

The Energy & Materials Research Conference

**EMR
2012**



Book of Abstracts

Torremolinos, Spain, 20-22 June 2012

<http://www.formatex.org/emr2012>

INTRODUCTION

The Energy&Materials Research Conference (EMR2012), which takes place in Torremolinos (Malaga, Spain) from 20 to 22 June 2012 (<http://www.formatex.org/emr2012>), brings together researchers and professionals from a broad set of science and engineering disciplines with the aim of sharing the latest developments and advances in materials, processes and systems involved in the energy generation, transmission-distribution and storage.

In the current situation, where world's energy system is likely to radically change in the next decades, research into materials, processes and systems is currently foreseen as a critical aspect in the development of cleaner and more efficient energy. In this conference series, researchers from very different academic backgrounds (from semiconductor scientists exploring new ways for improving conversion efficiency within solar cells, or electrochemists pursuing better performance and durability of fuel cell components, to microbiologists deepening on how engineered microorganisms can be exploited for generating useful energy, or materials engineers conceiving new designs for power plants), but with an unique interest in contributing to the global energy and environmental challenges, join together in a truly interdisciplinary atmosphere.

TOPICS

Conference topics include, but are not limited to:

Energy production from Biomass -Biofuels	<ul style="list-style-type: none"> • Extraction of biomass materials • Development/Improvement/Performance of materials for biomass systems/plants for heat & power and biofuels production (combustion, gasification, pyrolysis, anaerobic digestion, fermentation and composting). • Materials/Coatings of biomass combustion chambers • Materials for capturing CO2 • Second generation of biofuels • Corrosion resistant materials for biofuel processing • Materials, processes and systems for water filtration and desalination in biofuels production • Materials for biofuels storage
Solar Energy	<p>Photovoltaics (PV)</p> <ul style="list-style-type: none"> • Development/Improvement of processing techniques for thin film • Materials and techniques to increase capture of the full spectrum of sunlight. • Suitable coatings and coating techniques. Encapsulation methods • Characterization of materials degradation due to sunlight. Novel methodologies for characterization of defects in solar cells. • Recycling of solar system materials at end-of-life • Solar cells based on low-cost and nontoxic materials <p>Solar cells based on silicon (Si) (amorphous silicon, protocrystalline silicon nanocrystalline silicon)</p> <ul style="list-style-type: none"> - Improvements/Advances in silicon refinement and silicon growth and modeling - Gettering and passivation processes - Silicon nanowires and nanodots <p>CdTe-based and CIGS-based thin-film solar cells Multijunction cells Single crystal solar cells Organic/polymer solar cells</p>

	<p>Dye sensitized solar cells (DSSC) Nanocrystalline solar cells Low-cost solar cells</p> <p>Concentrating photovoltaics (CPV) and high concentration photovoltaics (HCPV)</p> <ul style="list-style-type: none"> • Manufacture and durability of lenses for high efficient optic concentrators. Assessment of optical errors of optics concentrators • Techniques to decrease the alignment error between the cell and the optic and to improve the efficiency • Thermal management of the module • Methods to avoid thermal dilatations, deformations of the materials and defects in the tracking control
Solar Energy	<p>Concentrating Solar Power (CSP) and Solar Thermal</p> <ul style="list-style-type: none"> • Development/Improvement of (key) materials (silica, iron and steel, concrete, plastic, aluminum, molten salts...) and coatings used in concentrating solar power systems: collectors, mirrors/reflectors, steam generator, heat storage systems and other components • Materials for solar thermal collectors and storage tanks • Methods/materials to improve solar absorbance. Heat transfer. • Development of thermal energy storage materials with improved heat capacity
Fuel Cells	<ul style="list-style-type: none"> • Novel high-performance materials for components and systems in PEM, solid oxide, microbial, alkaline, direct methanol, phosphoric acid, molten carbonate and regenerative fuel cells. • Anode, cathode and electrolyte materials • Development of new materials for fuel cell catalyst. Nanotechnology. Nanocomposite catalyst • Degradation of fuel cell components. Identification of fundamental corrosion mechanisms • Recycling of fuel cell materials
Hydrogen	<ul style="list-style-type: none"> • Materials for hydrogen production and purification • Characterization and analysis of high capacity materials for hydrogen storage. Carbon nanostructures. Metal hydrides... • Low-cost materials resistant to hydrogen embrittlement • Materials for hydrogen vehicles • Materials for hydrogen infrastructure: pipeline transport, tanks... • Biohydrogen
Wind Power	<ul style="list-style-type: none"> • Development/Improvement of advanced materials for high-speed, high volume processing, increasing gearing efficiency and harsh environments • Materials/Coatings/Methods to reduce fatigue and erosion-corrosion in constituent materials, sub-components and major structures • Rare earth metals in wind turbines • Nanoreinforcements
Geothermal Energy	<ul style="list-style-type: none"> • Development/Improvement of materials resistant to hot corrosion, for drilling hard rock... • Nanotech materials for geothermal energy

Hydropower	<ul style="list-style-type: none"> • Development/Improvement of materials resistant to high pressure, abrasion and corrosion for water turbines • Construction materials in dams, hydroelectric power plants
Wave and Tidal Power	<ul style="list-style-type: none"> • Materials/Coatings/Methods to reduce fatigue and corrosion in constituent materials, sub-components and major structures • New materials and methods for energy-efficient tidal turbines
Nuclear Energy and Materials	<ul style="list-style-type: none"> • Development/Improvement of structural materials capable of operating at high temperatures, resistant to radiation damage, corrosion, environmental degradation... • Development of advanced ceramics and coatings for fuels • Development/Improvement of materials to contain nuclear waste • Radioactive elements used in nuclear power plants. Uranium mining and processing. • Radiation detector materials • Advanced materials developed by computational modeling tools
Energy Production from Fossil Fuels	<ul style="list-style-type: none"> • Materials for fossil fuel extraction • Research into advanced materials and coating techniques to increase the efficiency of power plants • Materials for construction of advanced ultra-supercritical plants • New methods and materials for CO2 storage and sequestration
Energy Harvesting Materials	Piezoelectric, thermoelectric and pyroelectric materials (ceramics, single crystals, polymers, composites...)
Energy Transmission, Distribution and Storage	<p>Transmission and Distribution</p> <ul style="list-style-type: none"> • Materials for energy transmission and distribution. <p>Relevant topics:</p> <ul style="list-style-type: none"> - Materials/components of smart-, green- and micro-grids - Superconductors: <ul style="list-style-type: none"> o Superconducting materials. LT and HT superconductors. Iron-based superconductors o Real and promising future applications: medical physics, power grid, cryogenic technologies, materials for liquid energy carriers (liquid natural gas and hydrogen), hydro and wind power generators... o Cooling <p>• Materials for mechanical storage (compressed air storage, flywheel energy storage...)</p> <ul style="list-style-type: none"> • Materials for electrical storage: <ul style="list-style-type: none"> o Ultracapacitors - Supercapacitors— Nanostructured carbon electrodes, graphene or other electrode materials o Superconducting Magnetics Energy Storage (SMES) • Materials for electrochemical storage: <ul style="list-style-type: none"> o Batteries: lithium-based batteries, improved lead acid batteries, nickel-metal hydride batteries ... o Flow batteries o Fuel cells <p>• Materials for thermal storage</p> <ul style="list-style-type: none"> • Materials for chemical storage: hydrogen storage, biofuels storage...

Advances in Lighting Materials	<ul style="list-style-type: none"> • Materials for energy-efficient lighting. <p>Relevant topic:</p> <ul style="list-style-type: none"> - Solid-state lighting: Improvements in LEDs. OLEDs, Phosphor-based LEDs...
Energy-Efficient Buildings	Integration of renewable energy systems in buildings, phase-change materials for walls, floors and roofs, insulation materials, smart windows, energy-efficient lighting systems, appliances with Energy Star ratings...

Materials, Processes and Systems for Energy Saving and Sustainability

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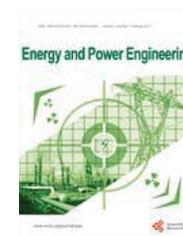
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THE VENUE

The Conference takes place at the "Palacio de Congresos y Exposiciones Costa del Sol-Torremolinos" (Torremolinos Congress Center), located at Calle de México, 3 29620 Torremolinos, Spain.



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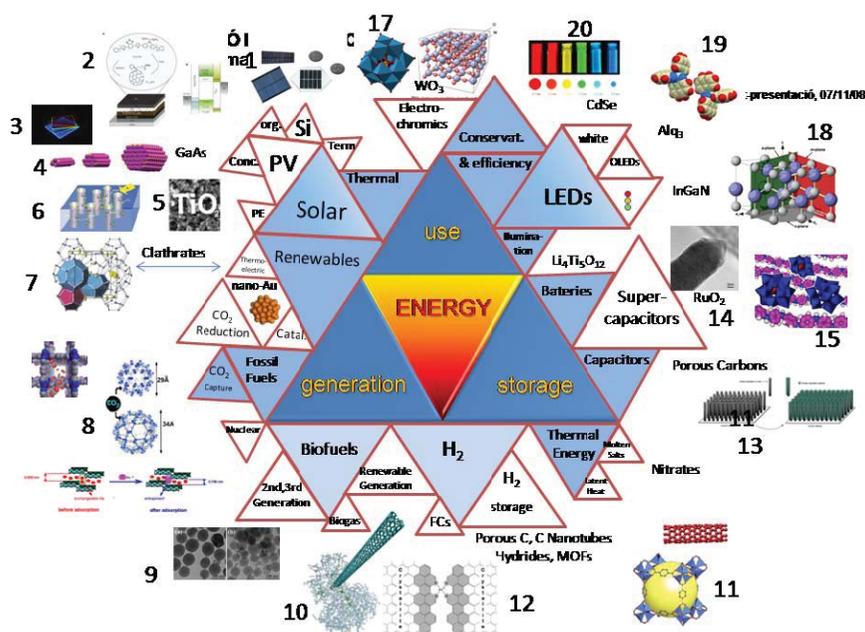
From Nanometers to Terawatts. Pending Revolutions in Materials Science

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With cheap oil is on its way to extinction and more abundant carbon threatening climate and environment, our present model for energy generation and consumption is doomed to a radical change or to a radical crisis. We are already living the beginning of a complex combined problem between energy and the environment, a problem that will not vanish miraculously through the chimney.

In this conference we will present a brief introduction to the overwhelming problem of energy and the many lines of action that should be taken to tackle this problem. This should include technological and social aspects, all intertwined to the limit, but we will center on science and technology. Hydrogen and fuel cells, biofuels, solar energy, batteries, supercapacitors, LEDs, CO₂ reduction, are all in bad need of radical improvement. But incremental technological evolution might not be enough to ensure the energy of our future. Not one but many pending scientific revolutions will be necessary for this task. Glancing at the intersection between Materials Science, Nanoscience and Electrochemistry, we will discuss some of those pending revolutions and the latest discoveries made along the path to a sustainable energy model.



Photovoltaic materials based on Small molecules: an emerging approach to organic solar cells

Jean Roncali

Group Linear Conjugated Systems CNRS, MOLTECH, University of Angers, France

The development of clean and renewable energy sources is one of the major scientific and technological challenges for the next decades. In this context, the photovoltaic conversion of solar energy appears as one of the most attractive alternative to address global environmental issues.

In recent years thin-film organic solar cells have attracting increasing fundamental and technological interest motivated by the possibility to develop light-weight, large-area and cost-effective photovoltaic energy sources by simple and low-environmental impact technologies.

Donor-acceptor heterojunctions solar cells combining soluble fullerene derivatives as acceptors and donor materials based on conjugated systems are among the most efficient devices reported so far. The intense multidisciplinary research effort developed in the past decade has generated considerable progress and conversion efficiencies exceeding 8.0% have been reported for solar cells based on soluble conjugated polymers as donor material. However, the synthesis of conjugated polymers pose various problems related to the control of their structural regularity, molecular weight, polydispersity, end-group defects and batch to batch variations.

In 2005 our group has proposed an alternative approach based on the replacement of polydisperse polymers by soluble monodisperse molecular architectures as donor materials in BHJ. In fact, molecular donors present several specific advantages in terms of unequivocal chemical structure and perfectly reproducible synthesis and purification.

After a general presentation of the state-of-the-art on the various aspects of organic solar cells including active materials, device architecture and evaluation, various series of active materials based on small molecules will be discussed with an emphasis on the relationships between the molecular structure and properties of the active material and the performances of the resulting solar cells.

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Energy production from Biomass - Biofuels

A comparison of the use of dilute aqueous *p*-toluenesulfonic acid and sulfuric acid in single step pretreatment - saccharification of biomass

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Efficient and economical saccharification of lignocellulosic biomass to fermentable sugars is the major hurdle for the production of cellulosic ethanol from abundant cellulosic biomass. The most widely tested technology for this step is the high pressure, high temperature dilute aqueous sulfuric acid pretreatment followed by the use of a cellulase enzyme cocktail for the saccharification step, but these operations are expensive. Therefore, the whole cellulosic-ethanol process is facing major challenges in bringing the cellulosic fuel-ethanol production cost competitive with gasoline. Single step pretreatment-saccharification using dilute aqueous sulfuric acid at high temperature and pressure is a viable alternative to the acid pretreatment-cellulase two step method, and in fact this is the older method used in the cellulosic ethanol process. However, this method was later replaced by enzymatic saccharification techniques developed in the last two decades due to poor sugar yields resulting low ethanol yields. Although, this direct saccharification gives lower sugar yields, several research groups have taken an interest in recent times taking a second look at this classical method due to its lower cost, and simplicity, compared to enzymatic saccharification, which however requires an energy intense pretreatment.

We have studied the saccharification of untreated biomass forms, corn stover, switch grass and poplar in aqueous medium using aryl/alkyl sulfonic acids as well as $-SO_3H$ functionalized imidazolium ionic liquids in water as catalysts in an attempt to improve the sugar yields of single step classical acid catalyzed saccharification method. Our studies on the use of aryl/alkyl sulfonic and $-SO_3H$ functionalized imidazolium ionic liquids have shown that these acids are superior catalysts than sulfuric acid at relatively lower temperatures and pressures. For example, a 100 mg corn stover sample heated at 150 °C for 1.0 hr, in aq. sulfuric acid produced 64 μmol of total reducing sugar (TRS), whereas the sample heated in *p*-toluenesulfonic acid produced 165 μmol of TRS under identical conditions. In the same experiment glucose yield also showed a similar trend, where in aq. sulfuric acid and *p*-toluenesulfonic acid mediums produced 29, and 35 μmol of glucose, respectively after 2.5 hr.

Advanced biofuels – bioethanol and biodiesel from lignocellulosic substrates

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The economic production of biofuels from lignocellulosic biomass requires quantitative fermentation of the cellulose as well as hemicellulose. The bioethanol production process consists of milling, a pretreatment step using steam explosion, increase of biomass concentration, enzymatic hydrolysis, recirculation of the hydrolyzed sugar solution to increase the sugar concentration, fermentation with yeast and downstream processing.

Only GMO yeast can ferment both sugars – glucose and xylose, but these yeast strains are not very stable during the industrial process and the use of these yeast strains enhances the strict security requirements and therefore the cost of the plant. Alternatively xylose can be used as substrate for feeding another microorganism.

The removal of C5 sugars derived from hemicellulose after the steam explosion step will be investigated. These sugars will be fed to oleaginous yeasts to produce appropriate fatty acid biodiesel while the C6 sugar from cellulose will be used for the production of bioethanol. The oleaginous yeasts will be screened and adapted to the inhibitors formed during the pretreatment and hydrolysis of lignocellulosic substrate. The improved bioethanol process and the coupling to the biodiesel production through oleaginous yeast enable the commercialization of bioethanol and biodiesel production from lignocellulosic substrates.

An experimental investigation of the biodiesel stability by means of oxidation and property determination

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As an alternative energy source attention has been focused on biodiesel which has lot of numerous advantages over petroleum diesel. However the concern over its stability made an issue for its applicability in automobiles. Since the chemical structure of biodiesel fuel consists of fatty acid methyl esters (FAME), thus it is susceptible to oxidation and thermal degradation. As time goes by, the oxidation and thermal stability of the fuels are being affected. Hence, in this research, these stabilities of petro diesel and different biodiesel such as palm oil and its blend, jatropha oil and its blend, and coconut oil are being studied by means of induction period (IP) and the change of the properties. The IP was measured by Rancimat instrument. The properties of biodiesels and diesel including density, viscosity, flash point, total acid number (TAN), and total base number (TBN), were determined at the interval of 180 hr. in a 2160 hr. (3 months) period using ASTM standard. The results showed that almost all biodiesel meet the standard specification regarding IP. The trend of density, viscosity and total acid number (TAN) was increasing while the total base number (TBN) was decreasing due to oxidation. For the flash point, the trend was also decreasing, but the rate was very low. In overall consideration among the biodiesel, palm oil biodiesel was the best while coconut oil showed the worst effect with respect to oxidation thermal and storage stability.

Application of Anaerobic Co-digestion for Utilization of Seaweed, Pectin and Carrageenan Waste

Dhan Prasad Gautam; Henrik B. Moller; Sutaryo Sutaryo

Co-digestion is an effective technology for utilizing different kinds of low value organic wastes, to reduce inhibition in biogas production during mono-digestion and optimization of methane production. This research was an experimental analysis of the co-digestion of four different type of biomass. The contextual scenario for this research was the interest of Solrød municipality of Demark for constructing a biogas plant for utilizing the locally available biomass with the collaboration of some food industries located on that region. The main goal this research was to determine the best method of utilization of seaweed which is creating problem on the environment of sea shore, and byproducts from some food industries. Considering the co – digestion of these materials as an appropriate solution, scientific investigation of the biogas production determining methane yield from these substance, level of inhibitions were carried out at different reactor conditions (mesophilic and thermophilic) and hydraulic retention times. Batch experiments were carried out in order to see the biogas potential of different substrates. Similarly continuous experiments were conducted in two small reactors of 25 liters and 7 liters total volumes both in mesophilic and thermophilic conditions. The experiments were prolonged for a period of around 3 months with different hydraulic retention times. The total solid (TS), volatile solid (VS) of the exit slurry were measured every week. Similarly, Ammonium (NH₄) and Volatile fatty acids (VFA) of the sample slurry were measured twice a week. Daily manual feeding of substrates was maintained according to hydraulic retention time. Total Nitrogen (TN) and Hydrogen Sulphide (H₂S) measurements were taken in every 15 days. The daily volume of the gas production was measured by gas meter and a Gas Chromatograph (GC) was used twice a week for measuring methane production. The results showed that the biogas potentials of industrial wastes were considerably higher compared to seaweed. Though the mono-digestion of these wastes is not considered worthwhile due to higher level of inhibitions; however, co-digestion of these byproducts with seaweeds showed significant methane production of around 280 liters per kg of VS. Grinding of seaweed as well solid liquid separation during evacuation of slurry was recommended for the experiments.

Artificial neural networks approach for the prediction of thermal balance of SI engine using bioethanol- gasoline blends

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This study deals with artificial neural network (ANN) modeling of a spark ignition engine to predict thermal balance of the engine. The thermal balance was respect of useful work, heat lost through exhaust, heat lost to the cooling water and unaccounted losses (i.e. heat lost by lubricating oil, radiation). To acquire data for training and testing of the proposed ANN, a four-cylinder, four-stroke test engine was fuelled with ethanol-gasoline blended fuels with various percentages of ethanol (0, 5, 10,15 and 20%), and operated at different engine speeds and loads. An ANN model based on standard back-propagation algorithm for the engine was developed using some of the experimental data for training. The performance of the ANN was validated by comparing the prediction data set with the experimental results. Results showed that the ANN provided the best accuracy in modeling the thermal balance with correlation coefficient equal to 0.997, 0.998, 0.996 and 0.992 for useful work, heat lost through exhaust, heat lost to the cooling water and unaccounted losses respectively. Generally, the artificial neural network offers the advantage of being fast, accurate and reliable in the prediction or approximation affairs, especially when numerical and mathematical methods fail. The experimental results showed as the percentage of ethanol in the ethanol-gasoline blends is increased, the percentage of useful work is increased, while the heat lost to cooling water and exhaust are decreased compared to neat gasoline fuel operation.

Keywords SI engine; thermal balance; ethanol-gasoline blends; artificial neural network

Atmospheric CO₂ sequestration through mineral carbonation of industrial solid wastes and their utilization in plant growth

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Sequestration of CO₂ from atmosphere in the form of solid carbonates through mineral carbonation is an option for reduction of atmospheric CO₂ concentration. In the present study carbon dioxide sequestration has been performed by using the industrial wastes like fly ash and red mud which are the wastes generated in huge quantity from thermal power plant and alumina industry respectively. Considering the reaction path of Al, Ca, Mg and Fe bearing minerals for carbonation, sulfatized mixtures are prepared with suitable additives in presence of water. The pH of the sulfatized mixture varies within 9.8-11.0. After thorough mixing each mixture is disposed to open place for atmospheric exposure. The mixtures are kept for 30 days in wet condition by addition of water for weathering and chemical reaction of mineral constituents. The atmospheric carbonation is a slow process and it takes about 30 days to initiate the reaction and formation of stable carbonate phases. This process is a cyclic path of sulfatization and carbonation which form polymorphs of carbonates. The mineral phases of carbonated fly ash studied through XRD resembles to calcite, aragonite, meionite, vaterite and magnesite etc. The quantitative estimation of CO₂ absorption through mineral carbonation has calculated from TGA analysis. From the experimental study it is found that 1tonne of fly ash mixture is absorbing 180kg and 1ton of red mud is absorbing 80Kg of CO₂ from the atmosphere. After carbon dioxide sequestration that carbonated fly ash and red mud has been used in plant growth. Utilization of carbonated material in improving the plant growth has been studied in two fast growing tree species i.e. *Acacia mangium* and *Dalbergia sisso* through pot culture study. Taking various parameters like PH, EC, and WHC into consideration, the periodical growth rate of *Acacia mangium* and *Dalbergia sisso* showed better response in carbonated materials.

Key words Carbon dioxide sequestration, mineral carbonation, industrial waste, hydrated mixture, plant growth.

Bioalcohols from biowastes: an assessment of current technologies

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While a transmutation from a petroleum-based economy to a bio-based global economy finds itself in its early infancy, agricultural wastes and residues have already begun their own transformation from high-volume waste disposal problems to being natural resources for the production of second generation liquid biofuels. Agricultural wastes contain high levels of organic carbon material and as such constitute inexpensive candidates for the biotechnological production of biofuel alcohols (e.g., biomethanol, bioethanol and biobutanol) without competing directly with the ever-growing need for world food supply. Since agricultural wastes are generated in large scales (in the range of billions of kilograms per year), thus, being largely available and rather inexpensive, these materials have been considered potential sources for the production of bioalcohols for quite some time and have been thoroughly studied as such. In the last decades, a significant amount of information has been published on the potentiality of agricultural wastes to be suitably processed into bioalcohols, with cellulosic ethanol being the main research subject. The production of biobutanol by fermentation of lignocellulosic material has experienced tremendous breakthroughs in recent years, both from the biochemical and technological points of view. Thus, it was the aim of this work to critically analyze the current technological situation and future needs for technological developments in the area of producing bioalcohols from biowastes. Lignocellulosic bioethanol is still the lead fuel currently being studied in terms of technology development for both production (pre-treatment, microbe and enzyme engineering, and process integration) and engine use and performance. However, several issues must still be addressed in order for commercial units to be built and become fully operational. Optimistic predictions estimate a 10 to 15-year horizon for the lignocellulosic bioethanol technology to be mature and fully operational. Biobutanol, as an alcohol fuel, presents distinct advantages over bioethanol in the sense that it can be used as is in unmodified spark-ignition engines (hence, it was coined the term 'biogasoline') and as a fuel it presents higher energy density than bioethanol. Major advancements in the production technology are related to the integrated fermentation-product recovery processes that also partly deal with the problem of fermentation inhibition caused by the presence of high concentrations of butanol in the fermentation medium. Other major issue is the lack of rigorous engine tests with this fuel. As a fuel for the transportation sector, butanol still has a long (but rather promising) research road ahead.

Keywords agricultural wastes; biofuels

Bioenergy in Sweden

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The biggest change in Swedish energy system over the past 30 years is that the biomass residual from forest and forest industry enters the energy market more and more in the place of fossil fuels, and Today accounts for more than one third of the total energy consumption in Sweden. This gives a clear picture of a shift of fossil fuel-based society to a sustainable society for an industrial country. The well established biofuel market in Sweden is, in principle, attributed to the good synergy of a strong forest industry with the energy sector, to a well-established district heating system, and to a favorable tax system. In this paper, the authors are trying to present a picture of how biomass residual is shaping the Swedish energy system in the past and for the future. The production of heat, electricity and transportation fuels will be discussed. A number of critic points associated to biofuel potential, economy, environmental impact, end-use, as well as to biomass conversion technologies such as combustion, gasification and biological processes will be discussed. The advances of research and technology development in Sweden will be overviewed.

Keywords biomass; bioenergy; biofuels

Biogas production from co-digestion by-products from biodiesel industry

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Anaerobic digestion is one of the most promising alternatives for waste treatment and energy production thanks to the production of energy by means of biogas valorization. In addition, this process allows the stabilization of organic matter and contributes to the reduction of greenhouse gas emissions. The present research deals with the co-digestion of swine manure with glycerines from two different biodiesel plants. The aim of this work was to improve the biogas production of swine manure by balancing C/N ratios through the addition of glycerine as an approach of the biorefinery concept.

Batch digestions test were realized in 250 ml batch reactors in order to determine the biogas potential of the different substrates (swine manure and glycerines denotes as A and B) and the co-digesting systems. The co-digestion of swine manure and glycerine was performed at four different glycerine ratios to assess the effect of the co-substrate over the biogas production. The co-digestion of glycerine and swine manure (denoted as Gly_X%) was carried out at 4, 8, 12, and 16% (dry weight). Four reactors were set for each system, two of them were used for measurement of the biogas produced and its composition (CH₄, H₂S), and the other two were used for analyses of the liquid phase (ph, TS, VS, VFA and LCFA). From results obtained, the digestion of glycerine A was carried out in 3 L continuous stirred reactor operating under semi-continuous conditions at a hydraulic retention time of 30 d.

Figure 1 shows the results from the digestion (Fig. 1a) and co-digestion (Fig. 1b) with glycerine A. Glycerine A presented high biogas production rate (890 mL/g VSfeed) along with high degradation rate during the first days of the experiment. The glycerine B presented lower biogas production (549 mL/g VSfeed) and the biogas curve shows a lag phase. Swine manure had the lowest biogas production (257 mL/g VSfeed). Methane composition ranged between 75 and 78% for all systems.

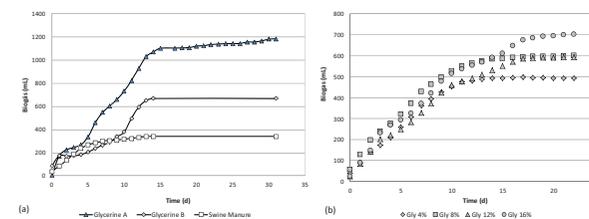


Fig 1. Accumulative biogas production for the single digestion tests (a) and codigestion tests (b)

Results obtained from the co-digestion with glycerine showed an increase in biogas production with the addition of glycerine A, ranging from 370 to 527 ml of biogas/g VSfeed for Gly 4% and Gly 16% respectively (see Fig. 1b). With regard to VFA analysis, results showed a high acetic and propionic acid concentration during the first days of the experiments that were gradually reduced as the digestion proceeded. The behaviour of the four systems did not show evidence of microbial inhibition. The comparison with the digestion of swine manure results in a clear increase in the biogas production between 1,5 to 2 fold. These increase could be explained by the increase obtained in the organic load in the digester and the better C/N ratio attained.

In addition, codigestion of swine manure and glycerine (5% v/v) was studied in semi-continuous mode using a 3L continuously stirred reactor to evaluate the effect of codigestion over the biogas production and VFA accumulation in a continuous digestion process. Results show an increase on the biogas production and a progressive accumulation of VFA during the experimentation, mainly acetic and propionic acid.

Acknowledgements:

This work was supported financially by project LE091A11-2 of the Junta de Castilla y León

Keywords: Anaerobic digestion; Glycerine; Swine manure; Biorefinery; Biogas;

Biomass energy from indigenous oil yielding plants in Pakistan

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Pakistan is a country which lies in between tropic of Capricorn and tropic of Cancer with diverse climatic conditions. Pakistan has rich biodiversity of oil yielding plants; some cultivated by local farmers while majority are wildy distributed in various zones of Pakistan. Among these oil yielding plants there is rich diversity of biodiesel yielding wild resources e.g. pongame, castor beans, carthame, wild bitter almond, neem, mesquite etc. Current energy crises throughout the world generally and Pakistan particularly need the energy from renewable sources like biodiesel. Biodiesel is an emerging solution for the present day concerns about rising oil prices and depletion of fossil fuel resources throughout the world. In current scenario due to shortage of energy resources, biodiesel is very good option for energy security in Pakistan. There are large arable lands with good climatic conditions for large biomass production of biodiesel yielding species. In this project we have identified rich diversity of oil yielding plants with biodiesel potential are identified based on biodiversity assessment, biodiesel production through transesterification and fuel properties comparison with ASTM standards. This study will provide pictorials of oil yielding plants, biodiesel samples, byproducts and their botanical aspects for wider interest which might be adopted by other countries to utilize these natural resources for biomass energy.

Build-up granulation of lignin sludge's as innovative process improving its energy efficiency

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The importance of bio-products production is enhanced with the abundance and renewability of lignocellulosic biomass in comparison to the depleting fossil fuels especially in producing environment friendly energy. Lignin is obtained as a residue from the pulp industry (black liquor) as well as from the bio-ethanol / bio-diesel industries. The extracted lignin is a renewable fuel with a heating value of 17 MJ/kg, low ash content. The extracted lignin in pulp mills is usually burnt at the mill directly to cover the energy production costs of the mill. The extracted lignin undergoes a reduction in heating value from 26 MJ/kg to 17 MJ/kg due to its high moisture content (30-75 %). The high moisture content reduces the total energy efficiency of the plant and simultaneously utilizes more amount of lignin sludge in producing the required energy. The energy efficiency can be increased with the efficient utilisation of fuel and at the same time reducing the percentage of lignin sludge required for energy production. This paper explains a possibility of integrating build-up sludge pelletisation in pulp mills. The integrated sludge pelletisation techniques would lead to an optimal utilization of lignin for energy and would simultaneously save the lignin resource for materialistic utilisation. The build-up sludge pelletisation was carried out with the help of a spray-granulation apparatus. The spray-granules were then treated with H₂SO₄ for stabilizing the lignin making it insoluble in water, regaining its original hydrophobic characteristics. The granulation process and the treatment with H₂SO₄ solves the problem of handling, storage, explosion risks of lignin, reduction of impurities and increases the energy density of the raw materials in comparison to the present situation.

Keywords: Lignin sulphonates; Kraft lignin; build-up pelletisation; energy efficiency; etc

Catalytic microwave-assisted pyrolysis of biomass for biofuels and chemicals production

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Pyrolysis of biomass produces liquid products (bio-oils) from a variety of biomass materials. However, the use of bio-oils has been hindered by its undesirable properties – complex, corrosive, and immiscible with hydrocarbons, etc. Subsequent treatment is essential to make bio-oils into usable fuels or chemicals. In this study, catalytic microwave-assisted pyrolysis (MAP) has been carried out with corn stover as main biomass feedstock and added in several metal salt catalysts. The addition of KAc, Al₂O₃, MgCl₂ were found to increase the bio-oil yield, which may be because these catalysts act as microwave absorbents and microwave plasma enhancers to speed up the heating rate. In addition, GC-MS analysis indicated that the bio-oil composition was significantly simplified with the use of catalysts. Furfural was the main product with the addition of 8% MgCl₂. The results suggest the possibility of the production of target chemicals with catalytic MAP.

Besides terrestrial biomass, microalgae received significant interests as a viable alternative to replace fossil feedstock due to their fast growth rate and environmental benefits. MAP of microalgae was also carried out under different heating rates to obtain optimum condition for bio-oil production. Compared to the bio-oils produced from lignocellulosic materials, those from aquatic microalgae have many desirable properties. The algal bio-oils had a higher pH (about 7-9) because of the presence of nitrogen bases. The bio-oil also had higher heating value (30.7 MJ/kg) and lower oxygen content than wood bio-oil. Gel permeation chromatography showed that algal bio-oils had lower average molecular weight than wood bio-oil. 22.2% of GC-MS peak areas were identified as aliphatic and aromatic hydrocarbons. In addition, algal bio-oils were found to be totally miscible with gasoline, which suggest potential direct use as fuel additives.

Keywords catalytic pyrolysis; catalyst; algae, bio-oil

Characterisation of corn starch content for bio-ethanol production purpose

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Maize is currently the single starting material of bio-ethanol production in Hungary. The cultivation conditions of Hungary are perfect for maize production, maize is grown on the quarter of cultivable land (1.2 million ha). Most of the current research is aimed towards improving the efficiency of maize-based bio-ethanol production. The most important measure of value of maize-based bio-ethanol production is starch yield of the starting material, namely the amount of starch harvestable from one hectare (t/ha). The ratio of amylose and amylopectin is essentially important, because it determines the gelification characteristics within the process of saccharification. In the course of production, alpha-amylase and amyloglucosidase enzymes are used in most cases; therefore it is important to know the content of starch resistant to alpha-amylase.

The aim of our examinations is the observation of yield and nutritional characteristics of commercial maize hybrids in Hungary from the aspect of efficient bio-ethanol production.

We set up a randomized block field trial. We determined the starch yield (t ha⁻¹) of the 51 maize hybrids involved in the field trial. In laboratory conditions, we also examined the amylose and amylopectin ratio and the amount of resistant starch of the selected 20 maize hybrids.

According to our results, there is a significant difference between the starch yield and the amylose component of the starch content of the examined maize hybrids. The difference amongst the amylose content of the maize hybrids was significant; we found twofold differences in some cases. The high amylose content of maize hybrids supports more efficient bio-ethanol production.

During the examination of resistant starch we found that resistant starch content may even reach 10 % of starch. Difference amongst starting materials may even be threefold.

Our studies reveal that maize starting materials shall be selected based on the cultivation objectives. If the objective is bio-ethanol production, detailed knowledge of starch content is necessary. There is a significant difference among commercial maize hybrids in Hungary in terms of characteristics determining the producible amount of bio-ethanol.

Keywords starch yield; amylose amylopectin ratio; resistant starch; corn

Characteristics of Biodiesel Fuels Applied to Diesel Engine

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So far research related to biodiesel fuel has been focused on its quality and property as a fuel and application to diesel vehicles mainly by government research centers and car makers. In the mean time, emission characteristics exhausted from biodiesel vehicles has been studied recently than ever before in environmentally friendly aspect. However, the study of emission characteristics of biodiesel fuel has been limited to experimental study of engine bench test, emission test in CVS-75 mode, unload test and etc. Through this research objective and quantitative data are secured by analyzing exhausted emissions and combustion characteristics from the experiment in which different blended ratio of biodiesel is injected to a constant volume chamber using a common-rail injection system. The pressure changes are measured by a piezometric pressure sensor and combustion processes are analyzed by securing heat release rates. The data of combustion pressure are collected by using DAQ (Data Acquisition: DAQ Card-6024E) and all the signals of ignitions and photographing timings is controlled by Code Vision AVR C language. Based on this fundamental experimental data this research aims to provide various technical materials in the preparation of emission reduction policy in future by confirming the potential applicability of biodiesel as a clean fuel for a commercial diesel engine..

Keywords Biodiesel; Compressed ignition; Ignition delay; Constant Volume Chamber (CVC); DTBP(Di-tert-butyl Peroxide)

Chemical interesterification of rapeseed oil with ethyl acetate using methanolic sodium methoxide and t-butanolic potassium butoxide solutions as catalysts

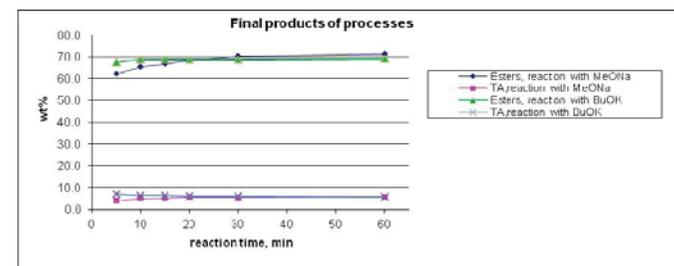
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Conventionally, biodiesel is produced by transesterification of triglyceride with alcohols in the presence of an acid or an alkaline catalyst. The by-product of the transesterification reaction is glycerol. In recent years much research has been aimed at improving biodiesel synthesis by interesterification with methyl or ethyl acetate using both enzyme and chemical catalysts. Fatty acid methyl or ethyl esters (FAME or FAEE) and triacetin (TAG) are the main products in this process. This leads to simplified downstream processes compared to conventional catalytic reactions as the mixture of FAME and TAG may be utilized as biodiesel, rather than FAME only. Moreover TAG has a much higher economic value than glycerol.

A. Casas et al. determined that methanolic solution of potassium methoxide gave higher yield of products than solid methoxide because the catalyst is completely dissolved in the reaction mixture from the beginning. However, it also causes transesterification side reactions, which lead to a lower yield of TAG production [1]. In the present work biodiesel synthesis from rapeseed oil and ethyl acetate was studied using two catalysts - methanolic sodium methoxide solution (MeONa) and t-butanolic potassium butoxide solution (BuOK). In addition to the FAEE, FAME and TAG, the reaction mixture may contain intermediates from interesterification -MADG (Monoacetyldiglyceride) and DAMG (Diacetylmonglyceride), as well as intermediates from transesterification -diglyceride, monoglyceride and glycerol.

In all experiments the optimal reaction conditions for interesterification were used: 75 °C, catalyst 0.8% of oil mass and molar ratio oil/ethyl acetate 1/18. Experimental results show, that in both reactions the content of esters and triacetin were similar, see fig. 1. In reaction with MeONa the equilibrium composition was reached within 30 min, but in reaction with BuOK - within 20 min. The greatest difference was observed in the MADG content. Using the MeONa catalyst, MADG content increased to 6.0% in 5 min and reached the steady value of 2.0% at 60 min. On the other hand, with BuOK, MADG reached a steady value of 2.0% already by 5 min. In accordance with the obtained experimental results the content of all products after reaching the chemical equilibrium in both processes are practically the same.



[1] Casas A., Ramos M. J., Perez A. Chemical Engineering Journal. 2011. 171, 1324– 1332.

Keywords chemical interesterification; ethyl acetate; rapeseed oil, biodiesel

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Chemometric study of biodiesel production from soybean oil

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The need to find alternative energy sources is mainly due to the shortage of oil reserves as well as the emission of toxic gases resulting from fossil fuels burning. Biodiesel has appeared as a promising substitute to diesel, widely used in cargo transportation vehicles, which in Brazil move the industry and agroindustry. Biodiesel is obtained from the transesterification of some oil, vegetal or animal, in methanol or ethanol means, using an acid or basic catalyst. Despite being a simple process, when carried out in unsuitable conditions, the oil transesterification remains incomplete, and if this substance is used as a biofuel it can result in serious damage do the vehicle engine decreasing its service life. For this reason, the study of variables in the process of obtaining biodiesel is very important. The main aim of this work is to establish, through chemiometric study, the best conditions of biodiesel production from soybean oil.

A chemiometric study was carried out with the aid of experimental planning in order to analyze the following variables: oil temperature (80 or 70 °C), solvent (ethanol or methanol) and basic catalyst (KOH or CH₃O). The response to the tests was in ester content, carried out using the Fuel Analyzer – ERASPEC, according to the EN 14078/NBR 15568 norm.

In figures 1 and 2, the results of chemiometric treatment are presented in the Cube format and interaction between factors, respectively.

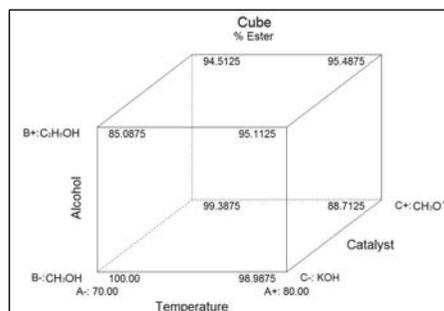


Figure 1 – Response in Cube format for the chemiometric study of the soybean oil biodiesel.

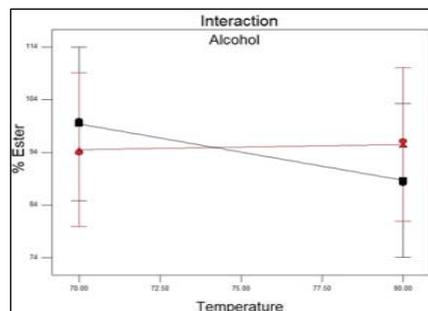


Figure 1 – Interaction between alcohol and temperature for the catalysis with methoxide.

When analyzing Figure 1, it can be noticed that the best biodiesel preparation conditions to obtain higher percentage of esters is: oil temperature equal 70° C, methanol as a solvent and methoxide (CH₃O) as a homogeneous catalyst. It is important to highlight that in general the biodiesel produced from methanol presented the highest levels of ester content, as it was expected due to its estereochemical properties.

The analysis of Figure 2 reveals an interaction between the alcohol employed and the temperature applied to the process, when the sodium methoxide is used as a catalyst, that is, when the kind of alcohol used and temperature are altered, this is probably due to the catalysis mechanism and the catalyst nucleophilic characteristic, besides esteric impediments that hamper the transesterification reaction.

Keywords: Biofuel; Transesterification; Renewable energy.

Co-product recovery from biomass during ethanol production

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The conversion of biomass to ethanol represents a sustainable alternative liquid fuel technology that does not need to compete with the supply of commodity crops such as corn and soybeans. Maintaining agricultural production of edible crops for the food supply and using agricultural waste or low input energy crops grown on marginal land for biofuel production is necessary although economically challenging. The separation and recovery of valuable co-products from biomass would improve the process economics of ethanol production. Available biomass is primarily lignocellulosic with minor components including waxes and other lipids that are potential co-products which could be separated and recovered from the biomass on-site prior to conversion using hot ethanol. Ethanol is not a traditional lipid solvent however at temperatures above 50°C ethanol can solubilize the waxes typically found on plant stems. Additionally, the lignin may also be separated from the cellulosic substrate and recovered for use in plastics and resins or decomposed into phenolic acid compounds such as the bioactive ferulic and coumaric acids. These phenolic acids have applications as antioxidant and antimicrobial agents, respectively.

The process for the recovery of co-products was evaluated for a 70 T/day facility using *Panicum virgatum* (switchgrass) as the biomass feedstock. Switchgrass is a perennial North American prairie grass with harvests of 5-11 tonnes/hectare. It was chosen for this investigation due to the amount of attention it has received as an energy crop rather than for the amount or unique co-products it contains. The amount of recoverable surface lipids was estimated at 0.1% dry weight and the lignin content was estimated at 5.5% in the leaf with 7.5% in the stem. The analysis assumed complete recovery of the lipids from the biomass with 0.5% residual lignin.

The evaluation was facilitated with the simulation software SuperPro Designer 7.5 (Intelligen, Inc., Scotch Plains, New Jersey, USA). The initial process design did not include a co-product recovery section. This was modified by adding a section to separate the lipids from the biomass in a continuous solid/liquid extraction operation using 50°C ethanol generated on-site. The lipids were recovered from the ethanol by cooling and centrifugation with recycle of the ethanol stream. This scheme produced 70 kg/day of mixed lipid extract which could be marketed as a natural wax product. The recovery of a lignin as co-product was addressed by considering existing fermentation process designs where a de-lignified cellulosic substrate is used for saccharification and the lignin fraction is combusted as a heating fuel. This becomes an economic comparison of the market value for the lignin as co-product versus the heating value of some alternative fuel (ethanol). It is possible to change the operation of the facility in response to fluctuations in the market price. At a high value for lignin it could be recovered as co-product otherwise used as fuel with minimal interruption to bioethanol production. The results of this study suggest two paths to improve the process economics of bioethanol production.

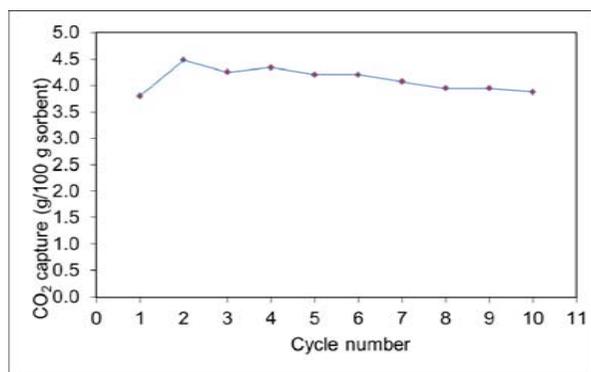
Keywords lignin; phenolics; process economics; simulation; sustainable

CO₂ Capture by a Synthetic, CaO-containing Sorbent in a Fixed-bed Reactor

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The Ca-based sorbents used in carbonation process can be divided into natural and synthetic sorbents. Examples of the natural sorbents are dolomite and limestone. The main problem associated with the natural sorbents is the rapid decay in capacity upon multiple sorption/desorption cycles. On the other hand, synthetic sorbent (CaO/Ca₁₂Al₁₄O₃₃) is more resistant to numerous cycles due to the higher reactivity and stability as shown in the figure below.



CO₂ breakthrough curves in the fixed bed reactor: T=600 °C, m₀=1 gm, dp=250-450 μm, P_{CO₂}=0.1 bar, F_{CO₂}= 10 ml/min, N₂ balance.

Capture of CO₂ using CaO-synthetic sorbent at high temperature in a fixed bed reactor being influenced by number of factors makes the characterization and prediction of carbonation process a difficult problem. In this study, the different operating parameters of the carbonation reaction have been investigated. Li and Cai [1] studied the carbonation reaction using the CaO/Ca₁₂Al₁₄O₃₃ sorbent in a thermo gravimetric analyser (TGA). However, we have used the fixed bed reactor to study the impact of diffusional limitations on the carbonation reaction. The carbonation reaction of the SE-SMR process is a non-catalytic gas-solid reaction system. It is well known that the carbonation reaction of CaO occurs in two successive stages. The initial stage in which the solid reactant is reacting with the gas reactant is fast and controlled by chemical kinetics. In this stage, the reaction rate is normally fast, resulting in a fast increase in the subsequent solid reactant conversion. After the fast initial reaction stage, a transitional towards a second slower reaction stage controlled by diffusion in the solid product layer takes place resulting in lower effective reaction rates. Until today, the published experimental data of the carbonation reaction were modeled to predict the reaction rate by neglecting product layer controlled diffusion regime. Hence, a kinetic rate expression has been developed using spherical grain model considering both the kinetic- and product layer controlled regimes. Moreover, a criterion has been proposed to divide the fast surface reaction regime and the slow diffusion controlled reaction regime. So, two different diffusional limitations can be calculated for the two different controlled regimes by the use of proposed kinetic expression. If we are interested to do simulation for the circulating fluidized bed reactor model, then we need the diffusional limitation which is valid for fast surface reaction regime only (because of the short residence time due to the fast fluidization). But, for the fixed bed reactor model, we need the value of diffusional limitation, which should be valid for both the fast- and diffusional controlled regimes.

Reference:

Li ZS, Cai NS, (2007) Modelling of Multiple Cycles for Sorption-Enhanced Steam Methane Reforming and Sorbent Regeneration in Fixed bed Reactor. Energy and Fuels 21:2909-2918

Cold flow properties investigation of some blended biodiesels from safflower and soybean

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One of the major problems associated with the use of biodiesel is poor low temperature flow properties, indicated by relatively high cloud points (CP) and pour points (PP). Within this paper, it has been demonstrated that cold flow behavior of soybean biodiesel can be improved by adding different proportions of biodiesel obtained from safflower. The oxidation stability of these mixtures was investigated too. The contribution of soybean biodiesel in this mixture doesn't change too much the induction period regarding oxidation stability, taking into account that soybean biodiesel has positive values of this quality parameter. All determinations were made according with European Standard EN 14214.

Key words: oil crops, biodiesel, cold flow properties, oxidation stability

Comparative performance analysis of a compression ignition engine fuelled with biodiesel blends

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Energy is the basic need for modern economy. Due to the rapid industrialization and modernization energy demand is increasing day by day. Biodiesel has an immense potential to be part of sustainable energy mix in the future because of offering more sustainability and less green house gas emission. This paper presents the comparative performance of biodiesel and their blends obtained from edible oil source such as palm oil and coconut oil compared with diesel together with some of its fuel properties. Seven fuel blends (B0, C20, C30, P20, P30, CP20 and CP30) were tested for their use as substitute fuel for a water-cooled single cylinder four stroke diesel engine. Test data were generated under full throttle position with different engine speeds from 1200 to 2400 rpm at an interval of 200 rpm. The properties were found to be comparable to diesel fuel. The brake power, torque and brake specific fuel consumption of the engine run by the biodiesel is comparable to that run by pure diesel and significant improvement of engine performance was observed when B30 is used.

Keywords: energy; biodiesel; performance; palm oil; coconut oil

Cultivation of microalgae with diluted primary olive mill wastewater for bio-fuel production

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The olive oil industry represents a very important agro-industrial sector in many countries of the Mediterranean region. Approximately 30 million m³ olive mill wastewater (OMW) effluents are produced as by-products annually of which about 370,000 m³ are produced in the Middle Eastern region. OMW is a significant source of potential environmental pollution due to its high content of polyphenols, tannins, and lipids which exhibit phytotoxic and antimicrobial activities, as well as a high potential to contaminate surface and ground water. The OMW has a very high organic loading, BOD and COD, which may reach 100 and 200 g/L, respectively.

Microalgae are good source of antioxidants mainly β -carotene and biomass for energy. Under optimized conditions, current yields of algae biomass are ca ~ 35 g dw m⁻²d⁻¹, but in theory, microalgae (marine or freshwater) can use up to 9% of the incoming solar energy to produce ca 70 g dry biomass m⁻²d⁻¹ and sequester ca 140 g CO₂. The main limitation of using these systems to treat agro-derived effluents is related to the composition of the wastewater and the possible presence of high concentrations of ammonia, organic acids, phenolic compounds, and pesticides or other compounds that can inhibit algal growth.

Our main objective was to cultivate different isolates of microalgae in primary OMW that has merely been diluted before use for the production of biomass to be used mainly for biodiesel production. Ten different cultures including *Dunaliella* and *Chlorella* were grown in different concentration of OMW and the biomasses as well as fatty acids were monitored. The biomass productivity of the microalgae exhibited a positive linear correlation with the initial COD values, which ranged from 370 to 1300 mg/L. Our results have shown that some of the microalgae, i.e. *Chlorella*, tripled within one week its biomass production compared to control. Some of the microalgae were rich with different fatty acids, i.e. oleic, linoleic and palmitic. The fatty acids were transformed to high quality biodiesel by using the in-situ transesterification method. Our results indicate that OMW is good source of nutrients for biomass and fatty acid production and suggests a convenient way to reduce the high organic content of OMW with the production of algal lipids.

Keywords COD; Biomass; Lipid production; Microalgae; Olive mill wastewater

Deconstructing sugarcane cell wall for the production of second generation ethanol

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Sugarcane is used worldwide as a feedstock for ethanol and sugar production. After sugarcane is milled for juice extraction, bagasse is obtained as a residue, which corresponds to about 25% of the total weight and contains 60-80% of carbohydrates [1]. Fractionation of bagasse components and their conversion to fermentable sugars is essential in enabling this renewable feedstock to be used for biofuel production, which can significantly improve bioethanol productivity and sustainability [2]. The classical approach to the production of second generation ethanol involves three key steps: pretreatment of the feedstocks to separate its cellulosic fraction from the hemicellulose and the lignin; enzymatic hydrolysis to break the carbohydrates into hexoses and/or pentoses; and finally, their fermentation into alcohol.

In this work, a consecutive two-step pretreatment was used to fractionate sugarcane bagasse. It included an acid step to remove hemicellulose mainly (H_2SO_4 1% m/v, at 120°C during 1h), followed by an alkaline step with NaOH to remove lignin (NaOH concentrations from 0.25 to 4% m/v, at 120°C, 1 h).

The chemical composition of the bagasse is severely changed after different pretreatment conditions, as shown by high proficiency liquid chromatography (HPLC), and nuclear magnetic resonance (NMR): up to 96% of the hemicelluloses and 85% of the lignin initial amounts were removed when sodium hydroxide concentrations of 1% or higher were used. Considering the sample morphology, lignin removal has a more noticeable effect than hemicellulose removal. Lignin withdrawal favors bagasse unstructuring by the loss of cohesion between neighboring cell wall bundles, as shown in Figure 1(a-b). Other morphological effects of the lignin removal are the changes in the inner cell wall structure, such as damaging, porous formation and loss of mechanical resistance (Figure 1c).

Changes on sample porosity are also confirmed by nitrogen adsorption isotherms (BET method), which showed that the total surface area of the bagasse increased from 0.75 m²/g before the pretreatments to 1.5 m²/g on samples undergoing treatments with acid and NaOH 0.5%. These effects facilitate liquid and enzyme access to crystalline cellulose and triplicate hydrolysis yields (using Accelerase 1500, Genencor, 25 FPU), showing the efficiency of the proposed method to improve the enzymatic digestibility of sugarcane bagasse.

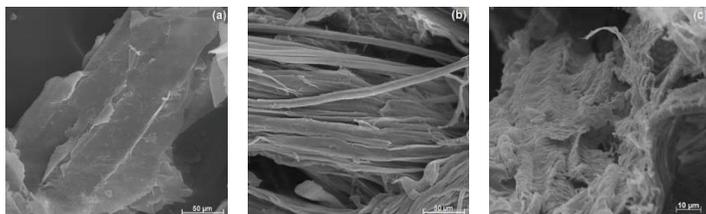


Figure 1. Surface images obtained by scanning electron microscopy: (a) untreated bagasse, showing an entire fiber; (b) bagasse treated with H_2SO_4 1% and NaOH 2%, showing unstructured fiber bundles and (c) bagasse treated with H_2SO_4 and NaOH 1%, showing the damaged surface of the cell wall.

Keywords sugarcane; bagasse; bioethanol; acid pretreatment; alkali pretreatment; chemical composition; scanning electron microscopy, enzymatic hydrolysis.

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Detection of greenhouse gas precursors from the biofuel combustion and binary mixtures of diesel measured by analytical techniques

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Abstract: Environmental pollution is directly related to the social and technological development causing serious damage to society. The consequences derived from different forms of atmospheric pollution vary from the local to the global scale, with deep impacts on climate, environment and human health. Fossil fuels are the major pollutants, particularly intensified by the transports sector. Thus the Brazilian government in order to try to reduce the pollutants emission since 2010 adopted the addition of 5% biodiesel in diesel. This study aims to simulate the emissions of different concentrations of binary mixtures (soybean biodiesel and diesel) in a diesel engine bench. Therefore, new methodologies based on selective and sensitive gas detection schemes must be developed in order to detect and monitor pollutant gases from this source. In this work, CO_2 Laser Photoacoustic Spectroscopy was used to evaluate ethylene (C_2H_4) emissions and electrochemical analyzers were used to evaluate the emissions of carbon monoxide (CO) and nitric oxides (NO_x) from the exhaust of diesel powered vehicles at different engine rotation speeds. The results indicate that the detection techniques used were sufficiently selective and sensitive to detect the gaseous species mentioned above in the ppmv range.

Keywords biodiesel; diesel engines; electrochemical sensors; photoacoustic sensors

Dual-frequency ultrasound-assisted reactor for transesterification of vegetable oils aiming at biodiesel production

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Increased environmental concerns and economic demands related to the use of fuels are the main driving force behind the increasing production of biofuels and biodiesel is one of the leading biofuels being produced and commercialized at large-scale [1]. The conventional process for industrial biodiesel production is based on the transesterification of vegetable oils with short chain alcohols in the presence of a homogeneous base catalyst (usually sodium methoxide) carried out in batch stirred reactors. Stirred reactors are employed to promote intensive agitation in order to create and maintain a stable emulsion of the reactants, thus minimizing the mass transfer limitations between phases (reactants) and improving reaction kinetics. However, the reaction times with this technology are still long and innovative technologies that would allow reduction in reaction time have been sought after in recent years. Intensification methods such as ultrasonication are being intensively studied and used for that purpose. The use of low-frequency ultrasound has demonstrated to be advantageous for biodiesel production for it is rather efficient (i.e., reduces reaction time and increases yields) and economically interesting (i.e., of low energy and catalyst consumption compared to the conventional processes). Thus, the objective of this study was to evaluate the performance of a transesterification reactor irradiated with ultrasound at two distinct frequencies (40 and 19 kHz) for the production of biodiesel. The configuration of the reactor allowed for the irradiation to occur either in series or in parallel. The irradiation of ultrasound in series was more effective in reducing the reaction time and increasing the biodiesel yield than the configuration with irradiation in parallel. Furthermore, in both cases, the reaction times ($t < 20$ min) were shorter than those with the conventional batch stirred reactor (~ 1 h) for similar degrees of ester conversion ($> 96\%$).

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Keywords transesterification; ultrasound

Economical bioethanol fermentation of different kind of corn hybrids

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The exhaustion of fossil energy sources, the growing importance of economical considerations as well as the protection of our environment give an ever growing role to the utilization of renewable energy in our life. Bioethanol could be one of the renewable energy sources. A widespread technology for ethanol production is the SSF (Simultaneous Saccharification and Fermentation). A profitable way to produce ethanol with this technology is the application of thermotolerant yeasts. *Kluyveromyces marxianus* is a yeast species with outstanding thermotolerance. Previously we developed a *Kluyveromyces marxianus* E1 mutant strain in order to produce the highest amount of ethanol at the highest possible temperature matching well to the SSF technology (Erdei *et al.*, 2011). Our aim was to produce bioethanol with this *K. marxianus* E1 strain using maize starch feedstock in order to confirm the fermentation would be more economical with the application of this strain. In these experiments we used 20 different kind of maize hybrids. We analysed the amylose/amylopectin ratio and resistant starch content of these hybrids in details. These qualitative characteristics fundamentally determine the amount of bioethanol producible from different maize hybrids. Besides we determined the starch yield which come from one hectare, because it is also very important value in order to define the economy of bioethanol production.

Keywords: maize starch, yeast, thermotolerance, bioethanol

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Economical sweet potato enzymatic hydrolysis for using as carbon source for single celloil production by thermotolerant oleaginous yeast

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In this work, the economical glucose syrup production from sweet potato hydrolysis and utilization of the obtained hydrolysate for single oil production by thermotolerant oleaginous yeast were studied. The Novozyme α -amylase and β -glucosidase were used for the liquefaction and saccharification steps of sweet potato hydrolysis, respectively. It was found that the highest sweet potato concentration which still could be able to stir after boiling was 60 g/l. This concentration was, thus, used for original substrate concentration for further studies. The optimum concentrations of α -amylase for hydrolysis of 60 g/l of sweet potato at 90 °C and pH 6.5-7.0 for 120 min were 100,000 Unit/ml. The obtained reducing sugar content after the hydrolysis was 26.4 g/l. In order to save the enzyme cost, 30 g/l of substrates were further added directly twice after the liquefaction step of α -amylase (total substrate was 120 g/l). The final obtained reducing sugar concentration was 50.8 g/l. The optimum β -glucosidase concentration in the further saccharification step for 48 hour at 60 °C and pH 4.3 - 4.5 was 10,000 Unit/ml. The final reducing sugar concentration of 99.1 g/l was obtained. The obtained glucose syrup from sweet potato hydrolysis was further used for single cell oil production by thermotolerant oleaginous yeast Scj01 strain at 40 °C. The result showed that the obtained lipid content was 2.24 g/l or 42.5% (w/w) on the cell dry weight basis, which was higher than some reported strains. The optimum conditions for the thermotolerant yeast Scj01 growth and oil accumulation by using the sweet potato hydrolysate could possibly improve the oil content accumulation and need further studies.

Keywords: single cell oil, sweet potato, Biodiesel, thermotolerant oleaginous yeast, glucose syrup

Effect of the biodiesel from waste oil in the metals composition in lubricative oil

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The use of biodiesel in engines without modifications of its intern design is usual when the main use is for auto consumption in tractors and energy generators in the farms. Therefore, the wear conditions and consequent lubricant oil contamination must be investigated. Biofuels unspecified cause serious problems in components life time and engine efficiency. Because of this, it is important to recognize the consequences of the type of biofuel. In this work, it is aimed to identify the components wear that it is observed like metals contamination in the lubricant oil, for example. Furthermore, in this work it was used biodiesel from frying residual oil (FRO) in an energy generator. The FRO biodiesel present high deterioration degree that contribute for a more intense engine wear than biodiesel from refined oil. The equipment used was a energy generator Tramontini TR22 model, with direct injection fuel system.

The analysis of the lubricant oil (SAE 15W40) was conducted in Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) after the acid digestion assisted by microwave. The study was accomplished during 280 h under fixed conditions of load and speed. The sampling and analysis was taken each 50 h.

The results showed variations in the Al, Cr, Cu, Fe, Mg, Mn, Pb e Zn concentrations in the lubricant oil (Table 1). It was observed positive correlation between the lubricant oil time of using and Cr, Cu, Fe, Mn and Pb contamination. For Fe Mn and Pb contamination, the correlation coefficient r^2 was higher than 95%. Such correlations can be explained because the Fe is a metal more abundant in tribologic system of the engine; Pb is a soft material founded in the piston rings, cylinder jacket and bearings and it also presented an increase along the assays; Mn is founded in the cylinder jacket, piston rings and in the piston, manufactured in alloy of Al and Mn, in such a way that the variation of its concentration in the lubricant represents a wearing on the surfaces of these materials; the concentration of Mg and Zn was reduced during the tests, and this can be explained by the combination of these materials with oxygen in the metallic surface of the engine; Al observed in the lubricant oil could be related to the piston or to the bearings wear; there are also Cu and Cr increase that correspond to corrosion of the componentes and wear of the bearings respectively. The ICP-OES showed continuous increase of the metals in the lubricative oil that consist in the contamination provoked by components wear during the use of the FRO biodiesel in the energy generator. It was observed wear in the internal components of the engine, but if the oil is changed periodically, this problem can be minimized and the FRO biodiesel will not be consider inappropriate for auto consumption in the farms.

Table 1- Medium levels of the metals in lubricative oil

AMOSTRA	Al	Cr	Cu	Fe	Mg	Mn	Pb	Zn
0 h	3,860±0,185	<0,25	<0,40	<1,70	266±1,732	0,340±0,023	<3,32	1136±5,774
50 h	3,6±0,115	<0,25	14,7±0,462	31,6±0,404	206±2,309	0,82±0,017	6,8±0,231	1082±9,238
100 h	6,5±0,231	<0,25	13,9±0,404	47,2±1,212	183±4,619	0,94±0,023	9,1±0,462	976±6,351
150 h	6,9±0,173	10,3±0,404	79,8±0,751	135,5±2,136	174±2,304	1,9±0,058	14,7±0,289	877±5,196
200 h	7,6±0,173	10,6±0,346	123,4±2,54	140,1±2,598	155±3,464	1,8±0,058	15,4±0,289	860±9,238
250 h	8±0,231	11±0,346	167,7±3,637	155,3±3,406	151±1,732	2±0,058	17,4±0,346	794±8,660

Acknowledgements: CNPq, SCIT-RS, Finep and Fap-UNISC

Keywords: metals, components wear, frying residual oil, biodiesel

Effect of the temperature in ethanol and xylitol production by *Hansenula polymorpha* using hydrolysates of sunflower stalks

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Hansenulapolymorphais a non-conventional methylotrophic yeast, particularly suitable to the bioalcohols production in fermentation process to high temperature (over 30°C) due to its thermotolerant nature. It was found that *H. polymorphais* able to ferment D-xylose, D-glucose, cellobiose and other lignocellulose sugars at elevated temperatures [1].

The use of lignocellulose materials for the production by biochemical processes of chemical products of high value is promising, because these represent an abundant and renewable source of carbohydrates. Sunflower cultivation in the European Union (EU-27) covers some 3.6 10⁶ ha[2] and generates yearly between 9.0 and 17 million tons of potentially useful agricultural waste. Thus the objective is to convert agricultural debris and other biomass feed-stocks into value-added products or biofuels.

In this work, the ethanol and xylitol production has been studied, carrying out fermentation processes with *H. polymorpha* at temperatures of 30, 40 and 50°C. In the fermentation processes, hydrolysates of sunflower stalks were used. Previously, hydrolysis processes were carried out with sulfuric acid 2 M. Results showed that for a similar initial sugar concentration, better results to xylitol concentration were obtained at 50°C. A higher specific sugar-uptake rate was observed at more elevated temperatures, and a major concentration of non-consumed sugars when the operation temperature was lower.

Keywords: Sunflower stalks, D-xylose, D-glucose, Ethanol, xylitol, *Hansenulapolymorpha*

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Energetic co-valorization of crude glycerol with lignite

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This paper summarizes the currently available and possible ways of valorisation of crude glycerol generated from the biodiesel industry and focuses on the innovative utilization of that waste product via co-pyrolysis with lignite in order to have sustainable and profitable biodiesel production. The idea of incorporating waste glycerol from the biodiesel manufacturing process with lignite is new. Towards the direction of producing an alternative to coal fuel, in this study, experimental results from thermochemical conversion of mixtures of waste glycerol and lignite are presented. Thermochemical conversion is discussed in this work, having a further insight on pyrolysis and gasification. Pyrolysis leads to the conversion of the fuel directly into liquid, charcoal and non-condensable gases, by heating the feedstock material in the absence of air while gasification process may be integrated with power generation. The characterization of the synthetic fuel material formed was carried out in order to investigate and evaluate the feasibility of utilizing that waste material in such process as well as in conventional combustion processes. Waste glycerol blend with lignite, at a percentage of 20% wt, was used for the experiments. Co-pyrolysis performed batch wise in a laboratory, non-continuous, captive sample, wire mesh reactor at atmospheric pressure. The process was studied, at an average heating rate over the range of 100 - 330 °C/s and a reaction time of 0,1 - 1 sec, by varying the temperature over a range of 500 - 850 °C. Glycerol content in the solid fuel resulted in greater decomposition rate. At specific pyrolysis temperature (630 °C), the results showed enhanced liquid production compared to the yields achieved from pure lignite pyrolysis and improved gas quality.

Keywords waste glycerol; lignite; optimal management; pyrolysis; fuel; energy

Engineering Bacterial Surfaces to Degrade Biomass

Timothy D. Anderson, Izaak Miller, Jimmy Zeng and Robert Clubb

To cost-efficiently produce biofuels, improved methods are needed to convert lignocellulosic biomass into fermentable sugars. One promising approach is to degrade biomass using cellulosomes, surface displayed multi-cellulase containing complexes present in cellulolytic *Clostridium* and *Ruminococcus* species. In this study we created genetically modified strains of *B. subtilis* that display on their surface heterologous proteins and protein-protein complexes. Proteins containing the appropriate cell wall sorting signal are covalently anchored to the peptidylglycan by co-expressing them with the *B. anthracis* sortase A (SrtA) transpeptidase. Greater than 300,000 heterologous proteins per cell are displayed in strains in which the WprA cell wall protease has been deleted. Two minicellulosomes were constructed that consist of a cell wall attached scaffoldin protein that non-covalently binds to cellulase enzymes secreted into the medium. Unlike the wild-type organism, *B. subtilis* displaying the minicellulosome robustly grow on biomass and can degrade greater than 60% of the biomass in 96 hours. Importantly, the cells exhibit greater cellulolytic activity than several previously reported *in vitro* and yeast displayed minicellulosomes. *B. subtilis* has a robust genetic system and is currently used in a wide range of industrial processes. Thus, grafting more elaborate multi-enzyme containing minicellulosomes onto the surface of *B. subtilis* may yield more potent cellulolytic bacteria that can be used to efficiently degrade biomass and to engineer consolidated bioprocessing organisms.

Key Words: Biofuels, Cellulose Degradation, Cellulosome

Environmental protection by the anaerobic methanisation of the cameline scrap of the slaughter-house of the city by a batch digester heated by solar energy

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In this work we studied the anaerobic digestion of waste coming from the slaughter-house of the town of Adrar located at the western south of ALGERIA. The used digester is of batch type heated by solar energy. During this study we followed the evolution of the pH and the biogas volume produced as well as the temperature inside the digester. The obtained results show that the temperature inside the digester varies in the interval [22-47] °C, which situated in the mesophile field (activity domain for the methanogenes bacteria), the biogas yield produced by the digester is of 62L/Kg M.O., the organic matter conversion rate corresponds to approximately 57%.

Key words: Batch digester, anaerobic digestion, methanisation, cameline scrap, methanogenes bacteria

Ethanol production by *Pichia stipitis* NRRL Y-7124 from olive-tree pruning hemicellulosic hydrolyzate

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Olive-tree biomass is a renewable, cheap and widespread resource that can be used to obtain fermentable sugars, mainly D-xylose and D-glucose. After finding the best conditions to sugars production by acid hydrolysis, the next step and the main objective of this research was to study olive-tree debris hydrolyzates fermentability to xylitol and ethanol production using *Pichia stipitis* NRRL Y-7124.

A representative sample of pruning material (branches and trunks with diameter lower than 50 mm) was collected in the corresponding period of time of this agricultural work (January and February) in a local farm localized in Jaén (Spain).

The conversion of this debris into bioethanol and others bio-products like xylitol or fuel gas is not an easy process. It is necessary a pretreatment in order to convert cellulose into D-glucose and hemicelluloses into D-xylose and others fermentable sugars. To obtain the hemicellulosic hydrolyzate, olive-tree pruning residue was submitted to acid hydrolysis in a 50 L stainless-steel pressure bioreactor (0.25 M H₂SO₄, solid:liquid ratio of 1:10 (w:v), 100°C, 150 min) and the resulting material was filtered under vacuum. The filtrate was kept at 4 °C and later concentrated 3 times (also under vacuum) in a 4 L evaporator at 70 ± 5 °C. The concentrated hydrolyzate was divided into 0.5 dm³ parts, which were prepared in different ways to be used as fermentation media.

The fermentative behavior of *P. stipitis* in raw and detoxified hemicellulosic hydrolyzates in agitated flasks was verified. Detoxification of hydrolyzate makes possible the kinetic behavior study. Temperatures assays were carried out at 25, 30 and 35 °C. The results shown that the yeast can consume substrate at 25 and 30 °C but not at 35 °C. The aeration was modified using a relation between volume of medium and Erlenmeyer flask (125 mL). For this, relations of 0.2, 0.4 and 0.6 were assayed. *P. stipitis* shown the best results between 0.2 and 0.4. The initial pH influence was studied and the cultures carried out at pH between 5.0 and 6.5 shown the best results. Finally, the initial biomass concentrations between 0.5 and 5.0 g/L were assayed too. A lag phase can be observed for all assays. For this yeast, the best initial cell concentration (in order with maximum ethanol yield) was 0.5 g/L, the maximum concentration of ethanol was 17.4 g/L at 96 h.

Keywords Olive-tree pruning debris; hemicellulose, fermentation; ethanol; *Pichia stipitis*;

Evaluation of genetic variability of *Jatropha curcas* L. accessions by means of RAPD and SSR markers

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The growing concern for the environment has given focus to the production and use of biofuels. *Jatropha curcas* is a promising oilseed plant species for biodiesel production, drought resistant and used for reforestation of degraded areas. It is also a viable crop for small farmers as an alternative source of income since it can be intercropped with other crops or livestock. Besides, it has a low production cost, ease of cultivation, and a high oil productivity (2 ton/ha). However, *J. curcas* not domesticated yet and it demands more studies on its agronomic technology and on the development of improved cultivars. Genetic breeding program needs variability. Therefore, we evaluated the diversity of 49 accessions of *J. curcas* from different regions of Brazil by means of 16 RAPD primers and 9 SSR primers. The RAPD primers generated 143 bands, 79.7% of them were polymorphic, while the SSR primers generated 11 bands, two of which were polymorphic. The genetic distance between pairs of accessions was calculated using the complement of Jaccard similarity index. The display representing the genetic distances was made using UPGMA algorithm. A cut for which was adopted the percentage of 61% of dissimilarity in the UPGMA dendrogram generated two clusters: a simple one with the accession 44 and another one involving all other accessions. A new analysis excluding the accession 44 revealed 13 clusters. These 14 clusters were very similar to the 15 clusters generated by a cut into the UPGMA dendrogram at a 35% of dissimilarity. However, they revealed a similarity among the accessions from different regions of Brazil, for example, the cluster comprising accessions from Minas Gerais, São Paulo, Mato Grosso and Mato Grosso do Sul States and another cluster with accessions from Minas Gerais and Ceará States, suggesting a common ancestry of these accessions. This result indicates a low genetic variability among the accessions evaluated. It should be highlighted that a new analysis that includes all 72 accessions of the Germplasm Bank has already started as well as the search for new SSR primers that could reveal the genetic variability of the plant.

Keywords Physic nut; genetic diversity; genetic improvement.

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Genetic algorithm and artificial neural network approaches to predict performance and emission parameters of a gasoline engine using TBA (Tertiary butyl alcohol) and gasoline blended fuel

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The purpose of this research is to study the effect of oxygenate additives into gasoline for the improvement of physicochemical properties of blends. Methyl Tertiary Butyl Ether (MTBE), ethanol, Tertiary butyl alcohol (TBA), has been blended into unleaded gasoline. Physicochemical properties of blends were analyzed by the standard American Society of Testing and Materials (ASTM) methods. Ethanol and TBA increased density of the mixtures, but MTBE, and DIPE decreased density. The addition of oxygenates lead to a distortion of the base gasoline's distillation curves. The Reid vapor pressure (RVP) of gasoline was found to increase with the addition of the oxygenated compounds. All oxygenates improve both motor and research octane numbers. This study presents genetic algorithm (GA) based model to predict the performance and emission parameters of a gasoline engine. The objective of this study is to develop alternative robust formulations based on experimental data and to verify the use of GA for generating the formulations for gasoline engine parameters. Experimental studies were completed to obtain training and testing data. All data sets, the training and testing sets consisted of randomly selected. Considerable good performance was achieved in predicting gasoline engine torque and brake specific fuel consumption by using GP. The performance of accuracies of proposed GA models are quite satisfactory ($R^2 = 0.9878$). The prediction of proposed GA models was compared to those of the neural network modeling, and strictly good agreement was observed between the two predictions. The proposed GA formulation is quite accurate, fast and practical.

Keywords SI engine; Ethanol, Gasoline, Engine performance, Exhaust emissions, Gasoline oxygenates,

Genetic programming approach to predict brake power and torque in SI engine using bioethanol- gasoline blends

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This study presents multigene genetic programming (GP) based model to predict the brake power and torque of a spark ignition (SI) engine. To acquire data for training and testing of the proposed GP, a four-cylinder, four-stroke test engine was fuelled with ethanol-gasoline blended fuels with various percentages of ethanol (0, 5, 10, 15 and 20%), and operated at different engine speeds and loads. Numerous runs were performed with model of GP and the performance of developed equations was evaluated for each run. The best models were selected according to statistical criteria including, root mean square error (RMSE) and coefficient of determination (R^2). The values of RMSE and R^2 for brake power were obtained 0.388 and 0.998 respectively, for training sets and 0.659 and 0.995 respectively for testing sets. Also the results showed that the values of RMSE and R^2 for torque were 0.524 and 0.999 respectively, for training sets and 0.731 and 0.998 respectively for testing sets. Considerable good performance was achieved in predicting SI engine brake power and torque by using GP.

Keywords SI engine; ethanol-gasoline blends; multigene genetic programming

H₂ production by glycerol steam reforming using CoRh/mixed oxide catalysts

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The H₂ production by glycerol steam reforming has been studied using mixed fluorite-type oxides of CeZrCoRh as catalysts. The effect of the Ce/Zr molar ratio on the catalysts properties and their influence on the catalytic behaviour was discussed. Three catalysts were prepared with different Ce/Zr molar ratio: Ce_{0.53}Zr_{2.97}Co_{0.47}Rh_{0.03}O_{8.8} (CZ^PCoRh - 0.20/0.80 molar ratio), Ce₂Zr_{1.5}Co_{0.47}Rh_{0.03}O_{8.8} (CZ^ICoRh - 0.65/0.35 molar ratio) and Ce_{2.59}Zr_{0.91}Co_{0.47}Rh_{0.03}O_{8.8} (CZ^RCoRh - 0.80/0.20 molar ratio). The different causes of deactivation are also presented. The catalysts were characterised before and after catalytic test by XRD, Raman spectroscopy, H₂-TPR, H₂-TPD, TPD-TPO and HR-TEM. The results showed that the increase in the cerium amount enhances the stability and selectivity towards H₂ production (fig. 1, zone A). This is related to the improve in different properties as the redox capacity, oxygen storage and metal support interaction. The decrease of the catalytic activity (zone B) was observed by the decrease of the global conversion along with a change of selectivity, increasing the formation of the condensable products (mainly hydroxyacetone) and decreasing the formation of non-condensable products. The H₂ production also decreased because of a change of selectivity in the gas phase being CO, CH₄ and C₂H₄ favoured with respect to H₂ and CO₂. In zone B the glycerol decomposition appears, decreasing the reforming capability by the formation of carbon deposits. According to the different by-products analysed, two reaction systems were proposed: (i) the non-condensable products, H₂, CO₂ and CO are formed by glycerol steam reforming, or (ii) can arise from the steam reforming of the condensable products, produced thermally before reaching the catalyst. The WGS reaction also plays an important role to convert CO into H₂ and CO₂. CH₄ could arise from methanation of CO, formed with H₂ by glycerol decomposition. The main condensable products, hydroxyacetone, acetaldehyde and acrolein were formed by glycerol dehydration on acid sites. The methanol production is related to ethylene glycol hydrogenation followed by irreversible C-C bond cleavage. Finally, the formation of carbon deposits can also be related to the formation of hydroxyacetone and acrolein: by the further dehydration of the molecule of acrolein and by the oligomerisation of hydroxyacetone to form polyglycerol species which may lead to coking reactions. Thus, the activity results demonstrated that the selective H₂ production is related to the capacity of the catalysts to activate the H₂O under reaction conditions. This step ensures the reforming of the by-products until H₂. The loss of this capability decreases the H₂ production decreasing the steam reforming capability and favouring the glycerol decomposition. In this last stage, the production of CO, CH₄ and C₂H₄ is promoted and also the formation of condensable products as hydroxyacetone, acetaldehyde and acrolein is favoured.

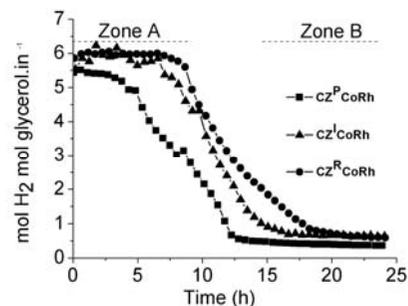


Figure 1. H₂ production at 650°C

Heterogeneous catalysis and Dark fermentation integrated system for the conversion of cellulose into biohydrogen

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1. Introduction

Fossil fuels contribute to about 85% of the total world energy usage causing a depletion of the reservoirs. The development of clean and sustainable alternative energy sources is a global priority. In the planet, the energy capture by photosynthesis is approximately 100 terawatts, about six times the energy consumption of the civilization. This makes biomass a natural renewable source for energy production. Cellulose is the most abundant non-food constituent available in plant biomass. It is a chain of glucose units bond by β-1, 4-glycosidic linkages which confers a highly recalcitrant nature [1]. Typically, the direct cellulose dark fermentation into hydrogen requires chemical or physical pre-treatments [2]. Here an integrated system between heterogeneous catalysis and dark fermentation was developed. The hydrolytic capacity of the ZrO₂ catalyst was modulated by different promoters for the cellulose conversion into smaller sugars. The resultant sugars were further submitted to dark fermentation.

2. Experimental

Promoted ZrO₂ was prepared by incipient wetness impregnation with different electronegative ions at 5 wt% and they were labelled as zirconium phosphated (ZrO₂-P), fluorated (ZrO₂-F) and sulphated (ZrO₂-S). The pure ZrO₂ was also studied. The ZrO₂ materials were structurally characterized by XRD. NH₃-TPD was performed for the total acidity determination. Surface area and porosity properties were evaluated by N₂- physisorption. The surface structure of the remaining cellulose after the reaction was studied by SEM. The hydrolysis of cellulose (16g/l) was carried out at 453 K and 30 bar for 15hrs. The resulting products were analyzed by TOC and HPLC to determine the cellulose solubilisation and selectivity to glucose, respectively. The dark fermenting was done in 100 mL serum bottle in anaerobic condition. *Enterobacter* sph1 and *Citrobacter freundii* H3 were employed. An overnight grown inoculum of 10% (v/v) was transferred to a synthetic medium having 0.5% (wt/v) of the catalytic treated carbon source. Hydrogen was measured using a tight syringe after an incubation of 72 hrs in GC-14B. The end fermentation products were analyzed by HPLC.

3. Results and Discussion

From the XRD patterns of the ZrO₂, ZrO₂-P and ZrO₂-S the zirconium tetragonal phase was mainly the observed. For the ZrO₂-F, the monoclinic phase was most dominant. The promoter effect over the ZrO₂ textural properties were also mirrored in the N₂-physisorption results (Table 1). The ZrO₂ surface area decreased from 113 to 52m²/g when promoted by phosphate. ZrO₂-S, ZrO₂-P and ZrO₂-F presented similar range of pore size. Based on the Figure 1 it is noteworthy that the cellulose conversion was enhanced for all promoted zirconium materials with respect to the pure zirconium oxide. The highest selectivity (15.8%) towards glucose was obtained by ZrO₂-P material. The ZrO₂-S presented the lowest selectivity (4.5%) towards glucose and the highest conversion (20%). This can be explained by the fact that the sulphate species confers highest acidity (Table 1) that induces higher hydrolysing capacity to the catalyst. Examination by SEM of the fibers from the cellulose surface after catalytic test revealed that they suffered degradation compared to the smooth ones of the pure cellulose. The product of the reaction catalysed by ZrO₂-P was effectively used by the microorganism, without any additional treatment, totally converting the remaining glucose into biohydrogen and other byproducts.

Table 1 N₂ adsorption and NH₃-TPD analysis data

Sample	BET (m ² /g)	Pore size (nm)	Acidity (μmol NH ₃ m ⁻²)
ZrO ₂	113	4.15	61
ZrO ₂ -P	52	4.15	307
ZrO ₂ -S	59	4.53	372
ZrO ₂ -F	63	8.15	31

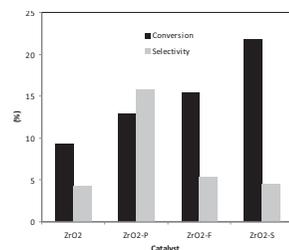


Fig. 1 Catalytic performance of the promoted ZrO₂ samples.

Keywords: cellulose, hydrolysis, ZrO₂, phosphated, catalyst, glucose, bacteria

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High Efficiency Microalgae isolated from Persian Gulf and large scale biodiesel production in 25.000 L. Open pond

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In previous study we are screening of 147 microalgae isolated from Persian Gulf for their biomass productivity and lipid content (Moazami et al., 2011). *Nannochloropsis* strain PTCC 6016 which attained 52% lipid and 46.4 mg/l/d productivities selected for large scale production in 2000 and 25.000 liters open pond.

The strain was grown outdoors in seawater and under natural sunlight condition. An average of biomass productivity of 2.81 g/l/day and 50 % lipid content was obtained.

The experiment showed that this microalgae has the potential for an annual production of 280 tons biomass and 140 tons of lipid / hectare / year.

Scale-up experiments with the Eustigmatophyte, *Nannochloropsis* sp. PTCC 6016 were carried out in 2.000 L. open pond under 50% sunlight illumination (greenhouse) and 25.000 L. outdoor open pond under direct sunlight illumination in seawater to evaluate the influence of light intensity, and concentration of nitrogen and phosphorus on culture productivity and fatty acid accumulation. The culture system used in these experiments consisted of four 2000 L. indoor and three 25.000 L. outdoor open pond.

Microalgae cultivated in sea water and batch condition for 2 weeks. Illumination was provided by daily sunlight (180 and 300 μmol PAR photons/m²/s indoor and outdoor respectively), the reactor was contained paddle well for mixing and gas exchange. Paddle well maintained with 20 rpm/min. CO₂ was added to pond to provide carbon source to microalgae and maintain pH at 7.5±2 for one week. In the second week with the rise of pH to over 8, microalgae cells concentrate high quantity of oil. CO₂ was injected into the culture through a gas diffuser for pH regulation.

The *Nannochloropsis* PTCC 6016 with a lipid content of 52% and lipid productivity, showing the best combination of biomass productivity and lipid content, perform well in outdoor conditions, were among the best producers in terms of biomass and lipid. Selection was guided not only by biomass productivity and lipid content, but also by the strain robustness and capacity to dominate for relatively long periods in high temperature and high radiation in outdoor culture

Table-1-Biomass productivity in indoor and outdoor Open pond

Pond	Light irradiance	Temp per culture	Paddle wheel speed	Biomass productivity
Indoor (Pond No. 1)	180 μmol PAR photons/m ² /s	30 °C	20 rpm	2.2 g/L/day
Indoor (Pond No. 2)	180 μmol PAR photons/m ² /s	30 °C	15 rpm	1.97 g/L/day
Indoor (Pond No. 3)	180 μmol PAR photons/m ² /s	30 °C	15 rpm	1.89 g/L/day
Indoor (Pond No. 4)	180 μmol PAR photons/m ² /s	30 °C	20 rpm	1.91 g/L/day
25.000 L. outdoor pond	300 μmol PAR photons/m ² /s	32 ± 3 °C	22 rpm	2.81 g/L/day



Generally under nutrient shortage, the fraction of lipids may increase, cellular growth declines with the overall effect being a decrease of lipid productivity

Nannochloropsis PTCC 6016, appears as a glaring exception, it was observed in our trials that lipid synthesis may continue in this organism culture period, not only at the expense of other cellular components, but starting from newly fixed carbon, and this generally is coupled with enhanced lipid productivity.

Key word: Microalgae; Biodiesel; *Nannochloropsis*; Raceway pond; Paddlewheel speed

High efficient bio-ethanol production method to offer competitive alternative spark ignition engine fuelling

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Biofuels have an increasing utilization in the internal combustion engines applications in order to improve the engines economical performances and to limit the levels of the exhaust emissions. Among these new types of fuels, alcohols, especially ethanol and methanol have received recognition of their capacities to replace the use of the classic fossil fuels.

Ethanol has been proved to be an efficient substituting fuel in the spark ignition (SI) engines due to its good miscibility with gasoline and to provide better results concerning the hydrocarbons and CO₂ concentrations from the exhaust gas emissions. Therefore UE market policies encourage the further development of the automation industry using ethanol-gasoline dual fuelling technologies. Ethanol produced from the biomass extracted from the rapid cycle poplar culture presents certain benefits in terms of production, environmental protection and fuel properties (caloric heat, viscosity and lubrication etc). Bio-ethanol seems to become an important agent to be used in the alcohols based on fuel-cells due to its safer storage and operation conditions.

This paper presents original results based on bio-ethanol obtained through enzymatic fermentation of the sugar compounds extracted from wooden biomass (obtained by bio-hydrolysis using Metha Plus L100 that contains β -glucanases, cellulases and xylanases) which is a new method for bioethanol preparation. This one has been harvested from special poplar clones with rapid growing cycle (coded as Sacrau 79, AF-8 and Monviso) coming from three different regions of Romania. The alcoholic fermentation process was achieved by using *Saccharomyces Cerevisiae*. The resulting product is submitted to breakage, azeotropic distillation and physico-chemical characterization for its mixing with gasoline. Due to its good miscibility with gasoline some tests could be performed using gasoline-ethanol mixtures within 0 and 30% ethanol substitution mass. Theoretical simulation of air-fuel mixture formation inside the engine cylinder as for its combustion and heat release is also to be described in order to highlight benefits consisting in SI engine increasing efficiency and emissions' levels decrease (especially in case of hydrocarbons and CO₂).

Key Words: bio-ethanol, wooden biomass, enzymatic fermentation, engine efficiency, low emissions

High methane gasification of biomass - experimental studies

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This paper presents the preliminary results of the experimental research on low pressure (atmospheric pressure) process of gasification of biomass in a dual-layer gas generator. The first layer is a biomass coke, and the second - biomass from agricultural waste. The gasing factor is the air. We point out the high proportion of combustible synthesis gas components including mainly CH₄ which translates to high efficiency of the generator process. High performative, especially highmethane synthesis gases generation technologies are justified by the possibility of development of low emission energy technologies. The synthesis gas with a high proportion of CH₄ is an excellent reburning fuel, used in combustion processes for effective NO_x reduction. Despite these technological perspectives suggesting favorable conditions for operating the system boiler-generator, so far there have been very few implementations of co-combustion e.g. of synthesis gas with coal.

In the processes of synthesis gas production, waste fuels are used mainly in the form of wood biomass (such as construction and forestry waste) or fuels formed from waste such as RDF. Such fuels are usually gassed in fixed bed technology, and at high water content the process is carried out in rotating chambers. Such arrangements are typical for small gas capacities, where the main combustible component is CO and H₂, and CH₄ yield is estimated to about 1%. Large capacities and performances of gas generators are obtained in the fluidized bed technologies. Their advantage is beneficial (of about 75%) chemical conversion of fuel to gas factor, which is justified with a relatively high proportion of combustible gases, e.g. CO- 22%, CH₄ - 3-7%. Higher concentrations of these gases are obtained by gasifying biofuels in an air environment with water vapor and oxygen with water vapor. Approximately 36% of CH₄ in the synthesis gas was obtained during the gasification in a fluidised bed, of fuel in the form of a mixture of coal, pine waste wood and plastic. The process was carried out using gasification agent which were air and water vapor. The increase in efficiency can be achieved by upgrading gas generators structures, such as: changes in shape and allocation of blast to nozzle gasifying agent, construction or shape of the grill gasifying chamber. Good results are obtained in the cyclone chambers, where with high fragmentation of biomass fuel the methane yield can reach a value of 10%. Given the quality of gas reburning fuel, gasification process can be implemented more effectively if it is proceeded in two layers, i.e. biocoke and agricultural biomass such as waste grain and wastes from the production of vegetable oils. This biomass, due to specific abilities to produce zones of reduction (fat content), naturally favors the formation of methane in the gasification process. Experimental studies presented in this paper have shown that the maximum yield of methane, in the case of gasification extracted rapeseed meal was 10.4 -14.7% at T = 541.5-563.8^oC, oat - CH₄ = 11.6% at T = 638.2 - 642.3^oC. While gasification in two layers, i.e. coke timber (layer I), extracted rapeseed meal (layer II) could result in the amount of methane CH₄ = 23% - 47.2% at T = 957.6 - 982.2^oC. The process was carried out continuously in the laboratory gas generator in air environment. Gas generator power was 3 kW.

The results of experimental studies show that in the case of two-layer gasification, methane rich gas can be effectively used as reburning gas in boilers fired mainly with coal dust. The results also suggest that in the longer term, research should examine the process of thermal treatment of the first layer, i.e. bio-coke in the stream of water vapor and air. High temperatures of around 900^oC are encouraging, where may occur favorable to the coal, complex process of carbonate activation according to the following sequence of equations: C+ H₂O→C (H₂O); C(H₂O)→H₂ + C(O); C(O)→CO, which involves the creation of additional products, valuable in terms of energy, such as H₂ and CO. High share of CH₄ in the synthesis gas also suggests the possibility of using steam reforming to increase the participation of hydrogen.

Keywords biomass, coke, gasification , high methane

Hydrogenation of animal fat and waste vegetal oils to biofuels production

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Nowadays, modern society relies deeply on solid, liquid or gaseous fuels from fossil sources to produce energy. Due to economical, social, and environmental issues, it becomes crucial to obtain alternative fuel sources. The combustion of transportation fuels contributes, considerably, to the emission of greenhouse gases, so it is essential to find new neutral carbon technologies that can lead to the production of clean and renewable transport fuels. The use of different materials, such as waste oils and animal fat, is one of the most promising ways to replace conventional diesel fuels with positive effects to the environment. Vegetable oils and animal fat have suitable properties (high triglyceride content and negligible sulphur, nitrogen and heavy metal content), to be used as an important source for the production of alternative fuels. Different technologies have been studied but hydrogenation seems to be a simple and efficient method for fuel production using this material.

The hydrogenation and cracking of these raw materials (with high triglycerides content) leads to the formation of a liquid product that can be further mixed with conventional fuels and used in conventional storage and distribution systems and in engines. The main advantage of this process is the possibility to use oils from several sources (including used oils) and also waste animal fat, to produce a liquid product with a consistent quality.

The studies that have been carried out, in this field, mainly use vegetable oils like soybean, rapeseed, sunflower and palm to produce biofuels. However, the high prices of these vegetable oils and the controversy around the use of materials which compete with food crops, lead to the necessity of finding alternative resources to produce biofuels. Moreover, the application of the transesterification process in animal fat and waste vegetable oils can present some problems due to their fatty acid profile. Consequently, it is very important to find other efficient technologies to process this kind of wastes.

In this study the conversion of different materials into a different biofuel by catalytic and non-catalytic hydrogenation were tested. Different materials, such as, animal fat, olive husk oil and waste fried oil were used. The effect of experimental parameters in the product yields and quality was evaluated with the aim of selecting the most favourable conditions to lead to liquid yield maximization and a better final product quality. The parameters tested were reaction temperature, reaction time and nitrogen initial pressure.

Hydrogenation experiments were carried out in a high temperature and high pressure batch reactor (Parr Instruments), at temperatures from 350°C to 450°C, nitrogen pressures of 80 and 160 psi and reaction times from 30 to 120 min. Also the effect of three different catalysts was assessed. The gaseous products were collected, measured and analysed by GC (gas chromatography). The liquid products obtained were fractionated by distillation and characterized by GC-MS (gas chromatography with mass spectrometry) and GC-FID (gas chromatography with flame ionization detector).

Experimental results obtained so far showed that, this three different material, can be efficiently converted to hydrocarbons mixtures with different applications. Regarding the effect of experimental conditions, higher temperatures and residence times seems to favors the gas yield, because besides hydrogenation, some cracking reactions also occurred. The gas fraction is, mainly composed by CO and CO₂. Hydrocarbons are also produced, being methane and ethane the compound present in higher concentrations.

Keywords hydrogenation; animal fat; waste oils; biofuel,

ILs for applications in biomass conversion and reprocessing

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Biomass, composed mostly of such biopolymers like cellulose, hemicellulose, and lignin, starch, chitin is currently one of the most underutilized renewable resources available to humans. So where is the main problem with utilizing this virtually endless resource? This state is mostly due to difficulty with processing biomass itself, which comes to a limited number of common solvents in which the biopolymers can be dissolved and fractionated. Current methods for the separation lignocellulosic biomass and recovery of pure fractions of individual components like cellulose and lignin, still in most cases involve chemical pulping, which accounts for almost ¾ of worldwide production of pulp. Such processes like Kraft and Organosolv besides being economically expensive (multiple reactors, caustic chemicals, large amount of water use, bleaching) often produce large amount of waist.

Even though there are over a 1000 literature reports on the dissolution and reprocessing of biomass utilizing ionic liquids, screening for new ILs capable of dissolution and reprocessing of biomass is far from over. This is mostly due to enormous amount of the ion combinations that can be prepared as ILs.

In our laboratory we have a privilege of being able to test hundreds of ILs at the same time as our ILs catalogue contains over 300 IL products and most of them we have in stock. Utilizing know-how about structure-property-relationships and available literature reports we have selected a matrix of 48 ionic liquids composed of various cations and anions (Figure 1) and tested their dissolution power toward three biopolymers: cellulose, lignin and starch. The IL selection criteria involved considerations of: (i) kind of cation core (pyrrolidinium, imidazolium, aromatic, aliphatic, cyclic), (ii) length of alkyl chains, (iii) functional groups on alkyl chains, (iv) anion kind.

Our initial results support our hypothesis that tuneability of properties of ionic liquids through modification of the structure of the cation and anion allows to select particular IL for specific applications, as in presented case, dissolution of biomaterials (Figure 2). In our presentation we will present initial results and an outlook on the applicability.

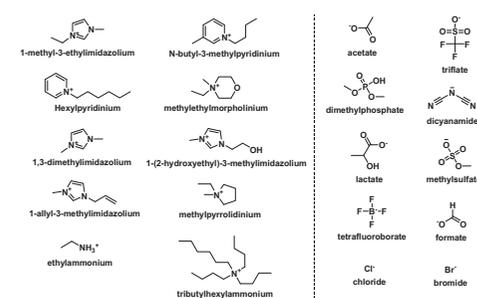


Figure 1. Examples of classes of cations (on the left) and anions (on the right) used for the biopolymers dissolution studies.

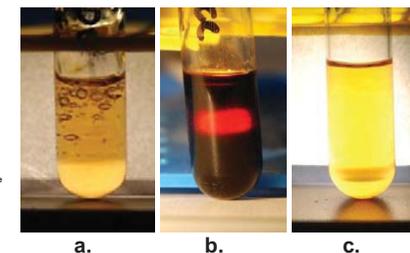


Figure 2. Successful examples of dissolution of biopolymers in ILs; a. 10% cellulose in IL; b. 5% lignin in IL; c. 5% starch in IL

Keywords ionic liquids; biomass; biomass dissolution; biopolymers

Influence of biodiesel fatty acid composition on exhaust emissions and engine performance

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The increase of the use of biodiesel in developed countries has promoted the study of different raw materials to produce this alternative fuel. Biodiesel (fatty acid methyl esters, FAME) is produced by transesterification of triglycerides from vegetable oils or animal fats. The most important physical and chemical properties of biodiesel, such as iodine value, calorific value, kinematic viscosity and cetane number depend on the fatty acid composition of biodiesel (Knothe 2008; Pinzi, Leiva et al. 2011). It has been demonstrated that engine performance and exhaust emissions depend on these physical and chemical properties; for this reason, it may be inferred that engine performance and emissions must be correlated to biodiesel fatty acid composition. The objective of this study was to evaluate the effect of fatty acid composition of the raw material used for biodiesel production on engine performance and exhaust emissions. Biodiesel was produced by the transesterification of sunflower oil, coconut oil, palm oil, linseed oil and pomace olive oil. Raw materials were chosen according to their variety in fatty acid composition, considering their unsaturation degree and hydrocarbon chain length. The most important physical and chemical properties of each biodiesel were analyzed according to the standard EN 14214. Next, biodiesel was blended with diesel fuel at 20% and 50% vol/vol and further tested in a farm diesel engine (Perkins model AD 3-152) by a portable dynamometer (Froment NJF). The higher the percentage of biodiesel in the blend, the higher the brake fuel consumption. Using a portable Testo 350-S exhaust emissions monitor, a reduction in emissions of carbon monoxide (CO) with the increment of the content of biodiesel in the blend was found. Also, the higher the fuel kinematic viscosity, the higher the noise (tested with a Soundbook instrumentation series) and CO emissions. In this sense, a linear correlation between kinematic viscosity and biodiesel unsaturation degree was found. Therefore, it may be concluded that the use of biodiesel in an internal combustion diesel engine produces an increase of fuel consumption and a reduction of CO emissions. Moreover, to reduce the noise and CO emissions, biodiesel from oil with a high degree of unsaturation is recommended.

Keywords Nitrogen oxides emissions (NOx), sunflower methyl esters, coconut methyl esters, palm methyl esters, saturated fatty acids

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Influence of the zinc, magnesium, thiamine and pyridoxine supplementation on the fermentation of sugar beet juice to bioethanol

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There are many attempts to scale-up the production of second and third generation of biofuels but ethanol from simple converting raw materials, like starch or sucrose containing, remains still one of the most important biofuels. It's expected that ethyl alcohol will be one of the dominating biofuels for next 10-30 years. Production of ethanol from sugar beet, due to high sugar concentration, is an easy way to obtain the sustainable fuel, ready to use in the transport. Bioethanol manufacturing process is strongly dependent on yeast activity. Despite that alcoholic fermentation seems a well-known process, fermentation activity of *Saccharomyces cerevisiae* depends on many factors, also on the presence of microelements like zinc and magnesium but also B-group vitamins.

Aim of this study was to establish the influence of zinc, magnesium, thiamine and pyridoxine addition to sugar beet thick juice based worts on the fermentation dynamics and ethanol yield.

3 hybrids (ER2, TSC8 and PM14) of distillery yeasts obtained by means of sexual hybridization in the Institute of Fermentation Technology and Microbiology (Lodz Technical University) were used as a biological material. Fermentations of thick juice diluted to 20°B_g enriched with mineral salts and nitrogen were carried out for 5 days at 30°C. Worts were also supplemented with thiamine (0-50µg/L), pyridoxine (0-100µg/L), Zn²⁺ (0-100mg/L) and Mg²⁺ (0-500mg/L). Yeast suspension in sterile water, was added in the dose of 1g of d.m./L to start the fermentation. Initial phase of fermentations lasted for approximately 30-48 hours and ethanol yield approached 76±91% of the theoretical.

Thiamine and pyridoxine dosage increased the ethanol yield. Additionally, thiamine supplementation resulted in the shortening of initial fermentation phase, whereas no such effect was observed for trials with pyridoxine. Fermentation of the samples supplemented with magnesium revealed that those elements, in the experiment conditions, had less significant impact on fermentation than vitamins. Zinc supplementation increased total ethanol yield by 2-3 %, comparing to samples without zinc sulfate addition, however no impact on fermentation dynamics was observed.

Concluding the results it may be stated that it's advisable to supplement worts prepared from sugar beet thick juice with zinc and magnesium (both in the dose 50mg/L), also with thiamine and pyridoxine in the dose 50 and 100 µg/L respectively.

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Keywords: sugar beet juice; bioethanol; zinc, magnesium, thiamine, pyridoxine

Investigations into combustion characteristics of fuels (Biomass) and influences on ceramic materials, to prevent heat exchanger/heat pipe corrosion

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In order to increase the efficiency of medium to high temperature processes – heat recovery extracted from waste gases through the use of heat exchangers has an overall significant impact. Currently metallic heat exchangers have been applied in various process plants, although their application has been limited in corrosive and high temperature atmospheres. Non oxide ceramic materials (e.g. SiC, SiSiC) inhibit features that make them appropriate as an alternative to metals. Comprehensive tests are required for these ceramic materials in terms of durability under such conditions prior to their use in heat exchanger modules.

The increase in energy requirements and the challenge to reduce CO₂ levels has led to the renaissance of biomass based fuels as opposed to the standard fossil fuels. On the other hand the biomass based fuels contain corrosive components like potassium (K) and chlorine (Cl) which can lead to corrosion in process plant components like the boiler, heat exchangers, superheaters. Thus the wide spread use of ceramic heat exchangers can be undertaken after investigations to their applicability in these conditions.

The presented work therefore focuses on the ceramic materials (SiC, SiSiC) investigations in the following atmospheres:

- Corrosive atmosphere – Biomass firing system
- Oxidative, reductive and abrasive atmosphere – Circulating fluidized bed

The investigations are thus important for the optimization of combustion processes, inclusive of biomass, heat and power plants.

Keywords: Heat exchanger; Biomass; Corrosive; Sintered silicon carbide (SiC); Silicon infiltrated silicon carbide (SiSiC)

Kluyveromyces marxianus mutant strains for improved ethanol fermentation with Jerusalem artichoke

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Kluyveromyces marxianus is a thermotolerant yeast species having characteristics of a short doubling time and a broad range of carbon utilization compared with *Saccharomyces cerevisiae*, the work horse in current ethanol production process. Therefore, *K. marxianus* is being investigated for potential applications in bioethanol production from various carbon sources in biomass including inulin from Jerusalem artichoke, lactose from whey, and hexoses and pentoses from lignocellulosics. In an attempt to improve carbon utilization in Jerusalem artichoke, we isolated *K. marxianus* mutant strains for improved ethanol fermentation with Jerusalem artichoke. *K. marxianus* NCYC2887 strain was subjected to UV mutagenesis, resulting in mutants with several-fold improved inulinase activity. The inulinase gene was also cloned from *K. marxianus* NCYC2887 strain and expressed in a *S. cerevisiae* for ethanol production from Jerusalem artichoke without inulinase pretreatment. The fermentation performance of *K. marxianus* mutant strains in ethanol production with Jerusalem artichoke was studied in comparison with the recombinant *S. cerevisiae* strain expressing the inulinase gene from *K. marxianus*.

The *K. marxianus* UV mutants behaved different from the wild type strain in carbon source utilization. The mutant strains could utilize lactose more efficiently than the parent strain. The lactose utilization was not dependent on aeration. The mutant strains could efficiently ferment a mixture of lactose and Jerusalem artichoke without significant sugar preference.

Acknowledgements

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Keywords *Kluyveromyces marxianus*; Jerusalem artichoke; ethanol

Microalgae production for biodiesel using mixed system (batch, turf scrubber and photobioreactor)

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Bioenergy is an important subject considering environmental issues and also a good opportunity for business. In Brazil, there are adequate conditions for bioenergy production, considering the diversity of aquatic resources, the solar position and large agricultural area, among other advantages.

Microalgae is an excellent alternative for biodiesel production associated with bioremediation of wastewater in relation to the removal of nitrogen and organic matter. The high biodiversity of microalgae combined with genetic improvement and the development of a technology for large scale cultivation, allows its use in various applications, in particular the treatment of wastewater from industrial processes, mitigation of greenhouse gases by the assimilation of carbon dioxide (CO₂), and the production of biofuels such as biodiesel and ethanol. In this context, this work involves the construction and operation of a conjugated system of microalgae cultivation at the University of Santa Cruz do Sul (Fig. 1), using the effluent from the sewage treatment plant of the university, assessing the growing capacity, nutrient removal and the oleaginous potential of the algae's biomass, in order to be used in the future for the production of biodiesel.

To monitor the cell density and biomass dry weight a method with UV/vis spectrophotometer was standardized and a good correlation coefficient ($R^2 > 0.98$) was obtained. For the recovery of microalgal biomass, an electroflotation method with iron plates electrode was also evaluated. The results indicated the development of various strains of microalgae, obtaining a maximum cell density of 25.48×10^6 cells mL⁻¹, 620 mg L⁻¹ of dry biomass and lipid percentage of 1.36 % without CO₂ injection. The values for the cultivation with addition of CO₂ in 15 days were 26.97×10^6 cells mL⁻¹, 720 mg L⁻¹ dry weight and lipid percentage of 6.07%. The averaged content of extracted oil was lower than the results obtained using a tubular photobioreactor for cultivation of the microalgae *Desmodesmus subspicatus* (CHLOROPHYTA). With *D subspicatus* the average content extracted oil was 18 and 12% for the cultivation with and without the input of CO₂, respectively.

Using the effluent from the sewage treatment plant of the university in the mixed system for microalgae cultivation, there was a remarkable reduction in the alkalinity, total phosphorus, ammonia nitrogen and total Kjeldahl nitrogen parameters. The results indicated that there was assimilation of nutrients (biomass growth) mainly in the culture with CO₂ injection. The variation of the effluent composition and the presence of carbon dioxide did not provide distinct fatty acid profiles compared to the conventional cultivation methods and without CO₂ injection. In all samples, the main fatty acids obtained were the C16: 0 (palmitic acid) and C18: 1 (oleic acid).

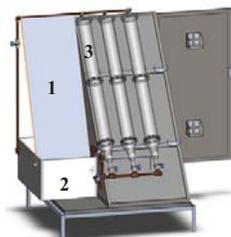


Figure 1 – Mixed system for microalgae Production. (1) turf scrubber system, (2) batch system and (3) photobioreactor.

Keywords microalgae, biodiesel, mixed system, biorremediation

Novel Techniques (Sonochemistry and Microwave) for the preparation of Biodiesel and Bioethanol

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I will report on the full conversion (~100%) of oils to biodiesel. This was accomplished by the transesterification of pristine (soybean) oil and restaurants cooked vegetable oil to biodiesel, based on microwave dielectric irradiation as a driving force for the transesterification reaction and SrO as a solid basic catalyst. This combination has demonstrated excellent catalytic activity and stability. According to ¹H NMR spectroscopy and TLC results, this new combination accelerates the reaction, so that the reaction was completed in 10 seconds when stirred, and 40 seconds when unstirred, maintaining a very high conversion (99%) and high efficiency. The catalyst was reused for 5 times and showed the same catalytic power.

We will also demonstrate the direct conversion of as-harvested *Nannochloropsis* algae into bio-diesel without separating the lipidic phase. The results are based on the use of two novel techniques. The first is a unique biotechnology-based environmental system utilizing flue gas from coal burning power stations for microalgae cultivation. This method reduces considerably the cost of algae production. The second technique is the direct transesterification (a one-stage method) of the *Nannochloropsis* biomass to bio-diesel production using microwave and ultrasound radiation with the aid of a SrO catalyst. In the early stages of this research the lipidic phase was extracted from the microalgae and transesterification followed it. Later we became courageous and carried out the transesterification directly on the as-harvested microalgae. Full conversion to biodiesel was achieved in 5 minutes.

Bioethanol is a renewable and environmentally benign substitute to the current fossil fuel based transportation fuels. Fermentation of sugars, which is in general a slow process, forms an inevitable step in the production of ethanol from renewable sources. The aim of the research work is to accelerate the fermentation process. Fermentation of glucose was carried out using *Saccharomyces cerevisiae* under continuous mild ultra sonication conditions. The kinetics of the fermentation reaction was monitored by ¹³C NMR spectroscopic analysis and weight loss measurements of the fermentation broth. The reaction rate constant was enhanced by 2.5 and 2.3 times as a result of sonication at 20 and 30 °C respectively compared to stirred control experiments, and 10 times faster than the non stirred fermentation. The acceleration in the fermentation of glucose is observed both at 20 and 40 % concentrations of glucose. Thus mild ultrasound has the potential to accelerate the fermentation process by a factor of 2.5.

I will also present preliminary work on glycogen which is related to conversion of commercial glycogen to glucose and also the glycogen synthesized from CO₂ using cyano bacteria into glucose. Microwave energy has provided an easy way to depolymerize (hydrolyze) glycogen. With 1 M of HCl, the complete conversion of glycogen (commercial) to glucose was achieved in 5 minutes. With 0.2 M HCl, complete conversion of the glycogen synthesized using cyano bacteria could be achieved in 10 minutes. Such a conversion under regular reflux conditions at 80 °C in 1 M of HCl requires more than 6 hours.

Finally, The best example of the conversion of biomass to ethanol is our successful conversion of Pine Cones to ethanol. A simple methodology based on the alkaline pretreatment of the biomass was developed to separate lignin from the pine cone and get cellulose and hemicellulose exclusively.



Figure 1. Pictorial representation of pine cone from *Pinus radiata*

Numerical identification of design parameters enhancing a mini-hybrid system of energy renewable “solar – biomass” for the electricity generation

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Because of global trends to deregulate the energy market and the reduction of energy costs, industrial manufacturers of Canada more opt for a way of bigger energy efficiency while using the alternative energies for the production of steam and/or electricity. With regard to the solid biomass, it can be converted into energy in several different ways. It can be burned directly to produce steam and electricity. The principle used to produce electricity consists in recovering the energy of biomass combustion for the production of steam, that, on its turn, is sent to a steam-powered turbine to drive an alternator. This process is profitable for the steam-powered turbine and the whole plant if the power to generate is higher. Other technologies have been developed that involve gasification of biomass fuels. In this process, biomass is converted to gas for direct biomass fired gas turbines. This leads, among other factors, to the corrosion and the fouling of turbine blades. However, for the ranges of weak power (until 5 MW), the concept of indirectly fired gas turbine is commonly utilized. This consists to use a heat exchanger to transfer heat from the biomass combustion to clean air, which passes through a turbine to create electricity. Due to material considerations in the combustion chamber and the heat exchanger, the turbine inlet temperature is fixed at full load conditions. This concept presents particular advantages for environmental and technic aspects. Indeed, turbine blades are solicited solely by the hot air that is cleaner than the gases of combustion of the biomass. Although the concept of use of this indirect principle seems to be simple to first seen, but, there are again big technical challenges for the improvement and the optimization of the global efficiency of biomass thermal power plant using an air turbine. Several research works have been published for air turbines and the utilization of biomass for the electricity production. However, many aspects of these cycles still need extensive study for the plant performances by using further component configurations for the regenerator and the combustion chamber.

In the frame of this work, a numerical model of a mini-hybrid system of energy renewable “solar – solid biomass” thermal power plant was developed to deeply study and identify parameters which improve its performances. This model included physical phenomena, inherent of real operating of a solar power plant and a biomass thermal power plant. For the solar energy, cylindro-parabolic solar collectors were used to collect heat by absorbing sunlight. A steam turbine and an air turbine were used for the electricity generation. The heat input to air for the air turbine and to water for steam production for the steam turbine was obtained by means of heat exchangers, solar system and a combustion chamber of solid biomass. A special emphasis was made on the biomass combustion chamber which was also modeled to accurately predict combustion products and to enhance its static and dynamic behaviors. Numerical simulations were accomplished to prove the effectiveness of the present work in model prediction of static and dynamic behaviors of a mini-hybrid solar-biomass power plant. The developed model was validated by comparing obtained numerical results with the published results in the literature relative to solar and biomass power plants. Further research work is planned to complete this study by designing and constructing a prototype of hybrid solar-biomass power plant for experimental validation.

Key words Solar energy; Biomass; Wood Residues; Modeling and Simulation

Optimization of biodiesel production from some wild non edible oil yielding plants

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In recent times, the world has been confronted with energy crises due to depletion of fossil fuel resources. At the same time increase in petroleum prices, environmental pollution and diminishing supply of fossil fuels are the key factors leading to search for alternative sources of energy. Currently the most often used type of biofuel is biodiesel which is renewable, biodegradable and non toxic fuel for diesel engines. It is derived from vegetable oils by transesterification with alcohols. The main hurdle to the commercialization of biodiesel is the cost of raw materials. The high value of edible oils a food product makes production of a cost effective fuel very challenging. To overcome these hurdles, non edible, inexpensive low grade seed oils with value added byproducts is utmost important to make the biodiesel production economical. This project is initiated in Pakistan with concept of mega tree plantation for green fuel for green Pakistan. The overall objective of this project is to reduce carbon in atmosphere using renewable green fuel. To investigate the impact of mega tree plantation on degraded barren and eroded land to overcome the energy crises, environmental pollution and promote biodiversity and ecosystem conservations in Pakistan. This study described in detail an optimized protocol for biodiesel production from non edible oil seeds i.e. hemp oil (*Cannabis sativa* L.), castor bean (*Ricinus communis* L.), neem oil (*Azadirachta indica* A. Juss.) and pongame (*Pongamia pinnata* (L.) Pierre.) Crude oil of these non edible oil seeds is converted into green fuel through base catalyzed transesterification by using an optimum ratio of 1:6 (Oil : Methanol) at 60 °C. The fuel properties of biodiesel blends i.e. B100, B50, B20, B5 were compared with ASTM standards. Based on qualitative and quantitative analysis of Biodiesel and their byproducts, the bioenergy from such resources can be feasible, cost effective, environment friendly, if mass plantation of such resources may initiated in suitable places at global perspective. The concept of green fuel from green plants have positive impact on climate stability and biodiversity promotion. The lesson learned from this study will be adopted in other countries with similar plant biodiversity, soil and climatic conditions.

Performance and stability of corundum and mullite hot gas filter candles in gasification environment

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As a basic component in advanced coal- or biomass-fueled gasification, hot gas filtration systems are designed to protect downstream components like gas turbines, catalysts, heat exchangers, or fuel cells from erosion, corrosion, and particle contamination. They are needed to clean the process gases, improve efficiency, and decrease costs. Nevertheless, char, ash, or additive fines can have a toxic effect on the reliable functionality of currently employed porous ceramic filters. Therefore, improvement of composition, long-term performance, durability, and operating life is essential to achieve a successful applicability of hot gas filter systems in advanced gasification applications. Hence, the understanding of microstructural composition and processes is indispensable.

In the present study six candles, five aluminum oxide-based and one mullite-based filter candle, were investigated. The corrosion experiments were done with five types of ashes: wood chips ash from the allotherm fluidized bed gasifier in Güssing (Austria) and four laboratory ashes from straw, miscanthus, DDGS (dried distilled grains with soluble), and a sulphur-rich lignite. The exposure experiments were done at a temperature range of 800°C to 950°C for 250 hours in a synthetic gasification-like atmosphere based on the gas composition of the biomass fired power plant in Güssing. The interaction between several gasification ashes and ceramic filter candles was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction.

Macroscopic interactions between each filter candle material and straw as well as miscanthus ash was found. The infiltration into the outer part of the candle seems to be strongly associated with the slag formation, which needs to be prevented to ensure a stable operation of the adopted candle. SEM/EDX analyses on cross sections reveal an effect to binder phases of nearly every filter candle material. Therefore, it is reasonable to discuss the exposure effects of the binder phases in detail.

Keywords: Hot Gas Filters, Alumina, Mullite, Corrosion, Alkaline Metals, Binder

Physicochemical characterization of biodiesel from weed *Cyperus esculentus*

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Biodiesel appeared as an alternative to fossil fuels mainly diesel, presenting the great advantage of being less pollutant due to the fact that it has no sulphur in its chemical composition, which minimizes acid rain, for example. The main raw material of this fuel is the soybean, which is also used as human food, nowadays in Brazil 85% of the biodiesel comes from this grain. The 2010/11 crop yield was 75 million tons, and about 7 million tons were used to produce biodiesel for the Brazilian market, this resulted in competition between energy production and the food market, raising the price of food made from soybean. One alternative to this competition could be the use of oleaginous grains that are not in the human food chain, for instance, the use of *Cyperus esculentus*, a kind of weed that exists all over the world. This weed oil content varies between 15-22% such variation depends on the cultivation and the soil, its productivity is about 15 tons per hectare, in an infestation area, and these characteristics qualify the weed to the production of biodiesel. This work aims to produce and characterize biodiesel generated from the *Cyperus esculentus* oil.

The biodiesel was produced through the heating of *Cyperus esculentus* oil up to 80°C, with the addition of a catalyst (potassium hydroxide) 3% v/v, along with 30% v/v anhydrous alcohol (methanol). Physicochemical analysis used for the quality control of the biofuel were: flash point, specific mass, visual color and aspect, thermogravimetry, gas chromatography and oxidative stability.

The physicochemical analysis results are summarized and presented in Table 1.

Table 1 – Result of physicochemical quality control tests of biodiesel from *Cyperus esculentus*.

Characteristic	Method	Specification	Biodiesel <i>Cyperus esculentus</i>
Visual aspect	Visual	L.I.I.	L.I.I.
Specific mass	NBR 7148	850-900 kg.m ⁻³	878,2
Flash point	ASTM D 56	min. 100°C	105
Conductivity	ASTM D 1125	máx. 350 µS.m ⁻¹	0
Hydrogenionic potential	-	7±1	7
Induction time	EN 14112	min. 6h a 110°C	1,93
Esters content	NBR 14598	min. 96,5%	96,54

Results in Table 1 reveal that the biodiesel from *Cyperus esculentus* is in accordance with the Oil National Agency (Brazilian ANP) resolutions, suggesting that this biodiesel can be used as a biofuel. The only test that was not in accordance with resolutions was the induction time, as it presented time lower than ANP regulations, this behavior is expected, however, due to the high percentage of esters with double bonds, moreover this study did not apply antioxidants to reach the requirements of specification.

Keywords: purple nutsedge, sustainability, biofuel;

Potato pulp as a modifier of biofuels rich in chlorine and alkali

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This paper presents the possibility of producing a new generation of biofuels from agricultural sources, which are characterized by a high softening point of ash. Such biofuels can be used for combustion in boilers of different power, not creating operational problems in terms of their endurance. This in turn reduces outbreaks of high-temperature corrosion of chlorine and chloride. It is well known that the combustion of biofuels such as agro cereal straw, waste grain, grass, etc., because of its low ash softening temperature (of around 700°C) and the risk of corrosion, do not constitute a full-value fuel for energy. This is due to a high proportion of alkaline elements, such as: potassium (K), sodium (Na) and calcium (Ca) in biomass of flammable substances. This concerns mainly potassium, whose share value often reaches around 20000 - 40000 ppm. At the same time the combustible substance of such biomass is rich in chlorine (Cl). Its share is often determined at the level of 0.6%. These elements occur in compounds with KCl, NaCl, CaCl₂. This fact is amply described in the literature, where many authors take on the research issues such as: reducing emissions of HCl. Chloride binding is accomplished through the use of fuel additives that are active in this respect. These activities are clearly aimed at improving the operating conditions of boilers, which plays an important role in reducing outbreaks of corrosion. Biomass material, subjected to the research (described in this paper), is the potato pulp constituting useless technological waste in the starch industry. In the potato starch which represents about 40% of pulp, there is phosphorus in the form of phosphoric acid, ester related to the 1st line alcohol group of glucose residue. Free valences of this acid are saturated with cations - usually potassium and calcium. There is a small content of Ca - 2568 ppm, K - 2949 ppm, and Na - 3263 ppm in dry mass. Noteworthy is the high content of chlorine (Cl) in the flammable substance, which based on the weight of dry mass can reach even 1,1%. It is known that if chlorine is in the fuel in the form of alkali metal salts or during the combustion process creates them, then it results in lowering the softening temperature of ash, which in turn leads to enduring boiler furnaces, defluidization of fluidized bed and high temperature corrosion. In order to demonstrate the anticorrosion properties of potato pulp, we demonstrate in this paper the results of the test experiment. For this purpose, biomass fuel was prepared, in which to the agro biomass rich in alkali and chlorine we used addition of potato pulp. To oat straw and oat bran, which moisture content was up to 10% in working condition, 20% of the fresh potato pulp with a moisture content of 86% was added. For such composed biofuel measurements of ash softening temperature were taken. The result is a significant increase in the ash softening temperature (characteristic of oat straw) from about 730°C to about 990°C, despite the high proportion of the element chlorine (Cl) in the potato pulp. It gives a hint that the potato pulp contains a component that causes the transformation of alkali metal chlorides present in the biomass constituting (along with pulp), the second component of fuel. Thereby it minimizes the ash liquefaction, causing high-temperature corrosion.

There are different techniques for solving problems of high temperature corrosion, such as blowing sediments, corroded equipment replacement, cleaning fluidized bed, adding chemicals to the process, introducing elements of a dedicated infrastructure. However, most of these methods removes only the identified impacts. Modifying the undesired properties of agricultural biomass by composing the fuel with the addition of potato pulp is an option of eliminating problems at their source. We can therefore believe that potato pulp binds effectively alkaline elements, including above all potassium. Thus, during combustion, fusible alkali metal chlorides do not appear, which significantly slows enduring of furnaces and the formation of high-temperature corrosion outbreaks and prevents agglomeration of bed in fluidized bed boilers. Undertaking research on the modern solution will help to develop low-emission and anticorrosion combustion technologies, which add to commercial potential of research results that will allow significantly greater than before energetic use of agricultural biomass.

Keywords potato pulp, combustion, high-temperature corrosion

Potential of Biochar Combustion in Blast Furnace Ironmaking

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For reducing CO₂ emission from the ironmaking process, utilization of carbon neutral material such as biochar is one of the promising solutions instead of conventional pulverized coal injection. This paper provides a numerical study for investigating the potential of injecting pulverized biochar in the blast furnace. Calculations were carried out in region from tuyere to raceway, which was surrounded by a packed bed of coke. In this region, the combustion process, which consists of inert heating, devolatilization of biochar particles, gaseous combustion of volatiles, and continuing with heterogeneous reactions of char, was simultaneously occurred. The effect of O₂ concentration and particle diameter of biochar on combustion performance was studied. Oak-char was subjected to numerical simulation. For comparison, the simulation was also done for conventional pulverized coal (Taiheiy coal). As a result, Oak-char provided lower temperature than Taiheiy because heating heat of Oak-char was lower than that of Taiheiy. Volatiles start to release after a preheating stage in tuyere. The highest temperature is situated approximately on the axis of tuyere. Moreover, an increase in O₂ concentration resulted in high gas temperature due to increase in combustibility. Oxygen in the raceway is quickly consumed as pulverized biochar injected. The position of the maximum CO₂ concentration coincides with that of the highest temperature. An increase in O₂ concentration increases temperature and CO₂ concentration due to the exothermic reactions of C(s)+O₂→2CO and 2CO+O₂→2CO₂. Particle diameter also affected combustibility. Decreasing particle diameter increased temperature due to rapid reaction of small particle. Increasing injection rate of biochar decreased combustibility. At high injection rates of biochar with 70 micrometers, pulverized biochar is not completely combusted in raceway. However, using hot blast of 27 wt% O₂ concentration and particle diameter of 40 micrometers, Oak-char provided the combustibility of 99% at biochar injection rate of 200 kg/(1000 m³ Feed Gas).

Keywords: Carbon neutral material; Biochar; Combustion; Blast Furnace Ironmaking; Numerical Simulation.

Potential of Sulphonated Carbonaceous Materials as Catalysts for Biodiesel Production

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The production and use of biodiesel as a fuel has greatly increased in recent years due to the fact that it is produced from renewable sources and is an environmentally benign alternative fuel for diesel engines [1]. The most widely used industrial process for the commercial production of biodiesel from vegetable oils is the transesterification process employing homogeneous base catalysts and methanol as the esterifying agent. However, homogeneous catalysis requires further glycerol separation and ester purification steps that increase the costs of production and hinders the achievement of high quality biofuels. Also, it faces difficulties in handling multiple and varied feedstocks. Thus, heterogeneous catalyzed production of biodiesel has emerged as an interesting process as it requires no purification steps, product separation can be more easily accomplished and the catalyst can be regenerated and reused several times. Many synthetic and non-synthetic catalysts have been proposed in the literature for use in transesterification of vegetable oils. However, the majority of them requires costly precursor materials and intricate synthesis pathways. Among the various support materials used for the preparation of solid catalysts, carbonaceous materials are one of the most relevant for they are usually inert in both acidic and basic media, present adequate mechanical strength and texture, and are quite easy to handle. Solid carbonaceous wastes, such as oilseed press cakes, are one of the most prominent candidates for precursor materials in the preparation of catalysts, since they are renewable, usually available in large amounts and potentially less expensive than other materials to manufacture a diversity of types of catalysts. In view of the aforementioned, in this work, we have investigated the preparation and use of a sulphonated carbonaceous catalyst for the transesterification of vegetable oils using *Raphanus sativus* press cake as a precursor material. The press cake was treated with sulphuric acid followed by thermal treatment to produce the sulphonated active surface. The prepared catalyst was used in a ratio of 10 g of catalyst for each gram of reactants in a stirred vessel irradiated by ultrasound (1000 W; 20 kHz) for the transesterification of soybean oil with ethanol (1:6). Samples were taken from the reacting medium and the ester yield analyzed by gas chromatography. After 75 min of reaction, the ester conversion was of 25%. As a preliminary result, it was demonstrated the feasibility of using oil extraction press cake as precursor material for the preparation of solid acid catalyst for the transesterification reaction of vegetable oils.

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Keywords transesterification; heterogeneous catalysis

Prediction of performance in combustion of vine shoots from La Rioja (Spain) based on their chemical composition

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Thousands of tonnes of pruned vine shoots are produced in the Spanish region of La Rioja every year. To date, no satisfactory system has been developed for making a reasonable use of them. Therefore, the main purpose of this article is to valorise this waste, mainly as an energy source.

Firstly, an assessment of this residual biomass was performed in La Rioja region. Data from *Oficina del Viñedo* of La Rioja Government were used. The annual quantity of available vine shoots was calculated for each municipality in the region. This allowed us to capture the distribution of this residual biomass on a map. A total amount of 150.000 tonnes of vine shoots was estimated for the harvest of 2010.

Subsequently, a representative sampling of the different varieties and vineyards in the region was taken. Each batch of samples was chemically analyzed to determine its moisture content, percentage of ash, elemental composition and high heating value. The influence of various agronomic factors on these thermo-chemical properties was studied. Only two factors showed to be important at a statistically significant level: variety and type of training.

Finally, the performance of vine shoots in combustion was predicted. Unquestionable advantages appeared, such as significant higher heating values and moderate quantities of ash and low heavy metal contents. Moreover, no problems of corrosion or emissions due to S or Cl compounds are not to be expected. However, levels of N higher than recommended for limiting harmful emissions were found. In addition, sintering cannot be ruled out according to ash compositions obtained.

Keywords Pruned vine shoots; thermo-chemical characterization; solid biofuel; combustion performance

Preparation of electrospun carbon nanofibers with increased specific surface area utilizing low cost lignin by-product

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Lignin, a naturally existing biopolymer contained in lignocellulosic biomass at 20-30% on average, is a high-volume by-product of wood pulping which in the U.S. alone exceeds 15 million tons per year. Nonetheless, lignin has been utilized mainly as a low-grade fuel for production of heat and power to date. Domestic pulp and paper mills in U.S. burn approximately 85,000 tonnes/day of lignin in "black liquor" to provide process energy and inorganic chemical recycle. Lignin is also dried and sold as an industrial chemical and used as a feedstock for polymeric products. There is however a growing demand to identify applications with higher economic value for lignin. Although production of carbon fibers from lignin has been reported in literature, the low mechanical properties obtained so far have prevented their commercial use in reinforcement applications. Nano-fibrous felts consisting of porous carbon nanofibers derived from low-cost lignin, however, have potential applications that rely on large specific surface area such as catalyst support, supercapacitor electrode, hydrogen storage materials, carbon fiber composites, etc. Furthermore, the domestic vehicle fuel consumption can be dramatically decreased by reducing the overall weight of production vehicles. Carbon fiber composites provide an attractive route to this goal. Significant automotive use of carbon fiber technology will require substantial increases in fiber production coupled with decreases in fiber price to \$7/kg. An earlier study which evaluated lignin production from renewable and recycled streams showed that diversion of 10% of U.S. lignin is sufficient to produce enough carbon fiber to replace half of the steel in all domestic passenger transport vehicles. In addition, lignin-based carbon fibers could be produced at lower temperature with shorter stabilization periods than other feedstocks because functional radicals derived from the polymer's own hydroxyls and ether linkages facilitate crosslinking. Use of only 10 kg of carbon fiber in each of the 13 million automobiles and light trucks produced in the U.S. each year would require roughly 5 times the estimated current worldwide production. Although lignin and lignin byproducts are recovered at a limited number of domestic mills, the pulp and paper industry is presently involved in development of high temperature gasification processes to increase net electric energy generation. Gasification processes would facilitate production of carbon fiber precursors from lignin and, in some cases, might make the recovery and storage of large amounts of lignin commercially attractive. In this work, innovative carbonaceous nano-fibrous felts with high specific surface area were developed by electrospinning of aqueous mixtures of alkali lignin and poly (vinyl alcohol) with varied mass ratios followed by heat treatments for stabilization and carbonization. The developed carbonaceous nano-fibrous felts had up to 19.4-fold larger pore volume and 7-fold greater specific surface area than the PVA-based control prepared without use of lignin, and are therefore expected to find important commercial applications.

Keywords: carbon nanofibers; lignin; electrospinning; specific surface area; applications

Production of biofuels that integrate glycerol into their composition by lipase catalyzed transesterification

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In this work, we report a methodology to produce biofuels that integrate glycerol into their composition by using immobilised Pig Pancreatic Lipase (PPL). Activated AlPO₄ was employed as support for the immobilization of PPL after functionalisation with p-hydroxybenzaldehyde (Figure 1) [1].

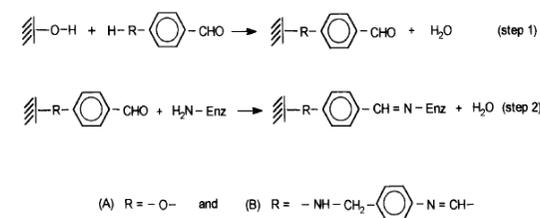


Figure 1. Immobilization scheme for PPL through the ϵ -amino groups of lysine residues.

The lipase was strongly fixed to the inorganic support (94.3%). Quantitative conversions of triglycerides (TG) and high yields to fatty acid ethyl esters (FAEE) were obtained under mild reaction conditions. All the conditions studied, for free and immobilized lipase, provided yields inferior to 66%, which correspond to the transformation of TG in a mixture of two moles of FAEE and a mole of glycerides, due to the 1,3-regioselectivity of this lipase [2, 3].

The immobilized catalyst was highly reusable preserving most of its initial activity after 42 runs, and the reaction mixture was easily isolated by decantation.

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Keywords: PPL, lipase, immobilized, biodiesel, biofuel.

Pyrolysis of *Jatropha curcas* wastes to produce bio-oil

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Increasing energy consumption has resulted in both the increasing use and the impending depletion of fossil fuel reserves worldwide (Demirbas, 2007). Additionally, the increasing rate of release of harmful emissions especially carbon dioxide from the increased usage of fossil fuels have led to the need for more sustainable and environmental friendly alternative fuels such as biodiesel, bioethanol and biomass. Presently, bio-oil or tar produced from the pyrolysis of biomass can be used directly or after further physico-chemical processes to heat up boilers or even drive diesel engines or turbines (Mohan *et al.*, 2006; Balat and Demirbas, 2009). The focus of this research is to determine the pyrolysis parameters required to achieve optimum quantity and quality of bio-oil production from *Jatropha curcas* pressed cake after oil extraction of its seed. Currently, *Jatropha curcas* is a drought free and inedible crop which can be planted economically in tropical and sub-tropical regions. Its seed is a promising source of oil especially for the purpose of commercial biodiesel production. A thermo-gravimetric analysis (TGA) shows that the *Jatropha curcas* pressed cake contains less than 4 wt% moisture content and over 70 wt% volatiles, both of which are indicative of potential bio-oil content. It also shows that 70% of the total volatile separation occurs at temperatures below 650 K, which is relatively low and hence optimises the energy consumption during the pyrolysis process (Figure 1). To achieve maximum bio-oil trap, a laboratory-scale convection pyrolysis reactor and a quencher are designed and fabricated. A corresponding Design of Experiment is performed for this work to determine the optimum pyrolysis parameters.

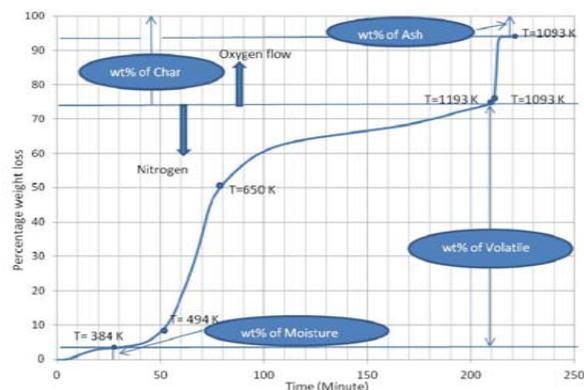


Figure 1: Thermo-gravimetric analysis of *Jatropha curcas* pressed cake

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Keywords pyrolysis; *Jatropha curcas*; bio-oil

Reducing furnace wall corrosion by coating the furnace tubes in a waste wood firing power plant

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The use of waste wood as a fuel in power plants is becoming more widespread in Europe, because it is a renewable energy source with a lower cost than forest fuel. However it is a heterogeneous fuel with a high amount of chlorine, alkali and heavy metals which leads to more corrosion than with fossil fuel or forest fuel combustion. A part of the power plant which is subjected to a high corrosion risk is the furnace wall or waterwall. Waterwalls are made of ferritic low alloyed steels, due to the low price, high stress corrosion cracking resistance, high heat transfer properties and low thermal expansion. However, ferritic steels corrode very rapidly when burning waste wood in a low NOx boiler and methods are being sought to reduce corrosion.

In this work, furnace tubes coated with Ni-alloys were compared to the uncoated tubes of 16Mo3. Specimens were cut out from test panels after three years of exposure in the boiler. Then they were chemically analysed by SEM/EDS and SEM/WDS methods.

The results showed that Ni-alloy coatings can change the corrosion mechanism by decreasing the production of low melting point chloride-containing compounds, which leads to a dramatic reduction in the corrosion rate. The role of alkali and heavy metals in the fuel is also discussed.

Keywords high temperature corrosion; water wall; waste wood; Nickel Coating; 16Mo3

Reproductive biology and artificial pollination of *Jatropha curcas* L.: a promising oilseed for biodiesel

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Scientific research ranks *Jatropha curcas* L., known as physic nut, as the most promising oilseed for biodiesel production. This classification is based primarily on its oil, which combines high content (38% on average) with oleic acid-rich (48% on average). Moreover, it is a hardy perennial plant, easy to manage and suitable for intercropping with food crops and other oilseed crops on small farms. These characteristics make it an alternative for rural development. However, there is a lack of basic scientific knowledge on the species, on its reproductive biology, genetics, physiology and crop science. The species does not have improved cultivars or a consolidated technology package for its cultivation. Our study aimed to facilitate the development of hybrids, to accelerate the registration process of cultivars and the availability of seeds for cultivation, since these are not yet available in Brazil. The research was carried out at the Universidade Federal de Viçosa, Viçosa, MG, Brasil, using six populations of *J. curcas*, which were introduced in November 2007. To make a detailed study of reproductive biology we have used the following procedures: i) pollinations were performed in inflorescences of plants selected at random, from December 2010 to February 2011, ii) inflorescences were marked randomly in every three plants of six distinct populations; iii) on each marked inflorescence were counted the number of male and female flowers, and the respective anthesis periods. We evaluated 12 traits: male flowers; female flowers; male:female flowers ratio; the onset of male anthesis; the onset of female anthesis; end of male anthesis; end of female anthesis; male anthesis; female anthesis; the onset of total anthesis; duration of total anthesis and end of total anthesis. All these data were processed by hierarchical classification analysis of variance, under fixed model. *J. curcas* is a diploid allogamous plant species with 22 chromosomes. The plant is monoecious and its flowers are unisexual and hermaphrodites eventually. The female/hermaphrodite flowers are surrounded by the males. Our study recorded an average of 119.5 male flowers (38 to 258) to 5.6 female flowers (0 to 13) per inflorescence. The male:female flowers ratio reached nearly 28:1, in line with literature, suggesting that this character has a high heritability. On the other hand, there were no hermaphrodite flowers this year, unlike the two previous years. Among the hermaphrodite flowers, 85.25% of them presented protogyny, warranting the xenogamy. The female anthesis lasted three days and the male anthesis about 14 days, with an overlap of only two days. The first one occurred from first to third day and the second one occurred from second to fourth day. The lack of variability for traits among populations and plants within populations reinforces the need of introduction of more populations in the population bank, in order to broaden the variability for reproductivity traits. The artificial pollination of the flowers of *J. curcas* can be performed both in open as in flower bud stage (pre-anthesis). When the hand-pollination is carried out in pre-anthesis, this waiver prior protection of the flower and prevent contamination with foreign pollen. In pre-anthesis it is necessary to remove parts or even the entire petals with fine point tweezers, to expose the stigma and not damage it. Whereas in hermaphrodite flowers, the emasculation should be made with the aid of tweezers. The removal of petals will not interfere in fruit development, since they are aborted very early in the process, leaving only the sepals to the complete formation of the flower. The protection of the flower with cotton should be performed immediately after pollination and the identification made with graphite plastic labels. Cover the flower with cotton was the most efficient way to avoid the presence of insect vectors which can bring pollen from other *Jatropha* plants. The presence of these insect vectors could lead to undesirable mixing of pollen or even promote the removal of the pollen grain of interest, previously deposited in the flower. The best periods to do the pollination are the early morning hours, when occurs the opening of the flowers and the presence of pollinators is lower. As the temperature rises, the flowers bloom more quickly and begin to exhale odoriferous substances which act as attractive to insects, both pollinators and those visitors which seek to feed on the nectar of plants. Insects goers of the bank populations of *J. curcas* belong to the orders: Coleoptera, Hymenoptera, Diptera, Hemiptera, Lepidoptera, among others, the beetles are the most abundant in number of species and individuals. However, only bees, flies, ants and wasps have proven effective in pollination.

Keywords: Physic nut; hybrids; genetic improvement.

Acknowledgements: Research supported by CNPq, CAPES and FAPEMIG

Retrofitting Practice of a 100kWth Coal/Biomass Air-firing Combustor to the Oxy-firing Mode: Experiences and the Experimental Results

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Air-firing of the fossil fuels results to relatively low concentration of CO₂ in flue gases which make the capture of CO₂ difficult and expensive. Oxy-firing combustion is a novel method of using enriched oxygen for coal/biomass combustion with Recycled Flue Gases (RFG) to control the adiabatic flame temperature and to increase the CO₂ concentration of the off-gases up to a 60-70% oxy-firing mode (compared to air-fired mode, around 12-14%). This new technology is being applied at Cranfield University to retrofit an existing 100kWth air-firing combustor to the oxy-firing mode. This paper presents the procedure of the modifications applied on the combustor and the excellent results obtained for co-firing of pulverised coal and biomass in this rig.

The retrofitting process of the 100kWth air-firing combustor consisted of two major phases and during that the following modifications and measurement systems have been implemented on the rig (see Fig.1):

- Installation of flue gases recirculation line (Recycle mode)
- Installation of the primary and secondary lines of oxygen
- Fitting an axial swirler in the air inlet port
- Installation of a gas tight fan for recirculation of the flue gases
- Employing a gas tight and CO₂ purged fuel feeder facility
- Gas Analyser, thermocouples and deposition probes for measurement of process environment
- Collection and analysis of ash deposits

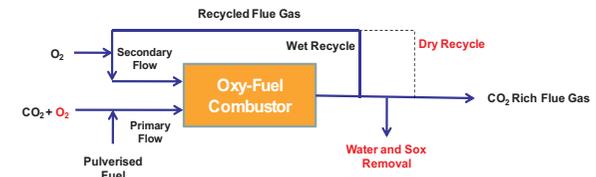


Fig.1: Flow diagram of the Cranfield oxy-fuel pulverised fuel fired combustor (red: ongoing modifications)

The experiments were carried out in this modified oxy-fuel combustion rig facility. In the recent experiments the fuel feed rates between 12-20 kg/hr for Daw Mill coal (100 %, wt), Cereal Co-Products (CCP) biomass (100 %, wt) and mixed fuel (coal:biomass, 50:50 %, wt), were introduced into the rig. Major emissions species (CO₂, O₂, H₂O), minor emission species (SO₂, CO, NO, NO₂, N₂O, HCl, HF), and gas temperature profiles were obtained and analysed for different fuel mixtures. Also the deposits formed on the ash deposition probes were also collected and analysed using SEM/EDX and XRD techniques to assess their corrosion potential in oxy-firing environment. The maximum concentration of about 57% CO₂ and 23% of H₂O were measured in flue gases which confirms a very successful conversion of the rig into the oxy-fuel mode with wet recirculation (see Fig. 2).

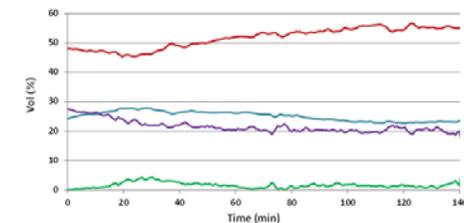


Fig.2: Major species of oxy-fuel combustion of 100% Daw Mill coal

Keywords: Oxy-Coal Combustion; Recycled Flue Gas (RFG); Carbon Capture Sequestration (CCS); Gaseous Emissions

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Role of intra-cellular and extra-cellular cues in triggering the switch from acidogenesis to solventogenesis in *Clostridium acetobutylicum*

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Biobutanol can be used as efficient vehicle fuel as its properties are closer to gasoline and comparatively advantageous over other fermentation based biofuels. However, *Clostridium acetobutylicum* is well known organism for biobutanol production since the history of ABE (Acetone Butanol Ethanol) fermentation. The organism has two distinguished phases, namely acidogenesis and solventogenesis, in its metabolic pathway. The first phase, acidogenesis, incorporates accumulation of acetic and butyric acids, whereas in the second phase, solventogenesis, sugars along with the acids produced in first phase are consumed simultaneously for production of organic solvents.

From the point of view of productivity of butanol, the duration of the acetogenesis phase delays switching of metabolic network from acidogenesis to solventogenesis. However, on completion of the acidogenesis phase, the cell can either enter the solventogenesis phase, or trigger the onset of sporulation. The precise cues which trigger the switch from one phase to another, and the choice between sporulation and solventogenesis are not well understood. Greater understanding of and control over the switching mechanism would enable design of strains for enhanced butanol production.

In present paper, we investigated the role of cellular and environmental cues which triggers the switch from acidogenesis to solventogenesis. We demonstrate that *C. acetobutylicum*, employs a hierarchical sugar utilization strategy, with the bacterium preferentially utilizing glucose over arabinose over xylose. This hierarchy is consistent with other sugar utilization patterns observed on other organisms. Our results also indicate that the cell utilizes intracellular cues (growth phase and growth rate) and extracellular cues (pH and organic acid) to determine the precise timing of the switch from the acidogenesis to the solventogenesis phase.

Keywords solventogenesis; acidogenesis; biobutanol; sporulation

Selection of Renewable Energy Technologies in Landfills: The M-Macbeth Decision Support

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The problem addressed in this work is the ordering problem. A set of alternatives – renewable energy technologies (RET) – must be ordered taking into account their attributes values and the preferences of the decision makers. This study therefore evaluates the characteristics of RET fuelled by biogas – three types of fuel cells (FC), one microturbine (MT), one Otto Engine (OTTO), one Stirling Engine (STIR), one gas turbine (GT) and one steam turbine (ST). The MACBETH method is associated to a user friendly decision support system called M-MACBETH which helps for the implementation of the whole multicriteria process and improves the decision makers' interaction over the multicriteria evaluation approach. Several criteria are used for the investigation: efficiency, lifecycle, environmental impacts, costs and power application range. The basic M-MACBETH model building can be described in 3 steps. 1st - The process began with the decision maker elicitation of the criteria. A tree was then created in the MACBETH decision support system - Figure 1. The options were then introduced into the model. 2nd - The next step was to create a value scale for each of the criteria. Judgments regarding the difference of attractiveness between options (alternative vs alternative) were elicited from the decision maker, who then responded with a "very weak", "weak", "moderate", "strong", "very strong" or "extreme" rating. The matrices were created for each criterion in analysis – Figure 2 presents the matrix for costs criterion. 3rd - As before judgments regarding the difference of attractiveness were elicited from the decision maker, but now between the criteria (criterion vs criterion). One matrix was then created for costs perspective, and another for environment perspective.

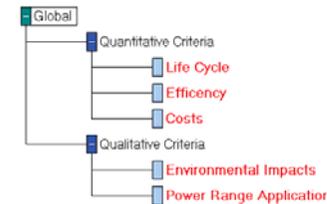


Fig. 1. The Macbeth value tree for RET selection.

	OTTO	TV	TG	MT	STIR	MCFC	PAFC	SOFC
OTTO		no	weak	moderate	strong	v.stig-extr	v. strong	extreme
TV	no		weak	moderate	strong	v.stig-extr	v. strong	extreme
TG				weak	moderate	v. strong	stg-vstr	v. strong
MT					no	moderate	v. strong	stg-vstr
STIR						no	stg-vstr	strong
MCFC							no	no
PAFC								no
SOFC								

Consistent judgements

Fig. 2. The matrix of comparisons: alternative vs alternative for the costs criterion.

The M-MACBETH software aggregates the scoring and weighting scales in an overall scale of attractiveness. Such aggregation leads to a final global ranking of the technologies. It is important to emphasize that weights are defined according to the experience of the selected decision makers taking into account social, political and economic aspects related to the particular region under analysis. The final results of the model are presented in Figures 3 and 4 for RET selection, according to costs and environmental perspectives.

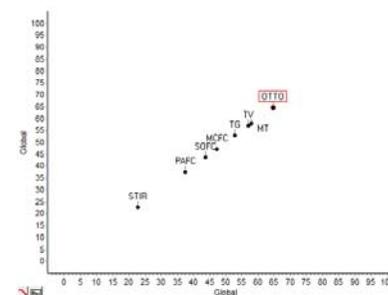


Fig. 3. RET ranking for costs perspective.

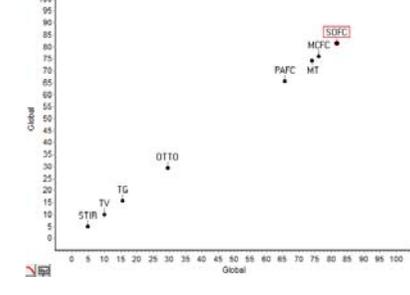


Fig. 4. RET ranking for environmental perspective.

By observing the methodology outcome, it is possible to conclude that the most appropriate systems selected by the MACBETH multi-criteria evaluation approach is the Otto engine for costs perspective and SOFC for environmental perspective.

Keywords: biogas, Macbeth approach, municipal solid waste landfills, renewable energy technologies.

Slag and fly ash from waste incineration – possibilities of management

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Incineration of waste results in a significant reduction in their weight and volume, eliminates any bacteriological risk, allows to recover the chemical energy contained in them. All processes related to the thermal conversion of waste and fuel and generate the formation of secondary waste – after process. These include furnace waste: fly ash, microspheres and residual grate as slag and fly ash. As a result of properly organized and conducted combustion, furnace waste should have a mineral character, with possibly a minimal amount of organic substances. As experience shows, these wastes contain products of incomplete and not full combustion. Due to the mineral composition of such recycled waste, it is possible to use them in industry. The industry use of slag and ash-slag mixtures is associated with their introduction into the environment. This in turn implies the possibility of harmful substances leaching by rainwater or groundwater. With qualification for the particular furnace waste for the use or storage, it is necessary to assess properly their impact on the environment. The elements of the environment most vulnerable to migration of leachable, mobile parts, are soil and groundwater.

This paper presents the results of research on solid residues from combustion of medical waste, animal fats and agricultural biomass. They are grate slag and fly ash captured. In order to verify the effectiveness of the combustion process, in the ashes of the furnace the content of combustible parts was determined, burning them to solid mass at temperature of 815°C. In the ash captured in the cyclone during combustion of medical waste and dust captured by the filter during the combustion of animal waste, we marked the greatest number of embers - about 30%. In addition, the content of 14-16% of combustible parts in grate residues (from thermal destruction of medical waste), and ash from the cyclone (from burning animal waste), shows poor organization of the combustion process. Waste incineration processes of plant biomass and coal co-firing of after refinery fatty acids and glycerine were proceeded with minimal amount of embers. In the slags we determined only a few percent (max.5.3) of combustible parts. Solid residue of the grate at the same time acted as absorbent material for the organic toxic substances. These substances are the products of incomplete combustion of combustible gas components. We identified among others, all groups of hydrocarbons (aliphatic, cyclic and aromatic), thiols, phthalates, and PAHs and their derivatives were determined in the range of 2 to 26ppm_m.

Potential load of leachable, harmful substances from the grate ash studied, was determined by analyzing the aqueous extracts. Markings of indicators of pollution in aqueous extracts were performed according to accepted methods of testing water and sewage. The values of pollutants in eluates met the standards for treated industrial sewage and sewage entered into water and soil. There is no risk of eutrophication, nor contamination with heavy metals, as these are at the level of trace.

Bioavailable forms of harmful chemicals may lead in plants to inhibition of respiration, photosynthesis, and restrictions on development, favoring the formation of dwarf forms or evoke a synergistic effect, which leads in effect to lodging of plants. Toxicity of ash and slag in relation to plants was verified by performing the phytotoxicity test. The plant material used was garden cress seeds. An aqueous solutions containing the components eluting from slag, showed a differential cytotoxic performance in relation to the tested seeds. Inhibitory effects were observed, as well as stimulating ones. The stimulation of plant growth, caused by the water extracts is not a desirable indicator, because of ash leaches that can get into the water, causing the blooms.

Solid residues tested before being introduced to the environment or storing, should be subjected to detoxification, stabilized with mineral binders or vitrified. This shall limit the migration ability of heavy metals contained, and other harmful substances as a result of rainwater leaching.

Keywords waste, combustion, fly ash, slag

Sludge valorization test issued from wastewater treatment plant after an anaerobic digestion as a bio-fertilizer for the Sahara soil

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The sludge application in agricultural land is to apply sludge on soils previously treated in agricultural land which is poor in organic matter. It is about a method of final disposition in accordance with ecological and economic principles of sustainable development, food security and reducing the amount of produced sludge. The fertilizing value improves the soil structure and its ability to retain water and nutrients. In this work we are interested in the study of the addition of natural lagoon sludge after anaerobic treatment as a fertilizer in the Saharan soil which is deemed as saline soils, having poor in organic matter rate and skeletal. The study demonstrated that the digested sludge addition to Saharan soil has increased the soil water holding capacity, by improving the permeability coefficient from 25.31 for the soil alone to 2.37 mixed soil with digested sludge. Owing to its fertilizing effects, the study also showed that the sludge induced a significant improvement of Millet growth.

Key words: sludge, agricultural spreading, fertilizer, food security, anaerobic digestion, biogas.

State of art of Biomass in South KOREA

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In August 2009, the South Korea presented the options of cutting GHG emissions by 21%, 27% or 30% relative to the projected level in 2020, which is based on a “business-as-usual” (BAU) scenario of a 36.9% rise in emissions between 2005 and 2020. In these agenda, there are various plans for developing the biomass as renewable energy. In this report, These are shown the development of new type of biofuel and overseas plantation for developing biomass. Moreover, These aim is to build a foundation for an additive mixing ratio on biodiesel and bioethanol, as well as stabilization in supply and demand of feedstock. Process to use living matter and livestock excrement which holds the potential to create renewable energy from waste and to produce biogas energy for transportation, are being supported constantly.

Keywords Biomass, Biodiesel, Bioethanol, Biogas, South Korea

Study of greenhouse gas emissions from combustion of biomass used to produce coal

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Air pollution is the major concern in today's society. Gases emitted by intensive use of fossil fuels produce serious damage to human health and environmental issues intensifies such as acid rain, photochemical smog, ozone depletion and global warming that generate the dreaded climate change. The IPCC report in 2007 indicates the use of renewable energy as a possible solution to this problem, including the use of biomass. We present a study of gaseous emissions from biomass burning (elephant grass), in the state of Rio de Janeiro/ Brazil. Brazil has an enormous potential for the use of biomass, due to their size, isolation, varieties of plants and water resources. We used infrared analyzer (URAS) and electrochemical sensors (Tempest100) to detect the gases emitted by burning elephant grass for coal production. We identified the gases carbon dioxide (CO₂) and methane (CH₄) by URAS and carbon monoxide (CO), nitric oxide (NO) and sulfur dioxide (SO₂) by Tempest 100 at ppmv range of concentration.

Keywords electrochemical sensors; photoacoustic sensors; elephant grass; air pollution.

Study of micro and nano bio-oil emulsions in fuel oil for use in power generation in thermoelectric plants

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With the increase in oil demand emerging economies, environmental and political concerns about the use of fossil fuel, we highlight the need to develop a cost-effective process for sustainable production of energy fuel and chemical products (HUBER et al., 2006). The increased use of bio-fuels in power generation, is of great interest, since they reduce the emission of greenhouse gases, are means to energy independence and can even collaborate in generating new jobs (DEMIRBAS & BALAT, 2006).

Biomass can be set to any fixed carbon source. The term generally used describes plant material such as wood, wood waste, agricultural crops and their waste (BRIDGWATER et al., 2002). One of the most efficient methods for converting biomass into fuel, however, is the pyrolysis (PŮTŮN et al., 2004). The use of pyrolytic bio-oil as potential source of fuel, is of great interest to the energy generation primarily part of thermoelectricity, since it uses petroleum fuels oils and therefore with high sulphur content. Thus, there is a serious interest in the adaptation of bio-oil as renewable fuel for thermal generation on a large scale, from agricultural biomass, agribusiness and urban organic waste.

The most significant problems of the use of bio-oil as fuel is low volatility, high viscosity, corrosivity and coking (CZERNIK & BRIDGWATER, 2004). The presence of lignin in its structure, which significantly contributes to the contruibui of instability have developed, therefore, to improve its stability and prevent the ageing of oil during storage the lignin must be removed (JIANG et al., 2010).

One of the adaptations of bio-oil in an attempt to replace fossil fuels, is through a mixture with fuel oil currently used. This mixing occurs due to the formation of two immiscible fluids consisting of emulsion by adding a surface active agent, which is able to stabilize the dispersed phase in the form of droplets, whose dimensions vary typically 300-400 nanometers to about 10 micrometers (CHIARAMONTI et al., 2003).

The purpose of this paper is to evaluate the stability of emulsions of oil with fossil fuel oil in various proportions, using or not surfactants, removing or not the lignin fraction of bio-oil for use in thermoelectric plants.

Bio-oil samples were obtained from the Fast Pyrolysis Plant, PPR-10 model, Bioware, Campinas-SP Technology using sawdust eucalyptus as biomass. The biomass was analyzed by Electron Paramagnetic Resonance and scanning optical microscopy. The bio-oil and its fractions were analyzed by molecular fluorescence and absorption; physico-chemical (ASTM and others). The extraction of non-lignin fraction pirolisada of bio-oil was held according to the patent: US 20080047674 A1. The fuel oil and mixtures of oil with the fuel oil were analysed according to Brazilian standards (ABNT NBR). In the process of emulsification fuel oil with nonionic surfactant used bio-oil.

The stability of emulsions was investigated and the size of its particles, nano and micro-detecting emulsions. The bio-oil emulsion with the fuel oil (PETROBRAS) was only when used the surfactant or when it removed the lignin fraction of bio-oil, but emulsions are not stable, probably due to water content present in bio-oil or in their fractions. Lies in the use of the test phase for the bio-oil pyrolygneous stratum emulsifiability in fuel oil. Adjustments are being made to increase the stability of emulsions.

Keywords surfactant; pyrolygneous extract; pyrolysis; fossil fuel

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Study of Solar Heated Biogas Plant

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Abstract

This work deals with the realization of an anaerobic digester heated by solar energy. The Batch digester is for 1.1 m³ biogas reactor. The cover serves to supply our digester by the required heat energy to maintain maximum of temperature to anaerobic digestion. Compared with an ordinary one with the same volume [1], [2] the biogas rate from the solar digester significantly increased. We concluded also that the insulation of lateral walls is important to avoid the decreasing of the nocturnal temperature below 27°C [3].

Keywords: Digester, solar energy, biogas, temperature.

Résumé

Le but de ce travail est d'essayer de réaliser un digesteur chauffé par énergie solaire. Le digesteur de type Batch est de capacité de 1100 litres. Le couvercle sert, par l'intermédiaire d'une plaque captatrice, à alimenter notre digesteur par l'énergie calorifique nécessaire pour maintenir une température favorable à la méthanisation. Comparé à un digesteur ordinaire avec le même volume [1], [2] le taux de production du biogaz du digesteur solaire pendant les trois mois d'été a augmenté de façon significative.

L'isolation des parois latérales est nécessaire afin d'éviter la diminution de la température pendant la période nocturne au dessous de 27°C [3].

Mots clés: Digesteur, énergie solaire, biogaz, température.

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Survivability of *Saccharomyces cerevisiae* strains selected for bioethanol manufacturing during storage in -70°C

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Saccharomyces cerevisiae yeasts are one of the earliest domesticated organisms. From ancient times to the present yeasts are employed for ethanol-making. Yeast strains are still improved by means of screening, sexual hybridization and genetic modifications to obtain organisms able to conduct fast and efficient fermentation of various sugar-containing media to ethanol. After laborious stages of the new strain's obtaining it's very important to choose the proper way for preservation of valuable yeast. Proper method of strain storage should be distinguished, inter alia, by: long-term storage ability with no losses of initial strain features, high survivability ratio and low cost of the whole process. One of the oldest, and still used methods is simple keeping strains living on the surface or in the liquid media such as malt wort or YPD medium. One of the biggest disadvantages of this method is laborious media preparation and requirement of the yeast strain passaging at least every six months. Frequentative passaging leads, very often, to losses of desired strain properties and this fact forces researchers to use other methods of strains preservation. One of such method is cryopreservation with use of freezers, able to keep the temperatures from -60 to -90°C.

Aim of this study was to establish the survivability hybrids of *Saccharomyces cerevisiae* yeast stored in the temperature of -70°C. Influence of cryoprotectants such as dimethylsulfoxide, glycerol and trehalose on cells survivability was also tested.

2 hybrids (ER2 and PAH6) of distillery yeasts obtained by means of sexual hybridization in the Institute of Fermentation Technology and Microbiology (Lodz Technical University) were used as a biological material. Yeast suspension in sterile saline (0,85 % w/v) or in YPD (yeast extract, peptone and glucose) was added to 5ml cryovials and immediately inserted into the freezer (-70°C). Survivability was assayed with use of plate method (expressing viable cells as CFU) after 2 and 7 days; 2 weeks; 1, 2, 6 months and 1 year storage time in -70°C. Influence of dimethylsulfoxide- DMSO (10 and 20% w/v); glycerol (10 and 50% v/v) and trehalose (5 and 15% v/v) addition to the cells suspension before freezing was also examined.

The most significant decrease of viable cells of the tested strains was observed after 2 days from freezing. Depending on the strain, viable cell count dropped to approximately 40-70% of the initial viable cell number. Longer storage (up to one year) in the same conditions resulted only in slight decrease (up to 7%) in the number of CFU formed from stored yeast cells suspensions after thawing. Survivability of the yeasts depended on the strain but also on amount and kind of cryoprotectant added. The most effective influence of the cryopreventive agents was observed for mixtures containing 20% of DMSO or 5- 15% of trehalose. The lowest survivability was observed during storage of the tested yeasts in saline and in the mixtures with glycerol. Cryopreventive properties of the YPG medium were also found out - up to 20% higher survivability comparing with the samples containing only yeast cells suspended in saline.

Concluding – to achieve high survivability of yeast cells after long-term freezing the proper profile of temperature changes during freezing and thawing seems crucial but it's also very important to optimize ratio and kind of cryopreventive agents to the specific yeast strain.

This work was financed from funds for Polish Science in 2009-2012 years as a part of projects: R N312 301037 and R&D N R12 0062 06

Keywords: cryopreservation; freezing; DMSO; trehalose; glycerol; *cerevisiae*; survivability

Synthesis of biodiesel in supercritical methanol using alumina, silica and zeolites as heterogeneous catalysts

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The synthesis of biodiesel (fatty acid methyl esters obtained from triglycerides) from renewable animal fats and plant-based oils has attracted considerable attention and has the potential to replace a fraction of the petroleum diesel. There are four principal approaches to the synthesis of biodiesel: base catalysis, acid catalysis, employing supercritical alcohol conditions and enzyme catalysis. The currently employed commercial processes rely on the methanolysis of triglycerides using homogeneous alkaline catalysts, which are difficult to separate from the glycerin phase, rendering them nonrecoverable and nonreusable. However, the use of heterogeneous catalysts offers various advantages including the recovery and recycling of the catalyst. Alumina, silica and zeolites are usually used as heterogeneous catalyst supports because of its high surface area, simple structure and availability.

In the present study, the activity and reusability of these simple supports for the synthesis of biodiesel from soybean oil will be tested in supercritical methanol in a batch reactor. The reaction was carried out at 275°C during 30 min and a methanol-to-oil molar ratio of 43 (optimal value); the pressure reached in the reactor was between 170 and 230 bar depending on the catalyst used and its concentration. The TG (triglyceride) conversion, MG (monoglyceride) yield, DG (diglyceride) yield, FAME (fatty acid methyl esters) yield and acidity index were studied during the reaction. In the following table are showing the main results obtained, observing that some of these catalyst supports can be used directly and efficiently for an improved supercritical synthesis of biodiesel.

Type of catalyst	Catalyst conc. (wt%)	Acidity index (mg KOH/g)	TG Conversion (mol%)	MG Yield (mol%)	DG Yield (mol%)	FAME Yield (mol%)
No catalyst	0.0	8.4	68.6	18.6	37.7	35.9
5A MS	5.0	12.2	71.2	20.5	36.0	38.0
5A MS	17.2	9.9	70.3	15.4	29.2	45.0
5A MS (1st reuse)	17.2	11.3	82.0	18.2	21.9	58.9
13X MS	2.5	8.2	68.6	17.6	33.7	37.9
13X MS	5.0	6.1	72.8	19.3	29.0	43.9
13X MS	9.7	6.8	74.0	21.4	27.9	51.3
13X MS	17.2	3.4	95.2	15.4	8.8	90.1
13X MS (1st reuse)	17.2	4.6	95.9	15.3	4.5	77.9
13X MS (2nd reuse)	17.2	4.7	95.5	13.4	7.4	81.1
13X MS (3rd reuse)	17.2	6.4	95.2	21.1	11.7	78.6
13X MS (4th reuse)	17.2	10.4	91.7	25.2	18.7	68.3
13X MS (5th reuse)	17.2	10.2	88.1	25.7	20.7	66.1
Z CBV 500	2.5	16.8	66.1	19.1	28.4	40.5
Z CBV 500	5.0	18.4	67.7	18.1	28.0	39.7
Z CBV 500	9.5	19.4	69.5	22.2	27.2	42.2
Z CBV 500	17.3	24.1	65.7	19.5	30.3	44.0
Z CBV 500 (1st reuse)	17.3	12.3	72.6	14.2	19.8	45.7
Z CBV 500 (2nd reuse)	17.3	9.6	73.2	13.8	21.5	48.8
Z CBV 500 (3rd reuse)	17.3	10.0	78.6	15.1	26.4	52.1
Z CBV 712	2.7	17.8	60.7	18.9	26.1	38.9
Z CBV 712	5.0	19.4	61.1	18.6	25.7	39.6
Z CBV 712	9.6	20.4	61.2	17.6	24.8	40.0
Z CBV 712	17.3	24.7	57.9	18.3	24.8	41.4
Z CBV 712 (1st reuse)	17.3	14.0	73.5	16.9	21.4	46.3
Z CBV 712 (2nd reuse)	17.3	11.1	75.6	17.9	21.3	51.2
Z CBV 712 (3rd reuse)	17.3	12.0	75.9	14.2	22.7	53.0
Silica KC AF125	5.0	7.7	68.3	19.4	32.5	43.3
Silica KC AF125	9.5	4.6	85.4	22.3	16.7	73.6
Silica KC AF125	13.6	2.1	96.7	11.1	1.7	96.9
Silica KC AF125	17.2	1.3	97.9	8.5	1.8	99.9
Silica KC AF125 (1st reuse)	17.2	1.6	99.8	7.8	1.3	91.4
Silica KC AF125 (2nd reuse)	17.2	2.3	99.8	8.4	1.7	86.2
Silica KC AF125 (3rd reuse)	17.2	4.7	99.8	13.5	2.6	84.2
Silica KC AF125 (4th reuse)	17.2	2.9	93.6	22.4	7.2	84.2
Silica KC AF125 (5th reuse)	17.2	2.9	92.6	18.7	10.3	73.4
γ -Alumina	5.0	11.9	68.1	17.6	32.0	39.2
γ -Alumina	9.4	10.1	76.7	16.7	27.6	52.4
γ -Alumina	17.3	8.2	77.4	20.0	26.6	55.9
Glass spheres	17.5	6.7	68.9	18.4	35.2	39.1

Zeolites [pellets of 1.6 mm of 5A molecular sieves (MS) (SiO₂/Al₂O₃ = 2), beads of 4-8 mesh of 13X MS (SiO₂/Al₂O₃ = 2.6-3.0), pellets of 3-12 mm of Zeolyst (Z) CBV 500 (SiO₂/Al₂O₃ = 5.2), and pellets of 3-12 mm of Z CBV 712 (SiO₂/Al₂O₃ = 12)], silica [beads of 4-6 mm of SiO₂ (AF125, Kali Chemie)], alumina [beads of 2-3.5 mm of γ -Al₂O₃], and glass spheres.

Keywords biodiesel; supercritical methanol; heterogeneous catalysts; soybean oil

Synthesis of DME from (H₂+CO₂). Effect of feed composition on catalyst deactivation

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Dimethyl ether (DME) is a clean fuel for diesel engines and an excellent source for obtaining H₂ by catalytic steam reforming, especially for vehicles, given that it is suitable for storage and transport and may be fed into cells without the need for pumping. DME is also a key intermediate to produce automotive fuels and raw materials (olefins and BTX aromatics) from alternative sources to oil (natural gas, coal, biomass) [1].

The synthesis in a single step following the syngas to DME process (STD) has advantages over the two-step process (synthesis of methanol and its dehydration to DME), due to the lower thermodynamic limitation of methanol synthesis. This thermodynamic advantage favours the incorporation of CO₂ as a co-feed with the syngas, or the transformation of (H₂+CO₂) mixtures into DME. Considerable attention has been paid in the literature to the use of CO₂ as a raw material in the synthesis of chemicals and liquid energy carriers, in order to mitigate the accumulation of CO₂ in the atmosphere. Amongst the different alternatives, STD process is an interesting route to combine the upgrading (via gasification) of alternative sources to oil, particularly lignocellulosic biomass, with the large-scale CO₂ sequestration.

The bifunctional catalyst used is composed of a CuO-ZnO-Al₂O₃ metallic function for the hydrogenation of CO₂ to methanol, and a γ -Al₂O₃ acid function for the dehydration of methanol to DME. The reaction equipment is provided with a fixed bed, and allows for operating at high temperatures and pressures. The combustion of the coke deposited on deactivated catalyst has been carried out in a tapered element oscillating microbalance (TEOM) coupled to a gas micro-chromatograph.

A kinetic model has been established for the transformation of (H₂+CO₂) into DME on a CuO-ZnO-Al₂O₃/ γ -Al₂O₃ bifunctional catalyst, with excess of γ -Al₂O₃ acid function [2]. This model fits the experimental data in a wide range of operating conditions. A fact to be noted in the kinetic model is the presence of a term with CO₂ concentration to quantify the attenuation of both the reaction rate of methanol and paraffin synthesis and the deactivation by coke of the metallic function.

In this work, a parametric study of the process has been conducted, in order to establish a suitable value of H₂/CO₂ molar ratio in the feed. The aim is to maximize DME production with catalyst deactivation being as low as possible. Runs have been carried out feeding mixtures of (H₂+CO₂) under the following conditions: 275 °C; 40 bar; space time, 42.0 (g of catalyst) h (mol of carbon)⁻¹; time on stream, 30 h.

When the amount of H₂ in the feed is increased, the conversion of CO₂ and the yield of products (DME, methanol and paraffins) steadily increases. This increase is attributed to the competition between the water gas shift reaction and the hydrogenation of CO₂ to methanol. Moreover, the conversion of CO₂ undergoes a very slight decrease with time on stream. Coke deposition after 30 h of time on stream is very low: 0.12 wt% for a H₂/CO₂ molar ratio of 2/1, 0.09 wt% for 3/1 and 0.08 wt% for 4/1. A high concentration of hydrogen in the reaction medium limits the deposition of coke on the metallic phase, following the same trend observed by feeding (H₂+CO). This effect is explained by the relatively high partial pressures of H₂ inhibiting the development of coke.

According to these results, the most suitable value of H₂/CO₂ molar ratio in the feed is 4/1 in the range of operating conditions studied, since although the catalyst undergoes a slight loss of activity with time on stream, DME yield peaks for this composition of the feed.

Acknowledgements This research has been carried out with the financial support of the University of the Basque Country, Department of Education of the Basque Government (Project GIC07/24-IT-220-07) and Spanish Ministry of Science and Innovation (Project CTQ2010-19188/PPQ).

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Keywords dimethyl ether; CO₂; syngas; bifunctional catalyst; deactivation

The heating liquids containing the component from fermentation processes

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The paper presents theoretical and experimental results of verification of the possibility of using the raw spirit (bioethanol) as a component for fuel using in municipal heating facilities of small scale energy. It has been defined technical and technological requirements as well as law and economic rules and the expected benefits of using bioethanol.

The scope of the paper include an assessment of the physical, chemical and functional properties of the raw spirit compare to the requirements of fuels for small scale energy sector, the evaluation of this component compatibility with fuels of different origin, determine the feasibility and advisability of light liquid fuel composition on the basis of the above mentioned components, assessment the feasibility of burning these fuels in devices equipped with flow burners, specifying the basic technical-economic indexes of the process.

This component belongs to the group of sulfur-free, high energetic products of the fermentation industry, available in Poland. Production capacity of this industry sector far exceeds the current demand and are not fully developed. Regardless of the search for new fields of application of the raw spirit (solvents, gasoline components), there are attempts to obtain low-cost, environmental friendly fuels for small heating devices, that are increasingly being modified from fueling by high emission, solid fuels (wood, peat, brown and hard coal) to fueling by liquid fuels (LPG, heating liquids).

Domestic distillery industry, as a result of multiple causes, has excess production capacity of the raw spirit. This is reflected negatively on the potential purchase of basic crops (rye, potatoes and others), and thus the rural economy. Hence, government intervention aimed at wider opening of market for this product. The relatively high calorific value and high purity encourage the use of bioethanol as a fuel. Research works carried out in many countries around the world have demonstrated the practical possibility of such development of bioethanol. The raw spirit used for that purpose must be dehydrated, which increasing fuel costs. The economy determines its cost of production and state excise policy in relation to fuel producers. It creates a positive climate for such solutions. While they are relatively well-recognized problem of using ethanol in gasoline production, it is no information on how to apply it as a component for production of fuels for heating (conventionally referred to as heating liquids). Regardless of the economic problems, there are differences in construction and technology of burn devices working continuously in compare to internal combustion engines, thus it is necessary to determine the feasibility and effectiveness of such use of the raw spirit. This is the source of the range scope planned in this paper.

Keywords heating liquids; the raw spirit, small scale energy facilities

The influence of metal loading and calcination temperature on the behavior of the Pt/SAPO-31 catalyst in the hydroconversion of sunflower oil

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In the past 10 years, the importance of biofuels has increased and this tendency is expected to be continued. Usually, the production of diesel fuel from natural raw materials is performed in two stages. On the first stage, the process over the conventional hydrotreating catalysts gives a deoxygenated hydrocarbon product, mostly a mixture of n-alkanes. A substantial drawback of diesel fuel produced in this way is its bad low-temperature properties. To improve them, the hydroisomerization of the n-paraffin-rich product over zeolites and silicoaluminophosphates is used.

In our previous work [1], we have demonstrated the possibility of the single-stage hydroconversion of sunflower oil over Pd/SAPO-31 catalyst for the production of diesel fraction with low freezing points. Unfortunately, we observed the decrease of hydrogenation and isomerization activity of our catalysts after 15 hours of TOS. Therefore, it was necessary to determine the primary reason of this to improve the stability of our catalyst.

Comparing IR-spectra of adsorbed pyridine for the samples before and after reaction, we have found detectable decrease in the Bronsted sites concentration for the samples after reaction. However, it looks doubtful that the acid sites blocking is a primary reason of activity drop in the sunflower oil transformation because the partially deactivated catalyst demonstrates a good activity in the hydroisomerization of n-undecane. Moreover, the n-undecane treatment of the catalyst returns its activity. Therefore, we have concluded that the noble metal poisoning or the sintering of metal particles is responsible for the low stability of Pt/SAPO-31 catalyst during the hydroconversion of sunflower oil.

From this point of view, it was important to know how the platinum concentration and the temperature of oxidation treatment influence on the Pt dispersion and the catalyst behavior. For 1wt% Pt/SAPO-31 samples calcined at different temperatures from 250 to 450°C, it was shown that the calcination temperature has a big effect on the catalytic properties but practically has no influence on the Pt dispersion calculated from the H₂-chemisorption data. The optimum values of oxidation temperature are within the range of 400-450°C. The lower and higher temperatures lead to the samples with low activity. It should be noted that the decrease in the Pt dispersion is observed when the oxidation temperature of samples exceeds 500°C.

According to data obtained by Vinek et al. [2], the deposition of 1wt.% of palladium on the SAPO-11 samples provides their good activity in the hydroisomerization of n-heptane. Further increase in the palladium content has no effect on the activity and selectivity. However, the situation is completely different for the hydroconversion of sunflower oil on Pt/SAPO-31. The increase of Pt loading from 0.5 to 2wt.% leads to decrease in selectivity because of large amount of cracking products corresponding to the hydrocarbons of gasoline fraction. Moreover, the significant improvement of the catalyst stability is observed. The additional increase in the catalyst stability can be obtained by varying the reaction conditions (for example, by increasing of reaction temperature).

Keywords hydroconversion; sunflower oil; Pt/SAPO-31; biodiesel

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The photosynthetic process of C-4 perennial energetic grasses in the climatic condition of Poland

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The targets contained in Directive 28/2009/EC imposed specific strategies to reduce fossil fuel consumption in Europe. In Poland, biomass is an important source of renewable energy. It is estimated that the demand for biomass energy will reach about 27 million tonnes in 2012. It will be necessary to introduce the cultivation of new plant species into biomass production, especially C-4 photosynthesis and utilization of marginal soils, unsuitable for food production, due to, for example, water shortage or chemical contamination. The aim of the research conducted by the Botanical Garden in Bydgoszcz is to assess the development of plants under adverse site conditions. Photosynthesis is the most essential process that determines the creation of plants dry matter. The investigations concerned the impact of selected photosynthetic parameters on the yield of biomass of grass species C-4 photosynthesis, planted in 2009 in three locations: Marcelewo (sandy soil, dry), Solec Kujawski (closed municipal landfill) and Bydgoszcz – Łęgowo (the area at the sewage treatment plant). The presented results are based on research conducted in the summer of 2011, the period of intensive growth of plants, by means of a portable measuring apparatus LCI ('s Li-COR). The intensity of net photosynthesis and transpiration of leaves was measured. The measurements were performed under comparable environmental conditions, in the afternoon, at constant – given intensity of PAR irradiation - 1200 $\mu\text{mol}/\text{m}^2/\text{s}$ and at an average air temperature of 25°C. Water use efficiency in photosynthesis was expressed in the coefficient of water use – WUE, calculated from the ratio of the intensity of net photosynthesis to the intensity of transpiration.

The species of plants differed from one another in terms of examined parameters. As for the experiment in Marcelewo, the highest intensity of photosynthesis (over 30 $\mu\text{mol}/\text{m}^2/\text{s}$) was observed for *Miscanthus sacchariflorus*, the lowest – for *Elymus elongatus* (9,1 $\mu\text{mol}/\text{m}^2/\text{s}$). The same species showed the highest degree of transpiration (from 4,7 to 5,6 $\mu\text{mol}/\text{m}^2/\text{s}$), while the lowest - *Spartina pectinata* (2,2 $\mu\text{mol}/\text{m}^2/\text{s}$). A high coefficient of water use (WUE over 8), indicates the effective management of water in the process of gas exchange of *Andropogon gerardi*. Twice as low rate of water use was observed in *Elymus elongatus*, species of C-3 photosynthesis. For the experiment in Bydgoszcz-Łęgowo the highest intensity of photosynthesis (over 24 $\mu\text{mol}/\text{m}^2/\text{s}$) was observed for *Spartina pectinata*. Prairie cord grass was a species with the highest rate of photosynthesis also in the experiment in Solec Kujawski. In both experiments the highest degree of transpiration was found for *Elymus elongatus* in the range from 2,7 (Solec Kujawski) to 3,1 $\mu\text{mol}/\text{m}^2/\text{s}$ (Bydgoszcz-Łęgowo). The knowledge of the intensity of photosynthesis allows to control factors connected with the increase of biomass, such as: the efficiency of light use and substrate taken up from the environment, stand density and row spacing.

The height of biomass yield of the studied species will be evaluated in the following growing season for plants in 2012.

Keywords: biomass, coefficient WUE, photosynthesis, transpiration

Thermo-Chemical Conversion of Municipal Green Waste in Central Queensland

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The thermo-chemical conversion process, Pyrolysis is considered as an efficient and environmentally sustainable technology to convert biomass to charcoal and condensate product. In this study, pyrolysis technique is employed to produce bio-coal, organic or bio-oil and aqueous liquids from municipal green waste which is yet to be characterised for the Central Queensland region in Australia. The sample green waste was pyrolysed in a short sealed rotary furnace with attached off gas condenser. The condensate was further processed in-situ and using a centrifuge to produce organic and aqueous fractions. The results of the pyrolysis and characterisation test work are presented in this study.

Keywords Building, Thermal Comfort, Energy Efficiency.

Trace elements in biogas production – Influence on the increase of the Organic Loading Rate

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The supplementation of trace elements (TE's) is a common practice in biogas production and especially in the mono-fermentation of energy crops and agro-processing wastes. The objective of this work is to give an overview on TE's in the anaerobic digestion process, to show TE deficiencies in different substrates, and to demonstrate the effects of trace element addition on the increase of the Organic Loading Rate (OLR).

Different substrates and TE additives were characterized regarding to their elemental composition (see table 1) and grain stillage was used as a substrate exemplary for TE'S deficiencies in continuous digestion experiments during a stepwise increase of the OLR and supplementation of Mn(II), Fe(II), Fe(III), and a commercial additive. The Acid Capacity (AC) was used as the parameter for the degree of accumulation of Volatile Fatty Acids (VFA'S) in the reactors.

Table 1 Recommended and analyzed trace element concentration in different biogas substrates in mg kg-1 TS

	Recommended concentration*	Grain stillage	Jatropha press cake**	Sugar beet	Maize silage	Rye corn	Cow slurry
Nickel	4–30	3.00	<3	1.41	2.67	2.132	7.6
Cobalt	0.4–10	<0.23	<3	0.045	0.008	n.d.	1.88
Molybdenum	0.05–16	0.47	0.35	0.549	1.09	1.4	2.79
Iron	750–5000	305.16	280	49.4	87.2	64.97	1072
Manganese	100–1500	63.00	87	28	20.4	23.47	337
Copper	10–80	96.00	27	4.07	4.67	4.038	63.2
Selenium	0.05–4	<0.23	0.31	1.37	2.02	1.505	0.631
Tungsten	0.1–30	<0.23	<0.34	n.d.	n.d.	n.d.	0.401
Zinc	30–400	n.a.	64	n.a.	n.a.	n.a.	319

n.d.: not detected; n.a.: not analyzed
* According to (Oechsner et al. 2008; EP EP 1 997 901 A2)
** According to (Schmidt 2011)

The work demonstrates that higher OLR's can be achieved in digesters operated with substrates with TE deficiencies by addition of TE's. All tested additives caused a lower AC and thus higher OLR's could have achieved compared to the reference digester. Astonishingly the addition of a single metal (Mn(II), Fe(II) and Fe(III)) caused lower AC values even when other deficient elements were not supplemented. This result supports the theory of a recomplexation of metals in the anaerobic digestion process, meaning that the addition of one element (e.g. Fe) leads to the release of other elements (e.g. Ni and Co) by replacing them in organic and inorganic complexes and making them more available for the microorganisms.

Analyses of the elemental composition of different substrates and especially grain stillage have revealed deficiencies in the content of some TE's. In parallel operated reactors with TE's supplementation the OLR could have been increased to higher levels compared to the reference reactor in which only stillage was used. By the addition of a commercial additive the OLR could have been increased to 5.0 g VS l⁻¹d⁻¹ while the reference reactor could not have been operated under stable process conditions at OLR's of 0.4 – 1.5 g VS l⁻¹d⁻¹.

The results demonstrate that a trace element supplementation can be obligatory to increase to OLR without acidification of the digester and thus improve the biogas production per m3 of digester volume.

Keywords biogas; trace elements

Transcriptome analysis of *Botryococcus braunii* race A by *de novo* assembly of pyrosequencing cDNA reads and real time PCR

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Botryococcus braunii race A is a green microalga, producer of alkadienes and alkatrienes (Metzger and Largeau, 2005), fatty acids and other compounds with commercial application (Dayananda et al., 2007), because of this, there is a great interest to develop its production at big scale. However, little is known about the physiology and biochemistry, as well as its pathways metabolic, key information to design methods of production and genetic transformation methodologies in this specie.

Through pyrosequencing by 454 of the transcriptome of *B. braunii* race A, cultured in massive systems of 1m³ (Bazaes et al., 2012), and a later bioinformatic analysis using Blast2Go software, it was determined that the pathways for fatty acids synthesis are related to the presence of enzyme acyl-binding protein besides of fatty acid desaturase. For the triacylglycerols (TAGs) formation it was identified the enzyme diacylglycerol o-acyltransferase 2. As responsible of the antioxidant activity (Ranga Rao et al., 2006) it was determined the presence of several enzymes manganese superoxide dismutase, iron superoxide dismutase, catalase, glutathione s-transferase, peroxidase and peroxiredoxin, among others. Finally to prove the expression of these genes in massive systems, specific primers were designed and it was evaluated using real-time PCR.

Keywords *Botryococcus*, biomass, pyrosequencing, transcriptome, triacylglycerols.

Use of Ultrasound in Biodiesel Synthesis

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The use of ultrasound (US) in the production of biodiesel has taken a keen interest in the last decade. The main handicap that slows down the transesterification process is the mass transfer speed between two immiscible phases, a non-polar phase (oil) and a polar one (alcohol). In this sense, the phenomenon of cavitation generated with ultrasonic devices produces more effective collisions between reactants and accordingly, could improve the mass transfer in the first step of the transesterification reaction. Moreover, US have been considered a clean energy owing to its high efficiency and low instrumental requirements. Ultrasonic probes allow modify the characteristics of ultrasound: frequency, amplitude and duty cycle.

Over 50 articles about biodiesel production assisted by ultrasound has been reviewed, showing that the use of US decreases reaction time considerably, compared to conventional transesterification reaction. To achieve high reaction yields, transesterification usually takes place in the order of hours, while in the case of sonicated reactions only few minutes are needed. Moreover, the use of US allows carry out the transesterification at room temperature without preheating the reaction, thereby saving energy. In many works, it has been found that the optimum catalyst amount and alcohol to oil molar ratio are lower in ultrasound-assisted transesterification reaction compared with conventional biodiesel production.

Although basic laboratory scale researches in ultrasound assisted biodiesel production have depicted interesting results, some problems remain unresolved. For example, although there are small-scale ultrasonic reactors providing optimized results, a large-scale reactor that allows the production of biodiesel in industrial scale is still to be designed. Moreover, kinetic studies to elucidate the reaction mechanism in sonicated transesterification are missing.

Variation in fuelwood properties of five tree/shrub species in the Sahelian and Sudanian ecozones of Mali: relationships with rainfall, regions, land-use and soil types

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Rural communities in the Sahelian and Sudanian ecozones of West Africa use more than 90 indigenous tree and shrub species for fuelwood, but there is very little published information about intra-specific variation in fuelwood properties. There are steep rainfall gradients with latitude and longitude in the Sahelian and Sudanian ecozones, and some computer models predict a hotter/drier climate. Information about variation related to rainfall gradients is important therefore for planning fuelwood production in a changing climate. In addition, it is important to know if fuelwood properties differ among regions, land-use and soil types.

We investigated variation in age-adjusted fuelwood properties [basic density (BDen), volatile matter (Vol), fixed carbon (Carb), ash content (Ash), air-dry moisture content (MC), gross calorific value (GCV), fuelwood value index (FVI = {net calorific value x BDen}/{MC x Ash})] of *Balanites aegyptiaca*, *Combretum glutinosum*, *Guiera senegalensis*, *Piliostigma reticulatum* and *Ziziphus mauritiana* along latitudinal transects in five regions extending from eastern to western Mali. The objectives were to determine if fuelwood properties varied with geographical coordinates (latitude, longitude, elevation), mean annual rainfall, land-use type (woodland or parkland agroforest) and soil type (sandy, sandy/loam or rocky).

Analysis of variance indicated that all fuelwood properties differed significantly among species, but there were significant species by region interactions. Fuelwood properties were generally best for *G. senegalensis* and worst for *P. reticulatum*. There were significant regional differences in Vol, Carb, Ash, MC, GCV and FVI of *B. aegyptiaca* and *Z. mauritiana*; Vol, Carb, MC and GCV of *G. senegalensis* and *P. reticulatum*; and MC only of *C. glutinosum*. Soil type had a significant effect on MC and FVI across species: MC was greatest on sandy soils, and since MC is in the denominator of FVI, FVI was greatest on rocky soils. The effect of land use was significant for *G. senegalensis* and *Z. mauritiana*: Ash of *G. senegalensis* was greater in parklands than in woodlands; while Vol of *Z. mauritiana* was greater and Carb was lower in parklands than in woodlands.

Linear regressions indicated that fuelwood properties of most species varied with geographical coordinates and/or rainfall. Fuelwood properties were generally better in drier locations for *B. aegyptiaca*, *C. glutinosum* and *P. reticulatum*, and in wetter locations for *G. senegalensis* and *Z. mauritiana*. MC of *B. aegyptiaca* and *G. senegalensis* wood was higher in drier locations in the driest regions, suggesting that these species may have evolved an adaptive mechanism to maintain high tissue moisture contents throughout the long dry period.

In general, fuelwood production is recommended in all regions for *G. senegalensis*, in drier regions for *B. aegyptiaca* and *C. glutinosum*, in more humid regions for *Z. mauritiana*, on rocky soils for all species, in woodlands for *G. senegalensis* (lower Ash) but in parklands for *Z. mauritiana* (higher Vol, which is positively correlated with FVI). Fuelwood production of *P. reticulatum* is not recommended.

In addition, based on this research, ecological-genetic reasoning and projected climate change, we recommend that seed of *B. aegyptiaca*, *C. glutinosum* and *G. senegalensis* should be collected in drier locations and used to establish fuelwood plantations in the Sahelian and Sudanian ecozones of Mali, and that similar research on these and other species should be carried out in the Sahelian and Sudanian ecozones of neighboring countries in order to make region-level recommendations for fuelwood plantations in a changing climate.

Keywords climate change; basic density; volatile matter; fixed carbon; ash content; moisture content; gross calorific value; fuel value index

Solar Energy

3C Concept for Control Strategies of Building Integrated Solar Energy Systems

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Research and development work on Building Integrated Solar Energy Systems (BISES) has become an area of growing interest worldwide. BISES has the potential to be more cost effective than separate photovoltaic (PV) and thermal systems as it could yield more energy per m², be more economic to install, make better use of limited roof space in urban areas and have improved aesthetics. The strategies for integrating and controlling the energy yield of BISES in a typical domestic situation is however a major concern as a balance has to be found between the thermal and PV output in relation to the needs of the household. In this paper the 3C concept is first introduced whereby the homeowner can choose the performance of their BISES based on a compromise between Comfort, Cost and Carbon. The fuzzy logic control algorithms to achieve 3C control strategies are then presented and the simulation methodology for evaluating their potential performance using TRNSYS and Matlab/Simulink explained. Finally, preliminary results from the simulations are presented that show the 3C concept could be an effective way controlling BISES.

A new solar concentrator and its performance analysis

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A compound parabolic concentrator (CPC) as a typical solar collector, which does not need the tracking system when the geometric concentrating ratio is lower, has large application prospects, especially in PV application. Truncation is a usually way to increase the acceptance angle of a mirror CPC, nevertheless, it also reduces the geometrical concentration ratio. In this paper, a new lens walled CPC is designed, which has a larger half acceptable angle than the mirror CPC. The shape of the lens is formed by rotating the parabolic curves of a CPC by a small degree internally around the top end points of the curves and the out surface of the new lens walled CPC is coated by the refractive material. Combining with PV, the lens-walled CPC-PV has the advantages of reduced PV cell size, increased efficiency, larger half acceptable angle and stationary operation. The investigation shows that when the incidence angle is smaller than 35°, the optical efficiencies of the lens-walled CPC of 2.5X always keep above 46.7%, which is more stable on the incidence angle changed than that of the mirror CPC and has great potential to promote the practical application for the large scope.

Keyword: lens-walled; CPC; concentration; optical; half acceptance angle

A Novel n-type Semiconductor for Organic Photovoltaics

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In this study, we present a new n-type organic molecule based on naphthalene with high electron withdrawing cyano moieties for OPV applications. The photophysical and the electrochemical properties of the acceptor material have been determined by UV-Vis, Fluorescence Spectroscopy, and Cyclic Voltammetry. For photovoltaic applications, bulk heterojunction type organic photovoltaics have been fabricated and CN₄NDI-EH used as the acceptor. The Photovoltaic performance measurements have been carried out under standard conditions while P3HT/PCBM has been used as the reference.

Keywords n-type organic semiconductor, organic solar cell.

A pattern search algorithm to extract optical constants and thickness of transparent thin films from transmittance spectra

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We propose the use of a pattern search optimization technique in combination with a seed preprocessing procedure to determine the optical constants and thickness of thin films using only the transmittance spectra. The approach is quite flexible, straightforward to implement, and efficient in reaching the best fitting. We demonstrate the effectiveness of the method in extracting optical constants, even when the films are not displaying interference fringes. Comparison to a real-coded genetic algorithm shows that the modified pattern search is fast, almost accurate, and does not need any parameter adjustments. The approach is successfully applied to extract the thickness and optical constants of spray pyrolyzed nanocrystalline CdO thin films [1, 2].

Keywords Thin Films; Optical Constants; Thickness; Pattern Search; Seed Preprocessing

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A Theoretical Study on Electron Injection and Recombination of Surface Complexes with TiO₂

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Adsorption geometry, nuclear vibrations, and molecular orientation of the dye with respect to the oxide surface affect significantly the performance of dye-sensitized solar cells [1-4]. We compute the influence of these factors on injection and recombination conditions in organic amino-phenyl acid dyes differing by the donor group on the anatase (101) TiO₂ surface [5]. *Ab initio* molecular dynamics simulations predict configurations in which dyes tend to lay flat on the oxide surface (Fig.1). The resulting proximity of the oxidation equivalent hole to the oxide is expected to promote recombination. Temporal evolution of the driving force to injection is found to be independent of dye orientation and uncorrelated to the oscillations of the O-Ti bonds through which the dye is attached to the surface. We conclude that the dynamics of $\Delta G(t)$ is explained by uncorrelated evolution of the energies of the dye excited state and of the conduction band minimum of the oxide due to their respective vibrations (Fig.2). This suggests that it must be possible to control independently conditions of recombination and of injection.

We also investigate the effect of deuteration on geminate recombination in photoelectrochemical cells operating by interfacial charge transfer absorption bands [6]. The trend in recombination in surface complexes of TCNX (TCNE, TCNQ and TCNAQ) with TiO₂ is treated as internal conversion (IC). The deuteration of TCNQ and TCNAQ significantly modifies the spectrum of vibronic coupling constants for many vibrational modes, but affects little the modes with the strongest contribution to IC. As a result, the overall effect on recombination / internal conversion is expected to be limited, slightly increasing its rate.

In dye design by changing the conjugation order, computational errors behave differently and are more important than when changing the size of conjugation. A different position of the methine unit in dyes induces an uncommonly large difference in absorption spectrum. Long-range effects cause a failure of TDDFT using *ab initio* and hybrid functionals to predict even relative transition energies in spite of a small degree of charge transfer. Orbital energies remain good predictors of the relative energetics and are used to compute the effect of nuclear motions on absorption spectrum [7].

Keywords Dye-sensitized solar cells, DFT calculations, *Ab initio* MD simulations

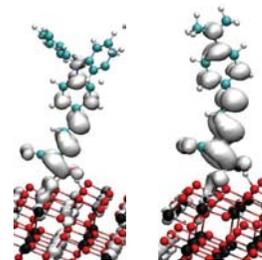


Fig1. Optimized geometries of NK1 and NK7 dyes absorbed on the anatase (101) TiO₂ surface.

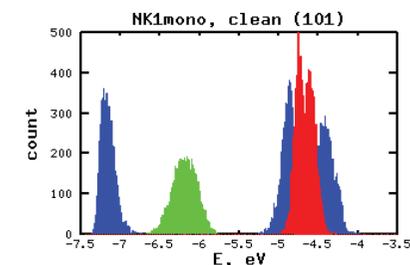


Fig.2 Distributions of energies of selected states during the MD trajectories for NK1 dye

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Advanced light management in Solid State Dye sensitized solar cells by quasi-1D hierarchical TiO₂ nanostructures

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Light trapping and advanced light management schemes are a promising, yet quite unexplored, route to enhance efficiency in Solid State Dye Sensitized Solar Cells. Indeed, these devices typically suffer from a low optical density due to the limitation in thickness connected to the use of a solid state hole transporting material (HTM). We present a novel photoanode architecture based on hierarchical TiO₂ nanostructures characterized by an high multi-wavelength scattering and light trapping efficiency. These quasi-1D tree-like structures are grown by self-assembly from the vapor phase on a glass-SnO:F substrate by means of Pulsed Laser Deposition (PLD). Morphological and optical properties can be finely tuned and optimized with deposition parameters and thermal post-treatments. Typically, they are annealed in air at 500°C to obtain an average grain size of 20 nm and anatase crystalline phase. The novel architecture was optimized for optical properties. All samples fabricated by PLD showed a higher absorption given by an enhancement in light scattering and light trapping (Fig. 1 a). Solid-state dye-sensitized solar cells (ss-DSSCs) were fabricated upon sensitization with N719 dye, spin coating of the HTM spiro-OMeTAD and Ag evaporation. Cells fabricated with the novel hierarchical TiO₂ photoanode showed higher short circuit current, J_{sc}, in accordance to the higher optical density measured. Overall, higher fill factor, FF, and similar open circuit voltage, V_{oc}, than reference cells made with conventional mesoporous TiO₂ determined an higher power conversion efficiency of the new architecture. Field emission scanning electron microscopy (SEM) and transmission electron microscopy are used to gain insights about the correlation between optical properties and photoanode morphology at different length scales, HTM infiltration, and the inorganic-organic interface. The performances of the devices were then tested using a solar simulator. The advanced light management and the outstanding HTM percolation shown by SEM images were thought to be the reason of an overall enhancement of the average photogenerated current density and efficiency of the nanotrees photoanodes compared to the nanoparticles ones. In figure 1b and 1c SEM images of the nanotrees used for cells fabrications and the J-V curves of the champion devices are reported.

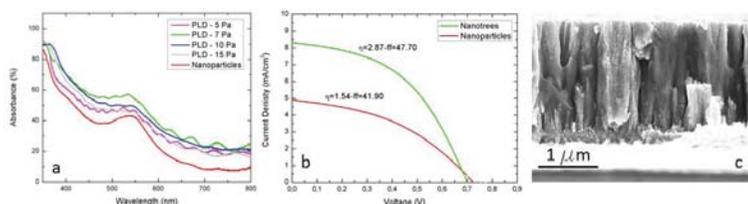


Figure 1a) UV/vis spectroscopy showing the absorbance and diffusive transmittance spectrum of the PLD fabricated devices compared to the one fabricated using standard nanoparticles paste; **b)** J-V curves of champion devices; **c)** SEM images of a device fabricated using nanotrees.

Keywords: Nanostructured titanium oxide; Pulsed Laser Deposition (PLD); photoemission spectroscopy; hybrid photovoltaics.

Al-doped ZnO nanostructured layers for increasing the efficiency of thin films solar cells

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1D nanostructures have been recently considered as key materials for increasing the efficiency of the photovoltaic devices. ZnO has demonstrated probably the largest family of nanostructured materials and the bottom-up solution-based synthesis of these nanostructures have triggered considerable interest for practical applications due to important advantages as low-cost and possibility of large-scale production.

The paper presents the effect of the morphology of Al-doped ZnO nanostructured layer, deposited by chemical bath deposition method, on the efficiency of modified silicon thin films solar cells deposited by CVD method.

The paper presents a new approach, the modification of photovoltaic cells consists in using ZnO nanowires film as the first layer for the deposition of TCO and p, i and n semiconductive silicon films. The effect of this layer on the solar cell efficiency was optimized by controlling the morphology of zinc oxide nanostructures. The morphology and optoelectronic properties of transparent Al:ZnO 1D nanostructured thin films used for the modification of silicon solar cells were investigated using HRSEM, optical transmittance, ellipsometry and solar simulator. Our experiments demonstrated that nanostructured layer containing a mixture of nanorods and nanosheets increase the efficiency of solar cells due to effects of light trapping and increasing the surface of *p/i/n* junction.

Key words: Al-doped ZnO, nanorods, solution synthesis, anti-reflective layer, *p/i/n* silicon junction, photovoltaics, cell efficiency.

AlGaAs/ GaAs Tunnel diodes grown on misorientated GaAs substrates for InGaP/ GaAs dual-junction solar cell applications

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The material properties of N⁺⁺-GaAs/P⁺⁺-AlGaAs tunnel diodes (TDs) grown on misorientated GaAs substrates, such as 2°, 6°, 10°, 15° off, are investigated, and these TDs are applied to the InGaP/GaAs dual-junction solar cells in this study. It is found that the misorientation influences both surface roughness and interface properties of the N⁺⁺-GaAs/ P⁺⁺-AlGaAs TDs. Smooth surface (rms roughness: 1.54 Å) and sharp interface for the GaAs/ Al_{0.3}Ga_{0.7}As TDs were obtained when the (100) tilted 10° off toward (111) GaAs substrate was adopted. Due to the reduction of the sticking coefficient and the number of anisotropic sites, the oxygen content of TDs layers grown on 10° off GaAs substrates was reduced. The conversion efficiency of InGaP/GaAs dual-junction solar cell with N⁺⁺-GaAs/P⁺⁺-AlGaAs TD grown on the (100) tilted 10° off toward (111) GaAs substrate is close to 20%.

Keyword: N⁺⁺-GaAs/P⁺⁺-AlGaAs tunnel diodes, misorientated GaAs substrates, InGaP/GaAs dual-junction solar cells

An experimental study of a hybrid photovoltaic-wind system with battery storage

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This paper describes the design and testing of a hybrid photovoltaic-wind system with battery storage, load and hybrid system controller for battery charging and discharging condition.

The experimental set up has been realized in the Unity of Research in Renewable Energies in Saharan Medium, Adrar (Algeria). The photovoltaic panel group constitutes the primary energy supplier of the system; while the wind turbine is the secondary supplier since the contribution of wind turbine is small as compared to the share of the photovoltaic subsystem (small wind turbine).

Keywords: Hybrid energy system, photovoltaic energy, wind energy, battery storage, load profile.

Analysis of heat loss of parabolic through collectors of Shiraz (Iran) solar power plant

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Solar thermal power plant employing parabolic trough collectors are constructed in various countries and it is going to be comparable with conventional system if one considers environmental impacts. Reducing electricity cost by means of increasing thermal efficiency and reducing heat losses are the main considerations among such power plant developers. In this respect heat loss of parabolic trough collectors for the collector field of 250 kW Shiraz (Iran) solar thermal power plant is evaluated for various conditions. For analysis, both experimental measurements and numerical modeling are made to find the impact of failure of heat collecting tubes (HCE). The amount of heat losses are compared numerically for 3 different types of tube; vacuum, lost vacuum (air) and broken glass (bare) tube. The experimental measured data are used to validate the numerical simulation. For temperature measurements around the glass tube and absorber tube an infrared thermograph (IR) camera is used. Thermal images are calibrated with measuring some local temperatures. For theoretical simulation a commercial code of thermal analysis of parabolic collectors are used. The field measurements and theoretical results indicate that for the present construction system of collectors field a vast amount of thermal loss occurs in the supports. An absorber tube with vacuum reduces significantly the heat losses in comparison with broken tube or tube without vacuum. During power plant operation poor isolation or any glass tube failure should be avoided for any collectors field.

Keywords: Heat loss; parabolic trough collector; thermal efficiency; infrared(IR) camera

Analytical approximation of external characteristic of solar cell

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The approximation of external characteristic (EC) of solar cell is proposed. Analysis is based on solar cell equivalent diagram shown in Fig.1. Elements of the circuit are as follows: emf E , open circuit voltage U_{oc} , short circuit current I_{sc} , current I and voltage U across load and resistors: radiation r_r , series r_s and parallel r_p . The emf E is constant to any solar power on the cell's surface P_s due to the linear connection between P_s and I_{sc} ; it is equal to $E = P_s / I_{sc} = \text{const}$. Under the certain radiation P_s the resistors' values are as follows: $r_r = (E - U_{oc}) / I_{sc}$ is constant; r_s and r_p vary with the load current changing ($0 \leq I \leq I_{sc}$) as $U_{oc} / I_{sc} \leq r_p \leq \infty$ and $0 \leq r_s \leq U_{oc} / I_{sc}$.

Two exponential approximations of the resistor r_s as a function of a load current I and/or as a function of an output voltage U are proposed:

$$\begin{aligned} r_s &= \frac{U_{oc}}{I_{sc}} \left(1 - e^{-a \frac{I}{I_{sc} - I}}\right) \\ r_s &= \frac{U_{oc}}{I_{sc}} \left(1 - e^{-b \frac{U_{oc} - U}{U}}\right) \end{aligned} \quad (1)$$

According to (1) the following is correct: $r_s = 0$ at $I = 0$, $U = U_{oc}$ and $r_s = U_{oc} / I_{sc}$ at $I = I_{sc}$ and $U = 0$. The coefficients a and b are found requiring that the approximation curves will pass through the MPP of the cell (I_m , U_m). The equations obtained are:

$$\begin{aligned} r_{sm} &= \frac{U_{oc} - U_m}{I_m} = \frac{U_{oc}}{I_{sc}} \left(1 - e^{-a \frac{I_m}{I_{sc} - I_m}}\right) \\ r_{sm} &= \frac{U_{oc} - U_m}{I_m} = \frac{U_{oc}}{I_{sc}} \left(1 - e^{-b \frac{U_{oc} - U_m}{U_m}}\right) \end{aligned} \quad (2)$$

Comparison of the approximations allows finding the EC of the solar cell. As examples the EC of the single crystal, poly-crystal and amorphous solar cells are calculated. The calculation results are compared with the characteristics obtained experimentally. A good matching is observed.

Keywords: solar cell; external characteristic; approximation

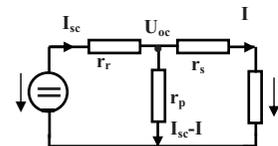


Fig.1. Solar Cell Equivalent Circuit

Band gap prediction of nanocrystalline tin oxide thin film solar cell using taguchi robust design method

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Nanocrystalline tin oxide thin films were deposited on glass substrates under various deposition conditions. Taguchi analysis was used to model the dependence of the band gap of transparent nanocrystalline tin oxide thin film on the process parameters. Comparison between the model predicted band gap value (3.23 eV) and the experimental observation band gap value (3.30 eV) predicted a remarkable agreement between them. The predictions of the model and sensitivity analysis showed that among the effective process parameters, deposition time and concentration were the main parameters having significant effect on the band gap of nanocrystalline SnO₂ thin film solar cell.

Keywords: Transparent conductive oxide; Solar cell; Band gap; Surface roughness; Taguchi robust design

Behaviour of steels in contact with liquid metals considered for thermal energy storage

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Energy storage in concentrated solar power plants is an important point for solving the mismatch between solar energy supply and electricity demand. Energy storage also improves the performance and the reliability of energy systems. Thermal energy storage is one of the methods which include sensible heat storage (SHS) and latent heat storage. The choice of materials for thermal storage is of course based on their thermal properties. These include inorganic salts, salt composites, metals and metal alloys. Thermal properties such as specific heat, thermal conductivity, thermal expansion, heat of fusion and melting temperature have to be carefully determined. For the SHS technique, liquid metals can be employed at high temperature but they have not yet been seriously considered because of weight penalties. Nevertheless, liquid metals remain an option for thermal energy storage. For the reliability of the plant, it is necessary to pay also attention on structural materials of components in contact with the liquid metals. This concerns tanks, pipes, heat exchangers...which can suffer from corrosion and mechanical loading, and especially environment assisted damage.

The objective of the paper is to present some results obtained these last years on the behaviour of steels deformed in presence of liquid metals.

A modified 9Cr1Mo martensitic steel and a 18Cr10Ni2Mo austenitic stainless steel have been investigated. These materials are frequently used for high temperature applications and in aqueous corrosive media respectively. They differ not only by their chemical composition but also by the heat treatment they can be submitted to. Especially, the 9Cr1Mo is subjected to quench and temper treatment which temperature plays a strong effect on hardness.

These materials have been deformed under monotonic or cyclic loading in several liquid metals: lead, lead-bismuth eutectic, tin and gallium in a temperature range between 300°C and 500°C except for gallium where the tests were carried out at 35°C.

It is shown that the liquid metals can modify the behaviour of the solid metals in different way considering the solid metal/liquid metal couple:

- a liquid metal assisted plasticity as for 18Cr10Ni2Mo austenitic stainless steel deformed in gallium
- no effect of liquid metal as for 9Cr1Mo steel tempered at 750°C and deformed in Pb-Bi eutectic
- a liquid metal restricted plasticity as for 9Cr1Mo tempered at 650°C or 700°C and deformed in Pb-Bi eutectic
- a liquid metal embrittlement for 9Cr1Mo tempered at 500°C, which is not the right tempering condition, and then deformed in Pb-Bi eutectic
- a liquid metal accelerated damage as for 18Cr10Ni2Mo austenitic stainless steel and for 9Cr1Mo steel under fatigue in Pb-Bi eutectic

The mechanical results are discussed according to metallographic investigation of the fracture surfaces and of the surface damage of specimens.

Finally, the study suggests that modified 9Cr1Mo martensitic steel and 18Cr10Ni2Mo austenitic stainless do not exhibit alarming behaviour in the considered liquid metals. Assessment of these effects would increase considerably the reliability of the plant. This encourages use of liquid metals for thermal energy storage.

Keywords: mechanical test; fracture; liquid metal modified plasticity

Bimodal nanostructured TiO₂ thin films for dye sensitized solar cells

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Dye-sensitized solar cell (DSC) is one of the most promising photovoltaic technologies for production of renewable, clean, and affordable energy. Since its invention by Graetzel et al. in 1985¹ it has been permanent subject of interest of research teams all over the world. One of the key issues in optimization of the Graetzel cells consists in the morphological engineering of the TiO₂ photoanode. High surface area, crystallinity and transparency predetermine mesoporous thin layers of TiO₂ to work effectively as photoanode in DSC. The presence of mesopores together with the anatase particle size of several nanometers is reflected by a high roughness factor (a specific surface area of the sample multiplied by its mass and divided by a geometric area of the thin layer). The solar performance of multilayer TiO₂ films sensitized with N-945 dye scales linearly for 1 – 3 layer films, but approached a plateau for thicker films^{2,3}. The solar conversion efficiency of 5.05 % was found for a 2.3 μm thick mesoporous TiO₂ film consisting of 10 layers. Nevertheless, despite the linear increase of roughness factor with the number of layers, the solar conversion efficiency reaches plateau values for more than 8 layers. Electron capturing and recombination with dye/electrolyte within extremely open mesoporous structure has been suggested to cause such a discrepancy. To eliminate this problem, TiO₂ anatase with fibrous morphology was incorporated into mesoporous structure. We have combined bottom fibrous TiO₂ layer with different kinds and thicknesses of mesoporous films and evaluate their performance in DSC. Performance of the DSC with 2.5 μm bimodal TiO₂ layer reached 5.35%. Recently we have started a new approach, combining well developed crystallinity of nanoparticulate anatase and high surface area of mesoporous TiO₂. Resulting layers are transparent, mechanically resistant and first IPCE measurements provide promising results.

Acknowledgement: Financial support of GA CR (P108/12/0814) is gratefully acknowledged.

Keywords: TiO₂ thin films, dye sensitized solar cell

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Building integrable luminescent photovoltaic systems

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In order to reach lower cost per installed capacity (€/W), concentrating photovoltaic (CPV) systems reduce the semiconductor quantity by optical concentrating systems and increase the efficiency by using more efficient solar cells. Within CPV sector, luminescent solar concentrators (LSC) represents a very attractive technology. Solar light incident on LSC devices is absorbed by dyes, re-emitted into a guided mode in the slab, and finally collected by a PV cell mounted at the edge of the slab.

LSCs show several advantages among CPV systems: i) use also the diffuse component of solar radiation; ii) do not require expensive solar tracking reducing the final cost and improving sensitively their architectural integrability. Moreover LSCs can be designed such that the luminescence energy closely matches the solar cell absorption edge for improving the system efficiency and reducing both the spectral and thermalisation losses.

This work reports the results obtained within PHOTOFUTURE, an European Project focused on developing high efficient LSC prototypes: in particular the work is focused on the development and testing of luminescent solar concentrators based on Eu(TTA)₃Phen, an interesting europium organometallic complex characterized by an extremely large Stokes shift which allows to minimize self-absorption losses. In particular in this work we reported: (i) fabrication of different LSC devices, characterized by different thicknesses and produced by different production procedures; (ii) characterization of the physical and optical properties of the different LSCs slabs; (iii) testing and comparison of the I-V performances of the different LSCs devices.

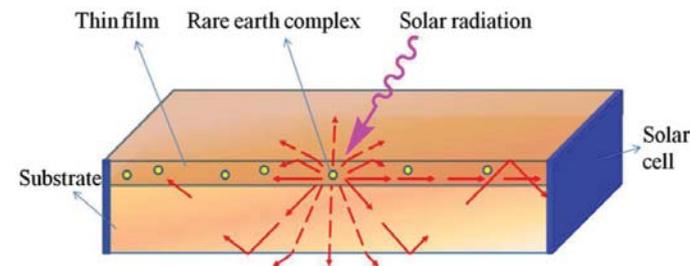


Fig. 1. Schematic of a thin film LSC: Light is collected over the top surface by luminescent centers. It is then re-emitted and wave guided towards the edges, where PV cells can be placed. The light trapping relies on total internal reflection.

Keywords: photovoltaic systems, luminescence, solar concentrators

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CdTe thin films for Solar Cells Application Prepared by Close-Spaced Sublimation and Magnetron Sputtering Methods

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Cadmium telluride became one of the most promising materials for its potential applications in solar energy technology since last decades. A lot of methods for preparing CdTe thin films had been reported [1]. The electrical, optical and structural properties of the films can change depending on preparation method and conditions. Our interest lies in taking advantage of the benefits offered by various methods to make films with desired properties.

This work presents comparison of XRD, atomic force microscopy, confocal Raman spectroscopy, and photoluminescence data's for two series CdTe thin films deposited on glass substrates by close space sublimation (CSS) and magnetron sputtering methods.

CSS-deposited CdTe thin films crystallized in the cubic sphalerite structure (space group F43m) with $a=6485\text{\AA}$ and showed a preferential orientation along the [111] direction. The films consist of grains 2–6 μm in size (Fig. 1a) and are dense. Grain sizes of magnetron sputtered films are smaller (around 1 μm , Fig. 1b) and are oriented mainly in [311] direction. The intensities of photoluminescence and Raman emission of CSS films are much higher than that of magnetron sputtered films.

The difference between the results for CSS-deposited and magnetron sputtered CdTe films are discussed in terms of the fact that CSS films are deposited at a much higher temperature (620°C versus 200–300°C) and therefore contain a lower concentration of structural defects [2].

Keywords cadmium telluride; close-spaced sublimation; magnetron sputtering

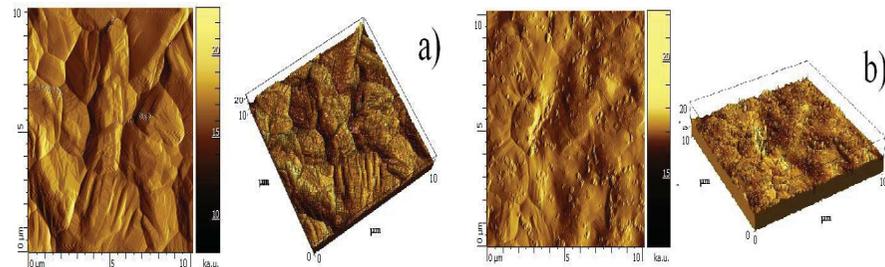


Figure 1. AFM images of CSS deposited (a) and Magnetron sputtered (b) films

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Challenges in materials selection for hydrogen producing solar reactors

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Solar thermochemical production of hydrogen requires high temperatures in the range of 1000 K to 15000 K. In order to house this process, a solar reactor is needed, where incoming solar radiation penetrates into the reactor cavity through an aperture. An example solar reactor which was recently developed and manufactured at Sustainable Energy Research Laboratory (SERL) of Texas A&M University at Qatar is shown in Figures 1 and 2. Building a solar reactor has many design challenges, where material selection plays a key role. Finding the most suitable material for each auxiliary part such as quartz window, internal coating of the cavity walls, insulation material, and aperture are some of the major design constraints to minimize heat transfer losses and to maximize hydrogen production efficiency.

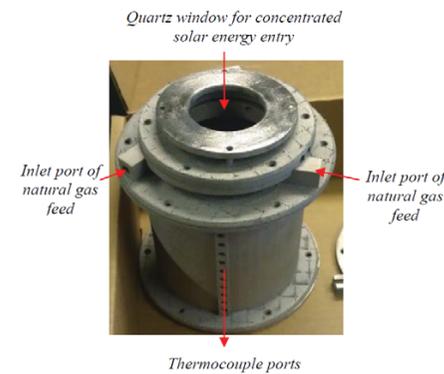


Figure 1: Solar reactor developed at Sustainable Energy Research Laboratory of Texas A&M Qatar

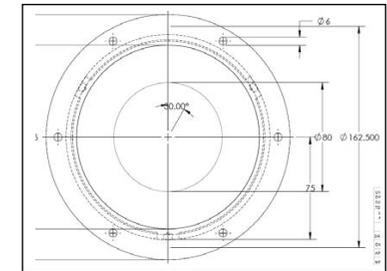


Figure 2: CAD drawing of the solar reactor cross section with dimensions in mm

In a solar reactor, it is important to reach high exergy efficiency in order to have smaller solar collection area and, therefore, reduced cost for the generation of unit amount of hydrogen. Because of the Carnot limit, it is favorable to run the thermochemical processes at high temperatures. But from the heat transfer point of view, high temperature process causes high losses due to re-radiation. By addition of metal or carbon based catalyst, methane decomposition in a solar reactors can be enhanced. However, metal catalysts deactivate very quickly because of the blockage of catalytic active sites by nano scale carbon particles formed during methane decomposition. As for the carbon based catalysts, they are not only cheap but also do not require preprocessing or recovery after processing. With the addition of carbon as catalyst, more nucleation sites in the reaction zone are obtained for heterogeneous decomposition reactions. Moreover, since carbon particles are directly exposed to the high flux radiation upon their entrance into the solar reactor, they absorb the heat and then exchange radiation with the nearby particles and gas molecules. Therefore, carbon addition as a catalyst creates an enhanced heat transfer mechanism inside a solar reactor and that yields with enhanced hydrogen production efficiency.

This paper describes materials selection methodology for a high temperature resistant and optimum heat transfer loss capacity solar reactor design. The paper also discusses impact of catalyst use on the hydrogen production efficiency, and provides information on the material properties of carbon black produced from solar cracking of natural gas process.

Keywords solar reactor; material selection; radiation losses; design constrains

Characteristic Solar Thermal Collector on Serial and Parallel Configuration

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This paper discuss the utilization of Solar Thermal Energy used as a fraction of energy source for Solar Cooling System and/or Organic Rankine Cycle (ORC) which will be developed. Eight units flat plate solar collectors was arranged as such that could be connected in series and parallel. Water – as the working fluid –, its flow rate inside the circuit regulated by valves.

Thermocouples measured working fluid temperature at the inlet and outlet of each collector, inside water tank and ambient temperature. Water from the tank circulated using a pump with maximum flow rate 33 liter perminutes, measured by a flowmeter at the inlet. Solar radiation measured by a pyranometer mounted paralel to the collector, and recorded every 5 minutes.

Simulation program was developed using ordinary equation, and the results compared to experimental data. The heat removal factor and collector efficiency from several test was compared for both series and paralel configuration.

Keywords Flate Plate Collector; Heat Removal Factor; Collector Efficiency

Characterization of materials degradation of photovoltaic modules

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The study of the source of degradation and the possibility to recycling materials that are part of photovoltaic modules is a subject of great interest. This paper presents the results of the characterization and degradation of photovoltaic materials, that come from polycrystalline silicon modules after 20 years of outdoor.

Besides to the defects observed after a visual inspection such as yellowing, delaminations and corrosion near the busbar, bubbles inside cells and cracks, etc, a disassembling process has been used to separate the panel components, following by specific treatment. After being classified, the chemical composition and morphology have been characterized using different techniques such as scanning electron microscopy (SEM) (Fig. 1a, b and c), thermogravimetric analysis (TGA), X-Ray diffraction (XRD), optical and IR measurements.

As a result, it has been able to determine the extent of EVA and glass degradation and also the presence of impurities in these layers, as well as the changes occurred in the silicon waffles over time.

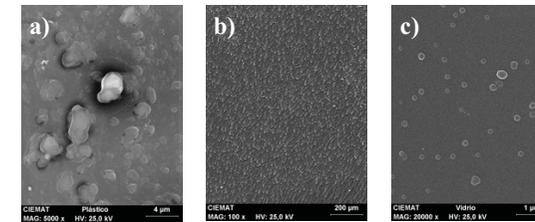


Figure 1: SEM sample images: a) EVA, b) silicon and c) glass, obtained from degraded panel.

Keywords Dregadation, Characterization

Characterization of transparent graphene electrode for dye-sensitized solar cell

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Recently, carbon material have been attracted in solar cells for electrochemical electrodes [1]. Especially, graphene is one of candiated materials for the electrode applications because not only its high optical and electrical properties but also excellent catalytic activity [2, 3].

In this letter, we prepared reduced graphene by chemical conversion of graphene oxides [4]. Then, graphene applied to devices deposited by electrophoretic method. The electrochemical properties of graphene electrode were examined by using half cells. Dye-sensitized solar cells (DSSCs) were fabricated with those graphene electrode in order to examine the conversion efficiencies. It could be tunable graphene counter electrode of transparency, electrochemical properties and conversion efficiency of DSSCs by controlling the electrophoresis deposition time, and electric field.

The results suggested that transparent GCE by electrophoretic method could be used as one of candidates for counter electrodes in DSSCs.

Keywords graphene; counter electrode; dye-sensitized solar cell; electrophoretic deposition

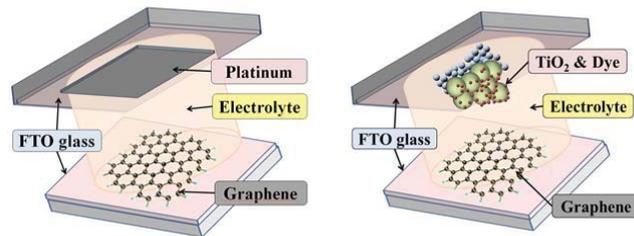


Figure 1 Schematic fo half cell and full cell for characteristics of DSSCs

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Comparison of different Scalar-Based control in the Photovoltaic pumping system

Chergui Moulay-Idriss; Pr. Mohamed Bourahla

We aim to arrive at an improved control and optimization between the different functions of the elements of a solar pumping system. The photovoltaic can supply maximum power only for defined output voltage. In addition, the operation to get the maximum power depends on the terminals of load, mostly a non-linear load like induction motor. In this work, we used an intelligent control method for the tracking module inserted in the photovoltaic system under variable temperature and irradiance conditions. The tracking module can be used to maintain the operation of the photovoltaic panel at maximum power; this can be done by means of the Maximum Power Point tracking by controlling the voltage or current generator independently of the load. The system was tested with the use of Scalar-Based control motor, with the Voltage/frequency control, by introducing the sine-triangle technique, but we ended up with a very high harmonic content, leading to control problems uncontrollable (noise, for oscillations of the torque and current disturbance on speed), which requires an increase in the value of the filter capacitor. To reduce these, we use other technical of inverter control as calculated PWM technique. At the end we presented a comparison between these two techniques by different electrical quantities to show the interest of technical Calculated PWM

Cu-doped TiO₂ by means of hydrolysis reaction at low temperature

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Introduction: Doping of TiO₂ with metal atoms is known to improve the properties for its use as semiconductor, both in photocatalytic and photovoltaic applications.^{1,2} In this work, we introduce a methodology based on the hydrolysis of a Ti-alkoxide at low temperature for obtaining Cu-doped TiO₂ with a low band gap energy.

Experimental: Cu-doped TiO₂ was synthesized using a hydrolysis reaction at low temperature using titanium n-butoxide as precursor. The procedure is: (a) 100 mL of water was cooled at 4 °C; (b) during the cooling process a stoichiometric amount of CuCl₂·2H₂O was added to get Cu/TiO₂ proportions of 2.5%, 5.0% and 7.5%; (c) 10 mL of titanium n-butoxide was added drop wise under magnetic stirring; (d) when the addition is finished, the solution was homogenised for 30 min; (e) 4 mL of HNO₃ (purity 65%) was added, and the mixture was kept under magnetic stirring for 2 hours; (f) solvent was evaporated under vacuum at 333 K using a rotavapor, and later on a hotplate at 373 K until complete dryness; and (g) as-prepared Cu-doped TiO₂ nanocrystals were annealed in air for 1 hour at 723 K.

The samples obtained has been characterized by: (a) ICP-AES for determining the amount of Cu introduced in the TiO₂ structure; (b) XRD and Raman spectroscopy in order to detect the crystalline phases in the samples; (c) UV-Vis spectroscopy for obtaining the values of band gap energy of the synthesized samples.

Results and discussion: Table 1 shows the real percentages of Cu versus TiO₂ which were introduced in the synthesized nanocrystals. In all cases, the results from ICP-AES technique show that the amount of Cu incorporated into the TiO₂ structure is about 80% with regard to the initial amount of Cu approximately results obtained for ICP-AES. Moreover, from XRD patterns, it can be seen that for all Cu-doped samples, only the peaks of anatase and rutile phases of TiO₂ were found. In addition, XRD did not reveal the formation of any crystalline phase of copper species.³ These results confirm that Cu ions are uniformly dispersed among the anatase crystallites. In turn, Raman spectra are in good agreement with XRD results. From Raman spectra, it is possible to see that several structural distortions occur because a structural copper doping. At last, from diffuse reflectance UV-Vis spectra, the values of the band gap energy have been calculated and using the Tauc formalism of the Kubelka-Munk reflectance plot. The obtained values are shown in table 1. We note that the band gap energy decreases with increasing Cu concentration. In addition, our Cu-doped samples show a decreasing of the band gap energy much higher than those reported in the literature.

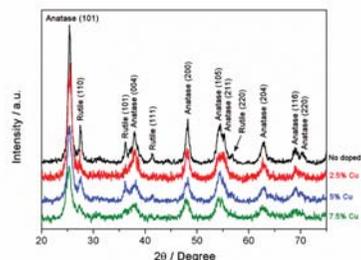


Figure 1. XRD patterns of undoped TiO₂ and Cu-doped TiO₂.

Conclusion: In this work, Cu-doped TiO₂ has been synthesized using a hydrolysis reaction at low temperature. We have obtained evidences for the presence of Cu in the samples. From XRD and Raman we can conclude that Cu is introduced inside the TiO₂ structure. In turn, the band gap energy decrease with increasing Cu concentration and this decrease is much higher than those reported in the literature.

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Keywords doping; Cu-doped TiO₂.

Table 1. ICP-AES results and band gap energy values obtained.

Initial %Cu	Real %Cu	E_g / eV
0.0	0.0	3.0
2.5	2.03±0.03	2.1
5.0	4.10±0.01	1.7
7.5	5.76±0.07	1.6

Deposition of Composite Thin Films by Electrophoresis using Two Kinds of TiO₂ Nano Particles

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The absence of cracks and a high optical transparency are critical factors for obtaining high performance when TiO₂ thin films are used as cathodes in dye-sensitized solar cells (DSSCs). The TiO₂ nano particles (here after, TiO₂ nanoparticles) used in this study is composed 100 % anatase and can smoothly transport electrons between nanoparticles by oriented attachment which makes the diffusion length of the electron comparatively long and are thus suitable for use as photocatalysts and as the cathode material for DSSCs^[1,2]. Electrophoresis deposition is an inexpensive process and has a high deposition rate. However, it is difficult to deposit thick films for the TiO₂ nanoparticles by electrophoresis. On the other hand, it is possible to deposit thick films for P25. P25 (Degussa) is the TiO₂ nano particle, is a commercially produced and is composed of 80 % anatase and 20 % rutile. However, the transparency of the thin film deposited using P25 is not high. The first goal of this study is to deposit transparent and thick composite TiO₂ thin films using powder mixture of TiO₂ nanoparticles and P25. The second purpose is to find the optimum condition of electrophoresis to deposit composite thin films with the high quality which improves the power generation efficiency (PGE) of DSSC.

The TiO₂ nanoparticles were synthesized according to the method by Adachi et al.^[1]. The synthesized TiO₂ nanoparticles were classified according to size by centrifugal classification^[2]. First, TiO₂ nanoparticles were precipitated at 4000 rpm by centrifugal classification. Next, TiO₂ nanoparticles were precipitated from the supernatant of the colloidal solution at 6000 rpm. Using the same method, 6000–8000, 8000–10,000 and 10,000–13,500 rpm nanoparticles were precipitated. In addition, TiO₂ nanoparticles precipitated at 13,500 rpm were prepared. Powder mixture of classified TiO₂ nanoparticles and P25 was dispersed in ethanol as dispersion medium and TiO₂ colloids were adjusted. Composite TiO₂ thin films were deposited on an indium tin oxide glass substrate by constant-current electrophoresis for various electrophoresis times and mass mixture rates of two kinds of TiO₂ nano particles^[2]. After adsorption of dye, the substrate was dried in air and the DSSC was fabricated. Current density-voltage ($J-V$) characteristics were measured in AM1.5. The surface of TiO₂ thin film was evaluated by optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy. The wavelength dependence of the transmittance of the TiO₂ thin films with adsorbed dye was measured using a visible light spectrometer.

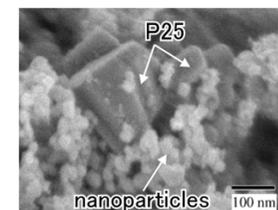


Fig. 1. SEM image for the composite TiO₂ thin film. Mass ratio of 10,000–13,500 rpm nanoparticles and P25 is 1:1. Film thickness is 12 μm.

The transparency of composite thin films was higher compared with that of only P25. Figure 1 shows the SEM image for the composite thin film deposited using powder mixture of 10,000–13,500 rpm nanoparticles and P25 with the mass ratio of 1:1. P25, of which size was larger than that of nanoparticles, were located as matrix material in the thin film. Nanoparticles filled up the space between P25 nano particles. Nanoparticles were connected each other. Figure 2 shows the $J-V$ characteristics of DSSCs fabricated using only classified TiO₂ nanoparticles or P25. All the thin films were approximately 500 nm thick. The PGE of a DSSC fabricated using thin film deposited only 10,000–13,500 rpm nanoparticles, only P25 and those powder mixture were approximately 2.4, 3.5 and 4.8 %, respectively. Therefore, we succeed to deposit thick film using powder mixture of TiO₂ nanoparticles and P25 as a matrix material and to achieve the high PGE.

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Keywords electrophoresis; dye-sensitized solar cells; TiO₂ nano particles; composite thin films; classification

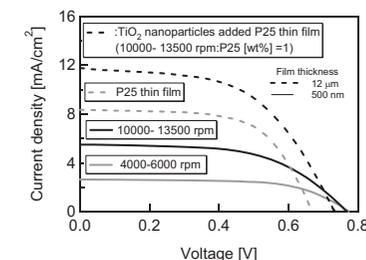


Fig. 2. $J-V$ characteristics of DSSCs fabricated using composite TiO₂ thin films and TiO₂ thin films deposited using classified TiO₂ nanoparticles.

Development of a pilot plant Solar Crop Drying System Using Liquid Desiccant

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In a pilot plant solar liquid desiccant drying system (LDDS) developed at Materials & Energy Research Centre (MERC), considerable reduction in the consumption of fossil fuels has been achieved for rice drying, while yielding improved rice quality. The quality of many food crops begins to deteriorate within hours of harvesting. Drying of the product soon after harvesting can avoid food spoilage and achieve storage lifetimes of 1-3 years. The moisture content of grains and seed products typically needs to be reduced from 20-40% to about 10% moisture by weight. Evaporating water requires heat energy and, for a crop containing 40% moisture, at least 1200 mega joules of heat energy is required for each ton of dried product. This heat is normally provided by burning diesel fuel or liquid petroleum gas (LPG). To reduce the moisture content from 40% to about 10% requires at least 30 litres of diesel fuel or 50 litres of LPG to be burned to provide the heat requirement for each ton of dried product. The results of this experimental work conducted in a hot and humid location in the north of Iran on the Caspian Sea indicate that by using the low temperature solar energy technique, in addition to the improved rice quality and energy savings, the drying time has considerably been reduced.

Keywords: Crop drying, liquid desiccant, desiccant regeneration, air dehumidification



Photograph of the solar LDDS pilot plant installed on the site

Development of a Pilot Plant Solar Liquid Desiccant Air Conditioner

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In a pilot plant solar liquid desiccant air conditioner (LDAC) developed at Materials & Energy Research Centre (MERC), dehumidification of the outside air is achieved through a honeycomb packed-bed heat and mass exchanger, using lithium chloride solution as the desiccant. The dry air obtained from the dehumidification process is evaporative cooled inside a cooling pad and directed into the conditioned space. The dilute solution thus produced, due to absorption of water vapour in the air, is concentrated in a honeycomb packed-bed scavenger air regenerator using hot water from flat plate solar collectors. Carryover of the desiccant particles has been avoided by using eliminators.

In this paper the experimental results obtained from testing the pilot plant absorber unit in a hot and humid location in the north of Iran on the Caspian Sea, have been presented and compared with a previously developed model for a honeycomb packed-bed. The comparison reveals that good agreement exists between the experiments and model predictions. The inaccuracies are well within the measuring errors of the temperature, humidity and the air and solution flow rates. The above tests further reveal that the unit has a satisfactory performance to control independently the air temperature and humidity when installed on a commercial site with an area of about 250 m².

A commercialization study reveals that the operating cost of a solar LDAC is significantly lower than its conventional counterpart. The costs would further reduce if a storage system was used to store the concentrated solution of liquid desiccant. A simple payback of five years was determined for the solar components of the liquid desiccant system in this study.

Keywords: Liquid desiccant, Dehumidification, Packed-bed, Solar regeneration.



Photograph of the solar LDAC pilot plant installed on the site

Donor-Acceptor Conjugated Novel aromaticfused polymer is High-performance Organic photovoltaic solar Cells

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Organic photovoltaic devices have gained a broad interest in the last few years due to their potential for large-area, low-cost solar cells. Various material concepts have been employed using small molecules, conjugated polymers, and combinations of inorganic and organic materials as the active layer. Among them, solar cells based on thin polymer films are particularly attractive because of their ease of film formation via solution process and mechanical flexibility. Although significant progress has been made, the performances obtained from polymer solar cells (PSCs) are still not satisfactory for commercialization. As a result of intensive investigations by many researchers, it is well known that by collaboratively lowering the HOMO energy level and band-gap, both high short circuit current (J_{sc}) and open circuit voltage (V_{oc}) can be achieved thus rendering high power conversion efficiency (PCE) upon thorough device and materials optimization. We reported the synthesis of novel polymeric semiconductors **Polymer1** for the fabrication of soluble polymer solar cells, these polymers with high yield were synthesized by Stille coupling reactions. The polymers were characterized by ¹H-NMR and IR studies. The photophysical properties for the polymers were investigated by UV-visible absorption. The polymers are good soluble in organic solvents such as chloroform, tetrahydrofuran, toluene and chlorobenzene. The polymers showed broad absorption peaks, **Polymer1** showed at 660 nm in solution and at 670 nm in film. The optical band gap for the polymers in film were calculated by UV edges. The electrochemical properties for the polymers were investigated by CV. The polymers showed HOMO energy level were -5.39 eV. The thermal properties for the polymers were investigated by TGA. The polymers showed T_d 5 % weight loss at 401°C. **Polymer1** showed higher device performances (PCE of 5.1%) compared to other PSCs polymer.

Dye Adsorption by Electrophoresis for Dye Sensitized Solar Cells

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In order to improve the power generation efficiency (PGE) of a dye-sensitized solar cell (DSSC), it is important to adsorb the dye molecule uniformly within the whole negative electrode material, such as titanium dioxide (TiO₂) thin films^[1]. Although immersion is typically used to adsorb dye molecules on the surface of TiO₂ by soaking in a solution in which dye molecules are dissolved (dye solution), the optimal adsorption time is extremely dependent on the kind of dye. On the other hand, for dye molecules which might be electrostatically charged in a colloid, the adsorption can be examined using electrophoresis^[2]. An electric field exists inside a TiO₂ thin film, which is a dielectric material, and as a result, the dye molecules are transported rapidly from the surface of the TiO₂ thin film to the interface of the thin film and the electrode material such as indium tin oxide (ITO). The first goal of this study was to determine the optimum conditions of adsorption of Cis-di(thiocyanate) bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II) bis-tetrabutylammonium (N719). The second purpose of this study was to find the optimum electrophoresis conditions by varying the concentration of the dye solution of N719, the electrophoresis time and the current density for electrophoresis to adsorb the dye molecules uniformly on a TiO₂ thin film.

Anatase TiO₂ nanoparticles were synthesized according to the method developed by Adachi et al.^[3], TiO₂ nanoparticle was dissolved in ethanol^[2]. TiO₂ nanoparticles were deposited on ITO glass substrate (negative electrode) by electrophoresis at 25 °C. The thickness of TiO₂ nanoparticles thin films was fixed approximately 1 μm. After deposition, the thin film was dried and annealed at 350 °C in air. The dye solution in which 10 mg of N719 was dissolved in 50 ml ethanol or fresh ion-free water as a dispersion medium for the dye was termed Conc-1 (1.68×10⁻⁴ M). The dye solution with 10×X mg dissolved N719 was termed Conc-X (X×1.68×10⁻⁴ M, 0.1 ≤ X ≤ 5). The ITO substrate deposited TiO₂ thin film was immersed in dye solution as a working electrode. An aluminum plate of 0.5 mm thickness was used as a counter electrode. The current density of electrophoresis was varied in the range of -0.1–0.1 mA/cm². The electrophoresis time was also varied. After adsorption of dye, the substrate was dried in air and the DSSC was fabricated. A solar simulator was used as the light source and the irradiation power density was set to 100 mW/cm² in AM1.5. Current density-voltage ($J-V$) characteristics were measured by changing the load resistance. The surface of TiO₂ thin film with adsorbed dye was evaluated by optical microscopy, scanning electron microscopy and atomic force microscopy. The wavelength dependence of the transmittance of the TiO₂ thin films with adsorbed dye was measured using a visible light spectrometer.

With the same current density, the short circuit current density increased with increasing the concentration of dye solution of Concs-0.1–1 and then decreased with increasing the concentration. The visible light transmittance of the TiO₂ thin films adsorbed dye using dye solutions of Concs-0.1-0.5 was larger than those of Concs-1-5 (Data are not shown). These results suggest that excess dye molecules adsorbed on TiO₂ thin films decreased the PGE of DSSCs^[2]. The PGE of DSSC fabricated using Conc-1 was the highest. It was revealed that the optimum dye concentration and current density exist for dye adsorption by electrophoresis. Figure 1 shows the $J-V$ characteristics for DSSCs using TiO₂ thin films with adsorbed dye by electrophoresis for 15 min in Conc-1 solution with 0.1 mA/cm² and immersion for 15 min or 24 h in Conc-1 or 5 solution. The PGE for immersion method was lower than that using TiO₂ thin films with adsorbed dye by electrophoresis for 15 min in Conc-1 solution with 0.1 mA/cm². It is revealed that the adsorption method of N719 using electrophoresis is effective compared with the immersion method.

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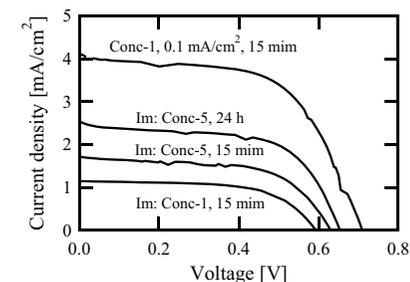


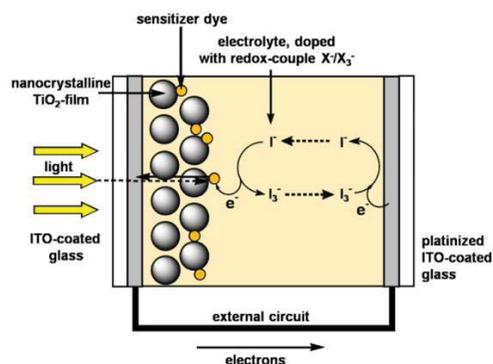
Fig. 1 $J-V$ characteristics for DSSCs using TiO₂ thin films with adsorbed N719 by electrophoresis for 15 min in Conc-1 and immersion for 15 min or 24 h in Concs-1 and 5. Im: Immersion.

Dye Sensitized Solar Cells – how far away from commercialization

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Dye-sensitized solar cells (DSSCs) use a synthetic dye, a nonporous semi-conductor and electrolyte to convert sunlight into electricity via a complex electrochemical process. Compared to silicon-based solar cells they offer the major advantage of producing significant electricity even under diffuse light. They are transparent and can therefore be used as translucent, power-generating architectural building blocks and design elements. In addition, it is also possible to produce flexible DSSCs via cheap roll-to-roll-processes.



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Ionic Liquids, compounds composed entirely of ions and liquid below 100°C, have enjoyed an increased popularity in past decade due to a unique combination of physical and chemical properties. Their low volatility and non-flammability, tunable conductivity and viscosity, combined with high electrochemical and thermal stability make them the most important electrolytes for the use in new sustainable processes like the conversion of solar energy in solar cells. The most widely used process is based on the I^-/I_3^- redox couple, and therefore the main components of the electrolytes are iodide containing ionic liquids. With these electrolytes efficiencies of more than 10% have been achieved in the laboratory.¹

In our talk we'll present our latest results about novel iodide-based electrolytes as well as the influence of important additives, reducing the so-called dark currents, which are responsible for the reduction of the overall performance as well as present the problems with the commercialization of this technology.

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Keywords ionic liquids; DSSC; dye sensitized solar cells; ready to use electrolytes

Dye sensitized solar cells based on metal-free organic dyes and aqueous electrolyte

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Dye-sensitized solar cells (DSCs) have recently emerged as promising candidates to utilize solar power because of their ease of fabrication and low cost as compared to conventional silicon based solar cells [1]. Till now, the most successful DSCs were obtained using porous TiO_2 nanocrystalline film sensitized with a ruthenium based dye with an efficiency of 11%. However, a further increase in conversion efficiency is found to be limited by slow electron transport in porous TiO_2 during the illumination. This requires replacement of TiO_2 by other suitable semiconductor material. In this regard, ZnO is potential substitute for TiO_2 in DSSC because of large band gap (3 eV), good electron affinity, and high electronic mobility ($100 \text{ cm}^2/\text{Vs}$) [2].

In this paper, we present fabrication of dye sensitized solar cells (DSSCs) which are free from toxic dyes and electrolytes. For this purpose, we have used 4,4-difluoro-1,3,5,7,8-pentamethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indecene (PM567) dye and aqueous electrolytes i.e. I^-/I_3^- or Fe^{+3}/Fe^{+2} . ZnO nanowires (Figure 1a) were grown onto ITO coated glass substrate by hydrothermal process using ZnO nanoparticles (dia ~ 30-40 nm) as seed layer and were used as anode. The photoanode was then prepared by sensitizing ZnO nanowire arrays on ITO with PM567 dye. A typical current density-voltage (J-V) curve in dark and under illumination (intensity ~50 mW/cm^2) is shown in Figure 1b. The open circuit voltage = 0.43 V, short circuit density ~ 2.84 mA/cm^2 and power conversion efficiency of 0.81 % was obtained for DSSC based on PM567 dye in aqueous iodide electrolyte, which was slightly higher than that found for N3 based DSSC.

Keywords Aqueous electrolyte; organic dyes, Dye sensitized solar cells

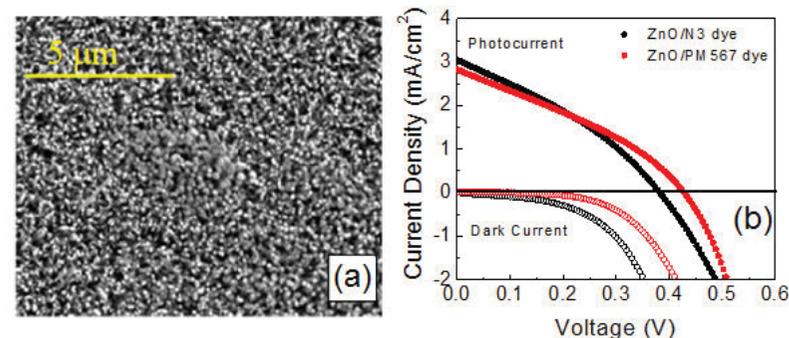


Figure 1: (a) Scanning electron microscopy image of ZnO nanowire on ITO electrode (b) J-V measurements of the dye sensitized solar cell using PM567 and N3 dye sensitized electrode in I_3^-/I^- electrolyte

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Effect of substrate temperature on properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films sulfurized from Cu-Zn-Sn alloy precursors

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In this study, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were prepared by sulfurization of single-layered metallic precursor sputtered from Cu-Zn-Sn alloy target. The effects of substrate temperatures on the structural, morphological, compositional as well as optical and electrical properties were characterized. XRD and Raman spectra have shown that CZTS compound can be synthesized without any secondary phases at substrate temperature up to 550 °C. Higher substrate temperature of 570 °C gave CZTS along with secondary phases of Cu_2SnS_3 and ZnS. The microstructure of CZTS thin films were affected by substrate temperature, in which good crystalline and dense structure was resulted at high substrate temperature. The direct band gap energies of the CZTS films were 1.45 eV, 1.47 eV, and 1.39 eV for CZTS thin films annealed at 530 °C, 550 °C, and 570 °C, respectively. The optical absorption coefficient over 10^4 cm^{-1} determined from the transmission and reflection spectra were found to be dependent on the substrate temperatures. From Hall measurement, all CZTS thin films were found to be *p*-type semiconductor, resistivity of 4.05 $\Omega \text{ cm}$, carrier concentration of $8.22 \times 10^{18} \text{ cm}^{-3}$, and mobility of $43.38 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$. These results showed that the optimal properties of CZTS thin films suitable for solar cells application were obtained by sulfurization at substrate temperature of 550 °C.

Table 1. Band gap, Electrical resistivity, carrier concentration, and mobility of CZTS thin films at substrate temperatures of 530 °C, 550 °C, and 570 °C.

Ts (°C)	Eg(eV)	Resistivity ($\Omega \text{ cm}$)	Carrier concentration (cm^{-3})	Mobility (cm^2/VS)
530	1.45	3.10	7.97×10^{18}	4.98
550	1.47	4.05	8.22×10^{18}	43.38
570	1.39	0.94	2.27×10^{19}	1.124

Keywords: $\text{Cu}_2\text{ZnSnS}_4$, thin films, sputtering, Cu-Zn-Sn precursor, sulfurization

Acknowledgments This work was supported by the Center for Inorganic Photovoltaic Materials grant funded by the Korea government (MEST-No.2012-0001170).

Effects of the position of the gas flow guidance device on carbon distribution during the growth of multicrystalline silicon ingots by the directional solidification process

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Directional solidification method is frequently used to produce the multicrystalline silicon ingots in the PV wafer industrial. The efficiency of an mc-Si solar cell depends strongly on the impurity content and level of the mc-Si wafers, which are cut from massive mc-Si ingots. One of the major impurities in multicrystalline silicon is carbon. In this study, numerical simulation has been performed to investigate the effect that installing a gas flow guidance device in a mc-Si crystal-growth furnace would have on the carbon impurity distribution in the melt during the growth process. The installation of such a gas flow guidance device changes the gas flow pattern in the furnace, which would affect the transport of carbon oxide and silicon oxide in the gas and oxygen and carbon in the melt. The results show that there is an optimum position to install the gas flow guidance device for obtaining a lowest carbon level in the melt during the solidification process.

Keywords keyword; solar cell, multicrystalline silicon ingot, directional solidification method, numerical simulation, impurities, heat and mass transfer.

Efficiency Enhancement of Dye Sensitized Solar Cell by Incorporating Li Ion In to ZnO Nanosturcures

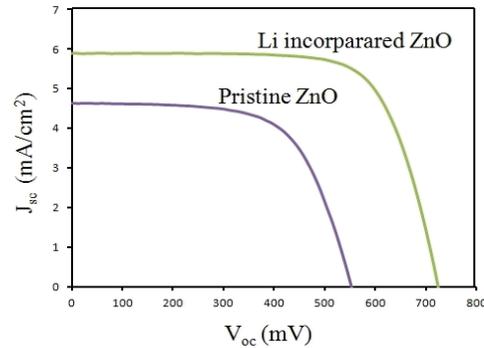
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ZnO nanostructures have been received broad attention in recent years as a promising alternative photoanode material for TiO₂ based Dye Sensitized Solar Cell (DSSC) due to its large band gap, high electron mobility and more importantly availability of simple nanostructure fabrication methods. However, the conversion efficiencies of ZnO nanostructure based DSSC are still inferior to those of TiO₂ based DSSC. The poor performance observed in ZnO nanostructure based DSSCs has been mainly caused by the formation of an inactive Zn²⁺ dye complex (Zn²⁺/Dye containing in acidic dye) layer on the ZnO surface, insufficient specific surface area and the slow electron injection flow from dye to ZnO.

In this study, the power conversion efficiency of ZnO based DSSC was enhanced by incorporating Li ions in to the ZnO nanostructure photoanode. ZnO nanostructures were fabricated using solution derived method and to incorporate Li salt in to the ZnO, Li salt was mixed with ZnO nanostructure during the photoanode fabrication step.

The typical photovoltaic behaviour of ZnO nanostructure DSSC in the presence and absence of lithium ions were measured under the AM1.5 simulated sunlight with a power density of 100 mW/cm². The current density (J_{sc}) of 4.64 mA/cm², open circuit voltage (V_{oc}) of 553.8 mV, fill factor (FF) of 63.9 % and overall efficiency (η) of 1.65% were achieved for of ZnO nanostructure based DSSC in the absence of lithium ions and in the presence of Li-salt, an efficiency of 3.06% was achieved. Enhance in overall performance was mainly due to high J_{sc} (5.89 mA/cm²) and V_{oc} (725.6 mV). The electron transport and recombination properties of the ZnO and Li-ZnO photoanodes were investigated.



Keywords Dye-sensitized solar cells, Li-ZnO nanostructures

Efficiency of energy transfer in nanomodified photocells via plasmons in metallic nanoparticles

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Noble metallic nanoparticles are under investigation in order to improve efficiency of photovoltaic devices. Collective oscillation of metallic plasma in such nanoparticles affect the interaction of device with incident light, which, under certain condition, can lead to increasing photocurrent. Electronic plasma in nanoparticle can absorb incident light resulting in surface plasmon oscillation. These oscillations are source of radiation itself which interact with active layer of semiconductor device. Efficiency of energy transfer via plasmon oscillation can be many times higher than in bare device.

This effects are however very sensitive for various parameters as size, material, shape of metallic nanoparticles and environment. Detailed analysis of underlying physics should provide to deeper understanding and harvesting of such phenomena in optoelectronic industry.

There are many experimental observations with noble-metal (particularly gold and silver) nanoparticles of diameters of few tens of nanometers. In range of diameters of 10-100 nm properties of system can be well-described in terms of semiclassical approaches like RPA (description of volume and surface plasmons were made in Random Phase Approximation in confined spherical geometry with analogy to well-known Pines and Bohm model of bulk plasmons). To include various types of interaction with environment special attention was paid to radiation effects, which seem to play main role in damping of plasma oscillation and causes dependency of nanoparticle size on resonant frequency [1].

Here we present detailed analysis of efficiency of plasmon-semiconductor coupling dependency of nanoparticles size made in terms of Fermi golden rule. Figure 1 presents calculated numerically probabilities rates and shows the limits for small nanoparticles (radius a equals zero) and approximation for large ones.

The second result of the work is the comparison of estimation damping rates corresponding to energy transfer from nanoparticle to semiconductor in classical damped driven oscillator, when this rate has both wavelength and particle size dependency with value for plasmon model in which damping rate depends only on nanoparticle size (fig. 2).

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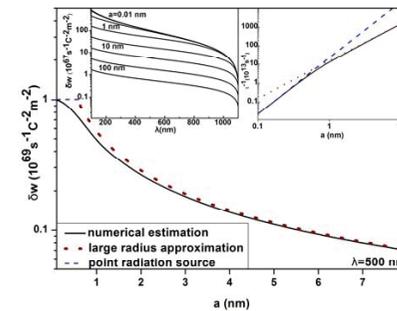


Figure 1. Transition probability vs. nanoparticle size (inset: dependency of the probability rate of wavelength and damping rate with nanoparticle radius).

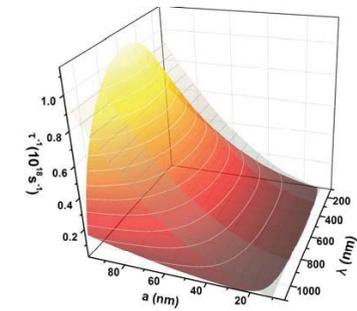


Figure 2. Damping rate associated with near field interaction in classical damped driven oscillator (yellow-red surface) and quantum-particle model (gray surface).

Keywords plasmonics; photovoltaic;

Efficiency Optimization of the CuInS₂ QD Doped Organic-Inorganic Hybrid Solar Cells Through the Nanocrystal Size and Composition Controlling

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The field of the organic hybrid solar cell based on quantum dots has attracted a great attention due to quantum dot's quantized optical and electrical properties and skills of designing new configurations with quantum confinement effect. Abilities of quantum dots in modification of the desired band gap, which depends on the quantum dot's diameter and production multiple excitons per photon¹ encouraged to improve performance for organic solar cell. Due to these unique properties, quantum dots have been subject of considerable study with organic-inorganic bulk heterojunction solar cells. Till now a variety of quantum dot design have been taken into account in order to improve the efficiency.

We present here the synthesis of CuInS₂ quantum dots with different sulphur ratios, different core diameters and investigation of gradually doping effect of these quantum dots on the conventional and inverted P3HT:PCBM bulk heterojunction organic solar cell efficiency.

References:

[1] A.J. Nozik "Quantum Dot Solar Cells," Physica E 14, 115 (2002).

Keywords Quantum dot, hybrid solar cell.

Electrical and photoelectrical characteristics of a rectifying diode based on a novel Cu(II) complex

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A Cu(II) complex of a novel Schiff base polymer with naringenin were synthesized and characterized by a combination of elemental analysis, Uv-Vis. spectroscopy, FT-IR, ¹H NMR, MS and TGA/DTA. An organic-inorganic rectifying diode was fabricated by forming a thin film of Cu(II) complex on an n-Si semiconductor and evaporating Au metal on the complex film. It was shown that the structure have a good rectification property. The electrical parameters of a device such as ideality factor, barrier height and series resistance were determined by the help of current-voltage (*I-V*) measurements in dark. The effect of light on *I-V* characteristics of the device was also examined by the help of a solar simulator with AM1.5 global filter and 100 mW/cm² illumination intensity.

Keywords Schiff base polymer; thin film; photoelectrical properties

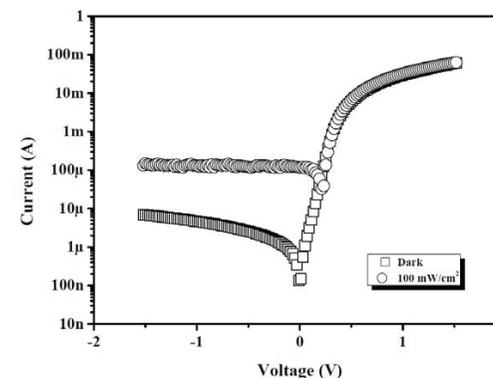


Fig1. Current-voltage characteristics of Au/ Cu(II) complex/n-Si device in dark and under illumination

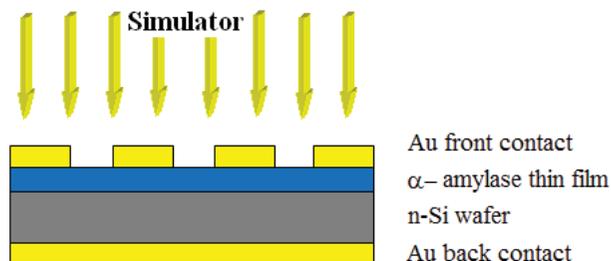
Electrical and photovoltaic parameters of an enzyme based heterojunction

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We successfully fabricated an Au/enzyme/ n-Si heterojunction device by forming α -amylase thin film on a n-Si semiconductor. It was seen that the structure showed excellent rectifying behavior. The electrical properties of the Au/ α -amylase /n-Si device including rectification ratio, ideality factor, barrier height and series resistance were determined. It was reported that the α -amylase enzyme could be evaluated as semiconductor with 3.65 eV band gap value obtained from optical method. We also executed the photovoltaic properties of the Au/ α -amylase/n-Si structures under 100 mW/cm² illumination condition.

Keywords α -amylase; optical band gap; electrical and photovoltaic parameters



The structure of Au/ α -amylase /n-Si device

Electrochemical characterizations of ZnO nanowires for dye-sensitized solar cells

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The dye-sensitized solar cells (DSSCs) using fluorine-doped tin oxide (FTO) supporting substrate for fabricating ZnO nanowires film electrodes were developed. Platinum was deposited at the counter-electrode surface to improve the electronic transfer between the electrolyte and the counter-electrode.

The obtained cells were characterized by electrochemical impedance spectra (EIS).

Based on the impedance spectra model, an equivalent electric circuit was proposed. This model gives access to the electrochemical parameters values of the cell components and their interfaces.

Keywords: ZnO; Nanowires; DSSC.

Electrochemical deposition of CIGS on electropolished Mo

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Copper indium gallium selenide (CIGS) is one of the most promising semiconductors for the absorber-layer of thin-film solar cells. CIGS alloys are of great interest because they show many advantages, including high absorption coefficients of visible light (up to about 10^3 cm^{-1}), facility to undergo band gap engineering through alloy composition and long-term optoelectronic stability. Thanks to these features, CIGS-based solar cells compete with poly Si-based ones and considerable efforts have been made for developing innovative devices using these materials. Molybdenum is the most common metal used as back contact for CIGS solar cells, owing to its stability at the processing temperature, resistance to alloying with Cu and In, and its low contact resistance to CIGS. Properties of molybdenum films are of fundamental importance because they could induce significant changes in the structural and electrical properties of CIGS deposited films.

In this work, we report some preliminary results concerning fabrication of CIGS thin films on molybdenum sheets, previously cleaned using an electropolishing treatment (Figure 1-a), in order to obtain a defect-free smooth surface. CIGS thin films (Figure 1-b) were obtained by electrodeposition from aqueous baths, at room temperature and under a N_2 atmosphere. Different deposition parameters, like bath composition and deposition time, were tested in order to obtain deposits with a composition close to the stoichiometric value. Film characterization was conducted using several techniques (EDS, SEM, RAMAN, XRD), in order to obtain information on both chemical composition and structure. Preliminary results on the photoelectrochemical behavior of CIGS thin films will be also presented and discussed.

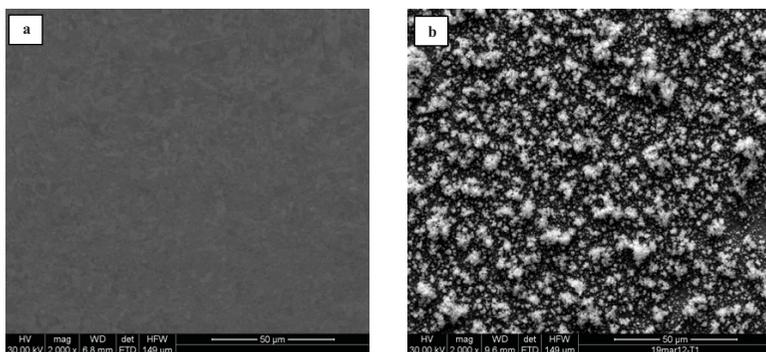


Figure 1. SEM images of electropolished Mo (a) and of electrodeposited CIGS (b).

Keywords: Molybdenum, CIGS solar cells, electrodeposition.

Acknowledgements. This work was partially funded by the European Community through the “Programma Operativo Nazionale Ricerca e Competitività 2007-2013” (PON01_01725 Project).

Enhanced Efficiency of Polymer Solar Cells by incorporation of Plasmonic Gold Nanoparticles

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Metal nanoparticles were suggested to improve the performance of many optoelectronic devices based on surface plasmon resonance: the collective oscillations of free electrons in metal NPs resonantly driven by incident radiation. By manipulating the dimensions of the metallic nanostructures, the surface plasmon resonance properties can be tuned depending on the applications. Application of noble metal nanoparticles was suggested also as one of the possible ways of increasing power conversion efficiency of organic photovoltaic devices.

In this communication, the role of Au nanoparticles incorporated in the bulk heterojunction solar cells consisting of active layer of poly (3-hexylthiophene) (P3HT)/fullerene derivative (PCBM), was investigated. The gold nanoparticles were prepared by vacuum thermal evaporation technique, in which the metal atoms form clusters by subsequent diffusion on the surface of a substrate. In the bulk heterojunction of P3HT-PCBM solar cells, containing Au NPs has higher value of incident photon to collected electron efficiency (IPCE), especially in the absorption range of Au NPs from 550-600nm that coincide with the localized plasmon resonance band of Au NPs. A clear increase in the power conversion efficiency (PCE) under white light illumination was observed which is attributed to strong local field enhancement around metal nanoparticles that locally increases optical absorption in a surrounding semiconducting polymer and as a result photocurrent increased. By careful control of the nanoparticles formation we were able to exclude the effects of variation of plasmonic resonance frequency and incident light scattering that would increase the interaction pathway of light within the active polymer layer.

Keyword Polymer solar cells; Plasmonics; gold nanoparticles

Acknowledgments: Financial support of the Czech Science Foundation projects P208/10/0941 and EU NoE project FlexNet are gratefully acknowledged.

Extended cylindrical projection method for assessment of sunshine in buildings

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Direct mathematical treatment of cylindrical projection technique for non rectangular shapes is generally considered too complex and recourse is made to other means such as spherical projection. Cylindrical projection method would be more manageable and able to give more sensitive results. The objective of this research was to use a computer-based mathematical analysis using trigonometric functions. This is to project building components and sun's position in the sky on a two-dimensional cylindrical projection chart for a wide range of plane shapes, inclined and non incline vertical planes, segment of a circular plane, semi-circular plane, and circular plane. This analytical method using Matlab programming language and its graphical potentialities will enable designers and architects to quick and realistic assessment of sunshine availability for buildings.

Key-Words: - Azimuth and altitude, Cylindrical projection, Segment of a circle, Semi-circular and circular planes.

Growth of high mobility metal phthalocyanine thin films

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Development of solar cells (and other devices) based on organic semiconductors is of interest as these have potential for lower cost compared to inorganic semiconductor devices and use simple fabrication techniques. Efficiency of organic solar cells and application of organic materials to other devices have however been limited by lower conductivity and mobility of thin films. Typical mobility reported for organic thin films is less than 10^{-2} cm^2/Vs . We have investigated metal phthalocyanine thin films by molecular beam epitaxy to identify methods to improve their structural organization and mobility. Consequently, mobility of cobalt phthalocyanine (CoPc) and iron phthalocyanine (FePc) thin films has been improved to ~ 100 cm^2/Vs . Results of the studies will be reviewed.

Films of 100 nm thickness were deposited on quartz and sapphire substrates and role of states in the energy gap was investigated using transport measurements that yielded band diagram shown in Fig. 1 and showed the importance of defects in controlling charge transport properties. Composite (CoPc + FePc) thin films deposited on sapphire substrate were studied [1]. Temperature dependence of resistivity showed that composite films are in metallic regime, while pure films are in the critical regime of metal-insulator transition (Fig. 2). Films showed face on orientation and composite films had two order of magnitude higher mobility (110 cm^2/Vs). High mobility and better structural ordering in composite films is attributed to the formation of CoPc-FePc dimers as seen by matrix assisted laser desorption ionization time of flight mass spectrometer (MALDI-TOFMS).

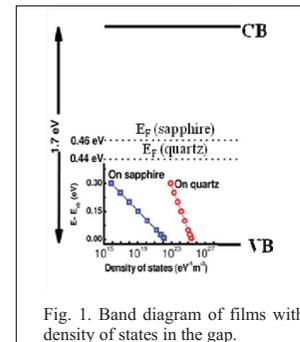


Fig. 1. Band diagram of films with density of states in the gap.

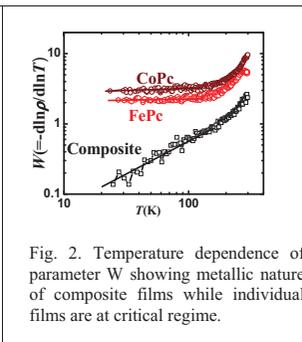


Fig. 2. Temperature dependence of parameter W showing metallic nature of composite films while individual films are at critical regime.

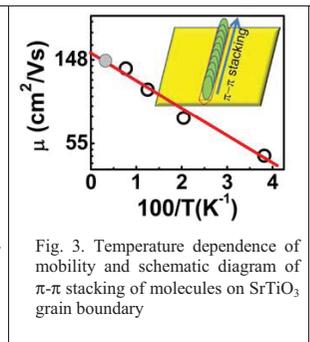


Fig. 3. Temperature dependence of mobility and schematic diagram of π - π stacking of molecules on SrTiO_3 grain boundary

Highly-oriented (rocking-curve width= 0.11°) CoPc films were deposited on LaAlO_3 substrates and these showed very high mobility that was attributed to well oriented edge on films with orientation controlled by natural twin boundaries in substrates [2]. The mechanism was confirmed by preparation of films on SrTiO_3 substrates [3] with grain boundary where the films in grain boundary region showed very high mobility (Fig. 3) while those on part of substrate without grain boundary showed much lower values as normally reported.

The results of the studies show that to obtain high mobility films, important factors are: (a) substrate crystallinity, (b) texture in a substrate such a grain boundaries, (c) thinner films so that these are organized due to interaction with the substrate and (d) composite materials as CoPc and FePc mixture. Using these techniques it is possible to prepare thin films with mobility exceeding 100 cm^2/Vs .

Keywords organic thin films; high mobility; CoPc, FePc

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High Efficiency Hybrid Photovoltaics with a Novel Hierarchical TiO₂ Photoanode

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Hybrid Photovoltaics (HPV) is an interesting technology with the potential of putting together the strengths of purely organic PV with those of Dye Sensitized Solar Cells. The ideal structure would consist in interpenetrated organic donor-inorganic acceptor morphology with the highest specific surface area per unit area of the device. In this work we present a novel hybrid cell architecture based on a forest of hierarchical nanostructures grown by Pulsed Laser Deposition (PLD). The structural characteristics of these nanostructures can be tuned by a proper choice of deposition conditions and post-deposition treatments (e.g. annealing). In particular Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) show that a hierarchical structure with 10-20 nm in size nanoparticles is formed when the O₂ pressure is in the 5-40 Pa range. Roughness factor, specific surface area, and average pore diameter of the device were 74, 55.22 m²/g, and 12.01 nm respectively. Hybrid cells were fabricated by spin coating high molecular weight (80,000 D) Poly(3-hexylthiophene) (P3HT) followed by Ag evaporation. A maximum power conversion efficiency of 0.65% under air mass (AM) 1.5 illumination has been obtained for devices 800 nm thick, deposited in 7 Pa of oxygen. This result represents a 50% increase with respect to an optimized device obtained with a standard architecture based on a mesoporous titanium dioxide photoanode ($\eta=0.43\%$). The efficiency gain arises mostly from a tremendous increase in J_{sc} from of 1.55 mA/cm² to 2.5 mA/cm² for the standard and the hierarchical photoanode respectively. This is attributed to the peculiar optical properties of the novel acceptor phase and to the close-to-optimal interpenetrating morphology obtained as confirmed by quantitative electron tomography. Further increase in efficiency is possible by treating the TiO₂ surface with suitable interlayers able to ameliorate the TiO₂-P3HT interface.

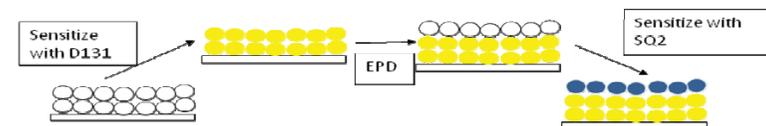
High performance plastic cosensitized dye-sensitized solar cells using multiple electrophoretic deposition

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Dye-sensitized solar cells (DSCs) are a potential low cost alternative to conventional silicon based solar cells. The efficiency of the device has exceeded 12%. However, light utilization in the near infrared (NIR) region of sunlight is still low. In this regard, novel dyes that have broad absorption to NIR can be developed. This is still challenging and such ideal dyes are yet to be developed. Alternatively, multiple dyes with different absorption region can be cosensitized within a single device in order to expand the absorption range of the device. The simplest way of cosensitization is to sensitize the photoanode with a solution containing two dyes, ie a dye cocktail. However, the device showed a low conversion efficiency using this method due to different speed of dye uptake and the interactions between the adsorbed dyes in close proximity on the photoanode.

In this work, we report a simple method to fabricate high performance plastic cosensitized DSCs using multiple electrophoretic deposition (EPD) technique. Low-cost commercial P25 TiO₂ and metal-free organic dyes are employed in our study. The dyes are chosen due to their large difference in absorption maxima (~425nm for D131 and ~670nm for SQ2 on TiO₂) and are ideal to show a proof of concept for this cosensitization method. As shown in Scheme 1, the two dyes were absorbed on different TiO₂ layers using layer by layer sensitization method. After sensitization with D131 dye, another layer of P25 TiO₂ nanoparticles is deposited on top of the previous layer by EPD. This fresh layer of TiO₂ is then sensitized with another dye, SQ2. As the deposition of the second layer of P25 did not cause a significant desorption of the D131 dye, layer by layer cosensitization can be achieved successfully. Finally, the film is subjected to compression to enhance particle connectivity.



Scheme 1

For comparison, D131, SQ2 and a D131 / SQ2 cocktail are used to sensitize similarly fabricated photoanodes, respectively. The photovoltaic J-V curves of these devices are shown in Figure 1. For D131 based device, power conversion efficiency (PCE) of 3.4% under illumination of AM 1.5G (100 mW cm⁻²) was achieved. The device sensitized with SQ2 achieved PCE of 2.7%. The device sensitized using the dye cocktail yields PCE of 2.4% due to reduction of photocurrent and photovoltage. The device cosensitized with the two dyes in discrete layers showed the highest conversion efficiency of 4.9%, outperforming the other devices. IPCE (Figure 2) indicate that light utilization of the devices has been expanded effectively.

In conclusion, high performance plastic cosensitized dye-sensitized solar cells have been developed using multiple electrophoretic deposition. This method can be extended to other dye pairs and with the proper optimization of the devices, it is hoped that high efficiency plastic DSSCs can be achieved.

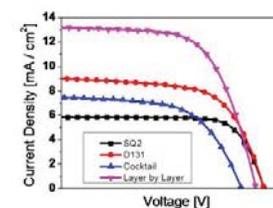


Figure 1

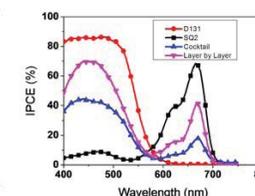


Figure 2

Keywords flexible dye sensitized solar cell; low temperature fabrication; cosensitization; multiple dye system

Highly oriented SnS thin films: preparation, post deposition heat treatments and characterisation

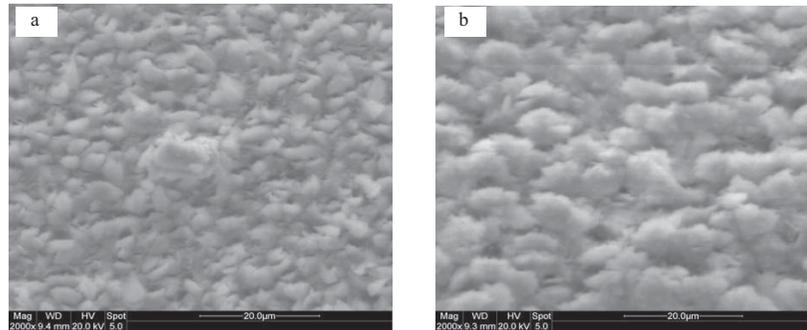
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Tin monosulphide (SnS) has the potential to be used as an absorber material in low cost photovoltaic solar cells. This is because SnS has a direct energy band gap close to the optimum for photovoltaic solar energy conversion (1.35eV), an optical absorption coefficient $> 10^4 \text{cm}^{-1}$ for photons with energies greater than the bandgap, the constituent elements (Sn and S) are abundant and environmentally acceptable, and also SnS also offers flexibility in device design, as it can be doped p-type or n-type. In the literature, laboratory device efficiencies $> 2\%$ has been reported for this novel semiconductor material.

In this work, the effects of annealing on the SnS thin films grown using the thermal evaporation technique were investigated. The layers were deposited using varying times (40seconds-3mins) keeping other deposition variables constant. In general the as-grown layers were single phase SnS and had the orthorhombic crystal structure. With an increase of deposition time, and consequently film thickness, the crystal structure remained orthorhombic, the crystallinity of the layers increased, the degree of preferred orientation increased, while the texture coefficient decreased. The effects of post deposition heat treatments in an H₂/argon environment were also investigated in detail. The consequences of the results on producing improved layers of SnS for use in thin film solar cell devices are discussed.



(a) A layer grown at a deposition time of 2 minutes, annealed in H₂S/argon for 30 minutes (b) The same layer annealed in the same medium for 60minutes.

Keywords; Highly oriented, SnS, post deposition annealing, thermal evaporation.

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Hydrogen dilution effect in film growth for amorphous silicon tin thin film solar cells

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We have been developing hydrogenated amorphous silicon tin (a-SiSn:H) thin film solar cells, because this material is a promising candidate for a bottom cell in a high efficiency multi-junction solar cell [1]. In this work, we studied the hydrogen dilution effect in film growth for a-SiSn:H solar cells.

The a-SiSn:H thin films were deposited on Asahi-U glass substrates by means of a very high frequency plasma enhanced chemical vapor deposition technique (VHF-PECVD). Vaporized tetramethyltin (Sn(CH₃)₄) and silane (SiH₄) gases were used as Sn and Si precursors. We fabricated devices with the structure identical to amorphous Si solar cell, where i-a-Si:H layer was replaced with a-SiSn:H. The performance of the a-SiSn:H solar cell prepared in low H₂ dilution in film growth were quite unsatisfactory.

In order to reveal the reasons of the low performance, we measured the conductivity and the electron spin resonance (ESR) signals of a-SiSn:H films. As a result, we observed ESR signal at g-value of 2.055 imposed on featureless broad ESR signal, which could indicate that the defect states in the deposited material were Sn-related. The intensity of this broad band in ESR signal drastically becomes small with increasing H₂ dilution in film growth. Moreover, the photosensitivity of a-SiSn:H films with Sn contents of ~5 at. % prepared in highly H₂ dilution in film growth was ~2 order magnitudes larger than that prepared in low H₂ dilution. According to improvement of photosensitivity, the solar cell performance drastically improved with increasing the H₂ dilution during the growth process as well.

Under these considerations, we concluded that improvement of photosensitivity and solar cell performance derived from reduction of Sn-related dangling bonds passivated by a large amount of generated atomic hydrogen. The effect of hydrogen dilution on the performance of a-SiSn:H thin film solar cell will be discussed in details.

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Hydrogen-induced effects in GaSe layers for solar energy devices

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New methods of fabrication, characterization and simulation of new functional and structural materials create the opportunities for understanding of perspectives of applications as manipulating and electronic parts of hydrogen and solar energy conversion equipments has discussed. Application of heterojunction on the base of $A^{III}B^{VI}$ for solar energy elements and high nitrogen steels for hydrogen energy structural elements - the new paradigms for design, funding the efficient conversion of hydrogen, solar energy into chemical fuels, and developing novel transparent conductors and structural management materials required the creation of new generation equipments with wided parameters.

It is experimentally established, that illumination of GaSe(Pb) semiconductor electrodes, hydrogen saturated in acids (H_2SeO_3 , H_2SO_4) and neutrals (water) environments has improved the anode and cathode reactions. Irradiation from the sun range leads to the increasing of the returning of electrons from electrode and also the dissolution of Ga, Se, stimulating their passing to the ionic state.

Liquid neutral, acid environments as films (or drops), which are formed on the spot of these electrodes has influenced on the surface characteristics of the investigated semiconductors, thus study of structure changing on nano scale and electrochemical properties are necessary for finding out of principle of action of new photoelectrochemical units for transformation of sun energy.

Hydrogen has influenced on mechanical characteristics (increased their anisotropy) of gallium monoselenides. Due to intensive intercalation between layers of crystals hydrogen exists in a molecular state, placed in the translation-ordered position. After definite concentration of hydrogen it is the possibility of penetration to matrix layer of crystals by hydrogen ions.

The complex investigations respect to establishment of physical features of forming of hydrogen localized states in the Van der Waals gap of GaSe layered films were carried out. The temperature diapason of GaSe hydrogen intercalated structure existence was determined. The topology and micro-local features of hydrogen dissolved structure of GaSe nanofilms formation were established using method of TEM analyses and changing the anisotropy of their kinetic parameters. The process of hydrogen adsorption by layered thin films and crystals has accompanied by changing of adsorption band position in GaSe due to the increasing of intercalation level.

Changing the hydrogen concentration leads to nonlinear increasing of unit cell parameter c and can be described by dependence $c(x) \sim \ln(x)$. For GaSe unit cell parameter c has increased from 1,589 nm to 1,594 nm, and further increasing of hydrogen concentration caused the increasing of unit cell parameter c only to 1,596 nm. In such case has formed the "nanoballs", which limited by linear sizes of crystallites, which can reversed adsorb and desorb the hydrogen. During the intercalation of crystals it has observed the increasing of unit cell parameter a (from 0,375 nm to 0,377 nm), which certified the partial introduction of hydrogen to matrix layer.

Keywords layered semiconductor; transformation of solar energy; neutral acid Environments

Immobilization of the I_3^-/I^- redox couple on lamellar solids and their application for dssc technology

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Dye-sensitized solar cells (DSSC) have been attracting the interest of the scientific community due to their potential advantages of high efficiency and low cost.¹ Recent studies have shown that the use of gel- or all-solid-state electrolyte DSSC may produce a significant improvement in energy-conversion efficiency and long-term stability, as compared with the usual organic solvent-based liquid-state electrolyte devices.²

This contribution will present the development of a solid state electrolyte for DSSC based on the I_3^-/I^- redox couple intercalated in a layered solid matrix, and dispersed in 3-methoxypropionitrile. Layered double hydroxides (LDH) are a large class of layered solids made of positively charged layers, that are balanced by exchangeable anions in the interlayer region. They show good anionic exchange properties, and they are suitable hosts for the I_3^-/I^- couple.³

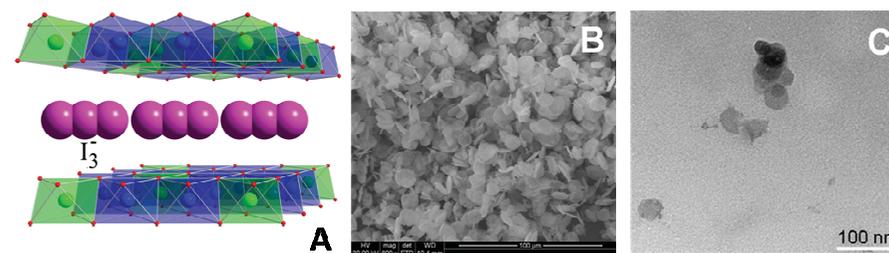


Figure 1: A) schematic structure of LDH; B) SEM image of microsized LDH; C) TEM image of nanosized LDH.

Molecular iodine was intercalated from nonaqueous solution into microsized ZnAl-layered double hydroxide (LDH) in the iodide form generating the I_3^-/I^- redox couple into the interlayer region. The intercalation compounds were characterized by thermogravimetric analysis, X-ray powder diffraction, UV-Vis spectroscopy, and scanning and transmission electron microscopy. In addition, nanosized, well dispersible LDH, synthesized by the urea method in water-ethylene glycol media, were also prepared and successfully functionalized with the I_3^-/I^- redox couple applying the conditions optimized for the micrometric systems. The X-ray powder diffraction data, UV-Vis and Raman spectra and TG analysis showed the presence of I^- , I_3^- and polyiodide, I_n^- , in the interlayer region of LDH. Finally, these intercalation compounds dispersed in methoxypropionitrile. (5wt% of solid in the solvent) have been in order to evaluate their performances in DSSC devices.

The electrochemical characterisation showed that the addition of microsized LDH does not influence significantly the solar cell efficiency. Interesting results were observed for nanosized LDH for which a progressive improvement of solar cell efficiency depending on iodine content was detected.

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Keywords: DSSC, layered double hydroxides, non-liquid electrolytes

Investigating the binding of ruthenium dyes to TiO₂ in dye-sensitised solar cells

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Dye-sensitised solar cells are devices which convert solar energy into electrical energy via photoexcitation of the dye molecules. Ruthenium-based dyes commonly feature bipyridyl ligands that can be easily tuned to enhance the optical properties of the dye.¹ Dye design is one of the key areas that need to be further explored.

There are several arrangements that the dye can adopt as it anchors itself to the semiconductor, but the number of acid linkages required for optimum efficiency, stability and rapid dye uptake remains unclear. It has been shown via theoretical modelling that binding through three linkages is energetically and sterically more favourable, however systematic experimental studies have not been carried out.²

Our research is currently investigating the number of anchoring groups required to successfully bind to the semiconductor whilst maintaining effective charge injection. We have synthesised a series of simple ruthenium dyes to explore this (Figure 1) and have characterised them through electrochemical, photophysical, spectroscopic, computational, dye uptake and solar techniques. This series show comparable optical and photophysical properties to the commercial Z907 dye.

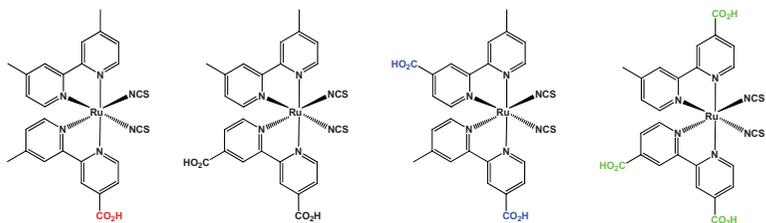


Figure 1 Series of ruthenium(II) dyes that feature either one, two or three carboxylic acids on the bipyridine ligand.

Keywords Dye-sensitised solar cells; ruthenium; dye uptake

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Investigation of electrodeposited ZnO thin films as transparent conducting oxide for application in CIGS-based solar cells

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The most widely investigated transparent conducting oxide for front contact CIGS-based solar cells is RF-sputtered Al-doped ZnO [1]. ZnO emerged as the dominant choice owing to its good transparency and conductivity, the most important requirements for application as front contact in a solar cell device. Transparency is necessary for a good light transmission to the underlying parts of the device, whilst a sufficient conductivity ensures transport of photo-generated current to the external circuit without high resistance losses [2]. Another important property of ZnO is the possibility to tune its conductivity by means of n-type doping, through substitution of Zn with elements of group III (B, Al, Ga) or substitution of oxygen with elements of group VII (F, Cl, I, Br) [3]. Efficiencies of 20% have been reported for CIGS solar cells with a sputtered Al-doped ZnO layer [4].

Despite the fact that efficiencies of some CIGS-based solar cells fabricated by the vacuum processes were even higher, this cheap and convenient technique attracts significant research interest as a potential alternative. Among the different procedures proposed for ZnO thin films fabrication, electrodeposition is one of the most investigated and appealing, thank to many advantages like low instrumental and materials cost, high deposition speed, efficient utilization of raw materials and feasibility for making large area films [5]. We have obtained CIGS nanowires [6] and thin films using a single step electrodeposition from an unbuffered sulphate electrolyte at different applied potentials and room temperature. After extensive investigation, suitable conditions were found for the simultaneous electrodeposition of elements having different standard electrochemical potentials.

Goal of this work is to show that electrochemical deposition can be also used for the fabrication of ZnO front contact of the CIGS-based solar cell, as an alternative to the more expensive sputtering technique. Thin films were grown on a conductive substrate (ITO) by potentiostatic deposition from aqueous baths. Different deposition parameters (like bath composition, time and temperature) were checked in order to obtain dense layers covering uniformly the substrate. Considering that Lincot et al. [3] reported high efficiency (up to 15.8%) for CIGS-based solar cells using electrodeposited ZnO:Cl as front contact, also this type of film was electrodeposited and the preliminary results will be reported. Finally, we have investigated the effect of a thermal treatment (performed at different temperatures and for different times) on ZnO thin films properties.

Films characterization was carried out by means of several techniques (EDS, SEM, RAMAN, XRD), giving information on both chemical composition and structure. Preliminary results on the photoelectrochemical behavior of ZnO thin films will be also presented.

Keywords: Zinc Oxide; CIGS solar cells; Electrodeposition; Transparent conducting oxide.

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Investigation of the Fundamental mechanisms that take part in the process of absorption of Si during rapid thermal process

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In-situ measurement of the silicon wafer temperature during solar cell processing is a difficult matter for high temperature process steps (>600 °C). Pyrometry often is used but causes problems since emissivity depends on wafer temperature, doping and surface finishing, also the access to the wafer is often difficult. Also the temperature dependence emissivity of silicon has been studied in several publications using different heating methods, including furnace in rapid thermal processing (RTP)¹⁻² and electron beam³. We describe the experimental procedure of measures in situ of the temperature of the silicon wafers p-type with thickness of 200µm, 300µm and 400µm, using to IR-transmission to high temperatures. This technique is new to this wavelength (1,45µm) that allows knowing the temperature the wafer with greater accuracy. The obtained results of transmission are compared with data experimental transmission with wavelength of 1,3µm and 1,5µm of other author. in-situ transmission equipment at an quartz tube furnace containing of a high power Hamamatsu small angle (5°) IR-LED (L 7850, λ 1.45 µm) in combination with a Hamamatsu IR-sensor (G8370) and a digital lock-in amplifier.

Keywords Absorption Coefficient, Silicon, IR-Transmission, Temperature.

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Kinetic studies of silicon epilayers obtained by epitaxial lateral overgrowth method for photovoltaic applications

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Epitaxial Lateral Overgrowth technique can be a promising technique in photovoltaic applications due to possibility of producing high-quality Si epilayer on silicon substrates of poor quality. The laterally overgrown parts of the layer are characterized by different growth rate in the two directions: parallel and perpendicular to the substrate (aspect ratio). The geometry of the layer depends on technological parameters like temperature of growth, cooling rate and mask fill factor. Finding optimal set of technological conditions of liquid phase epitaxy (LPE) experimental process is crucial to obtain thin and wide structures, which can be used to solar cell production.

In this paper the kinetics of silicon epitaxial layer growth on partially masked substrate have been examined in the temperature of 920°C for different growth time, cooling rate and geometry of the substrate. Time of growth was set in the range of 30 – 60 min and the cooling rates were equal 0.5°C/min and 1.0°C/min. Size of the opened window in the silicon substrate has been changed from 50µm to 200µm as well as the distance between the windows.

Keywords: Epitaxial Lateral Overgrowth (ELO), Liquid Phase Epitaxy (LPE), Computer modeling

Light soaking induced increase in conversion efficiency in solar cells based on In(OH)_xS_y/Pb(OH)_xS_y

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Light soaking characterization on complete SnO₂:F/TiO₂/In(OH)_xS_y/Pb(OH)_xS_y/PEDOT:PSS/Au, eta solar cell structure as well as on devices which do not include one or both TiO₂ and/ or PEDOT: PSS layers has been conducted. Additionally, studies of SnO₂:F/ In(OH)_xS_y/Pb(OH)_xS_y/PEDOT:PSS/Au solar cell have been performed. The power conversion efficiency and the short circuit current density have been found to increase with light soaking duration by a factor of about 1.6 - 2.7 and 2.1 - 3 respectively.

The increase in these two parameters has been attributed to filling up of trap states and / or charge – discharge of deep levels found in In(OH)_xS_y. These effects take place at almost fill factor and open circuit voltage being unaffected by the light soaking effects.

Light-harvesting excitons as solar energy carriers at functional temperatures

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Basic biological processes, such as photosynthesis, typically obey classical rules. However, since photosynthesis begins with absorption of solar quanta, it can be considered at a borderline of classical and quantum realms. It is generally agreed upon that absorption of a solar photon by light-harvesting antenna complexes creates a collective quantum excitation - exciton - that transfers its energy very efficiently to the photochemical reaction centre, where it is subsequently transformed into potential chemical energy. Yet this insight has primarily arisen from interpretation of the low-temperature spectroscopic experiments; evidence for the excitons at physiological temperatures is scarce at best. Thorough studies are, therefore, undertaken over a broad temperature range to prove the presence of photosynthetic excitons at functional temperatures and investigate their properties. Relevance of the results of these studies to excitons in polymer and dye sensitized solar cells is discussed.

Keywords light-harvesting; excitons; photosynthesis; dye sensitized solar cells

Low-Cost CIS/CIGS solar cell processing

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CIS/CIGS solar cell device technology is now days becoming most tempting within Thin Film Solar Cell (TFSC) technologies due to mutual interest in low-cost precursor materials and low-cost processing by maintenance of best efficiency. In the present work, several vacuum (e-beam PVD, PLD) and non-vacuum (CBD, ECD) techniques have been applied in processing the n-conductive part of chalcopyrite absorber based solar cells and conclusive remarks have been drawn in the quality assessment of the layers and the performance of the cells. Particular attention has been given to the processing of buffer- and window-layer by low-cost chemical (CBD) and electrochemical techniques (ECD) as demonstrated in Figs. 1 and 2. ZnSe buffer- and ZnO window-layers have been deposited on CGS (alternately CIGS) absorbers grown by standard vacuum techniques. Both, MOCVD and PVD grown absorbers have been considered aiming to investigate growth mechanisms critical for quality and thickness control of buffer- and window-layer. The grown layers have been characterized by a series of techniques for structural (XRD, SEM-EDAX, AFM), optical (Ellipsometry, Modulation Spectroscopy, Raman Spectroscopy, Transmittance/Reflectance Spectroscopy), and electrical characterization (Van-der-Pauw Resistivity). The I-V characteristics of the cells, inclusive cell efficiency and fill factor, have been analyzed using a sun simulator at standard AM1.5 conditions.

Keywords CIS/CIGS solar cells; low-cost processing; ZnSe buffer-layer; ZnO window-layer

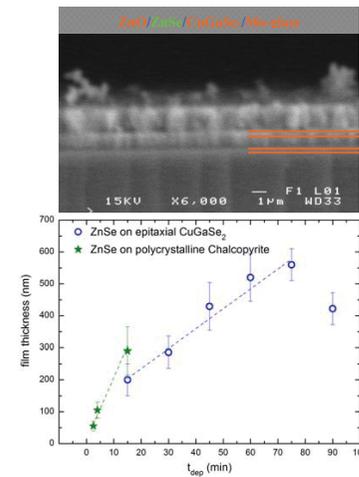


Fig.1. CBD ZnSe on CuGaSe₂/Mo/glass

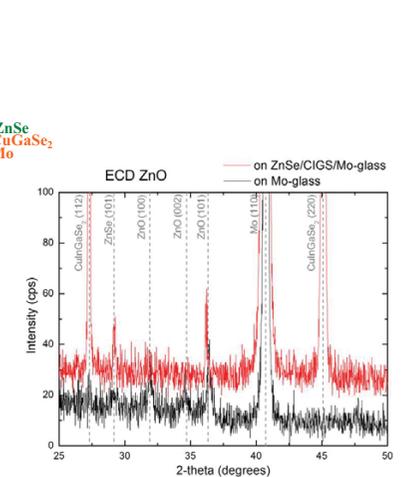


Fig.2. ECD ZnO / CBD ZnSe on Cu(In,Ga)Se₂/Mo/glass

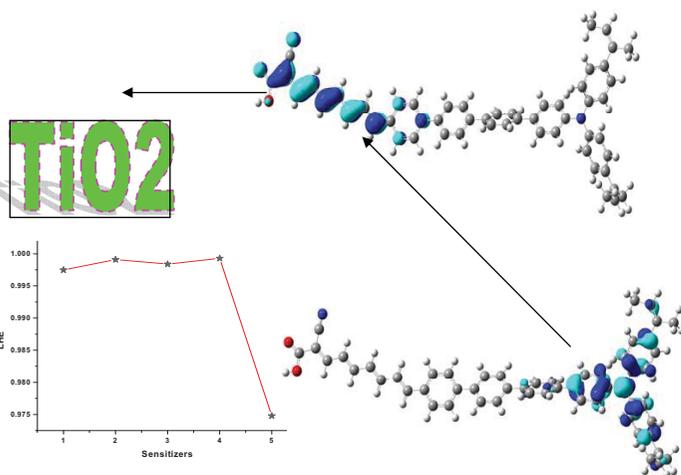
Modeling of highly efficient triphenylamine based sensitizers with improved electron injection

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The density functional theory has been applied to compute the ground state geometries. The excitation energies have been calculated by using time dependant density functional theory. The polarizable continuum model (PCM) has been used for evaluating bulk solvent effects at all stages. The long-range-corrected functional (PCM-TD-LC-BLYP) underestimate the absorption spectrum of parent molecule while PCM-TDBHandHLYP is in good agreement with the experimental data. The highest occupied molecular orbital (HOMO) is delocalized on TPA moiety while lowest unoccupied molecular orbital (LUMO) is localized on anchoring group. The LUMO energies of all the investigated dyes are above the conduction band of TiO_2 . HOMOs are below the redox couple and HOMO-LUMO energy gaps of studied dyes are smaller than TC4. The improved electron injection (ΔG_{inject}), electronic coupling constant ($|V_{\text{RP}}|$) and light harvesting efficiency (LHE) of new designed sensitizers revealed that these materials would be excellent sensitizers. The methoxy group as donor is better than the methyl which can improve the electron injection and coupling constant. The broken coplanarity between the benzene near anchoring group having LUMO and the last benzene attached to TPA unit in consequently would hamper the recombination reaction.

Keywords Dye-sensitized solar cells; Highest occupied molecular orbitals; Lowest unoccupied molecular orbitals; Absorption; Electron injection



Modified Solvothermal Synthesis of NiO Nanoparticles: Optical Properties and Surface Area Studies

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We report here a simple and modified solvothermal synthesis of NiO nanoparticles by using nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, hexamethylenetetramine $[\text{C}_6\text{H}_{12}\text{N}_4]$, sodium hydroxide $[\text{NaOH}]$ and ethanol $[\text{C}_2\text{H}_5\text{OH}]$ as refluxing solvent. Nickel hydroxide $[\beta\text{-Ni}(\text{OH})_2]$ nanostructures were first formed which were then calcined at 400°C to obtain nickel oxide (NiO) nanoparticles. The nano-powder was investigated by means of X-ray diffraction, scanning electron microscopy, transmission electron microscopy, high-resolution transmission electron microscopy, Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, photoluminescence and Brunauer-Emmett-Teller surface area studies. The size of the NiO nanoparticles was estimated by X-ray powder diffraction pattern, which was in close agreement with the particle size obtained by transmission electron microscopy analysis. Scanning electron microscopy studies revealed that the synthesized nickel oxide nanostructures showed various morphologies and the morphologies can be easily tailored by adjusting the pH value. The chemical structure information of the products was studied by Fourier transform infrared spectroscopy. Electronic spectra were used to clarify qualitatively the change in absorption band positions on changing the particle size of NiO. The optical band gap value of the NiO nanoparticles was calculated and indicated a direct transition. The values of the optical band gap of the NiO nanoparticles increases as the particle size decreases. The two strong characteristic UV emission peak were observed at 358 and 393 nm in the luminescence spectra for NiO nanoparticles. The specific surface area of NiO nanoparticles by nitrogen adsorption-desorption measurements using multipoint BET equation and found to increase from 58.3 to 131.4 m^2/g with decrease in the particle size from 20 nm to 5 nm respectively. It is also revealed that the pH value of the solution significantly affected the particle size, optical band gap energy and surface area of the synthesized NiO nanoparticles.

Keywords: Nickel oxide nanoparticles; X-ray diffraction; Electron microscopy; Optical properties; Surface area studies.

Nanocomposites derived from silica and carbon for low temperature photothermal conversion

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The most efficient solar collector for low to moderate temperature applications such as domestic water heating collectors is to use a selective surface that absorbs radiation solar to transform it into heat transmitted to a coolant. A selective surface has a low hemispherical reflectance of less than 10% in the wavelength range from 0.3 to 2.5 μm and a high hemispherical reflectance of greater than 90% for wavelengths greater than 2.5 μm . No intrinsic material is capable of this kind of selectivity that is why many studies try to tailor the optical and structural properties of the material or a combination of materials to achieve desired wavelength selectivity.

This paper presents preliminary results of the effect of various parameters such as composition, thickness, surface morphology on the selectivity of coating. The best results (absorbance=0.87, emissivity=0.1) were obtained for a nanocoating of silica and carbon derived from the pyrolysis of a gel (TEOS+carbohydrate) deposited on aluminium substrate.

Nanotubes of TiO₂ development for a flexible dye-sensitized solar cell

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Arrays of TiO₂ nanotubes were fabricated by the anodization of Ti foils and then used in assembling dye-sensitized solar cells. The Ti foil with the composite film was used as the photoanode of a flexible dye-sensitized solar cell (DSSC); a fluorine-doped tin oxide (FTO) substrate with a thin layer of platinum was used as the counter electrode.

The structures and morphologies of the films were studied by X-ray diffraction (XRD) patterns, field emission scanning electron microscopic (FESEM) images.

Power conversion efficiency was achieved for the DSSC, through back-illumination. Explanations are substantiated by electrochemical impedance spectra (EIS).

Keywords: TiO₂; Nanotubes, DSSC.

Natural dye photo-sensitizers and solid state electrolyte for DSSC application

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A solar cell was constructed of natural dye sensitized anatase-based nanostructure TiO₂ thin film, dip-coated on ITO conducting glass, solid state thin film electrolyte prepared by solution cast technique. The electrolyte is a blend of 50 wt% chitosan and 50 wt% polyethylene oxide (PEO). The polymer blend was complexed with ammonium iodide (NH₄I) and some iodine crystals were added to the polymer-NH₄I solution to provide I⁻/I₃⁻ redox couple. The ionic conductivity of the polymer electrolyte is 1.18x10⁻⁵ S cm⁻¹ at room temperature. Structural and optical properties of the semiconductor thin films were characterized by X-ray diffractometer and UV-Vis spectrophotometer. The XRD shows crystalline structures for TiO₂ thin films. The photovoltaic properties of the cell have been studied.

Keywords: natural dyes; DSSC; TiO₂; solid state electrolyte; photovoltaic

New flexible tracking-free solar concentrators

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Within "Next photovoltaic generation" devices, luminescent solar concentrators (LSC) represents an attractive technology. Solar light incident on LSC devices is absorbed by dyes, re-emitted into a guided mode in the slab, and finally collected by conventional PV cell mounted at the edge of the slab.

This approach allows two principal advantages: (i) reduce sensitively the cost of the system due to the low quantity of solar cells in the final system; (ii) maximize the conversion efficiency of the different solar spectrum window by optimizing the matching between the dye emission and the solar cell absorption external quantum efficiency.

These photovoltaic devices show several advantages also in comparison with concentrating photovoltaic (CPV) ones. In particular they: (i) use also the diffuse component of solar radiation; (ii) do not require solar tracking systems.

In this work we report recent results obtained within PHOTOFUTURE, an European Project focused on developing novel LSC devices, on the development of novel high flexible luminescent solar concentrators obtained by doping optically and mechanically stable silicone matrices with different perylene dyes. The produced flexible slabs were finally coupled with different typologies of solar cells.



Fig. 1. Picture of a 5*5 cm flexible luminescent slab. The light is collected by the luminescent centers dispersed in the slab and re emitted and wave guided towards the edges. The light trapping relies on total internal reflection.

Keywords: photovoltaic systems, luminescence, solar concentrators

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Numerical simulation of the thermal behavior of heat storage, for an application in the drying of cocoa beans

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The results of numerical simulation of thermal behavior of a storage of heat, sized to dry 13 kg of cocoa beans, in phase of storage and destocking are presented here. For the storage phase which occurs between 6 am to 4 pm, it is the evolution versus time of the temperature of the stones which is studied. For the destocking phase from 4 pm to 6 am, it was developments temperatures stones and working fluid (air) through the bed of stones (storage material), which are studied. Particular attention is focused on the evolution of the temperature at which the working fluid leaves the storer.

These simulations were performed in the meteorological conditions of the city of Yamoussoukro for the days of the study. The results show that the maximum temperature reached by the stones is 63 °C at 3,20 pm, for the storage phase. These results also show that the outlet temperature of the working fluid from the storekeeper is still 40 °C at around 6 am. The simulation results show that the quantity of energy stored is sufficient for drying the beans during non sunlight.

Keyword: storage of solar energy, solar dryer, thermal modeling, numerical simulation.

One-year comparison of different thin-film technologies at Bolzano Airport Test Installation

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The interest in thin-film PV technologies has recently increased thanks to lower costs of manufacturing and improved performance. 6 thin-film PV technologies have been installed at Bolzano airport outdoor test field and monitored since August 2010. The aim is to investigate the outdoor module behavior and to evaluate their performance.

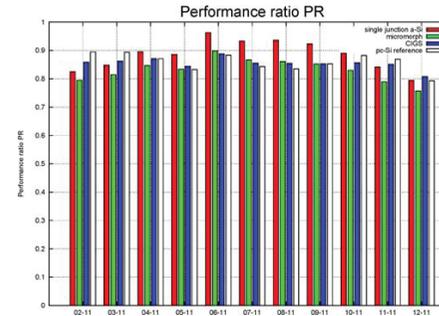


Figure 1: Performance ratio of an a-Si/ μ -Si, single junction a-Si and CIGS based module of the months February 2011 to December 2011 with a polycrystalline silicon based module as a reference.

This work presents the results of one-year comparison between technologies based on single- and multijunction amorphous silicon (a-Si), copper indium gallium diselenide (CIGS) and micromorph silicon (a-Si/ μ -Si). In order to understand better the outdoor behavior of thin-film technologies a polycrystalline silicon (pc-Si) based module is added in the comparison. The performance of the chosen reference module corresponds to the average of the installed pc-Si based modules at Bolzano airport outdoor test field. This multi-technological plant is divided into 24 arrays with a nominal power of 1-2kWp each. The comparison is carried out in a 12-month period between February 2011 and January 2012 where the first 7 months of operation - characterized by a strong degradation of a-Si based modules - are not taken into consideration.

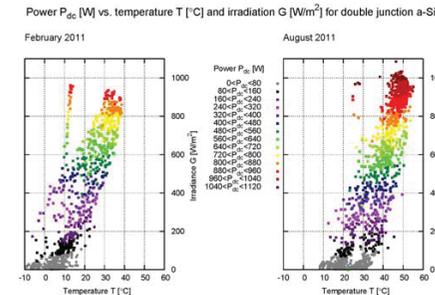


Figure 2: Performance matrix of a double junction a-Si based module of the month February 2011 and August 2011.

Fig. 1 shows the performance ratio of three different thin-film technologies. The a-Si reaches higher performances in summer, as expected, whilst the performance of CIGS is less prone to fluctuations during the year. The behavior of a-Si/ μ -Si lies between a-Si and CIGS: this is an effect of the implemented technology, which is a hybrid of a-Si and μ -Si.

A double junction a-Si based module is chosen as an example to show the performance matrix in a winter and summer month, see fig. 2. Under the same irradiance the module has a higher power output in summer, which is in good agreement with fig. 1.

In conclusion, the figures show a well recognizable seasonal oscillation of a-Si, whilst the oscillation of the micromorph is weaker. CIGS has a behavior similar to the pc-Si reference module, as also expected.

This work provides useful information for planners and energy advisers showing real-case energy production of different thin-film technologies available on the market, at Alpine latitudes. Furthermore, PV manufactures can gain more insight from the assessment of module performance under different outdoor conditions.

Keywords: thin-film, open rack, performance ratio, seasonal behavior

Optical and electrical properties of novel Schiff base polymers with naringenin

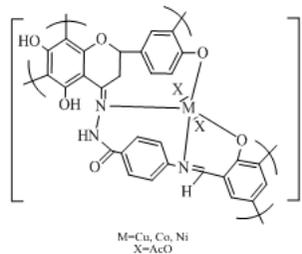
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The metal complexes of a novel Schiff base polymer with naringenin were synthesized and characterized by a combination of elemental analysis, Uv-Vis. spectroscopy, FT-IR, ¹H NMR, MS and TGA/DTA. Electrical properties of polymers including conductivity, mobility and carrier concentration were determined by means of Hall Effect Measurement system with 0.58 T magnetic field. It was seen that the polymers have conductivity about $10^{-5} \Omega^{-1} \text{cm}^{-1}$. The direct and indirect band gaps of the molecules were calculated from UV-vis data. Furthermore, photodiodes fabricated by forming thin films of the molecules on inorganic semiconductor were characterized using current-voltage measurements in dark and under a solar simulator.

Keywords Schiff base polymer; electrical and optical properties; photodiode



Molecular structure of the polymers

Optical design of Gallium Zinc Oxide/Zinc Oxide/Cadmium sulfide layers for Cu(In,Ga)Se₂ solar cells

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Cu(In,Ga)Se₂ solar cells have attracted much attention due to their power conversion efficiency over 20 % and wide energy band gap (1.02 eV ~ 1.6 eV). Cu(In,Ga)Se₂ is chemically stable and its energy band gap could be controlled by regulating the ratio of Gallium or Indium[1]. Also, since Cu(In,Ga)Se₂ layer possesses high absorption coefficient[2], it is possible to grow a thin light absorption layer of Cu(In,Ga)Se₂. Thus, manufacturing cost of Cu(In,Ga)Se₂ solar cells is economically cheaper than that of other solar cells. Furthermore, present Cu(In,Ga)Se₂ solar cells uses MgF₂ or Al₂O₃ as anti-reflection layer, which requires extra cost and time.

In this study, we suggest a new design for window layer without using anti-reflection coating of MgF₂ or Al₂O₃. Before deposition of window layer, we use a Macleod simulation program to design window layers for Cu(In,Ga)Se₂ solar cells by utilizing GZO/ZnO/CdS material system. From the simulation results, we obtained GZO 260 nm/ZnO 100 nm/CdS 60 nm, GZO 275 nm/ZnO 75 nm/CdS 60 nm and GZO 290 nm/ZnO 65 nm/CdS 60nm. Then, we fabricated window layer based on our simulation results. First of all, CdS layer was grown 60 nm by a chemical bath deposition on sodalime glass. GZO/ZnO films were deposited by radio frequency magnetron sputtering on the CdS layer. GZO/ZnO/CdS layers were measured by using scanning electron microscopy, atomic force microscopy. Also, they are measured for electronic and optical properties by using Hall measurement and UV/VIS-spectroscopy. From the results, we obtained growth thickness and transmittance of window layers of Cu(In,Ga)Se₂ solar cells. It was the best transmittance of 92 % at thickness of GZO 260 nm, ZnO 100 nm and CdS 60 nm. Finally, we achieved high transmittance window layers using anti-reflection coating effect.

Keywords CIGS Solar cells; anti-reflection; Macleod simulation; Window Layer

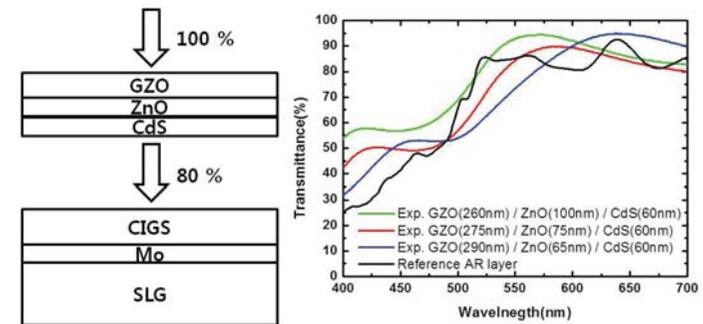


Figure 1. (a)Design structure (b)Simulation results

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Optical properties of silicon junction

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This paper presents an advance in optoelectronic silicon devices since it introduces and formulates a process for the creation of an optical active layer inside silicon devices. The model is based on a population inversion associated with a defect layer for carrier confinement and an electrical stimulation of light is demonstrated. In this work, defect layers have been created by managing the injection of energetic carriers through a silicon n-p junction. Hot carriers were produced by the application of a reverse bias to the emitter-base junction. Interactions of hot carriers with the silicon layer produce degradations processes near the junction which results in a generation of defects near the space charge region. When the emitter-base junction is reverse-biased, the electric field in the space charge region is high enough to heat the mobile carriers charge. These hot carriers can acquire sufficient energy to break weak bonds in the bulk of the junction and at interface layers giving rise to the insertion of defects in the base near the space charge region. The defects disturb the lattice periodicity by creating energy states situated in the band gap of the semiconductor, and engenders a defect layer in the base characterized by localized traps and a density of recombination centers.

Key words: Silicon, optoelectronic, defect layer, confinement, emission of light

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Optimisation of the utilisation of the solar energy: economic profitability of one telephony mobile network

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An important program of deployment and development of the telecommunication mobile network is doing in Algeria; the aim of our work is linked directly to kept energy usage very low in this network, and there are still great opportunities to reduce CO2 emissions to save the nature. In hence, our study permit the adapted utilization of the solar power in telecommunications mobile domain, this solution is very useful to change the polluted energy (diesel) by the green energy (solar power). Also the solar energy is considered as durable installation of the « ecologic telecoms ».

We have elaborated, developed and implemented one informatics program which is composed of many modules. The first data-processing module specifies the scope of application, namely mobile telecommunication. Our initially work; is study, conception and development of one informatics program to help us in the dimensioned of the UMTS network (Universal Mobile Terrestrial System) which means the third generation of the mobile network.

This developed tool makes it possible to estimate the number of transmitters which will give us uniform and continuous electromagnetic wave propagation; these transmitters are needed to cover one specific area.

The optimal dimensioning of the number of transmitters is useful to minimize the additional energy consumption of the transmitters. This optimization permits to optimize the optimal utilization of the energy consumption and help us to reduce the number of the panel solar used.

Then, other data processing module is developed and dedicated to deploy the solar energy to powered one UMTS site transmitter. This module concern the photovoltaic system sizing need to power the transmitters and ensured its autonomy.

At the end, one economic benchmarking has been done between the cost of the diesel solution alone and the hybrid solution based on photovoltaic and diesel to illustrate the importance to deploy the power station based on the photovoltaic modules.

Keywords: Solar energy, Green power sources, Ecologic telecoms, Energy consumption, Mobile telephony, Benchmark, Business plan.

Optimization of solar water heaters in Lebanon

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Non renewable resources have been overexploited by human beings in order to fulfill their needs and sustain their daily lives. For instance, fossil fuels have been the main non renewable resources used in producing energy, however on one side this has damaged the environment which is clearly noticed by the global warming effect and the climate change happening all over the world. On the other side, fossil fuels have been highly depleted, thus arising many concerns about finding new sustainable ways for producing energy. This has drawn attention to the use of renewable sources of energy such as wind and solar radiation.

This was the main reason behind looking further into the status of solar energy in Lebanon, and to assess its availability and accessibility regarding the thermal field in particular. Despite the fact that energy dependence on foreign sources exceeds 97% and a very important solar rate should support the development of solar technologies, the use of solar systems to heat water remains marginal. Electric water heater provides around 80% of hot water needs while electric power supply fails to meet the growing demand. This results in long period of discontinuous power failure in all Lebanese regions. Given these facts, Lebanon was among the leading countries with the most expensive energy production.

Lebanon, being located in an area with sunny condition (2200 KWh/m²/year), shows a large potential in the renewable energy field. However, the growth of solar thermal systems in Lebanon is faced with many challenges that should be overcome. These constraints can be illustrated by the absence of awareness regarding renewable energy, the dominance of vertical buildings in urban areas that complicate the installation of solar systems, the lack of credibility and the limited number of investments due to the lack of legislative support. All these factors play a vital role in limiting the ability of meeting local energy demands at low costs. Therefore, we will treat these constraints and take advantage of solar energy to heat water through developing a study on collective solar thermal system to ensure that people demands are met efficiently and in a reliable way.

During our presentation, we will expose the importance of solar thermal systems to heat water by analyzing the actual situation in Lebanon; then evaluate the approaches of synchronizing thermal and hydraulic theoretical aspects and practical applications efficiently according to many conditions such as location, weather, installation and cost. Not to forget the monitoring side by using the right measurement equipments to explore the parameters affecting its performance. Ending up by achieving several simulations on T-SOL software to fit the right parameters into the right equipments, and make a reliable efficient circulation and energy control.

At last, our target in Lebanon is to exploit the solar energy in a profitable and economical sound way. Thus many approaches to design a collective solar thermal system dedicated to heat water will be presented. Proper ways to reduce the constraints affecting the installation and the efficiency of collective solar thermal systems will be pointed out. In addition, demonstrations will be given regarding the benefit of using T-SOL to validate a general model able to optimize the selection of collective solar water heater systems that cover 80% of the market in Lebanon.

Preparation and characterization of CuI/PVA : PEDOT:PSS core-shell for photovoltaic application

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In the present paper, nano polymer composite of CuI/PVA blended with PEDOT:PSS has been prepared by growing CuI nano particles inside aqueous solution of PVA. The XRD characterization illustrated the growth of CuI nano-crystals of 23-52 nm size. The optical absorption showed direct transition with energy band gap in the range 1.2 and 1.3 eV for colloidal and thin solid films respectively. The frequency dependence of conductivity suggests hopping conduction where the bulk conductivity is thermally activated with an activation energy in the range 0.07 – 0.46 eV. The cyclic voltammetry technique has been used to determine the position of both HOMO and LUMO levels and subsequently the chemical band gap which decreases from 1.54 to 1.3 eV with increasing PEDOT:PSS concentration from 0.48 to 2.4 wt%

Quantum dots and nano-porous materials for solar energy conversion

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Solar energy conversion with high efficiency and economically competitive solar cells represent the main task of many research groups [1, 2]. The fabrication of solar cells has passed through a large number of improvement steps. The first generation solar cells were based on Si wafers, mainly single crystals. Permanent researches on cost reduction and improved solar cell efficiency have led to the marketing of solar modules having 12-16% solar conversion efficiency. Application of polycrystalline Si and other forms of Si have reduced the cost but on the expense of the solar conversion efficiency.

Based on thin film technology, a second generation solar cells have been developed. Materials like amorphous Si, CIS (copper-indium-selenide) and t-Si were used and efficiencies of about 12% have been achieved with a remarkable cost reduction due to less consumption of materials.

In the last decade, a third generation solar cells based on nano-porous materials and quantum dots have been developed [3, 4]. In Kansas State University, a research group has developed solar cells based on GaAs nanoparticles. An advanced photovoltaic cell, originally developed for satellites with solar conversion efficiency of 37.3%, based on concentration of the solar spectrum up to 400 suns was developed. It is based on extremely thin concentration cells.

New synthetic strategies have been developed to design nanostructure architectures of semiconductors, metals, polymers and light harvesting assemblies. Some examples have unique optical, photocatalytic and photoelectrochemical properties of nanostructures. New sensitizer or semiconductor systems are necessary to broaden the photoresponse in solar spectrum. Hybrides of solar and conventional devices may provide an interim benefit in seeking economically valuable devices [3]. In 2008 new quantum dot solar cells based on CdSe-TiO₂ architecture have been developed [4]. With increasing demand for clean energy alternatives an increasing interest from private sector and venture capitalist investment could be achieved, where a major breakthroughs in developing economically viable solar energy conversion devices are expected.

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Reuse of the Reflective Light in Concentrated Photovoltaic Cells

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In this study, a complex solar unit with microcrystalline silicon solar cells placed around the centered GaAs triple junction solar cell has been carried out. With the same illumination area and intensity, the result total power shows that the excess microcrystalline silicon solar cells increase total output power 13.59% by absorbing the reflective light from the surface of optical collimators. This mechanism provides a simple method to enhance the utility rate of high concentrated photovoltaic (CPV) solar cells. Such concept can be further applied to the aerospace industry and the development of CPV solar energy.

The CPV unit with optical rod prism is a well known mechanism which concentrates sunlight via Fresnel lens onto the GaAs solar cell to generate electricity. Optical rod prism is mainly made of aluminum and coated with silver-nickel mirror like films. Most of the light will guide to the GaAs chip surface; but still some reflective light is generated when the sunlight illuminates on their polishing surface. The structure of optical rod prism allows only part of the reflective light to illuminate again to the GaAs solar cell and resulting in limited increasing output power while other part of the reflective light spreads outward. This study aims at generating more energy by placing microcrystalline silicon solar cells around the CPV unit with optical rod prism in order to absorb residual reflective light from prism. (Shown in Fig. 1 (B)) The results in Table 1 show that microcrystalline silicon cells in Mechanism B generates excess output current at 3.98 mA and output voltage at 10.72 V. Therefore, compared with the present Mechanism A, the total output power of Mechanism B has increased 13.59% (shown in Fig 2.) under the same illumination area and same intensity.

Keywords: Silico, GaAs, solar cell; concentrated photovoltaic (CPV).

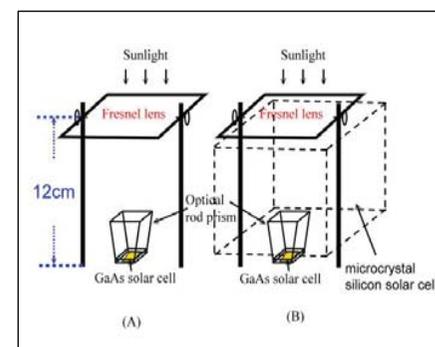


Fig. 1 Mechanisms used in this research.

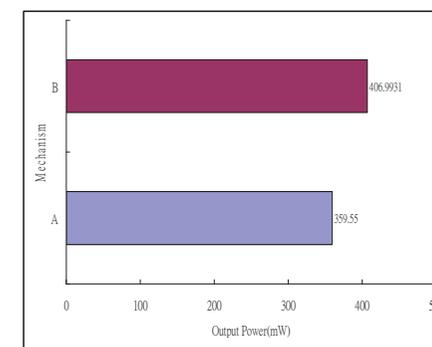


Fig. 2 The output power of mechanism A and mechanism B.

Table 1. The output property of mechanism A and mechanism B

Mechanism	GaAs solar cell of CPV			Microcrystal silicon solar cells		
	Output Current (mA)	Output Voltage (V)	Output Power (mW)	Output Current (mA)	Output Voltage (V)	Output Power (mW)
(A)	141	2.55	359.55	none		
(B)	142.85	2.55	364.27	3.98	10.72	42.67

Silica Enrichment as raw material for Silicon solar grade production

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The actual advances in mineral processing technologies aim mainly to increase the supply of newly mined metals and reducing the cost of enrichment process. In this context, the silicon solar grade SoG as feedstock for cells photovoltaic production requires a high purity. Its cycle of production consists on: enriching the silica, carbothermic reduction for obtaining silicon metallurgical grade and finally to purify the MG-Si for obtaining high solar grade silicon (SoG).

However, in order to achieve this goal a preliminary silica enrichment is needed in order to eliminate the maximum of impurities before the carbothermic and purification processes which will allow the obtention of required high quality silica (99 % of SiO₂) as a raw material for solar silicon grade production, this makes the processes downstream cited more efficient with a high yield.

In the present work we have studied the silica enrichment process using the acid leaching technology in laboratory scale, which consists firstly in silica characterization by EPMA SX-100 and X-Ray Fluorescence in order to locate the impurities incrustated in the crystal lattice or on its surface, secondly the leaching process by acids attack to increase the SiO₂ content and to optimize its technological parameters. After that, an alkaline attrition by (NaOH) takes part in order to eliminate the residual impurities on the silica surface.

Keywords: silica, Characterization, acid leaching, high purity silica, silicon solar grade.

Silicon thin films obtained by epitaxial lateral overgrowth for PV applications

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Due to the material savings and economical aspects thin film technologies for photovoltaic applications develop very dynamically. Recently market share becomes more significant for thin film solar cells,

One of methods enabling thin silicon films production is liquid phase epitaxy (LPE). By growth substrate special design, epitaxial lateral overgrowth (ELO) can be obtained. Structures grown as ELO are characterized by very important feature – density of structural defects are ten times lower than in a growing substrate, what translates to economical aspect of the process.

This method was used to obtain silicon active layers in order to produce solar cells. Presented article contains analysis of influence of LPE growth conditions like cooling rate (c.r.), geometry of growth substrate, temperature of growth on solar cells performance.

Keywords: thin film solar cells, liquid phase epitaxy, epitaxial lateral overgrowth

Size effect of synthetic saponite-clay in quasi-solid electrolyte for Dye-Sensitized Solar Cells (DSSC)

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Dye-sensitized solar cells (DSSC) have attracted the interest of the scientific community for their potential high solar conversion efficiency and for the possibility to prepare flexible and transparent devices with low cost of materials and deposition processes¹. Nevertheless, DSSC technology has some disadvantage mainly associated to a rapid degradation of composing materials under work conditions and evaporation of the CH₃CN-based liquid electrolyte. To overcome these limitations, recent studies have shown that the use of a gel- or quasi-solid electrolyte-based DSSC led to a significant increase in energy-conversion efficiency and long term stability. Quasi-solid electrolytes have been obtained by adding to proper ionic liquid mixture solid particles with different chemical nature². In this work, we propose the use of a synthetic saponite-clay³ with different morphological features as additive to obtain electrolyte suspensions for DSSC solar cells aiming at investigate the effect of particle size on solar cells efficiency and long term stability.

The saponite is a phyllosilicate belonging to smectite family characterised by a layered TOT structure. Synthetic saponite-clay materials were prepared by hydrothermal treatment at 513 K of a synthesis gel with the following molar composition: 1 SiO₂, 0.853 MgO, 0.056 Al₂O₃, 0.056 Na₂O and xH₂O. The H₂O/Si ratio of the samples have been varied from 20 to 150 aiming to modulate the saponite particle size. For DSSC applications, saponite solids have been dispersed in a methoxypropionitrile-based electrolyte (Z946, Solaronix) and injected in DSSC test cells.

As determined by X-ray powder diffraction and HRTEM analysis, the dilution of the synthesis gel allowed to decrease the saponite particle size from *ca.* 200 nm to *ca.* 50 nm (see Figure 1) with different textural and surface properties. The influence of these parameters on solar cell performances have been tested by dispersing 5 wt% of the clay in Z946 liquid electrolyte and using the dispersion as non-liquid electrolyte. The stability of saponite dispersions in methoxypropionitrile solvent have been studied by Dynamic Light Scattering (DLS). Spectroscopic data showed that depending on particle size, saponites form suspensions composed by aggregates of variable dimensions and with different stability.

The electrochemical characterisation showed that the addition of saponite with the largest particles (i.e. prepared by using H₂O/Si= 20) does not influence the solar cell efficiency, whereas the addition of solids with a progressive diminishing of particle dimensions led to an increase of solar cell efficiencies up to 8% with respect to the reference cell. This behaviour is probably associated to the fact that saponite with smaller particles favour scattering phenomena inside the electrolyte suspension. Proper tests to verify this effect have been successfully performed. Finally, tests devoted to investigate on the stability of DSSC prepared by using quasi-solid saponite-based electrolytes indicated that the addition of layered solids (especially the one with the smallest particles) increases the solar cell long term stability up to 1200 h under solar soaking.

Keywords: DSSC, synthetic clays, saponite, non-liquid electrolytes

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Solar pond technology to precipitate lithium carbonate from salt lake brine

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Solar pond is an important using way of solar energy. Generally speaking, a natural or artificial tank under sunlight illumination, has the heat absorption and the stored energy function, is called the solar pond. However, the salinity gradient solar pond (SGSP), a narrow sense solar pond, has been widely studied worldwide. In China, it has been widely applied in the production of Glauber's salt and in aquaculture during winter. Recently, solar pond technology has also been successfully used in the production of lithium carbonate from salt lake. As an ideal area to develop solar pond, the Tibet Plateau has the outstanding solar energy resources and the rich salt lake brine resources. Moreover, it lacks the mineral energy. SGSPs was operated in the Tibet plateau using natural brine of Zabuye Salt Lake. Through the experiment, it was discovered that a high temperature of 39.1°C-64.5°C can be achieved at low-convective zone (LCZ). This heat was used to precipitate lithium carbonate from Zabuye salt lake brine. After the experiment, we got lithium carbonate product directly from the brine which have an average grade of 78.9%.

Key word: Salinity gradient solar pond, Tibet plateau, Salt Lake, Lithium Carbonate, Solar Energy

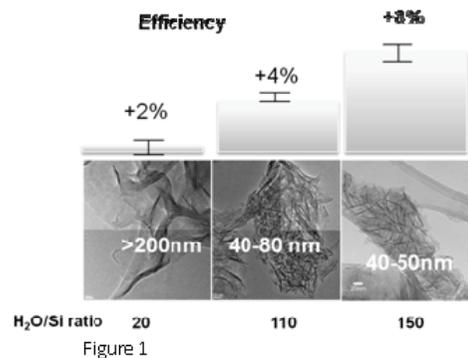


Figure 1

Spatially separated carrier multiplication in silicon Nanocrystals: towards high efficiency solar cells*

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Semiconductor nanocrystals can exhibit carrier multiplication (CM), a process in which absorption of a single photon creates multiple electron-hole pairs (excitons). This is of great interest for the development of highly efficient (third-generation) solar cells. However, the modest multiplication efficiencies and the high threshold energies found until now limit the practical benefit of CM. In this work, we present the results of investigations on CM mechanism in high density dispersion silicon nanocrystals embedded in a SiO₂ matrix by ultra-fast pump probe spectroscopy. We demonstrate efficient CM with an onset close to the energy conservation threshold of twice the bandgap, 2E_g. Moreover, under low pump fluence conditions, multiple excitons generated by CM do not undergo nonradiative Auger recombination, typically reported for CM in nanocrystals of other semiconductors, and thus have a long life time on the microsecond time scale. This enhances the extraction time window for charge separation by six orders of magnitude over previous results. We also show that multiple excitons are generated directly in adjacent NCs, rather than in a single NC with subsequent (< 100 fs) relocation.

Keywords Silicon nanocrystals; multiple exciton generation; carrier multiplication; high efficiency solar cells; third generation solar cells; quantum dot solar cells.

* the work has been accepted for publication in the Nature Photonics journal, DOI: 10.1038/nphoton.2012.36

Spray-pyrolytically deposited Ag-doped Cu₂O thin films for solar-hydrogen generation: Experiments & first-principles analysis

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We present here a combined study on photocatalysis by Ag-doped Cu₂O thin films using DFT band structure calculations and its experimental verification. The results of DFT calculations show that the top of valence band and bottom of conduction band of undoped Cu₂O lie at Γ point of Brillouin zone respectively (Fig. 1a), suggesting that pure Cu₂O is a direct band gap material. Minimal changes appear in the band gap and band gap energies in the Ag-doped Cu₂O system (Fig. 1b), keeping it still a direct band gap material. A defect band appearance can be seen between -2eV to -3eV in the valence band which is mainly due to the Ag 4d orbital and can be explained by a stronger interaction between the Ag 4d and O 2p, due to the larger Ag size.

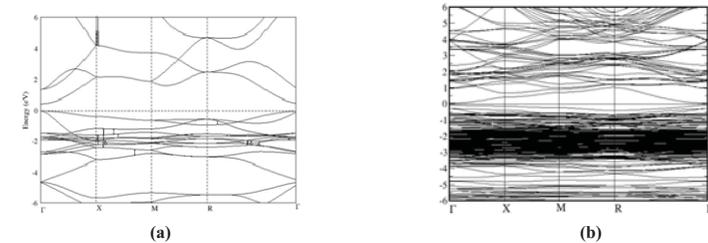


Fig. 1 showing the electronic band structure of undoped (a) and (b) Ag-doped Cu₂O

To validate the theoretical results experiments were carried out on undoped & Ag-doped Cu₂O by preparing thin films of Cu₂O doped with 0, 1.0, 3.0, 5.0 & 10.0 at.% Ag via simple spray pyrolysis method and characterized with X-Ray Diffractometry (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), UV-Vis Spectroscopy and Photoelectrochemical measurements. The results exhibited that Ag-doped Cu₂O samples produce significant photocurrent (2.34 mAcm⁻²) at 0.8 V/SCE with an experimental band-gap value of 2.35 eV as compared to undoped Cu₂O samples (0.62 mAcm⁻²) at 0.8 V/SCE with an experimental band-gap value of 2.52 eV (Fig. 2). The observed change in the electronic band gap and that estimated with first-principles calculations compare well, thus suggesting that such calculations have the potential to be used in screening various dopants before performing the experiments thereby saving precious chemicals, time and energy.

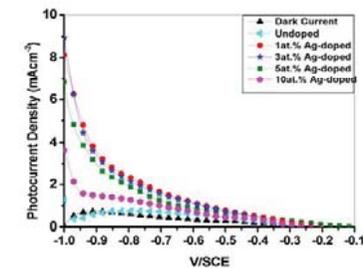


Fig. 2 showing photocurrent density of all undoped & Ag-doped Cu₂O samples

Keywords: Cu₂O; Ag-doping; Density functional Theory; Spray Pyrolysis

Structural, optical and electrical properties of a-Si:H thin films treated by femtosecond laser pulses

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Hydrogenated amorphous silicon (a-Si:H) has been attracting a lot of attention for last decades, because of its perspectives in thin film optoelectronics (e.g. solar cells, active matrix of liquid crystal displays). It combines low cost with a processing mechanism capable with large scale technologies. Low temperatures during the deposition process allow using inexpensive and low-melting substrates. The main issues with a-Si:H films is the high order of dangling bonds which act as recombination centers that strongly reduce the carrier lifetime and make the efficiency of the solar cell as low as around 10 %. Additionally, this initial efficiency will halfway decrease when exposed to sunlight which is known as the Staebler-Wronski effect (SWE). In order to reduce the SWE in solar cells, hybrid a-Si/nc-Si tandem modules have been developed. Such modules are able to achieve both higher efficiency and stability compared with single a-Si:H solar cells. For optimization of technological process of tandem solar cells production one can use a femtosecond laser-induced crystallization of a-Si:H thin films. The laser-based treatment of a-Si:H may solve its efficiency and stability issues in a one-step process.

a-Si:H films with a thickness of 300 nm were deposited onto quartz substrates using PECVD method. The a-Si:H film was deposited at a rate about 2 Å/s in an argon (Ar) diluted silane (SiH₄) environment at a substrate temperature of 250 °C. The samples were treated using a femtosecond Yb:KGW laser system. The laser system delivered pulses at a repetition rate of 200 kHz with a pulse wavelength of 1030 nm and a duration of 500 fs. The beam spot was circular with beam diameter of 15 μm on the film surface. To prepare the samples for measurements films were scanned by laser beam with the scanning speed of 5 mm/s. The scanning step was 2 μm. To carry out the electrical and photoelectric measurements aluminum contacts were deposited on the surface of prepared films. The gap between the contacts was perpendicular to the laser beam scanning direction. Distance between contacts and their length were 0.5 and 4 mm correspondingly. Averaged laser beam power was varied continuously from 25 to 100 mW.

We have investigated the effect of femtosecond laser treatment of hydrogenated amorphous silicon films on their structural, optical and electrical properties. When crystalline volume fraction of the treated samples was around 7 % sufficient increase (by 4 orders of magnitude) of dark conductivity was observed (Fig. 1). We have attributed such behavior to change in charge carrier transport mechanism from amorphous to nanocrystalline. However, the shape of the spectral dependences of absorption coefficient of all investigated samples corresponded to that of a-Si:H. This question still remains uncertain and needs further investigation. It was also found that starting from some values of laser fluence the effect of spallation and film oxidation occurred.

Keywords amorphous silicon; femtosecond laser crystallization

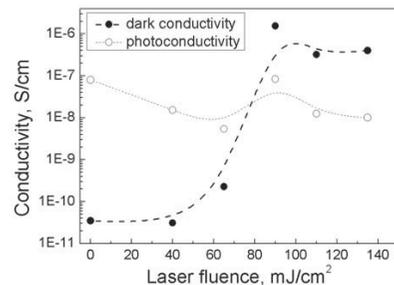


Fig. 1. Dark conductivity and photoconductivity of studied samples as a function of the used laser fluence. Dashed lines are guides for eye.

Surface selenization of CuInS₂ thin-film solar cell absorbers by rapid thermal processing

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Cu(In_{1-x}Ga_x)₂(S₂Se_{1-y})₂ ("CIGSSe") chalcopyrite-based thin-film solar cells are among the most promising candidates to supersede Si wafer-based photovoltaics. One of the advantages of the CIGSSe alloy system is that by changing the chemical x and y composition of the absorber, its optical band gap (E_g) can be varied between 1.04 eV (for $x = 0, y = 0 \rightarrow \text{CuInSe}_2$, "CISE") and 2.53 eV (for $x = 1, y = 1 \rightarrow \text{CuGaS}_2$, "CGS") [1]. Thus, it is easily feasible to engineer absorber bulk E_g values to match the optimum E_g for solar energy conversion (i.e., ~1.4 eV for AM 1.5 [2]). However, the highest solar cell efficiencies are obtained when using CIGSSe absorbers with E_g values of approx. 1.1 eV [3]. Devices based on chalcopyrite absorbers with higher E_g fall behind with respect to expectations. One reason for that could be unfavorable energy band alignments at, e.g. the respective buffer/absorber heterojunctions [4]. Deliberate surface modifications of "wide-gap" CIGSSe absorbers could be an optimization route, which may hold the key to improvements in corresponding thin-film solar cell devices.

In this contribution, we present an example of such surface tailoring. We will focus on our work of selenizing the surface of CuInS₂ (CIS) absorbers with the aim of producing a surface with an optimal electronic structure for alignment with the electronic energy levels of the CdS buffer [5]. KCN-etched CIS substrates were selenized by a rapid thermal process (RTP) in elemental Se vapor. The impact of different RTP process parameters (such as RTP temperature, RTP duration, and Se amount) on the chemical and electronic structure of the "Se:CIS" absorbers was studied. A non-destructive depth-resolved chemical and electronic structure analysis was performed using a suite of complementary spectroscopic techniques. The chemical surface structure of treated CIS absorbers was studied by x-ray photoelectron spectroscopy (XPS). Ultraviolet photoemission spectroscopy (UPS) was used to monitor the position of the valence band maxima (VBM) with respect to the Fermi level (E_F), giving some clue about changes in the surface band gap. Bulk elemental analysis was conducted via x-ray fluorescence analysis (XRF). The impact of the selenization treatment on the optical E_g was followed through optical ultraviolet-visible (UV/Vis) spectroscopy. Additionally, energy-dispersive x-ray spectroscopy (EDX) recorded in a scanning electron microscope allowed for laterally-resolved elemental mapping of Se:CIS cross sections. The combination of the results obtained by all these different x-ray spectroscopies allows us to paint a detailed picture of the (depth-resolved) chemical and electronic structure of the Se:CIS thin-film. We find that a substitution of Se for S takes place as a result of all RTP treatments. The VBM shifts towards E_F and a reduction of the optical E_g can be observed. Both observations are in agreement with the formation of a CuIn(S,Se)₂ (CISSe) like phase *on top* of the treated CIS substrate. However, this CIS \rightarrow CISSe conversion (i.e., its S/Se ratio) depends on the RTP process parameters. Furthermore, it was revealed that the RTP selenization process changes the initial Cu-poor CIS surface to a surface with a stoichiometric 1:1:2 = Cu:In:(S+Se) composition.

In summary, we have introduced an easy RTP-based process to incorporate Se into the surface of CIS absorbers; thus, tailoring its surface properties aiming for an optimized electronic heterojunction interface structure.

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Keywords Surface tailoring; RTP; XPS; UPS; XRF; UV/Vis spectroscopy; EDX

Synergistic effects of InN compact layer and different concentrations electrolytes for dye-sensitized solar cells

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This study examined the nanostructure nitrided indium compact layer (InN-CPL), different concentrations electrolytes and Au nano particles to dye-sensitized solar cells (DSSCs). We present the DSSCs with InN-CPL prepared by radiofrequency magnetron sputtering and doping Au particle in photoelectrode. When InN-CPL was applied to DSSC, the energy conversion efficiency was enhanced considerably compared with using InN-CPL prepared using a radiofrequency magnetron sputtering. The DSSC fabricated on InN-CPL covered ITO electrode shows the short-circuit current density and efficiency of conversion of solar energy to electricity were increased to 19.2 mA/cm² and 7.92 %, respectively, under illumination by a 1000 W xenon lamp.

Keywords Dye-sensitized solar cells; Nanostructure nitrided indium compact layer

Synthesis and characterisation of SnO₂ nanocrystallite films formed by electrodeposition in nitric acid solution

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SnO₂ thin films were electrodeposited on fluorine tin oxide substrate in nitric acid solution. The potential was swept from -0.4 to -1.6V with a rate of 50 mV/s. The films were found uniform, adherent to the substrate and amorphous. It pointed out by XRD patterns that after heat treatment at 600h for 1h, the films turn out to be crystalline. Indeed, the film becomes composed of SnO₂ nanocrystallite with a cassiterite tetragonal structure. The nanocrystallite size is about 50 nm. The films thickness was estimated to about 592 and 563 nm for as-deposited and after heat treatment, respectively. Some optical parameters of these films such as refractive index (n), extinction coefficient (k), absorption coefficient (α) and band gap were studied. These parameters were deduced by Swanepoel method in the wavelength range 300-800 nm using optical transmission data. It is shown that the band gap increases after heat treatment which is of order of 4 eV.

Keywords: Thin films; Optical properties; band gap; electrodeposition, cyclic voltammetry.

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Synthesis of new derivatives of Rhodanine dyes for Dye-Sensitized Solar Cells (DSSCs)

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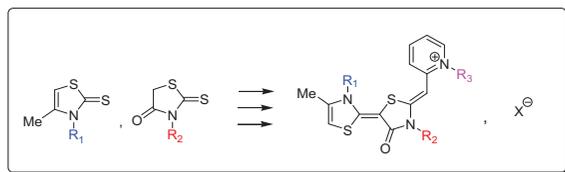
Solar energy is renewable energy par excellence. Environmentally friendly, it has many specific advantages because of the foreseeable depletion of fossil energy resources. The solar cells are currently dominated by silicon and expensive, hence the widespread enthusiasm of researchers interested in the possibility of manufacturing solar cells from plastic materials or organic.

These new cells have the advantage of being simpler and more malleable than those made from a silicon ^[1].

Several organic dyes, such as styryl ^[2], coumarines ^[3], polyenes ^[4] and indole derivatives ^[5], have been proposed as potential candidates for solar cells.

Rhodanine derivatives, electron acceptors are used in a wide range of organic molecules "Push-Pull" These have applications in optics and more recently non linéaire ^[6] are used in the manufacture of DSSCs ^[7] and are obtained with a high conversion efficiency compared to other.

We were interested in the synthesis of new chromophores containing the pattern rhodanine, a molecule from the leader aminothiazoline thione as a synthetic strategy developed previously in our laboratory.



Chromophores obtained and intermediate compounds were identified by spectroscopic methods (1H NMR, 13C, IR and mass spectrometry).

Keywords: DSSCs, Rhodanine, Merocyanine, Dye, Photovoltaic cells.

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The energy performance analysis of building integrated photovoltaic (BIPV) Trombe wall system for summer period

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In this paper, the energy performance analysis of a model BIPV Trombe wall built in Izmir, Turkey for summer period has been designated. For this, a-Si semi-transparent PV module has been integrated on the Trombe wall façade of a model test room. The system has been operated for 2 weeks and the results of the days July 29th – August 1st have been used for the simulation model. The Computational fluid dynamics (CFD) analysis for two-dimensional model has been applied to predict the temperature and velocity distribution in the test room model. The analysis is based on transient condition. The experimental results also show that 10% of solar radiation transmittance has been supplied by using a semi-transparent a-Si solar cell. Thus, the change in electrical efficiency by surface temperature of the PV module has been interpreted and the electrical power rate of the PV module has been designated. This project aims to designate the summer performance evaluation of BIPV Trombe wall system.

Keywords: BIPV Trombe wall; a-Si semi-transparent type PV; computational fluid dynamics; natural ventilation; electrical efficiency.

Thienopyrroledione-containing Donor/Acceptor alternating copolymers as new electron-donating materials for BHJ polymer solar cells

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Pi-conjugated polymers have attracted significant research interests during the past three decades owing to their tuneable by design (electro)chemical, electronic and optical properties. This remarkable and rare combination of features paves the way toward new generations of (opto)electronics devices such as organic FETs, LEDs, Laser & Solar Cells.

Designing efficient materials for boosting solar cell's external power conversion efficiency (EPCE) beyond state-of-the-art values exceeding 8.0% require, among other important issues, a strict and full control of their redox properties. Key material parameters are HOMO/LUMO levels and the band gap. Cyclic voltammetry (CV) & UV-Vis spectroscopic studies performed on the three synthesized D/A alternated copolymers showed band gaps inferior to 2.0 eV together with easily varied HOMO and LUMO levels in the -5.62 eV to -5.08 eV and -3.53 eV to -3.13 eV respective ranges as a result of our (macro)molecular engineering approaches. UV-vis-NIR spectroelectrochemical studies confirmed CV results, enabling moreover more accurate determinations of their HOMO levels. In addition, Raman spectroelectrochemistry was used for an in depth probing of the redox stability of these new semiconducting materials incorporating an electron-accepting thienopyrroledione sub-unit.

A preliminary and encouraging EPCE value of 1.6% has been obtained for non-optimized D/A bulk-heterojunction solar cells based on D/A alternated copolymer/PC61BM's active layers.

Keywords : Pi-conjugated polymers, D/A bulk heterojunction Solar Cells, Redox Properties, EPCE.

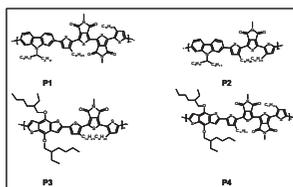


Fig.1. J-V Repeating units of the four push-pull band gap alternating copolymers of P2-P4

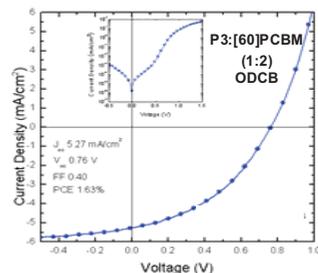


Fig.2. J-V characteristics of the fabricated photovoltaic cell (active area of 25 mm²) obtained under AM 1.5G illumination of 100 mW. cm.

Thin film layers of Amorphous SiCx:H intrinsic and phosphorus-doped for the manufacture of emitters in solar cells

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With annealing the thin hydrogenated amorphous silicon carbide films (a-SiCx:H) deposited on the wafers of silicon crystals using the technique of the Plasma Enhanced Chemical Vapour Deposit (PECVD) reactor, pn-junctions with very low inverse saturation current can be formed¹. This has proven suitability for the fabrication of thin film transistors [2] and is of increasing interest for crystalline Si thin film solar cells^{3, 4}. The most commonly used method to crystallize the amorphous layers is solid-phase crystallization (SPC) which requires annealing in a furnace at a maximum temperature of 600 degrees Celsius during a long time (20–60 hrs) or the rapid thermal annealing (RTA) that requires a high temperature near 1000 degrees Celsius together with a shorter time of process³. The characterization of the annealed structures indicates that the a-SiCx:H thin films partially recrystallize during the annealing process can form Si-nanocrystals embedded in the amorphous thin film causing significant changes in the emitter. To better understand this process and to further improve pn-junction we are studying the recrystallization process studying the process of change from amorphous to crystalline by X-Ray Diffraction (XRD) measurements and optical transmission measurements in the infrared (FTIR). The both layers, Intrinsic and phosphorus-doped a-SiCx:H layers were deposited using the technique of plasma enhanced chemical vapour deposition (PECVD) at 400 °C on a crystalline silicon substrate (c-Si) type-p of 300um-thick and crystallographic orientation <100> and subsequently annealed in a furnace with quartz tube at 900 ° C. The presence or absence of Si-nanocrystals changes the optical properties of the a-SiCx:H/c-Si samples. From the fitting of the FTIR transmission spectra, the refraction and absorption indices of the intrinsic and phosphorus-doped a-SiCx:H films have been calculated in the range of 1500-9000 cm⁻¹.

Keywords Annealing, Emitter, Intrinsic, phosphorous doped, crystallization, Thin Film, X-ray diffraction,.

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Thin film solar cells from nanocrystal inks of quaternary semiconductors

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The creation of a suitable inorganic colloidal nanocrystal ink for use in a scalable coating process is a key step in the development of low-cost thin film solar cells. We have developed an innovative method of synthesizing and using $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanocrystals as the building block for the fabrication of bulk CZTS based thin films. This presentation will focus on the synthesis of CZTS nanocrystals with different compositions and structures. We will also discuss our successful result on incorporating Ge in the CZTS structure to yield CZTGeS nanocrystals with tunable bandgap. The CZTGeS nanocrystal ink solution is applied directly on various substrates to form a thin film coating. The CZTGeS nanocrystals are then consolidated into large crystalline domains by a brief thermal treatment under Se vapor. Furthermore, the ability to control the composition for CZTGeS nanocrystals allows the unique capability to engineer the bandgap of the CZTGeS absorber using nanocrystals with different ratios of Sn/Ge. By optimizing processing conditions for the various layers in the solar cells, total area efficiencies in the vicinity of 8.5% under AM1.5 illumination have been achieved.

We will also briefly describe our work to date with copper indium gallium disulfide (CIGS) nanocrystals and the associated PV devices. For this system we have achieved efficiencies greater than 12%.

Keywords CZTS, CIGS, Thin Film solar cells, PV

TiO₂ Thin Films Prepared by APCVD for Organic Solar Cells Application

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The efficiency of organic solar cells depends on many parameters such as absorption, charge transport, interface states, etc. ...

The amelioration of the efficiency of photovoltaic conversion can be obtained by minimizing losses in reflection and absorption in the transparent electrode involving increased absorption efficiency in the active layer which can be achieved by the use of TCOs with special optical and electrical properties.

Titanium dioxide TiO₂ thin films have been prepared by APCVD method using the titanium tetrachloride (TiCl₄) as a starting material on glass and ITO. The surface morphology of the films deposited on ITO and glass substrates were investigated by scanning electron microscopy (SEM) and structural properties in terms of crystal structure were also investigated by XRD. Ellipsometry was used to determinate the refractive index for the films deposited at 490°C and the sheet resistance was measured using the Four-Point method.

TiO₂ films prepared on ITO during 5minutes present a sheet resistance of 19.57Ωcm⁻¹ and refractive index of 1.8 can be used as an interfacial layer in organic solar cells application to minimize the reflectivity. The total reflectivity of TiO₂/P3HT: PCBM obtained by using the films is less than 3%.

Keyword: TiO₂, APCVD; Reflectivity, Organic Solar Cells.

Transparent and hydrophobic nanocoating materials for photovoltaic cells

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Leveraging the durability of photovoltaic (PV) plants at an acceptable cost is becoming one of the most challenging issue to foster the diffusion of PV. For instance, stringent requirements for the modules life time of at least 30 years are carried out by the US Department of Energy. One of the most important technological factor to enhance the PV modules durability is represented by the availability of suitable coating materials with high barrier properties, flexibility, and affordable cost. These properties are of a special concern for thin film PV cells, which are more sensitive against the degradation effect due to atmospheric agents.

A lot of research effort has been devoted to study and to develop novel flexible and low cost coating materials with improved barrier properties against water vapour and oxygen. However, few studies have been carried out to leverage the barrier properties against liquid atmospheric agents of the coating materials for PV cells (e.g., acid and basic rains). As a result, these studies proposed the development of transparent hydrophobic and superhydrophobic surfaces suitable for solar cells applications by means of multi-step processes involving plasma treatment steps of the polymer surfaces as well as high temperature steps (>150°C). Nevertheless, these multi-step processes are likely to turn out to be expensive and difficult to be implemented at industrial level.

This work aims at studying and developing highly hydrophobic transparent and flexible coating materials for solar cells by means of a simple, but yet effective, single-step process, which is carried out at room temperature and specifically applied to PV standard coating materials.

The current barrier protective films for the PV applications are generally composed of one or more layers of polymer substrate with an inorganic coating. The inorganic coating is generally consisting of SiO_x or AlO_x, whereas the polymer substrate can be EVA, ETFE, PET or PEN.

This study investigates the chemical deposition of a transparent and hydrophobic nano-coating on a „standard“ bilayer material employed for the solar cells coating, consisting in a PET-SiO_x substrate of 12 micron width. The nano-coating has been deposited by applying the self-assembly of monolayers (SAM) of alkylsilanes (OTS: octadecyltrimethoxysilane) and fluoroalkylsilanes (FAS: 1H,1H,2H,2H-per-fluorodecyltrichlorosilane).

The hydrophobic properties of the obtained samples have been assessed by means of static contact angle measurement, showing high average values of 130° as a consequence of the FAS deposition with a 105% increase of the contact angle on the SiO_x side and a 83% enhancement on the PET side. Therefore, the chemical deposition of the FAS nano-coating successfully changed from hydrophilic to hydrophobic both the PET and SiO_x surfaces. The same measures carried out for the OTS modified samples indicated that only the SiO_x surface has been coated, with an increase of 36% and an average value of 86°, while a negligible increase of 6% has been relieved on the PET side. A chemical mechanism hypothesis has been proposed to explain the different reactive behaviour of the PET-SiO_x samples with FAS and OTS, respectively.

Moreover, the light transparency of the nano-coated films has been evaluated. A 90% transmittance value has been measured for the different coated samples, thus resulting adequately transparent for solar cell applications. The water vapour barrier properties (WVTR) have been also assessed in order to understand the effect of the deposition treatment on the gas barrier properties. Furthermore, the morphology of the obtained samples has been studied by AFM.

The preliminary results obtained demonstrated that a highly hydrophobic flexible and transparent coating may be successfully obtained by modifying a PV standard coating bilayer with a simple and single-step process carried out at room temperature. These results will be further deepened and investigated in the future research.

Therefore, an interesting contribution may be potentially provided from the accomplishment of the present study to the PV sector applications in terms of improved barrier properties of the coating materials against liquid atmospheric agents. This is expected to guarantee a higher durability for the PV modules.

Keywords photovoltaic; coating; self assembled monolayer; fluoroalkylsilanes; alkylsilanes

TTF/p-InP organic-inorganic heterojunction solar cell

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Tetrathiafulvalene (TTF) with C₆H₄S₄ molecular formula was used in the fabrication of organic-inorganic (OI) heterojunction. The Al/TTF/p-InP/Au-Zn structure was fabricated by forming a thin of TTF organic semiconductor on p-InP inorganic semiconductor and evaporating of Al metal on the film. It was seen that the barrier height value of the Al/TTF/p-InP/Au-Zn OI heterojunction is remarkable higher than the conventional Al/p-InP/Au-Zn metal-semiconductor contact. The characteristic parameters of the device were determined by using current-voltage (*I-V*) and capacitance-voltage (*C-V*) measurements in dark and room temperature. The *I-V* characteristics of the device were also examined between 40-100 mW/cm² illumination intensity by the help of a solar simulator with AM1.5 global filter.

Keywords Tetrathiafulvalene; InP; solar cell

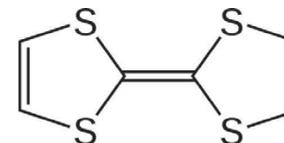


Fig1. Molecular structure of TTF

Using density functional theory to model dye-sensitized solar cells

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With negligible environmental footprint, easy deployment and simple manufacturing processes, the photovoltaic solar technology is expected to play a key role in future energy breakdown. Novel types of solar cells, extending into the field of low-cost and easily chemically tunable organic molecules and polymers, pave the way to a new generation of economic photovoltaic modules, possibly standing in competition against other energy sources.

Among these, dye-sensitized solar cells (DSSC)¹ are excitonic solar cells, in which a monolayer of dyes grafted on a surface of a highly porous semiconductor material (typically TiO₂ or ZnO) is the photoactive part. The driving force to the exciton separation into free charge carriers is a fast electron injection from the photoexcited dye to the conduction band of the semiconductor.

We present an efficient computational protocol² based on a unique density functional theory model, which allows for an accurate and balanced treatment of electronic and spectroscopic properties in different phases (such as gas, solution and interfaces). Through the support of some examples, we show how this computational protocol can be used not only to explain experimental observations, but also to design either new single components (dyes, anchoring groups, electrolyte component) or, more generally, new cell assemblies. This may thus allow to drive experiments through an efficient *in-silico* prescreening of all different basic components of DSSC, and therefore offer substantial time and resources savings at the experimental level.

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Keywords DFT; DSSC

ZnO Nanowire Arrays Sensitized with CuInS₂ and Cu₂ZnSnS₄ Absorbing Materials for Extremely Thin Absorber Solar Cells

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The use of less expensive materials, prepared by low cost techniques and their integration in the new generation solar cells is in intensive research. Aligned one dimensional nanowire arrays, providing a direct pathway for charge transport as well as a high junction area, are beneficial for the nano-photovoltaic device concept. The all-inorganic extremely thin absorber (*eta*) solar cell appears as a promising candidate to reduce the high cost and massive use of materials in their single-crystalline and thin film counterparts. The proposed nanowires-version of *eta*-solar cell, is composed by a thin semiconductor absorber ($E_g \sim 1.5$ eV) sandwiched between transparent electron and hole conductors (n and p-type semiconductors, respectively with $E_g > 3$ eV). The sensitization of ZnO nanowires with various narrow band gap semiconductors would allow the generation of electron-hole pairs through visible light excitation. As a consequence of the thinner absorber and the good electrical and optical properties of the nanostructured electrode, the photogenerated carries can be efficiently collected and transported through the nanowire channels (Fig. 1a).

Here we are reporting on the photosensitization of electrodeposited ZnO nanowire arrays with different light absorbing materials, as CdS, CuInS₂ (CIS) and Cu₂ZnSnS₄ (CZTS). The last one became very attractive in the last few years for the scientific and industrial communities due its abundance and non-toxicity. In our study the sensitization of ZnO nanowires is achieved by forming around them thin continuous films composed of quantum dots (Fig. 1b). These semiconducting quantum dots are prepared by two methods: Successive Ionic Layer Adsorption and Reaction (SILAR) and electrodeposition (ECD). The layer thickness for the SILAR method is determined by the cycle numbers whereas for the electrodeposition it is controlled by the passed charge density. As prepared quantum dots films are with good optical properties and only few nm are enough to reach full light absorption in the large range of visible solar spectrum (Fig. 1d).

With the aim to obtain more efficient light absorption from the available solar spectrum a double shell structure is proposed, where the first shell is composed of CdS ($E_g \sim 2.1$ eV) and the second of CIS or CZTS ($E_g \sim 1.5$ eV). The obtained structure is with good crystalline and optical properties (Fig. 1c, d). TEM images show that ZnO NW, with strong (002) orientation, is covered by a double shell: thin polycrystalline layers of: CdS (~7 nm) and CIS (~15nm).

Thus, SILAR and ECD appear as suitable low cost techniques for preparation of conformal photosensitizing extremely thin absorber layers of CIS and CZTS onto electrodeposited ZnO nanowires. The optical transmission results prove the enhanced photoresponse of the ZnO nanowires after being photosensitized with absorbing materials. While ECD produced layers of better crystalline quality, the SILAR technique proved to be more suitable for uniform layer preparation on the entire nanowires surface. The increased junction area by ZnO nanowires combined with controlled shell thickness, are crucial for preparation of heterostructures with good optical and electrical properties. The integration of these core/shell nanostructures (ZnO/Quantum dots (CdS, CuInS₂, Cu₂ZnSnS₄)) in *eta*-solar cells, where the cell is completed with a p type hole transporting layer (CuSCN) is going on.

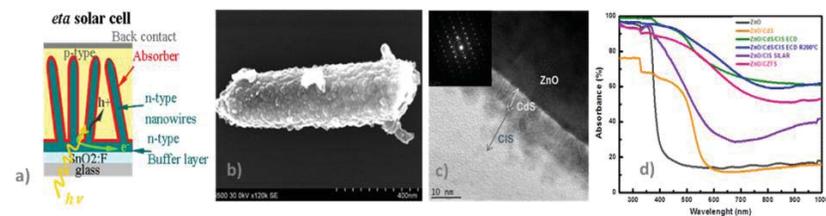


Figure 1. (a) Schematic of the eta solar cell; (b) STEM image of ZnO/ CuInS₂ (SILAR) nanostructure; (c) TEM images of core/double shell nanowire structure: ZnO /CdS (first shell)/ CuInS₂ (second shell); (d) Absorbance spectra of: bare ZnO nanowire arrays and after their sensitization with: CdS (orange curve); CdS/CIS-ECD (green curve), after annealing at 200°C (blue curve); CIS-SILAR (violet curve) and CZTS-ECD (red curve).

Keywords ZnO nanowires, Cu₂ZnSnS₄ (CZTS), CuInS₂ (CIS), eta solar cells

Fuel Cells

A distribution of relaxation times approach for PEM fuel cells electrochemical impedance data analysis

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Electrochemical impedance spectroscopy (EIS) was used as a base diagnostics technique for in-situ analysis, in order to better categorize irreversible changes in the kinetic and/or transport properties of a proton exchange membrane (PEM) fuel cell. This was based on the fact that polarization losses differ in their characteristic time constants and frequency response. An extensive study of fuel cell performance has been carried out for an open air cathode 8 cells PEMFC, in various operating conditions. The influence of different oxidant supply concentrations, fuel flow rate and fuel pressure were studied over a wide range of current densities. Measurements were carried out using a Solartron Frequency Response Analyser, Model 1250, connected to an Electrochemical interface also from Solartron, Model 1286. The frequency was typically spanned between 20 kHz and 0.1Hz.

The analysis of impedance data was made, at first, using an *a priori* equivalent circuit describing the transfer function of the system in question. Basically, two RQ elements connected in series are identified as describing the impedance response of the cell. A constant phase element (CPE) was chosen to describe the impedance observed behavior in an open air cathode PEM fuel cell. In the case of the cathode representation a Warburg impedance (finite length type) was added to the circuit.

An approach is proposed for computing the distribution of relaxation times (DRT) given the impedance model of the physical system. As a result a DRT expression was derived for an equivalent circuit composed by a CPE in parallel with both a resistance and a finite Warburg diffusion element.

The ac impedance data were associated in the high-frequency region (>100 Hz) to charge transport in the catalyst layer, whereas in the low frequency region they were associated to mass transport in the gas diffusion layer (GDL), catalyst layer and membrane. At high overpotentials gas diffusion in the GDL and the catalyst layer become dominant, which is to be expected in the present case where air is used as the oxidant.

Results show the higher resolution of DRT allowing the identification of losses with characteristic frequencies separated by half decade, which is not possible to find when using the equivalent circuit elements approach evaluated by a complex non-linear least square (CNLS) fitting algorithm.

A clearer understanding of the mass transfer diffusion processes occurring at the anode and cathode is achieved. In particular, the identification of diffusion limitations at the anode was possible in situations of air depletion and lack of hydrogen humidification.

Keywords: PEM fuel cells, electrochemical impedance, distribution of relaxation times

Atomic layer deposition of dense mixed ionic-electronic conducting membrane on porous tubular substrate for oxygen combustion

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Atomic layer deposition thin film deposition technique was studied for preparing robust and high performance mixed ionic-electronic conducting membranes for oxygen production in oxyfuel process.

There were two qualities for the final product pursued; nanometer scale membrane thickness and large reaction surface area of the membrane, both aiming at improved oxygen flux through the membrane compared to membranes prepared with powder/sintering methods, illustrated in **Figure 1**. In addition mechanical strength against pressure gradient across the membrane was sought with strong porous support material.

Non-functional dense thin films were deposited on the inner surfaces of mesoporous tubular alumina substrates and experiments were also done to coat through mesoporous tubular substrate conformally. Coating experiments were carried out with a flow type reactor, with modified forced flow for coating of tubular porous substrate. Pressure and flow rate data for different coating processes were gathered and gas tightness of coated samples were measured. Gas tight coatings on the inner surfaces of the porous tubes and some conformal coating of the porous tube material were achieved in the experiments.

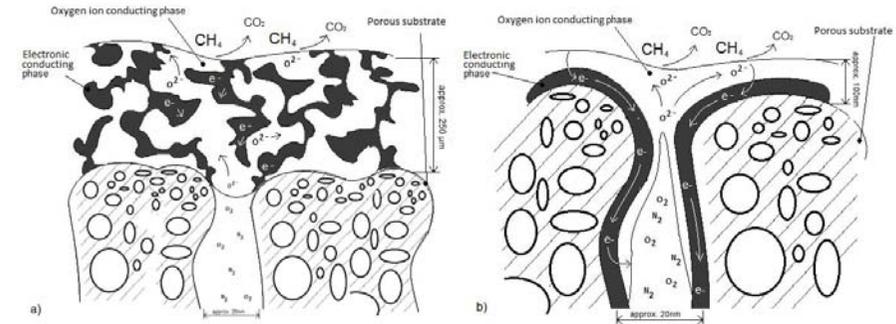


Figure 1 Dual phase mixed ionic-electronic conducting membrane on porous substrate; a) powder/sintering prepared b) ALD thin film

To demonstrate dual phase mixed ionic-electronic conducting membrane structure prepared with ALD, shown in **Figure 1** b), electronically conducting thin film platinum coating was prepared. From electrical measurements it was derived that Pt-coating's cross-sectional area on the inner surface of the tube was approximately three times larger than what could be derived from theoretical film growth rate and from the tube's inner diameter. Larger than expected cross sectional area of the coating can be explained as uncontrolled film growth on the inner surface of the tube, or improved surface area of the coating resulting from nanoscale thin film conform the rough inner surface of the tube, illustrated in **Figure 2**.

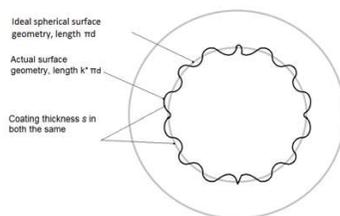


Figure 2 Improved cross sectional area of the Pt-coating

Keywords atomic layer deposition; mixed ionic-electronic conducting membrane; thin-film; porous; tubular

Carbon Aerogel as a Carbon Support for PEMFC Electrocatalysts

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Carbon aerogels (CAs) are prepared by pyrolysis of organic aerogels that are synthesized by supercritical drying of the gels obtained by the sol-gel polycondensation reaction of resorcinol and formaldehyde in aqueous solutions. Their microstructure and physical properties (pore volume, pore size) can be tuned by varying the processing parameters in the sol-gel polymerization, gelation, curing, and pyrolysis steps. Because of their high electrical conductivity, they are promising materials as carbon support for PEM fuel cells.

Carbon supported Pt catalysts are very efficient for both oxidation and reduction reactions in fuel cells. Particle size of platinum nanoparticles and dispersion are important parameters that affect the fuel cell performance and these properties strongly depend on the catalyst preparation methods. Among catalyst preparation techniques, supercritical carbon dioxide (scCO₂) deposition is a promising way of depositing Pt onto various carbon supports.

ScCO₂ deposition involves the dissolution of an organometallic precursor in scCO₂ and the impregnation of the carbon support by exposure to this solution. After the reduction of the precursor on the carbon support, carbon supported metal nanoparticles are obtained.

In this study, firstly carbon aerogel was synthesized and then CA supported Pt nanoparticles were prepared via scCO₂ deposition. Effects of different different reduction temperatures on the catalyst properties and electrochemical activity were investigated. Prepared Pt/CAs were characterized by XRD, TEM and CV. TEM results showed that when the reduction temperature was increased from 200 to 1000°C, the average particle size increased and this caused a drastic decrease in electrocatalytic activity.

Keywords supercritical carbon dioxide deposition; carbon aerogel; pemfc

Catalysts for Ethanol Oxidation in Ethanol Solid Oxide Fuel Cells (ESOFc)

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The finite resources of fossil fuels, along with environmental concerns are stimulating a broad intensive search for alternative energy sources. The direct ethanol-oxidation fuel cell (DEFC) or solid oxide fuel cells fueled with ethanol (ESOFc) could afford an excellent alternative solution to energy-generation problems, and entail major improvements in the prospects for a renewable energy economy. Catalyst which effectively oxidize ethanol and splits the C-C bond in ethanol at room were prepared at Brookhaven National Laboratory in 2009 [1-4]. Now, to improve the process of ethanol oxidation in ESOFc we tested several catalyst for the anodic decomposition of ethanol in anodic part of ESOFc. SnO₂, SnO₂/Sb₂O₅, CeO₂ and TiO₂ were tested as catalyst for ethanol decomposition. Physical properties of this catalysts were described by XRD and SEM techniques. This catalysts were deposited on Ni porous material and are placed before an anode in ESOFc. Power and current densities of solid oxide fuel cell fueled with ethanol (ESOFc), with and without a pre anode conversion catalyst were compared and studied in the function of temperature.

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Keywords: ethanol oxidation, solid oxide fuel cells, ESOFc

Characterization of hybrid membranes for PEMFC.

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The main component of low temperature fuel cells (PEMFC) electrolyte is Nafion®. This polymer is also present in the catalytic layer. The principal disadvantage concerning with the use of Nafion® is the high cost of this polymer. Recently, it was discovered that natural rubber, an electrical insulator, can be possible used like a membrane in a PEMFC[1,2]. Nevertheless, its protonic conductivity should be improved to be able to replace Nafion®. To obtain this aim, a mixture of this natural rubber with an inorganic protonic conductor can be prepared and thus preparing hybrid inorganic-organic membranes with enhanced protonic conductivity. In this work, the inorganic protonic conductor used is colloidal silica dispersed (8-33% wt) in a latex matrix, the prepared membranes will be doped with phosphoric acid to increase the concentration of functional groups. The results obtained showed that H₃PO₄ plays an active role in the protonic conduction mechanism of these membranes. The hybrid membranes were prepared from a mixture of a pre-vulcanized natural rubber solution and a colloidal silica suspension. pH has been wisely controlled and kept always basic. The membranes were prepared by casting the mixture in a film (120-150 microns), and then drying them between 60 and 90°C. Phosphoric doping was performed by immersing the membranes in concentrated H₃PO₄ at 25°C for more than 10h. The membranes characterization has been made using different techniques as FTIR in the ATR mode, SEM and Electrochemical Impedance Spectroscopy (EIS) with an Agilent 4294A impedancimeter (1·10⁷ – 40 Hz) or an Autolab analyzer (10⁶ – 1Hz). MEAs prepared with the membranes obtained were measured in a FCTS Arbin Instruments test station.

Five membranes with different SiO₂ % wt were obtained, all of them showed physical stability and were able to manipulate. The FTIR spectra comparison shows that the only difference between the obtained membranes is the presence of a band (1080-1060 cm⁻¹) which corresponds to silicon-oxygen bonds in the case of the SiO₂-modified membranes. SEM confirmed that the increase of silica content generates surfaces more bumpy. Besides, it is observed that the pores number increases with increasing silica content. EIS spectra shows that the membrane with lower resistance is the one that contains a 28 % wt of SiO₂. This film has been selected for preparing a MEA, and to measure its polarization curves. The maximum power density obtained, in this case, has been 0,66 mW/cm². Also, it is checked that phosphoric acid doping increases the conductivity (3,41·10⁻³ S/cm to 8,33·10⁻³ S/cm), and this improvement in the performance of the membranes has been also observed in the i-V curves measured (maximum power density 28 mW/cm²).

The obtained results show the viability of latex membranes doped with silica as an alternative to conventional electrolytes. In the future, it is proposed to replace totally the Nafion® from the catalytic layer, obtaining MEAs with competitive power densities.

Keywords: Fuel Cells, PEMFC, Membranes, Inorganic-organic hybrids, Natural Rubber, Colloidal Silica, MEAs, Conductivity.

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Cobalt Containing Perovskite Structures for Solid Oxide Fuel Cell Cathodes

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The majority of traditionally used cathode materials for Solid Oxide Fuel Cells (SOFCs) have perovskite or perovskite related structure. The research of new materials is focused on high electronic conductors with catalytic activity. Our work demonstrates the perovskite cuprate phases $\text{YSr}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7+y}$. Previous research in this area investigated the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ showing good results as a possible cathode material for SOFCs¹. However at higher temperatures (>900°C) and at low current densities material problem with significant decomposition arose. In order to improve thermal stability copper can be partially replaced by other transition metals cations. In the case of Co, additional Sr for Ba substitution has improved the stability.

Our initial goal was to investigate the solid state solution of the $\text{YSr}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7+y}$ system, to find the relationship between the conductivity behaviour and the structural changes and to improve the conductivity properties by introducing electronic carriers. The next stage after finding the best conductive material was to investigate the material for SOFC cathode usage, including compatibility tests with most commonly used electrolytes (SDC, GDC, LSGM) and the A.C. impedance measurement of a symmetrical cell. Varying Co doping levels a set of phase pure materials have been prepared. Their physical properties have been measured and compared to previous work². Significant improvement of conductivity properties has been achieved.

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Keywords: SOFC; cathode; conductivity

Conducting Polymer/Carbon Composites for PEMFC Electrocatalysts

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Membrane electrode assemblies (MEAs) are the heart of the proton exchange membrane fuel cells (PEMFCs) in which proton conduction and half cell reactions occur. The anode and cathode electrodes are mostly comprised of carbon supported platinum (Pt) electrocatalysts. The carbon surface oxide groups are formed during the long term operations of fuel cells and further oxidation of these groups resulted in carbon dioxide formation named as carbon corrosion which causes performance losses in the fuel cell. Oxidation of carbon can be resulted in a decrease in the active surface area and change in the pore morphology and pore surface characteristics. Surface oxide group formation over the carbon support is attributed to the hydroquinone-quinone (HQ-Q) redox couple.

The oxidation of carbon can be decreased by using the conducting polymers which are resistant to oxidation and having superior properties that include high electrical conductivity, high specific capacitance and good chemical and thermal stability, especially facile synthesis and being environmentally friendly.

In this study, polypyrrole/carbon and PEDOT/carbon composites were synthesized via chemical oxidative polymerization either at 25°C or 0°C which were doped with different dopants in order to increase the electrical conductivity of the composites. A commercially available carbon support, Vulcan XC72, was used. The composites were characterized with XRD and TGA. The electrical conductivities of the composites were measured by using four point probe technique. The carbon corrosion characteristics were evaluated by using cyclic voltammetry (CV) technique. CV curves showed that conducting polymer/carbon composites are promising materials and showed a better carbon corrosion resistance when compared to carbon black.

Keywords conducting polymer/carbon composites; electrocatalyst; pemfc

Development of informative methodology for half cell and fuel cell tests through incorporation of reference electrodes

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Nowadays, the methodology for characterisation of solid oxide fuel cells is mainly limited to describing the electrochemical performance of the fuel cells after anode reduction only. Moreover, it is difficult to differentiate the contributions of fuel cell components, in particular, during long-term operation of fuel cells or at a stage when new materials are being incorporated and tested.

The methodology presented in this work was based on incorporation of a reference electrode in the fuel cells and half cells with thin electrolyte and was proved by the example of fuel cells of rolled tubular design and planar half cells with different types of cell components.

This methodology, besides the measurement of the main fuel cell characteristics (OCV and IV-curves), enables:

- to differentiate cathode and anode losses during heating of the fuel cell to operating temperature in air;
- to monitor different types of losses (ohmic, diffusion, chemical and electrochemical polarisation) for the cathode and anode sides separately as well as heat distribution during the anode reduction;
- to consider correlations between different types of losses and overheat of the fuel cell due to a strong exothermic reaction taking place at the anode;
- to discover reasons for poor initial electrochemical performance and identify degradation rates of different fuel cell components and contributions of different processes in the total degradation during further electrochemical performance of fuel cell under current load;
- to vary two types of fuel cell components at the same time (one for cathode and one for anode sides).

Results will be presented demonstrating this capability.

Electrochemical recovery of platinum from PEM fuel cell electrodes

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Since platinum is used as the electrocatalyst in the MEA, recovery of this expensive noble metal from discarded fuel cell MEAs is of great interest. Ideally, the platinum should be recovered on a form which requires minimal processing prior to redeposition as electrocatalyst nanoparticles on fresh support material, keeping in mind that the majority of methods for preparing nanoparticles of platinum on various carbon supports involve hexachloroplatinic acid (H₂PtCl₆) or potassium tetrachloroplatinate (K₂PtCl₄) salts dissolved in water or various alcohols as the source of platinum [1].

The conventional way of recovering platinum from fuel cell electrodes is to dissolve platinum in *aqua regia* after combustion of the carbon support. However, this process involves emission of NO_x gas in order to get rid of the nitric acid derived components of the solution, and so a more environmentally friendly process is desired.

Several studies have shown that a) dissolution of platinum is one of the degradation pathways during the lifetime of a PEM fuel cell MEA, b) that it can be accelerated by subjecting the electrode material to potential cycling and c) the dissolution rate is strongly dependent on the presence of chloride ions, potential range, sweep rate, etc. [2,3,4]

This poster presents the exploration of the idea of putting the degradative process of platinum dissolution to good use by its deliberate application as a means to recover platinum electrochemically. By potential cycling of PEM fuel cell electrode material in hydrochloric acid electrolyte, platinum could be recovered as chloro complexes without the need for NO_x degassing. The chloro complexes could easily be converted to the appropriate platinum salts and redeposited as electrocatalyst nanoparticles.

Keywords platinum dissolution; platinum recovery; potential cycling; electrocatalyst; fuel cell electrode

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Electrospun PANi/PAN composite fibres for microbial fuel cell electrode

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The current socio-economic context requires the identification and deployment of new energy resources. Among various solutions, microbial fuel cells (MFCs) are devices which can use bacterial metabolism to produce an electrical current from wide range organic substrates.

The purpose of this paper is to present the preparation by electrospinning of the fibers composite polyaniline/polyacrylonitrile. Electrospinning has gained much attention in recent years due to its versatility and potential being a simple technique to produce fibers from a wide variety of polymers for fuel cell applications, tissue engineering, biosensors, drug delivery, and enzyme immobilization.

In the case of MFCs one of the limiting factors for high-power is the anode performance. The characteristics of anode play an important role in bacteria attachment, substrate oxidation and electron transfer.

The chemical composition and morphology of the new electrodes we have obtained by electrospinning were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM). FT-IR has confirmed the presence of structural units of polymers. SEM images show the nonofibers having diameters in the 200-400 nm ranges. The conductivity and the electrochemical behavior of the polyaniline (PANi)/polyacrylonitrile (PAN) composite fibers were evaluated in 0.5M H₂SO₄ aqueous solutions and buffer solution. The microbial tests show a friendly environment for bacteria cultures and a very good attachment of these.

The new electrode material we have obtained provides a large surface-area, a protective function for bacteria and directly contributes to electrocatalysis to give a high current density.

Experimental evaluation of the operating parameters impact on the performance of anode-supported solid oxide fuel cell

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The issue of renewable energy is becoming significant due to increasing power demand, instability of the rising oil prices and environmental problems. Among the various renewable energy sources, solid oxide fuel cell is gaining more popularity due to their higher efficiency, cleanliness and fuel flexibility. The performance of solid oxide fuel cells (SOFCs) is affected by various polarization losses, namely, ohmic polarization, activation polarization and concentration polarization. Under given operating conditions, these polarization losses are largely dependent on cell materials, electrode microstructures, and cell geometric parameters. Solid oxide fuel cells (SOFC) with yttria-stabilized zirconia (YSZ) electrolyte, Ni-YSZ anode support, Ni-YSZ anode interlayer, strontium doped lanthanum manganate (LSM)-YSZ cathode interlayer, and LSM current collector, were fabricated. The effect of various parameters on cell performance was evaluated. The parameters investigated were: (1) YSZ electrolyte thickness, (2) fuel composition, (3) anode support thickness, and (4) anode support porosity, (5) time and temperature impact. The effect of these cell parameters on ohmic polarization and on cell performance was experimentally measured. Cell parameter study, a cell with optimized parameters was fabricated and tested. The corresponding maximum power density at 800 °C was ~0.5 Wcm⁻².

Keywords Solid Oxide Fuel Cell, Performance, Polarization, Impedance, Fabrication

Hybrid polymer electrolytes Nafion-TiO₂ for PEMFCs: synthesis and characterization

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Nafion based hybrid membranes containing titanium dioxide (TiO₂) nano particle was synthesized and characterized. Nafion-TiO₂ membranes were produced by using in-situ sol-gel technique on Nafion membrane at room temperature. Commercial Nafion membrane was impregnated in Titan tetraisopropoxide (TIP) and then treated in micro-wave. The X-ray diffraction (XRD) shows the crystallization of TiO₂ in anatase phase. The Infrared spectroscopy IR spectrum of hybrid membranes Nafion-titanium dioxide confirm the presence of bonds Ti-O-Ti and Ti-OH which proves that the hybridization of the membrane by sol-gel method is successful. Atomic Force Microscopy AFM confirmed the good dispersion of TiO₂ nano-particles (figure 1). The interaction between the organic and inorganic phase is favorable for the improvement of the thermal stability of the hybrid membrane. The nano-TiO₂ film can be used to reduce the cross-over permeation of fuel through the PEM and increase electric power of the Fuel cells.

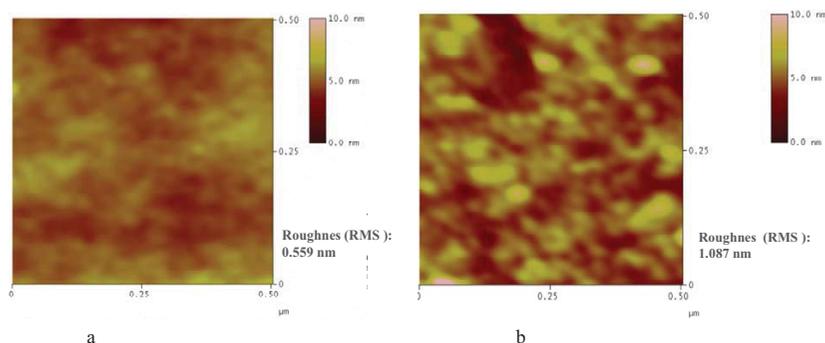


Figure 1: AFM image of nafion 212 membrane (a) and hybrid membrane of nafion with TiO₂ (b)

Investigation of Mn-polypyrrole-carbon nanotube composite as oxygen reduction catalyst and its application in microbial fuel cells

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A novel Mn-polypyrrole-carbon nanotube (MPC) composite was synthesized and tested as an alternative cathode catalyst for oxygen reduction reaction (ORR) in air-cathode microbial fuel cells (MFCs). Prepared by solution-based method, the MPC composite was comprehensively characterized by infrared spectroscopy, scanning electron microscope, elemental analysis, conductivity measurement, and its electro-catalytic activity in neutral electrolyte was investigated by cyclic voltammetry (CV), showing that MPC composite could catalyze ORR in neutral medium with quite good catalytic activity, possibly because of the coordination of Mn-N acting as an active site. MPC was further tested as the cathode catalyst in air-cathode cubic MFCs, in which mixed culture was inoculated by activated sludge and artificial wastewater (1 g/L sodium acetate) was used as the substrate in the anode chamber. It was found that MPC (1 mg/cm²) yielded good performance with power density of 181 mW·m⁻² (nearly 50% that of MFC with Pt catalyst which is the benchmark). Further experiment will be conducted on MFC with higher loadings of MPC, e. g. 3 mg/cm². It is reasonable to expect an even better performance as indicated by the CV test. This is the first study regarding the Mn-heterocycle polymer composite as ORR catalyst other than numerous studies on Fe, Co-porphyrin/ heterocycles, and it has successfully demonstrated that using MPC composite instead of Pt could potentially improve the feasibility of scaling up MFC designs for practical applications by lowering capital cost.

Keywords Mn-polypyrrole-carbon nanotube composite; oxygen reduction catalyst; microbial fuel cells

Investigation of Pt-CeO₂ Catalyst for Polymer Membrane Fuel Cell

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The using cerium oxide doped by platinum as a new catalyst material for fuel cell with the proton exchange membrane has been already publicized. The material based on very thin layer of cerium dioxide doped by noble metals prepared by rf-magnetron sputtering was presented. The loading of platinum is very low - lower than a few micrograms per square centimeter. The photoelectron studies showed that all platinum atoms are in state Pt²⁺ or Pt⁴⁺. This phenomenon is inherent to these rf-magnetron sputtered layers. The catalyst films were deposited on a microporous gas diffusion layer (GDL) or carbon nanotubes (CNT) directly grown on the GDL. For fast and easy performance testing of catalyst was designed a small fuel cell device. As a catalyst on anode was used very thin layer of sputtered cerium dioxide doped by platinum. The thickness was 30 nanometers which corresponds to 1 microgram of platinum per square centimeter. For reference measurement was used generally accepted Pt-Ru powder catalyst (in this case: Alfa Aesar, Pt50,Ru50 at.%) mixed with the Nafion solution and spreaded over the GDL surface with loading of 5 mg · cm⁻² of platinum and ruthenium together. And as a catalyst on cathode was used standard reference Pt-C powder (Alfa Aesar, Platinum, nominally 40% on carbon black) spreaded over the GDL by same way with loading 1.3 mg · cm⁻² of platinum. The relative high activity of the magnetron sputtered Pt-CeO₂ film was observed. The FC test showed high specific power of 70 W · mg⁻¹ of Pt approximately which is more than 1500 fold higher than 0.04 W · mg⁻¹ of Pt+Ru which was reached in the same device and under same conditions with reference catalyst. The resistance of platinum doped cerium dioxide catalyst to poisoning with carbon monoxide was tested with using hydrogen fuel containing carbon monoxide (from 50 to 500 ppm). The morphology of catalyst layer was investigated by scanning electron microscopy.

Keywords PEM FC; Pt-CeO₂

Mesoporous materials for direct methanol PEM micro fuel cells

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The increasing demand for reliable and durable power sources in modern, power hungry, portable electronics prompts the development of integrated systems for micro fuel cells feed with hydrogen or methanol [1]. The use of new types of nanostructured carbon materials as catalyst support or gas diffusion layer (GDL), and mesoporous electrodeposited or nanoparticulated catalysts could contribute to achieve the expected performance.

In our group a number of new materials have been prepared, characterized and tested in prototype fuel cells in order to assess its possible use in direct methanol fuel cells, which potentially could have higher energy density than current lithium-ion batteries [2]. Thus, hierarchical porous carbon containing nanopores and micrometric sized capillaries has been produced by a combination of hard and soft templates [3], and mesoporous platinum were electrodeposited on the monolithic carbon, using a surfactant template, to produce an integrated electrocatalyst with optimal platinum utilization [4].

In this work we report the comprehensive characterization of a mesoporous carbon (MC) used as catalyst support, grinded or as a monolithic, including morphology, pore distribution, electrical resistivity, contact resistance, wettability, imbibition and methanol permeability. The results are compared with those of commercial carbons and its use as catalyst support or GDL is discussed.

A number of bimetallic electrocatalysts, such as nanoparticulated PtRu and PdNi, were prepared on the grinded mesoporous carbon by reduction of the corresponding precursors with NaBH₄. Pt and PdNi catalysts were characterized for the oxygen reduction reaction (ORR) in the presence of methanol by resorting to conventional electrochemical techniques and differential electrochemical mass spectroscopy (DEMS). The obtained catalysts show high conversion to CO₂ and high CO tolerance.

On the other hand, PtRu catalysts supported on MC and Vulcan were studied for the methanol oxidation reaction (MOR) using electrochemical impedance spectroscopy (EIS) and DEMS. The electrochemical active surface area is higher for the catalyst supported on MC as well the conversion of methanol to CO₂. This result, along with the analysis of the impedance behaviour indicates a more facile diffusion of methanol through the MC.

Membrane-electrode assemblies (MEAs) prepared using mesoporous PtRu supported on MC and Nafion as proton exchange membrane, were tested in micro fuel cells feed with aqueous methanol in the anode and oxygen in the cathode. Power as high as 40 mW.cm⁻² at 30 °C and 60 mW.cm⁻² at 60 °C were obtained, while at high current densities (> 300 mA.cm⁻²) the power is much higher than that observed for fuel cells assembled with MEAs prepared using the mesoporous catalyst supported on commercial Vulcan. This is the practical verification that the accessibility of methanol to the catalyst is enhanced by the use of MC as support.

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Keywords: fuel cells; mesoporous carbon; mesoporous catalysts; methanol.

Metallic-ceramic composite on Crofer22APU channelled interconnect for cathode contact layer application in solid oxide fuel cells

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Cathode contact materials are used in Solid Oxide Fuel Cells (SOFC) stack assembly for better electrical contact between the interconnect and the cathode [1,2]. The goal of this work is to study the feasibility of ceramic-metallic composite as cathode/interconnect contact material on Crofer22APU channelled interconnect substrate. $(La_{0.8}Sr_{0.2})_{0.95}Fe_{0.6}Mn_{0.3}Co_{0.1}O_3$ (LSFMC) combined with FeCr(Ni,Ti) as austenitic stainless steel mesh were chosen as contact materials to form the composite. Small square-shaped substrate pieces with a dimension of 10 x 10 x 1 mm were cut from 1 mm thick steel plates. Channels with 1 mm width, 0.5 mm depth, 10 mm length and distance of 2 mm between two neighboring channels were then machined.

$(La_{0.8}Sr_{0.2})_{0.95}Fe_{0.6}Mn_{0.3}Co_{0.1}O_3$ ceramic oxide has been studied concerning the structural transitions by temperature and electrical properties. LSFMC-FeCr(Ni,Ti) mixture was heated in air at 950 °C and at 1050 °C for 2 h to determine the extent of reaction between the stainless steel mesh and ceramic oxides (Figure 1). Contact composite was oxidized at 800 °C in air for 1000 h to establish stability (Figure 1) and adhesiveness between both materials. These analyses have been made by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with an energy dispersive X-ray analyzer (EDX). Besides, the same study was carried on for Crofer22APU-LSFMC mixture. Ceramic powder is applied as a paste on stainless steel mesh which it is in contact with Crofer22APU to form a continuous layer through the channelled interconnects by aqueous tape casting technique. The interface contact between the Crofer22APU interconnect and FeCr(Ni,Ti) mesh has been investigated using different sintered conditions between both by SEM.

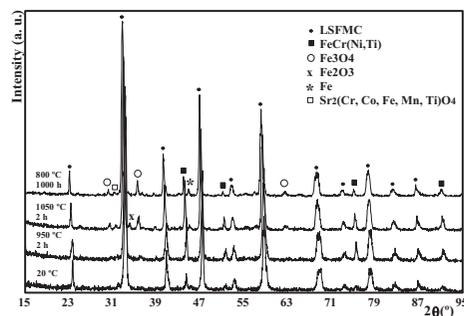


Figure 1. XRD patterns of LSFMC-FeCr(Ni,Ti) mixture at room temperature, after heated at 950 °C and 1050 °C for 2 h and after oxidized at 800 °C for 1000 h.

In the present work it was also studied the possibility the use a dense contact layer in order to increase electric conductivity without sacrificing the permeability for air through contact layer. For this, ultrashort pulse laser machining of composite materials was carried on using different conditions in order to limit the degradation.

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Keywords: SOFC cathode contact layer; Metallic-ceramic composite.

Modelling a CO₂ separation made by Molten Carbonate Fuel Cell

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Based on mathematical modelling, a Molten Carbonate Fuel Cell (MCFC) is shown to separate CO₂ from flue gas (e.g. taken from a Coal Fired Power Plant). The main advantages of this solution are: higher total electric power generated by a hybrid system, reduced CO₂ emissions and higher system efficiency. The model of the MCFC is given and described. The results obtained show that use of an MCFC could reduce CO₂ emissions by at least 56%, which gives a relative CO₂ emission rate of 288 kg_{CO2} per MWh.

Keywords Molten Carbonate Fuel Cell, mathematical modelling, CO₂ emission

Nanofiber-based SPEEK composite membranes for DMFC applications

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Direct Methanol Fuel Cells (DMFCs) are promising electrochemical devices for portable power generation from a few milliwatts up to 1 kW. Nafion[®] (DuPont Co.) is a standard membrane in this application which belongs to the family of perfluorinated sulfonic acid materials. However, they are costly compounds, lack of mechanical stability above 80°C [1] and present high methanol permeability values ($>10^{-6}$ cm²/s) [2].

Sulfonated poly(etheretherketone) materials (SPEEK) are potential candidates to replace Nafion[®] membranes at a low cost while exhibiting good chemical and thermal stabilities [3], what should enable operation at elevated temperatures in which electrochemical reaction rates speed up. Unfortunately, pristine SPEEK membranes typically dissolve in hot water when their sulfonation degrees are high enough to achieve acceptable proton conductivities. Thus, they would not be in principle suitable to be used in DMFC applications.

In this work we have studied the blending of SPEEK with PVA, a hydrophilic polyvinyl alcohol polymer, and with PVB, a hydrophobic polyvinyl butyral polymer, at different compositions with the purpose of stabilizing the membranes for their application in DMFCs operating up to 100°C. The materials have been characterized by means of their water uptake, ion-exchange capacity (IEC), swelling degree, proton conductivity, methanol permeability, Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).

SPEEK-PVB (IEC of SPEEK = 2.05 meq/g) membranes presented robust mechanical properties and very reduced swelling, methanol permeability (10^{-7} - 10^{-8} cm²/s) and water uptake values (Fig. 1), although proton conductivity was considerably low ($\approx 3 \cdot 10^{-4}$ S/cm for SPEEK-30%PVB) (Fig. 2 left). SPEEK-PVA (IEC of SPEEK = 1.75 meq/g) membranes showed rubber-like mechanical properties with much larger values of swelling, water uptake and methanol permeability (10^{-5} - 10^{-6} cm²/s) (Fig. 1) in comparison with the SPEEK-PVB membranes, but on the other hand, higher proton conductivities were achieved ($\approx 1.6 \cdot 10^{-2}$ S/cm for SPEEK-35%PVA) (Fig. 2 left). In both SPEEK-PVA and -PVB polymer blends, it was observed that water uptake, methanol permeability and proton conductivity were reduced with increasing polymer content (Fig. 1).

Compositions of SPEEK-30%PVB and SPEEK-35%PVA were found to be optimal in order to accomplish the preparation of novel nanofiber-reinforced membranes following the previous experience acquired by the authors [4]. The nanofiber framework of SPEEK-30%PVB (Fig. 2 right) is used to provide mechanical and methanol barrier properties while the matrix phase of SPEEK-35%PVA emphasizes the proton conductivity. However, interestingly, the proton conductivity of such nanofiber mat soaked in Milli-Q water reached a value near 0.1 S/cm, much larger than in the bulk membrane, and measurement of an analogous porous support (Whatman filter paper Grade 40) just achieved a value of $\approx 2 \cdot 10^{-4}$ S/cm (Fig. 2 left). The characterization of these nanofiber-based composite membranes will also be reported for their DMFC application.

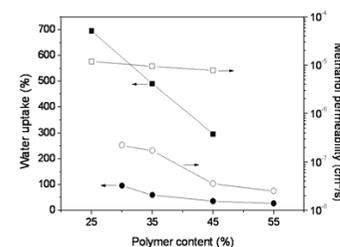


Fig. 1. Values of water uptake (closed symbols) and methanol permeability (open symbols) of SPEEK-PVA (square) and SPEEK-PVB (circle) membranes at different PVA and PVB contents.

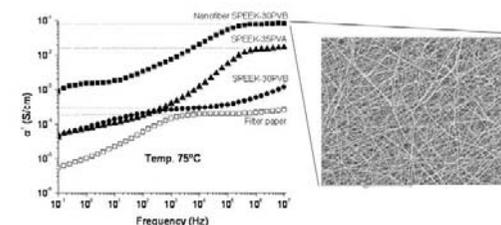


Fig. 2. Proton conductivities (left) at 75°C under fully hydrated conditions of SPEEK-30%PVB and SPEEK-35%PVA membranes as well as a nanofiber mat of SPEEK-30%PVB compared with a Whatman filter paper. SEM images (right) of the SPEEK-30%PVB nanofibers after annealing at 200°C for 1 h.

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Keywords: SPEEK; nanofiber; PVA; PVB; composite membrane; DMFC

Nanoimprinting and nanotransfer for electrochemical systems

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Nanofabrication is a core task performed and constantly further developed by today's and future semiconductor industry. The most challenging issues to overcome within this technology are minimizing process cost, increasing fabrication reliability and optimizing throughput. Printing techniques play a crucial role in efficient nanofabrication since they pave the way to large area patterning while keeping overall process time shorter and costs lower than any other traditional nanolithography technique.

We concentrated on nanoimprint lithography (NIL) and nanotransfer printing (nTP) as scalable, purely mechanical, lithographic techniques to fabricate semiconductor devices suitable for innovative applications both in photovoltaics and electrochemical energy conversion.

Therefore conventional protocols for nTP and NIL [1] were improved to transfer highly-ordered, repetitive Au and Pt nanostructures on various substrates, such as doped Si, SiO₂ and glass. The device structures showed high quality and fidelity and positive feature sizes down to 50 nm over extensive substrate areas. Furthermore, they were characterized successfully by conductive-AFM and cyclic voltammetry which demonstrated both their electrical and electrochemical functionality.

As an example, nTP and NIL were applied on Si substrates with Au to fabricate lines on which Pt catalyst particles were deposited electrochemically in order to investigate the hydrogen evolution/oxidation reaction (HER/HOR) [2]. In doing so we were able to control the particles' size and distance on the nanometer scale independent from each other. This offers the advantage to study the interdependence of geometry and electrocatalytic activity of such nanostructured electrode surfaces systematically.

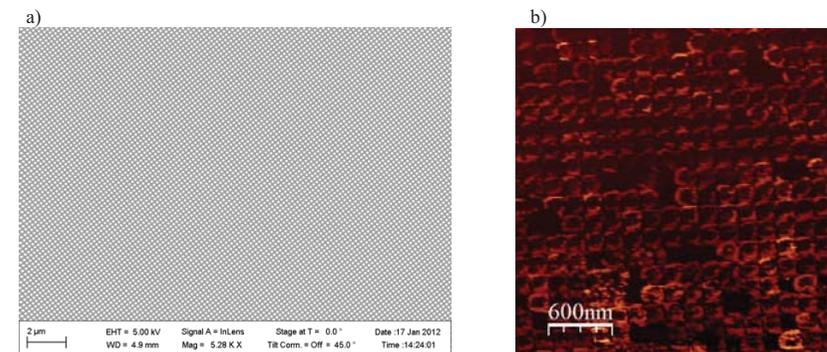


Figure 1. a) SEM image of nano-transfer-printed Au pillars (75 nm diameter, 100 nm spacing) on highly-p-doped Si substrate; b) electrical investigation of Si transferred-Au-contacts (pillars: 120 nm diameter; 80 nm spacing) by conductive AFM (contact mode)

Keywords nano imprint lithography; nano transfer printing; ordered nanostructures; electrocatalytic activity;

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Oxyanion doping in cathode materials for SOFCs: a new strategy to improve their performance

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Perovskite materials are widely used as cathode materials for use in Solid Oxide Fuel Cells (SOFCs) due to their generally high electronic conductivities and catalytic activity [1, 2]. Recently we have proposed an alternative doping strategy, instead of traditional substitution of aliovalent cations, for perovskite systems with potential applications in SOFCs. Traditionally doping studies on such materials has focused on simple cation doping strategies with similar size, e.g. Sr doping for La in LaMnO₃. Recently we have been investigating an alternative doping strategy for solid oxide fuel cell materials, namely the incorporation of oxyanions such as sulphate, silicate, borate and phosphate.

Our initial work demonstrated the successful incorporation of silicon into SrMO₃ (M=Co, Mn), leading to a structural change from a hexagonal to a cubic perovskite, and a large enhancement in conductivity [3]. In this work we have extended these studies to other cathode materials such as CaMnO₃ and Ca_{1-x}Sr_xMnO₃ (compositions not studied for cathode applications), La_{1-x}Sr_xMnO₃, La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ and Ba_{1-y}Sr_yCo_{0.8}Fe_{0.2}O₃. These systems can accommodate low levels of BO₄⁵⁻, PO₄³⁻ or SiO₄⁴⁻, enhancing the electronic conductivity. Also, we can report for these systems an improvement in ASR values for the doped-compositions in comparison with the undoped compounds. For instance, for B and P-doping on CaMnO₃, the ASR values, at 800°C, were 1.50, 0.37 and 0.30 Ω·cm² for CaMnO₃, CaMn_{0.95}B_{0.05}O_{3-δ} and CaMn_{0.95}P_{0.05}O_{3-δ}, respectively.

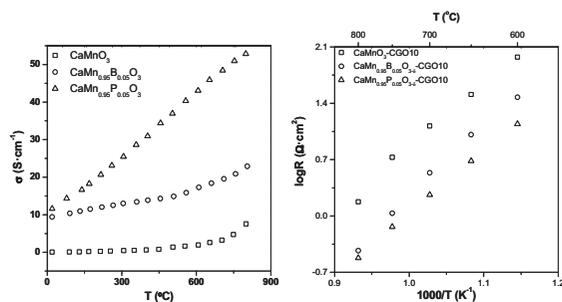


Figure 1. (Left) Conductivity plot and (right) ASR plot for CaMn_{1-x}M_xO_{3-δ} (M=B and P; x=0 and 0.05).

In addition, with these oxyanion doping strategies, we report the stabilization of higher symmetry forms and unstable compositions. For instance, with Si-doping in CaMnO₃ and Ca_{1-x}Sr_xMnO₃ we stabilize their cubic forms at room temperature (originally orthorhombic for undoped CaMnO₃ and hexagonal for high strontium contents in Ca_{1-x}Sr_xMnO₃) with an enhancement in conductivity. Also, with P-doping on Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-δ} (among the most promising oxygen permeable membrane materials [4] with a caveat that there are concerns regarding its stability at intermediate temperatures due to a gradual transformation to a hexagonal perovskite [5]), the samples showed no evidence of any transformation to a hexagonal perovskite, maintaining the electrical properties.

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Keywords SOFC; cathode; oxyanion doping

PEM electrochemical systems development at NRC “Kurchatov Institute”

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Development of PEM electrochemical systems was carried out at NRC «Kurchatov Institute» for more than 30 years. PEM systems development includes modeling, fundamental and applied RSD and also development of pilot plants.

A lot of attention is paid to electrocatalysts development. Chemical (precursor reduction in a liquid phase) and thermal (precursor thermal decomposition or reduction in gas phase) are widely used for metals, alloys and mixed oxide catalyst synthesis. At present time, new plasmachemical technologies are under development for electrocatalyst on carbon carrier synthesis.

Nanostructural Pt-based electrocatalysts (2-10 nm) on nanostructured carbon carriers were developed for fuel cells and electrolyzer cathodes using this technology. Average particle size could be easier varied due to ion current density and time of sputtering. Additional high-energy gas ion treatment (ion implantation) gives possibility to increase the specific activity (up to 10%) and lifetime (up to 20-30%) of the catalysts by modification of catalyst particles (radiation defects production) and of carbon carrier surface (purification). Pt catalyst with average particle size about 4-6 nm (specific surface up to 60 m²/g) demonstrated same activity at lower Pt loadings as chemically synthesized catalysts. Application of carbon nanotubes and nanofibers as catalyst carriers permitted to increase the catalyst activity but stability of such carbon carriers is not always sufficient and special surface treatment, for example, preliminary plasma sputtering of SnO₂ nanofilms on carbon, have to be recommended. When such catalysts with improved carbon carrier stability were used the increase of catalyst layer lifetime (up to 20%) was observed partially also due to well developed dimensional structure of catalyst particles on carriers in a catalyst layer. Specific activity of some alloy catalysts when Pt:Ni or Pt:Pd ratio was equal or higher than 1 was comparable with activity of pure Pt. From commercial point of view the technology is very attractive as gives possibility to provide one stage catalyst synthesis (no further catalyst purification like in case of synthesis in a liquid phase), no temperature limits for different crystal structure and amorphous structure production, no catalyst particle sintering. Magnetron-ion sputtering was also used for bipolar plates and electrolyzer current collectors protection from oxidation and hydrogen saturation (for titanium components).

Catalytic hydrogen burners (recombiners) were developed for solution of hydrogen safety problems and hydrogen purification in high pressure electrolyzers.

Using these technologies high efficient PEM electrolyzers operating at pressure 130 bar (without additional gas compression) and providing hydrogen purity 99,99% (energy consumption 4,0 – 4,2 kWh/m³, productivity 10 m³/h of hydrogen) were developed. At present time PEM electrolyzers for 300 bar are under development. Such high pressure electrolyzers give possibility to decrease energy consumption due to exclusion of hydrogen compression procedure and permit to simplify hydrogen storage problem as standard hydrogen tanks could be used. But gas diffusion through the membrane decreases current efficiency and gas purity. That is why membrane modification by inorganic compounds and application of hydrogen catalytic burners is necessary. For PEM fuel cells some increase of PEM membrane-electrode assembly's efficiency and increase of life time was reached. Reversible or unitized regenerative fuel cell stacks with power up to 1 kW were developed and successfully tested. All these electrochemical systems look very attractive for renewable energy and autonomous energy supply (including back up power).

At present time a new project on renewable energy system with 10 kW energy output based on hydrogen energy technologies is carried out.

Keywords: renewable energy, hydrogen, PEM electrolyzer, PEM fuel cell, unitized regenerative fuel cell, electrocatalysts, plasma technologies

Performance improvement of PEM fuel cells using new type of bipolar plates

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PEMFC performance depends on many factors, including the operating conditions, transport phenomena, kinetics of electrochemical reactions, membrane electrode assembly (MEA) and flow channel geometry [1]. In addition to distributing the reactant gases across the entire active MEA surface area, the mission of gas flow field channels is to evacuate optimally the reaction products, specially water from the cathode [2]. Therefore, its design can reach a significant impact on the performance obtained from a PEMFC. In this work, using a three-dimensional computational model (STAR-CD 3.26, es-pemf 2.2) [3], numerical simulations are performed to investigate the performance characteristics of a PEMFC, incorporating either a conventional serpentine gas flow channel, SSF (Mod#2), or a novel gas flow channel design with homogeneous distribution flow field, HDFF (Mod#1), Figure 1.

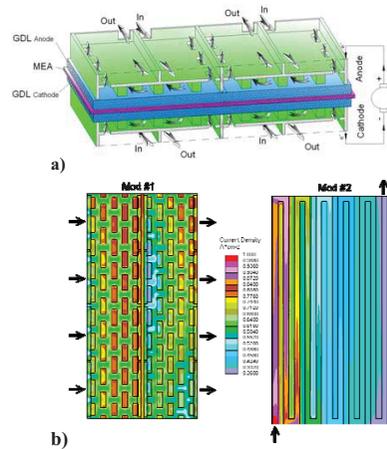


Figure 1. a) Original gas flow channel design with homogeneous distribution flow field, HDFF (Mod#1); b) Comparison of current density distributions of Mod#1 and Mod#2.

The numerical results reveal that Mod #1 yields a more uniform values of membrane water content (λ), net water flux per proton flux (α), temperature and current density distribution. Consequently, compared to a conventional gas flow field channel, the HDFF channels would be useful to promote the cell performance of PEMFC.

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Keywords: PEM fuel cell, bipolar plates, numerical simulation.

Performance of modified SPEEK membrane by inorganic nanocomposite for Fuel Cell

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Among the best way to enhance fuel cell performances, is the improvement of the polymer electrolyte membrane. Over the last 10 years, there has been increasing interest in the polymers sulfonated polyetheretherketone (SPEEK). SPEEK is considered as a possible alternative to Nafion for proton exchange membrane fuel cell application, for his low cost, low fuel permeability, good proton conductivity and high thermal and chemical stability. Recently the organic-inorganic hybrid membranes have been prepared by addition of various inorganic compounds such as SiO₂, TiO₂ and clay. Nanocomposite of clay can be used to ameliorate the proprieties of the SPEEK membrane^{1,2}

Smectite is a 2/1 phyllosilicate composed of negatively charged layers. It has a high cation exchange, high surface area and high barrier properties. In order to understand the effect of this clay on the structure and the ionic conductivity of the SPEEK, a composite cast SPEEK membranes containing smectite powder were prepared and characterized.

SPEEK was prepared using PEEK and concentrated sulfuric acid as sulfonation agent³. The degree of sulfonation was fixed at 70%. SPEEK was modified with various amounts (6, 5 or 4 wt%) of smectite. The synthesis was prepared in DMSO solution, stirred for 24h and heated at 80°C. The modified membrane was characterized by electrochemical impedance spectroscopy (EIS), field emission scanning electron microscopy (SEM) and thermogravimetric analysis (TG). The SPEEK-smectite membrane characterized concerning their water, ethanol and methanol solution uptake has amelioration of swelling behaviour and proton conductivity. The presence of clay in the membrane of SPEEK improves the absorbance of water which becomes two times as higher compared to the membrane without smectite (figure1). The modification of polymer SPEEK permitted the amelioration of the performance of membrane used as promising alternative to proton exchange membrane (PEM) for Fuel Cell (FC) compared to SPEEK membrane.

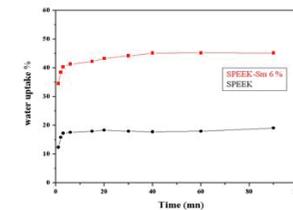


Figure 1: Water uptake of SPEEK and SPEEK-smectite membrane as function of time.

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Preparation of submicron Yttria Stabilized Zirconia films via e-beam deposition: Structural and optical properties

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Considerable effort has been devoted during the recent years in developing thinner solid electrolyte films for Solid Oxide fuel cells operating at lower temperatures. To this end we used the electron beam gun (e-beam) evaporation technique has been used to deposit YSZ (Yttria Stabilized Zirconia: ZrO₂ stabilized by 8 wt.% Y₂O₃) thin films on silicon substrates. Films ranging from 0.2 to 2.0 μm in thickness have been prepared. Operating technical parameters that influence the film properties were studied. The influence of the deposition rate has been investigated. The film thickness has been measured in situ via a quartz crystal monitor and ex situ using a stylus profilometer. Samples have been thermally treated and the morphology of the prepared films have been studied by scanning electron microscopy and atomic force microscopy. Finally, their structural and optical properties have been studied.

The results of these measurements show that the e-beam method produces films under controllable conditions that have the desired thickness and structural stability. The dependence of electron gun power and mode of operation – and subsequently the rate of deposition – played an important role on film morphology. The crystal sizes range between 40-70 nm, the prevailing crystallographic orientation is (1 1 1) and the transmittance of the films was measured to vary between 70% and 90%.

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Keywords: Fuel cells; Yttria Stabilized Zirconia; e-beam;

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Proton conductive nanofiber membrane for fuel cells

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Recently, nano-scale fibers prepared through an electrically charged jet of a polymer solution/melt (electrospinning) have received a lot of attention. Electrospinning is capable of producing fibers with diameters in a nanometer range, and the electrospun nanofibers possess many unique properties including a large specific surface area, superior mechanical properties, and use as nanoscale building blocks. However, there are only a few reports in the literature on proton conductivity of the electrospun nanofibrous mats, in addition, the fibrous structure was the isotropic non-woven mat. Here, we describe the composite membranes composed of uniaxially aligned nanofibers for the proton exchange membrane fuel cell, which reveal dramatically enhanced proton conductivity, lower gas permeability, and longer durability.

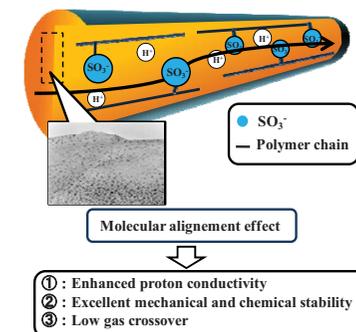


Figure 1 Proton conductive nanofiber.

We have synthesized the novel composite membranes composed of sulfonated polyimide nanofibers and sulfonated polyimide for proton exchange membrane fuel cell. It was clear that the polyimides within nanofiber were significantly oriented or aggregated when electrospun, as the result, the membrane stability, such as oxidative and hydrolytic stabilities, of the composite membrane was significantly improved with an increase in nanofiber, and oxygen permeability of the composite membrane also decreased when compared to that determined in the membrane without nanofibers. In addition, the proton conductivity in the parallel direction in the composite membrane significantly increased depending on the amount of nanofiber, compared with the dense membrane without containing nanofibers. On the other hand, although proton conductivity in the perpendicular direction of the composite membrane increased compared with the dense membrane without containing nanofiber, the rate of the increase was significantly smaller than that determined in the parallel direction, demonstrating that proton conductivity of the composite membrane strongly depends on the direction of aligned nanofiber.

Table 1 Proton conductivity of composite membrane containing aligned nanofibers.

Membrane	Weight ratio(%)	IEC value	Proton conductivity(S/cm) *	
	Membrane : Nanofiber (experiment/theory)		$\sigma_{//}^{(1)}$	$\sigma_{\perp}^{(2)}$
Membrane	100 : 0	1.44/1.50	0.034	0.032
Composite membrane	99 : 1	1.43/1.50	0.049	0.036
Composite membrane	95 : 5	1.47/1.50	0.081	0.061
Composite membrane	90 : 10	1.47/1.50	0.121	0.087

* : 80°C, 98%RH

1) : Proton conductivity in parallel direction to aligned nanofiber measured in transverse direction.

2) : Proton conductivity in perpendicular direction to aligned nanofiber measured in transverse direction.

Keywords : polyimide nanofiber; proton conductivity; composite membrane; electrospinning; fuel cell;

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Proton transport in poly-imidazole membranes: a fresh appraisal of the Grotthuss mechanism

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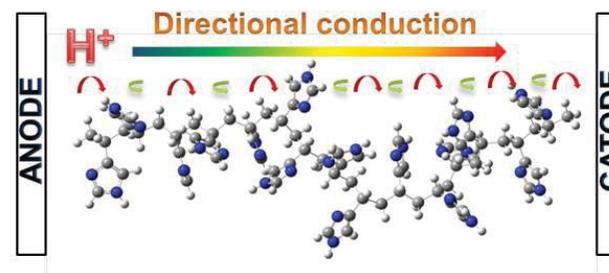
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The performances of Proton Exchange Membrane Fuel Cells (PEMFCs) are strongly influenced by the proton conductivity of the solid electrolyte. The N-heterocycles based polymers are today the most promising materials to improve the effectiveness of these systems. A detailed theoretical investigation of the charge transport mechanism in Poly(4-vinyl-imidazole) (P4VI), a parent prototype proton conductor, is presented. The results obtained applying a previously developed Density Functional Theory (DFT) protocol [1] on small model systems (protonated imidazole dimers and trimers), suggest that the commonly accepted (Grotthuss) conduction mechanism, based on a sequential proton transfer between imidazole moieties, could be impeded in this system because of the backbone constraint. Classical Molecular Dynamic (MD) simulations support an alternative mechanism of conduction hypothesized. This latter involves a rotation of the protonated imidazole, constituting the rate-limiting step, before each proton transfer reaction between adjacent imidazoles can take place (Figure 1). The obtained simulations show how the backbone constraints play a crucial role in the conductivity mechanism, thus indicating that models including the polymeric matrix are necessary to investigate theoretically these systems, in contrast with what has been done till date. Furthermore, these findings could pave the way for the design of new and better performing protogenic groups with minimum reorientation barriers for efficient proton transport. This design could, with a global approach for the organization at the nanoscale, leads to proton transport materials with advanced performances.

Keywords Proton Exchange Membrane Fuel Cells (PEMFCs), Grotthuss mechanism, Imidazole

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Reduction of perovskites with transition metal cations and composites made up of modified cerium oxide and perovskites in hydrogen containing atmosphere: kinetics and thermochemistry

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Complex oxides materials with rare-earth metals and transition metals in high formal oxidation states are important as catalysts, battery materials, electronic ceramics, and fuel cell electrodes. Fuel cell tests carried out with perovskite materials and ceria-based cermets as anode function layers showed promising electrochemical performance under hydrogen and hydrocarbons. However, there was a significant loss in the performance of the fuel cells at 700 °C after heating to high temperatures (800-900 °C), which was associated with changes in the ceria containing catalyst. To address this issue, long-term reduction behaviour of undoped cerium oxide, multi-cation doped cerium oxide, perovskites, and the following composite systems $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3 - \text{CeO}_2$ (LSCCe), $\text{La}_{0.95}\text{Ni}_{0.6}\text{Fe}_{0.4}\text{O}_3 - \text{CeO}_2$ (LNFCE), and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 - \text{CeO}_2$ (LSMCE) was studied under hydrogen containing atmosphere in a wide temperature range (500-900 °C).

It was found that reduction of the perovskites occurs at temperatures higher than 300 °C and can be interpreted as a multi step process. At 800 °C a small weight gain is followed by dramatic weight loss. The latest is related to the reduction of transition metal cations to lower oxidation states. Perovskites, depending upon composition, rapidly lose up to 6-12 mol% of the lattice oxygen which is accompanied by phase or structural transformations in the solid. Further mechanism and kinetics of reduction strongly depends on temperature. The complete reduction of perovskites can occur at 800 °C. Perovskites undergo reduction at 800 °C under H_2 -Ar atmosphere much stronger compared to undoped cerium oxides or doped by transition metal cations. The results obtained in the present study demonstrate that enhanced reduction of cerium oxide in composite materials with highly reducible transition metal cations occur under hydrogen atmosphere at the initial stage of reduction. During long-term exposure to H_2 -Ar atmosphere the involvement of cerium oxide in the reduction process seems to depend on its structural parameters that determine the length of the pathway for oxygen ion transport through the lattice. Kinetics and thermochemistry of the reduction has been discussed for perovskites and composite materials at 800 °C in more details. The role of ionic and electronic conductivity and their mobility through the bulk of materials has been considered.

Single-chamber solid-oxide fuel cells driven by thermal transpiration Knudsen Compressors

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Advances in microelectromechanical systems (MEMS) and micro electronics has fueled interests in miniature electrical power generation for ample military, space, and commercial applications including air or space reconnaissance vehicle, pneumatic power for micro-robots, and high-energy-density electrical power sources for autonomous or handheld electronics. One common requirement for these systems is to be operated either at an elevated pressure or in a vacuum environment, which leads to the need of a gas pumping system. Most of existing micropumps are scaled-down versions of the conventional pumping systems, which often have moving parts that cause inefficiencies due to frictions and consume a significant portion of the power source. Hence, the size and weight of the entire micro system would increase with the inclusion of extra pumping and power requirements.

A small-scale combined pumping and power generation device that can provide the necessary gas pressure and power generation would simplify the entire micro system. Additionally, the use of hydrocarbon fuels for electrical power generation provides numerous advantages over conventional batteries including higher energy storage per unit mass and more power generation per unit volume, even when the conversion efficiency from thermal energy to electrical energy is taken into account. Hence, a device that (a) has means for pumping to supply reactants and expel combustion products, with no moving parts; (b) uses fuel, not electrical power for the pumping, and (c) produces electrical power with no moving parts, would be ideal to be incorporated in the aforementioned micro systems.

Single-chamber solid-oxide fuel cells (SCSOFCs) are fuel cells with cathodes and anodes operating at the same gaseous atmosphere without mechanical separation of gases. The anode catalyst of SCSOFC serves as an electrochemical catalyst for H_2 and CO oxidation, and also generates thermal energy by the exothermic oxidation of the hydrocarbon fuel. Based on the molecular gas dynamics theory of thermal transpiration, the Knudsen Compressor induces a gas flow as well as a pressure gradient across a nanoporous membrane material due to a temperature gradient, which can be achieved by absorbing the thermal energy produced from the SCSOFC. Therefore, combining the Knudsen Compressor and SCSOFC, a self-sustained operation with hydrocarbon and oxidizer flows to generate electrical energy generation is constructed with no moving parts or parasitic losses all in one package.

A self-sustaining combustor with a thermal transpiration gas compressor using glass fiber filters to form a SCSOFC power generation system was reported by Ahn et al. The encouraging results obtained from Ahn's system lead to the present study, which outlines the operating parameters of efficiently incorporating the Knudsen Compressor to the SCSOFC power generation system. Since the thermal transpiration phenomenon is accomplished using nanoporous materials, these materials must have proper pore sizes, which are comparable to the mean free path of gas molecules (λ) at given operating conditions. In addition, these materials should have relatively low thermal conductivities to sustain a required temperature gradient without consuming excess thermal energies. The thermal transpiration behaviors and optimal properties of the nanoporous materials for this purpose were assessed via combined numerical studies and Direct Simulation Monte Carlo modeling here.

Keywords Fuel Cells, Aerogels, Molecular Gas Dynamics, Thermal Creep

Stability and conductivity of $\text{La}_{2-x}\text{Ce}_x\text{Zr}_2\text{O}_7$ pyrochlores

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Solid Oxide Fuel Cells (SOFCs) are highly efficient and environmentally friendly energy conversion devices with a large variety of potential applications. A SOFC consists of three main components, two porous electrodes (cathode/anode) separated by a dense electrolyte. The total cell is best described as a system of interfaces as most of the electrochemical reactions occur in narrow zones (so called triple phase boundaries [TPB]) where the electrode material, solid electrolyte and the gas are in contact. Due to the severe operational conditions regarding temperature (~800 °C) and atmosphere several physical-chemical and mechanical processes may occur in a fuel cell leading to changes in properties and ultimately a reduction in performance. One of these is the chemical interaction that can occur between the different components (electrode-electrolyte, electrode-interconnects, etc.) leading to the formation of new phases that may affect the electrochemical processes occurring at the interfaces.¹

Here we report on our investigation of the family of pyrochlores, general formula $\text{A}_2\text{B}_2\text{O}_7$ (where A is a trivalent ion, usually a rare earth, and B is a tetravalent ion) which are known to exhibit oxygen ion conductivities of the order of 10⁻² S/cm at 1000 °C, making them promising candidates as electrolyte materials. Examples include: $\text{Gd}_2(\text{Zr}_{1-x}\text{Sn}_x)_2\text{O}_7$, Ca-doped $\text{Gd}_2\text{Ti}_2\text{O}_7$ and Ca-doped $\text{Gd}_2(\text{Zr}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$.²⁻⁴

In particular we have focused on the $\text{Ln}_2\text{Zr}_2\text{O}_7$ (Ln= Lanthanide) family of materials, whose structure is mainly governed by the ionic size difference between Ln^{3+} and Zr^{4+} .⁵ For La-Gd they adopt the pyrochlore structure, while for Gd-Lu the fluorite structure. These materials have the properties needed to be a potentially good electrolyte (high melting point, high thermal expansion coefficient, low thermal conductivity, high thermal stability and high electrical conductivity) in SOFCs.⁶ Among the rare earth zirconates, $\text{Ce}_2\text{Zr}_2\text{O}_7$ bears additional interest due to the catalytic application of the CeO_2 - ZrO_2 in several chemical processes in industry and automobiles.⁷

We have studied the stability of the solid solution $\text{La}_{2-x}\text{Ce}_x\text{Zr}_2\text{O}_{7+\delta}$ and the effect of the Ce on the conductivity. Our X-ray diffraction data show that while under reducing conditions the whole solid solution can be obtained, in air up to a maximum of x=0.5 of Ce can be substituted for La. Once prepared, the pyrochlore structure is stable in air up to 1200 °C. We will also present the results of impedance measurements on these materials and discuss the change in conductive behaviour as function of Ce content.

Keywords SOFC; pyrochlore; electrolytes

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Study of methane electro-oxidation in solid oxide electrode assemblies under operando conditions

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Solid oxide fuel cells (SOFCs) are promising candidates for stationary power generation. In Intermediate Temperatures Solid Oxide Fuel Cells (IT-SOFCs), hydrocarbon fuels can be directly used in a temperature range (below 800 °C) where carbon deposition can be avoided. Ceria-based anodes demonstrated the potential for direct use of methane in SOFCs. Ni/CeO₂(Gd₂O₃) (Ni/GDC) are currently used in IT-SOFCs, due to their efficiency in preventing coke build-up with weakly humidified CH₄ fuels. In this study, ambient pressure photoelectron and near edge absorption fine structure spectroscopies (APPES and NEXAFS respectively) are used to detect *in situ* the surface oxidation state and adsorbed/spillover species of Ni/GDC electrodes under different gas atmospheres and applied potentials. Model Solid Oxide Electrode Assemblies (SOEAs), suitable for simultaneous electrochemical evaluation and surface characterization were examined. The SOEAs consisted of thin Ni/GDC anodes (WE) applied on polycrystalline YSZ electrolyte, using Pt as the counter electrodes (CE). The cell operated at 700 °C in 0.1 CH₄ under constant anodic and cathodic potentials, while *on line* mass spectrometry and chronoamperometry were applied simultaneously to the spectroscopic characterization, to detect changes induced in the gas phase and measure the ionic current in the cell. In addition, the anode was exposed to various gas atmospheres (O₂, H₂, H₂O) at 0.1 to 0.2 mbar at open circuit potential (OCP), in order to manipulate the surface oxidation state prior to CH₄ electro-oxidation.

The surface oxidation state of the mixed ionic/electronic conducting Ni/GDC electrodes is determined by the ambient gas. At 0.1 mbar CH₄, reduction of both NiO and CeO₂ to Ni and Ce₂O₃ occurs, and the surface amount of nickel decreases considerably. On the contrary, at 0.2 mbar O₂ complete oxidation of all surface elements was observed with parallel accumulation of NiO on the surface. In 0.2 mbar H₂, CeO₂ and Ce₂O₃ coexist on the surface together with reduced Ni. Finally, in 0.1 mbar H₂O, hydroxylation of cerium is observed while nickel can be either in the metallic or in oxidized state depending on the pre-treatment of the sample.

Changes in the oxidation state are observed when potential is applied. At open-circuit voltage (OC) with no net current in the cell, the NiO/GDC anode is in equilibrium with the gas phase. When constant anodic polarization (+1V) is applied, O₂²⁻ is driven towards the surface, while with negative potential (-1V) O₂²⁻ is pumped from the surface. In CH₄ atmosphere, CO, CO₂ and H₂ are detected in the gas phase with anodic potentials (+1V) obtaining the larger measured currents. Oxygen spillover was clearly observed in the APPES O1s peaks when anodic potentials were applied during methane electrooxidation. The ignition and maximum value of the measured currents was found to depend on the oxidation state of the surface elements and on the surface composition. Combination of APPES and NEXAFS data showed that NiO, CeO₂ and Ce(OH)_x species are deactivation agents of the electrocatalytic activity. A mixture of zero-valence Ni and Ce³⁺ species and a surface rich in O²⁻ were detected as the active phase. Last but not least, a Ni/ Ce surface atomic ratio close to 0.4 was found optimum for current production during CH₄ electrooxidation.

Keywords methane electro-oxidation, gadolinia-doped ceria, solid oxide fuel cells, ambient pressure photoelectron spectroscopy, NEXAFS

Suitability of different carbon supports for proton exchange membrane fuel cells

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A novel electro-deposition technique for preparing the nano catalyst layer in polymer electrolyte membrane fuel cells (PEMFC) has been designed, which may enable an increase in the level of platinum utilization currently achieved in these systems. Three different carbon supports ie. multiwalled carbon nanotubes, carbon nanofibers and graphene were synthesized for electrocatalyst deposition and compared with commercially available carbon supports (Vulcan XC-72). These three carbon supports were characterized by using FTIR to confirm the functional groups of the material. The thermal stability of this material was studied by TGA and DSC. The surface area and pore size were calculated from Brunner Emmett Teller (BET) method. The morphology of the carbon supports were confirmed from scanning electron microscopy (SEM) analysis. The intensity of D and G bands were confirmed by Raman spectroscopy. The Pt on three different carbon supports were prepared by reducing chloroplatinic acid using ethylene glycol as a reducing agent on their corresponding carbon supports (Pt/MWCNT), (Pt/CNF) and (Pt/G). The particle size of platinum nanoparticles and uniform dispersion of platinum on these three different carbon supports were confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) respectively. Four MEA sets were prepared and tested in the fuel cell assembly. Three were prepared using SPEEK membrane as electrolyte with the synthesized Pt/MWCNT, Pt/CNF and Pt/G catalyst. This was compared with the MEA fabricated using the commercially available Nafion 117 and Pt/C catalyst. The performance of the MEA was studied in single cell proton exchange membrane fuel cells of 25 cm² at ambient condition. It is therefore considered that this method can find important applications in reducing the cost and improving performance of proton-exchange membrane fuel cells.

Keywords: carbon supports; PEMFC; graphene; carbon nanofibers; carbon nanotubes

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Sulfonated Poly Ether Ether Ketone / TiO₂ Nano Composites As Polymer Electrolyte For Microbial Fuel Cell

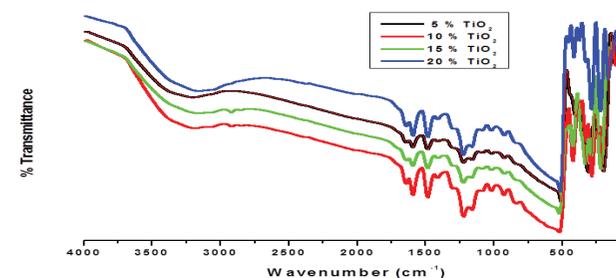
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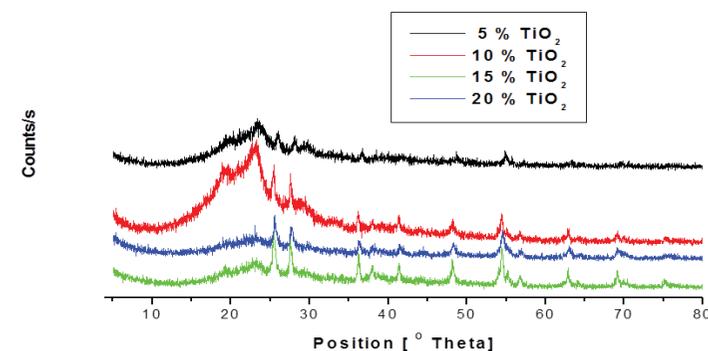
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Polymer Nano composites are promising alternative polymer electrolyte membranes for fuel cells because of its proton transfer, cost reduction, improves thermal and mechanical stability. E. coli an electro genic bacteria was used as a biocatalyst in anodic chamber with Pt/C coated air cathode. Four different compositions of SPEEK/TiO₂ membranes (5%, 10%, 15%, 20%) were fabricated by solvent evaporation method. Water absorption, ion exchange capacity of the fabricated polymer Nano composite membranes were studied and also characterized by FTIR, XRD, SEM. The maximum power obtained was compared with that of Nafion®.

Key Words: SPEEK, TiO₂, Polymer Nano composites, MFC.



FTIR Spectra of SPEEK /TiO₂ (5%, 10%, 15%, 20%)



XRD Patterns of SPEEK /TiO₂ (5%, 10%, 15%, 20%)

The development of fuel processor platform for micro-scale solid oxide fuel cells

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Recently, the development of micro-scale solid oxide fuel cells (μ -SOFCs) has become a promising research topic in the area of portable energy production. A μ -SOFC system, which can provide 1 to 2 W electrical power under an operating temperature of 550°C^{1,2}, mainly consists of a fuel processor, an electrochemical power generator, and a post combustor. The role of the fuel processor is to generate a hydrogen-rich product stream that is fed to the power generation module. In previous works, various micromachined fuel reformers based on microelectromechanical system (MEMS) technology have been demonstrated to achieve high-yield syngas generation from liquid hydrocarbons³⁻⁵. However, MEMS-based micro-reformers require time-consuming and expensive fabrication processes, and face critical issues concerning electrical and fluidic interconnects. Conversely, 'traditional' thick film-technology is a simple and low-cost fabrication route, allows integration of a wide palette of materials by a convenient printing technique, and has a proven track record in harsh environments⁶. Here, we propose to apply thick-film technology to a fuel-processing platform for the development of μ -SOFC systems.

The thick-film based fuel processor consists of a self-sensing heating element, a fluidic carrier comprising a catalyst chamber, and a ceramic substrate. The heating element consists of two independent thick-film platinum conductor meanders, which are screen printed at the bottom of the fluidic carrier, and provide relatively homogeneous heating of the catalytic reforming zone up to 700°C⁷. Due to their temperature dependence of resistance, the thick-film Pt heaters double as temperature sensors and thus allow integrated temperature control of the fuel processing. The fluidic carrier was made of two pieces of (12 mm \times 75 mm \times 0.7 mm) borosilicate glass (Schott AF32), bonded by a screen-printed glass frit seal (Ferro IP760c), which also patterns the fluidic channels in the carrier. Multiple glass paste prints allow for building up the channel height (i.e. distance between glass plates) up to ca. 150 μ m. The catalyst is placed into an open chamber on the top plate of the fluidic carrier by dispensing, and is capped by a piece of AF32 glass (12 mm \times 13.8 mm) using the same glass frit bonding technique. The elongated shape of the fluidic carrier and low thermal conductivity of the glass efficiently decouples the heat generated in the "hot" catalyst area from the other "cold" end of the carrier, allowing conventional low-temperature electrical and fluidic interconnections. With a heating power below 8 W, the platform is able to quickly heat the active zone to 700°C, while maintaining the electrical and fluidic connections below 50°C. The performance of isobutane reforming was evaluated, studying the impact of design parameters such as the catalyst chamber dimension, and geometry of the thick-film Pt resistor. The talk will present and discuss the studied fabrication processes including the glass frit and catalyst paste formulation, screen printing and dispensing processes, and show the performance of the platform with results obtained on thermal characterization and gas reforming. The heat output of exothermic reactions is well observed.

Keywords solid oxide fuel cell, fuel processor, hydrogen production

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The effect of LiAlO₂ ceramic particles addition to molten carbonate fuel cell anodes

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Abstract

Fuel cell is an electrochemical device that converts free chemical energy directly into electrical energy. One type of fuel cell is molten carbonate fuel cell which, like other cell types, including three parts: anode, electrolyte and cathode. In primary MCFC not alloyed porous nickel was used as anode. Disadvantages of this primary type we can point to the weakness against creep and sintering during its process. To eliminate these disadvantages some actions such as alloying nickel with chromium or aluminum which has higher creep strength were done, between these alloyed anodes Ni-Al anodes were better than others in creep but the electrolyte lithium reacts with anode's aluminum and LiAlO₂ will produce, causes corrosion of the cell's electrolyte by reducing cell's life time. In this research to increase cell's life time and creep strength LiAlO₂ was added to the anode and its effects were studied.

Key words Anode, fuel cell, carbonate, melting

A summary of experimental and results

In the first stage of experiment mixtures of nickel and aluminum's powders with purity of 99.99% and compositions of Al₃%-Ni₉₇% mixed and simultaneously mechanically alloyed in a planetary ball mill at argon atmosphere. Changes in the structure of the alloy powder and its particle size were tested and assessed, respectively, by X-ray diffraction device (XRD) and particle size measuring apparatus (PSA). Test results show that mechanical alloying for 4 hours formed the nickel-aluminum solid solution. It was observed that the particle size of 100- μ m alloy after 4 hours has been reduced to 10-1 \times 1 micron. In the second stage of experiment LiAlO₂ ceramic powder was prepared. In the third stage, binder solution was made so that the solution components include the adhesive PVA, corn oil as a dispersant, and the amount of water as a solvent in the solution and plasticizer. The reason for using corn oil instead of conventional instruments dispersants was that after casting, samples were dried in air and then sintered in a controlled atmosphere. The made anodes were compared with anodes with composition with Al₃%-Ni-free anode with ceramic particles. The number and distribution of porosity, morphology and creation phases. Analysis results show that the addition of ceramic particles improves the size and distribution of porosity and also creates phases by these particles which increases the creep strength of the anodes. On the other hand these particles increase wettability properties and at the end it increases the electrolyte's lifetime because of lithium consumption of aluminum in the anode and also anode reinforced with lithium aluminate. After cell function, some changes in the anode can be named as such: to increase the size of the catalyst chamber, reducing the active surface of catalyst, changing in the shape of anode because of pressure in the mass of the fuel cell, the anode reaction with the electrolyte components such as chromium reacts with lithium in the anode and electrolyte. Increase the strength as a result of lithium aluminate so in molten carbonate fuel cell's anode, so the changes can be greatly reduced.

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And...

VUV irradiation: towards an innovative process for PEMFC membranes synthesis

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Radiations are used efficiently and economically for the production of new or modified polymer electrolyte membrane fuel cells (PEMFC) membranes [1-3]. However, high energy radiation processes present some limitations as enhanced safety procedures and the cost of ionising sources and of their facilities. To overcome these drawbacks, we proposed herein an innovative process, based on VUV irradiation, to chemically modify the polyvinylidene fluoride (PVDF) bulk for PEMFC membrane synthesis [4]. The thickness grafting distribution of different vinylic moieties in PVDF film was investigated by EDX and infrared spectroscopy. The thermal stability, water uptake, swelling ratio, ion exchange capacity and proton conductivity were studied on the resulting membranes with different grafting yields. VUV-proton exchange membranes show a good thermal stability and proton conductivities in the range of Nafion 212 membrane. All membranes exhibit desirable proton conductivity which makes them a great potential in PEMFC.

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Keywords proton exchange membranes; VUV irradiation

Hydrogen

A sodium borohydride hydrogen generation reactor for stationary applications. Experimental and reactor simulation studies

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Chemical hydrides, in particular sodium borohydride (NaBH_4), have been mentioned over the past decade as one of the most promising technologies for hydrogen storage. Its high theoretical hydrogen storage capacity (10.8 wt.%) and potentially safe operation attracted the attention of countless research groups. Therefore, much work has been done in order to understand the reaction behaviour and to optimise the system for stationary and portable applications. In this work, a ruthenium on nickel-foam catalyst was prepared for hydrogen production from the hydrolysis reaction of an alkaline NaBH_4 solution.

In a first stage, experiments were carried out at five temperatures (30, 40, 45, 50 and 60 °C) in a small batch reactor. With the aim of understanding the kinetic behaviour of the hydrolysis reaction in the presence of this catalyst, the experimental data were fitted to three kinetic models (zero-order, first-order and Langmuir-Hinshelwood) using the integral method. Results showed that the Langmuir-Hinshelwood model described fairly well the reaction for all temperatures and for the entire time range. Zero-order could be applied only at low temperatures or until the concentration of NaBH_4 remained high in the solution; first-order could be only applied efficiently at 60 °C.

In addition to this kinetic study, a dynamic, three dimensional and non-isothermal computational model was developed to describe a pilot scale reactor for stationary use. The batch reactor with an internal volume of 21 dm³ could hold up to 60 bar of hydrogen. Experimental studies were done at different operational conditions varying catalyst mass, solution volume and NaBH_4 concentration. The experimental data, namely, temperature and pressure inside the reactor, were used to validate the numerical model. This model was developed using a commercial CFD solver and all relevant transport phenomena were treated in detail. The previously developed kinetic model was introduced in the CFD algorithm with the objective of generating reliable predictions and to analyse the impact of the reactor geometry in the reaction rate. Besides, the impact of several other key parameters on performance was studied, such as: position of the catalyst pellets in the reactor, operational temperature and catalyst concentration. It was also analysed different strategies to control the temperature inside the reactor throughout the reaction time. In particular, it was studied the impact of several insulation materials, and the properties of the fluids used to heat up or cool down the reactor. Results showed that the reaction rate was extremely affected by the mass transport resistance from the bulk to the catalyst surface. Optimisation procedures were proposed to reduce this resistance and to enhance performance.

Keywords: kinetics; sodium borohydride; hydrolysis; numerical simulation; modelling.

A solid state photoelectrochemical cell with gaseous water and methanol as reactants

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Photoelectrochemical hydrogen production is aimed at water electrolysis with most or all of the electrical energy needed provided by photogenerated charge carriers. The traditional approach is to use aqueous electrolytes, sometimes in conjunction with an ionic-membrane (salt bridge) between the anode and cathode compartments. The liquid electrolyte can present some difficulties during scale up and commercialisation, which we think will be minimised with an all solid state device. That would most naturally split water vapour, which is thermodynamically more favourable.

We report on the use of a nafion-inorganic oxide composite membrane in a PEM electrolyser-like set up for photoelectrochemical water splitting, with methanol added as a sacrificial agent. A schematic of the set up is presented in figure 1.

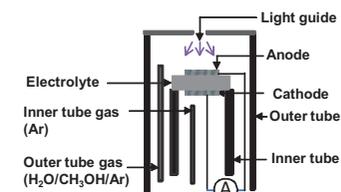


Figure 1: A schematic of the PEC cell

The anode and cathode catalysts are TiO_2 and Pt-carbon respectively, all deposited on carbon paper. Current-voltage and chronoamperometric measurements indicate that current is increased significantly with irradiation, also at zero external bias. A considerable photovoltage is thus set up upon irradiation.

Modification of the carbon paper on the anode side with titanium led to more ohmic response. In addition, it also induced instability on the photocurrent, which was however eliminated with time, probably due to passivation of the titanium layer. Electrochemical impedance spectroscopy provided evidence of significant increase in electrode resistance and capacitance with increasing light irradiance, in spite of the corresponding increase in photocurrent. This is attributed to accumulation of photogenerated product species at some surface or interface, leading to mass transport diffusion impedance.

Keywords: Water splitting, hydrogen, photoelectrocatalysis, solid state electrolyte, nafion, TiO_2

Acceleration of Hydrogen Desorption from MgH₂ by High-Energy Ball-Milling with Al₂O₃, TiO₂, Cr₂O₃, and ZrO₂ for Extremely Short Time

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To improve on the absorption-desorption processes for MgH₂, several approaches have been attempted, with various degrees of success. These include the alloying with intermetallics, the use of processing methods (e.g. grain size refinement) and the use of catalysts.

Grain size refinement of MgH₂ by mechanical grinding (MG) using high-energy ball milling has been shown to be an effective technique. While this process enhanced the hydrogen absorption-desorption kinetics, it required a significantly long time (generally longer than 20h)[1]. In order to improve the hydrogen absorption/desorption kinetics, Mg and MgH₂ doped with transition metals or transition metal oxides were recently prepared by ball milling [2-3].

In our previous work, it was shown that a significant improvement in the hydrogen desorption kinetics of MgH₂ was achieved by the ultra-high energy ball milling with 50 wt% Al₂O₃ [4]. The addition of 50 wt% Al₂O₃ reduced the hydrogen storage capacity of MgH₂ by half, however, the milling time became extremely short (10 min) and provided a material in which molecular hydrogen was released at 250°C within 1hr. The amount of Al₂O₃ played a role in reducing the grain size of MgH₂, and had the potential to prevent grain growth at the operating temperature. As a result, the onset temperature of hydrogen desorption decreased from 390 to 220°C. However, the relationship between the addition of Al₂O₃ and the acceleration of hydrogen desorption kinetics of MgH₂ was not well understood.

In this work, we describe the effect of Al₂O₃, TiO₂, Cr₂O₃, and ZrO₂ addition on the desorption kinetics of molecular hydrogen. The effect of the addition of Al₂O₃ (10-50 wt%) on the dehydrogenation of MgH₂ was investigated with the other metal oxides. Composites of Al₂O₃ and the hydride were prepared in two ways: by milling the components separately or by co-milling them together in a gear-driven planetary ball mill for 10 min. The co-milled composite (MgH₂-50wt%Al₂O₃) released approximately 90% of the maximum hydrogen storage capacity within 30 min under a pressure of 0.003 MPa at 250°C. In contrast, the composite of the separately milled components did not release hydrogen even after two hours under the same conditions. BET measurement with nitrogen gas showed a negligible difference in the specific surface areas between the co-milled and separately milled composites. However, the saturation amount of hydrogen gas for the co-milled composite was 30% larger than that of the mixture of separately milled hydride and oxide. For the other metal oxides, the co-milled composites also released hydrogen for the shorter time under a pressure of 0.003 MPa at 250°C. The activation energy for hydrogen desorption from the co-milled composite with Al₂O₃, calculated on the basis of the surface-controlled model was 80 kJ.mol⁻¹, a value that is 50 kJ.mol⁻¹ lower than that of mixture of the separately milled MgH₂ and Al₂O₃. The activation energies for hydrogen desorption from the co-milled composites including TiO₂, Cr₂O₃, ZrO₂ were 66- 70 kJ.mol⁻¹.

Keywords Magnesium hydride; Alumina; High-energy ball milling; Hydrogen desorption kinetics

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Analysis of solar hydrogen production potential in Algeria: case of an electrolysis-PV tracking system

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Concern about energy shortage and pollution generated by the use of the conventional energy sources is pushing for the search of a new source of energy. Hydrogen, as a clean energy source, is a serious contender first as an alternative then ultimately as a substitute to the conventional energy resources.

In the present communication, an analysis of the potential of renewable hydrogen production is carried out. The case of a PV-electrolyser system is considered. Taking into consideration projected technological advances in PV systems for solar energy harvesting as well as in electrolyser technology for hydrogen production, the available of natural resources and using economic variables, different scenarios are used to estimate the potential and cost of hydrogen production in different sites in Algeria. Special attention is paid to the effect of tracking on the potential and cost of hydrogen production.

To this end, the concept of technology learning curves is applied to the performance as well as to the cost of hydrogen production in order to assess its viability and its sustainability in Algeria. Using these results and taking into account the environmental parameters, the most promising sites are identified.

The present results indicate that hydrogen economy is viable and shows a promising prospect for most of the sites in the country. The production of hydrogen opens new opportunities for the country. It allows the country not only to diversify its energy resources but also to keep its share of the energy market.

Bio-inspired membrane electrode assembled with electrospun-fibres for catalytic evolution of hydrogen in water

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[FeFe]-hydrogenase is one of the three metalloenzymes found in microbes and algae in nature^[1]. Crystal structural analysis revealed that the active site, H-cluster, consists of an organometallic diiron subunit which is bridged to a [4Fe4S]-cubane, Figure 1^[2,3]. The remarkable feature of this enzyme is its reversible and rapid catalysis of hydrogen evolution with high efficiency at physiological conditions. Owing to the potential of hydrogen as a clean energy vector in the future, this finding has greatly inspired chemists. In the past decade, numerous diiron-carbonyl complexes as the mimics of the diiron sub-unit of the enzyme have been synthesised^[4]. Mechanistic investigation into the electron transfer and their binding with proton to form hydrides provide very much insight of the enzymatic catalysis. To further exploit those mimics in catalysing hydrogen evolution, there are a number of hurdles to be overcome. One of the problems is to assemble a catalytic electrode operational in water by using the mimics. Recently, we reported our success in functionalisation of polymeric materials with diiron-carbonyl mimics and assembly of electrodes^[5-7]. Those electrodes exhibited electrochemical responses in organic solvents but their stability and hydrophilicity remain problematic. To take on the challenges, we exploited electrospun-fibres to assemble membrane electrode.



Fig. 2 Membrane of Electrospun-fibres containing complex 1.

In this presentation, we will report our exploring cellulose acetate (CA) as main component to prepare electrospun-fibres and assembling membrane electrodes using the electrospun-fibres membrane in which were dispersed diiron mimics of $[\text{Fe}_2(\mu\text{-edt})(\text{CO})_6]$ (edt = 1,2-ethanedithiolate) (1) and $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{OH})(\text{CO})_6]$ (2). To ensure the conductivity of the membrane, multiwall carbon nanotubes (MWCNTs) were anchored onto the CA chains. The electrode showed electrochemical response in 0.1 mol L⁻¹ KCl in water and very much improved stability. Repetitive scanning by 150 cycles decreased the peak current of the electrode by only ca. 50%. This is a sharp contrast to our previous reports in which the electrodes lost activity after one scan. Upon the addition of acetic acid, steady increase of catalytic current was observed.

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Keywords Hydrogen evolution; membrane electrode; electrocatalysis; electrospun-fibre; [FeFe]-hydrogenase

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Biological hydrogen production in a packed bed reactor

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Immobilized-cell reactors provide an alternative to conventional continuously stirred tank reactor (CSTR) due to their capacity for maintaining high biomass concentrations and operation at shorter HRT without biomass washout [1].

The objective of this study was to evaluate the performance of a reactor to produce hydrogen containing immobilized biomass on polyurethane foam.

Firstly, experiments to check the availability of the support material were performed. The support material used consisted of 3 cm polyurethane foam cubes. The polyurethane foam and the inoculum were initially introduced in 2 erlenmeyer flasks with 500 mL volume (working volume of 250 mL). They were placed in a thermostatic water bath at mesophilic temperature (35°C ± 1°C) without stirring. They were continuously fed with sucrose-based synthetic wastewater during 50 d in order to verify the growth of microorganisms. The organic loading rate (OLR) was increased from 1.6 - 9.6 g COD L⁻¹ d⁻¹.

Afterwards, hydrogen experiments were carried out in a column made of methacrylate with a working volume of 4 L, filled with the support material. Feeding cycles consisted in withdrawing a fixed volume of reactor effluent and subsequently adding an equal volume of fresh feed, which was pumped into the reactor by a peristaltic pump. Agitation inside the reactor was carried out by periodical recycling of the reactor content.

During first part of experimentation, the performance of the system was not stable, with a high fluctuation in biogas production. These instability problems might be explained by the absence of stirring in the system that favoured the accumulation of dissolved hydrogen inside the reactor. It has been reported that stirring improves hydrogen production in comparison with static fermentation experiments [2,3].

The biogas production obtained during the experiments in the column ranged from 2.05 – 4.80 L/d with an average hydrogen content of 35.4%. Hydrogen production was accompanied by an increase in acid production in the fermentation system. When the system was evaluated at an OLR of 10 g COD⁻¹L⁻¹ and HRT of 2 days, the hydrogen yield reached a value of 48.4 L H₂/kg COD⁻¹.

Acknowledgements This work was supported financially by project ENE-2009-10395 of the Spanish Ministry of Economy and Competitiveness.

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Keywords hydrogen; Packed-bed reactor

Comparative study of biological hydrogen production using microbial fermentation

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An increasing number of human population and rapid growth of global economy, shortage of energy sources and environmental pollution by cause of abundant exploitation and usage of mineral energy sources which were coal, oil, recent concerns about renewable and clean energy sources have intensified the exploitation and usage all around world. Searching for new alternative energy and developing system of renewable energy resources have to become inevitably selection to come true sustainable development. Hydrogen is a promising alternative fuel for the future because its non-polluting and inexhaustible nature, it has high heating power and the potential to eradicate all the environmental problems.

As an importantly and specially industrial gases, hydrogen has a wide application and potentiality in petrochemical, electronics, metallurgic industry, food processing, refined organic synthesis and aviation. Compared to traditional fossil fuel, hydrogen has high energy density and quantity of heat inversion rate, which generally acknowledged new energy resources. Biohydrogen production can utilize the devil of a waste product, such as effluent water and waste residue from industry production. Among the various hydrogen production pathways, use of biological methods of hydrogen production has attracted increasing global attention, due to its potential for inexhaustible, low-cost and renewable source of clean energy.

The aim of this study was to observe the hydrogen production yield of 16 different pure strains and mixed culture, which contains hydrogen-producing strains (*Clostridium acetobutylicum* S512, *Clostridium butyricum* T11, *Enterobacter cloacae* Y219, *Enterobacter aerogenes* E9) and non-hydrogen-producing strains (*Bacillus stearothermophilus* U2, *Bacillus subtilis* B7, *Bacillus subtilis* B7-S, *Pseudomonas putida* P85, *Kluyveromyces lactis* B9, *Rhodotorula lactosa* C8, *Kluyveromyces marxianus* D10, *Kluyveromyces marxianus* 15D, *Rhodotorula rubra* R530, *Cantharellus* KX560JY, *Boletus edulis* KX920NG, *Clavicornia pyxidata* KX320SH). The experimental results compared the hydrogen production yield of these pure strains: A high hydrogen production yield was observed in the cultures with *Enterobacter cloacae* ATCC 13047 (12.5 mL/h⁻¹.L⁻¹). This yield was higher than that in cultures with *Kluyveromyces marxianus* 15D (8.9 mL/h⁻¹.L⁻¹) and lower than that in cultures with *Clostridium acetobutylicum* ATCC 824 (13.6 mL/h⁻¹.L⁻¹). While the pure *Cantharellus* KX560JY, *Boletus edulis* KX920NG and *Clavicornia pyxidata* KX320SH strains achieved the lowest yields i.e. no more than 1.5 mL/h⁻¹.L⁻¹ compared to the yields achieved by other strains. In addition, The biohydrogen production in mixed culture of *Enterobacter cloacae* ATCC 13047, *Kluyveromyces marxianus* 15D and *Clostridium acetobutylicum* ATCC 824 was greatly enhanced up to 33.7 mL/h⁻¹.L⁻¹, indicating that biohydrogen production in mixed culture is preferable for the fermentative hydrogen-producing system. These results confirmed *Enterobacter cloacae* ATCC 13047, *Kluyveromyces marxianus* 15D and *Clostridium acetobutylicum* ATCC 824 of hydrogen-producing bacteria (HPB) has potential and efficient applications in biohydrogen production. As a consequence, the fundamental knowledge derived from this study should provide a valuable platform for further investigation into the behavior of hydrogen-producing bacteria involved in microbial fermentation.

Keywords Alternative energy; Biohydrogen production; Microbial fermentation; Hydrogen

Consolidated bioprocessing of lignocellulosic biomass and waste for cost-efficient biohydrogen production

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Hydrogen (H₂) is considered the “energy of the future” and an ideal alternative fuel to the current energy scenario due to its high energy content (143 MJ/Kg compared to 26.9 MJ/Kg for ethanol, and 43.5 MJ/Kg for gasoline) and non-polluting nature (water is the only end product). The current global demand for H₂ is 45 million tons/annum of which the U.S. consumption of H₂ is about 20% of the global H₂ supply or 9 million tons per year. At present, approximately 95% of the current H₂ production is derived from fossil fuels (49% from natural gas, 29% from crude oil, and 18% from coal) via steam reforming, with the remaining 4% of H₂ produced through electrolysis of water. However, fossil fuel reforming generates greenhouse gases such as CO, CO₂ and NO_x, and the whole process is dependent on the supply of fossil fuels, which are non-renewable, polluting, and depleting. The United Nations Statistics show that the global CO₂ emissions increased 44% between 1990 (20.69 billion metric tons (MT)) and 2008 (29.86 billion MT). On the other hand, water electrolysis requires high capital investment for electrolyzers and is currently energy inefficient. Biological H₂ production offers two major advantages over the steam reforming process in that 1) it utilizes renewable sources, and 2) it produces very low or no net level of CO₂ as most of CO₂ produced during carbon metabolism is fixed back and used for the cell growth and energy metabolism. Biologically, H₂ can be produced via photolysis, photofermentation and dark fermentation. It is widely accepted, however, that dark fermentation by many facultative and obligate anaerobic bacteria is advantageous over the other biological methods as anaerobic bacteria can ferment a wide range of organic substrates including organic waste. In addition, dark fermentation exhibits a markedly higher H₂ production rate, compared to biophotolysis and photofermentation. However, an economically feasible dark fermentative H₂ production from renewable sources is still in an early stage of development for at least three major reasons: 1) feedstock costs; 2) lack of appropriate microorganisms which can hydrolyze biomass to fermentable sugars; 3) low stoichiometric H₂ yield. An environmentally friendly and potentially viable alternative for sustainable H₂ production is presented through the utilization of renewable resources such as lignocellulosic biomass such as switchgrass (SWG) and waste including municipal solid waste (MSW). SWG is viewed as one of the most promising energy crops for the U.S. conditions with low nutrient/water requirements and high adaptability to any weather/soil/land conditions. It is produced at yields of 25 t/ha or 10 t/acre, on average, and production is predicted to increase up to 10-fold within next 10 years - from the current 30 million tons per year to 300 million tons per year in 2010. Furthermore, its carbohydrate composition (>65%) and low lignin (<20%) content favors a bioprocessing route for biochemical (fermentative) utilization of SWG to biofuels and value-added bioproducts. On the other hand, the handling and disposal of MSW is of growing global concern as waste generated world-wide continues to increase - in the U.S. only it reached close to 5 lb per capita per day. However, MSW contains approximately 60% of biodegradable material such as food waste, yard trimmings, paper and cardboards which can be utilized to produce value-added products. This presentation will discuss the major opportunities that are offered by consolidated bioprocessing (CPB) of lignocellulosic biomass to hydrogen. CPB combined three major processing steps - enzyme production, hydrolysis and fermentation - in one single operation stage, and as such presents outstanding opportunities for cost savings of 40-60%. Results will be presented on utilization of a thermophilic bacterial isolate identified as *Caldicellulosiruptor saccharolyticus* in biohydrogen production. SWG appeared as the preferred substrate over MSW with a maximum H₂ production of 32.3 mmol/L (894.7 ml/L) after 72 h of fermentation at 65°C. The H₂ production on MSW peaked at 96 h with 14.2 mmol/L. Acetate and propionate were identified as the two major metabolites whereas degradative biomass-derived sugars included glucose, mannose and arabinose. This study demonstrates the principle feasibility of using *C. saccharolyticus* for establishment of a commercially viable process for H₂ production. Utilization of low cost carbon feedstock such as SWG and MSW without prior thermo-chemical treatment in a CBP process is expected to significantly improve the economics of the H₂ production process and its commercial feasibility.

Keywords: biohydrogen, switchgrass, municipal solid waste, consolidated bioprocessing, *Caldicellulosiruptor saccharolyticus*

Current challenges of hydrogen energy

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Recent advancements in hydrogen technologies and renewable energy applications show promise for the use of hydrogen for the electric utility and transportation sectors. During the last decades, notable developments have taken place in the science and technology of hydrogen energy and fuel cells. The main tasks of the hydrogen economy have been related to existing and being in demand hydrogen production methods (i.e. water electrolysis, gas reforming, methane decomposition), ways of purification and transfer of gas hydrogen for a distance, problems of hydrogen storage (i.e. under pressure, in a liquefied form, in metal hydrides), and finally, conversion of chemical energy of gas hydrogen into electric energy that can be applied in the industrial practice (Fig. 1).

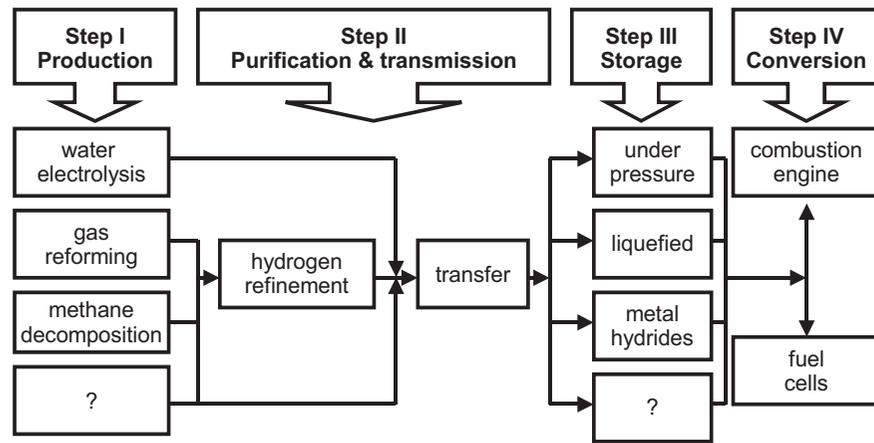


Fig. 1. Main tasks of the hydrogen economy.

Up to now, I and II steps of the hydrogen economy has been most investigated. At present, challenges of the hydrogen energy are focused on searching for new methods of hydrogen storage and conversion (III and IV steps). It has been postulated that insistent and expensive attempts of commercialization of fuel cells based on the materials that are not finished up, must be stopped. The most important aspect of hydrogen technologies should be the use of hydrogen as fuel for highly effective, silent and not burdensome for the environment generators of the electricity – fuel cells. It should be also note that theory, modeling and computer simulation can help in deeper understanding of the solid state phenomena and electrochemical processes proceeding during the work of fuel cell, and better tailoring of the electrode materials and cell construction.

Therefore, in this work the current key scientific issues concerning: (i) materials for fuel cells (electrolytes, electrode materials, interconnectors, constructional materials), (ii) membranes and gas segregation, (iii) materials for solid-state hydrogen storage with a special attention focused on nanostructural materials, and (iv) problems of catalysis, have been presented and briefly discussed. A critical review on the newest methods and techniques for investigations of fuel cells, particularly, electrochemical impedance spectroscopy techniques for determination of the mechanism and kinetics of hydrogen adsorption, absorption and evolution reaction on metals and its alloys, have been also carried out.

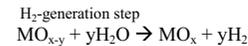
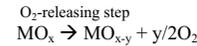
Keywords hydrogen conversion; hydrogen energy; hydrogen production; hydrogen storage; hydrogen technologies

Dopant Effect on Hydrogen Generation Step of Two-Step Water Splitting using CeO₂-ZrO₂-MO_x Reactive Ceramics

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The two-step water splitting reaction for a production of solar hydrogen using concentrate solar thermal energy has been extensively studied for reactive ceramics.[1,2] The red-ox reactions in the two-step water splitting process are given by the following chemical equations:



where MO_{ox} and MO_{red} denote the oxidized and reduced states of metal oxide, respectively. The O₂ and H₂ gases are obtained by repeating two alternating steps in the two-step water splitting cycle. Previous research on the two-step water splitting has presented the use of CeO₂ system compounds for the reaction.[3]

In this study, the dopant effect on the H₂-generation reaction using CeO₂-ZrO₂-MO_x reactive Ceramics has been investigated. Each metal(Mg, Ca, Sc, Sr, Y, Ba, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) was used for the dopant(M). A CeO₂-ZrO₂ has higher O₂-releasing reactivity. On the other hand, H₂-generation reactivity of this material is low. Therefore, a ratio between O₂ and H₂ is less than 1:2 within 3min H₂-generation reaction. This is advantageous for the investigation for the dopant effect on H₂-generation. If the ratio is 1:2, the H₂-generation reactivity increasing via dopant effect is difficult to observe because the dopant affect to not only H₂-generation, but also O₂-releasing reaction. Hence, in this study, we use each dopant as 2nd dopant of CeO₂-ZrO₂ solid solution. The ionic radius and valence of each dopant were compared with an oxidation ratio. The oxidation ratio increases with an increase in the ionic radii, and the effect become larger with an increase in the ionic charge (divalent < trivalent < tetravalent). The ionic conductivity of each sample was measured by an impedance spectrometer. The reaction time becomes shorter with an increase in the ionic conductivity.

Keywords Water Splitting; CeO₂; ZrO₂; Ionic conductivity

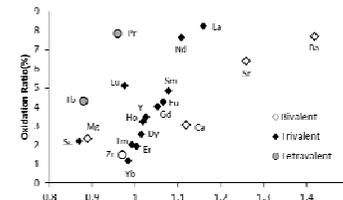


Fig.1 Oxidation ratio vs Ionic radii of dopant

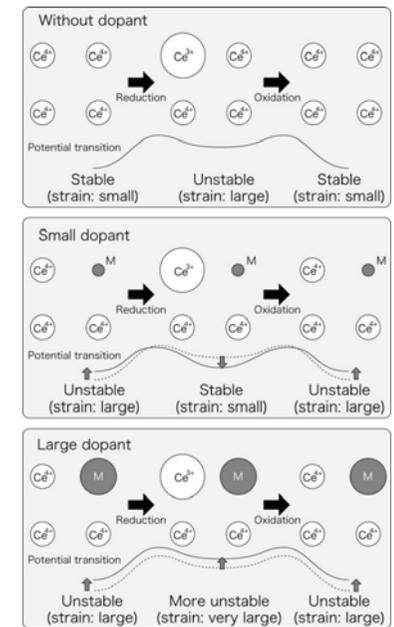


Fig.2 Dopant effect on lattice strain

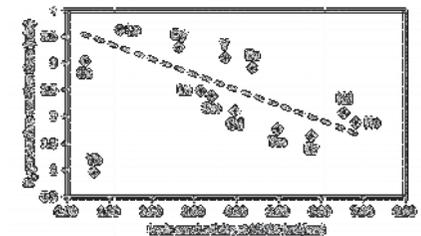


Fig.3 H₂-generation reaction time vs Ionic conductivity at 1073K (Trivalent dopants)

Effect of nickel distribution on alumina surface to the catalytic activity in biogas reforming reaction

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Biogas reforming has attracted considerable scientific interest in the past years, as it offers the possibility of simultaneous removal of two inexpensive and abundant carbon containing sources, which are also greenhouse gases, and their transformation into useful chemical products. Ni-based catalysts supported on different carriers have been extensively investigated because of the metal availability and economic considerations [1]. Although, in order to improve the catalytic performance and minimize coking of the nickel catalyst, several conditions can be modified, such as characteristics of the support, metal content, *preparation method* and the introduction of promoters into the catalyst formulation [2]. Nonuniform distribution of catalysts on supports has long been taken advantage of in the so called "egg shell" catalysts to minimize diffusion resistance. In recent studies, supported nickel on alumina catalysts with egg/shell structures showed good activity and thermal stability in all types of methane reforming reactions, such as POX and SR and DRM [3]. In the present work the Al₂O₃-supported Ni catalysts with core/shell and uniform structures, with 7 and 15 wt% nickel loadings, were tested in the dry reforming of biogas.

The nickel catalysts with a uniform structure (xNi/Al-wet) were synthesized using the wet impregnation method, whereas the egg-shell catalysts (xNi/Al-edf) studied were prepared by a combination of the *edf* method [4] with the wet impregnation technique. The physicochemical properties of the final catalysts were determined by using different techniques: N₂ adsorption – desorption isotherms, X-ray Diffraction (XRD), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Catalytic performance was evaluated for the biogas reforming reaction using a feed gas mixture of CH₄/CO₂=1.5, simulating a clean model of biogas. Biogas reforming reaction was carried out at atmospheric pressure in a fixed-bed continuous flow reactor at temperature values ranging from 700 to 900 °C and product gases were analyzed by online gas chromatography equipped with a TCD and a FID detector.

The results showed that the catalysts prepared with the "edf" method at pH=7.0, equal to the pzc of the support used, are characterized by smaller nickel species particle sizes, compared to the ones prepared with the wet impregnation method. SEM results reveal that following the modification of the edf method proposed by the authors, an egg-shell marked structure is accomplished (xNi/Al-edf samples), compared to the xNi/Al-wet samples with uniform metal distributions on alumina surface, that are accomplished following the conventional wet impregnation method.

The fact that the ratio H₂/CO is higher than unity during the reforming reaction for the egg-shell nickel catalyst, indicates that the egg-shell structure probably inhibits the reverse water gas shift reaction, which is related to hydrogen consumption and CO production. Specifically, at high metal loadings, the catalysts reveal similar catalytic performance, resulting in high conversion rates above 800 °C and similar H₂/CO ratios of 1.5. Otherwise, at low metal loadings, there are only slight differences in methane conversions at the range of 800-900 °C, but the catalyst with an egg-shell structure reveal an increasing hydrogen yield, resulting in a parallel increase in H₂/CO ratio. The improved catalytic performance of the above catalyst is attributed to its unique properties, as the high surface area, the high dispersion and the egg-shell structure that is optimum for the reforming reactions.

The supported Ni catalysts with a core/shell structure were proven to be relatively better catalysts for the reforming process of biogas, in comparison to the ones with a uniform structure. Such catalytic property is assumed to mainly arise from their core/shell structure and the study on their contribution to such catalytic properties will be discussed.

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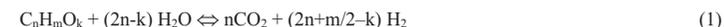
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Effect of the temperature in a pre-reforming reactor with dolomite for H₂ production by crude bio-oil steam reforming in a two-step reactor system

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Hydrogen and syngas can be sustainably produced by steam reforming (SR) of bio-oil (the liquid product derived from the fast pyrolysis of biomass), which might constitute a promising feedstock in a bio-refinery^[1]. The reaction network of bio-oil SR is complex although the overall process can be represented by Eq. (1) (which is the combination of the reforming reaction of bio-oil oxygenates to produce CO and H₂ and the WGS reaction). Thermal decomposition, Eq. (2), also occurs due to the thermal instability of oxygenates



Several catalysts of Ni supported on mixtures of basic oxides (such as MgO or La₂O₃) and alumina have been tested in literature for bio-oil SR under wide range of operating conditions. Total bio-oil conversion and H₂ yields between 63 - 80 % are achieved at 850 °C and steam-to-carbon ratio (S/C) ≈ 5^[2,3], but quite rapid catalyst deactivation (both by coke and by sintering) is observed under these operating conditions. Improvements in H₂ yield have been reported by using dolomite both as: i) *in situ* CO₂ sorbent in the SR of the aqueous fraction of bio-oil in a fixed bed reactor^[4], attaining an increase in H₂ yield from 20 to 70% and; ii) low-cost catalyst for the pre-reforming of bio-oil in a two-stage fixed bed reactor system^[5], in which the first bed (with dolomite at 900 °C) is used to convert the reactants into CH₄, and the second bed (with Ni/MgO catalyst) is used to reform the CH₄, obtaining a H₂ yield of 80 % at 850 °C and (S/C)= 16. It has been previously shown that a two-step system (thermal step + catalytic step) is efficient for attenuating catalyst deactivation by coke in catalytic processes for bio-oil upgrading^[6].

In this paper, a two-step reactor system consisting of a pre-reformer (with dolomite) + reformer (with Ni/La₂O₃-α-Al₂O₃), both fluidized beds, is used for the SR of crude bio-oil stabilized by the addition of 20 wt% of ethanol. The effect of pre-reformer temperature on the composition of the stream at the pre-reformer outlet and on the bio-oil conversion and H₂ yield obtained at the reformer outlet are analyzed. The bio-oil (obtained by fast pyrolysis of pine sawdust) is composed of 65 wt% organics (C_{4.2}H_{7.1}O_{2.7}) and 35 wt% water, and additional water is fed to the pre-reformer in order to fix a S/C ratio ≈ 6. The operating conditions are: i) pre-reformer: feed flow rate = 0.1 ml min⁻¹; 11 g of dolomite; temperature between 500-800 °C; ii) reformer: 1.3 g of Ni/La₂O₃-α-Al₂O₃ catalyst, 700 °C, WHSV = 3.64 h⁻¹. Prior to the reforming reaction, the catalyst was reduced at 700 °C for 2 h using a H₂-He flow (with 10 vol % of H₂).

Concerning the composition of the product stream at the pre-reformer outlet, a notable increase in the concentration of gaseous products is observed with the increase in temperature, from 11 wt% at 500 °C up to 98 wt% at 800 °C, which CO, CH₄ and CO₂ being the main components at 500, 600 and 700 °C, respectively. Above 700 °C a pronounced increase in CO and CO₂ content is observed (from decarbonation-decarboxilation reactions), which are the majority products at 800 °C. The liquid product composition also changes with respect to the bio-oil fed: i) most of the acids (especially acetic acid) are totally transformed while ketones content increases noticeably in the whole range of temperature studied; ii) ethanol totally disappears above 600 °C; iii) high contents of phenolic compounds (mainly phenol) are obtained at 600 °C, but they react at 700 °C and the concentration of aromatic hydrocarbons is increased. Consequently, an increase in the pre-reformer temperature decreases initial H₂ yield due to the promotion of CH₄ formation. Nevertheless, it also leads to a notable attenuation of catalyst deactivation, due to: i) a change in the oxygenated composition, responsible for coke deposition and ii) the gasification of the coke that deactivates both the dolomite and the Ni/La₂O₃-α-Al₂O₃ catalyst. Consequently, 700 °C is the optimum temperature for the pre-reforming unit with dolomite in order to obtain stable operation in the SR of crude bio-oil (with constant H₂ yield for 4 h).

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Keywords: hydrogen production, crude bio-oil, catalytic steam reforming, dolomite, two-step reaction system

Efficient conversion of agricultural lignocellulosic waste materials into biohydrogen by acid pretreatment

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Hydrogen must be produced sustainably to be economically feasible. This could be achieved from water through electrolysis powered by photosynthetic or other renewable energy, or by gasification or pyrolysis of biomass. It also may be possible to develop a cost-effective and reliable technology to produce hydrogen directly from renewable biomass or organic waste products through anaerobic fermentation. Lignocellulosic biomass contains approximately 70–80% carbohydrates. If properly hydrolyzed, these carbohydrates can serve as an ideal feedstock for fermentative hydrogen production. In this research, batch tests of biohydrogen production from acid-pretreated wheat straw were conducted to analyze the effects of various associated bioprocesses. The objective of the pretreatment phase was to investigate the effects of various sulfuric acid pretreatments on the conversion of wheat straw to biohydrogen. When sulfuric acid-pretreated solids at a concentration of 2% (w/v) were placed in an oven for 90 minutes at 120°C, they degraded substantially to fermentative gas. Therefore, wheat that is pretreated under the evaluated conditions is suitable for hydrolysis and fermentation in a batch test apparatus. Different conditions were evaluated in the tests, which were conducted in accordance with standard batch test procedures (DIN 38414 S8): fresh straw, pretreated straw and Simultaneous Saccharification and Fermentation (SSF). The SSF method proved to be the most effective and economical way to convert wheat straw to biohydrogen. The hydrogen yield by this method was 1 mol- H₂/mol-glucose, which resulted from 5% carbon degradation (η_C gas) or the equivalent of 64% of the hydrogen volume that was produced in the reference test (glucose equivalent test).

Key words: Biohydrogen, Wheat Straw, Acid pretreatment, Bioenergy

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Keywords: H₂ production; steam reforming; dimetil ether; cupper-ferrita spinel; reaction-regeneration cycles

Equilibration treatment of a CuFe₂O₄/AlOOH bifunctional catalyst for the stable operation in successive reaction –regeneration cycles in the DME steam reforming

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Dimethyl ether steam reforming (DME-SR) is a promising alternative to produce H₂ rich gas for low-temperature fuel cell systems¹. DME-SR proceeds over bifunctional catalysts, via hydrolysis of DME (over an acid function, such as γ -Al₂O₃)², followed by steam reforming of methanol (over a metallic function, typically based on Cu)^{1,4}. The Cu/ZnO/Al₂O₃ (CZA) metal phase has been extensively used in literature for MeOH-SR³, but it suffers from sintering at relatively low temperature, which is a handicap for i) its use in DME-SR together with γ -Al₂O₃ as acid function (which requires T>300 °C for a high activity in DME hydrolysis) and ii) the regeneration of the bifunctional catalyst by coke combustion. CuFe₂O₄ spinel has recently been regarded as an attractive metallic function because of its stability at higher temperature^{2,4}, compared to CZA metal phase, which allows the regeneration of the catalysts by coke combustion at high temperatures (500-550 °C) without sintering of Cu.

In this work, it has been studied the operation of a catalyst with CuFe₂O₄ spinel as metallic function for the DME-SR in successive reaction-regeneration cycles carried out in an isothermal fluidized bed reactor. Pseudoboehmite (aluminum oxi-hidroxide, AlOOH) has been used as acid function, because it has enough activity for the hydrolysis of DME and, moreover, it confers the bifunctional catalyst enough resistance to attrition for its use in the fluidized bed reactor. The CuFe₂O₄/AlOOH catalyst (1/1 mass ratio) was prepared by wet physical mixing of both functions. The reforming conditions were 350 °C, P_{DME} = 0.21 bar, steam/DME = 3. The regeneration consisted in combustion with air at 500 °C for 2 h, which totally removed the coke deposited on the catalyst.

The evolution with time on stream of DME conversion (X_{DME}) and of MeOH virtual conversion (X_{MeOH}, that is the conversion for the MeOH-SR stage in the DME-SR), in 3 successive reaction cycles for a low value of space time ($\tau = 0.03$ g_{cat}h/g_{DME}, which assures high deactivation by coke) (Figure 1) shows that a noticeable activation of the metallic phase occurs in the regeneration steps (especially in the first one), which is due to the creation of a new phase (Cu-Fe₂AlO₄) by the solid-state reaction at the interface between the metallic and acid functions⁴. Nevertheless, the activation of the metallic function is not observed when the fresh catalyst is subjected to the oxidizing treatment used for the regeneration, and under conditions of low deactivation by coke (high values of space time) the activation of the metallic phase is slow and high number of reaction-regeneration cycles are required for attaining the stable behavior of the catalyst.

These results indicate that the presence of high amounts of coke over the metallic and acid functions favours the solid-state reaction for the creation of the new phase. Consequently, an equilibration treatment of the bifunctional catalyst is proposed consisting in subjecting it to a previous reaction at 350 °C for 2 h by feeding only DME (without steam, which provokes a very rapid deactivation of the catalyst by coke), followed by a regeneration with air at 500 °C for 2 h. The performance of this equilibrated catalyst in the DME-SR is notably improved compared to the fresh catalyst, and its behavior in successive reaction-regeneration cycles is totally reproducible.

Acknowledgements: This work was carried out with the financial support of the Ministry of Science and Innovation of the Spanish Government (Project CTQ2009-13428/PPQ).

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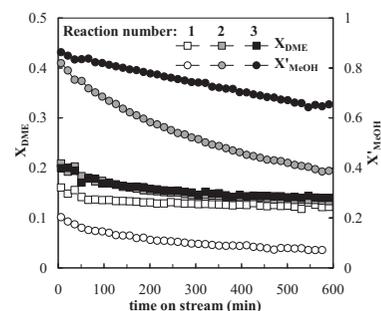


Figure 1. Evolution of DME and MeOH conversions for successive reaction cycles over a non-equilibrated CuFe₂O₄/AlOOH catalyst.

Experimental study of hydrogen generation from water using activated aluminum for portable power sources

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An important part of the hydrogen energy problems is the search of hydrogen sources for feeding hydrogen-air fuel cells. These sources of hydrogen should be compact, capacious, safe in use and working at normal conditions. Water is the capacious hydrogen source, the mass fraction of hydrogen is 11 wt.%. However, to reduce hydrogen from water the active metals are needed. For a portable application one of the most convenient methods for hydrogen generation is based on the hydrogen reduction from water by means of aluminum. The hydrogen content in the reaction is 3,7 wt.%.

But it is known that aluminum does not react with water at normal conditions. So, the new method of aluminum activation was developed [1]. This method is based on using of gallium alloys (gallams). The moistening of aluminium by gallam leads to the destruction of oxide film on the surface of aluminium, cracking of aluminium sample and formation of the powder. Such activated aluminium powder can react with water even at normal condition.

In this work the kinetic parameters of the reaction of activated aluminum with water (hydrogen generation rate and hydrogen yield) depending on the gallam's amount and composition, powder particle sizes and reaction temperature are studied.

Reached high reaction rate allowed us to develop a hydrogen generator based on the reaction of activated aluminum with water. The kinetic parameters of oxidation reaction in generator are studied. Based on this hydrogen generator, the prototype of portable power source was developed.

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Keywords activated aluminum; hydrogen generation; gallam; portable power sources

Exploitation of pre-treated olive mill wastewater for hydrogen photoproduction by *Rhodospseudomonas palustris* 42OL

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Olive mill wastewater (OMW) is the liquid waste resulting from the olive oil extraction process; this wastewater is one of the main pollutant products in the Mediterranean area. Since the worldwide annual production of OMW is estimated to be more than 30 million m³/year [1], a process for OMW biodegradation is mainly required. At the beginning, light dependent microorganisms like microalgae were used for biomass production using OMW as nutrient medium [2]. In the first decade of this millennium, a different strategy was proposed using a photofermentative process by purple non-sulfur bacteria (PNS) [3]. In our recent study, *Rhodospseudomonas palustris* 6A was grown on pre-treated OMW diluted with distilled water (25 % v:v) and it produced biogas rich in hydrogen [4]. In the present study the exploitation of fresh olive mill waste (OMW_F), pre-treated with an eco-technological process, was investigated to produce bioH₂. The culture broth containing OMW_F (30%) and distilled water (70%) was tested for hydrogen photoproduction using the non-sulfur photosynthetic bacteria *Rhodospseudomonas palustris* 42OL. The photofermentative process was studied in batch growth conditions, at three different light irradiances (18.5, 37 and 74 W/m²). The lowest cumulative hydrogen (439 ml/l) was attained at 18.5 W/m², the highest one (1030 ml l) was achieved at 74 W/m². The average hydrogen evolution rate, based on the culture volume (HPR_{avg}), achieved at the three different irradiances (18.5, 37 and 74 W/m²) were 1.40, 3.17 and 5.28 ml/l/h respectively. The culture age, at which hydrogen photoevolution stopped, showed an inverse proportionality with respect to the irradiance: the higher the irradiance the lower the culture age. The light conversion efficiency (η) was maximal (1.07 %) at 37 W/m² and decreased (< 1.0 %) at lower and higher irradiances.

Keywords photofermentative process; hydrogen photoproduction; olive mill wastewater; *Rhodospseudomonas palustris*

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Hydrogen adsorption on Fe₅₀Ni₅₀

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Iron promoted nickel based catalyst has been developed for high yield hydrogen generation through ethanol reforming [1]. The reaction results show a remarkable improved durability in catalytic activity as well as selectivity. On the other hand, the perturbations in the electronic properties of the bimetallic surfaces are considered to be a contributory factor to the change in the catalytic action [2]. Investigations have reported that binary Fe-Ni catalysts decreased the reaction temperature and yielded 70-90 percent of hydrogen [3, 4].

In the present work, we have analyzed at theoretical level, the adsorption of hydrogen on the Fe₅₀Ni₅₀(111) surface by Atom Superposition and Electron Delocalization calculations [5]. Different sites on the surface were selected in order to establish the preferential H location and the optimum H-surface distance. The two most stable sites for H on Fe₅₀Ni₅₀(111) are those where H bonds on top Fe at 1.50 Å from the surface, and the H bonds on the Fe-Fe bridge site at 0.70 Å from the bimetallic surface. We found that the minimum energy site corresponds to the H bonding on top Fe atom. The Fe-H interaction is formed and the bond is mainly due to the overlaps between the H s orbital with the Fe p_z, s, d_{z²} and p_y orbitals. As a consequence, it is observed a local Fe-Fe bond weakening of 12 %. On the other hand, when the H is located on the Fe-Fe bridge site, the Fe-H interactions weaken the Fe-Fe nearest bonds to about 33% and the Fe-H interaction is mainly formed with participation of Fe p_z, p_y, s and d_{yz} orbitals. In general, after H adsorption, the Fe-Ni and Ni-Ni bonds are slightly affected. The Ni-H interaction is not evidence on the Fe₅₀Ni₅₀(111) surface.

Keywords: iron; nickel; hydrogen; modelling studies

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Hydrogen Production by Aluminum Corrosion in Hydrochloric Acid and Using Inhibitors to Control Hydrogen Evolution

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This study reports on the systematic assessment of hydrogen (H₂) production by corrosion of aluminum alloy (AA) in hydrochloric acid (HCl) at different temperature. Rare earth inhibitors, lanthanum (La) and cerium (Ce) have been applied to control the H₂ production process. The production process is based on electrochemical reaction of aluminum (anodic reaction) in the HCl solution, which has a high concentration of hydrogen ions (H⁺), the H⁺ ions are reduced and H₂ is evolved. Preliminary results showed that an increase in temperature of working solution produced an increase of the H₂ production rate. The H₂ production rate increases because acid can prevent aluminum passivation during H₂ evolution. The rare earth inhibitors La and Ce control the H₂ evolution, especially, when using mixture of both inhibitors. This result demonstrates a synergistic effect between the La and the Ce inhibitors. X-ray diffraction studies were performed on the surface structure before and after immersion, and a scanning electron microscope (SEM) was used to study the morphology of the AA.

Keywords: Aluminum Alloy; Hydrogen Production; Rare Earth Inhibitors; Controlling Hydrogen Evolution.

Hydrogen production by means of catalytic gasification of plastic waste

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Gasification processes are expected to play a key role in the future of solid waste management since the conversion of municipal and industrial solid wastes to a producer gas or a synthesis gas significantly increases its value. Of all waste gasification technologies, fluidization allows use a catalytic bed allows to completely change the composition of output products and, in particular, to avoid the formation of heavy hydrocarbons by means of an “in situ” catalytic destruction of tar precursors and intermediates. The tar precursors, such as cycloparaffins, naphthenes and aromatics, forming during ternary reactions of the wax-like intermediates produced by primary cracking, can be decomposed to carbon and hydrogen by means of metal-based catalysts. This paper reports the comparison between the results obtained by carrying out the gasification tests without the use of a catalytic bed and those obtained by using a bed made of an allumino-silicate of iron and magnesium (olivine). The main result is that, under the right value of bed temperature, fluidising velocity and oxygen concentration, the test performed with the catalyst allows to obtain a complete de-hydrogenation of the polymer macro-molecules. The process is completely auto-thermal thanks to the exothermic partial oxidation reactions of a part of the fuel fed in the reactor. Therefore, the gasification of poly-olefins can be considered an interesting and economically sustainable way to produce hydrogen with high yield.

Keywords: hydrogen; gasification; polymers; catalytic cracking; fluidized bed

Hydrogen production by methanol steam reforming over Cu-based catalysts: Insights into the role of Cu

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Copper-based catalysts are commonly used for steam reforming of methanol (MSR) due to their high activity and selectivity along with their low cost [1]. Cu–Mn spinel oxide catalysts synthesized by the combustion method, showed comparable activity to commercial Cu–Zn–Al catalyst for H₂ production via MSR, despite their low surface areas [2]. In the present work the surface state of Cu–Mn (30:70) and Cu–Al–Mn (30:7:63) spinel oxides is investigated *in situ* under methanol steam reforming conditions by ambient pressure X-ray photoelectron and absorption spectroscopies (APPEs and NEXAFS respectively). The reaction was performed at 250° C at overall pressure of 0.2 mbar and the catalytic performance was monitored simultaneously to the surface characterization by *on-line* mass spectrometry. The results showed that the actual Cu surface atomic fraction is significantly lower compared to the nominal, which might be related to diffusion of Cu in the bulk or spillover of oxide species (*e.g.* MnO). Interestingly no direct correlation between the amount of Cu on the surface and MeOH conversion or CO selectivity was found, in contrast to the common belief, that increasing copper dispersion should benefit catalytic activity [1].

In situ NEXAFS was mainly used in order to determine the surface oxidation state of the working reforming catalysts, due to its high sensitivity to the local electronic structure. Reference spectra and theoretical simulations were utilized for the interpretation of NEXAFS results. It was indicated that spinel oxide decomposes under reaction conditions and the surface is dominated by MnO and metal-like Cu species. The presence of Al in Cu–Al–Mn spinel seems to hinder reduction of Cu compared to Cu–Mn. Unreduced Cu species (probably still in the spinel oxide structure) do not have any notable effect on the activity, but they do have a pronounced effect on CO selectivity. Finally, subtle but reproducible differences at NEXAFS Cu L-edge features between reference samples and Cu–Mn and Cu–Al–Mn catalysts will be discussed to shed light on the active Cu state during MeOH reforming reaction.

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Keywords hydrogen production, steam reforming reaction, PEM fuel cells, ambient pressure photoelectron spectroscopy, NEXAFS.

Hydrogen production with TiO₂ photocatalysts modified by Pt nanoparticles in different sizes

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In the present work platinum deposited Aeroxide P25 titanium dioxide photocatalysts were prepared with 1 wt% noble metal content. The aim of the experiments was to investigate the differences in the photocatalytic performance when these photocatalysts were deposited with differently sized Pt nanoparticles (2.5-5 nm).

In the literature there are numerous references that platinum doped titanias have high efficiency for H₂ production when these catalyst suspensions are irradiated with UV light due to the low overpotential of hydrogen evolution on Pt. It is also known that the optimal Pt content on TiO₂ is around 1 wt%. H₂ production with Pt-TiO₂ catalysts can be achieved even from pure water, although the process is more effective when the suspension contains an easily oxidable organic compound as a hole scavenger (also known as sacrificial reagents).

The noble metal deposition onto the titania surface was achieved by chemical reduction *in situ* on the titania photocatalysts (CRIS) or by mixing chemically reduced Pt nanoparticles in sols with the aqueous suspensions of the photocatalysts (sol-impregnated samples, CRSIM). During the synthesis trisodium citrate was added. Varying the citrate concentration differently sized noble metal particles were prepared. The reducing agent was sodium borohydride. UV photoreduction and these two chemical reduction processes were compared under different reaction conditions. The catalysts were washed by centrifugation in order to remove chloride, borohydride and citrate ions and any unreacted traces from the surface.

The samples were examined with transmission electron microscopy (TEM) to determine average platinum particle size. TEM images revealed the presence of 2.5-5 nm platinum-domains on the surface of the Pt-TiO₂ catalysts.

Hydrogen production measurements were carried out in the absence of dissolved oxygen. Photocatalytic activity of the samples was examined in a special well-sealed reactor containing aqueous TiO₂ suspensions and irradiated with UV light ($\lambda_{max} = 365$ nm), using oxalic acid (50 mM) or methanol (50 mM and 100 mM) as model compound. The hydrogen flow was measured by gas chromatography and the decomposition of oxalic acid by HPLC. In these measurements, the H₂ production rates were dependent on the platinum particle size. The optimal particle size was ≈ 3.2 nm, at which the photocatalytic activity was the highest. The photoreduced samples containing larger Pt nanoparticles were less efficient, than the chemically reduced ones. Oxalic acid adsorption was measured both on bare Aeroxide P25 (49 m²/g) and platinum-modified P25 TiO₂. Comparing the quantum yield of the most effective Pt-TiO₂ catalyst for H₂ production and for the oxalic acid decomposition it turned out that hydrogen mostly evolves from the organic sacrificial compound but there should be still a significant rate of water splitting. Interestingly there is a high peak in hydrogen evolution in the first 40 minutes of the measurement. After this period, the H₂ evolution falls back but it stays at a constant rate in the rest of the experiment. This phenomenon can be caused by the change of noble metal particle size as a matter of UV irradiation. There should be a process in which the smallest particles on the surface are slowly disappearing, while the bigger ones are slightly growing. Using methanol as a sacrificial reagent, the hydrogen production was nearly constant during the experiments and these rates were notably higher than in the cases using oxalic acid.

These experiments confirmed that suitable platinum modified catalysts can be synthesized for efficient hydrogen production. These catalysts are potentially able to utilize the UV component of solar irradiation. Despite the presence of the relatively expensive platinum, the amount of noble metal is so low, that this method could be used for cost-effective hydrogen production.

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Keywords: size dependent activity; platinum nanoparticles; titanium dioxide; solar energy; hydrogen production; photocatalysis; oxalic acid; methanol

Hydrogen storage capacity of activated carbon pellet bounded by Lignocellulose liquid

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Hydrogen adsorption capacity of different treatment activated carbon namely granular and pellets bounded by Lignocellulose liquid have been studied. It was found that mixing between the liquid Lignocellulose and nano particle powder of activated carbon to form pellets is suitable for use with mass ratio 3:4, because after the reactivation process during 1 hour, the form of activated carbon pellets remained stable. The surface area of the samples is shown in Table 1, the pellet has lower surface area, it is because of the Lignocellulose liquid tends to close the pores of the activated carbon. The capacity of hydrogen adsorption on activated carbon pellet form is tested using the adsorption volumetric method with a variation of isothermal temperature -5°C and 35°C and pressures up to 4 MPa as shown in Figure 1. The adsorption capacity of activated carbon pellet is better than the of granular activated carbon as shown in Figure 2, it is because after the reactivation of an increase in the electrostatic forces between the molecules and the content of the element carbon (C) and the reduction of elemental impurities in the activated carbon pellet form. Maximum capacity of hydrogen adsorption on activated carbon pellet occurs by reactivation of an hour which is 0.0016873 kg / kg at a temperature of -5°C and pressure of 3854.83 kPa. The effect of the isothermal temperature on the adsorption capacity for pellet activated carbon is shown in Figure 3; the lower temperature the higher adsorption capacity. Adsorption isotherm data obtained correlated to the three-equation model of the Langmuir, Toth and Langmuir-Freundlich. It turned out that the Langmuir-Freundlich equation model has the smallest deviation is 7.1% for granular activated carbon and 5.5% for pellet 1 hour reactivated.

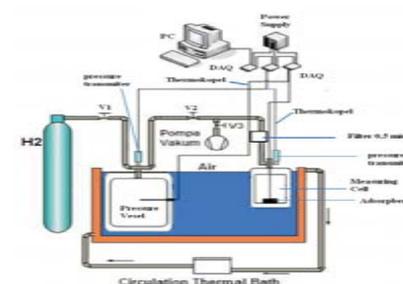


Figure 1. Volumetric adsorption testing apparatus

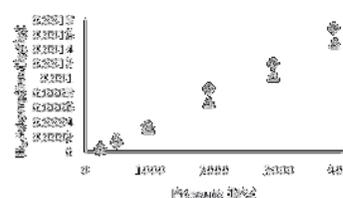


Figure 2. H₂ Adsorbed on granular (▲) and pelleted (◆) activated carbon

Sample	Surface area (m ² /g)
Granular	729.944
Pellet Reactivated 1 hour	331.921

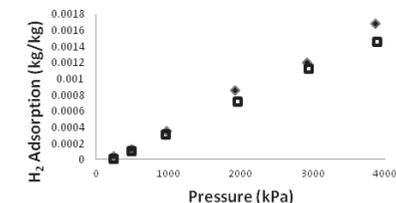


Figure 3. H₂ Adsorbed on 1-hour pelleted activated carbon at -5°C (◆) and 35°C (■)

Keywords hydrogen storage; adsorption; activated carbon; pellet

Hydrogen storage via liquid organic carriers: a microscopic view

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The most serious challenge of hydrogen technology is related to storage, with existing technologies requiring either high pressures or cryogenic temperatures. Chemical hydrogen storage represents an interesting alternative, with so-called Liquid Organic Hydrogen Carriers (LOHCs) providing particularly promising properties. N-ethylcarbazole (NEC) has been identified as one attractive candidate which is reversibly hydrogenated to dodecahydro-N-ethylcarbazole (H12-NEC), taking up 5.8 wt% of hydrogen. As H12-NEC has many physico-chemical similarities to Diesel, LOHC systems based on NEC/ H12-NEC could make use of the existing energy infrastructure and, therefore, enable step-wise replacement of the existing hydrocarbon fuels.[1] Besides, LOHC technology provides a very attractive new way to store temporary energy over-production from renewable sources, even at longer timescales. The current challenge for implementation of LOHCs in mobile applications is related to the noble-metal demand of conventional dehydrogenation catalysts. Sufficiently fast and dynamic dehydrogenation requires catalysts containing large amounts of supported Pt or Pd. Careful design of dehydrogenation catalysts that combine highest activity, selectivity, and stability with low noble metal content could pave the way for LOHCs in future energy technology.

Despite the great technical potential of the concept, very little is known on the underlying reaction mechanisms at the microscopic scale. Such detailed insight, potentially guiding knowledge-based improvement strategies for existing catalysts, could be provided by appropriate surface science and model catalytic studies.[2]

In this contribution we summarize recent results from a joint project that aims at elucidating the catalytic reaction mechanisms and associated microkinetics of H12-NEC on noble metal model catalysts, ranging from single crystal studies to oxide-supported noble metal nanoparticles. We use a broad range of surface science and in-situ spectroscopic methods to study the interaction of H12-NEC with these systems, including time-resolved infrared reflection absorption spectroscopy, high-resolution photoelectron spectroscopy also using synchrotron radiation, molecular beam techniques, temperature programmed desorption, and temperature programmed reaction spectroscopy, complemented by theoretical studies using density functional calculations.

Detailed insight into the mechanism of adsorption, dehydrogenation, and decomposition of H12-NEC on Pd and Pt catalysts is obtained. Initially, H12-NEC adsorbs molecularly, before on Pd activation occurs via C-H bond scission at specific positions of the carbazole skeleton. Differences in the activation barriers are identified comparing various model catalysts which indicate structure-sensitivity due to a reduced activation barrier at specific nanoparticle sites. Successive dehydrogenation competes with breakage of C-N bond. The activation barrier for the latter process depends on the catalytically active metal and particle structure and size. These findings could explain the different stability of technical dehydrogenation catalysts and may provide strategies towards the development of more stable and metal-efficient catalytic materials. The decomposition intermediates reside on the surface and finally decay into small fragments and atomic species which selectively block part of the reactive sites. We show that sustained dehydrogenation occurs in the presence of these surface species, indicating that they play an important role in moderating the reactivity of dehydrogenation catalysts.

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Keywords hydrogen, liquid organic hydrogen carriers, heterogeneous catalysis, model catalysis

Indoor versus outdoor biohydrogen photoproduction by *Rhodospseudomonas palustris* 42OL

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Hydrogen is a promising energy carrier of the future, nevertheless biohydrogen technologies are still in their infancy. If biohydrogen systems are to become commercially competitive, they must be able to synthesize hydrogen at rates that are sufficient to power fuel cells of a sufficient size to carry out practical work [1]. Before the concept of hydrogen economy becomes a reality, a safe, economical, sustainable way of production needs to be developed [2]. Biological hydrogen photoproduction by photosynthetic bacteria could be a promising process for solar energy conversion. Advancements in hydrodynamic aspects, bioreactor design, gas separation, light intensity and its distribution through culture thickness are the key points for improving the hydrogen yield [3]. Besides, the growth strategy could be a relevant way to attain high hydrogen yield. We investigated the hydrogen photoproduction by *Rhodospseudomonas palustris* 42OL cultured under both artificial and natural light radiation. For indoor experiments, four cylindrical photobioreactors (PBR) of different internal diameters (i.d. of 4.0 cm; 7.6 cm; 9.6 cm and 13.0 cm) were used. Indoor experiments were carried out at the irradiance of 480 W/m² and at constant temperature (30 °C); outdoor investigations were performed in autumn using an underwater tubular photobioreactor (UwTP) with a pipe i.d. of 4.8 cm. The organic carbon source was malic acid, which is a compound of wine-distillery waste [4]. In the future, the use of cheaper materials would undoubtedly make hydrogen production process more competitive than the conventional hydrogen generation process [5]. Nevertheless, the high hydrogen yield remains the ultimate goal and the main challenge for the biohydrogen research and development [6]. We used two growth strategies: (i) batch and (ii) semi-continuous regime. The daily average hydrogen production rate (HPR_{av}) attained under batch-growth operation was 222 ± 18 ml(H₂)/l/day, which increased to 655 ± 85 ml(H₂)/l/day under semi-continuous regime, corresponding to 27.3 ± 3.5 ml(H₂)/l/h. This rate reduced drastically outdoors (9.8 ml (H₂)/l/h). Peaks of 32.7 ml (H₂)/l/h and 15.5 ml (H₂)/l/h were obtained indoors and outdoors respectively. The hydrogen yield of 3.03 mol H₂/mol malic acid was achieved indoors under the semi-continuous regime. Our study demonstrated that the hydrogen production rate (HPR) is greatly affected by the diameter of photobioreactors and an inverse relationship links the HPR to the diameter of the reactor.

Keywords *Rhodospseudomonas palustris*; hydrogen production rate; photobioreactors

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Kinetics of $Ce_{0.95}Li_{0.05}O_{2.6}$ solid solution in the O_2 -releasing step for solar hydrogen production

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Thermochemical two-step water-splitting cycle includes two steps: O_2 -releasing step and H_2 -generation step. These two steps proceed cyclically to produce hydrogen. This work investigated the reaction mechanism in the O_2 -releasing step. The valuable information obtained could provide a new insight into developing reactive ceramics and designing reactors for solar hydrogen production.

$Ce_{0.95}Li_{0.05}O_{2.6}$ was synthesized by a polymerized complex method. Powder X-ray diffraction (PXRD) of synthesized sample suggests that synthesized $Ce_{0.95}Li_{0.05}O_{2.6}$ solid solution has a cubic fluorite structure. Thermogravimetric analysis (Fig.1) shows that the reaction mechanisms are different at different temperatures: 2nd-order reaction mechanism in the low temperature range and R2 (contracting-area model) in the high temperature range. The activation energy in the high temperature range is approximately two times of that in the low temperature range. The totally different activation energies indicate that the reaction mechanisms shift during the O_2 -releasing step as temperature goes up. PXRD patterns before and after O_2 -releasing step display that there is no phase transition during O_2 -releasing step. SEM images before and after O_2 -releasing step shows that particle size increases during O_2 -releasing step because of sintering at high temperatures, and thus the shift in reaction mechanisms in the O_2 -releasing step is due to sintering at high temperatures.

Keywords reactive ceramic; two-step water-splitting cycle; O_2 -releasing step; solar hydrogen

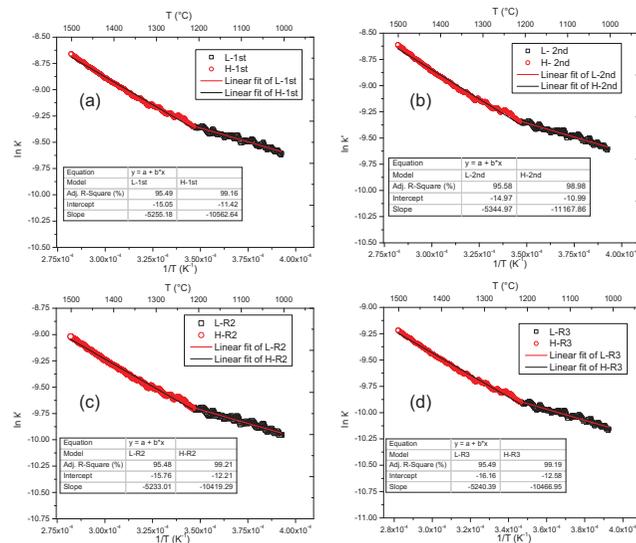


Fig. 1 Arrhenius plots of different models of the $Ce_{0.95}Li_{0.05}O_{2.6}$ solid solution fitted by two-stage linear fit within the whole temperature range (low-temperature range and high-temperature range, L and H denote the lower temperature range and higher temperature range, respectively.) in the O_2 -releasing step; (a) 1st-order model; (b) 2nd-order model; (c) R2 model; (d) R3 model.

Microbial Hydrogen and Ethanol production from biodiesel waste glycerol via “dark”fermentation

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The need of hydrogen (H_2) is increasing globally for its demand in fertilizers, chemical plants, and food production and mainly as a sustainable energy carrier since it has a high energy yield (122 kJ/g), which is about 2.75 times greater than that of hydrocarbon fuels.

Biohydrogen production via dark fermentation is preferable because it uses different spectrum of substrate and requires less energy [1 and 2]. Glycerol is selected as a substrate because 1 kg is generated for every 10 kg of biodiesel produced, and the rapid increase in biodiesel production will result in a considerable surplus of glycerol in the near future. Therefore, developing a new method to treat the waste containing glycerol is important. Several biological treatments of glycerol-containing wastes have been reported. Production of H_2 and ethanol from glycerol wastes by using microorganisms is attractive because H_2 can be applied to fuel cells to generate electricity and heat while ethanol can be used as a raw material, a gasoline supplement and a feedstock for biodiesel production instead of methanol.

Biodiesel waste glycerol was used as a substrate for H_2 production in 1.2 L batch bioreactor dark fermentation system using a mixed culture of comparatively selected strains of *Enterobacter* spH1 and *E.coli* CECT432. *Enterobacter* spH1 was selected as a best hydrogen and ethanol producer from our previous comparative study between new isolated strains. This strain showed higher glycerol uptake efficiency (85.75 %) than glucose (75.5 %). It had also produced 156.6 mM of H_2 and 178.3 mM of ethanol from glycerol (217.4mM). The same procedure was followed for the comparative study of *E.coli* CECT432, *E.coli* CECT434 and *Enterobacter* MCM2/1. *E.coli* CECT432 was selected due to its higher productivity of H_2 (1306.6 mL/L). The end fermentation product from this strain was similar to the *Enterobacter* spH1 especially in the small amount of 1,2-propanediol production. Therefore, constructing a microbial co-culture (1:1) of *Enterobacter* spH1 and *E.coli* CECT432 was found to have a higher H_2 production (4774.77 mL/L) from pure glycerol (217.4mM). This synergistic effect of co-culture was tested for H_2 production using biodiesel waste glycerol which we found from a biodiesel company in Barcelona, Spain. The glycerol waste mainly consist of (w/v): glycerol 47.5%, water 40.5%, ash content 4.8% and Material Organic Non-Glycerol (MONG) 7.2%. The amount of total soluble organic carbon (TOC) in the glycerol waste was 320 g/L. An overnight cultivated co-culture of 10 % (v/v) was transferred to 450 MY medium contained 20 mL of the glycerol waste. The co-culture produced 3718.06 mL H_2 /L medium, 9.5 g ethanol /L medium and small amount of other end metabolites. This production was attractive because the biodiesel waste containing glycerol was not purified to avoid extra costs. All the H_2 production was carried out over 72 h, by purging continuous argon at 20 mL/L, at a temperature of 37°C and at 200 rpm of agitation.

Keywords: Hydrogen; Dark fermentation; *E. coli*; *Enterobacter* ; Biodiesel ; Glycerol

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Nanocatalyst: Electrospun nanofibers of PVDF- dicationic tetrachloronickelate (II) anion and their effect on hydrogen generation from the hydrolysis of sodium borohydride

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In this work, we report poly(vinylidene fluoride) (PVDF) - dicationic tetrachloronickelate (II) anion (dicationic ionic salt $[C_6(\text{mpy})_2][\text{NiCl}_4]^{2-}$) nanofiber composites as catalyst for hydrogen generation from alkaline sodium borohydride. The nanofiber composites were produced by electrospinning method. The synthesized nanofibers are characterized by SEM, TEM, EDX, and FTIR. The rate of hydrogen generation from catalyzed hydrolysis of alkaline NaBH_4 solution was determined as a function of temperature, substrate concentration, and catalyst concentration in the presence of prepared catalyst. The result shows that IL based nanofiber composite is a highly efficient and most important advantage that it can be easily recovered and repeatedly reused.

Keywords Nanofiber composites; Hydrogen generation; NaBH_4 ; PVDF; Dicationic ionic liquid; Recyclability.

Nobel Bioethanol Steam Reforming Catalysts Based on Delaminated Zeolites Promoted with Cobalt

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Introduction

Support plays an important role in the preparation of highly active and selective bioethanol steam reforming catalysts since it helps in the dispersion of metal catalyst and enhances its activity via metal-support interactions [1]. The singular structure of delaminated zeolites, and particularly the very high and well-defined external surface area, makes these materials attractive to be used as supports for dispersing active metal phases. We have explored the activity of Co metal particles supported over two delaminated zeolites (ITQ-2 and ITQ-18) in the steam reforming of bioethanol. For comparison purposes a commercial amorphous SiO_2 was also used as Co support. The characterization of the catalysts by DRX, BET area, TPR, SEM and TEM, has allowed to establish interesting relationship between the catalytic performance and their physico-chemical properties.

Experimental

Pure all silica delaminated zeolites were prepared as described in [2,3]. Amorphous SiO_2 was supplied by Fluka (silica gel 100). Steam reforming experiments were carried out in a continuous fixed bed reactor at atmospheric pressure, $\text{H}_2\text{O}/\text{BioEtOH}$ molar ratio of 13, GHSV 4700 h^{-1} , atmospheric pressure, and a range of temperatures between 673 K and 873 K.

Results and Discussion

Delaminated zeolites promoting with Co were found more active and selective catalysts than Co supported on amorphous silica, **Figure 1**. The high activity, selectivity, and stability of these zeolitic catalysts have been attributed to the absence of acid sites in the pure silica ITQ-2 and ITQ-18 zeolites, to their high external surface ($>800 \text{ m}^2/\text{g}$ and $>600 \text{ m}^2/\text{g}$, respectively), which would provide a large surface for coke deposition helping to slow down the deactivation effects, and to the especial structure of these delaminated zeolites formed by array of “cups” (**Figure 2**), which would provide an excellent position for the stabilization of the Co metal particles improving their dispersion and preventing their agglomeration.

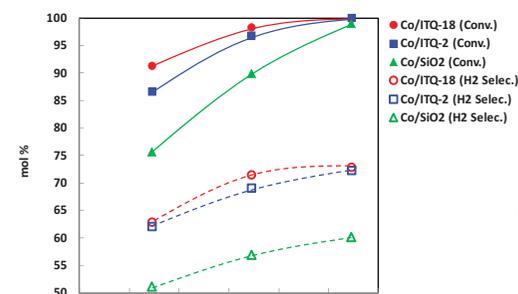


Figure 1. Bioethanol conversion and hydrogen selectivity in the steam reforming of bioethanol using Co supported on delaminated zeolites and amorphous silica. Reaction conditions: $\text{H}_2\text{O}/\text{BioEtOH}$ molar ratio of 13, GHSV 4700 h^{-1} and atmospheric pressure

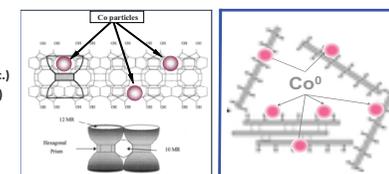


Figure 2. Structure of delaminated zeolites ITQ-2 and ITQ-18

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Keywords: Zeolites, ITQ-12, ITQ-18, Hydrogen, Bioethanol, Steam Reforming.

Noble metal deposited TiO₂/WO₃ composite photocatalysts for hydrogen production: the role of the localization of the gold or platinum nanoparticles

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The synthesis of nanomaterials capable of photocatalytic hydrogen production is nowadays a major research field in materials science. To raise the H₂ production yield, noble metal deposited composite photocatalysts (i.e. WO₃-TiO₂-Au) were obtained and successfully tested.

The main role of the individual oxides combined with the proper noble metal particles in the composite for the hydrogen production is not clarified yet in the literature. In order to find answer for this important question, TiO₂/WO₃/noble metal (Au or Pt) composite materials were obtained using commercial TiO₂ and WO₃. The following WO₃ concentrations were achieved in the composite materials: 1, 3.5, 7, 10, 14, 19, 24 and 33%. The noble metal nanoparticles (1 wt% in the final composite) were deposited selectively by photodeposition (under UV light).

The obtained nanocomposites were successfully characterized by several techniques such as XRD, HRTEM, DRS, etc. The impact of the selective noble metal deposition was successfully investigated by evaluating the photocatalytic hydrogen production from aqueous solution of oxalic acid and the obtained data were further comparatively discussed from the perspective of the achieved structural results.

Acknowledgements: This work was financially supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-ID-PCE-2011-3-0442 and also by the Swiss National Science Foundation (SH/7/2/20). Károly Mogyorósi thanks the financial support of the Hungarian Research Foundation (OTKA PD78378) and the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

Keywords: titanium dioxide; WO₃; hydrogen production; platinum; gold; composite photocatalysts

Novel periodic nanoporous organosilicas for hydrogen and methane storage

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Novel periodic nanoporous organosilicas (PNOs) synthesized by direct co-condensation of tetraethylorthosilicate and triethoxy(naphthalen-1-yl)silane were evaluated for their hydrogen and methane storage ability. Evacuation of the pores from the surfactant of the pristine material (Naph-PNO) was achieved either by treatment with HCl 37 wt % (sample: Naph-PNO-H⁺) or by heat treatment at 623 K (sample: Naph-PNO-350). The naphthalene-based PNO materials exhibit regular hexagonal arrangement of uniform pores, high naphthalene content up to 17 wt %, specific surface areas above 1000 m²/g and pore size distributions (PSD) in the microporous/mesoporous boundary. Methane and hydrogen storage properties, at different temperatures, have been investigated for these samples by Sievert-type apparatus. The samples exhibit a reversible methane/hydrogen surface excess adsorption capacity, with measured maximum uptake of up to 5.27 wt % at 298 K

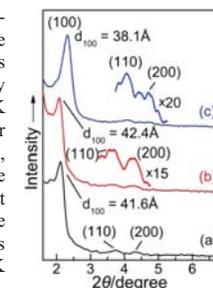


Figure 1. XRD patterns of Naph-PNO (a), Naph-PNO-H⁺ (b) and Naph-PNO-350 (c).

and 3.5 MPa and 2.05 wt % at 77 K and 4.3 MPa respectively. The analysis of the obtained isotherm curves by Tóth equation shows high grade of surface homogeneity of the samples. Total storage capacities were also estimated. For methane a maximum 41.6 v/v at 298 K and 3.5 MPa was found, while for hydrogen a maximum 15.8 g/L at 77 K and 4.3 MPa was calculated.

Table 1. Structural properties and gravimetric and volumetric surface excess adsorption and total volumetric storage capacities of methane (3.5 MPa at 298 K) and hydrogen (4.3 MPa at 77 K) for samples Naph-PNO-H⁺ and Naph-PNO-350.

Sample	S_{RET} (m ² /g)	V_{pore} (mL/g)	d_{BJH} (Å)	d_{app} (g/mL)	Grav. CH ₄ (wt %)	Vol. CH ₄ (v/v)	Vol. CH ₄ (v/v)	Grav. H ₂ (wt %)	Vol. H ₂ (g/L)	Vol. H ₂ (g/L)
Naph-PNO-H ⁺	1016	0.43	20.4	0.13	4.33	8.35	39.86	1.91	2.53	15.66
Naph-PNO-350	1076	0.57	22.0	0.13	5.27	10.26	41.60	2.05	2.72	15.77

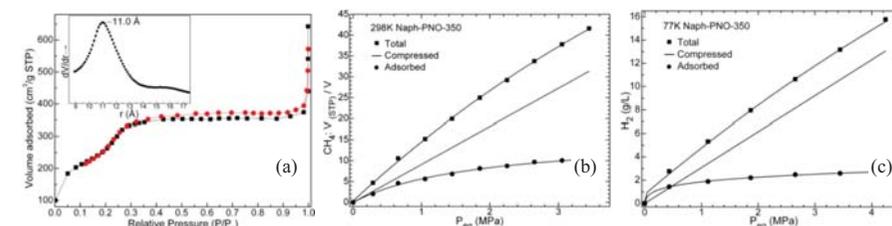


Figure 2. (a) Nitrogen adsorption-desorption isotherm of Naph-PNO-350. Inset: corresponding PSD calculated with the BJH method. (b) Total, compressed and adsorbed CH₄ volumetric (v/v) storage capacity of Naph-PNO-350 up to 3.5 MPa at 298 K. (c) Same for H₂ volumetric (g/L) storage capacity up to 4.3 MPa at 77 K.

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Keywords naphthalene; grafting; periodic mesoporous organosilicas; nanoporous; hydrogen storage; methane storage

On-site sodium metal production for hydrogen generation on sea and on-demand hydrogen power generation on land

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Hydrogen can neither be stored nor transported at room temperature under the atmospheric pressure, but coal and oil can be done. The storage and transportation barriers of hydrogen have been broken through by sodium metal "Source of Hydrogen". A large amount of hydrogen is generated immediately when water is added to the sodium metal at a thermoelectric power plant, and power whose energy is 4.4 times as much as the fossil fuel is generated by hydrogen combustion. Salt that is the raw material of sodium is distributed evenly in the sea and widely on the Continents as rock salts and salt lakes in the world, and there is neither maldistribution nor worry of exhaustion. It not only removes the maldistribution of the fossil fuel, which is one of the factors to threaten the energy security, but also limits the damage or disorder caused by a natural disaster, terrorism, or accident as much as possible by delivering the sodium metal produced on site to a thermoelectric power plant in the consumption place. The power plant waste is water only, and no CO₂ and radioactivity at all. Therefore, it contributes to the environmental protection of the earth as an environmentally friendly power plant.

Figure 1 shows the conceptual diagram of the sodium metal production with seawater and offshore wind power generation. Generally, sodium metal needs high power for production, which is very expensive. In the process of manufacturing sodium metal and generating hydrogen, however, fresh water, sulfuric acid, hydrochloric acid, sodium hydroxide, and magnesium are produced as by-products. They are also the ones that consume electricity at high rate in production. These by-products alone are payable, so the economical efficiency is high. Moreover, the production site is conveniently located on the raw material, seawater, and the indoor power plant is operated by natural resources such as wind, tidal, or solar energy. The economic benefit, therefore, is collectively enormous. And, the sodium metal is transported to the land, where it reacts with water to generate hydrogen; hydrogen produced is used to generate electricity at a thermoelectric power station, and sodium hydroxide, a by-product, is supplied as raw material to soda industries for almost nothing.

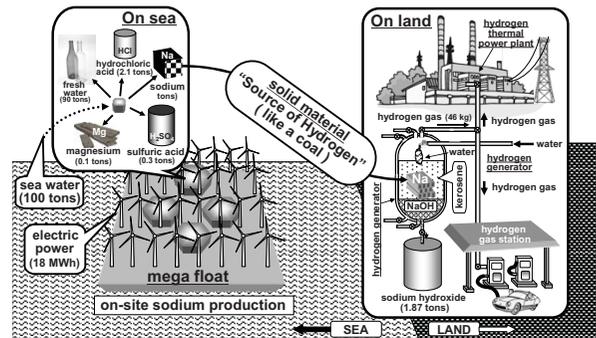


Fig. 1 On-site sodium metal production from seawater by wind power on sea and on-demand hydrogen power generation on land.

Keywords sodium metal production for hydrogen generation; source of hydrogen; hydrogen storage material; offshore seawater electrolysis; offshore wind power generation

Optimal operational conditions to work on alkaline water electrolysis with stainless steel 316L electrodes

Lavorante, M.J., Kenigsberg, J., Gavarini, A., Franco, J.I., Fasoli, H.J. y Sanguinetti, A.

In this work we investigated the effect of the physical separation, the gap between electrodes and the use of the same electrode material (stainless steel 316L) with and without a chemical acid treatment and agitation of the solution, with the purpose of establishing the optimal operational conditions in alkaline water electrolysis for a specific electrolyte prototype. In order to study the effect of the separation distance between electrodes, we designed and built different devices and further analyzed important parameters such as current density, resistance and voltage needed to break the water molecules into oxygen and hydrogen, in different experimental conditions. The results obtained in our experiences showed that the presence of a physical separation for the hydrogen and oxygen separation process increases resistance but when the electrodes are near each other (no more than 5 mm) the current density increases. The resistance increased almost linearly with the distances proposed in this work (6 to 22 mm) when the same type of electrode was used; no evidence of bubble resistance were observed in the nearest gap between electrodes, tested, although this could not be confirm in smaller distances. The behavior of the resistance of all the types of electrodes used is also analyzed in this work in order to select the most suitable type of electrode to use for a specific distance. We observed that agitation improves the performance of the system when electrodes with a chemical acid treatment where tested because it favors the removal of the bubbles formed in their tortuous surface.

Optimization of the synthesis method and gold nanoparticle size of TiO₂-Au photocatalysts for hydrogen production

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In the present work gold deposited Aeroxide (Degussa) P25 and Kronos VLP7000 titanium dioxide photocatalysts were prepared with 1 wt% noble metal loading. Our main objective was to investigate the photocatalytic performance of these photocatalysts for hydrogen production. For efficient hydrogen production in irradiated titanium dioxide suspension, there are two prerequisites: (i) efficient hole scavenging by an organic compound that might be easily oxidized even in the absence of molecular oxygen and (ii) the presence of active surfaces without having overpotential for hydrogen evolution. The noble metal deposition onto the titania surface was achieved by chemical reduction in situ on the titania photocatalysts (CRIS) or by mixing chemically reduced gold nanoparticles in sols with the aqueous suspensions of the photocatalysts (sol-impregnated samples, CRSIM).

UV photoreduction and these two chemical reduction processes were thoroughly compared under different reaction conditions. The catalysts were washed by centrifugation in order to remove chloride, borohydride and citrate ions and any unreacted traces from the surface. We investigated the influence of the noble metal and the titania particle size on the photocatalytic activity.

To determine gold particle size, the samples were examined with X-ray diffraction (XRD) measurements and with transmission electron microscopy (TEM). A representative diffraction peak at 38-39° (2θ) can be used to estimate the average gold particle size of the samples using the Scherrer-equation. TEM images revealed the presence of 2.5-10 nm gold-domains on the surface of the TiO₂-Au catalysts.

Hydrogen production measurements were carried out in the absence of dissolved oxygen. Photocatalytic activity of the samples was studied in near-UV light irradiated ($\lambda_{\text{max}} = 365 \text{ nm}$) aqueous TiO₂ suspensions in a photoreactor, using oxalic acid or methanol as model compound. The hydrogen-flow was measured by gas chromatography and the decomposition of oxalic acid by HPLC. In these measurements, the H₂ production rates of the Au-deposited photocatalysts were dependent on the gold particle size. We obtained the optimal particle size, at which the photocatalytic activity is the highest. It was observed that the samples made by the photoreduction process were significantly less efficient compared to the chemically reduced gold deposited TiO₂ samples due to the large gold particle size. The optimal diameter for gold nanoparticles was found to be about 5 nm for both titania samples. Although Kronos vlp7000 owns significantly higher specific surface area (296.5 m²/g) compared to Aeroxide P25 (49 m²/g), the best measured photocatalytic performance was approximately the same for both titania due to the similar adsorption capacity of the substrate. Comparing the quantum yield of the most effective TiO₂-Au catalyst for H₂ production and for the oxalic acid decomposition it turned out that hydrogen mostly evolves from the organic sacrificial compound.

These experiments confirmed that suitable gold modified catalysts can be synthesized for efficient hydrogen production that are potentially able to utilize solar irradiation and purify different industrial wastewaters containing organic pollutants. This method could be useful for the disposal of environmentally harmful or toxic solutions and organic solvents and for hydrogen production at the same time.

Acknowledgements: This work was financially supported by the Swiss National Science Foundation (SH/7/2/20). KM thanks the financial support of the Hungarian Research Foundation (OTKA PD78378) and the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

Keywords: size dependent activity; gold nanoparticles; titanium dioxide; solar energy; hydrogen production; photocatalysis

Optimizing metal alloys for H₂ separation from gas mixtures

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Membrane reactors used to enhance the efficiency of industrially important chemical reactions are limited by the lifetime of the membrane material and the related costs of downtime and replacement. The need for high permselectivity and stability, both under high pressure, temperature and in a corrosive environment, puts stringent requirements on the materials used.

Computational materials design speeds up the development and optimization of metal alloys because relatively fast screening of potential alloys can be achieved, thereby obtaining quantitative information about the solubility of hydrogen, volume changes upon hydrogenation, indications of the effect of alloying on diffusion and phase boundaries. The newly developed computational scheme starts from ab-initio calculations through statistical thermodynamics to the representation of actual alloy systems. It will be shown that relaxation and short-range ordering play a fundamental role in the potential performance of alloys.

By means of these combined calculations the hydride formation and critical temperature can be predicted as a function of the composition of the metal-matrix and the hydrogen content. The principles of this method and its ability is illustrated by examples of newly designed, multi-component metal-based membranes of high thermal and mechanical stability that meet criteria such as a critical temperature for hydride formation below a pre-defined operating temperature and high hydrogen solubility.

Optimum Conditions for Efficient Hydrogen Generation in Water Electrolyzer Powered by a Solar cell or by a Power Supply

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Water electrolysis to hydrogen and oxygen can be carried out by potential control or by current control in a single compartment electrochemical cell with two or three electrode systems. In a practical electrolyzer two electrodes are used without the use of a reference electrode as third electrode. In this study we report the optimum electric power needed to be supplied by a solar cell or a power supply for efficient electrolysis of water to hydrogen and oxygen. Water electrolysis experiments were carried out using different combinations of current and voltage to different powers. During the electrolysis hydrogen current density decreased considerably within 5 minutes from 88.0 mA to 4.0 mA when an external power of 175.8 mW (= 87.9 mA x 2.0 V) was supplied from a power supply, but from an initial 88.0 mA to 15.9 mA in the case of an applied power of 222.0 mW (= 88.8 mA x 2.5 V), from initial 88.0 mA to 48.0 mA when power of 310.8 mW (= 88.8 mA x 3.5 V) was applied from the external power supply, and finally from an initial 88.3 mA to 88.0 mA when power supply supplied a power of 353.2 mW (= 88.3 mA x 4.0 V). These results indicate that the initial current or current density cannot be maintained if power and voltage supplied from power supply are not optimum to overcome the extra resistances developed due to oxygen gas and hydrogen gas evolution at the anode and cathode respectively. According to the experimental observations during this study the power of 353.2 mW (= 88.3 mA x 4.0 V) was found to be optimum since the initial hydrogen current was closely maintained at 88.0 mA. Similar experimental results were observed for photoassisted water electrolysis when the external power was solely supplied by a silicone based solar cell. Within 5 minutes hydrogen current decreased from its initial value of 75 mA to 10 mA when a solar cell (solar cell-1) supplied a power of 194.7 mW (= 88.5 mA x 2.2 V) under solar simulated light illumination of 1 sun (100 mW.cm⁻²), and from an initial value of 75.0 mA to 70.0 mA when an external power of 255.2 mW (= 88 mA x 2.9 V) was supplied from another silicone based solar cell (solar cell-2) under the same illumination conditions. Solar cell 2 with a photoactive surface area of 9.6 cm² that generated the steady state current of 70.0 mA shows a solar to hydrogen (STH) efficiency of 8.97 %, whereas solar cell-1 having a photoactive surface area of 4.90 cm² that generated the steady state current of 10.0 mA shows a STH efficiency of 2.51 % under the same illumination conditions. These results clearly indicate that it is vital to have a solar cell with an optimum power and voltage to achieve and maintain a high desired STH efficiency of ≥ 10.0 %.

Permeation of hydrogen and other types of buoyant gases through foils for balloons and their tensile properties

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The application of novel materials for buoyant, rotating, cylinder shaped balloons filled with hydrogen or small (buoyant) gases requires an analysis of optimal solution considering permeation and mechanical properties. In order to make a materials selection for this wind power system easier, it is desirable to have more information on potential envelope materials.

In this work different monolayered and multilayered foils for such balloons are considered, all of them purchased by respective producer. The foils tested are Polyester-Polyurethane of 100 μm thickness, Heptax of 25 μm thickness, Octax of 25.3 μm thickness, EVAL of 60 μm thickness, Epurex of 80 μm thickness, Aerofabrix of 50 μm thickness, and Aerofabrix blue of 70 μm thickness. All the foils are thermally bondable and all the tests are performed both on thermally seamed and seamless foils.

Permeation tests are performed by means of the time-lag method, with hydrogen, helium and nitrogen. Mechanical properties are tested under long time and short time tensile stresses, by means of a standard tensile machine and an impact tensile apparatus (Charpy), respectively. Since machining influences molecular orientation, leading to a potential anisotropy, both mechanical tests are performed on the machining direction and on the direction perpendicular to the machining. First tests on dynamic mechanical behavior of the thin foils on a large temperature range from -190 °C up to 140 °C are performed as well giving information on complex modulus, mechanical damping and energy losses depending on temperature. These dynamic tests under tensile tests are performed by means of Dynamic Mechanical Analysis (DMA).

There is not any generally superior foil. The final choice has to be made considering conditions under which the foil will be used.

Keywords gas permeation; mechanical tests; hydrogen; buoyant gases; foils; balloons

Reforming methane towards hydrogen and aromatic hydrocarbons on highly stable Mo and Re/H-ZSM5 catalysts modified with La

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Catalytic performance of highly stable catalysts for dehydroaromatization (DHA) process of methane with few percent of CO₂ and H₂O in stream was studied. The direct conversion of methane to aromatics, for instance, benzene, naphthalene and hydrogen was studied over Mo and Re/H-ZSM5 modified with selected rare earth element- lanthanum. Catalysts were prepared by incipient wetness impregnation and by physical mixing. Significant decrease in coke selectivity, while at the same time increasing in selectivity towards ethane, ethylene and benzene was observed under the typical reaction conditions when Mo and Re/H-ZSM5 were doped with a small amount of La. Longtime experiments displayed very good stability of Re and Mo/H-ZSM5 modified with La. Lanthanum promoter led to the lower oxidation temperature (TPO experiment) and reduced amount of coke on the Mo and Re/H-ZSM5 catalysts. X-ray diffraction experiment revealed that La₂O₃ transforms under CO₂ atmosphere at 773 K and 0.1 MPa to crystallographic form La₂O₂CO₃. It was proposed that La₂O₂CO₃ as a transitional phase reacts with surface carbon (C), than transforms to La₂O₃ and CO under the reaction conditions and thereby prevents mouth clogging of zeolite pores. DHA process was suggested as possible adoption in biogas plant, Fig.1. Recently much of methane has been found in remote locations in Poland eg. shale gas, which makes it difficult to monetize the gas. A process that converts methane to hydrogen and aromatics would have significant commercial value.

Key Words: biohydrogen; dehydroaromatization; Mo/ZSM-5, Re/H-ZSM5 catalyst; promotion by La; benzene; methane valorization; biogas; shale gas; biorafinery

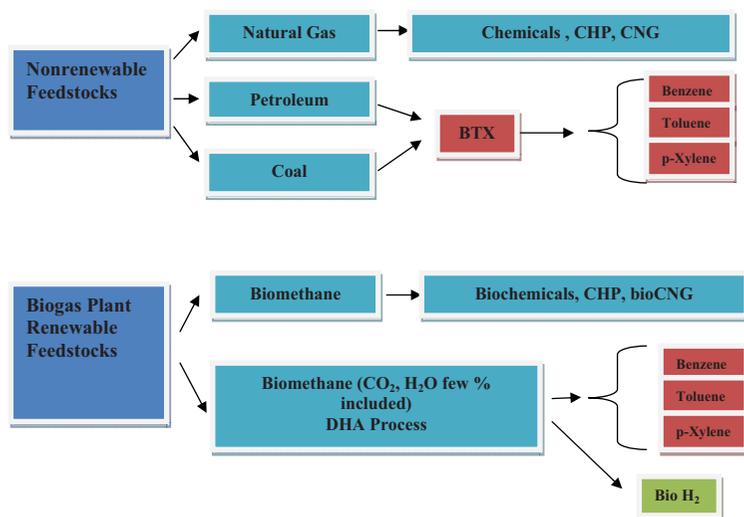


Fig.1 Comparison of simplified scheme of Petrochemical Refinery and Biogas Plant as a Biorefinery with adopted process of dehydroaromatization of methane (DHA)

Relationship between structural features and catalytic activity in WGS and PROX reactions over gold catalysts on Fe-modified ceria

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Hydrogen is an ideal fuel with the advantage of high efficiency and zero emissions. Following the reforming process, water gas shift reaction (WGS) and preferential CO oxidation in H₂-rich stream (PROX) are widely applied as catalytic processes for CO removal regarding pure hydrogen production for fuel cells application. Recently, gold catalysts on ceria based supports have attracted a significant interest as low-temperature shift and PROX catalysts. In the present study two series of Fe-modified ceria supports with 5, 10 and 20 wt% Fe₂O₃, were prepared by incipient wetness impregnation (IM) or by mechanochemical mixing (MM). Gold (3 wt%) was loaded by deposition-precipitation method. The catalyst were denoted as AuxFeCe (x = 5, 10 and 20). The catalysts were characterized by XRD, HRTEM, AFM, XPS and TPR. A detailed investigation by Mössbauer spectroscopy of fresh and used in WGS and PROX samples was carried out as well. The aim was to shed light on the relationship between the gold particles size and supports' structural features, and catalytic properties.

In Fig. 1 is illustrated the comparison of the catalytic activity (expressed as degree of CO conversion) in WGS at 250°C (a) and in PROX at 100 °C (b). Significantly higher WGS activities exhibited the gold catalysts on Fe-doped ceria prepared by MM. Concerning PROX, the differences in the catalytic activity and selectivity depending on the preparation method and dopant amount, were not very significant. The best Au10FeCeMM catalyst showed not very significant drop of the activity and selectivity after adding CO₂ and H₂O to the gas feed.

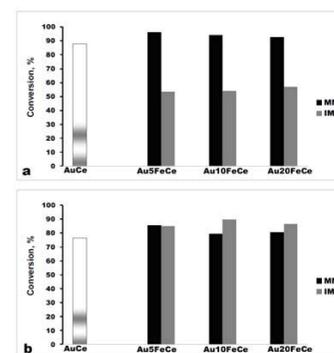


Fig. 1. Bar diagram on the CO conversion: (a) in WGS and (b) in PROX.

The XRD and HRTEM data showed that the supports' preparation by MM was beneficial for growth of highly dispersed gold particles controlling the high WGS activity. In addition, the cooperative effects of the Fe-modified ceria and the formed under WGS conditions defective magnetite phase (Mössbauer results), contribute for the significantly better catalytic performance in WGS of gold on MM prepared mixed Ce-Fe supports. Mössbauer results revealed higher cation deficiency in the magnetite phase for the gold catalyst with 5 wt% Fe₂O₃ correlating with its highest activity in WGS.

The comparison of Mössbauer parameters of the fresh samples and that after testing in PROX, showed insignificant changes in the initial Fe-phases for both preparation methods. The role of iron is like ceria modifier, improving the ability of ceria supports for supplying oxygen to facilitate the CO oxidation in the presence of H₂. These results, together with the fact that differently from WGS the extremely small gold particles are not beneficial for high PROX activity, could explain the observed

performance in PROX, insignificantly depending on the used preparation method and the Fe-dopant amount. However, the impregnation mode has an important role related to the coverage of the CeO₂ grains with nanosized hematite phase (confirmed by Mössbauer results and in agreement with AFM images), which could lower the surface basicity and by this way could explain the improved resistance toward CO₂ in the feed.

Acknowledgements: The study was performed in the frame of NATO Project CLG 984160 and COST Action CM 0903/02. L.I. is grateful for the financial support via project BG051PO001/3.3-05-001.

Keywords gold catalysts; Fe-doped ceria supports, WGS, PROX

Resent progress in storage of compressed hydrogen in glass multi-capillaries

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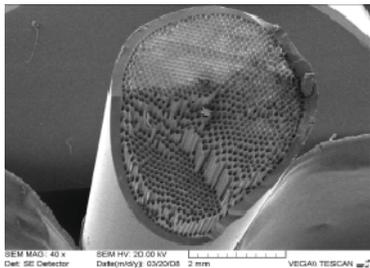
Compressed hydrogen may be the best near-term solution for mobile hydrogen storage due to the relative simplicity of producing gaseous hydrogen and rapid refuelling capability. Unfortunately, hydrogen diffuses more easily through many conventional materials used for vessels, and through gaps that are normally small enough to seal other gases safely. It can cause metal material embrittlement resulting in serious reduction in ductility, cracking and failures well below the normal yield stresses. Obviously, there is the need for more safe and cost-effective hydrogen storage vessels compared to usual steel or advanced composite tanks. To solve the existing problems of hydrogen storage we developed [1, 2] a revolutionary technology that has ground-breaking implications on the ability to utilize compressed hydrogen as an alternative energy resource in a cost effective, safe and environmentally friendly manner. Particularly, using glass capillary arrays shown below we achieved 48.3 g/l volumetric and 10.2 % gravimetric capacity of hydrogen storage vessels [3]. The values are above the US Department of Energy 2010 targets for the on-board hydrogen storage systems and we believe that the 2015 targets are achievable. The developed technology of gas storage is applicable to methane and hythane (H₂ - CH₄ mixture), which bridge the gap between conventional fossil fuels and the clean future of a hydrogen economy, as well as to other gases, i.e. oxygen.

The present paper describes the results of our resent experiments with various glass capillaries and capillary arrays compounded with epoxy resins or polyimides. We demonstrated that the theoretical strength of glass 70 GPa, far above the strength of steel, can be reached in thin enough glass capillaries drawn from the melt. We discuss methods of gas injection to and withdrawal from the capillaries to a fuel cell, as well.

The work is performed according to the contract 16.516.12.6009 with the Ministry of Education and Science of Russian Federation.

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Keywords hydrogen storage; pressurised gas, glass capillary; gravimetric capacity, volumetric capacity



SEM image of a glass capillary array

Selectivity of MCH dehydrogenation over monometallic and bimetallic Pt catalysts

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Hydrogen storage for mobile and stationary applications is an expanding research topic. One of the more promising storage techniques relies on the reversibility, high selectivity, and high hydrogen density of liquid organic hydrides, in particular methylcyclohexane (MCH). Catalyst evaluation for MCH dehydrogenation to toluene is based on three catalytic parameters: activity, selectivity, and stability. Current catalysts, optimized for catalytic reforming, do not meet the targeted aromatic selectivity (+99%) for MCH dehydrogenation. Therefore, a range of Pt catalysts was prepared and compared with commercially available ones in a fixed bed reactor under operating conditions suitable for mobile and stationary applications. It was found that the best overall performance was realized by a particular monometallic Pt catalyst. This catalyst showed superior activity, selectivity, and stability compared with other prepared and commercial catalysts. As an effort to further enhance the aromatic selectivity, this study identified the main side-reactions associated with MCH dehydrogenation, the effect of operating parameters on by-product yields, and the effect of catalyst deactivation on the long-term selectivity.

Keywords: Hydrogen Storage, Organic Hydride.

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Simultaneous photoelectrochemical hydrogen generation and organic compound oxidation under W/WO₃ photoanode

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The photoelectrochemistry is a technique based on the irradiation of a semiconductor often a p type. When the semiconductor materials is under illumination, holes (h⁺) are generated in the valence band and electrons (e⁻) are generated in the conduction band. In order to minimize the h⁺/e⁻ recombination, the system is biased as the electrons are redirected to the auxiliary electrode. The photoelectrocatalysis is being widely employed in the oxidation of organic compounds for many years. The hydrogen generation is a challenging research topic which has received much attention in recent years for its potential to provide H₂ as a clean and renewable energy resource by the reduction of protons. Although the possibility of oxidizing organic matter and simultaneously generate hydrogen is real, this research field is not being appropriately explored. For this purpose, the development of new materials which can be activated by both visible light and then used for hydrogen generation and organic compound oxidation is of great importance. Semiconductor electrodes of nanoporous W/WO₃ obtained by anodization method in a 0.15 mol L⁻¹ sodium fluoride solution (2 hours, 60 V) were prepared, characterized and after that applied on the oxidation of a synthetic organic dye (reactive black 5) and hydrogen evolution. Finally, the optimized electrode was employed as photoanode on the photoelectrocatalytic oxidation of 1.0x10⁻⁵ mol L⁻¹ of reactive black dye under visible light and UV light, a Pt gauze was used as the counter electrode and Ag/AgCl (sat) as the reference electrode. This system was biased at +1V, the pH at de anodic compartment was 6 and pH at the cathodic compartment was 4. Under these best experimental conditions, a pseudo first order kinetic of 2,67x10⁻² min⁻¹ under visible light and 2,90 x10⁻² min⁻¹ under UV light were observed after 120 minutes of photoelectrocatalysis leading to 96% and 97% of color removal, 55% and 62% of TOC removal and the hydrogen efficiency was of 14% and 28% under visible and UV light respectively. This results indicate that the photoelectrochemical method is promising for both organic compound oxidation and hydrogen generation.

Keywords hydrogen; textile dye, photoelectrocatalytic oxidation, W/WO₃, visible light.

SiN films as an efficient hydrogen permeation barrier

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An efficient reduction of gaseous hydrogen isotope permeation through a metal wall is essential in several applications like hydrogen storage & distribution, hydrogen embrittlement protection, and control of the tritium inventory in future fusion reactors like DEMO. Normally, a thick metal construction provides the necessary mechanical stability of the membrane or device while a deposited coating is supposed to impede the migration of the hydrogen isotopes. Several materials known to have low diffusivity and/or low solubility for hydrogen are therefore expected to act as an efficient hydrogen permeation barrier. In this work we present our research on the efficiency of SiN films as hydrogen permeation barriers.

Amorphous SiN films, 500-nm and 700-nm thick, were deposited on Eurofer substrates applying reactive radio frequency magnetron sputtering from pure Si targets in an argon/nitrogen atmosphere. The hydrogen permeation through such double-layered, 40-mm-diameter membranes at 400 °C and 1 bar upstream pressure involved using a conventional technique with enhanced sensitivity. Extremely high barrier efficiency for these SiN films with respect to hydrogen, expressed as a permeation-reduction factor in excess of 2000, was only achieved with films containing 6–7 atomic percent of hydrogen. The achieved permeation reduction factor at 400 °C corresponds to SiN permeability which is as low as $P = 1 \times 10^{-17}$ mol H₂ / s m Pa^{0.5}. Hydrogen concentration in the SiN films was determined by Elastic Recoil Detection Analysis, which indicated that this high hydrogen concentration represents only the strongly bound hydrogen that is not mobile at this low temperature but impedes the mobility of the diffusive hydrogen. A SiN film with a low H content is shown to be a far less efficient barrier.

The hydrogen evolution reaction on electrolytic nickel – based composite coatings containing molybdenum or tungsten nanopowders

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The electrocatalytic processes occurring on the electrodes depend considerably on the chemical nature of the substrate, dimension of its crystallites, morphology of the surface, presence of structural defects and chemical and phase composition. The factors mentioned above depend strongly on the method of preparation of electrode materials. They are exceptionally important when the electrode surface is covered by a layer of electrolytically deposited metal and when this metal is enriched by additional component playing the role of activator in electrochemical processes.

This study was undertaken in order to obtain Ni+Mo and Ni+W composite coatings by electrolytic codeposition of crystalline nickel from an electrolyte containing suspension of molybdenum or tungsten nanopowders. A scanning electron microscope was used for surface morphology characterization of the coatings. Chemical composition of obtained coatings was determined by X-ray fluorescence spectroscopy method (XRF) and phase composition investigations were conducted by X-ray diffraction method. The behaviour of obtained coatings was investigated in the process of hydrogen evolution reaction (HER) from 5 M KOH using steady-state polarization and electrochemical impedance spectroscopy (EIS) methods. It was found that Ni+Mo composite coatings are characterized by enhanced electrochemical activity towards hydrogen evolution as compared with Ni+W composite coatings. Thus obtained coatings may be useful in application as electrode materials for the hydrogen evolution reaction in comparison with Ni+W composite coatings.

Keywords: Ni+Mo coatings, Ni+W coatings, electrodeposition, hydrogen evolution reaction

Theoretical study of H adsorption on FeNi(111) surface

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Iron promoted nickel based catalyst has been developed for high yield hydrogen generation through ethanol reforming. The reaction results show a remarkable improved durability in catalytic activity as well as selectivity to hydrogen.

The adsorption of H on FeNi(111) has been analyzed at theoretical level by tight binding calculations. Different sites on the surface were selected in order to establish the preferential H adsorption location and the optimum H-surface distance. The two most stable sites for H on FeNi(111) are the top Fe and the Fe-Fe bridge. We found that the minimum energy site corresponds to the H bonding on top Fe. Fe-H bond is formed on the FeNi(111) surface and the interaction is mainly due to the overlaps between the H s orbital with the p_z , s, d_z^2 and p_y Fe orbitals. On the other hand, when the H is located on the Fe-Fe bridge site, the Fe-H interaction is formed with mainly participation of p_z , p_y , s and d_{yz} Fe orbitals. In general, after H adsorption, the neighbouring Fe-Fe bonds are weakening while Fe-Ni and Ni-Ni bonds are slightly affected. The Ni-H interaction is not evidence on the FeNi(111) surface.

TiFe – based alloys with nanocrystalline/amorphous structure as a material for hydrogen storage application in nickel metal-hydride batteries

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The composite nanocrystalline-amorphous TiFe alloys were obtained mechano-chemically by high-energy ball milling in a planetary type mill. The duration of milling was varied with the aim to produce alloys with defined microstructure. The average size of the powders was reduced from 50 μm to <1 μm after 30-40 hours of grinding. The end product of milling consists mainly of nanocrystalline fcc TiFe with CsCl-type structure. Presence of nanocrystalline Fe was also detected. The synthesized composite material showed relatively high thermal stability. The electrochemical hydrogen charge-discharge behavior of materials with different microstructure was investigated. It was obtained that small microstructural changes result in significant discharge capacity and cycling stability differences. The material milled for 40 h revealed discharge capacity comparable to that of alloy milled for 30 hours, but its stability was greatly improved.

Two dimensional Mathematical Modeling of Hydrogen storage device for fuel cell Plant

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Hydrogen storage in a fuel cell plant can be modeled and simulated using two dimensional approaches. Previous research on hydrogen storage in a fuel cell plant only considered the absorption /desorption of the gas in radial direction only. In this project, a mathematical modeling of fuel cell plant which results in a system of partial differential equations (PDE) based on heat, momentum and mass transfer of hydrogen in two dimensions using software COMSOL were implemented and the obtained results are simulated. The effect of variables such as pressure, temperature, concentration, viscosity and time on the gas was also verified. The porosity of the gas in the media is also investigated. (This is a function of time).

The simulations results obtained proved that the model applied is sensitive to agitations of some of its parameters; activation energy of absorption, effective conductivity and heat of reaction which are considered as the most important ones.

Also the effect of internal geometries on the rate of hydrogen absorption/ desorption in the metal hydride bed reactor was investigated.

Keywords – Hydrogen; Storage; Absorption; Desorption; Metal hydride

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Understand the high photocatalytic activity of $Zn_xCd_{1-x}S$ by hybrid DFT study of the formation of bulk defect states

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Semiconductor photocatalysts have been widely used in photocatalysis to harness solar energy.¹ A key issue that attracts a lot of interests is how to enhance their quantum efficiency. The quantum efficiency of photocatalysis is defined as the percentage of incident photons utilized for chemical reactions. Two key factors restrict the quantum efficiency. The first is the wavelength range that a photocatalyst can absorb. The second is the transfer of photogenerated electrons and holes from the bulk to the surface. Defect states in semiconductor photocatalysts have been reported to significantly influence the transfer of photogenerated carriers.²

It has been reported that the photocatalytic activity of a solid solution photocatalyst, $Cd_{0.44}Zn_{0.56}S$, is about 30 times higher than that of CdS. Therefore, it is of necessary to understand the mechanism behind the high photocatalytic activity of $Zn_xCd_{1-x}S$. Shi et al³ have reported that the surface defect states act as electron pools to promote the photocatalysis process. There is no report on the bulk defect states in $Zn_xCd_{1-x}S$ until now.

We studied the formation of bulk defect states in both zinc-blende and wurtzite $Zn_{50}Cd_{50}S$ by using the Vienna ab-initio Simulation Package (VASP). The generalized-gradient approximation (GGA) with the standard norm conserving Perdew-Burke-Ernzerhof (PBE) and Heyd-Scuseria-Ernzerhof (HSE06) exchange-correlation functionals are employed. We use 128-atom SQS cells to represent $Zn_{50}Cd_{50}S$ solid solution.

Taking wurtzite $Zn_{50}Cd_{50}S$ as an example, we find that: (1). Similar to CdS and ZnS, Zn vacancy (V_{Zn}) and Cd vacancy (V_{Cd}) are the most stable acceptor-type defects and S vacancy (V_S) is one of the most stable donor-type defects. The formation energies of V_{Zn} & V_{Cd} are higher than those in CdS and ZnS but the formation energy of V_S is lower. (2). Differing from CdS and ZnS, the formation energies of interstitial defects (Zn_i , Cd_i and S_i) are about 0.5 ~ 1 eV lower than those of antisite defects. (3). Under metal-rich growth condition, major donor-type defects are negative-U defects. The Fermi level is pinned at close to the conduction band minimum (CBM), indicating $Zn_{50}Cd_{50}S$ is a stronger n-type semiconductor than CdS and ZnS. The transition energy levels of these donor-type defects are higher than the pinned Fermi level, showing that there are less electron-hole combination centers in $Zn_{50}Cd_{50}S$ than in CdS and ZnS. Therefore, we can conclude that $Zn_{50}Cd_{50}S$ synthesized under metal-rich condition is a better photocatalyst for water splitting.

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Keywords Photocatalyst, Solar hydrogen, Hybrid DFT, Native defect, Solid solution

Wind Power

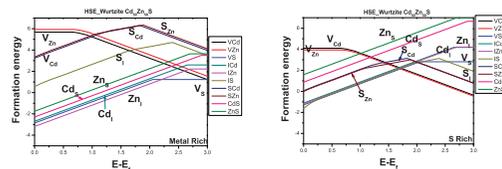


Figure: Formation energies of native defects in wurtzite $Zn_{50}Cd_{50}S$ as a function of the Fermi level under (a) metal-rich (left) and (b) S-rich (right) growth conditions.

A model about windfarms and collision risk of birds: an Italian example

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The risk of collision is one of the major threats that wind turbines determine on birds. This threat is related with the rapid expansion of windfarms across Italy, and by now requires the development of adequate conservation decision-support tools to identify areas of high impact on birds.

A geometric and mathematic model to evaluate an estimate of the potential number of some species of *Falconiformes* collisions likely to occur at an operational turbine was implemented at a local scale (in the territory of Fornelli, Molise Region). Our model was based on Scottish Natural Heritage guidelines and relates technical and aerodynamic elements of wind turbines with biological characteristics of *Falconiformes*. The area swept by the rotors and the "risk window" are a virtual wall that increases the probabilities of bird collision. The ratio of these parameters represents the number of birds flying through rotors, upon on we calculated the collision risk of individuals that potentially across the risk zones. These parameters and velocity, type of flight, length and wingspan of *Falconiformes* allowed us estimating the collision risk coefficient per annum. The model allows synthesizing the several elements influencing the relationship birds-wind turbines and shows the different sensitivity of each species to the windfarms.

Keywords windfarms, collision risk model, *Falconiformes*

Assessment of wind energy technologies in Nigeria

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The wind energy resource situation in Nigeria including the estimated potential, economic competitiveness, technical assessment, cost comparison of wind energy technologies with other energy technologies, available amount of the resource, and global wind energy utilization are presented in this paper. The status of the database is discussed, indicating its degree of adequacy and an identification of the gaps.

Wind speeds in Nigeria range from a low 1.4 to 3.0m/s in the southern areas and 4.0 to 5.12m/s in the extreme North. Wind speeds in Nigeria are generally weak in the South except for the coastal regions and offshore locations. In Nigeria, peak wind speeds generally occur between April and August for most sites. Initial study has shown that total actual exploitable wind energy reserve at 10m height may vary from 8 MWh/yr in Yola to 51 MWh/yr in the mountain areas of Jos Plateau and it is as high as 97 MWh/yr in Sokoto. Hence, Nigeria falls into the poor/moderate wind regime.

Key words: Energy potentials, Wind, Energy, Database, Resource, Wind regime, Economic competitiveness, Global.

Comparison of Aerodynamic Performance of Curved and Straight-blade Darrieus Wind Rotors

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A wind rotor constitutes a major component of any wind turbine system. It is the direct means by which the turbine extracts the wind energy and transforms it into shaft power. This power may then be used directly or else converted into electrical power through an electric generator. A particular type of such turbines is the Darrieus wind turbine which generally offers several advantages for small scale applications. Darrieus wind rotors appear in one of two distinct configurations where its blades are set in either a curved or straight manner. The main purpose of the study described here is to investigate and compare the aerodynamic performance of these configurations through the development and validation of a computer program based on a well documented mathematical model tailored to the aerodynamic design and performance analysis of Darrieus wind rotors. Results indicate that the straight-blade configuration offers better performance.

Econometric Forecasting of Wind Power Production

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Precise short term forecasts (one to 36 hours ahead) are crucial in the wind energy industry for several market participants. Power producers as well as power distributors (energy traders) require reliable forecasts to achieve market clearing and fair pricing in the power markets. Transmission system operators (TSOs) are also in need of efficient forecasts of the foreseeable power production since they have to manage the network load. Their challenge to find the best possible match of power supply and power demand, i.e. to find a balance of production peaks and heavy power loads has become more difficult since the massive increase of strongly volatile renewable energy in the energy mix started one or two decades ago.

This paper presents a forecasting model that focuses on the non-linear relationship between wind speed and wind power production, called "Power Curve". In addition to the classical usage of that term we utilize wind direction as an explanatory variable and observe the non-linear relationship as a two-sided censored set of data. Therefore, our model uses an important additional ex-ante known information: The power range of the turbine(s) that determines the two censoring points. Using this we are able to show that our model returns an efficient and unbiased forecast of wind power production that is more precise than forecasts of models in current use by the industry. It should be emphasized that the model mainly aims at running at a turbine specific level, but can also be used at a more macro-oriented perspective WLOG, e.g. at a wind park level including several turbines.

Numerical study on a vertical axis-helical savonius wind turbine

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This paper presents the performance of Savonius-type vertical axis wind turbine (VAWT) with various twist angles. A number of numerical simulation has been made to predict the power and torque of the VAWT with the aiming to apply for the future application in the real site. For the numerical simulation of VAWT, The unsteady RANS(Reynolds-Averaged Navier-Stokes) equation are solve. As one of key parameters in the VAWT design, the twist angle was chosen and changed in angle - 0°, 45°, 90°, 135°(see Fig 1). The ratio of rotor height(H) and diameter(D) was set to be 1.33:1. The numerical results include coefficient of torque and coefficient of power against the TSR(Tip Speed Ratio). In order to get a optimum design, the model shape of maximum performance was chosen in the end.

Keywords Helical Savonius wind turbine; Performance analysis; Numerical simulation

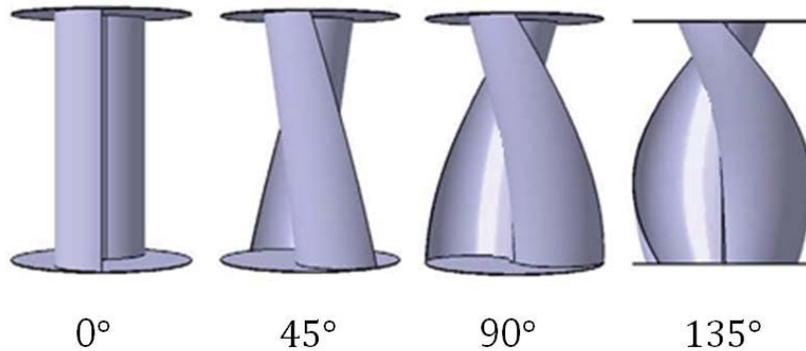


Fig. 1 Vertical axis wind turbines with various twist angles.

Performance of a hybrid wind- grid- load energy system

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A wind driven generator (WG) and a power utilities grid are interconnected together to make a hybrid energy system. The hybrid system provides a constant power to an AC load regardless the surrounding weather conditions. A general scheme of the study system is represented in Fig. 1. The figure consists of three main parts: a wind driven generator (WG) operated by a controlled single phase full wave bridge rectifier, an AC voltage source representing the power utilities side or the grid, and an AC power load. The bridge operates in the inverter mode of operation. The desired powers flow is simplified by the arrows direction.

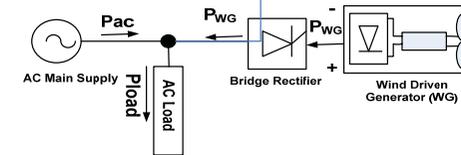


Fig. 1. Study System

The extracted power from the wind generator is supplied to a constant AC load and any excess of power from the wind renewable energy source is injected into the power utility grid. At any pretended surrounding weather conditions, maximum extraction of power from the renewable energy source is also targeted. This is done through the realization of a self-adjusted firing angle controller. The performance of the proposed system has been simulated in MATLAB/SIMULINK environment and tested practically by building a laboratory prototype model. Table 1 depicts the computer steady state values of the powers recorded at certain pretended wind speeds.

Table 1. Computer Simulations Steady State Results

Wind Speed (m/s)	Pload (W)	P _{AC} (W)	P _{WG} (W)	Targeted Wind Generator Power (W)	Firing angle (degree)
5	19.99	-5.388	36.5450	38.3408	159.433
6	19.99	-18.461	63.1498	64.4882	166.9262
7	19.99	-32.576	100.2796	101.0944	158.9950
8	19.99	-42.706	149.6885	150.4174	142.1763

By fixing the firing angle at certain value and driving the wind driven generator at certain speeds, the powers are recorded and reported in Table 2.

Table 2. Experimental Recorded Measurements

Wind Motor Speed (rpm)	When the firing angle is set to 110°			When the firing angle is set to 120°			
	Pload (W)	P _{AC} (W)	P _{WG} (W)	Wind Motor Speed (rpm)	Pload (W)	P _{AC} (W)	P _{WG} (W)
300	21.10	16.61	6.87	300	21.08	18.09	10.89
500	21.74	7.89	25.75	500	21.32	12.83	34.37
600	21.92	1.21	44.44	600	21.32	8.72	52.91
800	22.09	-3.63	64.74	800	21.55	1.61	93.93

Keywords: Integration of Renewable Energy Sources to Grid Systems, Wind Driven Generator, Maximum Power Point Trackers, MATLAB/SIMULINK Applications

Reliability evaluation of off-grid small hybrid solar pv-wind power system for the rural electrification in Nepal

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Nepal being a small and developing country, awareness on generation of renewable energy resources is mounting with the rapid depletion of fossil fuel resources, increase in oil prices and environmental concerns. Among the various renewable resources, off-grid small hybrid solar pv and wind power system (HSWPS) seems to be the promising solution to provide reliable power supply with improved system efficiency for the remote rural areas in Nepal. This paper is focused on the study and analysis of hybrid system reliability for the electricity supply for off-grid applications with focus on solar photovoltaic-wind hybrid system using current load profile and model generation capacity for a real system. Various reliability indices like Loss of Load Expectation (LOLE), Expected Energy Not Served (EENS), Energy Index Reliability (EIR), Expected Customer Interruption Cost (ECOST) are evaluated through Probabilistic Approach using Analytical Method. The paper assesses the reliability of hybrid generation system of a recently completed HSWPS at a remote location in Nepal. The wind turbine generator (WTG) is the primary source of supply to the system; while the solar PV array is the secondary source of supply since the contribution of photovoltaic is small as compared to the share of the wind turbine subsystem (small solar PV array generation) along with the battery backup system. It is expected that the findings for this project would be useful for similar hybrid system reliability studies in the future.

Keywords: Off-grid, HSWPS, reliability indices- LOLE, EENS, EIR, ECOST, Probabilistic Approach

Geothermal Energy

A geochemometrics approach to determine the reaction time required to reach quasi-steady state conditions of mineral dissolution reactions in geothermal systems by water-rock interaction experiments, Na-K geothermometry and regression tools

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Dissolution rates of minerals decrease with time at such a slow rate that true steady state may not occur; however the attainment of steady state in water-rock interaction experiments has been an important parameter to validate in mineral dissolution studies.

In laboratory, the dissolution rates of minerals is generally affected by temperature, initial concentration of starting materials, water-rock ratio (W/R), surface area, and reaction time, among other experimental variables. Reaction time plays an important role when designing costly and efficient water-rock experiments. Analytical costs and their problems of reproducibility may be reduced when estimating the time necessary to approach a quasi-steady state in water-rock interaction experiments. Equilibrium temperatures are also important parameters to determine for a reliable study of such water-rock interaction experiments.

With these objectives, geochemical and statistical (geochemometrics) studies have been carried out both to estimate the reaction time needed to approach a quasi-steady state in water-rock interaction experiments, and to determine the theoretical equilibrium temperature of the reaction using Na-K geothermometry. The geochemometrics methodology was comprehensively designed to study cation exchange reactions in rock samples with feldspar using experimental data previously published (granite-water interaction at 200 °C, 50 MPa, W/R ratio values of 2 and 10) and new geochemical data compiled from water-rock interaction experiments. The new experimental data were recorded in a Parr stirred reactor system which was successfully operated at 90 °C and 150 °C. These experiments were performed for trying to improve the calibration of the current Na/K geothermometers for low and medium hydrothermal systems.

Polynomial regression models were successfully used for fitting fluid composition [$\log(\text{Na/K})$] and reaction time (t) data. The $\log(\text{Na/K})$ values inferred from Na-K geothermometry equations were assumed to be the most probable fluid chemical composition under quasi-steady state conditions. Considering previous water rock interaction experiments with W/R=2, we found that a reaction time between 3.8 and 5.0 months would be required to approach the quasi-steady state, whereas for experiments with W/R=10, the estimated reaction time to approach quasi-steady state would be between 12.7 and 28 years.

Using the same methodology, new geochemical data from basalt-deionized water interaction experiments are also presented, indicating that fluid composition is still far from the theoretical equilibrium after 9 months of reaction at 150 °C. Details of the experimental and mathematical methodologies are outlined.

Keywords geothermal energy, equilibrium temperature, Na-K geothermometer, feldspar dissolution, quasi-steady state conditions

A new improved mathematical method to estimate stabilized formation temperatures using thermal recovery data of geothermal boreholes

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The exploitation of geothermal resources is currently considered as a clean energy option to face future energy challenges. Technological and sustainable developments achieved in several world geothermal fields have demonstrated its capability to produce electricity from the exploitation of their endogenous resources. Although, this remarkable progress, new improved techniques are still needed for a reliable estimation of the heat reserves stored in geothermal systems.

The determination of stabilized formation temperatures (SFT, also known as undisturbed or static formation temperatures) constitutes a fundamental task for an early thermal evaluation of the geothermal systems. SFT are commonly used in a wide variety of applications, such as: (a) the calibration of chemical geothermometers and water-rock interaction experiments for exploration applications; (b) the estimation of geothermal gradients and heat flows for exploration mapping; (c) the optimal design of borehole drilling and completion programs; and (d) the estimation of the heat reserves of geothermal systems; among others. Numerous analytical methods based on heat source models (either conductive or conductive-convective) have been developed for the estimation of SFT using transient thermal recovery data [i.e., bottom-hole temperature (BHT) and shut-in time borehole logs]. Although the research advances reached in this area, the application of these methods to borehole drilling data has led to unreliable prediction of SFT (either under- or overestimation) with large uncertainties and inconsistencies among the methods commonly used. Most of these problems have relied on unrealistic and simplified physical and mathematical-statistical algorithms that have not described the complex borehole drilling process (which greatly affects the SFT surrounding the borehole).

Drilling fluids (also known as drilling muds) are commonly non-Newtonian fluids which are used for drilling deep geothermal boreholes. Drilling muds are an integral part of the drilling due to their tribological and rheological properties, which serve in a wide variety of operations. Although the technical benefits provided by the drilling muds, unfortunately its circulation greatly affects the formation-rock temperature nearly surrounding the borehole. Temperature changes are disturbed by the time of drilling mud circulation, the temperature difference between the drilling mud and formation, the wellbore radius, the thermophysical properties of the system (wellbore, formation, and fluid reservoir), and the drilling technology used. Given these factors, the accurate determination of formation temperatures at any depth requires a certain length of time (also called thermal recovery time) in which the borehole is not under operation.

With the main objective to solve all these problems, a new improved mathematical method to estimate geothermal SFT is proposed in this work. The new practical method uses rational polynomial regressions applied to thermal recovery data of geothermal boreholes. The new method has the enormous advantage to use early BHT and shut-in time data logged during geothermal borehole drilling operations. Additional data, commonly required by other analytical methods, such as drilling circulation times, and thermo-physical properties of drilling fluids, drill pipe and formation materials, are not needed by the new mathematical approach. The requirement of a large number of parameters with high accuracy actually constitutes a strong weakness or disadvantage of previous analytical methods in comparison with the new proposed method. It was clearly demonstrated that the rational polynomial method provides a much better statistical fit (either at short or at infinitely longer shut-in times) than those previous analytical methods, which finally enables the SFT to be reliably determined with smaller uncertainties. Mathematical details and some field applications of the new method are outlined in the present work. For these purposes, some well-known actual borehole data (logged from several world geothermal fields) and synthetic experimental data have been used to highlight the advantages of the new practical method.

Keywords borehole completion; shut-in time; bottom-hole temperature; thermal recovery; drilling mud

Low temperature geothermal energy

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High temperature geothermal energy has been exploited for a long time for energy production (electricity and heat). However, the exploitation of low temperature geothermal energy is generally limited to direct applications (drying, fish farming, balneotherapy, etc.), despite the abundance of low temperature geothermal resources in many countries.

This paper gives an overview of low temperature geothermal energy and discusses the energy production from low temperature geothermal resources.

Keywords Geothermal energy; Low temperature; Exploitation; Resource

Wave, Tidal and Hydropower

Designing and Numerical Simulation of a Pump-Turbine Runner

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The possibility of storing and recovering a large amount of energy very quickly, is one of the main challenges confronting the energy industry at present time. Pumped storage power plants are presently one of few ways of satisfying these two criteria.

The development of renewable intermittent energies makes energy production highly dependent on meteorological conditions. Wind power, solar energy and marine energy are all fatal energies, meaning that the energy produced is lost, if it is not immediately consumed and generated during peak consumption hours. Energy storage is therefore the only means for managing production according to demand by smoothing production and consumption curves. Pumped energy storage plays therefore an important role in the development of a new forms of energy.

In the present paper, the runner of a pumped-storage power plant (Pump-Turbine) has been designed, with the predefined requirements in both pump and turbine modes, using conformal mapping method. The requirements are presented in table.1. A CFD (Computational Fluid Dynamics) simulation has been then performed. In this Simulation, the $k-\epsilon$ turbulence model has been used. This model, because of its accuracy and robustness, is very popular and preferable in the industry. For modeling the multi phase flow "mixture model" has been used, as it has the capability to model interpenetrating phases which allows the phases to have any volume fraction between 0 and 1. This capability makes the multiphase flow simulation more accurate. Using the results of this analysis, the design was improved to meet the requirements in both modes. The independency from the grid has been investigated. The hydraulic phenomena, such as the flow separation and cavitation, which can affect the runner performance has been also investigated. In order to avoid the destroying effects of these phenomena, the design has been again changed. Finally a good design, that meets the requirements in the best way, has been obtained. This design has a high efficiency in both modes (pump and turbine) and a good performance in off-design conditions. The characteristic curves of both modes have been also presented, which show good performance in the off-design conditions.

Table 1. defined requirements

Mode	Expected head(m)	Rated Flow rate(m ³ /s)
Pump	530	44
Turbine	480	60

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Keywords Pumped-storage HydroPower plant, Designing, Numerical Simulation, Hydraulic Phenomena

Experimental Study of the operating conditions of a modified micro hydro

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A 45° degree axial flow Kaplan type micro hydro turbine was originally designed to operate without guide blades. Later due to a research program at the Iranian Research Organization for Science and Technology (IROST) it was developed to operate under low head and limited flow potentials in Iran . The original design of the main shaft of the turbine was supported by a bearing housing consisting of three bearings outside the main casing, leaving the rest of the shaft, hub and the runner without any supports inside the turbine .Later a suitable support near the runner and inside the casing was designed and installed. Standard turbine tests showed considerable improvements in operating characteristics of the turbine due to these design modifications. This paper presents details of these improvements and the related outcomes.

Keywords: micro hydro turbine, operating point, main shaft, second support.

Optimal control of wave energy converters using deterministic sea wave prediction

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Abstract: We demonstrate that deterministic sea wave prediction (DSWP) combined with constrained optimal control can dramatically improve the efficiency of sea wave energy converters (WECs), while maintaining their safe operation. We focus on a point absorber WEC employing a hydraulic/electric power take-off system. Maximising energy take-off while minimising the risk of damage is formulated as an optimal control problem with a disturbance input (the sea elevation) and with both state and input constraints. This optimal control problem is non-convex, which prevents us from using quadratic programming algorithms for the optimal solution. We demonstrate that the optimum can be achieved by bang-bang control. This paves the way to adopt a dynamic programming (DP) algorithm to resolve the on-line optimization problem efficiently. Simulation results show that this approach is very effective, yielding at least a two-fold increase in energy output as compared to control schemes which do not exploit DSWP. This level of improvement is possible even using relatively low precision DSWP over short time horizons. A key finding is that only about 1 sec of prediction horizon is required, however, the technical difficulties involved in obtaining good estimates necessitate a DSWP system capable of prediction over tens of seconds.

Keywords: wave energy; float; heave plate; synchronous machine; constrained optimal control; bang-bang control; dynamic programming; deterministic sea wave prediction

Theoretical and Numerical Analysis of a Marine Current Turbine and Introducing a Novel Self-Adaptive Model

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A theoretical and numerical approaches is developed to marine current with horizontal axis like an underwater wind turbine which is used in regions with high amount of tidal currents. Concerning velocity of currents, we develop analytical solve of momentum equations on the blades and obtain the torque, axial force, power output and efficiency. In the numerical simulation, the same parameters are calculated to compare with the theoretical ones. This kind of turbine should be operated in two directions of the currents (offshore to onshore and vice versa). We develop a uni-directional blade which does not need to spin mechanically due to direction of the currents which is a common practice in the modern tidal turbines. This innovative model is also evaluated numerically and compared with the present tidal turbines.

Keywords marine current turbine; tidal turbine; numerical simulation; theoretical analysis; self-adaptive

Nuclear Energy and Materials

An analytical study on the molten nuclear fuel coolability after severe accidents

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After Fukushima nuclear power plant accident due to unexpectedly large earthquakes, cooling strategies of the molten nuclear fuel under station black-out scenario draws heavy attention. However, the cooling of molten nuclear fuel with only external water, so called in-vessel retention (IVR), has been known to be marginally successful due to focused heat flux from a thin molten metallic pool compared with the heat removal capability (or critical heat flux) of externally flooded water in a large power reactor as shown in Fig. 1. Therefore, for such large power reactors, ex-vessel cooling strategy has been pursued which is a concept of molten fuel cooling outside the reactor vessel assuming reactor vessel failure. However, this ex-vessel cooling strategy is not favorable for public acceptance of nuclear energy. Thus, in order to deduce more effective design option to increase thermal margin of IVR for such large power reactors, analytical investigation of the coolability by IVR is performed for the APR1400 (Advanced Power Reactor 1400), a Korean large evolutionary pressurized light water reactor with rated thermal power of 4000 MW. The coolability analyses begin with selection of accident scenarios with meaningful probabilities and the simulation of the fuel melting processes of such scenarios by using the MAAP4 code, which models thermodynamics, heat and fluid flow and chemical reaction processes of nuclear fuel melting. The coolability is represented by the ratio of focused heat flux from the molten metallic pools versus the critical heat flux. The focused heat flux is obtained from a two-layer lumped heat balance model for molten metal and fuel pools as shown in Fig. 1. Analysis results show that there is a definite cooling potential of molten nuclear fuel inside the reactor vessel without failure as provided in Fig. 2 when we flood both in- and outside of the vessel with water as in Fig. 1 due to additionally increased heat removal by internal water through film boiling which is greater than radiative heat transfer dominating in case of no water inside.

Keywords Fukushima, nuclear reactor, fuel melting, in-vessel retention, APR1400

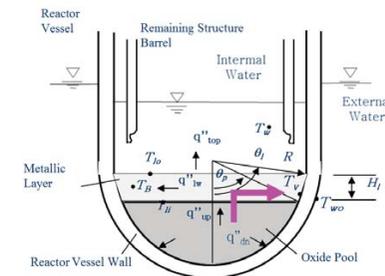


Fig. 1. Heat transfer model for molten fuel and materials inside a nuclear reactor.

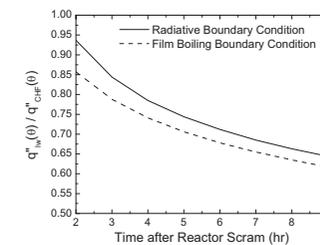


Fig. 2. Coolability molten fuel with both internal and external flooding of water (dashed line)

Composite zirconium materials with increased level of properties for active core components of new type light-water reactors with more rigid operation conditions

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Development of new type light-water reactors (LWR) with more rigid operation conditions requires using zirconium alloys with increased level of properties to manufacture active core components of these reactors.

We analyzed traditional methods used to change properties of metals and alloys including zirconium alloys: 1) selection of alloying elements and their quantity; 2) choice of annealing and tempering optimum modes; 3) use of thermo-mechanical treatment different methods. The analysis results have shown limitation of capabilities of such approach to provide an optimum combination of technological effectiveness of an obtained metal and a complex of operational characteristics of products made thereof: strength and plasticity, corrosion stability, resistance to high-temperature creep and radiation growth.

It is considered promising to develop methods to influence physical-mechanical properties of zirconium alloys due to developing their heterogeneous (composite) structure with dispersion principle of hardening.

The ordered phases are formed on the basis of principle fcc, bcc and hcp lattices as a result of regular arrangement of atoms along clusters (long-range order formation) during crystallization from a liquid condition or phase transformation in a solid condition. Under ordering with long-range order formation there are radical changes of mechanical, magnetic, thermal, electrical, corrosion and other properties in an arrangement of different grade atoms, that is a basis to develop materials with a complex of optimum characteristics. An abnormal feature of alloys described by presence of areas (volumes) with the ordered structure is an increase in deformation resistance, increase in yield strength and coefficient of strengthening at temperature rise.

Such material has been developed using a casting process due to liquid-metal reinforcement, i.e. an alloy transfer in some localized volumes into an ordered state by introducing small amounts of super-structure (ordered) compounds in a melt.

Besides, a promising principle to build a structural material structure with high values of short-term and long-term strength, creep and fatigue resistance, resistance to development of fatigue cracks is to make a heterogeneous structure in the material with plastic layers between strong bearing elements. In such composite materials the reduction of sensitivity to dynamic loads is achieved due to faster absorption of energy by an elastic component of a composite material than by a plastic one, and a decrease of sensitivity to crack formation is achieved by the intended redistribution of accumulated damages in the component which does not reduce the material bearing capacity. In this work a granule technology was used to produce the composite material.

The investigation results have shown the possibility to improve operation properties of the components made of existing industrial zirconium alloys and to prolong their operation duration.

Several versions of composite materials with an increased level of properties have been developed.

Keywords new type light-water reactors; active core components; composite zirconium materials; heterogeneous structure; liquid-metal reinforcement; carbon nanostructures

Development of higher order shear element for the static analysis of composite lamina

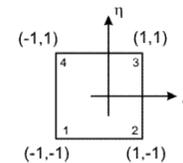
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In this paper a higher order shear element, which is a 4 noded quadrilateral element used in nuclear energy production, is developed. This element is used for the static analysis of composite lamina. Using the Higher order shear deformation plate theory for basic displacement field equations, the B matrix, (Strain-Displacement relationship matrix) the D matrix (material matrix) and the resultant K (global stiffness matrix) are formulated. These B, D & K matrices were used in formulating the 4 node element with 3 degree of freedom at each node. This element was also formulated to incorporate 5 degrees of freedom per node to obtain increased accuracy in the analysis. MATLAB, a numerical analysis package, is used for the calculation of nodal displacements as basis for coding principles. The modeling is initially done for an isotropic material then extending it for the composite lamina with different angles of orientations. Knowing the position of the quadrilateral in the coordinate system, geometrical dimensions, its material properties and the loads which it is being subjected to, the above said entity can be calculated. Developing a MATLAB code is meticulously done to make sure that all the formulations are rightly interpreted in the code. Eliminating rows and columns after removing corresponding constraints is one such example. This code is helpful in eliminating all the paper work that is needed to solve problems in FEM based on theory used and can obtain results as accurate and precise as possible.

For the development of the four noded quadrilateral element with five degrees of freedom per node with quadrilateral plane stress element (Fig. 1), we have,

Fig. 1 Four noded quadrilateral plane stress element



$$\begin{aligned}
 u_0(x,y,t) &= N_1 u_1 + N_2 u_2 + N_3 u_3 + N_4 u_4 \\
 v_0(x,y,t) &= N_1 v_1 + N_2 v_2 + N_3 v_3 + N_4 v_4 \\
 \Phi_x(x,y,t) &= N_1 \Phi_1 + N_2 \Phi_2 + N_3 \Phi_3 + N_4 \Phi_4 \\
 \Phi_y(x,y,t) &= N_1 \Phi_5 + N_2 \Phi_6 + N_3 \Phi_7 + N_4 \Phi_8
 \end{aligned}$$

where,

$$N_i = 1/4 (1 + \zeta_i) (1 + \eta_i) \quad i=1,2,3,4$$

i.e. $N_1 = 1/4 (1 - \zeta) (1 - \eta)$;
 $N_2 = 1/4 (1 + \zeta) (1 - \eta)$;
 $N_3 = 1/4 (1 + \zeta) (1 + \eta)$;
 $N_4 = 1/4 (1 - \zeta) (1 + \eta)$;

The finite element formulation for isotropic material presented in this study, based on higher-order shear deformation theory, gives reasonably good results for both 3 and 5 degrees of freedom with different materials and fiber orientations. A single lamina is taken to analyze displacements then a lamina with fibers of different orientations is considered. MATLAB program is used for applications where ever user needs to calculate resultant displacements of an element when point load is applied on it. Advantage of this MATLAB program over other programming languages is that the user does not only get the direct result but, will also have access to all other entities that are required to be calculated while solving the problem to find out displacements. Working on this paper offers advantage of getting to know the intricacies that go into dealing with FEM, working with Matlab and also gives the real time hands-on experience.

Keywords: MAT LAB, Static analysis, Shear element

Diversification of processes to measure thermal power of nuclear reactors

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Nuclear reactor instrumentation is designed so as to emphasize the reliability, redundancy and diversity of control systems. Other criteria such as accuracy, and speed in response are also of major concern. Power monitoring in nuclear reactors is of crucial importance with respect to safety and efficient operation. Since the first criticality of a nuclear reactor carried out by Fermi and collaborators on December 2, 1942 at the Chicago University, there has been concern about safely monitoring the parameters involved in the chain reaction. Power monitoring of nuclear reactors is always done by means of neutronic instruments, i.e. by the measurement of neutron flux. The greater the number of channels for measuring power, the greater is the reliability and safety of reactor operations.

The aim of this research is to develop new methodologies for on-line monitoring of nuclear reactor power using other reliable processes. One method uses the temperature difference between an instrumented fuel element and the pool water below the reactor core. Another method consists of the steady-state energy balance of the primary and secondary reactor cooling loops. A further method is by calorimetric procedure whereby the reactor power is monitored as a function of the temperature-rise rate and the system heat capacity constant. Another methodology, which does not employ thermal methods, is based on measurement of Cherenkov radiation produced within and around the core. The first two procedures, fuel temperature and energy balance, has been developed and experimentally validated in the IPR-R1 TRIGA nuclear research reactor at Belo Horizonte (Brazil) and are the focus of the work described here. The thermal balance method developed in this project is now the standard methodology used for IPR-R1 reactor power calibration, and measuring power by using the fuel temperature is the most reliable way of on-line monitoring of this reactor power.

The methodologies and graphical interfaces implemented provide greater reliability and transparency in its operations. Besides allowing visualization in real-time, transmission through the internet or in the networks, the data is stored and can be made available to the authorities and to the public. Developments and innovations used for research reactors can be later applied to larger power reactors. Their relatively low cost allows research reactors to provide an excellent testing ground for the reactors of tomorrow.

Knowledge of the reactor thermal power is very important for precise neutron flux and fuel element burnup calculations. The burnup is linearly dependent on the reactor thermal power and its accuracy is important in the determination of the mass of burned ²³⁵U, fission products, fuel element activity, decay heat power generation and radiotoxicity. This research project primarily aims at increasing the reliability and safety of nuclear reactors using alternative methods for monitoring their power.

Keywords: nuclear reactor; power; TRIGA; instrumentation.

Elastic and electronic properties of YVO4 under pressure

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The elastic, electronic and some thermodynamic properties of the zircon-type and the scheelite-type YVO4 using first-principles method and by considering generalized-gradient approximation for exchange correlation energy functional. YVO4 under pressure are investigated by first-principles calculations. The ground state properties and equations of state are obtained, which agree well with available theoretical calculations and experiments. Moreover, the elastic constants with the increasing pressure are analyzed. By the elastic stability criteria, we predict that zircon-type YVO4 is not stable above 5.92 GPa.

Influence of structural and microstructural parameters on fluorite-type (An,Ln)O₂ mixed oxides dissolution

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Actinides mixed dioxides are currently used in PWR nuclear reactors and considered as reference fuels for several Gen III and Gen IV concepts. Moreover, they could act as matrices for the recycling of minor actinides, either directly in the reactor core or in fertile blankets. In these conditions, the consequences of the incorporation of trivalent elements, such as americium or curium (and lanthanides as surrogate elements), in the fluorite-type structure of MO₂ should be carefully assessed when dealing with key-steps of the nuclear fuel cycle, such as reprocessing. This study was then focused on the dissolution of (An^{IV},Ln^{III})O_{2-x} and (An^{IV},An^{IV})O₂ samples (An^{IV} = Th, U ; Ln = La-Yb) as model compounds for future mixed oxides fuels. Since the influence of conventional parameters such as temperature or acidity was mainly described in the literature, a particular attention was paid to structural (chemical composition and homogeneity, crystal structure...) and microstructural (crystallization state, density, pore size and distribution, ...) parameters.

On the one hand, the incorporation of trivalent lanthanides in both CeO₂ and ThO₂ matrices was found to drastically increase their normalized dissolution rates, due to the formation of oxygen vacancies weakening the crystal structure [1]. As instance, the normalized dissolution rate of Ce_{1-x}Ln_xO_{2-x/2} solid solutions was increased by 4 orders of magnitude when shifting from Ce_{0.9}Ln_{0.1}O_{1.95} to Ce_{0.5}Ln_{0.5}O_{1.75} [2]. On the contrary, the nature of tetravalent cation did not induce great modification in the chemical durability of the ceramics. Another significant effect of composition was found to arise from the cationic homogeneity of the solid solutions considered. Such effect was particularly observed for Th_{1-x}U_xO₂ samples, whose dissolution is often promoted by redox reactions involving U(IV). In these conditions, the kinetics of alteration was generally slowing down when improving the distribution of cations at the microscopic scale, namely by using wet chemistry routes of preparation [3].

On the other hand, microstructural parameters were generally found to be significant only for samples of high chemical durability, *i.e.* ThO₂, CeO₂, and derived solid solutions [4,5]. In these conditions, the crystallization state of the samples could influence the kinetics as much as the acidity of the leachate while density or grain size remain second order parameters. Nevertheless, these later parameters must be taken into account when studying the evolution of the solid/solution interface. Indeed, ESEM observations performed *in operando* during the dissolution process allowed imaging the preferential alteration zones for several solids which can be located either within the grain boundaries, triple junctions or through intragranular corrosion pits. Also, it allowed pointing out the effect of surface heterogeneities on the dissolution kinetics as well as the strong evolution of the reactive surface during the dissolution of the ceramics. This information appears of main importance when working with normalized dissolution rate and led to consider limit cases for using such variables.

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Keywords : actinide oxide ; lanthanide oxide, dissolution; microstructural parameters, ESEM.

Investigations of dissimilar electron beam welds on P91 and PM2000 steels

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Compared to present reactors, modern nuclear power plant concepts are based on materials which can be operated at higher temperatures and up to higher fuel burn-up. Oxide dispersion strengthened (ODS) steels – produced by mechanical alloying – with chromium contents of 9 and 14 wt. % (or even more) are typical candidate materials. Preliminary studies have shown that these ODS steels have superior thermal creep strength and they are much more resistant to irradiation damage than standard 9Cr Ferritic/Martensitic steels. Irradiation swelling, helium embrittlement, and irradiation hardening were observed on a much lower level.

The European research program GETMAT (GEneration IV and Transmutation MATerials) deals with the characterization of ODS steels for nuclear applications at elevated temperatures, at high neutron doses, and for extended operation times [1]. One GETMAT task is dedicated to feasibility studies for joining ODS steels. In this context, the present work discusses the welding of ODS steels with common weld procedures.

In extended investigations on joining, the ferritic ODS steel PM2000 [2] and the ferritic/martensitic nuclear standard steel P91 were used. After joining by EB (electron beam) welding several heat treatments were performed and investigated. First, the samples were annealing at 1050°C for 1 hour and then tempered at 770°C for 2 hours. To characterize the joints, creep and Charpy tests were made. The microstructure was analyzed using optical microscopes, SEM and TEM.

This paper presents and discusses the results of the mechanical tests focusing on the microstructure of the dissimilar welds. A comparison of Charpy and creep tests of dissimilar with similar welds shows that the later are much easier to produce. Therefore, further investigations of dissimilar welds are necessary for a full characterization, understanding, and possible optimization.

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Manufactured new energy source from hot waste seawater of nuclear power plant <production of sodium metal for hydrogen power generation >

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180 nuclear reactors that are equivalent to 40% of the total existing reactors in the world use seawater for cooling and discharge 70% of the heat generated by the power plants into the sea. A nuclear reactor that has a capacity to generate electric power of one million kW uses about six million tons of seawater daily and returns warm wastewater whose temperature increased by 7°C to the sea again. The six million tons of seawater contains fresh water 5.4 million tons, sodium 65,000 tons, hydrochloric acid 128,000 tons, sulfuric acid 17,000 tons, and magnesium 7,700 tons; moreover, the warm water discharge has the thermal energy of 42 billion kcal, which costs 4.5 million dollars if generated by oil. It is simply a waste to keep discharging the hot wastewater. Thus, a new technology for manufacturing an energy source from the hot waste seawater is proposed. If the heat is directly used to distill seawater, fresh water and concentrated seawater are made. The hot concentrated seawater is subjected to electrolysis of aqueous solution to produce sodium hydroxide, and the sodium hydroxide is then subjected to molten-salt electrolysis to produce sodium metal. In addition, fresh water, sulfuric acid, hydrochloric acid, and magnesium are produced as by-products. It is, therefore, a very rich process in payability.

As shown in Fig. 1, the seawater cooling tube in a condenser is divided into upper and lower ones. The seawater that flows through the lower tube is warm wastewater, which is discharged into the sea. On the other hand, the seawater for fresh water and condensed seawater recovery runs in the flash vacuum distillers before getting into the upper tube, where fresh water is recovered. The hot seawater dehydrated by vacuum distillation is 20 to 30% high-density, concentrated salt water and is sent to the electrolytic plant. The concentrated salt water is subjected to electrolysis of aqueous solution to produce sodium hydroxide, and the sodium hydroxide is subjected to molten salt electrolysis to generate sodium metal.

Sodium metal is slightly lighter than water, and it is safe if stored in oil. At the thermal power plant, the sodium metal reacts with fresh water violently to generate a large amount of hydrogen for hydrogen combustion power generation and supplies the soda industry with the waste, sodium hydroxide, as a raw material.

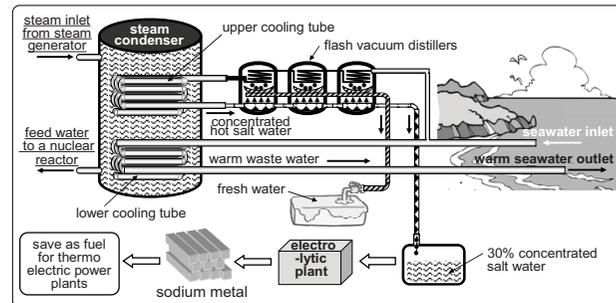


Fig.1. Condenser having a hot seawater production tube and a cooling tube and production system of fresh water and concentrated salt water

Keywords hot waste seawater of nuclear power plant; sodium metal; hydrogen power generation

Microchemistry of dislocations loops in Fe-based ferritic alloys studied by atomistic Metropolis Monte Carlo techniques

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Iron-based materials such as ferritic steels are important for many structural applications requiring high strength and good ductility, such as for turbine blades, pressure vessels and components in nuclear setups. With respect to the latter, a good resistance against irradiation is another important feature of low alloyed (Fe-Cu-Ni-Mn) or high-Cr ferritic (Fe-Cr) Fe-based steels for reactor pressure vessels. Yet, neutron irradiation causes a certain degradation of the mechanical properties in these steels due to the formation of radiation defects and up to some extent due to the enhanced diffusion leading to non-equilibrium segregation. In particular, the segregation of solutes is expected to occur at lattice defects that induce an essential lattice distortion, which acts as a sink for mobile point defects. Under neutron irradiation, these would be nano-scale voids and dislocation loops, constantly generated in displacement cascades. Non equilibrium segregation, in turn, may contribute to hardening due to the formation of solute clusters or modification of the properties of dislocation loops as obstacles to moving dislocations.

In order to cast some light on the effect of solute enrichment at dislocation loops and voids, we performed an atomic level study by using Monte Carlo (MC) techniques in Fe-0.5%Cu-1%Ni-1%Mn and Fe-9%Cr, corresponding to the content of solutes in the RVP and high-Cr steels. We employed recently developed Fe-Cu-Ni-Mn and Fe-Cr interatomic potentials in combination with an atomistic Metropolis MC method, allowing for local atomic relaxations. In this way the equilibrium arrangement of solutes in the above specified matrices as a function of ambient temperature, defect type and size was investigated.

The preliminary results suggest that in RPV-model alloys segregation of Ni and Mn indeed occurs on small dislocation loops, thus making them possible nuclei for heterogeneous solute precipitates, capable of leading to the precipitation outside the equilibrium solubility.

In the high-Cr alloys, it has been revealed that Cr atoms segregate to and form clusters at the tensile region of the edge dislocation segments on both $\langle 100 \rangle$ and $\frac{1}{2}\langle 111 \rangle$ loops. The temperature, for the dissolution of the Cr clusters attached to $\langle 100 \rangle$ loops is ~ 100 K higher than that corresponding to the solubility limit. Therefore, the presence of $\langle 100 \rangle$ loops may actually influence the solubility limit.

In both cases, the observed segregation effects suggests that small nano-metric dislocation loops in Fe-based alloys are stabilised by decoration of solutes, which implies a significant reduction in the mobility of loops and their ability to be dragged by moving dislocations. As a result, we conclude that the segregation may have an essential impact on the evolution of microstructure and post-irradiation deformation processes.

Keywords ferritic steels; radiation defects, dislocation loops, solute atoms segregation, Metropolis Monte-Carlo.

Modelling of fission gas behaviour applied to nuclear fuel rod analysis

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In order to compete with other forms of power generation, it is fundamental to the future of nuclear power that reactors can be run safely and economically. For this purpose, it is essential to refine the understanding of nuclear materials behaviour, and to embody this knowledge in codes to provide best estimate predictions of materials performance. In particular, reliably predicting the in-reactor thermo-mechanical behaviour of the nuclear fuel rods constitutes a basic demand for safety-based calculations and design purposes. As a complement to experiments in the nuclear reactors (which require tremendous resources), the fuel rod analysis codes [1,2] are presently used by industries, research centres, universities and safety authorities. With the aid of fuel rod analysis, operating rules can be derived to prevent fuel failures and the release of gaseous fission products to the environment. Fuel rod performance assessments may also lead to a reduction in operating restrictions, flexibility in fuel management and improved operating economics, without jeopardizing the safety. Although many mature fuel rod analysis codes are in active use, there are still significant incentives to improve their predictive capability. One particular aspect is related to the strong trend of reactor operators to extend the flexibility of use and the discharge burn-up of the nuclear fuel beyond the current licensing limits. The progress of fuel rod modelling is supported by many International Projects, such as the FUMEX-III (*Fuel Modelling at Extended burn-up*) co-ordinated research project of the IAEA [3], in which framework the present work was carried out.

Among the various issues involved in fuel rod analysis, the modelling of the complex behaviour of the fission gases xenon and krypton is of special importance in view of the relating detrimental effects on fuel rod performance [4]. On the one hand, the fission gases generated in the fuel tend to precipitate into bubbles resulting in fuel swelling, which promotes pellet-cladding mechanical interaction (PCMI) and possible cladding failure at high burn-up or during accidental conditions. On the other hand, the inter-connection of the gas bubbles developing at the grain boundaries brings about fission gas release to the free volume of the fuel rod, which causes pressure build-up and thermal conductivity degradation of the rod filling gas, leading in turn to higher cladding stresses and fuel temperatures. The inherently coupled kinetics of the fission gas swelling and release calls for the development of physics-based, integrated models of these phenomena to be employed in the fuel rod analysis codes. As of today, however, empirical correlations are often adopted, which are inexpensive to use but unfit for providing insight into the underlying mechanisms, and cannot be applied beyond their range of calibration.

The present work provides a contribution to the modelling of fission gas swelling and release in oxide nuclear fuels employed in current light water reactors, with application to fuel rod analysis. Through an engineering approach, which practically combines a physics-based treatment and the essential computational efficiency, a new integrated model of fission gas swelling and release is developed. The model is effectively implemented in the TRANSURANUS fuel rod analysis code [2] and verified through an extensive set of simulations of fuel rod irradiation experiments. The results show a physically sound representation of the phenomena, a satisfactory agreement with the experimental irradiation data, and improvements of the TRANSURANUS code. Compared with the semi-empirical treatments commonly adopted, the innovative aspects mainly lie in (i) the physical foundation of the developed model, allowing higher flexibility of application, (ii) the consistent coupling between the fission gas swelling and release, and (iii) the appropriate evaluation of the role of the stress field in the fuel. The latter aspect is of high importance for properly analysing the conditions of PCMI, and is topical in view of the tendency to extend the operating margins of the nuclear fuel.

Keywords nuclear fuel; fuel performance; thermo-mechanical analysis; swelling, fission gas release; Transuranus code

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Nanocrystalline Al₂O₃/a-Al₂O₃ composite coatings for protection of steels from heavy liquid metal corrosion

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Heavy liquid metals (HLMs), such as Pb or Pb-Bi eutectic, are under wide investigation for use as coolant materials in advanced nuclear systems due to their attractive thermal and neutronic properties. Nevertheless, a major bottleneck for the deployment of these systems is the ability of the foreseen structural steels to withstand erosion degradation and corrosion phenomena at high temperatures [1]. Although several protection techniques are already being developed [1-3], a breakthrough in corrosion protection of materials is still required to allow further improvements in the field.

In this work, a novel technique, namely pulsed laser deposition (PLD), was employed for synthesizing advanced Al₂O₃ barrier layers on 9Cr1Mo type martensitic steel. The characterization of the environmental barriers was performed using scanning electron microscopy (SEM), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM). The tribological and mechanical performances were investigated through nano-scratch tests and a combination of nanoindentation, ellipsometry and Brillouin spectroscopy (BS). Metal-like mechanical properties and enhanced hardness were attained, owing to the nanostructure of the coatings. The latter consists of an embedding of ultra-fine nano-domains (2-5 nm) in an amorphous alumina matrix. Our results show that these ductile ceramic coatings are moderately stiff ($E \approx 200$ GPa, $\nu \approx 0,29$, $H \approx 10$ GPa), and that they possess a unique combination of compactness, superior plastic and tribological behaviour, and strong interfacial bonding.

The corrosion resistance of the barrier layers was tested at a preliminary stage by exposing samples to HLM environment at 600°C for 500 hours. No sign of corrosion was found (figure 1). The proposed technology is therefore a suitable and promising candidate for protection of steels from HLM corrosion.

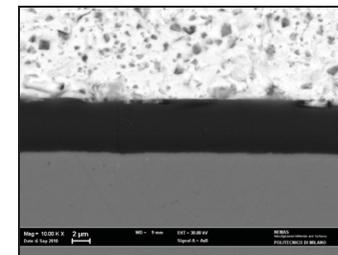


Figure 1. SEM micrograph of a cross-section of Al₂O₃-coated martensitic steel after exposure to liquid lead at 600°C for 500 hours. No signs of corrosion were found.

Keywords alumina; coating; heavy liquid metal (HLM); HLM corrosion

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Prerequisites to manageable surveillance programme development for the RPV materials resistance to radiation damage and hydrogen embrittlement monitoring

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As a main barrier against radioactivity outlet reactor pressure vessel (RPV) is a key component in terms of safety and extended nuclear power plant life.

The surveillance programme (SP) calls upon to predict ahead RPV materials characteristics conservatively to guarantee RPV structural integrity without any compromise. General vice of existing SPs is an impossibility of SP changing and development during reactor operation (30, 60 and even more years). Up to day approach based on initial hard nomenclature of surveillance specimens installed in capsules. Therefore practically it is impossible to change anything in SP during RPV service life. Anachronistic principle of ahead of time, for some decades of years in advance fabrication and installation into reactor vessel the sets of surveillance specimens (SS) without taking into account quantitative and qualitative changes of norms; state of the present-day science, testing methods and technique contradict to request of RPV operational monitoring technologies innovative development during long-term RPV operation.

Besides there is a deficiency of SP portliness relative to conditions of the RPV irradiation during operation. Most important is the discrepancy of the actual thermal condition of RPV wall from SSs irradiation temperature. At any case as a result of γ -heating it exceeds the real RPV temperature. This fact carries in the element of non-conservatism into the system of control. Moreover because of specimen-to-specimen clearance existence temperature gradients through the SS set take place. Ideally surveillance metal has to be irradiated in contact with coolant.

Metal placement in perforated capsules that is immediately in running water provides the minimum irradiation temperature and therefore guarantees the most conservative data on mechanical properties getting. Clearly that at this case there is no need in temperature monitors. Moreover today there is no hard confidence in SS capsules integrity during RPV operation. In the event of capsule depressurization SSs degradation occurs.

In reality it is impossible to exclude environmentally assisted cracking of the primary circuit stainless steel components during 60 years of operation. Surveillance metal contacting with water in perforated capsules emulate base metal-water corrosion reaction appearance as a result of possible RPV cladding cracking and hydrogen (as a corrosion product)-base metal interaction. By this means for materials susceptible to hydrogen embrittlement the degree of SP conservatism grows.

We propose to improve RPV SPs by means of passage from existing «hard» SPs to «flexible» manageable SPs (MSP) which would give the possibility of SP adaptation to requirements of time and to strengthen technical and scientific potential of investigators and researchers in the future. So, we believe that is no sense to leave present-day level of knowledge and technology in congeal state to next generation of researchers. Thus for new LWRs with the service life of 60 and more years we propose pass on from the SSs of routine nomenclature to MSP i.e. sets of archive materials coupons placed in non-hermetic containers and cooled directly by running water. It gives a perspective in case of need put into practice an innovative MSP taking into account the state-of-the-art safety standards, technical progress, level of science and technology.

In support of the above-mentioned conception the 7-year duration prototype version of the MSP was performed at operating LWR. The test specimens were fabricated from irradiated coupons with following notches machining immediately before testing. Encouraging results were obtained.

Keywords: RPV steel, manageable surveillance programme, radiation damage, hydrogen embrittlement, monitoring

Radiation-hydrogen embrittlement of the reactor pressure vessel steel

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As the service life of an operating nuclear power plant (NPP) increases, the potential misunderstanding of the degradation of aging components must receive more attention. Integrity assurance analysis contributes to the effective maintenance of adequate plant safety margins.

In essence, the reactor pressure vessel (RPV) is the key structural component determining the NPP lifetime. Environmentally induced cracking in the stainless steel corrosion-preventing cladding of RPV's has been recognized to be one of the technical problems in the maintenance and development of light-water reactors [1]. Extensive cracking leading to failure of the cladding was found after 13000 net hours of operation in JPDR (Japan Power Demonstration Reactor) [2]. Some of the cracks have reached the base metal and further penetrated into the RPV in the form of localized corrosion.

Failures of reactor internal components in both boiling water reactors and pressurized water reactors have increased after the accumulation of relatively high neutron fluencies [3]. Therefore, in the case of cladding failure, the problem arises of hydrogen (as a corrosion product) embrittlement of irradiated RPV steel because of exposure to the coolant.

The effects of neutron fluence and irradiation temperature on steel/hydrogen interactions (adsorption, desorption, diffusion, mechanical properties at different loading velocities, post-irradiation annealing) were studied. Experiments clearly reveal that the higher the neutron fluence and the lower the irradiation temperature, the more hydrogen-radiation defects occur, with corresponding effects on the RPV mechanical properties.

Hydrogen accumulation analyses and thermal desorption investigations were performed to prove the evidence of hydrogen trapping at irradiation defects. Extremely high susceptibility to hydrogen embrittlement was observed with specimens which had been irradiated at relatively low temperature. However, the susceptibility decreases with increasing irradiation temperature. To evaluate methods for the RPV's residual lifetime evaluation and prediction, more work should be done on the irradiated metal-hydrogen interaction in order to monitor more reliably the status of RPV materials.

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Keywords: RPV steel, radiation-hydrogen embrittlement, combined action, corrosion, hydrogen.

Recycling of Zircaloy from nuclear fuel fabrication scraps

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A great effort is being done worldwide in order to develop clean energy sources and also to reduce and optimize energy consumption. At the present scenario, nuclear generation is the most reliable non-carbon-emitting way to meet the energy demand for economic and social development. The new generation of nuclear plants and nuclear fuels aims, not only to achieve more secure and efficient technologies but, also, to minimize the energy consumption in the construction of these plants and their operation processes.

In most nuclear power reactors, the fuel is composed of uranium dioxide pellets conditioned in cladding tubes, forming the fuel rod. A set of fuel rods, disposed in an assembly, forms the fuel element. The cladding and the structural materials of the fuel elements have to present very specific mechanical, corrosion and nuclear properties. The materials which best meet these requirements are the zirconium alloys, so-called Zircaloys. The processes of fuel elements fabrication generate machining chips which cannot be discarded as ordinary scrap, once nuclear grade Zircaloy is considered controlled material, besides being pyrophoric and presenting high costs of production. Furthermore, the fabrication of these alloys demands high consumption of energy and highly controlled processes. Therefore, the recycling of Zircaloy scraps presents great relevance in economic and environmental aspects.

In Brazil, a research program is being developed for the recycling of the Zircaloy scraps generated in the fabrication process. In this case, additionally to the economical and environmental interests, there is a strategic aspect to be considered, once Brazil does not produce zirconium alloys in industrial scale. There are two routes being studied for this purpose: by vacuum arc remelting (VAR) and by hydriding/sintering processes. In both processes, it is necessary to ensure that the composition of the alloy is not changed nor contaminants are introduced. Therefore, besides the development of these processes, the establishment of the analytical methodology to assure the reliability of the results is of paramount importance in the development of the processes.

In this work the recycling processes are described and the results for microstructural characterization and chemical analysis for the recycled materials are, also, presented.

Energy dispersive X-ray fluorescence spectrometry was used for chemical composition determination once it is a non-destructive and multielemental analytical technique, besides being fast and presenting adequate precision and accuracy. Cr, Fe, Sn and Hf were determined in recycled samples using the experimental sensitivity curve, obtained by the Fundamental Parameters method. The precision and accuracy were evaluated applying statistical tests according to the EURACHEM/CITAC guide, using Zircaloy-4 BCR098 certified reference material from Commission of European Communities.

Conventional and Synchrotron light diffraction was used to characterize the structure and phase composition of the material. The X-ray diffraction analysis shows that both, the melted and the sintered Zircaloy, presented α (hexagonal) zirconium structure. Optical and scanning electron microscopies were used to evaluate the microstructures resulting from the processes.

The sintered material presents better compositional homogeneity and more refined microstructure compared to the remelted material. It is shown that the powder metallurgy process may, additionally, purify the starting material from possible contaminations by other alloys, like steel. These good results suggest the possibility of production of Zircaloy parts of nuclear reactors, like the cladding end-caps, by the so-called "near net shape" powder metallurgy process.

Keywords: Zircaloy; recycling; hydriding; sintering; X-ray fluorescence; X-ray diffraction.

Segregation at radiation defects in Fe₇₀Cr₂₀Ni₁₀ austenitic alloy studied by atomic scale computer simulation

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Austenitic stainless steels are commonly used materials for in-core components of nuclear light water reactors (LWRs). In service, such components are exposed to harsh conditions: intense neutron irradiation, mechanical and thermal stresses, and aggressive corrosion environment. This combination of factors allows the occurrence of irradiation assisted stress corrosion cracking (IASCC), radiation induced creep and swelling, which all limit the life time of in-core components. So far, the available knowledge on degradation of the internal components of LWRs originates mainly from either the analysis of materials extracted from power reactor components, or tests on materials irradiated in test reactors or using accelerator facilities. In order to optimize in-service lifetime and to avoid costly replacement campaigns, a deeper fundamental understanding of the above mentioned degradation mechanisms is desirable, which hopefully could serve as input for engineering- and design-level modelling.

In this framework we perform atomistic simulations to investigate the effects of radiation damage on the alloy's micro-structure and micro-chemistry. Using a newly designed ternary Fe-Ni-Cr interatomic potential, we apply an atomistic computer simulation approach by combining Molecular Dynamics (MD) and Metropolis Monte Carlo (MMC) techniques (within the isothermal-isobaric statistical ensemble) to study segregation effects at stacking fault (SF) boundary interfaces and Frank loops (both interstitial and vacancy types) in the Fe₇₀Cr₂₀Ni₁₀ model alloy. In order to reveal the local stress effect, restricted number of simulations were repeated by a rigid lattice MMC. Re-arrangement of Cr and Ni near the interfaces, as well as the sensitivity of these effects on the temperature and local stress are analyzed and discussed.

The preliminary results suggest that, in the Fe₇₀Cr₂₀Ni₁₀ austenitic model alloy, re-arrangement of Ni and Cr indeed occurs on small dislocation Frank loops in a quite wide range of temperatures: (300-1400)K. Enrichment of Cr and in some cases depletion of Ni is found at the stacking faults regions of vacancy loops; near the dislocation segments of the vacancy loop, enrichment of Ni is observed. For interstitial-type loops the trends are basically opposite: depletion of Cr and enrichment of Ni are observed at the stacking faults regions, whereas near the dislocation segments Cr depletion is observed. Rigid lattice MMC simulations demonstrate similar trends qualitatively, but quantitative estimations of segregation deviate from those obtained by full MMC techniques.

Keywords austenitic model alloy, radiation defects, Frank loops, solute atoms segregation, Metropolis Monte-Carlo.

Separation of Re(VII) and Tc(VII) in simulated HLLW using a column packed with xerogel microcapsules enclosing MIDOA extractants

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Recently, significant attention has been focused on the selective separation, recovery, and effective utilization of ⁹⁹Tc from high-level radioactive liquid waste (HLLWs). MIDOA (2,2'-(methylimino)bis(N,N-dioctylacetamide)) was developed as a new extractant for Tc extraction by JAEA. The purpose of this study is to develop a method of microencapsulation of MIDOA and to examine the uptake properties of Re(VII) and Tc(VII) ions for hybrid microcapsules enclosing MIDOA by the column method using simulated HLLW (SHLLW, 28-component solution, JAEA, **Table 1**). The present study deals with the irradiation stability of MIDOA-HALG xerogel microcapsules, the breakthrough/elution properties of Re(VII) and Tc(VII), the uptake properties of metal ions in SHLLW, and the chromatographic separation of Re(VII) in SHLLW.

As for the irradiation stability test, MIDOA-HALG MCs were irradiated by ⁶⁰Co-γ rays up to 3.51×10⁷ R (Tohoku University). There was no appreciable alteration on the surface of the irradiated specimens after irradiation below 0.9×10⁷ R, while a part of the thin film of alginate gel matrices on MCs was damaged above 1.84×10⁷ R. The IR spectra for the irradiated specimens were almost unchanged, suggesting that MIDOA is stable up to 3.5×10⁷ R irradiation. Re(VII) uptake tended to gradually decrease at higher irradiation doses. This may be due to the release of the fine oil drops of MIDOA from the surface of the MCs. The uptake (%) of Re(VII) for the irradiated specimens at 3.5×10⁷ R was still above 85%.

The breakthrough (BT) curves of ReO₄⁻ for the MIDOA-HALG column showed symmetrical S-shaped profiles, and the 5% BT capacity of Re(VII) was estimated to be 0.23 mmol/g. Even after the third run of the column test, the BT capacity was almost constant. As for the elution, the recovery of ReO₄⁻ was estimated to be 95% and was almost constant after the third run, indicating the high reusability of the column. The uptake (%) of ⁹⁹TcO₄⁻ was estimated to be 75% in the presence of 1 M HNO₃, while the uptake (%) tended to decrease above 1 M HNO₃. The elution percentage of ⁹⁹TcO₄⁻ was estimated to be 95–97% in the 3-cycle runs, indicating high reusability, similar to the case of Re(VII).

The uptake (%) of Re(VII) and Tc(VII) in SHLLW was estimated to be 60% and 80%, respectively. The elution percentage of ⁹⁹TcO₄⁻ in SHLLW was estimated to be 99%, and the elution property was similar to that in the single-component solutions. By using basic breakthrough/elution data, the chromatographic separation of Re(VII) in SHLLW was effectively performed (**Fig. 1**) and the recovery (%) of Re(VII) was estimated to be 98.5%.

Thus, MIDOA MCs are effective for the selective separation of Re(VII) and Tc(VII) from HLLWs.

Keywords: Re(VII); Tc(VII); high-level liquid wastes; xerogel microcapsules; MIDOA; irradiation stability; chromatographic separation; recovery

Table 1 Chemical Composition of Simulated HLLW (SHLLW, 28-component solution, SW-11E, JAEA)

Element	Concentration (M)	Element	Concentration (M)
H ⁺	2.5	Rh	3.39 × 10 ⁻³
Na	0.981	Pd	8.66 × 10 ⁻³
P	1.27 × 10 ⁻²	Ag	3.45 × 10 ⁻⁴
Fe	7.77 × 10 ⁻²	Cd	4.67 × 10 ⁻⁴
Cr	3.95 × 10 ⁻³	Sn	3.32 × 10 ⁻⁴
Ni	9.37 × 10 ⁻³	Se	5.41 × 10 ⁻⁴
Rb	3.64 × 10 ⁻³	Te	3.57 × 10 ⁻³
Cs	1.61 × 10 ⁻²	Y	4.87 × 10 ⁻³
Sr	8.78 × 10 ⁻³	La	7.92 × 10 ⁻³
Ba	9.72 × 10 ⁻³	Ce	5.89 × 10 ⁻³
Zr	3.61 × 10 ⁻²	Pr	7.46 × 10 ⁻³
Mo	3.06 × 10 ⁻²	Nd	2.50 × 10 ⁻²
Re	4.70 × 10 ⁻³	Sm	5.10 × 10 ⁻³
Ru	1.69 × 10 ⁻²	Eu	7.96 × 10 ⁻⁴
		Gd	3.86 × 10 ⁻⁴

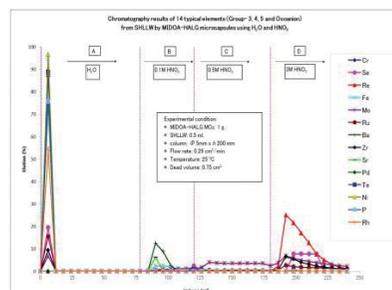


Fig. 1 Chromatographic separation of Re(VII) by MIDOA-HALG columns.

Simplification of elastomeric sealing of fast breeder reactors based on a few material formulations, analysis procedures, coating technique and manufacturing processes

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The advantages of grouping low pressure, moderate temperature elastomeric sealing applications of sodium cooled Fast Breeder Reactors (FBRs) are depicted using examples of 500 MW(e) Prototype Fast Breeder Reactor (PFBR) and the 13 MW(e) Fast Breeder Test Reactor (FBTR) presently under construction and operation.

Seals are grouped under the major categories of operation (static and dynamic) and size (below and above 500 mm diameter). Large and small diameter seals are manufactured by extrusion and molding respectively. Further classifications based on factors such as self-actuation (o-rings), aiding by differential pressure (lip seals) and actuations by external source (inflatable seal) are considered along with their effects on material compositions and design. It is shown that of one representative seal, chosen based on the most demanding operating conditions in each category, can encompass most of the major sealing applications of PFBR reactor assembly in terms of material, finite element analysis (FEA) based design, antifriction coating and manufacture. The bisphenol cured fluorohydrocarbon rubber (FKM) and ethylene-propylene-diene-methylene (EPDM) formulations developed for the inflatable (large diameter, dynamic) and backup seals (large diameter, static) of PFBR and FBTR rotatable plugs could be tailored for other reactor seals and combined with a uniform FEA procedure, plasma enhanced chemical vapor deposition (PECVD) based Teflon-like coating and manufacture (molding and extrusion) to standardize the applications in the form of a universal design code.

The gross simplification of reactor sealing based on a few material formulations and compound (as well as geometry) specific FEA, coating and manufacturing processes promise large cumulative gains in efforts, time and economy in design, development, operation and maintenance of future FBR seals.

Keywords FBR; elastomeric sealing; simplification; design code

Sintering of Fluorite-type MO₂ (M = Th, Ce) : New Insights from Coupled HT-ESEM and Dilatometry Approach

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Sintering is usually considered as a key-step in the fabrication of nuclear fuel which can allow monitoring the final microstructure of the pellet. Nevertheless, even if numerous studies were already conducted concerning the densification processes of actinide dioxides, only very few of them were related to microstructural control [1], particularly through the elaboration of a sintering map that links the density of the samples with their average grain size. As the determination of such data in various experimental conditions is generally strongly time-consuming, a novel approach based on the combination of *in situ* High-Temperature Environmental Scanning Electron Microscopy (HT-ESEM) observations and dilatometric measurements was developed to investigate the densification of fluorite-type dioxides such as CeO₂ and ThO₂.

Both samples were first prepared from an oxalate route then shaped as green pellets by uniaxial pressing. On the one hand, small pieces of such samples were heated up to 1200-1400°C directly in the ESEM chamber under 100 Pa air atmosphere. In such conditions, the *in situ* observation of the sample allowed monitoring the average grain size all during the heat treatment then establishing the corresponding kinetic laws [2]. This latter excluded the existence of exaggerated growth regimes in both cases. Also, it appeared possible to observe the various phenomena leading to the densification of the pellet, mainly through grain growth and pore elimination (Figure 1). Moreover, grain boundaries mobility, which was previously unreachable by conventional techniques, was determined as well as thermodynamic data, such as activation energy related to grain growth.

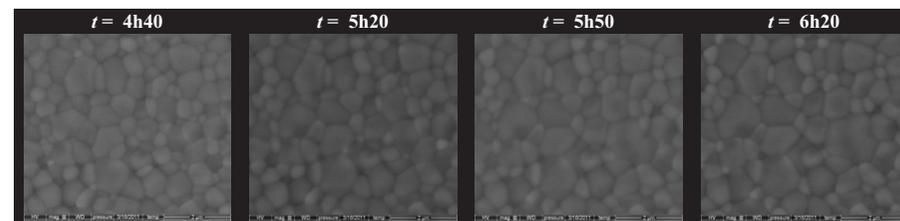


Figure 1. HT-ESEM images recorded during heat treatment of ThO₂ pellet at T = 1400°C.

On the other hand, dilatometric measurements gave access to complementary information such as that obtained through the Dorn's method [3]. These latter confirmed the activation energy value determined by HT-ESEM and led to the diffusion mechanism involved in the grain growth process. Moreover, the determination of the relative shrinkage allowed evaluating the relative density of the pellet during the heat treatment. In these conditions, the combination of dilatometry and HT-ESEM data led to the establishment of the sintering map and to the subsequent sintering trajectories. The rapid collection of such data thus appears as a promising way to explore the influence of various parameters, including those related to the powdered precursor such as grain size or morphology.

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Keywords : Sintering; HT-ESEM; dilatometry; thorium oxide ; *in situ* observations ;

The onset of flow instability under research reactor's operating condition

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Two phase flow instabilities have been studied by many researches since flow excursion was first discovered by Ledinegg in 1938. These studies were prompted by potential harmfulness caused by instabilities in large scale nuclear reactor systems. The 1979 accident TMI reactor proved the importance of the concept of Inherent safety. Two-phase flow instabilities can cause heat transfer crisis, mechanical vibrations, problems with system control, and tube failure. For instance, the Ledinegg instability has received much attention recently. The ongoing research was motivated by the need to establish safe operation margins of the special purpose reactors such as the advanced neutron source reactor (ANSR).

The present work focuses on a simulation of pressure drop in forced convection boiling in vertical narrow and parallel uniformly heated channels. The objective is to determine the point of Onset of Flow Instability by varying input flow rate. In addition to closure relationships based upon the drift flux model and other constitutive equations are considered to determine the channel pressure drop under steady state boiling conditions. The model validation is performed by confronting the calculations with the Oak Ridge National Laboratory THTL experimental data set. Further verification of this model is performed by using the results of RELAP5/Mod 3.2 code. Good agreement is observed, and the prediction of the OFI instability at which the minimum point in the demand curve occurs within 12 percent over the all range of experimental results

KEYWORDS Ledinegg instability, two phase flow, Onset of flow instability, Pressure drop, Onset of significant void, Drift-flux model, Void, RELAP5/MOD 3.2.

Unification of elastomeric sealing applications of fast breeder reactors based on peroxide cured fluorohydrocarbon rubbers

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The large improvement in simplification of Fast Breeder Reactor (FBR) elastomeric seals and enhancement of their safety, reliability and life by use of peroxide cured fluoroelastomer compositions of advanced architecture is described. It is demonstrated that the major elastomeric sealing applications of 500 MW(e) Prototype Fast Breeder Reactor (PFBR) could be based on the advanced fluorohydrocarbon rubber formulation obtained during development of inflatable seals of rotatable plugs and its three variations.

Peroxide curing minimizes the release of volatiles during manufacture of large diameter (> 500 mm) seals of any cross-section by cold feed extrusion and continuous cure using microwave and hot air at atmospheric pressure. The improved chain chemistry in advanced formulations and positioning of Iodine cure site monomers at mid as well as ends of the macromolecules result in superior curing rate and processability while ensuring long-term thermal stability typical of bisphenol cured fluoroelastomers. Peroxide curing also minimizes release of harmful, low molecular weight volatiles from seal during reactor service because of negligible unsaturations in the cured product. Sodium aerosol compatibility of the seals is likely to increase because of lower unsaturations and presence of Tetrafluoroethylene in the formulations apart from Vinylidene fluoride and Hexafluoropropylene. The lower ionic interactions in these formulations result in much better hot tensile properties which increases the factor of safety on material strength and elongation at elevated service temperature to more than 4 compared to 2 in the bisphenol cured fluoroelastomers which is reflected in life and reliability. Faster cure and higher hot tensile properties enable mass production of small diameter (< 500 mm) seals by injection moulding.

These indicate that founding the sealing applications based on the 4 formulations, axisymmetric element and Mooney-Rivlin based finite element analysis, plasma enhanced chemical vapour deposition (PECVD) based coating and manufacture by cold feed extrusion as well as injection moulding can unify, codify and standardize FBR elastomeric sealing while maximizing their safety, reliability, life and economy simultaneously using minimum effort and time. It is shown that the concept could be extended to nuclear reactors of other genres to encompass the nuclear sealing applications on a unified foundation.

Keywords FBR; unification; seals; FKM; peroxide cure

Uptake properties of Re(VII) and Tc(VII) for xerogel microcapsules enclosing MIDOA extractants

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The novel organic extractant MIDOA (2,2'-(methylimino)bis(N,N-dioctylacetamide)) with high extractability for oxoanions was microencapsulated by the sol-gel method using alginate xerogel polymer matrices. The uptake behaviors of nuclear rare metals (oxoanions, Re, and Tc) were examined using the highly functional xerogel microcapsules (MCs) enclosing MIDOA (Fig. 1) and its derivatives (IDOA and MIDDdA). The characterization of these xerogels was examined by SEM/EPMA, CHNS elemental analysis, and IR analysis, and the basic uptake properties of the nuclear rare metal ions (Tc(VII), Re(VII), Zr(IV), Mo(VI), Se(VI), and Te(VI)) were investigated by the batch method.

The oil droplets of MIDOA extractant were uniformly dispersed in MCs (matrix: alginate acid (HALG)), and the MIDOA content was estimated to be 63.7%. The uptake (%) of Re(VII) ions was above 90% in the presence of 0.01–0.1 M HNO₃, while it markedly decreased with increasing HNO₃ concentration. Here, the Re(VII) uptake corresponds to the formation of a 1:1 complex of HMIDOA⁺ and Re(VII). The lowering of Re(VII) uptake (%) is probably due to the competition with NO₃⁻. At higher HNO₃ concentrations above 1 M, the uptake (%) order for Re(VII) was MIDOA-HALG > IDOA-HALG > MIDDdA-HALG. In the presence of Na⁺ ions, the lowering of uptake (%) of Re(VII) was observed above 0.1 M Na⁺, which is due to the swelling of xerogel matrices. On the other hand, the uptake (%) of Re(VII) was independent of the reaction temperature up to 50°C.

The uptake of Re(VII) ions for MCs (MIDOA-HALG) followed the Langmuir adsorption isotherm, yielding an uptake capacity of 0.75 mmol/g. The uniform incorporation of Re(VII) ions into MCs was confirmed by EPMA analysis. The uptake order of nuclear rare metal ions for MIDOA-HALG was Zr(IV) > Mo(VI) > Re(VII) > Se(VI) > Te(VI) in the presence of 10⁻²–5 M HNO₃. The uptake (%) of ⁹⁹Tc(VII) ions exceeded 90% below 0.1 M HNO₃, and the uptake behavior was similar to that of Re(VII) ions (Fig. 2).

Thus, the MCs are effective for the selective separation of oxoanions (Re(VII) and Tc(VII)) from radioactive waste solutions containing HNO₃ and NaNO₃.

Keywords: uptake; Re(VII); Tc(VII); xerogel; alginate; microcapsule; MIDOA; oxoanions

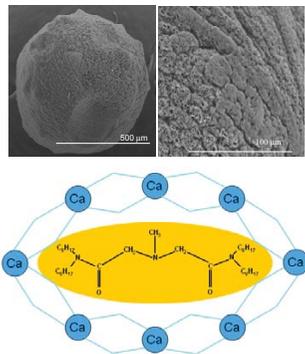


Fig. 1 Digital microscopic picture of MIDOA-HALG MCs and a schematic view of MCs.

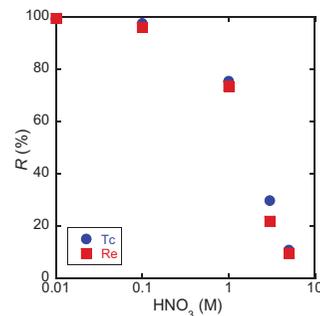


Fig. 2 Effects of HNO₃ concentration on the uptake (%) of Tc(VII) and Re(VII) for MIDOA-HALG. MCs: 0.1 g; ⁹⁹Tc: 9 kBq, [Re(VII)]: 10 ppm, [HNO₃]: 0.01–5 M, 5 cm³; 25°C.

Ways to improve the radiation resistance of pressure vessel materials for water-moderated reactors by their structure refinement

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Degradation of reactor pressure vessel (RPV) steels mechanical properties (that appears in ductile-to-brittle transition temperature (the critical brittleness temperature) shift) is mostly determined by their structure degradation. Changes in mechanical properties of the BCC-lattice steels under long-term operation are stipulated by action of two mechanisms: the hardening one (radiation hardening due to the formation of radiation defects and radiation-induced precipitates) and non-hardening one (formation of intragranular and intergranular segregations of impurities – the known phenomenon of reversible temper brittleness).

The influence of the primary austenite grain size on the critical brittleness temperature of RPV steels in the initial state and after provocative embrittlement heat treatments in the temperature range of reversible temper brittleness was studied. It is shown that the smaller grain size corresponds to a lower critical brittleness temperature in the initial state, as well as after embrittlement heat treatment.

TEM and fractographic studies of the samples of VVER reactor pressure vessels steel with different nickel contents in the states after thermal exposure, as well as after thermal exposure under irradiation were carried out. It was found that high nickel content in steels leads to an additional increase in the rate of embrittlement of these materials due to the intensification of reversible temper brittleness as well as an increase of the density of radiation-induced nickel-enriched precipitates.

The dependence of radiation-induced structure changes and the share of brittle intergranular component in the fracture surfaces of Charpy specimens on the chemical composition, test temperature and irradiation dose (fast neutron fluence) was studied. The correlation between the increase of the yield stress and the density of radiation defects and radiation-induced precipitates depending on the fast neutron fluence was set. Moreover it was shown that there is a temperature dependence of the share of brittle intergranular component: this value increases from the lower shelf on the KCV curve, reaches a maximum in the temperature range of ductile-brittle transition, and decreases to zero on approaching the upper shelf. The presence of large columnar grains in weld metal is shown to promote the phosphorus concentration at grain boundaries, which results in increasing of the share of brittle intergranular fracture.

According to the results of fractographic studies the dependence of the share of brittle intergranular fracture on three parameters: nickel content in steel (for a given phosphorus content), time of isothermal exposure at RPV operating temperature and fast neutron fluence was plotted. It was established that the share of brittle intergranular fracture increases with the fast neutron fluence, thermal exposure time and nickel concentration. Moreover, we showed that the share of this structural component in the fractures of irradiated Charpy specimens is higher than in similar samples subjected to the equivalent time of exposure to operating temperatures, but without irradiation. Increasing of the exposure time at the operating temperatures was found to enhance segregation processes, and increasing of the radiation dose, in addition, increases the density of radiation-induced nanoscale precipitates, i.e., radiation hardening. Effect of nickel on the share of brittle intergranular fracture is both embrittlement strengthening due to the formation of grain boundary impurities segregations and yield stress increasing due to the formation of radiation-induced nanoscale precipitates on nickel basis.

Thus, it was shown that grain refinement and reduction of nickel content in steel improves their resistance to radiation and thermal embrittlement. New compositions of steels and their manufacturing technology for reactor pressure vessels with higher capacity and resource were developed based on the obtained regularities of the structure influence on service characteristics of steels.

Keywords: reactor pressure vessel steels, radiation embrittlement, electron microscopy, radiation-induced precipitates, grain-boundary segregations

Energy Production from Fossil Fuels

Design of experimental facility to study partial oxy-combustion CO₂ capture technology

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Currently processes to implement CO₂ capture both in large pulverized coal power plants and new installations are based on either postcombustion or oxycombustion technologies, due to the gas conditions: low partial pressure of CO₂, large volume of gas and the presence of pollutants such as SO₂ and NO_x. These technologies feature significant penalties on the overall performance of the plant, mainly derived from the CO₂ removal from the gas stream in postcombustion, and from O₂ separation in oxy-combustion. Various researchers have showed that intermediate operating conditions approach (partial oxycombustion) could minimize the energy requirements to implement CO₂ capture (Figure 1). [1]

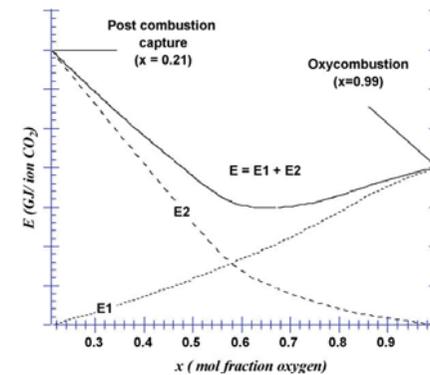


Figure 1. Energy cost postcombustion, partial oxycombustion and oxycombustion technologies

The main objective of this research work consists of analyzing the feasibility of a new CO₂ capture process for existing power plants under partial oxycombustion conditions by using oxygen-enriched combustion air combined with postcombustion through regenerative chemical absorption. The aim is to develop a new technology that becomes best available technology. It is expected to minimize investment and operating costs and to increase energy efficiency of CO₂ capture in large power plants.

The research group has carried out the design, construction and commissioning of a versatile and flexible experimental facility so as to explore a wide range of operation for a partial oxycombustion process. The facility consists of a 1.5 MWth boiler for the generation of combustion gas and a CO₂ capture system using regenerative chemical absorption.

The oxyfuel boiler is fed with a mixture of oxygen-enriched air and flue gas recycle (FGR) with a maximum concentration of 30% v/v O₂. The nominal gas flow is 300 Nm³/h, which allows working with concentrations up to 80% v/v O₂ in enriched air. Thereby, the experimental facility covers the entire operating range for partial oxycombustion process. The CO₂ capture system consists of a packed column and a pulverized column, where the CO₂ absorption takes place, and a regeneration column. In addition, the facility allows the study and development of new absorbents to minimize regeneration energy requirements and the fuel consumption in utilities.

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Electrochemical production of fuel from coal or CO₂ in mini-plants: a thermodynamic and quantum mechanical study

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In the past the authors demonstrated a unique way of silicon solar cell manufacturing [1] in substituting expensive equipment by electrochemical processes.

For the desire of making fuel out of coal or CO₂, this conference contribution is a first communication of ideas, which are formulated in inserting well established molecular data into the most fundamental formulas of physical chemistry. Given the well known processes of synthesizing fuel out of CO and H₂, or much more difficult with CO₂ and H₂ (Fischer-Tropsch), as well as the direct conversion of coal to fuel with hydrogen at high pressures and temperatures (Bergius-Pier), the following questions arise:

First, is it possible to substitute the provision of molecular hydrogen by the provision of protons in electrolytic solutions in order to avoid high pressures, and second, is it possible to substitute high temperatures by voltage on cathodes possibly covered with catalysts.

In any case proton selective membranes are needed.

In the case of reduction of concentrated CO₂ which is dissolved in electrolytes, cathode processes easily lead to CO, see e.g. [2]. The exiting new question is, if the provision of protons on the same or the other side of the, eventually porous, electrode can continue the extent of the CO₂ reduction to methane or small alcohols, or if a 2-electrode assembly is advantageous, where at the first electrode the reduction to CO occurs, and at the second electrode the synthesis of CO and protons in solution to hydrocarbons or alcohols is possible.

Much easier seems to be the possibility of synthesizing fuel out of coal and very acid electrolytes when switching the coal as a cathode. The electrolytic production of at least methane had been reported already in the very old literature [3]. Again, a proton selective membrane is needed. The exiting question to be answered experimentally is, if mixing particles of catalytic metal into the milled coal as electrically floating catalysts will lead to liquid hydrocarbon molecules needed for fuel.

Details of the questions will be discussed with the computer code CHEMIE.BAS. Experiments are in preparation, but cannot be performed before the conference date.

[1] F. Kröner et al; Solar Energy Vol. 86 pp. 548-557

[2] Y. Hori et al; Electrochimica Acta Vol. 39, pp. 1833-1839

[3] Gmelin; Kohlenstoff C [B] p. 743 ff

Experimental assessment of fuel production from waste plastics

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Recently more than 150 million tonnes of plastics were produced in the world. On the one hand, the consumption and production of polymers is increasing, on the other hand as landfill and incineration become more expensive and less accepted, the increasing amount of polymer wastes from them generates further mainly environmental problems. In present work catalytic cracking of waste plastics blend with heavy gas oil (HGO) was investigated using H-ZSM5 and H-BETA. Reaction systems that were studied included high density polyethylene HDPE and polypropylene blend with HGO. Reactions were carried out in 1L micro autoclave reactor under different conditions of weight, temperature and type of catalyst. The optimum conditions were 2.5% catalyst by weight of total feed stock, 60 min residence time, working at atmospheric pressure and three temperatures selected 400°C, 425°C and 450°C. The product distribution for the system [plastics and HGO] provided promised results of high yield of liquid [gasoline] up to 210°C, gases and small amount of heavy oils.

Keywords: Waste plastics, Gasification, Catalytic cracking, Rotary kiln reactor

Experimental Study Based on the Sorption and Flow in Porous Media of Oil to Delay or Inhibit Asphaltene Precipitation using Nanoparticle Type Differents

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The deposition of asphaltene is considered to be one of the most difficult problems during oil production. The presence of asphaltene in crude oil and consequently adsorption and deposition of asphaltene on the surface of the rocks has some effects on the properties of rock such as porosity, permeability and wettability. The aim of this study is to analyze the effect of chemical nature of twelve nanoparticles on the asphaltene sorption, hence the delay or inhibition of deposition and precipitation of asphaltenes on porous media under flow condition at reservoir pressure and temperature. Complete asphaltene sorption from nanoparticles can be effectively reached at relatively short times (around 2 min), making these sorbents good candidates for delaying or inhibiting of deposition and precipitation of asphaltenes. The sorption equilibrium of asphaltene for nanomaterials were determined using a static method in the range 150 - 2000 mg/L. The equilibrium adsorption data were fit to the Langmuir and Freundlich models. In addition, in this study investigated the transport of nanoparticles using an porous media at a typical pressure and temperature of reservoir. The results of the nanoparticles flow were successfully, showing the inhibition of the precipitation of asphaltenes in the porous media.

Keywords Asphaltene, nanomaterial, adsorption, precipitation, inhibition

Influence of turbulent mixing intensity on the MILD combustion and pollutant formation

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Mild combustion has been acknowledged as one of the most interesting combustion technologies to meet both the targets of high process efficiency and low pollutant emissions. Therefore the potential for its implementation in gas turbine combustors is investigated in recent research activities. In the Mild combustion regime, we find that the characteristic times of kinetics and turbulence become comparable and the two phenomena are coupled with each other. In this work, a Partially Stirred Reactor (PaSR) is applied to investigate the influence of the turbulent mixing intensity on the combustion process as well as its impact on NO_x formation. The proposed model is based on a combination of simple turbulent mixing approach with a detailed chemistry sub-model for methane oxidation and NO_x formation. The computational results demonstrate that the combustion processes as well as the pollutant formation are very sensitive to the mixing intensity. However, the total NO_x emissions after complete combustion are seen to be only slightly influenced by the mixing intensity.

Keywords Mild combustion; turbulent mixing intensity; gas turbine combustion; NO_x emission

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Modeling and Optimization of DME Direct Synthesis in Experimental exothermic Reactor

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In this research, modelling and reactor optimization of direct synthesis of Dimethyl ether considering four main catalytic reactions of production was performed and validated. Given that one-step production of Dimethyl ether is extremely exothermic, selection of an appropriate reactor for the temperature control of reactions have been considered.

For modeling, slurry bubble reactor, due to its good ability in temperature and mass transformation, was utilized. In this regard, the effect of temperature, pressure and reactor length on the productivity of reactor was also studied.

The reactor was modeled in steady state and isothermal situation. The equations were solved by CFD method of k-e model. The validation of them for the model was performed separately assuming 10% intensity.

Also the impacts of pressure and temperature parameters on CO conversion and DME selectivity were examined. Then the results were compared with those obtained under H-Mordente Zeolite modified catalyst with Alumina for methanol dehydration reaction and Cu_o/Zno/Al₂O₃ for water gas shift and CO consumption reactions. For each case the maximum error was less than 11%.

Taking into account the influence of reactor length increase on its productivity, the results of this study showed that efficient reactor length was 15 cm.

Keywords optimization, DME, direct Synthesis, experimental reactor, CFD

Modeling of the Reaction Kinetic for Direct Oxidation of Methane to Methanol

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In the present study the modeling of the reaction kinetic for direct oxidation of methane to methanol, using the ferric molybdate catalyst has been discussed. The operating temperature range was 643-723K and the pressure was 34 bar.

The Eley-Rideal based mechanism with surface reaction as rate determining step has fitted the experimental data well. In this model assumed that at the start of the reaction adsorbed oxygen, in dissociative form reacts with gaseous methane.

The kinetic parameters (rate constants and adsorption equilibrium constants) are determined by means of Ant Colony Optimization algorithm (ACO). The selected model parameters were determined and their correspondence with temperature have been discussed.

The reaction rate constants were obtained from Arrhenius temperature expression and the equilibrium adsorption constants are obeyed from van't Hoff equilibrium expression.

Keywords kinetic model; partial oxidation; methane; methanol; reaction rate

Molecular view on natural gas production from shales

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In the context of high fuel prices the reserves of natural gas stored in shales is too large to be ignored. Shale gas reservoirs are defined as highly porous organic-rich sedimentary rocks. These organic-rich patches ("kerogen") are responsible for the creation of methane, that is contained within them. In this study, we present a molecular model of kerogen based on Reverse Monte Carlo method. Arrangement of the kerogen atoms is driven by a systematic refinement of simulated radial distribution functions to match experiment. The porosity, pore size distribution and simulated methane isotherm are compared with experiment. We then focus on the transport properties such as diffusion and permeability. Figure 1 shows a snapshot of the simulation cell used for permeability calculations. High density and low density regions are settled at each end of the simulated kerogen cell that allows to attain a steady flow. The densities in these regions are controlled by Grand Canonical Monte Carlo simulation; the molecular motions are described by molecular dynamics simulations. Quantitative estimates of the permeability and conditions under which the gas production reaches a maximum are presented.

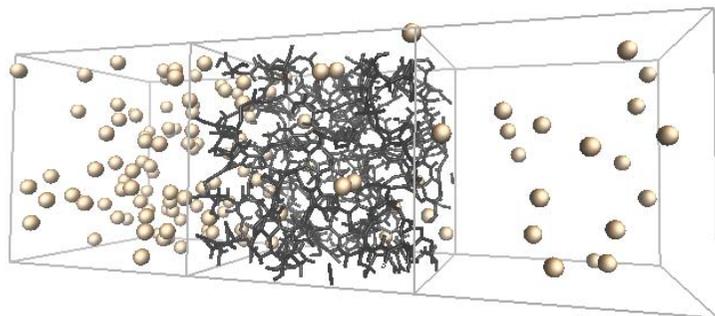


Figure 1: Snapshot of the numerical experiment. Gas molecules permeate through the kerogen from the high to low density region.

Optimal cogeneration selection in response to power and water growth

Rojin Derakhshan, Hossein Ahmadi Danesh, Jala Ghelichzadeh, Amirali Dolatshahi

Nowadays due to significant increasing in power and water demand, most of the improvement challenging focuses on selecting the optimum cogeneration option considering technical and economical aspects of the project. Recently, MAPNA Group is intended in designing and constructing turnkey EPC cogeneration plants. In response to the surging demand of power and water especially in southern region of Iran, MAPNA is designed typically simple cycle power plant coupling with MED-TVC thermal desalination system due to low initial cost. Mentioned alternative based on GT-HRSG-MED is a blocked design each including one 25MW gas turbine, one HRSG and two 5000m³/d capacity MED-TVC units to satisfy a given demand of power and water for awarded projects. This paper offers a proven alternative for new units for best utilization of GT exhaust gas potential, based on combined gas/steam turbine cycle, which make steam turbine electricity production as a byproduct of delivering steam to desalination process, while meeting the minimum desired market requirement. For each of the above configuration, thermodynamic modeling and optimization is presented and life cycle cost analysis based on direct cost allocation method is carried out. The comparative analysis between two mentioned alternatives shows that the proven configuration will be more thermodynamically efficient and economically feasible in association to current water and electricity tariffs. Finally a sensitivity analysis will be presented to determine the effect of power and water price on financial return of the project.

Porous polycarbonate membranes with Ni and Cu nano catalytic additives fabricated by selective laser sintering

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Optimal regimes of laser synthesis for three-dimensional porous membranes by selective laser sintering method were determined depending on laser influence parameters, metal-polymer powder compositions and fraction size of metal nano inclusions. As a metallic filler agent the copper ~ 50 μm , 70-120 nm and the nickel 15-200 nm were used. SEM equipped energy dispersive x-ray microanalysis are indicated about of relative stability of nano inclusions after liquid-phase laser sintering of polycarbonate.

In the comparison the catalytic characteristics of micro- and nano- copper were studied by the gas chromatography dates of benzene hydrogenation reaction. It was shown that reaction velocity increases up to 2.5 times. We have studied low temperature oxidation of carbon monoxide and propane on nickel nano powders differing in particle size and extent of oxidation. The nano nickel with optimized characteristics has been shown to have a marked catalytic effect on these processes.

The benefit for the understanding of catalytic properties of thin membranes in the form of Cu/CuO and Ni/NiO oxides, prepared by laser-assisted nanofabrication, was discussed in frameworks of perspectives for NEMS applications in fuel cells and hydrogen storage.

Key words: selective laser sintering, Ni and Cu nano oxides, nano – electro - mechanical systems

Preparation of Ni-MOF-74 membrane for CO₂ separation by layer-by-layer seeding technique

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Continuous and defect-free Ni-MOF-74 membranes were prepared on α -alumina support via a layer-by-layer seeding technique followed by secondary growth crystallization. The seeded supports were examined by SEM-EDX and AFM which evidenced that a uniform and compacted seeding layer can be formed on porous substrate surface through four alternated immersion cycles. Then Ni-MOF-74 seeding layer can grow into continuous Ni-MOF-74 membranes under optimal synthesis solution conditions. The as-synthesized Ni-MOF-74 membranes were characterized by XRD, SEM, BET and TGA. The continuous and crack-free membranes can be synthesized based on comparatively more concentrated solution and yet excessively concentrated solution is disadvantageous to obtain the uniform and defect-free membranes. Gas permeation properties of the membranes were investigated for small gases such as H₂, N₂, CH₄ and CO₂. Compared with other gases, Ni-MOF-74 membrane exhibits the stronger adsorption affinity to CO₂ and thus the permeation of CO₂ through Ni-MOF-74 membrane is dominated by surface diffusion. The high H₂/CO₂ ideal selectivity can be obtained for Ni-MOF-74 membranes.

Keywords Metal-organic framework; Membrane permeation; CO₂ capture; Diffusion; Ni-MOF-74.

Qualification of Materials and Their Welded Joints for Advanced Ultra-Supercritical Power Plants

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For advanced ultra-supercritical fossil power plants operated at a steam temperature of 700/720°C, new materials have to be used and integrated in the design process. Economical and cost effective construction demands for adequate materials for each component considering the temperature range where the component is operated. Therefore the ferritic steel T24, the martensitic steels T/P92 and VM12 as well as the nickel-base alloys 617, 263 and 740 are under investigation. Material testing - based on the manufacturing and design criteria - is necessary in order to have a reliable database of the relevant design characteristics. Investigations and experiments aimed to optimize and qualify welding consumables have been done. Additionally work to obtain expanded knowledge about the specific material behaviour under service like loading conditions for the evaluation of possible damage mechanisms is essential.

Results of basic qualification programs with standard specimens including welded joints show the applicability of the materials. In the paper beside results of creep rupture tests of base materials and welded joints, Weld Strength Factors (WSF) are discussed. Microstructural investigations to obtain information on precipitation and dislocation state in the virgin and aged conditions are presented.

Keywords ferritic / martensitic steel, Ni-base alloys, welding, creep, microstructure

Rapid Removal and Enhanced Catalytic Decomposition/Gasification of Colombian Asphaltenes by Hybrids Nanomaterials Containing Dispersed NiO Nanoparticles

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Hybrid nanomaterials can be used as adsorbents and catalyst in oil industry for in-situ upgrading. The main objective of this study was obtain the kinetic and thermodynamic equilibrium of asphaltene sorption onto hybrids nanoparticles of nickel oxide (NiO) supported on nanoparticulated matrices (silica gel or alumina) at different temperatures, times and concentrations, followed by subsequent thermal catalytic cracking of asphaltenes. Complete asphaltene sorption from hybrid nanoparticles can be effectively reached at relatively short times (around 10 min), making these sorbents good candidates for sorption and thermal catalytic steam gasification/cracking of asphaltene. The sorption equilibrium of asphaltene for hybrids nanomaterials were determined using a static method in the range 150 - 2000 mg/L. The equilibrium adsorption data were fit to the Langmuir and Freundlich models. Regarding to the silica-supported nanomaterial, the experimental data on asphaltene sorption isotherms were adequately adjusted by the Freundlich model. On the other hand, experimental data of the alumina-supported nanomaterial was adequately fitted by the Langmuir model. The pseudo-first-order and pseudo-second-order kinetic models were applied to experimental data at different concentrations of asphaltene, showing that the pseudo-second-order model agrees well. Thermogravimetric experiments showed that the catalytic action of the hybrids nanomaterials caused a significant decrease in the steam Gasification/Cracking temperature (270-300 °C with respect to pure asphaltene). This result was obtained with NiO onto alumina, which was the best hybrid nanomaterial evaluated in this study. Experimental results suggest that a correlation may exist between the sorption and the catalytic activity when the amount of NiO increases onto the surface of the supported nanoparticle.

Keywords Asphaltene, Hybrid nanomaterial, adsorption, steam Gasification/Cracking, catalyst

Spectroscopic study of heavy fuel oils (HFO) aging using specific cell and chemometric data treatment

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Heavy fuels, used with ferry boats or cargo boats could be considered as refining waste. Nevertheless they have to respond to stringent specifications as burning, stability and sulfur content. As structural and functional composition of fuels is usually affected by the crude oil origin and refined conditions, heavy fuels present a large variability of composition. All around the world, the sulfur content in particular covers a large range, between 0.2% in Argentina to 3.49% in Panama. Some sulfur compounds present a good antioxidant activity, so the fuel stability could be studied as a function of sulfur content.

One of the most suitable analytical techniques used for oil quality control is Fourier transform mid-infrared spectroscopy (FT-IR). In this paper FT-IR was used to continuously characterize the aging of various heavy fuels with a specific aging cell. This cell (Fig1) was initially developed for studying the aging of polymer modified bitumens (PmBs) or lubricating oils under thermal and oxidative conditions (air, N₂). A chemometric treatment, such as SIMPLe-to-use Interactive Self Modeling Analysis (SIMPLISMA), has been used to identify more precisely the chemical species produced or degraded during the thermal treatment of HFO and to track their evolution. This mathematical method allowed to obtain pure spectra of different species present and their concentration profiles. Interesting informations were obtained, about the ability of samples to support the oxidative treatment. The interest is to supply relative quantitative informations which traduces the temporal evolution of the relative abundance of the different product compounds during the thermal aging process according to the sulfur content in heavy fuels.

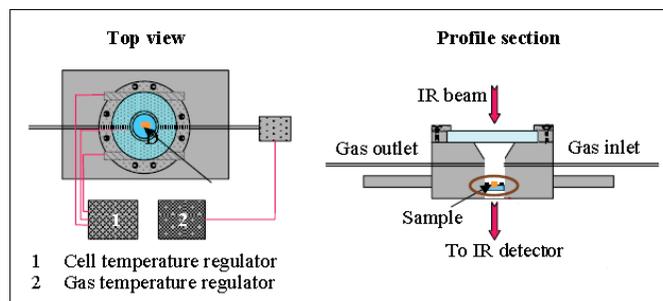


Fig1 : Specific cell from infrared microscopy

Keywords: Infrared spectroscopy, Aging, Heavy fuel, Antioxidant, SIMPLISMA, Sulfur

Study of the Kinetics and Mechanisms of Thermal Decomposition of Ellajjun Kerogen

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Extracted kerogen from Ellajjun oil shales was studied for kinetic parameters estimation. Estimation of activation energy and frequency factor was performed using different standard procedures. The employed standard methods are used to estimate the kinetic parameters using TGA/DGA data. Heating rates; 1, 3, 5, 10, 30, and 50 °Cmin⁻¹ are used with a 100 mlmin⁻¹ nitrogen flow rate.

The kinetic parameters determined using Friedman, Kissinger-Akahira-Sunose (KAS) Method, Flynn-Wall-Ozawa (FWO) and other methods. The values of activation energies and pre-exponential factor estimated using the different methods were used to model the conversion rate produced by experiment.

Keywords: Pyrolysis, Oil Shale, TGA, Kinetics, Parameters.

The influence of creep-corrosion interaction on the residual life of high temperature applications

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Particular attention is paid to the creep behaviour of materials used for high temperature applications like radiant tubes, flame tubes and industrial furnaces. These applications generally do not experience the classical low cycle fatigue as the occurring stresses are significantly lower than the flow stress of the material. The significant damage mechanisms are creep and corrosion in a combustion atmosphere.

The interaction between creep and corrosion plays an important role in determining the operating life of these components. Corrosion under ongoing creep processes would be influenced by the spallation of the oxide scale due to its deformation. This would accelerate the loss of the oxide-forming element from the alloy. On the other hand dissolution of the precipitates in particle strengthened alloys due to corrosion may lead to a reduction of the cross section and thereby creep strength. Precipitate coarsening further reduces creep strength.

The current study dealt with the experimental and computational investigation of the interaction between creep and corrosion processes in high temperature Ni alloys at a temperature of 1100°C. Exposure experiments in a synthetic combustion atmosphere without and under a tensile load were conducted over an accumulated duration of around 6000 h. Samples of different section geometries were loaded with tensile stresses encompassing the range of stresses occurring in the mentioned applications. The experiment allowed a direct comparison of the behaviour in air and in combustion atmosphere by exposition of samples with equal load and for equal exposure time in both atmospheres. This enabled a comparison with the data obtained through standardised creep rupture tests performed in air. The measured creep strains under the two conditions were compared to quantify the effect of the corrosion in combustion gas. A microstructural analysis of the samples was conducted to evaluate the effect of the creep deformation on the grain size growth and precipitate dissolution.

A carbide free zone was observed in the particle strengthened alloys which broadened with increasing exposure time. The broadening of the zone accelerated under tensile loading. In the carbide free zone voids were also observed. An optical analysis of the carbides before and after exposure showed a coarsening of the precipitates in the interior of the sample. Grain size increased over time and a larger increase was observed in the carbide free zone than in the centre of the sample.

Under the same tensile load a lower creep rate was observed for the samples loaded in the combustion atmosphere. The reasons for this are currently being investigated. An influence of corrosion on the tertiary creep regime is however likely due to the change in the distribution of the strengthening carbides. The loaded samples displayed a higher initial loss of chromium as compared to the unloaded samples. The total loss of chromium from the sample was used to model the depletion of chromium from the alloys. Different rate constants as observed for the unloaded and loaded samples were used to compute the rate of chromium loss.

Results of these observations were used to develop a computational procedure for the residual life assessment of a radiant tube. The modelling of creep strains was accomplished with the Theta Projection concept. A penalty factor was devised to integrate the effect of corrosion. Prediction of the time to creep rupture failure was accomplished with the Wilshire-Scharning methodology. Residual life estimates were obtained by the damage summation rule. The life assessment procedure was implemented in a spreadsheet program to estimate the operating life of a radiant tube under given component dimensions, operating conditions and residual life criteria. A module based structure of the program enables the user to input data and visualise results through plots and tables.

Keywords Ni alloys; creep-corrosion interaction; residual life assessment

Thermoeconomic analysis for optimum load allocation for a dual purpose cogeneration plant

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From a beneficial aspect of view, it is very important to optimize new plant designs considering each project's unique requirements. This paper presents a techno-economic study for a selected dual purpose power/water cogeneration plant employing a combined cycle power generation and a thermal desalination system. Simulation and thermodynamic analysis for such cogeneration plant is performed based on the Original Equipment Manufacturer design information. The system incorporates two SGT5-2000E gas turbine sets, two Heat Recovery Steam Generators, a back pressure steam turbine (supplying motive steam to MED-TVC system), and a MED-TVC thermal desalination system which is designed for a minimum water demand of 22MIGD. This study allows defining the optimum load allocations for steam turbine subject to satisfying power and water demand constraints. Moreover an indirect pro-rating cost allocation method is used for estimating unit water and electricity cost. The proposed scheme is capable of determining cost proportions and allocating correlated cost between the electric power and steam generation. Using cost estimating results, allows optimal selection for plant configuration to achieve the best financial return and competitive water and electricity pricing according to current energy and water tariffs while meeting market requirements.

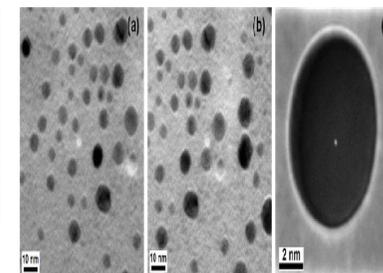
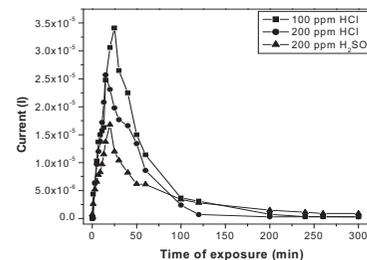
Energy Harvesting Materials

A facile method for synthesis of polyaniline nanospheres and effect of doping on their electrical conductivity

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The synthesis of polyaniline (PANI) nanospheres by a simple template-free method has been described. The polymerization of aniline in aqueous medium was accomplished using ammonium persulfate without any protonic acid. The UV-vis spectrum of PANI nanospheres displayed the characteristic absorption peak of $\pi-\pi^*$ transition of the benzenoid ring at 355 nm. The oxidation state of PANI nanospheres was identified with FT-IR spectroscopy by comparing the two bands at 1582 (ring stretching in quinoid unit) and 1498 cm^{-1} (ring stretching in benzenoid unit). The X-ray diffraction patterns demonstrated the low crystalline nature of PANI nanospheres. The morphology of PANI nanospheres was spherical and the mean diameter of nanospheres was found in the range of 5-12 nm. The thermal behavior of PANI nanospheres was studied by thermogravimetric analysis. The effect of doping of HCl and H_2SO_4 on PANI nanospheres was studied by measuring the current as a function of time of exposure. The high electrical conductivity of $6 \times 10^{-2} \text{ S cm}^{-1}$ was obtained for PANI nanospheres at their optimum doping state by 100 ppm HCl.



I Vs t of exposed PANI nanospheres films.

TEM images of PANI nanospheres doped with HCl and H_2SO_4 vapors

Keywords: polyaniline; nanospheres; electrical conductivity; effect of doping; polymerization

All-solution based engineering of aggregation effects in photon up-converting layers of organic binary composites

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Herein we present results of our studies on photoactive layers of solution-processed organic composites that could be potentially utilized as solid-state photon up-converting layers [1]. As a model system we use binary composites consisting of the organometallic complex (2,3,7,8,12,13,17,18-octaethyl porphyrinato) platinum(II) (PtOEP) mixed with the polymeric matrix poly[9,9-di-(2'-ethylhexyl)fluorenyl-2,7-diyl] (PF26) [2]. The effect of PtOEP aggregation on the photophysical properties of the PF26:PtOEP blend films is addressed with the use of time-integrated UV-vis and photoluminescence spectroscopy. The experimental data are supported by quantum chemical density functional theory (DFT) and time-dependent (TD-DFT) calculations with the aim to investigate the ground and the excited state properties of PtOEP in the form of single molecule and molecular aggregate (dimer). Tuning of the PtOEP aggregation in PF26 matrix is achieved with i) varying the PF26:PtOEP ratio, ii) performing thermal annealing of the PF26:PtOEP blend films at temperatures defined by differential scanning calorimetry and iii) casting the PF26:PtOEP from solutions of solvents with increasing boiling point. For all studied systems the photophysical process of resonant energy transfer from photoexcited PF26 to PtOEP is monitored as a function of PtOEP aggregation and a modified Stern-Volmer photokinetic model [3] is applied that is appropriate for the solid state. For reference purposes, control blend films of poly(styrene):PtOEP samples are also investigated spectroscopically. Optical probes of PtOEP aggregation have been identified by comparing the experimental absorption spectra of solution-processed blends with DFT/TD-DFT calculations. A discussion is presented on the impact of PtOEP aggregation on the process of photon up-conversion in the PF26:PtOEP blend films that can be useful for the sensitization of organic electronic devices such as photodiodes, light-detecting transistors, dye-sensitized and bulk heterojunction solar cells.

Keywords: organic composites, resonant energy transfer, aggregation, quenching, phosphorescence, delayed luminescence

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Argon Plasma Treated Flexible CNTs Bulky Paper with Improved Thermoelectric Properties

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With over 60% of the energy generated from primary energy sources wasted as dissipated heat, conversion of this huge amount of waste heat back to useful energy has been identified to play a significant role in improving sustainability. Typical experimentally reported figure of merit, ZT, values of CNTs are in the range of 10^{-3} to 10^{-2} , which is too low for thermal energy conversion applications. Herein, Ar plasma treated CNT bulky papers that are highly processible, mechanically flexible, durable and chemically stable are explored as a new type of thermoelectric material. The ZT values of these CNTs were greatly enhanced as compared to its predecessors. Plasma treatment duration was found to have a profound effect on the ZT values of the bulky papers as a result of enhanced phonon scattering and tuning of carrier concentration. The ZT values of the CNT bulky papers were significantly enhanced through Ar plasma treatment, i.e. increasing it from 0.01 for pristine CNTs to 0.4 for Ar-plasma treated CNTs. The improved thermoelectric properties were mainly due to the drastic increase in Seebeck coefficients and a reduction in the thermal conductivities, at the expense of reduced electrical conductivities.

Keywords Carbon Nanotubes; Thermoelectrics; Figure of Merit; Seebeck coefficient; Plasma treatment

Calendar aging and post mortem analysis of a Graphite/LiFePO₄ cell

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Graphite/LFP commercial cells are stored under 3 different conditions of temperature (30°C, 45°C, and 60°C) and SOC (30, 65, and 100%) during up to 8 months. The calendar aging phenomena was evaluated by employing a various set of non-destructive electrochemical tests at different storage times. After storage, the cells stored at 45°C and 60°C exhibit capacity fade while those stored at 30°C do not. The extent of capacity fade strongly increases with storage temperature and to a lesser extent with the state of charge. The data analysis identifies the loss of cyclable lithium as the main source of capacity fade. This loss mostly arises from side reactions taking place at the anode, e.g., solvent decomposition leading to the growth of the solid electrolyte interphase. However, the existence of reversible capacity loss also suggests the presence of side reactions occurring at the cathode, which are less prominent than those at the anode. The differential voltage analysis does not show any evidence about active-material loss in the electrodes and the EIS analysis shows an overall impedance increase of 70% or less. In addition, XRD (X-ray diffraction), SEM (scanning electron microscopy), and half-cell studies were carried out on the fresh and used electrodes (LFP and graphite electrodes) harvested from the dismantled cells. The contribution of each individual electrode to the overall degradation of the cells is investigated. The results obtained are in accordance with those suggested from the nondestructive analysis, i.e., (i) loss of cyclable lithium, and (ii) no loss of active material in the electrodes.

Keywords Graphite/LFP cells; Storage; Capacity fade; Impedance; Rate capability; PITT

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Effect of spark plasma texturing on the thermoelectric properties of doped bismuth telluride

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Thermoelectric materials are being explored as suitable materials for waste heat recovery and other applications. The performance of thermoelectric materials is indicated by the dimensionless figure of merit ZT defined as $ZT = S^2\sigma T/\kappa$ where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity. Bismuth telluride shows the maximum figure of merit close to 1 and the anisotropic behavior of this compound makes the thermoelectric behavior more dependent of the microstructure. Bismuth telluride can be suitably doped with elements such as Sb, and Se to obtain p or n -type behavior respectively. We have studied the thermoelectric properties of p -type ($\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$) and n -type ($\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$) powders using spark plasma texturing method. Spark plasma sintering method allows rapid sintering at considerably low temperatures, texturing and high densification as compared to conventional sintering. The obtained results will be discussed in details taking into account the dependence of thermoelectric properties such as resistivity, Seebeck coefficient and thermal conductivity on the microstructure of the textured and non textured specimens.

Keywords: Thermoelectrics, Spark Plasma Texturing, Microstructure.

Effect of thermal gradient on spin-wave amplification in a ferromagnet: numerical study and phenomenological model

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Recent experiments have shown that a temperature gradient across a magnetic material (conductor or insulator), generates a pure spin current. This phenomenon, known as Spin-Seebeck Effect (SSE) [1, 2] has opened a research field in which temperature, magnetism and electronic transport are strongly related [3]. In conducting ferromagnets, pure spin current is generated mainly by itinerant electrons with opposite spins, flowing in opposite directions. In insulating ferromagnets, spin current cannot be carried by electrons, so that a spin wave spin current [2] associated to the magnetization dynamics in the sample, is at the basis of spin current propagation.

The SSE offers a simple and effective way to transfer information using heat, and a theoretical investigation on the effect of thermal gradient on the magnetization dynamics is necessary, both for a deep understanding of the phenomena and for possible applications [3]. We report on numerical simulations, which describe the magnetization dynamics of a Permalloy nano-structure in presence of thermal gradient. Our simulations show that heat flow acts as a *thermal torque*, that compensates the damping and leads to an exponential amplification of the SW signal, in qualitative agreement with a recent experiment [4].

In order to find the optimum material for applications, our computations have been performed for different values of damping, applied field and exchange stiffness, and show how SW amplification is influenced by those parameters.

Moreover, we have developed a simple theoretical model, based on a classical continuity equation for SW power, that allows to understand qualitatively our simulations.

Keywords Spin-Seebeck effect; thermal gradient; spin current; spin waves; magnetization dynamics

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Improvement of photo-active functions of solar cell and photoelectrochromic cell for energy and environment application

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The use of certain technologies requires reliable and effective ways of storing energy, and the improvement of chemical and physical properties of materials which can improve the current energy systems and lead to energy alternatives that can compete with existing technologies. In all green energy, the effective use of solar energy is an interesting and challenging topic. Application of nanotechnology can improve the photo-electric transfer efficiency of solar cell and overcome the recent complex global issues of energy, environment and aged society-related problems. The transfer efficiency can be improved up to 5 % by the use of nanostructure composite based solar cells. The cycling stability of the photoelectrochromic devices can be improved with the use of certain dopant materials in the electrochromic films. The response time and reversibility of photo-electrochromic WO₃ films are enhanced using polyethylene glycols (PEG). This nanostructure tungsten oxide film also has higher coloration efficiency and fast response time. Using different process technology and materials, we have increased the energy transfer efficiency of solar cell. Proper combination of technology and materials, we can also construct a low pollution and intelligent life environment. Details of the materials, technology and process development will be presented during presentations.

Nickel and Iron Co-substituted Lanthanum Cobaltates as New Thermoelectric Oxide Materials

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The ability of thermoelectric materials to convert heat flux into electricity determines them as a key source of the “clean” energy of the future. The classical thermoelectric materials are the semiconductors based on bismuth and tellurium. Their economic importance is greatly restricted because of their toxicity and low chemical and thermal stability at high temperatures. Contrary, oxide-based materials are usually more stable and less toxic that makes them alternative candidates for future thermoelectric applications. In the last years the most intensive studied thermoelectric oxides are cobaltates with layered and perovskite type structures.

In this contribution the formation of a new thermoelectric oxide material is reported. The oxide composition comprises LaCoO₃ perovskites where cobalt is partially replaced by nickel and iron. When Ni and Fe ions are in equal amounts, their effects are balanced and cobaltates with improved thermoelectric efficiency are formed: LaCo_{1-2x}Ni_xFe_xO₃, 0 < x ≤ 0.25. All perovskites are obtained from freeze-dried citrate precursors at 900 °C. This method is shown to be effective for the preparation of substituted perovskites, where Ni and Fe are randomly distributed. Structural and morphological characterizations are carried out by powder XRD and SEM analysis. The thermoelectric efficiency of the perovskites is determined by the dimensionless figure of merit which is calculated from the independently measured Seebeck coefficient (S), electrical resistivity (ρ) and thermal conductivity (κ).

The replacement of cobalt with nickel and iron in LaCo_{1-x}(Ni,Fe)_xO₃ for the concentration range 0 ≤ x ≤ 0.5 yields oxides with a rhombohedrally distorted perovskite structure. The single substitution in LaCoO₃ affects the thermoelectric parameters (S, ρ and κ) in a different way for Ni and Fe additives. The electrical resistivity decreases significantly during the progressive replacement of cobalt by nickel. This is a consequence of the increased carrier density. In the same order, there is a decrease in the values of the Seebeck coefficient and the thermal conductivity. As a result, slightly doped LaCo_{1-x}Ni_xO₃ oxides (0.05 ≤ x ≤ 0.10) display a higher thermoelectric efficiency as compared to LaCoO₃: ZT=0.07. The substitution for cobalt with iron leads to an increase in ρ, while κ decreases and S tends to increase. As a result, LaCo_{1-x}Fe_xO₃ (x=0.05) exhibits a dimensionless figure of merit ZT=0.04 which is slightly higher than that of LaCoO₃. Using the specific effect of Ni and Fe additives on S, ρ and κ, new perovskite-type thermoelectric materials are prepared by double substitution (i.e. LaCo_{1-x}Ni_{x/2}Fe_{x/2}O₃). In these perovskites, the effect of the nickel ions on the electrical conductivity and on the Seebeck coefficient is more pronounced than that of the iron ions. It is noticeable that the double substituted perovskites have an enhanced electrical conductivity as compared to that of LaCoO₃, which does not depend on the total Ni+Fe content. The synergetic effect of Ni and Fe is demonstrated by the effective reduction of the thermal conductivity in comparison with the single substituted perovskites. The perovskite with the composition LaCo_{0.8}Ni_{0.1}Fe_{0.1}O₃ exhibits the best thermoelectric efficiency with ZT=0.16, which is an order of magnitude higher than that of LaCoO₃ at room temperature. These results open new possibilities for optimization of the thermoelectric activity of LaCoO₃-based ceramics.

Acknowledgment: Authors are grateful to the financial support from the National Science Fund of Bulgaria (IDEAS No D0-02-309/2008).

Keywords thermoelectric oxide materials; perovskites

Optimal design of transparent and conductive electrodes using « multiobjective optimization/data clustering » coupled approach, application to thin film solar cells

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The development of optically transparent, electrically conductive oxides (TCOs) is relevant to a broad range of optoelectronic applications [1]. The design of new TCOs and the optimization of existing ones require powerful modeling tools and algorithms that would be able to handle the multi-objective nature of the problem. Here we present a new approach that merges TCO physics to multi-objective evolutionary optimization algorithms. In contrast to conventional figure-of-merit relations, our approach discards any weighting-induced bias and hence provides accurate information on the material's performance. Moreover, it allows identifying optimization guidelines for many TCO structures. We show that once we envisage a device application (e.g. thin film solar cells), the analysis of the calculated Pareto optimal set by data clustering techniques yields essential information on performance enhancement. Our approach opens the way towards *in silico* design of optoelectronic materials and devices [2].

Keywords Optimal Design; Genetic Algorithms; Pareto Set; Data Clustering; TCOs

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Photo-Electron Injection into TiO₂: Molecule vs Quantum Dot vs. Water

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We presented a detailed comparison on the similarities and differences of the ultrafast photoinduced electron transfer (ET) from three kinds of donor species, namely water, PbSe quantum dot (QD), and alizarin, into the acceptor TiO₂ surface via *ab initio* nonadiabatic molecular dynamics (NAMD) simulations. The similarities contain the all ET events occur on sub-10-fs due to the strong donor-acceptor coupling. The main differences stem from the size and dimensionality of the donor species. For example, both the QD and the molecule are localized species; however, the QD is notably larger than the molecule. In contrast, the water layer in the wet-electron system is delocalized two dimensional object. The ET mechanism depends on the dimensionality of the donor. The injection from the localized donor states of the QD and the molecules is dominantly adiabatic. In contrast, the injection from the two-dimensional water layer in the wet-electron system exhibits a high, 50% NA component. The NA mechanism is efficient for the wet-electron because it is delocalized over two dimensions and is able to couple with a dense manifold of delocalized TiO₂ conduction band states. The high density of acceptor states in this case favors the NA mechanism. All three systems exhibit diverse scenarios for individual electron injection events, involving a complex interplay of ET mechanisms, time scales, and phonon dynamics.

Keywords: TiO₂, Electron Transfer, Nonadiabatic Molecular Dynamics, Electron-Phonon Coupling

Plasmonic applications: New designs for high-efficiency thin film photovoltaics

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Thin-film solar cell technologies continue to stand out as the most promising low-cost “next generation” technology with photon-to-current conversion efficiencies (η) in excess of 20% reported for lab scale cells [1,2]. The efficiencies of these devices primarily depend on the properties of the absorber material and the interfaces. However, with improved understating of absorber and interface structures, these record efficiencies and the manufactured cell efficiencies fall far short of the thermodynamic limits to photovoltaic energy conversion.

Plasmonics is an emerging field that makes use of the nanoscale properties of metals, and its application in solar cells has seen a recent surge of interest. Metal nanostructures (e.g. nanoparticles, NPs) support surface plasmons that are the collective oscillation of free electrons and characterised by a set of resonant frequencies that depend on the nanostructure topology. In the case of NPs, the surface plasmon resonance (SPR) is affected by the NP shape, size, and the dielectric properties of the surrounding medium. By choosing an appropriate shape and surrounding medium, it is possible to shift the SPR frequency into the visible or IR region of the electromagnetic spectrum, which is the range of interest for photovoltaic (PV) applications [3].

In this work, our approach addresses several solar-cell architectural designs that may pave the way towards enhancing efficiency beyond thermodynamic limits in thin film photovoltaics. Although many practical challenges await the work described in this presentation have considerable potential to enable very high photovoltaic efficiencies.

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PVDF-TrFE coated stainless steel flexible blender for energy harvesting from wind flow

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PVDF-TrFE piezoelectric copolymer has attracted great attention in piezoelectric energy harvesting applications over the past years. In this presentation, we come up with the idea that coating flexible stainless steel substrate with PVDF-TrFE piezoelectric copolymer and analyze the ferro, piezoelectric property, further using this blender to scavenge energy from wind flow. The method employed to the coating process is tape casting. If we could get strongly adhered, flatly coated PVDF-TrFE on the flexible stainless steel substrate, prospecting applications of this blender are over our imagination. We could use this blender to fabricate large area piezoelectric sheet and then modify it with various structure like multi-stacking layers. To obtain the essential piezoelectric and ferroelectric characteristic we needed to carry out appropriate heat treatment from 100-150°C after the end of tape casting in a manner sweeping the PVDF-TrFE solution poured at the edge of stainless steel over the whole substrate with doper blade. After the heat treatment process, we measured the film thickness using Tencor alpha step-500 and performed x-ray diffraction and FTIR measurement for detecting whether the coated polymer had increased crystalline of ferroelectric beta phase or not and involved ferroelectric all-trans conformation in it. Our observation had showed that it had the best results at 130°C with its thickness around 7-8µm. In order to enhance the piezoelectric performance the process of polling is imperative. So we gave the device top Al electrode and executed the polling process at 1.5kV for 10minutes and the corresponding d_{33} and g_{33} parameters are 30pC/N and 6Vm/N, respectively. After that we fixed it firmly on self-customized brace so as to measure the relative power output generated from the device under varied wind speed. The electric circuit used here was a variable resistor directly connected to piezoelectric device. We also tried to obtain the maximum output with different load resistance.

Keywords: PVDF-TrFE copolymer; piezoelectric property; energy harvesting; heat treatment; tape casting.

Room-temperature photoluminescence properties and corresponding size-effect of p-CuAlO₂ nanoparticles for energy-related applications

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P-type semiconducting, transparent oxides have recently gained renewed interest for possible applications in UV-based solar cells and 'Transparent Electronics'. Amongst these materials, p-CuAlO₂ is one of the very important transparent oxides having a wide range of applications in solar cells, light emitting diodes, field emitters, thermoelectric converters, hydrogen generator, and sensors among others. We have observed a strong excitonic effect in sputter-fabricated p-CuAlO₂ nanoparticles via photoluminescence studies. The nanoparticles show room-temperature photoluminescence peaks of near-band-edge emission due to recombination of free excitons, depicting the presence of room-temperature excitons within the nanoparticles. Also, a size-dependent blue-shift in the emission peaks is observed, which is attributed to the quantum confinement effect within the CuAlO₂ nanoparticles. Theoretical calculations of bandgap enhancement values are found to be matching fairly well with that of the experimentally obtained values, confirming the existence of the quantum size effect within the nanomaterial. The nanocrystalline structure and phase of the as-deposited nanoparticles are confirmed by X-ray diffraction and electron microscopic measurements. The room-temperature and size-dependent photoluminescence properties of this nanomaterial will be very useful for light emitting diode and similar optoelectronic applications. Also the proper tuning of the nanoparticle size will provide the necessary flexibility of using a wider range of solar spectrum for potential energy applications, especially in the field of 'Transparent electronics'.

Keywords p-CuAlO₂ nanoparticles; room-temperature excitons; size-effect; Transparent electronics.

Substitution Strategy for Controlling the Thermoelectric Efficiency of Layered and Perovskite Oxides

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Depletion of oils and climate changes are the main drive in development of new class of materials that are able to store and convert energy effectively. The classical thermoelectric materials are the semiconductors based on bismuth and tellurium. Their economic importance is greatly restricted because of their toxicity and low chemical and thermal stability at high temperatures. Contrary, oxide-based materials are usually more stable and less toxic, that make them alternative candidates for future thermoelectric applications. In the last years, the most intensive studied thermoelectric oxides are cobaltates with layered and perovskite type structures.

In this contribution, a formation of new thermoelectric oxide material is reported. The oxide composition comprises LaCoO₃ perovskite, where cobalt is partially replaced by nickel and iron. When Ni and Fe ions are in equal amount their effects are balanced leading to the formation of cobaltates with improved thermoelectric efficiency: LaCo_{1-2x}Ni_xFe_xO₃, 0 < x ≤ 0.25. All perovskites are obtained from freeze-dried citrate precursors at 900 °C. This method is shown to be effective in the preparation of substituted perovskites, where Ni and Fe are randomly distributed. Structural and morphological characterizations are carried out by powder XRD and SEM analysis. The thermoelectric efficiency of the perovskites is determined by the dimensionless figure of merit, calculated from the independently measured Seebeck coefficient (S), electrical resistivity (ρ) and thermal conductivity (κ).

The replacement of cobalt with nickel and iron in LaCo_{1-x}(Ni,Fe)_xO₃ for the concentration range 0 ≤ x ≤ 0.5 yields oxides with a rhombohedrally distorted perovskite structure. The single substitution in LaCoO₃ affects its thermoelectric parameters (S, ρ and κ) differently for Ni and Fe additives. The electrical resistivity decreases significantly during the progressive replacement of cobalt by nickel. This is a consequence of the increased carrier density. In the same order, there is a decrease in the values of the Seebeck coefficient and the thermal conductivity. As a result, slightly doped LaCo_{1-x}Ni_xO₃ oxides (0.05 ≤ x ≤ 0.10) display a higher thermoelectric efficiency as compared to LaCoO₃; ZT=0.07. The substitution for cobalt with iron leads to an increase in ρ, while κ decreases and S tends to increase. As a result, slightly doped LaCo_{1-x}Fe_xO₃ (x=0.05) exhibits a dimensionless figure of merit ZT=0.04 which is slightly higher than that of LaCoO₃. Using the specific effect of Ni and Fe additives on S, ρ and κ, new perovskite-type thermoelectric materials with double substitution (i.e. LaCo_{1-x}Ni_{x/2}Fe_{x/2}O₃) are prepared. In these perovskites, the effect of nickel ions on the electrical conductivity and on the Seebeck coefficient is more pronounced than that of the iron ions. It is noticeable that the double substituted perovskites have an enhanced electrical conductivity as compared to that of LaCoO₃, which does not depend on the total Ni+Fe content. The synergetic effect of Ni and Fe is demonstrated by the effective reduction of the thermal conductivity in comparison with the single substituted perovskites. As a result, the perovskite with a composition LaCo_{0.8}Ni_{0.1}Fe_{0.1}O₃ exhibits the best thermoelectric efficiency with ZT=0.16, which is an order of magnitude higher than that of LaCoO₃ at room temperature. These results open new possibilities for optimization of the thermoelectric activity of LaCoO₃-based ceramics.

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Keywords thermoelectric oxide materials; perovskites

Synthesis and Characterization of Gold Nanoparticles- Cationic Polythiophene nanocomposites for Optoelectronics Applications

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Hybrid nanocomposites of metal nanoparticles (NPs) and π-conjugated polyelectrolytes (CPEs) have recently shown great interest due to their potential applications in photovoltaics, non-volatile memory devices, surface enhanced Raman scattering (SERS) probes [1]. A combination of optoelectronic properties of π-conjugated polymers with plasmonic effects of noble-metal NPs can bring about or alter phenomena such as a local enhancement of charge transfer or excited state quenching, which affect the efficiency of the photovoltaic energy conversion. We report the synthesis and characterization of the nanocomposites of regioregular cationic polythiophene poly {3-[6-(1-methylimidazolium-3-yl)hexyl]thiophene-2,5-diylbromide}, PMHT-Br with gold (Au) NPs. The effect of Au nanoparticles on the optical and electronic properties of the cationic polythiophene has been studied in the solution and film form. The UV-visible spectra of the composites film show the broadening of peak at 532 nm at the same position for PMHT-Br due to the overlapping of the plasmon band of Au NPs and π-π* transition band of pure polymer. The measured electrical conductivity for the composites exhibit one or two orders of magnitude higher conductivity depending upon the concentration of the Au NPs. Mixed ionic and electronic conductivity is demonstrated by the break at ca 80 °C that is due to the steep increase in the mobility of ions caused by the increased segmental motion of polymer chains above 80 °C as confirmed from the impedance spectroscopy. In fluorescence spectra of composites, the observed quenching of the polymer fluorescence, particularly at lower polymer concentrations, points to the efficient energy dumping from the photo-excited conjugated polyelectrolyte to the nanoparticles. It suggests that Au NPs serve as efficient fluorescence quenchers for conjugated polyelectrolytes.

Keywords Cationic polythiophene; gold nanoparticles

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Energy Transmission, Distribution and Storage

A holistic evaluation plan for agent-based brokerage systems for neighbourhood electricity usage optimization

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This paper outlines the evaluation methodology implemented in the context of the EU funded project NOBEL (Neighbourhood Oriented Brokerage Electricity and Monitoring System) of the 7th Framework Programme. NOBEL developed and implemented an integrated system of services and applications, that enables all users of an electricity network to manage their energy behaviour in a more efficient way and to optimize energy usage produced from clean energy sources. To achieve these objectives, NOBEL applications were addressed to different clusters of users, namely the energy distribution network operators (DSOs), private energy retailers (PSs) and different end-users of energy within the grid. The end users were clustered to simple consumers and to prosumers (was defined from the words *producer* and *consumer*). By the term prosumer is meant a user that consumes and produces energy (for example a household that has installed small scale photovoltaic generators). The role of prosumers is crucial as the project aims to use energy from mainly small scale prosumers (e.g. roof photovoltaic systems, electric vehicles) within the local grid and to achieve more dynamic interplays between energy network operators and prosumers. On the other hand, the energy distribution network operators using NOBEL applications have an overview of real-time demand and clean energy production and optimize the match between them. In the bargain, NOBEL end-user applications, using data from smartmeters installed, enable prosumers to achieve more efficient energy management. NOBEL high level objectives are related with energy impacts, mainly increase of energy efficiency, reduction of energy consumption, reduction of CO₂ emissions, etc. These impacts are translated also to monetary and social impacts, whenever possible.

This paper describes the integrated approach followed for the evaluation of the system and the assessment of its impacts, focusing on energy impacts, aiming to an overall energy consumption reduction 20%, in conformance to the European Council targets for 2020.

The holistic assessment encompasses the following evaluation categories: technical assessment, user assessment and impact assessment. Technical assessment evaluates all technical components and applications developed within NOBEL via lab-test and pilot tests, while user assessment evaluates the performance of the system under the influence of the human factor. These results will formulate the basis of the impacts assessment, to be performed with a post-pilot analysis.

The main indicators to be measured are namely the overall consumption reduction, the production by clean energy, the energy efficiency, the energy imported, the CO₂ emissions, the prosumers' expenses and revenues for/from energy, the DSOs revenues and long term environmental impacts.

The evaluation of these indicators will be realized via log files from smartmeters, log files from NOBEL applications, DSOs data, questionnaires for all users, etc. The impacts will be assessed through comparisons with reference cases or with objectives defined by the project and are clustered to impacts on energy, economic and social. In specific, all data will be compared to historical data from the same site (Alginet, Spain) or to a defined by the project objective e.g. overall energy consumption reduction 20%.

All results will be extended by assuming business models for different levels of scalability and different environments and performing a socioeconomic analysis.

Keywords NOBEL project, clean energy, prosumers, electric vehicles, energy management system, CO₂ emissions, evaluation plan, smart grid

Capacity fading in Li-ion batteries: Thermal and state of charge effects

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An extensive testing programme has been implemented at LNEG for the study of Li-ion batteries including thermal and state of charge effects, ageing by cycling and post-mortem analysis. In this work, cells with a nominal capacity of 10 Ah are used.

An ARC calorimeter allowed the evaluation of the generated heat in the various stages of the life of the battery and electrochemical diagnostics was done by electrochemical impedance spectroscopy (EIS).

Impedance measurements of the lithium-ion battery at several states of charge were carried out by a Solartron 1250 Frequency Response Analyser coupled to a Solartron 1286 Electrochemical Interface. All EIS measurements were made in a galvanostatic mode, in a four-terminal configuration with ac signal amplitude of 300 mA and frequency range from 600 Hz to 0.01 Hz. The connection to the test cell was done in order to minimize the phenomenon known as mutual inductance that limits the ability of EIS system to make accurate measurements of low impedance values at high frequencies, which is usual in lithium-ion batteries. The analysis of impedance spectra was made on the basis of equivalent circuits proposed a priori and the associated parameters, estimated by adjustment based on the "Complex Non-Linear Least Squares" (CNLS) method. The identification of interfacial reactions and the determination of characteristic parameters are instrumental in the study of a correlation with the battery state of charge.

Results are reported on 300 and 600 cycles aged batteries, which present, after normal charge/discharge cycles, a capacity fade of 8.3 and 11.9 % in relation to tested virgin cells.

A study of the state of charge (SOC) and its relationship with the EIS response of the battery was carried out. In between partial charging cycles a period of stabilization of 3 h, at the open circuit, was allowed. An equivalent circuit with 3 time constants was selected in order to account for the several processes occurring in the battery charging, including the response of the so called SEI film at the solid electrolyte interface. The resistance of the SEI film was found to increase with SOC, stabilizing at values higher than 60%.

The effect of temperature on performance was study at 45°C. Tests were conducted for virgin cells in the fully charged state after 4 and 8 weeks, demonstrating a decrease of the open circuit potential. Discharge/charge cycles were analyzed together with the generated heat. A decrease in the discharge capacity higher than 3% was observed. Drastic variations in the impedance spectra as a result of thermal ageing will be discussed.

Keywords: Li-ion batteries; state of charge; thermal effects; ageing; electrochemical impedance spectroscopy

Carbon foams derived from Polyacrylonitrile-Formaldehyde Resins -prospective electrode for hybrid supercapacitors

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Carbon, in its various forms, is currently the most extensively examined and widely utilized electrode material in hybrid supercapacitors. The major scientific and technical challenges that have to be addressed to determine the feasibility of hybrid supercapacitors include: new and/or optimization of electrode materials (increase of the active surface and control of pores size and their distribution, increase affinity between electrode and electrolyte, reduce overlapping effect of the electrical double layer, improve conductivity and decrease leakage current, low cost), control of the charge storage at the solid-liquid interfaces, the electrolyte composition, reduced life of devices due to redox processes, increase the operating voltage.

The double-layer capacitance of carbon materials is proportional to their specific area and capacitance in terms of area. Carbon foams represent a group of lightweight materials that have been widely used due of its unique properties. Beside traditional applications (heat-shielding systems in aerospace, bone surgery materials, etc.), supercapacitor electrodes, battery and fuel cell electrodes have been of significant interest to this research.

A new form of highly porous carbonized polyacrylonitrile-formaldehyde resins microcellular foam in the presence of ferrocene has been developed by a method involving two stages of pyrolysis: 1. early pyrolysis in thermo-centrifugal field and 2. final pyrolysis up to 900°C. This method provides uniform dimensions and size distribution of pores inside the foam.

The chemical composition and morphology of the new supercapacitor electrodes we have obtained were characterized by Optical Microscopy (OM), Scanning Electron Microscopy (SEM), and Raman Spectroscopy (RS). OM and SEM studies show uniform and highly porous structures with 50 - 100 µm pores dimension of the carbon foam. RS has confirmed the presence of D and G lines of carbon. The electrochemical measurements were performed in a three-electrode cell system where synthesized carbon material is used as working electrode. The obtained results offer a promising perspective for the obtained material to be used as electrode for supercapacitors.

Keywords: Carbon foams, Hybrid supercapacitor, Supercapacitor electrode

Charge monitoring and control system for Li-Ion batteries with modular communication interfaces

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Smart charging batteries and Vehicle-to-Grid (V2G) solutions have been pointed out as being key developments towards large scale deployment of Electric Vehicles (EV's) and Renewable Energy production equipments into smart-grids. Nevertheless, the system's integration of these cell batteries requires flexible, accurate monitoring and control of the charge/discharge processes, the introduction of new cell balancing technologies and algorithms and the inclusion of data communication interfaces for exchanging battery's condition relevant information with smart-grid's controlling and management infrastructures. These functionalities are fundamental to guarantee and optimize battery operating conditions and to prevent degradation of its performance or autonomy.

Despite the fact that there is nowadays some offer of on-the-shelf Battery Management Systems (BMS) and that some battery's manufacturers integrate such OEM devices into their products, there is still need for improvements in cell's accurate charge monitoring and estimation, based on real-time determination of relevant cell functional parameters, and in local equalizing control algorithms to extend battery's autonomy and lifecycles.

A modular and programmable system for battery management and charge/discharge monitoring and control, currently under development at LNEG, is described. This system offers a flexible choice of communications interfaces with other external systems, useful for smart-grid interactions, and is primarily intended to real-time monitor and manage the relevant physical parameters for accurate charge estimation of large string Li-ion cell packs. It has a modular architecture and offers the possibility to use custom algorithms for cell's charge estimation. This system can be easily configured to be used with various electrochemical cell types and can also be integrated with smart battery charging systems, important issue for of a full integration of V2G Electrical Vehicles into smart-grid applications. It can be programmed and configured with custom management and control functionalities, offering several hardware and firmware expansion possibilities, like an active non-dissipative charge balancing control module that is also under development. The active equalization method implemented in this expansion module, which architecture is also presented, works both during charge and discharge stages and is more energy efficient than the traditional passive energy dissipation approaches, followed on most of the actual OEM and commercial BMS systems. The functionalities included in the described BMS modular architecture are discussed, referring their advantages in the context of smart battery management systems for EV's and renewable energies smart-grid integration.

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Keywords: low cost modular BMS, cells charge equalization

Corrosion mechanism of copper in palm biodiesel

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As compared to diesel, biodiesel is more corrosive for automotive materials. The present study aims to investigate the corrosion mechanism of copper in palm biodiesel. Static immersion tests were conducted in biodiesel at room temperature for 200-2880 h. Corrosion of copper was investigated by measuring corrosion rates and examining the exposed surface through SEM/EDS, XRD and XPS. Fuels were characterized by TAN analyzer, FTIR and GCMS. Corrosion patina is found to be composed of Cu₂O, CuO, Cu(OH)₂ and CuCO₃. Dissolved O₂, H₂O, CO₂ and RCOO⁻ radical in biodiesel seem to be the leading factors to enhance the corrosiveness of biodiesel.

Efficiency of Catalysts in Rechargeable Lithium-Air Batteries

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Aqueous Li-air batteries have attracted a great deal of attention due to their high theoretical energy capacities. The novel battery system has the potential of replacing gasoline engines in automobiles so as to reduce pollution and dependence on foreign oil. However, while still in the early stages of research, the reported energy capacities of Li-air batteries are far from what has been theoretically predicted. In this research, we have designed a Li-air battery that has a Li | organic liquid electrolyte | Li⁺-conducting glass ceramic plate (LiGC plate) | DI water | air electrode structure and also developed more cost-effective and high-performance alternative cathode catalysts (MnO₂ and hybrid catalysts CoPc/MnO₂) to replace carbon and Pt. The impacts of the catalysts for air electrode on the battery performance were studied.

Highly improved voltage efficiency was observed with this system by using MnO₂ and hybrid catalysts CoPc/MnO₂. The observed open circuit voltages (OCV) for the battery system containing various catalysts C, MnO₂ and CoPc/MnO₂ are 3.60 V, 3.65 V and 3.67 V, respectively. The discharge voltage plateaus (vs. Li⁺/Li) for the batteries with the catalysts C, MnO₂ and CoPc/MnO₂ are observed to be 3.07 V, 3.45V and 3.46V, respectively, at the current rate of 0.05 mA/cm² or 100 mA/g_{carbon} with the charge voltage of around 4.27 V, 4.00 V and 3.90 V at the same current rate. Our new Li-Air battery showed the highest discharge-charge voltage efficiency (88% in pure DI water) of all other efficiencies reported in other works. MnO₂ and hybrid catalysts CoPc/MnO₂ are more cost-effective and higher-performance catalysts for rechargeable Li-air battery.

Keywords: Lithium-air; battery; catalyst

Enhanced Lithium Storage Properties of Tin-based Anode Materials Prepared via Melt Spinning Process

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Lithium ion batteries (LIBs) is one of the most widely used form of rechargeable batteries for consumer portable electronics. Driven by the move to cut down carbon emission, the emergence of electric vehicles as well as efficient storage of electricity generated from renewable energy sources placed a huge demand on advanced LIBs that possess higher capacity and faster charge/discharge rate. Potential anode materials with higher capacities are highly sought after to replace the conventional graphitic anode. Among them, tin is actively studied as it is known to electrochemically alloy and dealloy reversibly with larger quantity of lithium, hence giving a high gravimetric capacity of 990 mAhg⁻¹. However, during lithium alloying/dealloying process, the structure undergoes drastic volume changes that cause the active material to become deprecipitated from the current collector and leads to rapid capacity fading.

One of the widely pursue strategy is the formation of active/active phase composite, where the more reactive phase reacts first and the unreacted phase helps to buffer the volume expansion before taking part in the reaction itself. In this work, melt spinning is explored as a rapid and high throughput process for the fabrication of various Sn-based active/active phase anode materials. Carbon nanotubes are added to improve both electronic and ionic transport. Enhanced lithium storage properties are demonstrated in the systems explored. For example, SnSb shows a good initial Coulombic efficiency of 79 % and a reversible capacity of 860 mAhg⁻¹ during the 40th cycle at a current density of 160 mA g⁻¹. This anode material also demonstrates good rate capability, with capacity that surpasses that of graphite (522 mAhg⁻¹) at high current density of 3300 mA g⁻¹. Apart from SnSb, Sn-Ge material will also be discussed.

Keywords Melt spinning; Carbon Nanotubes; Tin Antimony; Lithium ion batteries

Fabrication and Characterization of Ionic Polymer Metal Composites Prepared by Electro-less Plating of Nickel

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Ionic polymer metal composites (IPMCs) are electro-active polymers (EAPs) that show the electromechanical transduction. IPMCs are promising materials as soft actuators in many applications because IPMCs in hydrated state show relatively large displacement under small electric voltage (<5V). IPMCs are consisted of an ionic polymer with metal plated on both sides. The conventional metal electrode is noble metal such as platinum and gold. However, non-noble metal can substitute for noble metal because noble metal is expensive. Among these, nickel can be a candidate of the metal electrode because the nickel electrode can respond under the magnetic field as well as electric field. Depending on the electro-less plating bath condition such as time, temperature and concentration, the bending response may differ because of the different electrode properties such as thickness, density and sheet resistance. The bending response depends on not only the electrode properties but also the morphology of interfacial area between the electrode and polymer layer because the interfacial morphology affects capacitance of IPMCs. We could also control the interfacial morphology by varying the electro-less plating bath conditions. Therefore, we investigated how the bath conditions of nickel electro-less plating have influence on the electrode properties, interfacial morphology and bending response of IPMC.

Keywords Ionic polymer metal composites (IPMCs);nickel electroless plating;bending response

In situ characterization of battery materials using x-ray diffraction

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The performance of a Li-ion battery depends upon several factors, such as the choice of electrode materials and their evolution during charge/discharge cycles. During the cycling process, Li ions are migrated between the cathode and anode, while the intercalation compounds undergo structural and electronic changes. Therefore, with respect to the application, the identification of the material evolution inside the battery is important. A variety of cathode and anode materials (including nanostructured materials [1]) are being investigated in order to reduce cost, while improving performance and usage. In order to improve the structural stability of battery-related materials and to enhance the battery cycling performance, modification as well as reduction of crystallite size of the involved materials are studied. All these structural features, including phase transitions and the formation of multiple phases are easily observed and monitored with X-ray diffraction. In the present work, detailed design of the in situ experiments, data collection and analyses on various doped battery materials will be discussed.

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Keywords Li-ion battery; X-ray diffraction

Near-neutral pH stress corrosion cracking in a straight seam welded X80 pipe

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Stress corrosion cracking (SCC) can occur in welded steel pipelines that are used to transport oil and gas under high pressure when the pipe surface is exposed to the ground water. While SCC in high pH environment is well studied, near-neutral pH stress corrosion which was first identified in Canada in 1985, is continuing to be studied with small-scale and full-scale testing in the laboratory [1-2]. Recently, there is a renewed interest in this subject as a result of new high-pressure X80, even X100 pipelines being considered for northern parts of Canada and the USA. However, the influence of complex microstructures of X80 pipe steel, seam weld metal and its heat affected zone have yet to be explored in terms of susceptibility to near-neutral SCC.

In this contribution, stress corrosion cracking tests were conducted using small-scale cylindrical tensile specimens cut in the hoop direction to include seam weld metal, HAZ and base metal of an X80 pipe. New test protocols were developed for constant-load testing for 55 days, 110 days and 220 days in a NS4 solution to simulate the typical soil conditions of pipelines in North America. Results show that while large microcracks (10-16 microns long) occurred in the weld metal, much smaller microcracks (less than 5 microns long) were observed in the base metal after the 55-day incubation time at an applied stress level of 95% SMYS (Fig. 1). The results for the longer incubation times 110 and 220 days will also be reported. Detailed analysis of microstructural features differentiating the near-neutral SCC behaviours of the pipe steel base metal, seam weld metal, and HAZ will be discussed.

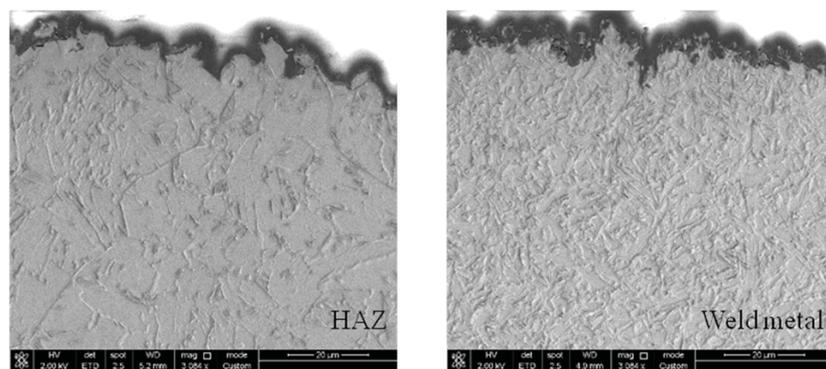


Fig. 1. Stress corrosion cracking on small-scale tensile specimens containing seam weld metal and HAZ of an X80 welded pipe after 55-day incubation time in a NS4 solution at an applied stress level of 95% SMYS.

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Keywords near-neutral pH stress corrosion cracking; X80 pipe steel; seam weld; heat affected zone

New electrolytes for ultracapacitor devices using manganese oxide as electrode material

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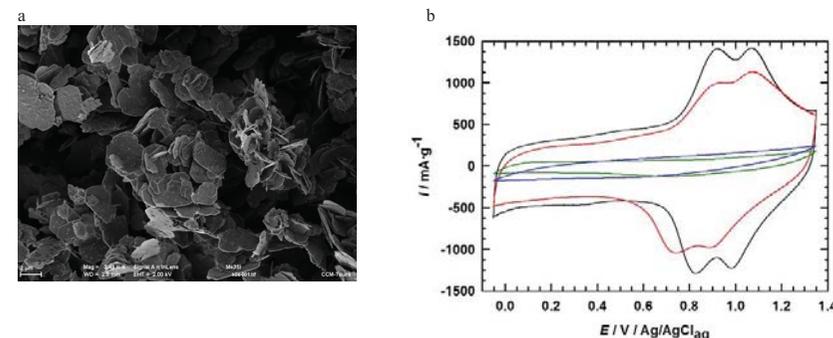
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Based on its low cost, low toxicity and in fact, its limited environmental impact, MnO₂ Birnessite is generally considered as a promising metal oxide able to substitute RuO₂ materials^[1,2]. Even if Birnessite is well known to have a good performance in capacitance and cyclability in aqueous media, its electrochemical behavior in non-aqueous electrolytes is, to date, not yet described into the literature.

Ionic liquids are considered as promising solvents, and electrolytes for sustainable chemistry due to their negligible vapor pressure, high potential window, high thermal stability and large liquid temperature range. Based on a higher electrochemical window than usual aqueous electrolytes, the protic ionic liquids are intensively considered as promising non-aqueous electrolyte for supercapacitor applications^[3,4].

The originality of our recent works is based on the study of new Birnessite synthesis ways in modified aqueous and non-aqueous media, and their interactions with the aqueous and non-aqueous electrolytes. Our aim is to link the electrochemical behavior of MnO₂ materials to the properties of electrolyte. So, different properties - such as thermal, electrochemical, transport and volumetric properties - were at first investigated for a wide range of electrolytes - including PIL, aqueous and low vapor pressure non-aqueous electrolytes containing different lithium salts. Another originality of this work is then driven by the investigation of the relationship between electrochemical behavior of MnO₂ Birnessite with the nature of anion in the electrolyte, as well as the cation size/structure effects on its solvation in such material. The first Birnessite cycling results seem to demonstrate that it is not easy to obtain efficient electrochemical storage despite good transport properties of the electrolyte.



Figure

^a Scanning electron micrographs of MnO₂ birnessite powder.

^b Cyclic voltammogram of MnO₂ in aqueous 5M LiNO₃ (black), aqueous LiNTf₂ (red), Et₃NH LiNTf₂ (green), Deep Eutectic Solvent with LiNTf₂ salt (blue).

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Keywords ultracapacitor; manganese oxide; birnessite; ionic liquids

Organic-Inorganic Hybrid Materials for Supercapacitors

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The design and development of hybrid organic – inorganic materials with improved electrochemical performance to be used in energy storage applications (e.g. supercapacitors) is presented. The systematic study carried out shows various carbon-based materials working as active substrates where the anchoring of inorganic species takes place (i.e. polyoxometalates, such as $H_3PMo_{12}O_{40}$, PMo_{12}) in search of synergic properties[1-3].

One gram of dried activated carbon, AC (kindly supplied by Norit Chemicals®) was added into a 50 ml 10mM H_3PMo_{12} aqueous solution. The mixture was stirred for 24 h at room temperature, then filtered, washed and dried at 80 °C for 24h in a vacuum oven [4]. The amount of PMo_{12} impregnated was obtained by weight difference (54 wt.%). The electrochemical characterization of the materials was carried out by cyclic voltammetry and galvanostatic charge – discharge tests. Pt wire and Ag/AgCl were used as counter and reference electrode, respectively, in the 3-electrode set-ups. 1 M H_2SO_4 was used as electrolyte.

Figure 1 a) shows CVs for AC and the hybrid material. The former shows a typical rectangular shaped capacitive behavior. The hybrid (AC/ PMo_{12}) material shows well – defined redox peaks on top of a rectangular-shaped envelop, indicating the coexistence of double layer and pseudocapacitance in that material. The specific capacitance values of carbon electrodes were improved by following this hybrid approach, not only in terms of, F/g, but more importantly in terms of F/cm^2 , from $10 \mu F/cm^2$ in AC to $28 \mu F/cm^2$ in AC/ PMo_{12} , which can be considered more relevant for practical applications. Symmetrical supercapacitors with AC/ PMo_{12} electrodes were characterized in synchronous experiments (two- and three- electrode configuration). In such set – up, the cell works as a two electrode cell and the variations of potential of each electrode are monitored. Figure 1 b) shows a galvanostatic cycle (left Y-axis) and the positive and negative electrode potentials (top blue and bottom green line, respectively). Efficiencies ranged 95 – 100% in the range on current tested. The overall cell voltage is split between positive and negative. The stability of the materials was evaluated by means of long-term cycling where a two electrode assembly was cycled over more than 10,000 cycles (1.3 A/g) showing no reduction in capacitance values demonstrating the strong interaction between the carbon substrate and the POM thus, validating the suitability of such material to be used in supercapacitors.

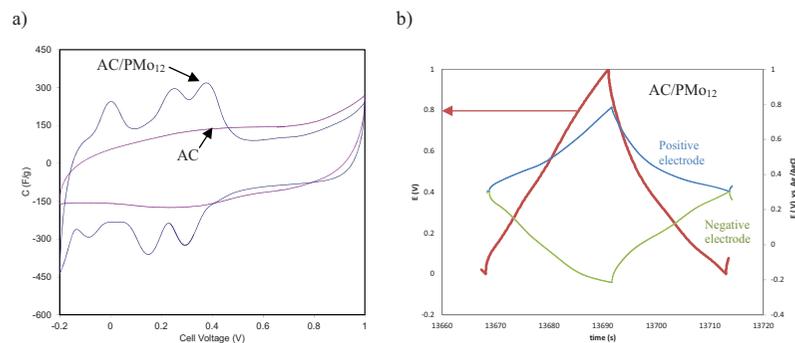


Fig.1. a) CVs - 5mV/s. b) Galvanostatic cycling at 15 mA - 1V (left Y-axis) and positive (top) and negative (bottom) electrode potentials.

Keywords Supercapacitors; polyoxometalates

Piezoelectric Energy Harvesting Converters: A Survey

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Piezoelectric energy harvesters, PEH gained a great interest in the literatures due to the surge applications of remote sensors that need sustainable power supply. Although PEH produces a small amount of power it plays a significant role in this applications because replacing the battery may be not that easy or sometimes impossible in some applications. Output power from PEH is characterized by variable frequency and high variable amplitude of output voltage. This unregulated voltage needs power converter to make it suitable to supply the load and battery and also to track the maximum power. Two main topologies used to perform this job, direct energy transfer and power conditioning converter. The first technique uses diode rectifier to convert ac output from PEH to dc to charge the battery and the load without dc-dc converter. Synchronized switch harvester inductor, SSHI technique is implying a switch and inductor in ac side to flip the voltage across the PEH from positive to negative of the battery voltage through this switch and inductor instead of charging the internal capacitor of PEH through the internal resistance of PEH. This technique will considerably reduce the losses and increase the PEH efficiency. Power conditioning converter technique uses dc-dc converter to extend the operating limit of the PEH to track the maximum power and to increase the efficiency. Buck converter is the most converters used in this application because of its voltage step-down characteristic which is suitable for high voltage output from PEH. Synchronized dc-dc converter is achieved by replacing the diode with MOS switch to increase system efficiency. Market available power converters support energy harvesting are employing low losses elements for diode bridge and dc-dc converter such as LTC 3588

Keywords Piezoelectric energy harvesters, maximum power tracker, direct energy transfer, Synchronized switch harvester, dc-dc converter, buck converter, buck-boost converter

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Protic ionic liquid electrolyte for supercapacitor applications

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Ionic liquids (ILs) are organic molten salts with melting points below 100 °C. Because of their unique physicochemical properties, such as their thermal stability, the favourable solubility of organic and inorganic compounds, low vapour pressure and non flammability, ionic liquids are attractive as new solvents for various applications like an alternative to volatiles organic compounds intensively used in industry. ILs can be classified into two groups: protic (PILs) and aprotic (AILs) ionic liquids [1,2]. PILs are synthesized by equimolar amounts of a Brønsted acid and Brønsted base [3-5]. The proton transfer from the acid to the base creates proton donor and acceptor sites and can lead to the formation of hydrogen bonds. Besides, PILs have a higher electrochemical stability window and thermal stability than aqueous electrolyte, but their use as electrolyte for supercapacitors is relatively recent [3,4,6].

ILs based on ammonium, phosphonium and sulfonium cations were synthesized and studied. Physico-chemical characterisations were realised in order to study their electrochemical properties for supercapacitors applications in pure ionic liquids or in mixture with solvents like water or acetonitrile. Electrochemical study were realized on activated carbon and modified activated carbon with metal-oxide nanoparticles electrodes, by cyclic voltammetry and galvanostatic charge-discharge curves in symmetric devices at different temperatures and current voltage, comparing pure PILs with optimal mixtures in solvents. Electrochemical performances were also compared with a classical electrolyte, tetraethylammonium tetrafluoroborate in acetonitrile.

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Keywords Protic ionic liquid; Supercapacitors; Activated carbon, Metal-oxide

Synthesis and Morphology Control of Novel Nanostructures of LiFePO₄ Cathode Materials for Li-ion Battery

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Solid state syntheses methods, which rely on using very high temperatures and multiple step procedures, are still the most commonly used method for commercial production of LiFePO₄ although these methods normally lead to a poor control of morphology and larger particles sizes. On the other hand, other approaches, such as solvothermal and reflux reactions provide a better alternative, offering the possibility to use cheaper precursor materials, lower working temperatures (≤200 °C) and leading to better morphology and size control.

This work aims to verify the solvothermal and reflux approaches for improving the size, morphology and electrochemical properties of lithium iron phosphates. In this work, solvothermal and reflux reactions were used to synthesize novel architectures of LiFePO₄ cathode materials, and their particle sizes and shapes were controlled from the nanometer to sub-micrometer scales leading to peculiar self-organized nanosheaf formations. In these lower temperature (180-200°C) approaches, environmentally benign and inexpensive precursors have been used. These approaches are shown to be simple, highly reproducible and cost-effective. Therefore, they could be a good alternative to replace the commonly used high-energy solid state techniques employed for the production of LiFePO₄. The crystalline structures of the synthesized cathode materials were characterized by X-ray diffraction, and their morphologies were analyzed by SEM and TEM.

The LiFePO₄ nanostructure materials synthesized by reflux approach (LFP_R) in this work exhibited uniform and beautiful morphology. A SEM photograph shows a very homogeneous sample consisting of intricate agglomerates (approx. 4 μm lengths and 3 μm widths; Figure 1.A) in the shape of dense, space-filling sheaves. The grown sheaf particles are formed of self-assembled needles (approx. 2-4 μm length and 30-40 nm diameters; Figure 1.B). Each sheaf consisting of two urchin-like sub-structures. The nanostructured LiFePO₄ material shown in Figure 1.B was synthesized using a solvothermal method ((LFP_S) by using a different iron precursor, different synthetic method, and different molar ratios from the one obtained using the reflux approach described above. This method has led to those astonishing superstructures formed in turn by sheaf blocks. The resulting fuzzy octahedra (approx. 5 μm diameter) consist of monodispersed sheaf-like units with a diameter ranging from 1 to 2 μm formed in turn by nanometer sized self-assembled needle primary particles. Additionally, it has been proven that this unusual and previously unreported morphology is directed simply by controlling the synthesis parameters such as temperature, time, precursor's type and precursor's molar ratio. This curious morphology is possibly grown via solvothermal Ostwald ripening process of sheaf-like units. Nevertheless, the detailed formation mechanism of the presented nanostructured LiFePO₄ materials has not been fully explained yet.

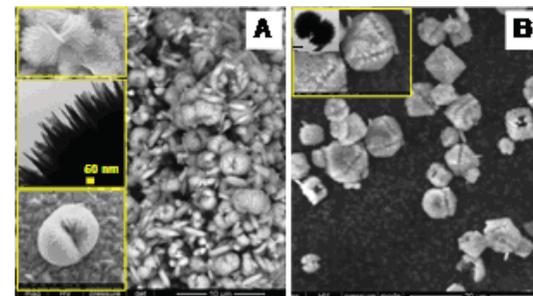


Figure 1. SEM and TEM images of pristine LiFePO₄ nano and microstructures synthesized through Reflux method (A) and Solvothermal method (B).

Keywords LiFePO₄; cathode; Li-ion battery; solvothermal synthesis; hierarchical structures; morphology

Synthesis conditions of the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ electrolyte and compatibility with cathode material in solid-state lithium-ion batteries

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Lithium containing perovskites have attracted a lot of attention in search of inorganic materials displaying a high lithium ion mobility, which are of interest for applications as cathodes or solid electrolytes in lithium batteries and other electrochemical devices [1].

In recent years, all solid state lithium ion batteries have been attracting more attention owing to their properties of high power density and good safety. As an important part of the battery, inorganic solid state electrolytes ($\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$, LLTO) become a significant issue because of their advantages over other electrolytes such as higher safety and better capacity retention [2].

The overall conductivity of LLTO ceramics is significantly affected by the grain boundaries, which bring additional barriers to the transport of lithium ions. Until now most of inorganic solid-state electrolytes have been obtained by solid state reaction. As known, this conventional preparation method needs high sintering temperature and long sintering time [3], which result in serious lithium loss during sintering process and in a particle size increase that is not propitious for micro-electrolyte layer in applications. As alternatives, some other synthetic methods have been employed to prepare LLTO ceramics pellets or thin films [4-5].

In addition, for these batteries, the stability between electrolyte and cathode material during the system fabrication is an important concern. The LLTO and cathode in order to enhance their crystallinities and properties, have to undergo a heat treatment. Therefore, the microstructure stability and chemical reactions in the interface between electrolyte and cathode during the treatment would affect the properties of these batteries.

In this sense, this study is focused on the synthesis route, sintering temperature, crystal stability and reaction between $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ and the cathode material (LiMn_2O_4) in order to find out a suitable processing condition for the materials to use in Lithium-ion battery systems.

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Keywords electrolyte; lithium battery; perovskite

The optimum design methods of integration system with PV and EV

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Recently, carbon dioxide emission is a worldwide concern. The Japanese government has aimed the target that the country's carbon dioxide emission will be cut off 60 to 80% until 2050 compared with 1990 level. In order to achieve the target, it is important to introduce the integration energy system with natural energy and energy conservation, and to manage the energy supply and demand. As a practical method, the Smart Grid has been proposed.

In the Smart Grid, it is proposed that EV is travelled by the electricity of PV and EV supplies the electricity to the home and factory. In the conventional energy system, the energy flow has gone only one direction from supply side to demand side. On the other hand, a consumer can generate the electricity and supply to other consumer in the Smart Grid. So, it is assumed that the energy system will become more complex system in which the energy flows interactively in the consumers. In order to design and manage the interactive energy system, not only the conventional electric power system but also the electricity with EV should be managed. However, the method has not been established.

In this study, we have developed the new design methods of integration system with PV and EV. Whole energy which is supplied from electric power system and pipe line, transported with EV and generated by PV is able to be managed through the use of this method. Also, we have developed the simulator which is based on this method. It can optimally design the installing place and generating capacity of PV, and battery capacity of EV as on the basis of the index of CO₂ economic and cost performance.

The content of study is as follows,

- ① We have developed the HEX model in order to manage the whole energy in a region. In the HEX model, the region is divided its area into the hexagon (HEX), also the energy of inflow, outflow, generated, consumed and stored are calculated in each HEX.
- ② Mileage, place and holding energy of vehicles were evaluated in each vehicle using the measured data of GPS which was installed 21 cars.
- ③ We have simulated the combination system with PV and EV. In the simulation, PV charges the EV which is commuter car. EV consumes the electricity to move and supplies the charged electricity to the home. Also, we have evaluated the reduction value of gasoline and electricity which is purchased from conventional electric power system. We have used the each hourly data and considered the factors of holiday and seasons.

The result is as follows,

- ① HEX model can evaluate the energy with EV which cannot be evaluated through the use of the network model. It has been verified the validity and flexibility whether HEX model can evaluate the unit from the single house to the city to be changed the each side of HEX.
- ② In the developed system which use EV as the commuter car, PV should install at the place of work, because commuter EV is parked for a long time during the daytime. So, it is effective to reduce CO₂ emission and cost performance.
- ③ The developed system which supply the electricity to the home through the use of EV can cut off the 33% out of the CO₂ emission of home without the reverse current to the conventional electric power system.

Keywords Photovoltaic power generation(PV); Electric Vehicle(EV); HEX model; Simulation; Energy System

Theoretical study of CO adsorption over a B2 FeTi (111) slab

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Iron-titanium materials have been developed and use over the last years for hydrogen storage properties. However, due to the low cost of these catalyst, it uses has been moved towards other applications, such as catalytic combustion and catalytic adsorption for vehicles exhaust emissions.

The adsorption of CO on B2-FeTi (111) has been studied at very low coverage using a theoretical level by tight binding and DFT calculations. Bridge, top, and hollow were considered.

It has been found that the minimum energy location is when the CO is adsorbed on a hollow site with the carbon pointing towards the slab surface. The interaction is due to the interaction of the orbitals 2s and 2p of the Carbon atom with the orbitals 4s and 4p from Fe. The main role of d orbitals is the geometry orientation, while the energy of the bonds comes mainly from s-s interactions. We have also studied the changes in the intermetallic bond after CO adsorption and the stability of this molecule at different surfaces sites.

Advances in Lighting Materials

Cu-doped ZnO nanostructured layers obtained by hydrothermal method for light-emitting-diode (LED) applications

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1D nanostructured oxide semiconductor materials have focused a high interest as potential optoelectronic materials. The band-gap engineering of doped ZnO nanowires is of high importance for applications in tunable light-emitting-diode (LED), the nanowires acting as light emitters.

Low-cost ZnO homojunction structures for LED application, composed of a *n*-type Al-doped ZnO sol-gel thin film and a *p*-type Cu-doped ZnO nanowires grown by hydrothermal method, were fabricated on Si (100) substrates.

The morphology, optical and electrical properties of Cu-doped ZnO nanowires were investigated by scanning electron microscopy, optical transmittance within UV and visible regions and dark conductivity. The band gap energy and the optical constants such as index of refraction, extinction coefficient, dielectric constants and optical conductivity were determined using the transmission at normal incidence of light in the wavelength range of 200-1100 nm.

The electroluminescence emission wavelength of Cu-doped nanowires was investigated as a function of Cu-doping and the temperature of synthesis.

Keywords: Cu-ZnO nanowires arrays; light-emitting diodes; hydrothermal method

Impact properties and dislocation evolution of Ti-6Al-4V alloy at cryogenic temperatures

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The aim of this study is to investigate impact response and dislocation substructure of Ti-6Al-4V alloy using a compressive split-Hopkinson pressure bar and transmission electron microscopy technique. Cylindrical specimens are deformed at strain rates ranging from $8 \times 10^2 \text{ s}^{-1}$ to $4.0 \times 10^3 \text{ s}^{-1}$ and temperatures of 0°C and -200°C , respectively. It is shown that the impact properties of Ti-6Al-4V alloy depend strongly on strain rate and temperature. For a constant temperature, the flow stress and strain rate sensitivity increase with increasing strain rate, while the activation volume decreases. Meanwhile, for a constant strain rate, the activation volume increases with increasing temperature, while the flow stress and strain rate sensitivity decrease. Transmission electron microscopy (TEM) observations show that the dislocation density increases with an increasing strain rate, but decreases with an increasing temperature. By contrast, the dislocation cell size decreases with increasing strain rate, but increases with increasing temperature. The mechanical properties of the impacted specimens are related to the microstructural evolution. The strengthening effect in deformed Ti-6Al-4V alloy is a result primarily of dislocation multiplication.

Keywords Ti-6Al-4V alloy; strain rate; cryogenic temperature; dislocation

Energy-Efficient Buildings

A comparison between lighting and daylighting performance in an office building and an economic comparison of daylighting and lighting control system

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During the last quarter of the 20th-century and early years of this century, architects and designers have recognized the importance and value of introducing natural light into buildings. Daylight in buildings has impacted human behaviour and human factors and has reduced the stress and discomfort of users. The urgency of increasing energy efficiency in new building design and retrofits has moved lighting simulation into a central role in sustainable lighting design.

Daylighting is a key strategy in reaching the contractual energy use.

In this study an office building model is studied and the lighting control range is determined by employing a daylight analysis simulation using Radiance that gives the most information regarding incoming daylight.

Indoor illumination was analysed to determine the lighting rate then was studied setting of artificial zoning for lighting control, analysis of lighting control range and setting the standard illumination for the turning off the artificial lighting through the simulation.

When the lighting control was applied, an economic analysis was performed by utilizing the payback period that was calculated by comparing the initial cost of installing the electric lighting control system with the annual energy cost which was reduced by the application of lighting control.

The energy cost was calculated by using the daylight and building energy analysis simulation.

The objective of this study is to perform an economic analysis of the daylight and automatic on/off lighting control system installed for the purpose of energy savings in office buildings.

Keywords Daylighting,; office building; Radiance; lighting control system; economic analysis

Analysis of Thermal Comfort and Energy Efficiency of Building Using Novel Building Envelop

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The paper aims to analyse the impact of new construction methodology, incorporating the building envelop and internal walls, on energy efficiency of buildings and examine the thermal performance of a residential building in subtropical climate. In this study, a novel residential building wall construction system is employed that is completely different from current brick veneer building wall. A novel building envelop with superior energy efficiency is employed to reduce the energy consumption and to enhance thermal comfortability of the occupants. Here, the new envelop is technologically and environmentally sustainable and primary consists of 10 mm render outside, 60 mm polystyrene, 100 mm reinforced concrete, 60 mm polystyrene and 10 mm plaster board from inside. The internal wall panel, made of compressed rice/wheat straws, is completely recyclable, biodegradable, and free from any chemical bonding elements, fire resistant and sound proof. The study reports an overall energy efficiency and better thermal comfort achieved by using the novel building envelop.

Keywords Building, Thermal Comfort, Energy Efficiency.

Development of photoelectrochromic devices for energy saving applications

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In recent years a considerable research effort has been directed towards materials and devices intended for the dynamic solar control of buildings (often referred to as “smart windows”) [1], such as photoelectrochromics (PECs thereafter) [2]. A typical PEC device layout is shown in figure 1. It consists of:

1. A glass coated with a transparent conductive oxide (such as SnO₂:F or Indium Tin Oxide).
2. An electrochromic (EC thereafter) layer of optical quality (usually WO₃).
3. A nano-structured wide band gap semiconductor film (usually TiO₂) sensitised by an appropriate dye.
4. An electrolyte with high ionic and low electronic conductivity that contains a redox couple (such as I⁻/I³⁻) and Li ions.
5. A counter electrode consisting of a transparent conductive oxide with a thin Pt layer.

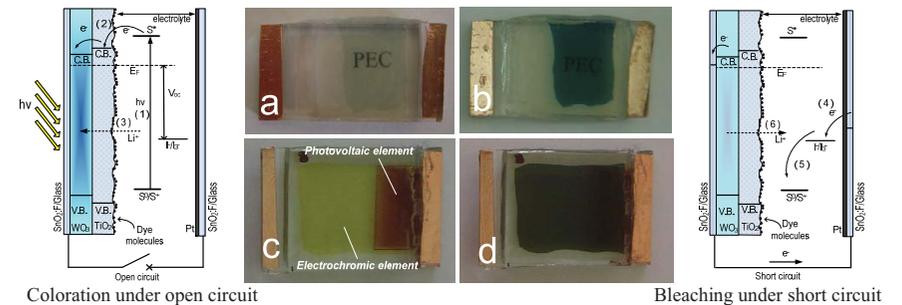


Fig. 1. Layout and operation of a typical PEC device. Pictures of the fabricated devices in the bleached (a,c) and coloured (b, d) states. Fully covered (a, b) and partly covered (c, d) devices are shown.

Parts 1, 3, 4 and 5 of the above device comprise a dye-sensitized solar cell [2] that provides the electrical potential for the coloration of the EC layer. The PEC device operation involves six different processes shown (in parentheses) in figure 1. They are: absorption of photons by the dye (1), injection of electrons into TiO₂ (2), and then into WO₃, intercalation of Li⁺ into the WO₃ layer (3) for charge equilibration, causing coloration of the WO₃ film [1] under open circuit. Under short circuit in the dark, electrons reduce I³⁻ at the counter electrode (4). Then, I⁻ reduces the dye molecules (5), Li⁺ is transferred back to the electrolyte (6) and the WO₃ film is bleached [2].

In our earlier work, [2] we have developed “fully covered” PEC devices in which a thin, transparent TiO₂ layer covers the entire device area. The requirement for high transmittance in the bleached state, imposes limitations on the device performance. One way round this problem is the spatial “decoupling” of photovoltaic and electrochromic elements and thus the “partly covered” type comes about [3]. It employs a thick, opaque TiO₂ film, that covers only a fraction of the WO₃ film, on one end of the device (see Fig. 1).

PEC cells of both designs have been fabricated and tested. Their properties (optical and electrical) have been assessed and compared with similar devices developed by others, with promising results.

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Keywords: Photoelectrochromics; tungsten oxide; titanium oxide; solar control.

Different photovoltaic systems and the use of natural lighting for energy saving in a building

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The attention to quality and environmental comfort of the living space is affecting a growing number of people: designers, manufacturers, producers, up to the end users of buildings and urban spaces that comfort and energy savings are now two objectives to be achieved simultaneously. Many interesting experiences are taking place around the theme of building sustainable, both nationally and internationally, seen as a conscious choice directed towards the concept of sustainable development. In the civilian sector strategies for the rationalization of energy consumption have a wide range of interventions characterized by a high degree of flexibility. The objective of this research is that of environmental comfort and energy savings by integrating the energy from photovoltaic systems and the use of natural lighting. The research has been conducted experimentally using a building model tested in the laboratory using an artificial simulator of the sky and numerically using Radiance to determine the distribution of illuminance and daylight factor inside the building. The numerical results are validated by comparison with experimental ones in order to come to the determination of correlation that may be of practical use to designers. Then the architectural PV integration has been studied. The photovoltaic modules offer solutions to high aesthetic value and can be integrated into every part of the buildings construction. Meet the requirements of its quality of construction materials (mechanical strength, water resistance, thermal and acoustic insulation, etc.). The solar panel also becomes an architectural element that offers many new possibilities of expression. For these reasons three different PV systems are studied and analysed for the building model as solar shading and photovoltaic glazing. The electricity which is generated by all these systems is purchased according to the Italian program called "Conto Energia". Economical analysis and the amount of the avoided CO₂ are elaborated for the PV systems. The combination of all these technological devices (daylighting system and photovoltaic systems,) in building structures, including non-residential, is certainly essential for achieving results of energy saving.

Keywords Energy saving; building; photovoltaic shading; photovoltaic glazing; economic analysis

Diffusion of solar radiation through plastic shading nets

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Plastic nets are widely used in the Arabian Peninsula for shading plants under arid climatic conditions. Nets are able to diffuse a considerable amount of solar beam radiation over plants. However, the diffusion characteristics of solar radiation through nets are still unknown because nets are non-homogeneous materials. In this study, a simple measuring method was presented and used to estimate the ability of different nets to diffuse the transmitted solar beam radiation. This was achieved by determining the beam that is diffused during transmission. Experiment to measure radiation parameters for determining the diffusion abilities of nets were conducted on clear sunny days in Riyadh, Saudi Arabia. Nets with colors and porosities that are most commonly used were selected for the study. The results showed that the diffuse radiation transmitted through the selected nets was enhanced by 17-170% depending upon the structure of the net textures rather than colors. This is because a proportion of the transmitted beam radiation was diffused and added to the transmitted diffuse radiation. This proportion was in the range from 2% to 20% depending upon the colors, texture structures and porosities of the nets.

Keywords: Plastic nets; solar radiation transmission; diffused beam.

Energy demand side management of building complexes cooling load using renewable energy sources

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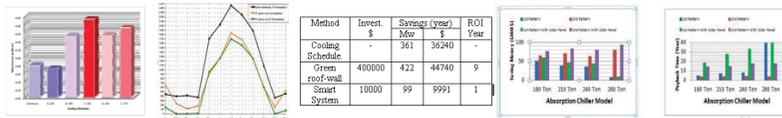
Energy consumed in buildings is about 30% to 40% of the total world energy demand, which makes it vital to decrease it as much as possible. Two important aspects in the proposed methods to reduce energy consumption in buildings are: to focus on the management of the energy demand rather than energy consumption optimization, and, also, to utilize renewable energy sources rather than conventional fossil based energy sources. In this paper the focus is on the buildings cooling and heating and building lighting is not considered. Also, the building complex investigated is in the hot and humid climate, and therefore, the energy demand is essentially for the cooling of the complex.

The building complex investigated with a total substructure area of about 4545 m² is located at the north of Ahwaz (Latitude = 31°, Longitude = 48°, Elevation from sea level = 20 m), south west of Iran, with a hot and humid climate: the temperature goes beyond 50 degrees Celsius and humidity reaches up to 100% in summer. Therefore, cooling and reduction of temperature and humidity is required in offices from April to November which creates a large demand for cooling.

The building complex demand side energy management new methods investigated are as follows:

- 1-Hybrid compression-absorption chillers: substitution of the current compression chillers which have a vast demand of electricity, with hybrid compression-absorption chillers which allow use of solar and natural gas energy sources instead of electricity.
- 2-Development and implementation of cooling system operation scheduling: The continuous operation of cooling system is substituted by a pre-planned scheduled optimum operation with minimum demand for energy.
- 3-Green roof and walls: green plants act as a good insulator for heat transfer through roof and walls which reduces the demand for space cooling or heating substantially.
- 4-Smart control of chiller room equipment: based on the data collected at specified locations, and pre-defined algorithms, these equipment are controlled in a smart way to optimize cooling load and energy demand.

All data needed for the calculation of the building cooling demand, including building architecture, walls, roof and windows specifications, weather data, human's latent heat, office equipment and lighting; were collected and properly fed to the software provided in this research. The software results accuracy were checked before using it for cooling load calculations.



Reduction of energy demand, savings in energy consumption and its related costs, and the return on investment (ROI) period in each case are calculated and presented. Even though it sounds that all methods may decrease building cooling energy demand, however, it is crucial to use them carefully: only in some particular cases the proposed methods are beneficial and feasible which could result to a decrease of the energy demand up to 40%.

Keywords building complex, energy demand side management, renewable energy

Energetic and Exergetic Performance Evaluation of an AC and a Solar Powered DC Compressor

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HVAC and refrigeration systems occupy the largest portion of overall energy consumption in domestic use. Domestic refrigeration systems have a big opportunity to be powered by green energy technologies such as solar and wind energy because of their low power demand. In this case, there are two different options for the compressor which are alternative current (AC) or direct current (DC) powered compressor. Green energy technologies can be used for DC compressor directly while AC compressor requires an inverter.

This study represents energetic and exergetic performance analysis of an alternative current (AC) and a direct current (DC) type refrigeration compressor used on a 79 liter mini fridge. Energy usage reduction potential of both systems was investigated. Experiments were carried out at ON and ON_OFF operation mode of the compressors. Temperature, pressure and power input measurements were obtained at every 30 seconds. The data was analyzed in terms of cooling capacity, power input, coefficient of performance (COP), Carnot COP and percentage of Carnot COP and exergy efficiency. The comparison showed that DC compressor can be much more efficient than AC compressor on the mini fridge. Although both compressors yielded almost same cooling capacities,

- DC system has higher COP than the AC system because of lower power input.
- DC compressor resulted in a higher COP_{CARNOT} because of smaller temperature span between the condensation and evaporation temperatures.
- DC compressor's exergy efficiency and COP_{CARNOT} percentage value is higher as well.

Also, DC compressor has lower compressor surface and discharge temperatures than that of the AC compressor. High temperature at the compressor side affects the life of lubrication oil and refrigerant in the compressor, unfavorably. Furthermore, DC compressor vibration level is lower with respect to the AC compressor. This may be an important selection criterion for some applications where noise and system reliability are highly considered. Higher performance of DC compressors employed in refrigeration systems makes them a strong candidate for improved HVAC&R units. In addition, the ability to use renewable energy such as solar, without a need for inverters, brings on added benefit to these systems.

Fabrication and characterization of triple vacuum glazing at low temperature using an indium-based seal

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Triple vacuum glazing (TVG) is a new generation of thermally insulating windows which consists of three glass sheets with two vacuum gaps hermetically sealed together around the edges. A high level of thermal insulation is achieved by evacuating the spaces between the glass sheets to a very low pressure; the low pressure greatly reduces conduction and convection within the space, therefore heat transfer through vacuum glazing is significantly lower when compared with double or triple glazing with an inert gas fill. The separation of the sheets which would otherwise touch under the influence of atmospheric pressure is maintained by an array of small support pillars. Triple vacuum glazing samples were fabricated at low temperature using an indium edge seal; a pump-out system enabled a high level of vacuum to be achieved between the panes. The TVG samples fabricated in this study comprised three, 4 mm thick 400 mm by 400 mm glass panes with low-emittance coatings separated by an array of stainless steel support pillars spaced at 25 mm with a diameter of 0.4 mm and a height of 0.15 mm. The thermal performance of the TVG samples were characterized using a guarded hotbox calorimeter and theoretically analyzed using a finite volume model. The experimentally determined thermal performance of the fabricated glazing was in good agreement with that predicted theoretically.

Keywords: triple vacuum glazing (TVG); double vacuum glazing; pump-out; thermal performance; finite volume model

Finite Element simulation of heat transfer through single-leaf walls in buildings

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Several studies about factors influencing the heat transfer in single-leaf walls composed by lightweight ceramic bricks of large format have been made, in order to reduce energy losses. Separate works have highlighted the relevance of some parts composing the wall.

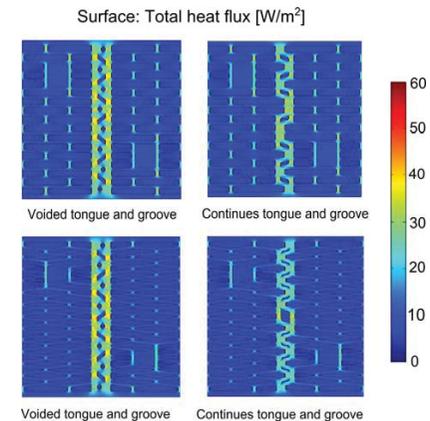
This paper seeks to integrate these studies in order to give an overview of factors that influence the heat transfer. For this we will show the heat flux diagrams of each of the characteristic sections of the wall ("clay/air cross-section", "clay/mortar cross-section" and "tendel cross-section or horizontal joint"), solved by Finite Elements Method, and we will compare the thermal resistances of sections.

Finally the influence of each section, according to their height, in the equivalent thermal transmittance of the exterior wall, will be compared, for two types of assembly the wall.

It is noteworthy that a substantial improvement in the characteristic clay/air cross-section of brick by improving the internal geometric distribution and tongue and groove system, is produced. A significant reduction in heat loss is observed and therefore an increase in thermal resistance.

Depending on type of assembly, the thermal transmittance of the exterior wall is extensively modified. In a thin horizontal joint assembly, the height of the tendel cross-section is reduced, and the clay/mortar cross-section (with a very low thermal resistance) is removed. This involves an increase of the height of the clay/air cross-section (with a high thermal resistance). In this way, the resistance of the wall significantly increases, reaching reductions in thermal transmittance up to 36%.

Keywords: Lightweight clay block; heat flux; horizontal joint; tongue and groove system; single-leaf wall; thermal resistance; grinding



Global warming and building energy use and environmental implications

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Buildings, energy and the environment are issues facing the building professions worldwide. Recent work by the Inter-governmental Panel on Climate Change (IPCC) has raised public awareness of energy use and the environmental implications, and generated a lot of interest in having a better understanding of the energy use characteristics in buildings, especially their correlations with the prevailing weather conditions. It was estimated that in 2002 buildings accounted for 33% of the global greenhouse gas emissions. For instance, let us consider the two largest energy-consuming countries - China and the US. It was reported that the building sector accounted for 38.9% of the total primary energy requirements in the United States, of which 34.8% was used for heating, ventilation and air conditioning (HVAC). In China, building stocks accounted for about 24.1% of the total national energy use in 1996, rising to 27.5% in 2001, and was projected to increase to about 35% in 2020. It had been found that the total annual CO₂ emissions due to energy consumption were 119 kg CO₂/m² and 178 kg CO₂/m² in large commercial buildings in Shanghai and Beijing, respectively. In addition to the energy used for operation, buildings embody the energy used in the mining, processing, manufacturing and transporting of the building materials, and the energy consumed in the construction and decommissioning of the buildings. This embodied energy, together with the energy used during the life span of a building constitutes the life-cycle energy and emissions footprint.

Buildings typically have a long life span, lasting for 50 years or more. It is, therefore, important to be able to analyse how buildings will respond to climate change in the future, and assess the likely changes in energy use and the corresponding impact on carbon footprint. A priori hypothesis is that climate change or global warming would lead to less energy use for winter heating and more for cooling during the summer months. The extent of reduction in heating and increase in cooling varies from one region/climate to another and depends very much on the prevailing local weather conditions and energy efficiency measures. Even in severe cold climates, where the reduction in heating is expected to outweigh the increase in cooling requirement there can still be an overall increase in CO₂ emissions because of the difference in carbon footprint of heating and cooling. Space heating is usually provided by gas- or oil-fired boilers whereas cooling relies largely on electricity, except buildings with gas absorption chiller plants. The aim of the present work was to investigate the impact of climate change on the energy use and carbon emissions in air-conditioned office buildings in the different climate zones across China.

Future trends of energy use for heating and cooling and the corresponding carbon emissions in five major cities with different climates across China in the 21st century were estimated. It was found that under the medium forcing emissions scenario the estimated increase in cooling energy use was 23.7% in Harbin, 24.5% in Beijing, 14.1% in Shanghai, 29.2% in Kunming and 15.5% in Hong Kong; and the reduction in heating 26.2% in Harbin, 34.1% in Beijing, 60.4% in Shanghai, 17.3% in Kunming and 25.7% in Hong Kong. In Harbin, although the reduction in heating energy use (10.6 kWh/m²) outweighed the increase in cooling (4 kWh/m²), because of the higher carbon footprint of electricity the overall carbon emissions would still be greater during the 21st century. To mitigate the impact of climate change on building energy use and thus carbon emissions, energy-efficient measures involving the building envelope, internal condition, lighting load density and HVAC system were considered. Given the growing awareness and recognition of adaptive thermal comfort, raising the summer set point temperature by 1-2°C could have great energy saving and hence mitigation potential. This can be readily applied to both existing and new buildings at no extra cost. In Beijing and Shanghai it was found that reduction in lighting load density had both positive and negative effects on building energy consumption. It resulted in savings in cooling energy use in the summer but an increase in heating energy use in winter. In cooling-dominated office buildings in subtropical climates, however, lowering the lighting load density would be very effective because of the savings in not only the electricity use for artificial lighting but also air conditioning due to less heat dissipation from the electric lighting.

It is generally believed that that our climates are changing. It is hoped that the work presented could form a basis for discussion about building energy efficiency and sustainable development at the EMR2012 Conference.

Keywords building energy use; different climate zones; climate change; mitigation and adaptation measures; China

Nano insulation materials for energy efficient buildings: from theory to practice

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The nanotechnology revolution has been making a ground-breaking impact on several science, engineering, and commercial sectors, also including the construction industry. The application of nanotechnology may enhance some vital characteristics of building materials, hence leading to, among others, super-strong structural components, self-cleaning façades and windows, and high-performance thermal insulation materials and envelopes [1]. Among these, the advanced thermal insulation materials and solutions have been receiving an ever increasing attention due to their significance to energy efficient buildings. For example, nano insulation materials (NIMs), which are proposed as homogeneous materials with a closed or open nanoporous structure and an overall thermal conductivity of less than 0.004 W/(mK) in the pristine condition, appear to be very attractive for many applications [2]. However, turning the conceptual NIMs into practical building materials may require substantial research efforts dedicated to this field.

Theoretically, an effective thermal conductivity λ_{eff} of NIMs at a given temperature T can be expressed as the sum of the thermal conductivity of the solid backbone λ_s , the thermal conductivity of the gaseous phase λ_g (also correlated to the gas pressure p_g), the radiative conductivity λ_r , and the contribution from the coupling effect λ_{coup} among these thermal transport components (2nd order effects) [3]:

$$\lambda_{eff}(T) = \lambda_s(T) + \lambda_g(T, p_g) + \lambda_r(T) + \lambda_{coup}(T), \quad (1)$$

where the solid and gaseous thermal conductivity λ_s and λ_g , respectively, are the dominant components. In order to achieve the lowest possible thermal conductivity λ_{eff} of NIMs, one straightforward method appears to design and optimize the architecture of NIMs, where the solid and gaseous thermal transport can be suppressed by taking advantage of their size-dependence at nanoscale [4].

In this contribution, we discuss the possibility and methodology for making NIMs by using hollow nanoparticles with controlled dimensions and compositions (Figure 1). We have noticed a significant reduction on thermal conductivity of hollow nanospheres compared to the bulk material values, clearly indicating a prominent size-dependent thermal conductivity at the nanoscale [3]. By controlling the diameter and the wall thickness of the hollow nanoparticles, it is now possible to achieve a thermal conductivity of about 0.020 W/(mK) in hollow silica nanosphere NIMs, comparable to ~0.015 W/(mK) for typical aerogel materials. With a proper design, optimization and selection of wall/solid materials, it is also possible to decrease the thermal conductivity of NIMs even further, which may open new possibilities and applications in the building sector.

Keywords: Nano insulation material; NIM; hollow nanosphere; size effect.

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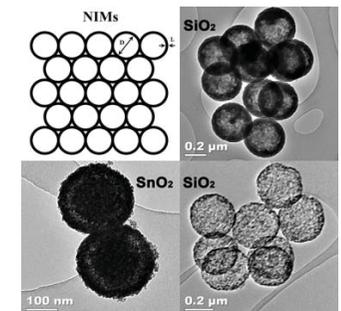


Figure 1. Nano insulation materials: conceptual methodology and representative material systems.

Natural lighting in the indoor environment

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Achieving visual comfort in building interiors is directly related to the lighting levels necessary for typical functions assigned to certain spaces, as well as to the avoidance of visual glare and to the visual connections with the exterior space. Educational buildings require a high degree of visual comfort for their users. Natural lighting in educational spaces is ensured with the provision of external openings. The linear disposition of classrooms in typical educational buildings in Cyprus allows for openings along the two long sides of these spaces.

The present study quantitatively analysed lighting levels and glare issues in classrooms using the software programs Ecotect v.5.5 and Desktop Radiance v.1.02 with the aim to create spaces with high levels of visual comfort.

The geo-specific simulation of natural lighting conforms to Nicosia area, latitude 35° 10' and longitude 33° 21', and it addresses varying orientations under conditions of overcast sky conditions - 8/8 for the Winter Solstice, intermediate sky conditions - 4/8 for the solar equinox and clear sky conditions - 0/8 for the Summer Solstice, at 09:00, 12:00 and 15:00. To validate the results obtained, natural lighting levels were measured on site. Conclusions regarding the most suitable orientation in relation to the average values of natural lighting were based on a comparative basis.

The presence of significant contradictions in the visual field, as well as abrupt alterations in luminosity, results in a disabling glare and negatively affects the visual comfort of users. Glare may be caused either directly from the luminous source or through reflections. In a classroom, glare causes disadvantageous teaching conditions, especially whenever it occurs on desks or blackboards. In simulating natural lighting conditions for the control of glare in a typical educational space with furniture, the above-mentioned software was used.

The results of the analysis enabled a comparative evaluation of visual comfort, lighting levels and issues of glare in classrooms of typical educational buildings in Cyprus.

Keywords visual comfort; lighting levels; glare; classroom; educational buildings in Cyprus

Performance analysis of a PV-array mounted single-span plastic greenhouse

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Electricity consumption is increasing in modern greenhouse cultivation to operate heating, cooling, ventilation, irrigation, and lighting appliances for plant environment control. For this reason, using renewable energy in greenhouses is an important objective for sustainable greenhouse crop production. Recent studies have examined electricity generation and shading (Yano et al., 2010), crop yields, and the system costs (Kadowaki et al., 2012) of a photovoltaic (PV)-array mounted greenhouse. The PV modules were mounted inside the south roof of an east–west oriented single-span plastic greenhouse, either in a straight-line (PV_s) (Fig. 1) or checkerboard (PV_c) arrangement. The cultivation experiment results show that the negative shading effects on plant growth can be mitigated by consideration of the PV module arrangement without reduction in the PV generated electric energy. Crop revenue losses were estimated in the PV_s greenhouse in comparison to those in the PV-less control greenhouse. Electricity revenues and the cost-payback time of the PV array and the inverter were also estimated under the assumption of cloudless skies and a practical electricity prices. Under actual sky conditions in the author's region, 690 kWh yr⁻¹ electrical energy is expected to be generated by the PV_s or PV_c array. Using this energy, for example, 75 W greenhouse appliances such as window ventilation control motors or supplementary lighting lamps can be operated year-round or 1.8 kW greenhouse loads, such as those of pumps or fans, can be satisfied for 1 h every day. These appliances promise to improve the greenhouse environment greatly, thereby enhancing crop yields. The use of appropriate scale and arrangements of PV modules with reasonable price and efficiency would be beneficial for greenhouse crop production. It is noteworthy that the balance of PV electricity production and allowable plant shading would vary according to the plant species, geography, meteorology, season, and greenhouse materials and structures. The greenhouse orientation also strongly affects the performance of electricity production and crop shading in a PV greenhouse. More extensive studies are necessary to explore the compatibility of crops and electricity production in PV greenhouses.



Fig. 1 Welsh onion cultivated hydroponically in the PV_s array mounted greenhouse.

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Keywords solar cell; photovoltaic; agriculture; horticulture; greenhouse; shading; crop; plant

Switching properties of switchable mirrors based on magnesium-yttrium alloy thin films

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Thin films of alloys of magnesium and 3d transition metals, such as nickel or titanium, capped with thin palladium, known as “switchable mirrors”, can change their optical properties reversibly between reflective and transparent states by alternately exposing the film to hydrogen and oxygen containing gas. Because these films can control the transmittance by changing their reflectance, they are promising materials as the switchable glazing in smart windows, which contribute to saving energy for air-conditioning. The switching properties required for the application are as follows: 1) high visible transmittance in the transparent state, 2) high achromatic property in the transparent state, 3) high switching durability between the reflective and transparent states. In this paper, we studied the above mentioned properties about switchable mirrors based on Mg-Y alloy thin films.

Mg-Y alloy thin films were prepared on glass substrates using direct-current (dc) magnetron co-sputtering of Mg and Y targets. These thin films were subsequently covered with a thin Pd film sputtered with a Pd target without breaking the vacuum. The base pressure of the deposition chamber was 5×10^{-5} Pa and the working pressure during deposition was kept at 0.3 Pa using a mass-flow controller of Ar. The composition of the alloys was controlled by adjusting the sputtering power ratio of Mg to Y targets. The thickness of the Mg-Y alloy layer was about 40 nm and that of the Pd layer was about 7 nm. The optical reflectance and transmittance spectra of the prepared switchable mirrors were measured at wavelengths between 200 to 2500 nm using a UV-vis-NIR optical spectrophotometer. The switching durability was evaluated by monitoring the transmittance at 940 nm with alternately exposing to hydrogen and oxygen containing Ar gas.

Figure 1 shows the transmittance spectra of Mg-Y switchable mirrors in the transparent state. The visible transmittance evaluated from these spectra is about ~33%. As evidenced by the fact that the spectra in the visible range are fairly flat, these mirrors show considerably color-neutral appearance. With increasing Y composition of Mg-Y alloy, the switching durability between the reflective and transparent states increased sharply up to over 5000 times.

This work was supported by the Grant for Industrial Technology Research Program of the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

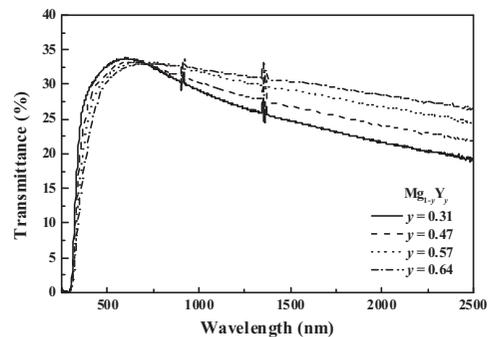


Fig.1 Transmittance spectra of Mg-Y switchable mirrors in the transparent state

Keywords switchable mirror; Mg-Y alloy; switching durability; visible transmittance; color neutrality

The study of native's materials used in residential houses roof in the mild and humid climate of the Caspian Sea region

HAJAR SADEGHI

The use of local materials in buildings construction is a strategy employed in the concept of sustainable development. The use of native material was more common in the traditional architecture in comparison to the current modern architecture.

Today these materials have been forgotten in the modern architecture. Recognition of native materials and investigation on the possibility of using of those materials is a particular importance. So, this study discusses the climatic solutions in the design and construction of housing, applying the local materials in the Caspian Sea region. With regard to the subject, firstly we identify the target group's climate in the zone climatic classification. This identification lead us the major design goals in the region. Thensome features of materials which compliance in the building that influenceclimateis described and with considering the solution some suggestions on the re-use of local materials are presented.

Towards zero energy buildings in central Europe – GIS-based mapping tool of urban solar energy potential

Attila Talamon, Tamás Csoknyai PhD, Gábor Szendrő

One of the major challenges faced by European countries today is the reduction of CO₂ emissions that contribute to climate change, and one of the key areas where improvements could be made easily and at low cost is the energy efficiency of buildings. There is an urgent need nowadays to reduce current levels of GHGs emissions. On the other hand the EU countries largely dependent on energy imports are vulnerable to disruption in energy supply which may in turn threaten functioning of their current economic structure. The EU imported 54% of its energy sources in 2006 and was projected to increase even further by 2030. Reducing its import dependency EU is one of the main goals of the 20-20 by 2020 target – this legislative package is believed to reduce the expected imports of energy by 26% compared to the development before the 20-20 initiative. One of the most important environmental problems is the energy consumption of the buildings. The current paper shows that buildings can deliver large energy and CO₂ emission reductions at low costs. The directives and the methods of the energy certification of the buildings spread across Europe. Only 1-2% part of the building stock is exchanged every year, so it is very important to increase the energy efficiency of the existing buildings, too. Present paper focuses on the buildings built in urban environment only. For the follow-up programs the question has been posed: How can we use GIS-tools to estimate the solar energy efficiency of the building stock in urban environment?

Vacuum insulation panels with melamine-formaldehyde rigid foams as core material

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Air-conditioning and heating represent approximately one half of the total energy consumption applied for buildings and building related processes in the temperate climate zone. Reduction of heat losses of home appliances in the domestic sector and that of machines in the industry is an essential part in the strategy for CO₂ emission reduction. This reduction by further increase of the conventional insulator thickness is in most cases not acceptable or even not a feasible solution, thus more efficient new materials are sought.

Vacuum insulation stands as the most promising alternative option. When micro or nanostructured foam or powder (core material) is encapsulated into a gas-tight envelope and evacuated to ~ 0.1 mbar, a vacuum insulation is obtained. Low pressure is required to keep the mean free path of molecules larger than characteristic size of caverns or pores. Since such materials are most often packed into sheet-like enclosures, the Vacuum Insulation Panel (VIP) is a common designation. The thermal conductivity of a VIP is roughly an order of magnitude lower compared to a conventional insulation material

There is no short and simple answer what prevented their widespread use so far since several factors are involved. The price was definitely the major obstacle; due to complex production of the porous filling material and particularly due to the VIP processing. Basic demands that the VIP must fulfill are the following: a) porosity of the core must be preserved, despite the atmospheric pressure on the envelope that can increase the density and consequently the thermal conductivity, b) pressure in the envelope must remain several orders of magnitude below the air pressure, c) expected lifetime of the VIP requires extreme seal tightness and low permeability of the envelope, as well as extremely low outgassing of the core material and envelope itself.

In this talk I will present our research on the VIP that contains melamine-formaldehyde (MF) rigid foam as a core material. Due to their unique properties, the MF polymers are gaining an increasing interest on the market. Even non-expanded MF polymers have good thermal and acoustic insulation properties, are non-flammable and chemically inert. Their application can be found in the aircraft, car and spaceflight industry, building construction and acoustics. Preparation of rigid foams from MF resin has been recently developed and patented by company Melamin, Slovenia. Low density (50-100 kg/m³), high porosity and extreme mechanical stability of such rigid foams indicate high potential as a VIP core material.

MF rigid foam is an organic material and is thus conventionally expected to have high outgassing rate in vacuum. Our measurements reveal that proper pre-treatment at 150°C in air (drying) and vacuum can reduce the outgassing rate to a level that warrants several decades of lifetime. Moreover, the overall thermal conductivity of prototype VIP with this core material and 0.1mm thick stainless steel envelope was measured to be $\lambda \approx 0.006$ W/m K, while non-evacuated core has $\lambda \approx 0.04$ W/m K. Treatment & measurement procedure will be presented along with the measured outgassing rate and its correlation to MF rigid foam synthesis.

Materials, Processes and Systems for Energy Saving and Sustainability

A first-principles investigation of Fe/MgO/Fe junctions by inserting ultrathin Co interlayers

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Recently, the tunnel magnetoresistance (TMR) effect became increasingly important for the fast developing field of spintronic devices. The first industrial applicable TMR contacts have been built using crystalline MgO insulators which are epitaxially grown on as well as coated with iron electrodes (Fe/MgO/Fe). Looking for improving the interface quality of Fe/MgO/Fe junctions, an alternative means is found in the specific manipulation of the spin-dependent conductances by embedding ultrathin interlayers. In this work, we report on systematic ab initio investigations of the effects of Co interlayers embedded into Fe(001)/MgO/Fe(001) MTJs, focusing on the changes in the electronic structure with interlayer thickness. We specifically studied the thickness dependence of ultrathin Co interlayers which are inserted at both Fe/MgO interfaces. Since Co grows epitaxially only up to few monolayers on a bcc substrate, the Co thicknesses $d(\text{Co})$ are restricted to $x \leq 6$ ML. Substituting all Fe atoms with Co atoms is studied in addition. The characteristics for embedded Co interlayers are considerably influenced by interface resonances which are analyzed by the local electronic structure.

Keywords: Magnetic tunnel junction, spin polarization, electronic properties, FP-LAPW, Co interlayers

A review of vacuum insulation technology for building insulation: current and future use

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Vacuum insulation technology has existed for many years, but only recently has it become commercially viable for building insulation elements. The development of vacuum insulation is a significant advance in the area of low heat loss systems with great potential to reduce building heating and cooling loads when combined with other insulants. Here the basic concept of vacuum insulation is reviewed and the procedures and research undertaken in the development of domestic and industrial vacuum insulation are outlined. The achieved thermal performance of current laboratory systems and those that are now commercially available are presented. The potential levels of performance that may be achieved using different materials and fabrication techniques of are reported. Research into heat storage systems that incorporate vacuum insulation to achieve improved thermal performance is also outlined. Some current applications of vacuum insulation such as vacuum insulation panel, vacuum insulated pipe and vacuum glazing are reviewed and the merits and drawbacks they offer are discussed. The research concludes that vacuum insulation technology has a very wide range of applications and also has significant potential to provide energy savings in the built environment.

Keywords: vacuum glazing; vacuum insulation panels; vacuum insulated pipes; thermal performance

A Study of the Installed Capacity and Electricity Quality of an Independent Microgrid with Tidal Power Generation, Photovoltaics, and Fuel-Cell

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Large-scale solar power generation has been increasing in Japan in recent years [1 and 2]. Local supply and consumption of energy is greatly needed domestically, as shown by the accident at the first nuclear power plant of the Tokyo Electric Power Company at Fukushima in March 2011. This paper describes the development of an independent distribution energy system that enables the local production of energy for local consumption via a fuel cell microgrid. The fuel cell microgrid investigated in this paper is not connected to a large commercial electrical power plant; rather, it supplies green energy to a surrounding area as much as possible. To supply stable electrical power on demand from a microgrid with unstable green energy, power sources that can provide output changes of green energy are required. Generally, changes in electrical power can be classified as short, when they involve several to approximately ten seconds, and long, when they involve tens of seconds or more. In this work, changes in electrical power that occur over a period of several seconds or more are accomplished by control of the number of SOFCs (solid-oxide fuel cells) in operation and by part-load operation. In this paper, the Saroma Lake green microgrid (SLMG, Fig.1), a fuel cell microgrid with tidal power generation and PVs (photovoltaics), was planned. Energy balance equations were used to investigate the method of operation of the system. Further analysis of the facility and the operation cost and analysis of the electric power quality of the network were conducted using MATLAB/Simulink, and the relationship between the capacity of a facility and the cost and supply rate of green energy and electric power quality (interphase voltage, frequency and higher harmonic wave) of the power network were clarified. Increasing the supply rate of green energy and reducing the facility cost will require the introduction of biofuels and the reduction of the facility costs of SOFCs in the SLMG.

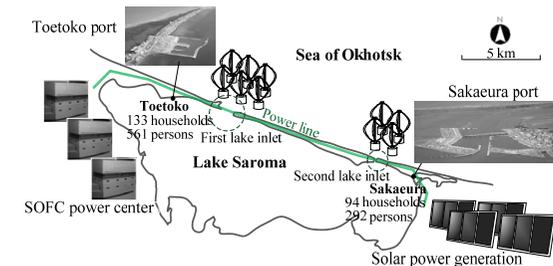


Fig.1 The electrical power system of the Lake Saroma green microgrid

Keywords keyword; SOFC; tidal power generation; microgrid; photovoltaics; numerical simulation; Okhotsk Sea

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Assessment of current methods for determination the stability of fuels in the context of development online system

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Traditional liquid fuels were characterized by stable structural-group composition. It was possible for these fuels to determine the time limit in the data storage climate conditions. The present fuels can contain up to 7% (v/v) FAME for diesel or 5% (v/v) ethanol for gasoline. According to the prevailing tendencies of the fuel containing bio-components will increase their market share. Currently, the primary criterion for assessing the degree of aging of fuel during storage is the change in the normative values of qualitative parameters. These parameters are determined in stationary laboratory using costly and time-consuming testing methods. Recently, a few of devices allowing for rapid and multiparameter analysis of fuels on the storage had appeared on the market. Examples of such devices are Eraspec Eralytics™ GmbH and MINISCAN IRXpert Fuel Analyzer from Grabner Instruments. These devices allow the use of spectral analysis to measure several parameters of the fuel at an acceptable accuracy. These fully mobile laboratories mainly determine the quantitative parameters of fuels. However, interpretation and evaluation of fuel has to be done by a specialist. It seems appropriate therefore to develop a new methodology for measuring the stored fuels.

Methodology for monitoring of the aging of fuels will be based on Raman spectrometer using a 785 or 1064 nm excitation laser. Alternative is considered measurements by IR with assisted optoelectronic system in order to ensure certainty of measurement. It is assumed that the designed analyzer system will collect information from three levels of the tank separately and combine them to give the equivalent of homogenization of the sample - as in the normative methods. In addition to information about aging of fuels we receive data about water content. The final device will be monitoring the aging of fuel giving clear messages to the dispatcher. A simple three-color scheme - green - the fuel can be safely stored, the orange - note, the rate of aging increase and approaches the critical value of the red - the need for swift action, the decision to release fuel and marketing, will allow the quick response of warehouse operator. Development of novel methods for examination of fuel during storage is an alternative to conventional testing, especially when it is not required for accurate and fast assessment of the quality parameters.

Key Words: fuel storage; biofuels; stability; FT-IR spectrometry; Raman spectrometry

Challenges and Barriers for the End of Life Depolymerisation: The Depotec Life⁺ Project

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Used tyres is a continuously growing environmental problem, with impacts to economy and health concerning every modern society. Used tyres can be further treated by different ways and processes. Taking into consideration the used tyres management trend in the EU for the last decade, several ways of processing used tyres are presented: retreading and reuse/export of used tyres can consume up to 20% of the rejected tyres per year.

Furthermore, end of life tyres can be used as a raw material for energy or material recovery. Over the last 15 years, the combination of material and energy recovery of end of life tyres, increased from 31% to 78% of total used tyres treatment whilst in the same time period the landfilling decreased to a dismal 4% (compared to nearly 50% in 1996).

Used tyres consist a high calorific waste and can be used in dedicated energy-to-waste plants, as fuel substitutes in industrial and as feedstock to alternative pyrolysis plant for both energy and carbon material production. Used tyres cover a wide range of materials which can be recovered (steel, fibers, shredders, energy, oils, carbon filler, activated carbon etc) and could be processed to fulfill guideline, regulatory or industry specifications mainly to achieve a high calorific value gas and carbon materials.

The aim of this study was a survey on the current practices of energy recovery of end of life tyres and especially pyrolysis for the production of gas, liquid and solid products in European Union and worldwide as well as to undertake an overview of the legal and policy framework for pyrolysis and use of the product. An assessment of the environmental impacts and of the economic aspects and a review of alternative outlets of the tyre waste streams is also presented.

Keywords: used tyres, pyrolysis, policy, legislation; energy

Comparative evaluation of biodiesel processing solid residues as adsorbents for wastewater treatment

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Currently, over 95% of the world's biodiesel production is derived from edible oils, easily available on large scale from the agricultural industry. However, continuous and large-scale production of biodiesel from edible oil without proper planning may cause problems, including depletion of food supply. A solution would be the use of non-edible oils for biodiesel production, employing seeds such as *Crambe abyssinica* and *Raphanus sativus* L. However, this process generates an extensive amount of solid residues (pressed seed cakes), which present environmental problems in terms of adequate disposal, given their limited application as animal feed or silage [1]. Given that one of the effective uses of agricultural waste biomass that has gained much attention over the last decade is the production of adsorbents for wastewater treatment [2], the objective of this study was to compare the performance of two types of pressed seed cakes, *Crambe abyssinica* and *Raphanus sativus*, as adsorbents. Methylene blue (MB) was selected as adsorbate in order to allow for performance comparison with other press cakes employed in the production of adsorbents. Both press cakes were employed directly as biosorbents, i.e., without submitting the agricultural waste to any thermal and/or chemical activation procedure. Batch adsorption tests were performed at 30 °C. Adsorption kinetics was satisfactorily described by a pseudo second-order kinetic model. Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich (D-R) equilibrium models were tested, with Freundlich providing the best fit. Maximum adsorption capacity values were 30 and 79.7 mg g⁻¹ for *Raphanus* and *crambe* pressed seeds, respectively. Such values were deemed quite satisfactory in comparison to other biosorbents employed for MB removal, such as banana and orange peels – 19 to 21 mg g⁻¹ – and wheat shells – 16.6 mg g⁻¹ [3,4]. Furthermore, adsorption capacity was high in comparison to adsorbents produced by thermal or chemical activation of similar types of residues, including sunflower oil cake – 16.4 mg g⁻¹ – and defective coffee beans press cake – 14.9 mg g⁻¹ [1,5]. Results showed that both types of press cake, without any thermal treatment, presented higher adsorption capacity than activated carbons produced from other seed press cakes, confirming that this type of waste material is a suitable candidate for use in the production of adsorbents, thus contributing for the implementation of sustainable development in the biodiesel production chain.

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Keywords sustainability; biodiesel;adsorption; biodiesel solid residue;dye removal

Critical Metals in Strategic Energy Technologies

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Due to the rapid growth in demand for certain materials, compounded by political risks associated with the geographical concentration of the supply of them, shortages of materials could be a potential bottleneck to the deployment of low-carbon energy technologies. Consequently, an assessment has been carried out to ascertain whether such shortages could jeopardise the objectives of the EU's Strategic Energy Technology Plan (SET-Plan), especially in the six low-carbon energy technologies of SET-Plan, namely: nuclear, solar, wind, bioenergy, carbon capture and storage (CCS) and electricity grids. The work identified 14 metals for which the deployment of the six technologies will require 1% or more (and in some cases, much more) of current world supply per annum between 2020 and 2030. Following a more critical examination, based on the likelihood of rapid future global demand growth, limitations to expanding supply in the short to medium term, and the concentration of supply and political risks associated with key suppliers, 5 of the 14 metals were pinpointed to be at high risk, namely: the rare earth metals neodymium and dysprosium (for wind technology), and the by-products (from the processing of other metals) indium, tellurium and gallium (for photovoltaic technologies). In addition, the work has explored potential mitigation strategies, ranging from expanding European output, increasing recycling and reuse to reducing waste and finding substitutes for these metals in their main applications. Furthermore, recommendations are provided which include closely working with the EU's Raw Materials Initiative; supporting efforts to ensure reliable supply of ore concentrates at competitive prices; promoting R&D and demonstration projects on new lower cost separation processes; and promoting the further development of recycling technologies and increasing end-of-life collection.

Keywords: critical metals, rare earth metals, strategic energy technologies, SET-Plan, Solar PV, wind energy

Developing innovative photovoltaic materials in the dawn of a new era: self-generation and small scale electricity consumption

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A few years ago, the use of solar photovoltaic panels in residential buildings seemed to be something remote and rather expensive for individuals, being only economically affordable through investments by large property owners' associations, being visible on public buildings or big infrastructures located on the outskirts of cities.

The emergence of new thin film materials such as, OPV (Organic photovoltaic) and CIGS (copper indium gallium selenide) respectively, opens up a new field, which get such solar devices closer to the families. Laboratories, the real developers of these technologies, have been working hard for several years in order to obtain new photovoltaic materials with better performance than the traditional rigid crystalline silicon modules. The advantages and possibilities that they offer are clearly demonstrated when compared to the costs of generating solar energy through the former modules. Nevertheless, large surfaces needed to install these panels the solar incidence angles and the high temperatures reached by the devices, made them inappropriate to be implemented at home in such a way. Once those problems are solved with the emergence of lighter and more flexible materials, the manufacture of such devices becomes affordable.

All European Union energy directives are aimed to reduce energy consumption through an efficient use of energy and the implementation of renewable sources. Energy in buildings represents approximately 40 % of the total energy consumption and about 36 % of the CO₂ emissions, which are responsible for the global warming.

On the one hand, under the heading of energy savings, the recent implementation of the Royal Decree-Law 1/2012, which either, constitutes a setback to financial assistance grants for self-generation via renewable energy and its later dumping onto the general electricity grid; and on the other hand it represents an innovative manner within our legislation, leaving the door open to self-consumption. The new legislative framework coupled with the emergence of new more efficient and malleable solar collectors, will enable to see facilities with new mechanisms generating solar energy, within our own residential homes, in such a way as to be more efficient, cheaper and profitable.

Perhaps we are not aware of it, but we are in the dawn of a new energy era, represented by self-generation and small scale consumption.

Key words: Photovoltaics; OPV; CIGS; Thin film; self consumption, efficiency.

Development of a thermal storage system based on phase change material as storage medium

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Thermal energy storage systems are a key component in utilization of solar energy or waste heat recovery. In the last 20 years more attention has been paid in development of energy storage systems based on phase change materials as storage medium, due to environmental and climate change challenges. However, most phase change materials suffer from some technical drawbacks such as low thermal conductivity, subcooling and corrosion which makes the charging and discharging process take longer time and consequently, influence the efficiency and reliability of the thermal energy storage systems.

My research focus on tackling the technical problems which face this technology by selecting a suitable phase change material and investigating ways to enhance heat transfer properties of this storage material. In addition, it is also important to reduce the interfacial thermal resistance between thermal storage material and heat transfer surfaces as well as to prevent corrosion that a heat storage material may cause. Furthermore, among the key aspects which are being targeted by this study are the prevention of phase separation, super cooling and superheating of the heat storage material. Finally, comprehensive experiments will be carried out using the illustrated lab scale thermal storage unit, and perform analyses of the data for understanding the dynamics of heat storage and release, as well as to find out the energy storage density of the system.

Development of guidelines for help on a platform wiki as a tool to support the process of self-learning in materials engineering of the technical Industrial Engineering degree

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There exists diverse tools, didactic resources and materials to be used in the learning process in academic environments. This work presents the experience conducted in different subjects of the studies plan of the technical Industrial Engineering degree speciality in chemical engineering taught in the University of Jaén. A review of the knowledge has been done and a set of forms have been generated. These resources can be made available to the students in wiki platform or virtual teaching of the own university based on ILIAS.

To generate the diverse resources for virtual teaching platform based on ILIAS LMS (Learning Management System), Reload Editor has been considered. It is an application based on SCORM that allows editing meta-data and packing contents with the aim of generating resources for self-learning. It can use previously generated contents, such as web pages, flash animations, Java applets, Javascript, etc. and pack them to be loaded. This standard allows the creation of structured learning objects that can be housed in different learning management systems (LMS) without having to make changes to suit each of them.

For guidelines on wiki platform, different materials have been developed. We have created a basic user guide and advanced guide to create content. They guide oriented script language used to create Wikipedia-style content.

The use of these didactic and pedagogical resources provides multiple advantages such as:

- Ease of integration of the contents of the learning platforms.
- Access to the teaching components in a remote way, exploiting the advantages of the web technologies.
- Self-learning and self-evaluation of the contents.
- Reutilization of the components and possibility of integration with other applications.
- Existence of visual tools for generating contents.

Keywords: guideline, self-learning, materials engineering

Effect of energy technologies on water consumption

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Water consumption is emerging as an important issue potentially influencing the composition of future energy generation technologies and networks, especially as projected urban populations are expected to outpace water availability. In this paper, we will examine the effect of different energy generation technologies on local water consumption. Water consumption is defined as freshwater withdrawals which are evaporated or incorporated in products and waste, whereas water use is defined as all water that goes into a system (most of this typically leaves the system as waste water). Water consumption, therefore, has a more severe impact due to the fact that the water is lost for use in the community. The significance of water consumption of different energy generation technologies is often not well understood. To highlight this, we will focus the discussion in context of alternative transportation technologies like battery electric vehicles. As will be shown, the effect of changing electricity generation types can significantly affect the water consumption of Battery Electric Vehicles (BEV) and Plug-in Hybrid Electric Vehicles (PHEV), and may result in significant water consumption fluctuations. The effect of variations in energy generation will be presented using a number of scenarios where the water consumptions for 2010 and 2030 Electric Vehicles for different electricity generation options has been totaled from fuel extraction to plant operation. Electricity fuel options include coal, nuclear, natural gas and petroleum, as well as wind and solar.

Keywords water; energy; transportation

Exciton absorption in GaSe layered crystal hydrogen intercalates

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Layered crystals, and in particular InSe and GaSe crystals, due to their specific chemical bonding between atoms: strong ion-covalent forces inside crystalline layers and low van der Waals ones between them, attract special attention of researchers, as heterostructures based on them possess good photosensitivity and can be used not only in solar cells [1, 2] and accumulators of electrical energy [3], but in accord with investigations [4] are rather promising in creation of gamma-radiation sensors.

Besides, as it was shown in a number of recent works [5, 6], the layered crystals InSe and GaSe can be applied in hydrogen energetics as operation elements in solid hydrogen storage. The hydrogen concentration in them can reach values close to $x = 5 \dots 6$, where x is the amount of embedded hydrogen atoms per one formula unit in the intercalated crystal matrix.

As it was shown in NMR investigations of GaSe crystals [5], in the process of intercalation hydrogen atoms recombine in layered crystals up to the molecular state. At the same time, an insignificant fraction of atomic hydrogen (about 0.01 %) passivates defects of crystalline lattice. Intercalation with hydrogen also results in growth of the lattice parameter and width of van-der-Waals gap. In addition, optical investigations of InSe crystals at $T = 80$ K [6] showed that growth of the molecular hydrogen concentration in the crystal interlayer space results in two-dimensional localization of exciton motion inside the plane of crystalline layers.

Represented in this work are low-temperature ($T = 4.5 \dots 250$ K) investigations of exciton light absorption in GaSe crystals intercalated with hydrogen in the concentrations $x = 0 \dots 5$. It is ascertained that, with growth of the intercalated hydrogen concentration in these crystals, one can observe localization of exciton motion inside the layer plane. However, by the contrast with InSe crystals, this localization takes place at higher hydrogen concentrations, which is related with difference between Bohr exciton radii in InSe and GaSe crystals, as it has been shown in this work. Growth of the hydrogen concentration in GaSe, like to that in InSe, results in widening the exciton absorption bands.

The performed temperature investigations allowed ascertaining that, despite the above factors causing localization of exciton motion as a consequence of changing the dielectric permittivity in interlayer space (when introducing molecular hydrogen to it), the character of exciton-phonon interaction does not change in the whole and is caused by the exciton scattering by homopolar optical phonons. This scattering leads to growth of the integrated intensity of exciton absorption bands as a result of decay of exciton polaritons, which is caused by homopolar optical phonons.

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Keywords layered crystals; hydrogen storage; GaSe; exciton-phonon interaction

Hybrid organosilica membranes for energy-efficient molecular separation

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Molecular separation with inorganic membranes provides an energy-efficient alternative to (cryo-)distillation. However, large-scale application is hampered by the low hydrothermal stability of nearly all existing materials. We have developed a nanoporous organic-inorganic hybrid silica membrane (HybSi®) that displays superior resistance under hydrothermal and acid conditions at realistic operating temperatures (150°C) for periods up to at least 1000 days [1,2]. While the architecture of the hybrid material is mostly similar to that of inorganic silica, a substantial part of the Si–O–Si bonds has been replaced by organic Si–R–Si bridges. It was found that these bridging moieties are an essential structural element, making hybrid silica less susceptible than inorganic silica to hydrolysis of siloxane network bonds and the nucleation and propagation of cracks. Hybrid silica is also stable under conditions in which polymer membranes generally provide no alternative, including high pressures, liquid separation up to 190°C and aggressive organic solvents.

To allow wide application of hybrid silica membranes, the separation performance requires extensive tailoring. We have shown that this can be done by adjusting the size, flexibility, shape, and electronic structure of the organic bridging group [3]. A single generic procedure has been applied to synthesize nanoporous membranes from bridged silsesquioxane precursors with different reactivities. Membranes with short alkylene (CH₂ and C₂H₄) bridging groups show high H₂/N₂ permeance ratios, related to differences in molecular size. The highest CO₂/H₂ permeance ratios, related to the affinity of adsorption in the material, were obtained for longer (C₆H₁₆) alkylene and aryl bridges. Materials with long flexible alkylene bridges have a hydrophobic surface and show strongly temperature-dependent molecular transport as well as a high butanol flux in a pervaporation process, which is indicative of organic polymerlike properties. The versatility of the bridging group offers an extensive toolbox to tune the nanostructure and the affinity of hybrid silica membranes and by doing so to optimize the performance towards specific separation challenges. This provides excellent prospects for industrial applications such as carbon capture and biofuel production.

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Keywords energy saving; sustainability; molecular separation; membrane; hybrid material; hydrogen purification; biofuel production; CO₂ sequestration

Influence of the thermal capacity of the hot active wall on the 2D transient free natural convection in diode cavities

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This work concerns the transient natural convective heat transfer that occurs in an air-filled parallelogrammic cavity represented in Fig. 1(a). This type of enclosure can be applied in many engineering fields as in building, aeronautics or renewable energy. The active hot and cold walls of height H and depth W remain in vertical position and parallel to each other, separated by a horizontal distance equal to his height (H).

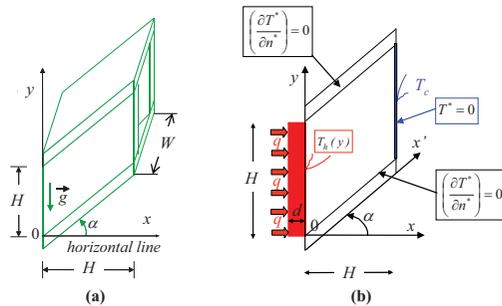


Figure 1: The treated enclosure

The cold wall is maintained isothermal at temperature T_c (Fig. 1(b)). The hot wall is constituted by a solid mass with specific physical properties that are fixed according to the considered engineering application. The external face of this wall ($x=-d$) is submitted to a constant heat flux q . Hence the temperature on the inner face of the wall ($x=0$) depends on y and is denoted as $T_h(y)$. The channel of the cavity is thermally adiabatic, being the top and bottom walls inclined at an angle α with respect to the horizontal. This angle is either positive (hot wall below the level of the cold one) or negative, giving rise respectively to a conducting or insulating enclosure in the convective sense of the term. In this study, α is set to the particular values of 0° (square section), $\pm 15^\circ$ and $\pm 30^\circ$. The considered thermal boundary conditions and the dimensions of the cavity (large depth W) allow to consider as 2D the flow taking place in the median plane of the cavity.

The governing equations of continuity, momentum and energy corresponding to the 2D transient case are solved by means of the Volume Finite Method in order to examine the characteristics of the flow inside the cavity submitted to the mentioned thermal conditions. Many calculations have been done by varying the dominant parameters as the angle inclination, the Rayleigh number and the thickness to height ratio ($A_w=d/H$) of the hot wall. The dynamic and thermal fields are presented and different instants during the transient regime and at steady state. This study allows to examine the influence of the mass of the wall on the convective transfer inside the enclosure. The local and mean Nusselt numbers are determined for each configuration as well as the maximum temperatures. Finally a comparison with the case of a wall of negligible thickness is carried out showing that the combined conduction-convection-heat transfer is significant and cannot be neglected. This result is important for the design of engineering devices.

Keywords Natural convection, diode cavity, energy saving, engineering applications, heat transfer

Making cool roofs compatible with low heating and cooling loads

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A cool roof has high solar reflectance (R_{sol}) and high infrared emittance. It reflects most incident solar energy and can pump heat by radiating efficiently to the sky, when warm and down to temperatures slightly below ambient on clear nights. While its ability to reduce total seasonal cooling loads and peak summer loads in hot zones is well established, its compatibility with reducing heating loads in climates with warm-hot summers and cool to cold winters is not so well understood. This issue is of high importance in temperate zones. When examined in detail the need to better understand the inter-play between a range of building design settings in terms of comfort, cost and energy savings becomes clear. The degrees of cross-coupling between various design parameter influences in a building's thermal response ranges from strong to weak. Understanding these cross-influence effects, opens up more design options for similar energy efficiency levels, while enabling large cost savings and more pleasant interiors. For example if one parameter setting is most influential in summer but not in winter, another in winter not summer, and if they weakly cross-couple, it becomes possible to save much energy in both seasons. The data and simulations in this cool roof study contain examples of strong and weak cross-coupling which can be exploited to save energy in summer and winter. Specifically we quantify the strong cross-influence between roof albedo and emittance values, and sub-roof insulation (R-value), first in summer alone and then in winter, to find an optimum year round combination. The lack of cross-coupling we find between a cool roof and air exchange rate settings, air changes per hour (ACH) in winter is of particular value since moderate to high infiltration, ACH values lead to high heating loads.

To quantify these issues measurements are gathered in two outdoor small scale buildings which have identical geometries with a single interior zone, sloping roof oriented with its axis east-west. Walls, floor and roof are insulated with 60 mm rigid polystyrene (R-value 1.4), roof infrared emittance in both is 0.9 but with different solar reflectance to compare the differences in the roof temperature and room air temperature. Simulation studies using "Energy Plus" are used to validate this data, then to explore the impact of a more complete parameter set on heating and cooling loads in a typical single family house occupying 186 m² located in Sydney (Australia) facing north with roof a space. From one hundred and forty-four simulations a matrix of heating, cooling, and year round energy outcomes results with roof solar absorptance set at 0.2, 0.4, 0.6, 0.8; ceiling insulation R-value at 0.5, 1.63, 2.5, 4.1; infiltration rates per hour at ACH 0.5, 1, 2; and internal loads at 9Kwh/day, 14.5Kwh/day, 20Kwh/day. Statistical and cross coupling analysis has been used to define optimum combinations of roof coatings, sub-roof insulation and infiltration rates considering cost and energy savings.

Example results include; on increasing roof solar absorptance by 0.1 cooling loads rise by 4.07 MJ/m²/year while heating loads fall by 1 MJ/m²/year. There is a diminishing return when increasing the R-value of insulation. Relative to the sensitivity of other parameters the effect of increasing R-value above 1.63 or 2.5 is on average small. If R_{SOL} is large, high insulation R-values are not needed in Sydney, are quite poor from a cost benefit viewpoint and may reduce cooling at night. R-value of 1.63 or more is still recommended but only needs to rise if R_{SOL} is too low, ACH too high. With low infiltration rates, high energy savings occur for the heating system. The year round cross-correlation matrix allows parameter ranking and the first thirty-three positions of our hundred and forty-four correspond to lowest infiltration. This is because heating loads are highest and ACH dominates them. Other key findings from this matrix will be presented. The core finding is that high solar reflectance, with low infiltration and an intermediate R-value is the preferred combination.

Keywords cool roof; solar reflectance; solar absorptance; R-value; infiltration; air changes per hour (ACH); cooling load; heating load

Modelling and experimental validation for the thermal performance of a hybrid vacuum glazing

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Hybrid vacuum glazing (HVG) is the combination of a conventional double vacuum glazing and a third glass sheet, separated by an edge spacer bar and a gas filled cavity. The double vacuum glazing comprises two sheets of glass separated by an array of stainless steel support pillars with a diameter of 0.4 mm and a height of 0.15 mm, spaced at 25 mm within the vacuum gap. The edge of the vacuum glazing was sealed by an indium alloy with a width of 6 mm. The vacuum glazing glass panes were 4mm thick, each with a low emittance (low-e) coating with emittance of 0.18 on the internal surfaces. A 12mm high warm edge spacer separated the double vacuum glazing and third glass pane and was sealed with butyl rubber. The total thickness of the HVG was approximately 24 mm. The thermal performance of the HVG with dimensions of 0.4 m by 0.4 m was modelled using a finite element model (FEM). A HVG was fabricated and its thermal performance was measured using a guarded hot box calorimeter constructed in accordance with the requirement of ISO 8990 standard to validate the simulation results.

The simulation results showed that for the 0.4 m by 0.4 m HVG with configuration parameters shown above, the thermal transmission U-value was $0.70 \text{ Wm}^{-2}\text{K}^{-1}$. Before integration with the third glass sheet, the U-value of the double vacuum glazing with dimensions of 0.4 m by 0.4 m was $1.08 \text{ Wm}^{-2}\text{K}^{-1}$. No low-e coating was employed on the third glass sheet. For comparison, the centre-of-glazing area U-value of a conventional air filled double glazing with two uncoated glass panes is $2.7 \text{ Wm}^{-2}\text{K}^{-1}$. The U-value of the HVG calculated using the analytic model was in good agreement with the U-value predicted using the FEM. The experimentally determined U-value of the HVG was $0.74 \text{ Wm}^{-2}\text{K}^{-1}$. This was in very good agreement with the prediction with a deviation of 5.4%. Compared to conventional triple glazing, the HVG offers improved thermal performance with a reduction in glazing thickness. With the use of high performance coatings of emittance 0.04, the U-value can be reduced further.

Key words: hybrid vacuum glazing (HVG), thermal transmission U-value, finite element model (FEM), thermal performance, low emittance coating

New evidence of anti-herding of oil-price forecasters

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The dynamics of the price of oil were characterized by large “bubble-like” swings in 2008/2009. These swings may reflect herd behavior of traders. A natural question is whether such herding, to the extent that it occurred, was driven by herding in the projections of professional oil-price forecasters.

We used the oil-price forecasts of the *Survey of Professional Forecasters* published by the European Central Bank to analyze whether oil-price forecasters herd or anti-herd. Oil-price forecasts are consistent with herding (anti-herding) of forecasters if forecasts are biased towards (away from) the consensus forecast.

Based on a robust empirical test developed by Bernhardt et al. (2006) we studied whether professional oil-price forecasters did, in fact, herd. We found strong evidence of anti-herding among oil-price forecasters. Evidence of anti-herding indicates that professional oil-price forecasters deliberately placed their forecasts away from the cross-sectional consensus forecast.

Evidence of anti-herding of professional oil-price forecasters is consistent with evidence of anti-herding of stock analysts (Naujoks et al. 2009) and macroeconomic forecasters (Batchelor and Dua 1990). Evidence of anti-herding, thus, is mounting, implying that it becomes an urgent issue for future research to analyze the consequences of anti-herding of forecasters for bubble-like price swings in financial market in general and in oil markets in particular. Anti-herding may also explain the significant extent of cross-sectional heterogeneity of forecasts documented in recent literature (e.g., Menkhoff et al. 2009).

Anti-herding of forecasters may provide a behavioral explanation for the wide range of forecasts observed in virtually every forecasting cycle. While we have reported evidence of anti-herding of oil-price forecasters, we have not analyzed reasons for why forecasters anti-herd. Given that evidence of anti-herding of forecasters is mounting, it would be interesting to analyze in future research why forecasters anti-herd.

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Keywords oil price; forecasting; herding

Opportunities for rare earth metal recycling

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Rare Earth (RE) metals are critical to energy technologies like energy efficient light bulbs and wind turbines, because of their unique chemical, magnetic, electrical, and luminescence characteristics. REs consist of the fourteen lanthanide group metals, Scandium, and Yttrium. Nearly 200 minerals contain $>0.01\%$ RE metals but only a dozen have high enough quantities to be economically extractable. In the United States, the National Minerals Advisory Board, the National Academy of Science, the National Academy of Engineering, the National Research Council, the National Academy of Medicine and Department of Energy all conclude that REs are critical to our Nation's industrial interests. In October 2010 H.R. 6160 was approved by the House of Representatives and if passed by the Senate will establish a research and development program in the DOE to assure long-term supply of RE metals.

In addition to opening up new mines, recycling is also considered to be an option to reduce the dependence on foreign supplies of rare earth metals. Even though processes are available to extract RE metals from waste products, most of them are still at laboratory scale and very few examples exist where they have been applied in industrial size recycling settings. In this paper, we will also some of the economical challenges in recycling rare earth metals. We have quantified the amount of rare earth metals and their financial value for a number of products to be recycled at an urban level. Because they are used in small amount, a key challenge is the lack of information about the amount of rare earth metals in products. Nevertheless, preliminary findings show that specialized rare earth recycling lines may be technically feasible, but not necessarily economically profitable unless a broader systems perspective is taken.

Keywords rare earth metals; renewable energy technologies; recycling

Pipe friction reduction with guar gum solutions in rough pipes flow

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Turbulent flow of dilute polymer guar gum (latex) solutions in smooth and in rough pipes was studied. This experiment use in 25.4 mm of diameter pipe (PVC), which roughened by (k) 0.34, 0.8 and 1.59 mm roughness value of sand grain and 250, 500 and 1000 ppm for additive concentration. The result show that flow properties are influenced by polymer addition and surface roughness. In the transition and turbulent flow regime without additives, the increasing of friction coefficient appeared to be effected by wall condition alone. Addition of polymer to water is effective for rough pipe. For example with addition of 1000 ppm of polymer reduced drag in $k/D = 0.03$ rough pipe by 26 percent at Reynolds number 2×10^4 , whereas in 250 ppm addition tested drag was reduced only 7 percent.

Keywords turbulent flow; dilute polymer guar gum; roughness; friction coefficient; ppm; Reynolds number

Production of sintered lightweight aggregates using wastes of brewing industry

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1.- Introducción. The continued growth of waste requires not only measures to reduce their generation, but also recycling and reuse at all levels, as stated in the National Integrated Waste Plan 2007-2015. It is estimated that in Europe there are more than 850 million tons of industrial waste, which shows the enormous importance of appropriate alternatives for treatment and/or recovery [1]. In this regard, the ceramic industry or the cement manufacturing processes have made especially viable waste recovery [2], or by taking the calorific value from the combustion products, either incorporating the residue into the internal structure materials as part of its own parent company and becoming an inert element, or both as may be the case at hand [3]. Similarly to cement, lightweight aggregates fabrication offers interesting capabilities of high incorporation levels, as the final product do not have to show a fixed shape and size [4]. Besides the environmental benefits, this solution might represent an important income to the acceptor industry [5]. Some studies report attempts to reuse several wastes in expanded clay-based formulations, such as quarry minerals, industrial wastewater sludge, paper-pulp and wood or textile residues, etc [6]. This study describes preliminary attempts to design new lightweight aggregate formulations from brewing industrial wastes: wastewater sludge, bagasse and land of diatoms.

2.- Experimental. The actions carried out are: 1) Drying of raw materials: clay and wastes in an oven 24 h at 105 ° C. 2) Characterization of raw materials by techniques of X-ray fluorescence and thermal analysis. 3) Creation and consolidation of materials. 4) Sintering the materials developed in oven for 1 h at 900, 950 and 1000 ° C. 5) Study of the properties of products.

3.- Results and discussion. Wastes and clay were characterized in terms of chemical (XRF) and mineralogical (XRD) composition, and their thermal behaviour (TGA/DTA) was also evaluated. Different compositions were then prepared and tested. The results show than incorporation of three wastes in the body clay increased the loss ignition and the water absorption when increases the waste percentage added. This trend is maintained independently of the sintering temperature employed. It can check that there is no significant variation of these properties in the assayed sintering temperature range.

4.- Conclusions. Resource efficiency and industrial symbiosis are important drivers for innovation and economic development. There is increasing demand for lightweight aggregate for use in precast products for off-site manufacturing. Research has demonstrated the potential for manufacturing lightweight aggregate from brewing industry wastes. Development of appropriate vesicular microstructures to give the required properties of lightweight aggregate requires rapid firing and sintering processes. Lightweight aggregate production may offer further opportunities for organic wastes valorization.

Keywords: brewing industry waste; waste reuse; lightweight aggregate

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Public lighting control systems

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The human need for light at night by artificial light sources led to the development of public lighting. Public lighting is a system that consists of a large number of extensive circuits whose elements are connected in a network structure beginning with the distribution substation and ending with electric light sources and associated equipment.

In recent years great progress has been made in developing the modern public lighting, widening the possibilities of their control and maintenance methods with positive impact on energy efficiency.

A large number of public lighting control systems have been developed for controlling and reducing energy consumption. These range from controlling the circuits of public lighting and/or individual control with special lamps and ballasts with appropriate network operating protocols. This may include sending and receiving instructions via a separate data network, as a high frequency signal injected into the voltage waveform or wireless.

Public lighting costs can be a significant expense for city utilities, it is therefore important to take all the opportunities for efficiency improvements. New solutions are being developed for all applications, but, increasing traffic, residents demand for safety, many regulations and an ever tightening budget, creates a wide area for continuous research.

The paper will describe public lighting system with special emphasis on control, its impact on the distribution network and environment.

Study of biobutanol compatibility with polymer materials in gasoline engine systems

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Traditionally the two most widely used biofuels in the automotive sector are bioethanol and biodiesel, due its use in gasoline and diesel engines, respectively. Nevertheless, the chemical nature of bioethanol presents a number of limitations. A biofuel that could complement or even replace the bioethanol is the biobutanol. Biobutanol is proposed as one of the most promising second generation biofuels as it can be mixed with gasoline and it is fully compatible with existing vehicle technology and existing fuel distribution infrastructure.

The development of new fuels leads us to the need of developing compatibility tests with the current materials used in fuel systems for vehicles.

This work studies the compatibility of polymeric materials found in the fuel system after introducing them in gasoline, bioethanol and biobutanol mixtures, at a 30°C temperature for 2000 hours of exposure. For this, materials currently used in the manufacture of fuel systems have been selected and the analysis of samples at 0,1000 and 2000 hours have been proceeded, in order to study the effects of fuel in the properties of the materials.

There has been an assessment of thermoplastic materials and elastomers. The materials studied are as follows:

- PA66
- POM
- HDPE
- Gaskets of FKM
- Evaporator pump hose of NBR.
- Fuel tube of PA6/PA12.

The fuel mixtures to be used, according to different studies and stability analysis, were the following:

- Gasoline 100%
- BU30. Mixture of 30% of butanol with gasoline
- E10BU15. Mixture of 10% of ethanol, 15% of butanol and gasoline.

In order to study the performance of the materials, the specific properties analysed were:

- Dimensional variation
- Resistance to the Charpy Impact
- Tests of tensile strength and extension
- Determination of the hardness

The obtained results will be shown in the full paper

Study of the effect of oxidation time on ZnO nanowires formation

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In the present work we fabricate ZnO nanowires deposited on LiNbO₃ substrates by oxidation at 500°C during 24 and 54h respectively. SEM results show clearly formation of ZnO nanowires, XRD patterns show the presence of ZnO diffraction peaks. Electrical measurement using STM give us information about ZnO nanowires gap. Effect of oxidation time on ZnO nanowires properties was discussed.

Keywords: ZnO nanowires; oxidation; LiNbO₃ substrates

Sugarcane straw cellulose as reinforcement in composite materials

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Incorporation of lignocellulosic fibers to reinforce polymeric materials for the production of composites has been intensively investigated over the last two decades. Advantages of these fibers compared to synthetic fibers are related to their lower cost, low abrasion in processing equipment, low density and they are obtained from renewable sources. Polyurethane resins (PU) are attractive due to their structural versatility, as well as the fact that they can be derived from either petroleum or vegetable oils. They still present the particularity to be more compatible to lignocellulosic fibers in relation to other resins, due to possible reaction of hydroxyl groups of the fibers and the isocyanate groups of the polyurethane. This work is concerned with the study of the utilization of sugarcane straw cellulose as reinforcement in castor oil polyurethane composites. For the obtainment of cellulose, sugarcane straw was pretreated by steam explosion, followed by a delignification with NaOH. For the production of the PU, the polyol (castor oil) to diisocyanate mass ratio was 1.5:1.0 (w/w). Reinforcement of the matrix was done changing the concentration of cellulose fibers (5,10,15,20% w/w). The efficiency on the obtainment of cellulose fibers was verified by chemical characterization and the fibers morphological aspects by SEM. Likewise, the influence of fibers content in the composites was studied by thermal (TGA and DSC), moisture absorption and mechanical (flexural tests) analyses. The results obtained by thermogravimetry showed that the process of decomposition of the matrix occurs in one step, while for the composites it occurs in two steps. The thermal decomposition of the matrix starts above 300°C. The addition of reinforcement almost did not change the thermal stability of the composite. The DSC curve of pure PU shows two glass transition temperatures (T_g), one near 40°C, and one higher around 163.7°C. Comparing the DSC curves of the composites reinforced with cellulose fibers with the pure PU, it was observed that probably the process of cure was not complete because the presence of cellulose did not permit the movement of the molecules. The addition of cellulose fibers to the matrix improved the flexural modulus, making it clear that the inclusion of cellulose fibers influence mechanical properties. The fracture region showed a poor dispersion of fibers in the matrix, fibers fractured along the polymer and a good fiber-matrix adhesion. Moreover, there was no presence of pull out. In the study of moisture absorption, it was observed a high level of water absorption by increasing the amount of fiber, mainly due to the hydrophilic character of cellulose. For the pure matrix it was also observed a high level of water absorption, probably linked to the fact of the cure reaction of the matrix was not complete, as verified by DSC analysis. Acknowledgements due to FAPESP, CAPES and CNPq (Brazilian agencies).

Keywords Composites; Sugarcane straw; Natural Fibers; Cellulose; Castor oil Polyurethane

Sustainable Assessment Method in Limestone Mining Management

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Sustainable assessment method in limestone mining management deals with elaboration of sustainable mining assessment in conditions of Estonian limestone mining's. It is known, that the mining processes impacts on the environment, economy and people social life, although there may be positive and negative impacts to the different scope activities.

The aim of this new study is to elaborate sustainability assessment methodology which will be suitable and comparable for limestone mining's in Estonia. An exergia analyze were developed and applied to measure the mining influence. This analyze allows also to define hazardous influence, for aspects comparison and gradation were used British Standard scale and data evaluations for 1 worker by 5 point scale, not including the zero point value.

The urgency of the research consists in management efficiency in the current market conditions in the mining. The work is to develop the scientific output of the optimal activity analyze, which can be also used in other EU countries to provide an optimal assessment of the capacities of different groups based on the company needs. As the fact this analyze is easy comparative and has an analogy with the workplace safety risks estimation. It is conveniently and quick analyze, which helps to find optimum decisions for existing problems in different mining scope activities.

Keywords sustainability analyze; socio-cultural aspects; work safety; risk analyze; environmental parameters; safety manuals;

Towards an environmentally responsible architecture: Architectural design proposals for public buildings in Cyprus

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Public buildings in general can help inform and educate the public on environmental issues and energy efficiency. At the same time, public buildings constitute city landmarks, and, especially if they are selected by a competition jury, their design and construction tend to follow, to some extent, contemporary architectural trends.

In the last years, the continuously growing concern for climate change and environmental degradation has inevitably lead to the introduction of bioclimatic and environmentally-friendly design principles to the already complex and demanding architectural design of public buildings.

This study presents the design process of three different public buildings, which participated and received prizes in architectural competitions in Cyprus. These are a town-hall building in Deryneia, an environmental information centre in Larnaca and a public school in Nicosia.

The first step of the process included bibliographic research for the general data of each study area (geographic location, climate, topography, ground composition, historical data), which, due to the restricted size of the paper, are briefly presented.

Throughout the process and until the finalisation of the design proposals, the bioclimatic behaviour was analysed both qualitatively and quantitatively with the use of software. The analysis of the bioclimatic behaviour of the proposed buildings concerns the prevailing thermal and visual comfort conditions throughout the year, is based on computer-aided analysis with the use of software, and is analysed separately for every proposed building in the present study.

Finally, conclusions are drawn in order to outline the design principles, which can be integrated into the design of public buildings in order to ensure both their architectural quality and their improved environmental performance in terms of comfort and energy conservation.

Keywords public buildings; architectural design competition; building envelope; bioclimatic principles; indoor comfort

Utilization of Sugarcane Straw to obtain products with higher added value: Bioethanol and Carboxymethylcellulose

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The use of agroindustrial residues from lignocellulosic sources to obtain chemicals products is an alternative to contribute for the valuation of these subproducts. In this context, ethanol produced by lignocellulosic materials is an interesting option to increase the production of this fuel without increasing the agriculture area for production of biofuels, since the ethanol demand has raised in the last years, with the objective of substitute the oil and his derivates, contributing for reducing the negative impacts for environment. In addition, other products may be obtained from these agroindustrial residues, as pulps and cellulose derivatives. Aiming the utilization of sugar cane straw as raw material for the production of bioethanol and carboxymethylcellulose, the goal of this work was to evaluate the best conditions for two types of pretreatments, hydrothermal and ultrasound, to produce bioethanol and evaluate the best method to obtain carboxymethylcellulose (CMC).

Aiming bioethanol production: For hydrothermal pretreatment, it was studied two temperatures, 160 and 180 ° C, and the times of 10, 20, 30, 40 and 50 min, under a solid:liquid ratio of 1: 10 (w / v). For ultrasound, the tests were carried out in a medium with 1% NaOH (w / v) or 1% H₂SO₄ (w/v), in the times of 1, 5, 10, 15, 20, 25 and 30 min, 25 ° C. The frequency of the equipment kept constant (40 kHz) and the ratio solid:liquid was 1:10 (w/v). Yields were determined for both reaction processes of pretreatment. Subsequently, the chemical characterization of samples submitted to hydrothermal and ultrasound treatment to quantify the levels of cellulose, hemicellulose and lignin was performed.

Aiming CMC: Sugarcane straw was chemically cooked by soda/anthraquinone process under the following conditions: NaOH 4.0 % (w/v), AQ 0.15% (w/v), 100 ° C for 60 min. After the stage of chemical cooking by soda/anthraquinone, the pulp was subjected to chemical bleaching with hydrogen peroxide in different concentrations (3, 6 and 9 %(v/v)) and was analyzed for kappa number and viscosity. The bleached pulps have gone through two distinct processes of carboxymethylation and were characterized by mass gain, degree of substitution and affinity for water.

Preliminary results: For hydrothermal treatment, the best yields were 82% and 78.92% for periods of 10 and 20 min, respectively, at a temperature of 160°C. In the case of pretreatment with ultrasound, both in alkaline and in acid medium, the yields achieved were similar, around 85%. Subsequently, chemical characterization of samples submitted to hydrothermal treatment to quantify the levels of cellulose, hemicellulose and lignin was performed. There was a greater preservation of cellulose at 160°C for 20 min. The same procedure was performed to characterize the samples treated by ultrasound and these analyses are underway.

For carboxymethylcellulose, the pulp bleached with H₂O₂ 6% (v/v) furnished the best results and the characterization of obtained carboxymethylcellulose is underway.

[Acknowledgements due to FAPESP, CNPq, and CAPES - Brazilian agencies]

Keywords cellulose; bioethanol; carboxymethylcellulose; sugarcane straw; biorefinary.

Other topics

An Analysis of Energy as a Precondition for the Improvement of Living Conditions and Poverty Reduction in Sub-Saharan Africa

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This paper examines the link between availability of energy and improvement of living condition and poverty reduction in Sub-Saharan Africa. It argues that modern sources of energy are required for the improvement of living standards may be helping to create jobs and boosting productivity. For energy exporters, particularly oil producers, they provide revenues that may bring about sustainable poverty reduction. And the supply of energy improve living conditions by providing better lighting of homes, cleaner fuels for cooking and heating.

The study found that, essential aspects of human welfare (leading long and productive life, enjoy good health, have access to knowledge and education opportunities, have the potential to earn sufficient income to supply themselves with ample nutrition, shelter, and other material and aesthetic needs) may improve only if modern energy becomes available for all; yet there are nearly two billion people still without electricity in developing countries. The study also found that, energy can have major favorable effects in remote rural areas and renewable energy technologies offer a key prospect in areas where the grid cannot reach. Reliance of the poor on their natural surroundings indicates that any step towards poverty alleviation should incorporate environmental and economic sustainability as a priority for sustainable livelihoods.

This paper is a contribution in a process towards the use of energy to be one of the instruments to reduce poverty in developing countries especially in Africa.

Keywords: Energy, Poverty reduction, Human development, Standard of living.

Electrochemical characterisation of Ti6Al4V alloy in simulated body fluid

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The aim of this work is the study of the influence of an alkaline medium, simulated to the human body, on the behavior of titanium alloy Ti6Al4V. Titanium and its alloys are widely used in aerospace and marine applications due to their interesting properties, mainly their excellent corrosion resistance associated with a low density and good mechanical characteristics as well as high melting points. Moreover, their good biocompatibility, make titanium alloys materials of choice in orthopaedic and implantology. As well in seawater as in the human body, its excellent behaviour with corrosion is due to the spontaneous formation of stable passive film on the surface and provides a barrier between the aggressive medium and substrate

In our experiments, two electrochemical techniques are used, cyclic polarisation and impedance measurements. The obtained Polarization curves show a large field of passivation, coming from the formation of a protective oxide film, generally of TiO₂. In addition, the negative hysteresis which appears during a cyclic polarization with ennoblement of the corrosion potential may be explained by a reduction of the corrosion products. We found that decreasing scanning rates weaken the passivation current with no significant effect on the potential and the current of corrosion. Impedance measurements were in a good agreement with cyclic polarization. Nyquist and Bode diagrams show that Ti6Al4V reacts according to a pseudo capacitive behaviour in the passive field, related to the formation and growth of oxide film.

Keywords :Titanium Alloy Ti6Al4V,SBF,passivation

High performance AlGaIn MSM ultraviolet Photodetectors

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We present Al_{0.25}Ga_{0.75}In ultraviolet Schottky barrier photodetectors on Al₂O₃, it was modeled using The two-dimensional device simulator Silvaco and ATLAS. It was found that the device has very low dark current about 16pA at 1 V bias and the peak responsivity of 0.07A/W was achieved at 308nm. We have performed a comparison between our modeling and the experimental results.

Nitride-based materials are the most suitable candidates for the fabrication of semiconductor photodetectors PDs in the UV spectral. The bandgap energy of Al_xGa_{1-x}In can be adjusted by changing Al content to match up requisite detector cut off wavelength. Various types of AlGaIn based detectors and photoconductors. The wide direct bandgap provides an intrinsic visible blindness, which is a critical advantage for a number of applications and can operate under severe conditions (high temperature and energy levels). Among these structures, MSM photodetectors has a special place. It is a planar photodiode based on simple technology, it is easy to integrate, it has fast response, small capacitance and dark current, as well as large active device area. It consists of two Schottky electrodes, often interlinked in the form of a comb structure, leaving a free semiconductor surface between the two contacts which forms the active region in which light will be absorbed.

One of the key issues in nitride semiconductor epitaxy in general has been, and remains, the substrate choice. Aluminum nitride (AlN), gallium nitride (GaN) and sapphire (Al₂O₃) are potential candidates which are all under investigation.

The active detector was a 3 μm thick unintentionally doped AlGaIn layer which was grown on top of a 10nm thick AlN buffer layer and the AlN buffer layer was on a 1 μm thick GaN. The electrode fingers are 5 μm wide, 500 μm long, and with a 5 μm spacing. A 200nm thick Au was deposited.

In comparison with an exclusive experimental procedure for this optimization the TCAD methodology exhibits the advantages of reduced development costs and development time. ATLAS is a physically-based two and three dimensional device simulator. It predicts the electrical behavior of specified semiconductor structures and provides insight into the internal physical mechanisms associated with device operation. ATLAS was used also to extract the optical characteristics such external quantum efficiency, responsivity, and frequency response characteristics when the photodetector is illuminated.

Index Terms— AlGaIn, Schottky, UV, Photodetector.

Performance comparison of CCHP systems using different fuzzy multi criteria decision making models for energy sources

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The environmental, technical, economical and social performances of combined cooling, heating and power (CCHP) system are evidently dependent on its design work and process strategy. This article investigates the energy sources of CCHP system and uses the fuzzy multicriteria decision making models such as fuzzy AHP and fuzzy TOPSIS. Here, four criteria and seventeen sub-criteria are evaluated for different energy sources. The results indicate that gas-steam combined cycle CCHP system is the optimum alternative among the five options.

Keywords: CCHP system, energy sources, fuzzy multicriteria decision making.

Synthesis and characterization of Lithium Zirconate based adsorbents for CO₂ capture

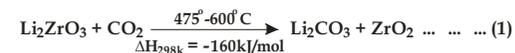
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Long before lithium based ceramics were considered for CO₂ adsorbent, it was known to material scientists and nuclear industries as a candidate for breeder materials due to its high tritium release rate, thermal stability, low thermal expansion coefficient and good compatibilities with structural materials such as beryllium. Although reaction between ZrO₂ and Li₂CO₃ is well known and used for synthesizing Li₂ZrO₃ (Equation (2)), the reverse reaction Equation (1) was not considered for CO₂ capture until 1998. Nakagawa et al from Toshiba Research and Development Centre in 1998 had shown that Li₂ZrO₃ is a potential candidate for CO₂ capture.

Lithium zirconate capture CO₂ through chemical reaction at high temperature as follows:



Regeneration takes place by the following reaction at $\geq 700^\circ\text{C}$:



Lithium zirconate does CO₂ capture in temperature swing adsorption (TSA) mode. Successful exploitation of these classes of sorbents industrially, should have the following characteristics: high CO₂ adsorption capacity, high selectivity, good adsorption/desorption kinetics and stable multicycle performance.

In the present study a series of lithium based sorbents were synthesized, starting from pure Li₂ZrO₃, 'Li' substituted by 'Ba', Zr substituted by Ce compounds. These compounds have synthesized from different types of starting precursors to vary the sorbents particle morphology. Particle morphology plays an important role on absorption/desorption kinetics and its operational cyclability. The morphologic and structural characteristics of the adsorbents are characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Isothermal absorption capacity and kinetics studied in the temperature range between 500° and 650°C have been conducted using thermogravimetric analyzer. Some of these samples show excellent absorption capacity and kinetics. Adsorption studies show the maximum weight gained by the sample Li₂ZrO₃+LiYO₂ is about 20 weight% whereas commercial pure Li₂ZrO₃ has a maximum weight gain of about 3 weight%. Multicycle adsorption-desorption revealed that the adsorbents exhibited good cyclic stability when regeneration is conducted at about 720°C.

Keywords Lithium Zirconate; CO₂ Capture; Solid Sorbents; Temperature Swing Adsorption

The best energy policy selection using VIKOR methodology

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The main purpose of this paper is to present a fuzzy multi-criteria decision making (FMCDM) model for energy policy selection in Turkey. As we search to achieve sustainable development and substance, energy security and efficiency should be viewed not only through the perspective of addressing short-term challenges, but also a necessity for long-term growth of the economy. In this paper, VIKOR approach is suggested for the selection among energy policies in Turkey. Finally, an empirical study for identifying the energy policy selection is conducted to demonstrate the computational process and effectiveness of FMCDM proposed by this paper.

Keywords: energy policy, VIKOR, FMCDM

Clean-up of Biogas from H₂S by selective oxidation on the V-Ce catalysts

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Biogas produced by waste biomass has become one of the most important alternative energy sources since it is derived from non-fossil sources [1].

It can be used in non conventional systems for energy production as the Molten Carbonate Fuel Cells.

Because the molten carbonate fuel cells have a poor tolerance to these compounds, it's necessary to reduce the H₂S concentrations at values about 1-5 ppm [2].

The removal of H₂S from biogas is a great concern in environmental technology; a large number of processes based on physical-chemical treatment (adsorption, absorption in aqueous solutions, physical solvent, membrane separation, biological desulfurization) have been used to treat gas stream containing low concentrations of sulphur containing-gases, but they are characterized by high costs and a limited overall efficiency [3][4].

Direct selective oxidation of H₂S to sulphur at low temperature appears to be the greatest promise for the removal from biogas to feed to MCFC. The optimization of the process of the catalytic oxidation is fundamental to achieve almost total H₂S conversion, so it isn't need to introduce after catalytic stage, a further stage of purification.

In a preliminary study it was performed a screening of catalysts for H₂S abatement to order to find active and selective catalysts for the partial catalytic oxidation. Vanadium-based catalysts supported on CeO₂, CuFe₂O₄ and TiO₂ were investigated in the range of temperature of 50-250°C in terms of H₂S, O₂ conversions and SO₂ selectivity. The better results were obtained on the V₂O₅/CeO₂ that has showed a high catalytic activity and a low SO₂ selectivity; for this reason further experimental tests were performed on this sample by varying some operative conditions (H₂S feed concentration, hourly space velocity, feed molar ratio).

Any significant variations of the H₂S, O₂ conversions and SO₂ selectivity were obtained by changing the H₂S concentration (250-1000 ppm) and the gas hourly space velocity (15,000-45,000 h⁻¹).

An interesting result in terms of SO₂ selectivity was obtained for the O₂/H₂S value of 0.4, for which the SO₂ selectivity was drastically reduced from 13% to 4% without any significant reduction of the H₂S and O₂ conversions.

Starting by this very good result, the work will be focused on the effect of Vanadium load, by studying samples in the range of 2,5-10%wt of V₂O₅, in order to determine the optimal catalyst formulation and operative conditions to obtain a very high H₂S conversion and the SO₂ selectivity minimization.

After found the optimal sample, additional tests will be performed to individuate the main kinetic parameters, and try to obtain preliminary indications concerning the main steps of reaction mechanism, and the basic kinetics parameters in order to determine the reaction rate expression.

Catalytic activity tests suggested the presence of a chemisorption step for both reactants. In this regard, Langmuir-Hinshelwood model has been proposed, where both molecules adsorb and the adsorbed molecules undergo a bimolecular reaction on the catalyst surface between the reduced vanadium in the form of sulphide with the adsorbed oxygen to give the sulfur and regenerate the vanadium oxide.

Keywords Clean-up Biogas; H₂S catalytic oxidation

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Design, Modeling, Fabrication, and Characterization of Defect-Free InGaN Nanowire Arrays/Metal and Metal Nanoparticles

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Generation of hydrogen in one step process and directly on site would be an important breakthrough to solve the urgent energy issue in military operations. The effective utilization of virtually unlimited solar energy for photochemical splitting of water and hydrogen production will offer a practical approach for this challenging problem. For a long time, however, its practical application has been limited by the low efficiency of direct solar-to-hydrogen conversion, due to the lack of appropriate photocatalytic materials that can effectively absorb the solar spectrum. The direct conversion of light to fuel requires the creation of novel materials that could be made at a low-cost, while demonstrating efficiency and durability. We have developed innovative nanotechnologies that can fundamentally address the efficiency bottleneck. We are developing metal-nitride nanowire arrays that can absorb nearly the entire solar spectrum and can drive ultrahigh-efficiency (>10%) solar-to-hydrogen conversion. More importantly, major obstacles have been solved, including the device scalability and yield, for the practical application of this novel solar-fuel technology. This innovative technology will offer Canadian Forces a costless viable renewable alternative energy source for battlefield operations. The work well also demonstrated that Atomic Layer Deposition technique (ALD) is a precise route to synthesize 1D nanostructures of TiO₂. The resultant nanostructured TiO₂ can be potential candidates in many applications, such as water splitting, solar cells, lithium-ion batteries, and gas sensors. In parallel, density functional theory (DFT) calculations have been carried out for polar surfaces of the InGaN material with and without adsorption of water molecules on the surfaces. The DFT calculations allowed to determine the atomic and electronic structures of these surfaces as well as surfaces with water. Nudged elastic band method was applied to determine the hydrogen evolution reaction pathways, energetic barriers, and transition states.

Methane auto-thermal reforming in a compact thermal integrated ATR reformer: monolith and foams structured catalyst performances

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Up to now, hydrogen and fuel cells combination is the most viable answer to the antithetic problems of energy growing demand and environmental pollution reduction. The well note difficulties in hydrogen transport and storage increase the industrial interest toward the distributed H₂ production, that so results as the most promising solution. In order to follow this pathway, very compact and small size production plants are required. To this goal, hydrocarbons auto-thermal reforming reaction assures a self-sustaining process and high reactor compactness, resulting as the best method for distributed H₂ production to couple to a fuel cell system. In spite of the increasing interest in renewable sources, due to the low costs, the widespread existing delivery pipelines, fossil fuels still remain the best choice in a transition period towards hydrogen based economy.

In this work the auto-thermal reforming of methane (as natural gas surrogate) was analysed. Structured catalysts (commercial monolith and foams) performances in methane processing were studied: the different catalyst geometry covers a fundamental role in the process performances. The activity tests were conducted in a compact catalytic reactor: in reactor design, great attention has been paid to the thermal integration in order to obtain a total self-sustainability of the process, without additional external heat sources, and so improving plant compactness. Through a heat exchange system, integrated in the reactor, water and air stream are preheated by exploiting the heat from exhaust stream, so allowing to feed reactants at room temperature as well as cooling product stream at a temperature suitable for further purification stages (WGS, PROX). In order to achieve a very comprehensive process analysis, temperatures and composition are monitored in 6 point along the catalytic bed. The influence of catalytic system geometry as well as thermal conductivity in the process performances was also analysed.

Preliminary tests showed high thermal system efficiency, with a good hydrocarbon conversion at different operating conditions. The low start-up times makes the system extremely versatile, and suitable for batch operations. In one hand the monolith catalyst allows a flatter temperature along the catalytic bed, so reducing hot spot phenomena and improving reaction performances in the thermodynamic point of view. On the other hand, the continuous reaction stream mixing realized by the foams catalysts (as well as by a special configuration of monolith catalyst) assure a products composition very close to the thermodynamic equilibrium, and allows higher gas space velocity.

Keywords ATR reforming; fuel processor; hydrogen production; structured catalysts

A method for wood fuel/charcoal of the alien invasive species mesquite (*Prosopis juliflora*) to support local incomes with better energy efficiency in arid land of Sudan

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In the 1980s, mesquite (*Prosopis juliflora*) was considered an ideal anti-desertification tree due to its high capacity to stabilize sand dunes, survive inhospitable environments, and provide fuel, timber, fodder, and edible pods. However, once planted, the mesquite seedlings failed to take root on sand dunes, but rather, became well established in oases, where they contributed to the lowering of the water table and suppression of native vegetation. The invasion of mesquite not only changed the regional ecosystem, but has also caused livelihood degradation of local communities (Babiker 2006, Nawata in press).

The authors seek to learn from “mistakes” made unintentionally by scientists, administrators and NGO workers and go beyond criticism in order to continue doing the high quality scientific research. An improvement of the negative legacies left from ineffective anti-desertification measures and the development of comprehensive procedures to control the alien invasive species mesquite is necessary. Scientists from universities, research institutions, NGO members, consulting firms, developmental organizations and local people must work together, pooling together the best knowledge available to build an effective mesquite management plan (Nawata 2010).

The Japanese-Sudanese interdisciplinary research teams are developing comprehensive measures to control this invasive species. Hydrologists, plant physiologists, weed scientists, remote-sensing specialists, range managers, agricultural economists, nutrient physiologists, and cultural anthropologists are working together doing the field surveys on riverbanks, *wadi* beds, seashores and mountainsides in arid to semi-arid areas of Sudan (Hoshino et al. 2011, Nawata in press, Yoda in press).

Scientific research results from the Research Institute for Humanity and Nature (RIHN) project (“A Study of Human Subsistence Ecosystems in Arab Societies: To Combat Livelihood Degradation for the Post-oil Era” led by Hiroshi Nawata)’s weed control team now is being applied to the Japan International Cooperation Agency (JICA) development project “Capacity Development Project for the Provision of Services of Basic Human Needs in Kassala” (2011-2013) in cooperation with Sudan University of Science and Technology.

A new method for making wood fuel and charcoal would be applied to villages to support local incomes with better energy efficiency. We organized a training course for extensionists of Technical Transfer and Extension Administration, State Ministry of Agriculture, Forestry and Irrigation, Kassala State in December, 2011.

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Keywords wood fuel, charcoal, alien invasive species, mesquite, Sudan, rural development

Estimation of Performance of the H Wind Turbine Using the Multiple Double Disk Stream Tube Theory

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The performance of the H vertical axis turbine is comparable with that of the more common horizontal axis machines. It has a number of aerodynamic and structural advantages over HAWT'S. However the H straight blade turbine are not self- starting at low wind speeds which is a considerable disadvantage for a simple small scale installation. Generally, papers concerning vertical axis turbine do not study the behavior of the rotor at low tip speed ratios. Therefore they do not deal with the self starting problem.

A number of analytical methods were investigated to see whether they could predict the starting performance of vertical axis turbines. The Chosen methods used “actuator disc theory” for multiple Stream tubes. In this paper the multiple stream tube model is applied using two discs in tandem. The computational analysis of all models simulates the blade aerodynamics throughout the full range of incidence from -180° to 180°. The effects of varying various geometric parameters of the windmill upon the performance of the rotor are investigated to find a design with improved self starting characteristics. . The results include the variation of angle of attack “ α ” and the variation of the torque coefficient as a function of both tip speed ratio “ λ ” and azimuth angle “ β ”. The theoretical results also demonstrate the effect of varying various geometric parameters (solidity) on both torque and power of the rotor for low and high tip speed ratios. Finally The results include the variation of the local torque coefficient as a function of azimuth angle.

Key words: (H rotor, Wind turbine, Windmill, blades, Vertical axis turbine)

Fabrication and test of Co-Sb thin film heat flux gauges

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Transient heat flux is difficult to be measured in thermal measurement field. Developing transient heat flux measurement, especially measurement in miniature space has a great significance in energy and power fields. In this paper, the vacuum evaporation technique was applied to produce thin film heat flux sensors. Calibrations and performance test have been conducted to study the reproducibility, sensitivity and dynamic response of self-made heat flux gauges.

In order to measure heat flux inside narrow space, such as the miniature fuel cells, silicon dioxide (SiO₂) was selected as insulating substrate, the overall dimension of which was 8 mm long, 8 mm wide, and 0.1 mm thick. Two different metals cobalt and stibium were chosen as thermode materials. Thin film heat flux gauges were designed and fabricated using Co-Sb thermopiles consisting of 11 Co-Sb junctions deposited on both sides of the 0.15 μm thick thermal resistance layer. Thin film heat flux gauges designed in micro scale are fabricated on the surface of SiO₂ substrate. Film electrodes of cobalt and stibium, with thickness of 0.08 μm, were manufactured by vacuum coating system, respectively. Thin film sensor were patterned with stainless steel masks of thickness of 0.01 mm during the plating cobalt and stibium films. The overall dimension of transient thin film heat flux gauge was 6mm long, 6mm wide (Figure 1), and 0.47 - 0.48 μm thick.

The experiment results showed that the thin film sensors had advantages in response time, application range and small dimensions, which could satisfy the requirement of transient heat flux measurement inside the tiny space. The sensitivity of self-made thin film heat flux gauge was $2.20575 \times 10^{-8} (\text{m}^2 \cdot \text{V})/\text{W}$. Thin film heat flux gauges had the immediate response to variation of heat flux loaded and good reproducibility. In addition, we measured heat flux evolution near a match using the thin film heat flux gauge. We recorded data from the moment of lighting up to flame extinction, find a very transient process of heat-flow density zooming-up, decrease, rising again in 175 milliseconds (Figure 2). Cause of the heat flux trough formation was discussed. The response time of thin film heat flux gauge in this case was 10.5565ms approximately.

Keywords transient heat flux measurement; thin film sensor; dynamic response; cobalt; stibium



Figure 1 Thin film heat flux gauge

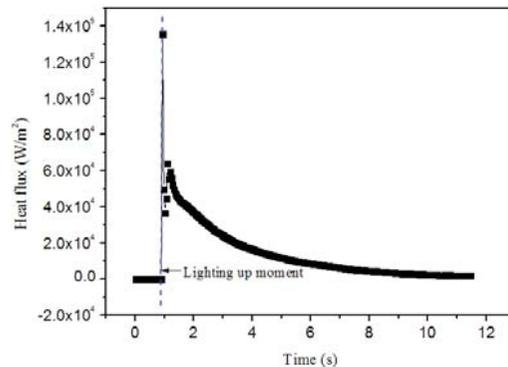


Figure 2 Transient heat flux of a match lighting up

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Inverters for grid connected photovoltaic systems

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The market for photovoltaic systems has, since now more than 10 years, a very high increase rate around 30 to 40% per year. This exceptional increase, is mainly due to photovoltaic system (PV) connected to the electricity distribution, and result of course by technological innovation and lower costs of PV modules but also significant efforts in research and development in the field of electronics power.

In PV systems connected to the grid, the inverter which converts the output direct current (DC) of the solar modules to the alternate current (AC) is receiving increased interest in order to generate power to utility.

In fact, the technical performance and reliability of inverters used for connection of photovoltaic systems to the electricity distribution are parameters that can greatly vary the annual electricity power and thus the financial viability of a system.

The purpose of the present work is to give an overview of topologies and power configuration for photovoltaic systems connected to the grid. Some control structures for single phase and three phase inverters are presented and some solutions to control the power injected into the grid are offered. The functional structure of each configuration of the system connected to the grid is investigated.

Lithium-ion capacitors: study of a new co-solvent (MiPC) with LiTFSI salts in electrolyte ternary mixtures

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Li-ion capacitors are based on electrochemical intercalation of lithium ions in an active materials such as graphite (negative electrode), and on an electrochemical double layer interface on the positive side of the device. Usually, the positive electrode consists of an activated carbon with high surface area. Such device, require also the use of an organic electrolyte containing a lithium salt [1], and its performances (i.e faradic efficiency and cycleability), are closely related to the composition of the electrolyte at the negative electrode which conditions the cycling ability at high charge-discharge rates.

Electrochemical storage systems such as batteries generally use electrolytes based on mixtures of alkylcarbonates and LiPF_6 as salt. These electrolytes exhibit a high conductivity and are able to provide both the formation of a "stable" solid electrolyte interface (SEI) layer onto graphite and to passivate aluminium collector at the positive electrode [2]. Nevertheless, some drawbacks still remains, such as their low stability at high temperatures (more than 55°C - 60°C) and their degradation (in the presence of residual water) with the generation of hydrogen fluoride [3,4].

As an alternative to LiPF_6 , we suggest to use bis-(trifluoromethylsulfonyl)-imide lithium (LiTFSI) as this lithium salt presents both better thermal and chemical stabilities. Hence, this work will be focused on the comparison of the physicochemical properties of LiPF_6 and LiTFSI in a mixture containing alkylcarbonates (1:1 EC/DMC mixture by volume) and a new co-solvent methyl-isopropyl carbonate (MiPC), in order to increase the performances at low temperature.

The thermal behavior of these electrolytes has been studied by mean of scanning differential calorimeter (DSC). In order to evaluate the specific capacitance and cyclability of such electrodes in the MiPC and LiTFSI based electrolytes, an electrochemical study has been realized. The influence of the separator in a practical cell has also been taken into account by determining, at different temperatures, the conductivities of the bulk electrolyte and the membrane soaked in the electrolyte.

The composition of the EC-DMC-MiPC in LiTFSI electrolytes was optimized in terms of conductivity and viscosity. Then, the optimized mixtures were used as electrolyte in graphite/activated carbon hybrid lithium-ion capacitors device. The cycling ability of the graphite electrode/activated carbone has been evaluated and the performances (energy and power) were compared to those obtained with a conventional symmetric supercapacitor.

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Optical and structural properties of $\text{SiO}_2/\text{SiN}_x$ graded refractive index layers.

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This work is a contribution towards the understanding of the optical and structural properties of graded refractive index layers $\text{SiO}_2/\text{SiN}_x$ to lead to antireflective coating and efficient passivation of multicrystalline silicon wafer. We investigate the influence of the thermal annealing on optical properties and chemical bonding of DLARC $\text{SiO}_2/\text{SiN}_x$ dielectric stack structure. Transparent hydrogenated amorphous silicon nitride ($\text{SiN}_x\text{:H}$) coating is prepared by plasma enhanced chemical vapor deposition (PECVD) using a gas mixture of NH_3/SiH_4 on multicrystalline silicon wafer substrates. We have deposited silicon oxide (SiO_2) thin films on the top of SiN_x by using dip-coating and thermal oxidation methods in the aim of creating graded-index refractive coating. The effects of annealing temperatures (500 to 1000°C) under nitrogen atmosphere are investigated. Based on Fourier Transform Infra-Red analysis (FTIR) (Fig.1), it was observed that after annealing temperature, IR absorption of Si-N bonding decreased, while the integral intensity of Si-O bonding increased. This is due to a partial conversion of the phases Si-N and Si-O to Si-O-N phase. On the other hand, the change on the weighted reflectance in the range of 400 - 1100 nm (Uv-Vis-IR) is observed. We have found a decrease of minimum reflectivity $R=0.77\%$ ($\lambda=690\text{nm}$) and weighted reflectance $R_w=7.71\%$ (Fig.2). Thus, the N_2 annealing method might have the tremendous potential for antireflective coating and surface passivation of solar cells applications.

Keywords: PECVD, $\text{SiO}_2/\text{SiN}_x$ DLARC, optical and structural properties, annealing temperature.

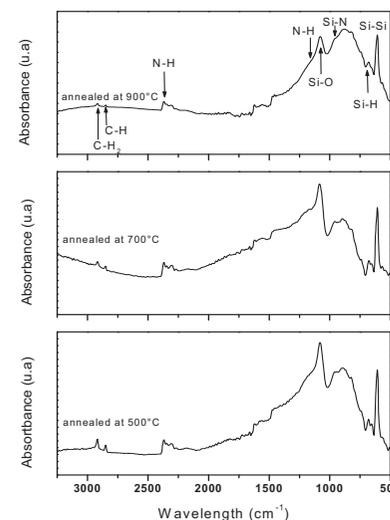


Figure 1: Absorbance spectrum for various annealing temperature.

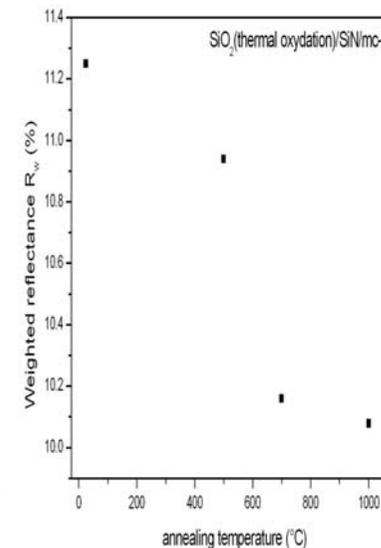


Figure 2: weighted reflectance (R_w) vs. annealing temperature.

Phosphorous Emitter redistribution study under Laser doping

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In this paper, we examine the influence of laser treatment to activate or drive in dopants atoms through PSG in the aim to decrease emitter sheet resistance from 60 Ω /sq to 20-30 Ω /sq.

Two parameters, speed and power, have been used by the YLiA M20 laser to treat areas of 1cm². The patterning is made by a laser pulse with a spot of 10 microns scanning the surface at different speeds (2 to 20 mm/sec) and power (0.5 and 20 Watt). We used surface emitters as diffused with phosphosilicate glass (PSG). We analyzed three parameters of the emitter: sheet resistance, profile concentration and surface morphology. The Sheet resistance (Rs_q) summarized on figure1 shows a decrease from 60 to 18 (Ω /sq). The figure1 indicates the higher the power the lower the Rs_q and also the lower the laser speed the lower the Rs_q. The emitter treated by laser presents a low dispersion of the Rs_q which has a mean value of 19.37 Ω /sq and uniformity of 3.54%. The measurement is made on twelve aligned points and spaced with a step of 0.8mm. This means that the surface is uniformly doped even so the laser spot does not treat the whole surface. The Emitter Profile measured by ECV (figure 2) shows a very strong enhancement of junction depth from 0.303 μ m to 2.0 μ m. The higher the laser power the higher the X_j. In contrast, the surface concentration is spread between 10¹⁹ to 6.6x10²⁰ cm⁻³. This indicates that the phosphorous has been redistributed from PSG layer into the emitter and also probably electrically activated from the dead layer. The shape of the profile also changes near the surface and in the tail. About the surface morphology, a pattern can be observed on the laser doped surface. This pattern is more pronounced when the power is high and/or the speed is low. Figure 3 show the morphology after treatment for P=7W and speed 2, 5 and 15mm/sec. A 30 μ m large channels parallel to the laser scan are created on the surface. A cross section (figure 3.c) show that the channels are not in depth. A reflection measurement shows that the surface is not significantly perturbed by the laser treatment and presents the same value for different power.

This study has shown that the laser treatment can redistribute the inactive phosphorous present in the PSG layer. With the latter we obtain a more uniform emitter sheet resistance. With this we can proceed to realize selective emitters for solar cell application.

Keywords : laser treatment, emitter profile, drive in, selective emitter

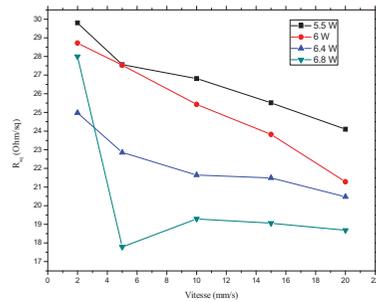


Fig 1 : Rs_q evolution with laser for different power

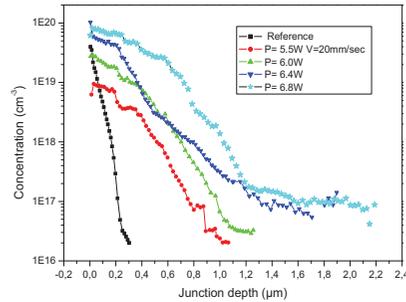


Fig 2 : ECV profiles of as diffused (reference) and after laser treatment at P=5W and v=5mm/sec

Thermochemical conversion of fuels to synthesis gas by using ICE recuperative heat

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One of the promising methods to improve energy- and cost-efficiency of internal combustion engines (ICE) consists in the using waste heat for thermochemical transformation of a primary fuel to another fuel characterized by high energy content, for example, synthesis gas.

In principle, two types of recuperation approaches could be realized – call them “external” and “internal” ones. Term “external” recuperation implies performance of endothermic reaction of a fuel due recovery of heat absorbed by cooling system and heat of exhaust gases. Choice of the fuel is of key importance here. In principle, catalysts allow reforming of any fuel to synthesis gas. It is reasonable to use lower homologues of saturated hydrocarbons, lower alcohols and ethers for synthesis gas generation. The following reactions proceed in the system: steam reforming $C_nH_{2n+1}OH + (2n-1)H_2O \rightarrow nCO_2 + 3nH_2$; hydrogenation $CO_2 + H_2 \leftrightarrow CO + H_2O$; and methanation $CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$. The choice of the fuel for hydrogen (synthesis gas) generation is a compromise between fuel energy content, temperature of steam reforming reaction, product gas composition and cost-efficiency. Taking into account methanol and ethanol low heat of steam reforming reactions, these alcohols can be considered as a source of cheap hydrogen (next to methane). Important factors in favor of methanol and ethanol fuels are low temperature of the steam reforming reactions and relatively cheap catalysts for their thermochemical conversion. The reported analysis on the use of thermochemical recuperation for the alcohols reforming to synthesis gas showed that in case of methanol and exhaust temperature of 500-600°C, a 12-20% increase in ICE efficiency can be expected. In case of ethanol (the same temperature interval), the expected increase is 14-24%.

“Internal” recuperation implies a more complex system, because in this case, besides heat recovery, the exhaust gases are mixed with primary fuel (e.g., natural gas) to produce synthesis gas by tri-reforming reactions $CH_4 + H_2O \leftrightarrow CO + 3H_2$; $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$; $CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2$ [C. Song and W.Pan. Catalysis Today 98 (2004) 463-484]. Here, the effect of thermochemical recuperation is stronger. The problems related to selection and application of tri-reforming catalysts, and the effect of tri-reforming processes on ICE energy- and cost-efficiency are considered.

Keywords: hydrogen, synthesis gas, thermochemical recuperation, methanol, ethanol, catalyst, tri-reforming, internal combustion engine.

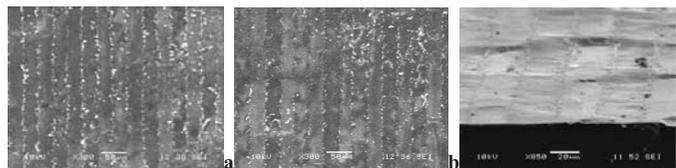


Fig 3 : Surface morphology after different laser speed doping at P= 7W a:2mm/s, b:5mm/s and c:15mm/s

Two phase flow in Pin-type positive flow field of PEM water electrolyzer

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Using hydrogen as the energy storage medium, fuel cell / water electrolyzer-based energy storage system allows separation of power conversion and energy storage functions. The fuel cells/ water electrolyzers comprise regenerative fuel cells (RFCs). Use of excess regenerative energy, electrolyzer converts water into hydrogen and oxygen. The fuel cell then recombines the hydrogen and oxygen back into water and provides electrical power when needed. Proton exchange membrane (PEM) electrolyzers that similar to the PEM fuel cells are often used for RFC systems.

The electrolyzer is one of the key elements of the RFC technology. In positive electrode of electrolyzer, the electrolysis reactant is water, the production is oxygen. Oxygen bubbles and liquid water form two-phase flow in positive flow bed. A mathematical model of the positive pin-type flow field in the proton exchange membrane electrolyzer was developed in the paper. The results indicated that the oxygen mole fractions in diffuse layer are far more than in the flow field. In diffuse layer, large amount of oxygen accumulated under the ribs due to the block of the ribs. The shape and size of flow field inlet have great influence over the two-phase flow of electrolyzer.

Keywords electrolyzer; positive; pin-type flow field; two-phase flow; energy storage

