3rd Zing Hydrogen & Fuel Cells Conference

Omni Cancun Hotel & Villas
Cancun, Mexico.

17th November – 20th November 2015

Conference Chairs
Bruno G Pollet & Walter Mérida

ZING CONFERENCES

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The Abstract Collection

Zing Conferences was established in 2007 to serve as an opportunity for the global community of scientific activity and interest to meet, exchange ideas and stimulate fruitful collaborations. Set in glorious locations, in luxury four and five-star accommodation, each conference aims to bring together a range of expertise, from Academia to Industry, from the Professional to the Student, and provide a beautiful and serene environment in which to present and discuss their respective work.

Zing Conferences is the promotion of inter-disciplinary communication; of the successful cross-pollination of theories and research amongst the many allied scientific fields. To promote this free exchange and dissemination of new ideas and research, all delegates are invited to compete for a place in the main lecture programme, of some 40 speakers, or to present their work as part of the larger Posters sessions by submitting abstracts for Chair-lead consideration.

In 2015 Zing were proud to become a Not-For-Profit company and receive a CIC status. A CIC (Community Interest Company) is a not for profit company with social objectives that works to earn profits for the purpose of reinvesting back into this specific community.

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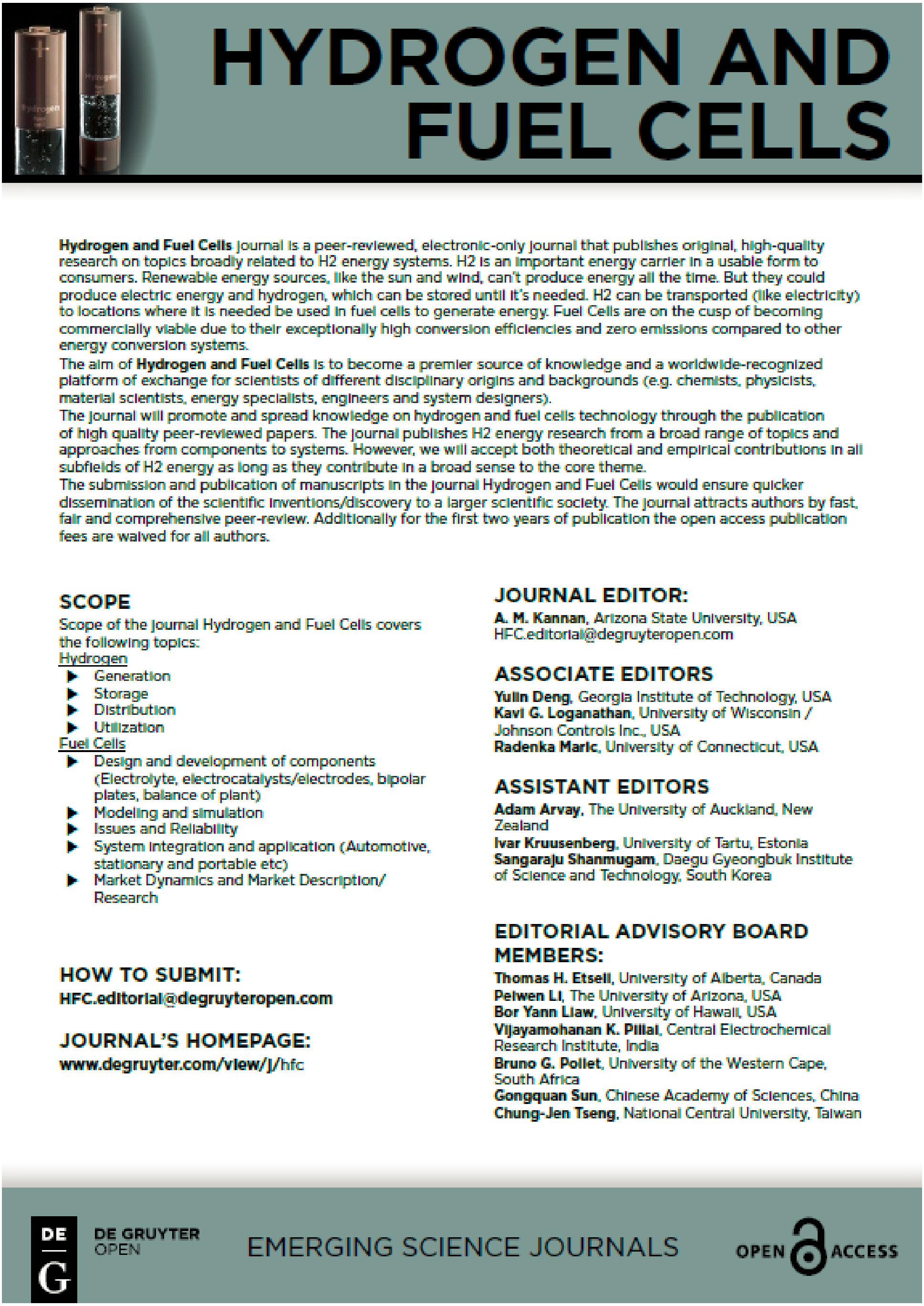

HYDROGEN AND FUEL CELLS

Hydrogen and Fuel Cells journal is a peer-reviewed, electronic-only journal that publishes original, high-quality research on topics broadly related to H2 energy systems. H2 is an important energy carrier in a usable form to consumers. Renewable energy sources, like the sun and wind, can't produce energy all the time. But they could produce electric energy and hydrogen, which can be stored until it's needed. H2 can be transported (like electricity) to locations where it is needed be used in fuel cells to generate energy. Fuel Cells are on the cusp of becoming commercially viable due to their exceptionally high conversion efficiencies and zero emissions compared to other energy conversion systems.

The aim of **Hydrogen and Fuel Cells** is to become a premier source of knowledge and a worldwide-recognized platform of exchange for scientists of different disciplinary origins and backgrounds (e.g. chemists, physicists, material scientists, energy specialists, engineers and system designers).

The journal will promote and spread knowledge on hydrogen and fuel cells technology through the publication of high quality peer-reviewed papers. The journal publishes H2 energy research from a broad range of topics and approaches from components to systems. However, we will accept both theoretical and empirical contributions in all subfields of H2 energy as long as they contribute in a broad sense to the core theme.

The submission and publication of manuscripts in the journal Hydrogen and Fuel Cells would ensure quicker dissemination of the scientific inventions/discovery to a larger scientific society. The journal attracts authors by fast, fair and comprehensive peer-review. Additionally for the first two years of publication the open access publication fees are waived for all authors.

SCOPE

Scope of the journal Hydrogen and Fuel Cells covers the following topics:

Hydrogen

- Generation
- Storage
- Distribution
- Utilization

Fuel Cells

- Design and development of components (Electrolyte, electrocatalysts/electrodes, bipolar plates, balance of plant)
- Modeling and simulation
- Issues and Reliability
- System integration and application (Automotive, stationary and portable etc)
- Market Dynamics and Market Description/ Research

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Welcome

For the past five years, the fuel cell industry has received a lot of interest, as fuel cells are zero-emission technologies with much higher efficiencies than competing technologies. Demand is expected to increase well into the 21st century. Indeed, latest projections estimate that the global fuel cell industry will be a multi-million US$ market in which emerging countries will play an important role. The current focus is on the development of hydrogen and fuel cell technologies and their associated supply chains that offer significant quantitative improvements in (a) lowering costs (by a factor of 10-100) and significantly improving durability, reliability and performance for the stationary, transport and portable markets; (b) addressing the challenges related to hydrogen generation, storage and use; and (c) the acceleration of hydrogen and fuel cell technologies deployment to various markets such as cars and buildings.

The 2015 Zing International Hydrogen and Fuel Cells Conference is chaired by Professor Bruno G. Pollet (Eau2Energy, UK) and co-chaired by Dr Walter Merida (The University of British Columbia, Canada) who have gathered distinguished Hydrogen and Fuel Cells Scientists, Engineers, Economists and Governmental bodies to present their latest findings in a unique and relaxed atmosphere. This conference (third in its series) will focus on modern aspects and new developments of Hydrogen, Fuel Cells and their applications with a focus on Novel PGM based and Non-Platinum based Nanomaterials to Systems for the Portable, Stationary and Automotive Sectors. The conference themes are as follows:

Theme 1: Hydrogen Production and Materials
Theme 2: Renewable Hydrogen
Theme 3: Materials for Fuel Cells and Hydrogen Storage
Theme 4: Fuel Cell Research & Development
Theme 5: Hydrogen and Fuel Cell Applications
Theme 6: Hydrogen Safety Engineering.

The Chairs strongly encourage young Scientists and Engineers to attend as well as invite attendees to submit a manuscript for the conference proceedings, which will be published in a Special Issue in *Hydrogen and Fuel Cells*, a journal published by De Gruyter Open. *Hydrogen and Fuel Cells* is a peer-reviewed, electronic-only journal that publishes original, high-quality research on topics broadly related to H2 energy systems

We hope that this conference offers everyone the opportunity to interact, learn, reflect and share ideas with each other supported by the relaxed atmosphere offered by the venue.

Thank you very much for joining the 3rd Zing Hydrogen and Fuel Cells Conference!

Sincerely

Bruno G. Pollet and Walter Merida

The Conference Chairs

Bruno G Pollet

Eau2Energy, UK

Professor Pollet has recently joined industry to head up a R&D Centre in a young, dynamic and forward-thinking High Tech company in the UK. He is also Visiting Professor at the University of Ulster (UK) and the University of Yamanashi (Japan). Professor Pollet was a (full) Professor of Energy Materials and Systems at the University of the Western Cape (RSA), R&D Director of the National DST Hydrogen South Africa (HySA) Systems Competence Centre (an industry oriented and led RD&D Centre with a strong emphasis on demonstrator/prototype development and Energy Materials manufacturing), SAIAMC Programme Director and Member of the RSA Department of Trade & Industry Electric Vehicle Industry Steering Committee.

Professor Pollet is known both in academia and industry to be a dynamic, energetic, enthusiastic, positive and visionary individual with expertise and experience in the research fields of Hydrogen Energy, PEMFC, Fuel Cell Electrocatalysis and Electrochemical Engineering. He has excellent business development, networking, leadership and communication skills.

He was formerly a co-founder and an Associate Director of the Birmingham Centre for Hydrogen and Fuel Cell Research, and Operations and Delivery Director of the Engineering and Physical Sciences Research Council (EPSRC) Doctoral Training Centre in Hydrogen, Fuel Cells and their Applications led by Professor Kevin Kendall FRS in the UK.

The Conference Chairs

Walter Mérida

The University of British Columbia

Dr Mérida was born in Guatemala and he completed his higher education in Italy and Canada (Physics, Chemistry, and Mechanical Engineering). His graduate research included work on natural gas liquefaction and fuel cell technology.

From 1996 to 1999 Dr. Mérida worked at the Institute for Integrated Energy Systems, coordinating joint research between Ballard Power Systems, British Gas Investments Canada, and two universities (UVic and Simon Fraser). He served on the Board for General Hydrogen Corporation prior to private financing (1999-2000).

Dr. Mérida joined the faculty at UBC in 2002: he is a professor in Mechanical Engineering, and an associate member in Chemical and Biological Engineering. He was a visiting professor at the Fraunhofer Institute for Solar Energy Systems (2010), and he was co-appointed at the National Research Council (Institute for Fuel Cell Innovation) from 2002 to 2011. He is currently the director at UBC’s Clean Energy Research Centre.

Plenary Speakers

Christophe Coutanceau

Université de Poitiers

Christophe Coutanceau obtained his Ph.D. degree in 1994 working with Prof. Claude Lamy at the Laboratory of Catalysis in Organic Chemistry (LACCO - University of Poitiers, France). In 1995-1996, he worked with Prof. Ramao Ribeiro, at the Instituto Superior Tecnico of Lisbon (Portugal) and obtained in 1998 a position of Assistant Professor at LACCO before being promoted as full professor in 2005. At present, he is Professor at the University of Poitiers (France) and Director of the “Catalysis and Unconventional Media” group of the Institute of Environment and Material Chemistry of Poitiers. He has responsible of the “Low temperature Fuel Cells and electrolysis cells” axe of the French “Hydrogen-Systems-Fuel Cells” Research Grouping from CNRS. His current research interests include development of synthesis methods for nanostructured supported metal nanoparticles using green processes (microwave activation, electrochemical methods, etc.) and solvents (polyols, water) and their application as electrocatalysts in fuel cells, electrolysis cells and electrosynthesis reactors. He is also interested in the conversion of agroresources into value-added compounds using electrochemical methods. He presented and published about 240 papers (incl. 106 articles in reviewed international journals, 8 book chapters, 14 invited lectures and 2 world patents), and he has reached h-indexes of 37 (Web of Science, 5643 citations) and 39 (Scopus, 5988 citations). He is a fellow of the International Society of Electrochemistry.

Søren Linderoth

Technical University of Denmark

Prof. Søren Linderoth is a professor (Functional Ceramics for Energy Purposes) at the Technical University of Denmark (DTU). He is also Head of Department of Energy Conversion and Storage (DTU Energy), with 240 persons doing R&D in the areas of sustainable energy technologies, such as fuel cells (SOFC and PEMFC), electrolysis (SOEC and AEC), solar cells (organic, perovksite etc), batteries (especially metal-air), ceramic superconductors, thermoelectric generators (RT-1000 oC), caloric cooling and heating (magnetocaloric and elastocaloric), and flue gas purification (electrochemical, SCR). The research is based on strong competences in ceramic processing, organic and inorganic materials, electrochemistry, modelling from atomic scale to components, devices and systems. In the past three years five start-up companies have evolved from the department. Prof. Linderoth has co-authored more than 220 scientific papers, and is the co-inventor of more than 25 patents.

Plenary Speakers

Vladimir Molkov

University of Ulster

Prof Vladimir Molkov is a physicist graduate from Moscow Institute of Physics and Technology (1977). Scientific degrees: PhD in Chemical Physics, including Physics of Combustion and Explosion, and DSc in Fire and Explosion Safety. Since 1999 he is Professor of Fire Safety Science at the University of Ulster. Since 2004 Prof Molkov is specializing in hydrogen safety. In 2008 he established and leads the HySAFER (Hydrogen Safety Engineering and Research) Centre at the University of Ulster with internationally recognised research and education activities. The thrust in research is on analytical and numerical studies of hydrogen releases and dispersion, including high pressure under-expanded jets, spontaneous ignition of sudden releases, indoor jet fires, deflagrations and detonations, innovative hydrogen safety strategies and engineering solutions. Prof Molkov has coordinated and participated in major European projects related to hydrogen safety. He is a Visiting Professor at Karlsruhe Institute of Technology (Germany). Since 2013 he represents UK as an expert in ISO TC/197 “Hydrogen technologies”. In 2012 published free download eBook “Fundamentals of Hydrogen Safety Engineering” (bookboon.com).

Steven Holdcroft

Simon Fraser University

Dr. Steven Holdcroft is a Professor of Chemistry and Departmental Chair at Simon Fraser University (SFU). He is known for his contributions to the design of π-conjugated and ionic polymeric materials and their application to organic electronics and fuel cell technology. He is author/co-author of more than 200 peer-reviewed articles and several book chapters and patents.

He has served on numerous research advisory boards throughout North America, Europe and Asia, and is a member of the Board of Directors of the Canadian Hydrogen and Fuel Cells Association. He sits on the editorial advisory boards of several, international scientific journals and national and international grant selection committees. He is the Technical Program Chair and Congress Vice-Chair of Pacifichem 2015 and Director of CaRPE-FC, a national network for Catalysis Research for Polymer Electrolyte Fuel Cells. For services to the community was awarded the Macromolecular Science and Engineering Division Award of the Chemical Institute of Canada (CIC) and is an elected Fellow of the CIC.

Plenary Speakers

Gregory Jerkiewicz

Queen's University

Gregory Jerkiewicz received Master's degree in Engineering Chemistry from Gdansk University of Technology, Poland, in 1984. In 1980 while being an undergraduate student in Poland, he became deeply involved in the Solidarność movement and was a co-founder of the Independent Student Association. In December 1981 during the crackdown on the freedom movement by the communist authorities of Poland, he was interned for six months. In 1985, he immigrated to Canada. He completed his Ph.D. (1991) at the University of Ottawa under the supervision of the late Prof. Brian E. Conway. He joined the Department of Chemistry, University of Sherbrooke, as Research Associate in September 1991 and became Assistant Professor in June 1992. He was promoted to Associate Professorship with tenure in June 1997. In June 2002, he joined the Department of Chemistry, Queen's University, as tenured Associate Professor and was promoted to the rank of Professor in 2005. He has authored over 125 publications that include peer-reviewed papers (80), peer-reviewed book chapters (6), papers in volumes of conference proceedings (24), editorials (5), and has co-edited one (1) book and three volumes (3) of conference proceedings. He has delivered over 145 invited keynote lectures, seminars, and conference presentations, and over 210 contributed conference presentations. He has been an active member of the International Society for Electrochemistry, The Electrochemical Society and the Canadian Society for Chemistry, where he has served on several executive committees. He is Editor-in-Chief of Electrocatalysis. He has trained fifty-five (55) highly qualified personnel, including graduate and undergraduate students, postdoctoral fellows and research associates, and has hosted six (6) visiting faculty members. In 2012, the President of Poland, Mr. Bronisław Komorowski, conferred on him the Knight's Cross of the Order of Polonia Restituta in recognition of his outstanding contributions to the Polish society in the 1980s.

Federico Rosei

Institut National de la Recherche Scientifique

Federico Rosei has held the Canada Research Chair in Nanostructured Organic and Inorganic Materials since 2003. He is Professor and Director of Institut National de la Recherché Scientifique, Énergie, Matériaux et Télécommunications, Université du Québec, Varennes (QC) Canada. Since January 2014 he holds the UNESCO Chair in Materials and Technologies for Energy Conversion, Saving and Storage. He received MSc and PhD degrees from the University of Rome "La Sapienza" in 1996 and 2001, respectively.

Dr. Rosei's research interests focus on the properties of nanostructured materials, and on how to control their size, shape, composition, stability and positioning when grown on suitable substrates. He has extensive experience in fabricating, processing and characterizing inorganic, organic and biocompatible nanomaterials. He has published over 200 articles in prestigious international journals (including Science, Nature Photonics, Proceedings of the National Academy of Sciences, Advanced Materials, Angewandte Chemie Int. Ed., Journal of the American Chemical Society, Advanced Functional Materials, Nanoletters, ACS Nano, Biomaterials, Small, Physical Review Letters, Nanoscale, Chem. Comm., Applied Physics Letters, Physical Review B, etc.), has been invited to speak at over 210 international conferences and has given over 170 seminars and colloquia and 20 public lectures in 42 countries on all inhabited continents. His publications have been cited over 5900 times and his H index is 41.

In 2014, he has been elected Fellow of the Royal Society of Canada. He is Member of the European Academy of Sciences, Fellow of the American Physical Society, Honorary Fellow of the Chinese Chemical Society, Fellow of the American Association for the Advancement of Science, Fellow of SPIE, Fellow of the Canadian Academy of Engineering, Fellow of ASM International, Fellow of the Royal Society of Chemistry (UK), Fellow of the Institute of Physics, Fellow of the Institution of Engineering and Technology, Fellow of the Institute of Materials, Metallurgy and Mining, Fellow of the Institute of Nanotechnology, Senior Member of the IEEE, Fellow of the Engineering Institute of Canada, Member of the Global Young Academy, Fellow of the Australian Institute of Physics and Member of the Sigma Xi Society.

He has received several awards and honours, including the FQRNT Strategic Professorship (2002–2007), the Tan Chin Tuan visiting Fellowship (NTU 2008), the Senior Gledden Visiting Fellowship (UWA 2009), Professor at Large at UWA (2010–2012), a Marie Curie Post-Doctoral Fellowship from the European Union (2001), a Canada Research Chair (2003–2013), a Friedrich Wilhelm Bessel Award from the Alexander von Humboldt foundation (2011), the Rutherford Memorial Medal in Chemistry (Royal Society of Canada 2011), the Herzberg Medal (Canadian Association of Physics 2013), the Brian Ives lectureship award (ASM international / Canada Council 2013), the Award for Excellence in Materials Chemistry (Canadian Society for Chemistry 2014), the NSERC EWR Steacie Memorial Fellowship (2014), the José Vasconcelos Award for Education (World Cultural Council 2014), the IEEE NTC Distinguished Lectureship 2015, the Lash Miller Award (Canada Section, Electrochemical Society 2015), the Chang Jiang Scholar Award (Government of China), the Khwarizmi International Award (2nd Laureate) from the Iran Research Organization for Science and Technology (IROST), the Recognition for Excellence in Leadership from the American Vacuum Society and the Selby Fellowship from the Australian Academy of Sciences.

Invited Speakers

Chris Reid
Hydrexia

Esteban Durán Herrera
Universidad de Costa Rica

Jens Oluf Jensen
Technical University of Denmark

Brant A. Peppley
Queen's-RMC Fuel Cell Research Centre

Dmitriy Makarov
University of Ulster

Shangfeng Du
University of Birmingham

Karen Swider-Lyons
U.S. Naval Research Laboratory

Sergio Miguel Durón Torres
Universidad Autónoma de Zacatecas

Kamiel Gabriel
University of Ontario Institute of Technology

Odne Burheim
Sor-Trondelag University-College

John Jostins
Coventry University

Contributing Speakers

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Simon Fraser University

Marco A. Rodriguez
Binghamton University SUNY

Torsten Berning
Aalborg University

Patrick Nonjola
CSIR, South Africa

Shouzhong Zou
American University

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University College London

Erik Engebretsen
University College London

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University of Kwa-Zulu Natal

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University of the Punjab

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Karlsruhe Institute of Technology

Ki Bong Lee
Korea University

Harby Alexander Martinez Rodriguez
Universidad Nacional de Colombia
sede Manizales

3rd Zing Hydrogen & Fuel Cells Conference

Day 1 Oral Presentations

Session 1

Catalysis

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Platinum Electrochemistry and Electrocatalysis: Unraveling the Origins of Its Unique Behavior

Gregory Jerkiewicz*

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, ON. K7L3N6, Canada.

In the hydrogen economy involving electrochemical technologies, electrical energy is converted to chemical energy (H_2, a stable, reusable product) in water electrolysers and such generated H_2 is used to produce electrical energy in hydrogen fuel cells. It is a wonderful cycle, in which water is initially a reactant and eventually a product. The processes occurring in water electrolysers and hydrogen fuel cells, hydrogen evolution (HER), oxygen evolution (OER), hydrogen oxidation (HOR) and oxygen reduction (ORR) reactions, drive an interest in hydrogen and oxygen electrochemistry and electrocatalysis. Platinum is the most effective electrocatalyst in these reactions, but the origin of its unique activity is poorly understood. However, it exceptional electrocatalytic activity needs to be explained in order to develop guidelines for the design and fabrication of non-noble electrode materials possessing similar properties. The contribution focuses on three phenomena taking place at Pt electrodes: (i) the under-potential deposition of H (UPD H); (ii) surface oxide growth; and (iii) Pt and Pt surface oxide dissolution.

Electrochemical, analytical and surface science research sheds new light on the unique interfacial behavior of Pt in aqueous electrolyte solutions. Temperature-dependent cyclic-voltammetry studies combined with theoretical data treatment facilitate the determination of thermodynamic state functions of UPD H ($\Delta_{\text{ec-ads}}G°$, $\Delta_{\text{ec-ads}}S°$, $\Delta_{\text{ec-ads}}H°$) and the Pt-H_{UPD} surface bond energy ($E_{\text{Pt–Hupd}}$). The data show that on a thermodynamic basis H_{UPD} is equivalent to H_{chem}, and suggest H_{chem} and H_{UPD} occupy the same surface adsorption sites and are embedded in the Pt surface lattice. Electrochemical quartz-crystal nanobalance (EQCN) analysis of interfacial mass changes in the potential range of UPD H and HER reveals the existence of potential of minimum mass (E_{pmm}), that value of which coincides with the completion of saturation layer of H_{UPD} and the onset of HER. It is observed that HER does not take place on bare Pt but on Pt modified with a layer of H_{UPD}, which modifies the electrode's interfacial wetting ability making the surface hydrophobic-like. The discharge of H_3O^+ in HER or the dissociative adsorption of H_2(g) in HOR proceed easily on Pt than on other metals because the species do not have to displace H_2O molecules or hydrated ions due to weak surface dipole–H_2O dipole and surface dipole–hydrated ion interactions. Effective and cheap non-Pt electrocatalysts for HER and HOR should mimic the interfacial behavior of Pt; thus, they should: (i) be chemically and mechanically stable; (ii) adsorb H; (iii) dissociate H_2; and (iv) have weak interactions with H_2O molecules and hydrated ions. The electro-oxidation of Pt at well-defined conditions, i.e. polarization potential (E_p), polarization time (t_p), and temperature (T), leads to very thin oxide layers. Their surface chemical composition is analyzed using X-ray photoelectron spectroscopy (XPS) and reveals that PtO is the main species formed at $E_p < 1.60$ V. Application of higher potentials leads to slow growth of PtO_2 on top of the PtO layer. Treatment of the Pt oxide growth employing oxide-growth theories results in the evaluation of the reaction's mechanism and kinetics. Formation of Pt surface oxides is accompanied by their slow but unavoidable dissolution. Stability of Pt oxides depends on the potential that they experience, exposure time, and electrolyte composition and concentration. Electrochemical and chemical Pt and Pt oxide dissolution pathways are discussed.

The Mexican Hydrogen Society / Mixed Oxides as Catalyst-Supports for Oxygen Evolution Reaction

Sergio Miguel Durón Torres
Unidad Académica de Ciencias Químicas, Universidad Autónoma de Zacatecas,Km. 6 Carr.Zacatecas-Guadalajara, 98610, México.

Today's world energy scenario faces big challenges for our societies such as increasing environmental problems, limited fossil resources and the geopolitical dependence on crude oil. Mexico is not between the ten principal countries that contributes to CO_2 generation, however in the last years has been observed an increase in the global emissions because the development of the country is demanding more transport facilities. In Mexico the main sectors that generate gas emissions are the services sector that includes electricity, transport and manufacturing and in the last decade the electricity and transport sectors has increased in more than twice their emission level. From all potential energy options, hydrogen used as a fuel is a clean candidate because it only produces water as a by-product when burned. Hydrogen can be produced from different renewable energy sources, and Mexico is rich in alternative resources. In the country, R&D efforts related to hydrogen technologies are leaded by the members of the Mexican Hydrogen Society (SMH), The SMH has as main objective to promote fundamental and applied research to advance in the use of hydrogen as clean energy source in Mexico.

/ Platinum-based catalysts on a conductive support are commonly used as electrode materials in low-temperature fuel cells. Similarly, iridium oxide is the usual anode material in polymeric exchange membrane electrolyzers. The performance and, in particular, the stability of these catalysts strongly depends on the characteristics of the support. Doped metallic oxides have received great attention because their interesting properties as supports. As a contribution to this field, antimony-doped tin oxide (ATO) was synthesized by a chemical coprecipitation method and a minimum calcination time, the material obtained presented a nanometric size (4-9 nm) that can be used as a support for IrO_2 and Pt in electrodes for PEM electrolyzers and fuel cells. Some mixtures of synthesized ATO and Vulcan carbon (VC) were assayed as mixed supports for ORR and OER and for acquiring a protective effect of ATO on the degradation of the carbon support [1]. By the other hand, novel material, with a general formula of Ir–Sn–Sb–O, was synthesized for use in solid polymer electrolyte water electrolyzers (SPEWEs). The results indicate that the catalyst-support materials presented nanometric sizes (1–2 nm) and electrocatalytic properties similar to IrO_2 supported on Vulcan carbon but with higher stability toward the oxygen evolution reaction [2].

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Concave PtNi nano-octahedra as high performance catalysts for oxygen reduction reaction

Shouzhong Zou,[1,2*] Hongzhou Yang,[1] Yongan Tang,[1] Jonathan Winterstein[3] and Renu Sharma[3]

1 Department of Chemistry & Biochemistry, Miami University, Oxford, OH 45056, USA
2 Department of Chemistry, American University, Washington, DC 20016, USA
3 Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Increasing the kinetics of oxygen reduction reaction (ORR) is a key challenge in the development of proton exchange membrane fuel cells (PEMFCs). Recent research efforts have been largely focused on developing Pt-based alloys to improve the ORR activity and stability. A particularly promising family of materials is the facet-controlled Pt-Ni nanocrystals, especially of octahedral shape. For example, a mass activity of 3.3 A/mgPt was reported recently on 9 nm $Pt_{2.5}Ni$ nanoctahedra supported on carbon.[1] An even higher mass activity has been observed on larger Pt_3Ni nanoframes.[2] In this presentation, we will discuss the synthesis and characterization of 18 nm concave $Pt_{1.2}Ni$ nano-octahedra, and their ORR activity. The concave structure was confirmed by TEM tomography. These nanocrystals exhibit very high specific activity and mass activity, which are about 70 and 7 times of that reported on Pt/C at 0.90 V vs RHE, after thermal annealing in an inner environment. More importantly, these catalysts show remarkable stability against potential cycling between 0.6 and 1.0 V and have a very long shelve life. The high ORR activity remains even after one year storage in aqueous/ethanol mixture. These properties make them very promising practical catalysts for PEMFCs.

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Direct catalyst electrodes based on PtPd nanodendrites for PEFC applications

Yaxiang Lu, Shangfeng Du*, Robert Steinberger-Wilckens
School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

In this work, the crystal growth mechanisms of PdPt bimetallic nanodendrites are studied with gas diffusion layers (GDLs) as the direct growth support to develop three-dimensional (3D) nanostructured electrodes for PEFC applications. The GDLs with 3D nanostructures are directly employed as gas diffusion electrodes (GDEs) for the oxygen reduction reaction (ORR) at the cathode in H_2/air PEFCs [1-2]. Experimental results show that the introduction of Pd not only manipulates the catalytic activity and durability of bimetallic PdPt nanodendrites, but also can be an efficient tool in tuning the morphology and distribution of nanodendrites on the large-area GDL. At an optimal Pd content of 5 at%, uniformly distributed PdPt nanodendrites with a branch diameter of ca. 4 nm and length of 10–20 nm are achieved on 16 cm^2 GDLs (Fig. 1). Other than with most other reported data, a better durability is achieved for PdPt bimetallic nanodendrites than Pt nanowires but a lower intrinsic mass activity and specific area activity are observed. Despite this, the uniform distribution of nanodendrites still leads to a better fuel cell performance due to the improved mass transfer losses. Since a similar challenge is faced with other advanced nanostructures for their poor performance in practical applications, the understanding gained here could aid in the design of practical catalyst electrodes from advanced nanostructures.

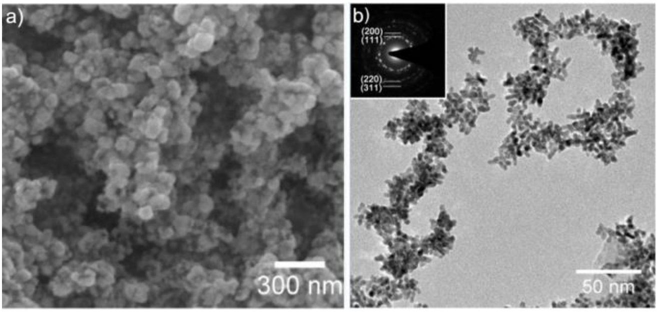

Fig.1 SEM and TEM images of Pd_5Pt_{95} bimetallic nanodendrites in-situ grown on GDL.

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Polymer Electrolyte Membrane Fuel Cell (PEMFC) power density optimization based on using graded Catalyst Layer (CL)

Sasan Ebrahimi[a*], **Krishna Vijayaraghavan** [a]
[a] *School of Mechatronic Systems Engineering, Simon Fraser University, 250-13450 102 Avenue, Surrey, BC V3T 0A3 Canada*
** sasane@sfu.ca*

The aim of this work is determining the optimum catalyst distribution which can produce the maximum Polymer Electrolyte Membrane Fuel Cell (PEMFC) power density. In many previous PEMFC models, the catalyst distribution in Catalyst Layer (CL) was assumed to be uniform and there are just few models in which the variation of catalyst loading across the CL was taken into account. In this work, first, a numerical approach is presented to evaluate the effect of catalyst loading gradient in the CL of a PEMFC. A two dimensional implicit model for PEMFC cathode has been developed. The model is steady state and isothermal and the numerical domain which is shown in Fig. 1, includes Channel, land, Gas Diffusion Layer (GDL) and CL. A spherical agglomerate model is considered for CL in which the transport of both chemical species and charges are also taken into account. Optimum catalyst loading distribution along catalyst layer is determined using a novel algorithm based on combining the numerical model and downhill simplex optimization method. In this novel algorithm, the optimum catalyst distribution is assumed as polynomial functions with unknown coefficients. Unknown coefficients are calculated by considering the numerical model as sets of constraints for optimization method. The optimum polynomial functions are shown in Fig. 2. In optimum case, maximum PEMFC power density is increased about seven percent.

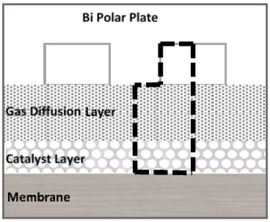

Figure 1. Numerical Domain

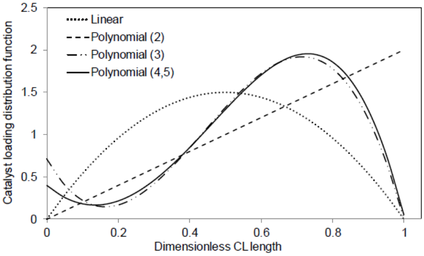

Figure 2. Optimum Catalyst Distribution

3rd Zing Hydrogen & Fuel Cells Conference

Day 2 Oral Presentations

Session 2

Membranes & Characterisations

Advances in Polyaromatic Membranes/Ionomers for PEM and AEM fuel cells

Benjamin Britton, Andrew Wright, Thomas Skalski, Timothy Peckham, Thomas Weissbach, Steven Holdcroft

Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, V5A 1S6, Canada

Perfluorinated proton-exchange materials form the basis of standard high-performance PEMFCs, but difficult chemistry hampers further material development to meet performance targets. Hydrocarbon proton-exchange materials have well-established chemistry that allows for rapid material development, and offer the potential for easier catalyst recycling, lower fuel crossover. In the corollary case of AEMFCs, the search continues for a stable and versatile polymeric hydroxide-conducting medium.

In this presentation, fuel cell data is presented using highly stable, sulfo-phenylated polyaromatic solid polymer electrolytes for in PEMFC membranes and ionomers. Separate investigations of these materials as membranes and ionomer in the catalyst layer were undertaken in conjunction with perfluorinated reference materials. The performance of PEMFCs based on these materials will be shown to be exceptionally high. Also presented will be the performance of a promising class of alkaline-stable AEMs exhibiting some of the highest-performance AEMFCs, with several avenues for performance optimization yet to be investigated. The material's solubility in methanol in addition to hydroxide stability makes them attractive candidates for AEM ionomers in catalyst layers, for it is capable of forming highly conductive, porous electrodes without the typical annealing required for those based on high-boiling solvents.

Challenges in the accurate measurement of oxygen reduction electrocatalyst activity in RDE and CCMs

Karen Swider Lyons,[1] **Yannick Garsany,**[2] **Megan Sassin**[1]

1. *Chemistry Division, U.S. Naval Research Laboratory, Washington DC*
2. *Excet Inc., Springfield, VA*

A key to achieving efficient, cost-effective hydrogen fuel cells is having a highly efficient, durable cathode electrocatalyst for the oxygen reduction reaction, while minimizing the amount of platinum and other expensive precious metals. Accordingly, the identification of new low-Pt electrocatalysts has been a productive research area. At the Naval Research Laboratory, we attempted to reduce the platinum content of cathode electrocatalysts by supporting the Pt on a range of oxides and oxyphosphates and take advantage of metal support interactions. The challenge then became, how good was our electrocatalyst vs. a platinum standard? We started with measurements by rotating disk electrode (RDE) voltammetry. Over several years, it became apparent that uniform film thickness of the electrocatalyst film on the RDE was one of the most important factors in reproducibility. After developing a standard RDE method for characterizing Pt/C, we then were able to confirm that our platinum tantalum phosphate (Pt-TaOPO/C) electrocatalyst had 2x higher activity than Pt/C. However, in catalyst-coated membranes (CCMs), the Pt-TaOPO/C performed poorly compared to commercial Pt/C ones. We have since tried to resolve this puzzle by embarking on a path to make reproducible CCMs in house, first starting with the optimization of Pt/C CCMs. We have found that the gasket thickness impacts the microporous layer structure of the gas diffusion layers, and thus the mass transport of O2 and H2O to and from the Pt in the catalyst layer. With such mechanical issues resolved, we could tackle the problems of how to make an oxide and/or phosphate based electrocatalyst active in CCMs, for which the hydrophilicity of the electrocatalyst plays a significant role. Understanding such issues are critical as researchers move to oxygen- and nitrogen-containing non-precious metal electrocatalysts.

Employing hot wire anemometry to directly measure the water balance in proton exchange membrane fuel cell

Torsten Berning, **Saher Al Shakhshir**
Department of Energy Technology, Aalborg University, Pontoppidanstr. 101, 9220 Aalborg, Denmark.

While proton exchange membrane fuel cells are nearing the commercial phase there are still technical hurdles to overcome in order to make this technology more reliable and affordable. Many problems that concern fuel cell performance and durability are still related to the fuel cell water management: at high current densities the danger of anode dehydration exists, and this can potentially limit the maximum current and thereby the maximum power that can be drawn from the cell. A thorough understanding of the fuel cell water balance is therefore highly desirable.

While there have been several studies of experiments on the fuel cell water balance published in the literature, previous methods to measure the fuel cell water balance are limited in their accuracy and can be very complex. Our group has recently suggested employing hot wire anemometry to measure the fuel cell water balance. When placing the hot wire sensor into the anode outlet, the sensor voltage can be directly converted into the fuel cell water balance, thus giving an almost real-time electrical signal of great accuracy. This method is also suitable for ad-hoc use in fuel cell vehicles as added diagnosis tool.

We will present the underlying theory and first experimental results that show the accuracy and convenience of this method.

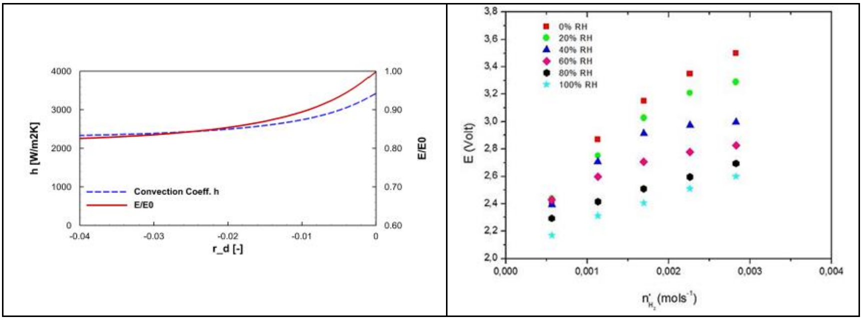

Figure 1. In theory, the fuel cell water balance, r_d, can be directly determined out of the relative voltage signal of the hot wire sensor, E/E_0, where E_0 is a pre-determined voltage signal for dry hydrogen and E is the sensor signal as received by the hot wire in high frequency (left). The voltage signal as received in ex-situ experiments shows a strong sensitivity to the molar flow rate of dry hydrogen as well as humidified hydrogen (right).

Characterisation of Thin Film Alkaline Anion Exchange Membranes for Fuel Cells Using a Quartz Crystal Microbalance and Crystal Admittance Spectroscopy

V. J. Bharath, [a] T. P. Neville, [a] T. Mason, [a] J. Millichamp, [a] P. R. Shearing, [a] R. J. C. Brown, [b] G. Manos, [a] D. J. L. Brett [a]*

a, Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK
b, National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK

Fuel cells are seen as one of the most promising technologies in the fight against climate change and achieving low-carbon energy conversion. Alkaline anion exchange membrane (AAEM) fuel cells are a novel solid polymer electrolyte (SPE) version of the alkaline fuel cell (AFC). Operating in an alkaline medium has the benefit of more facile oxygen reduction kinetics at the cathode, compared to traditional acid-based proton exchange membrane (PEM) fuel cells, and AAEM fuel cells are therefore able to utilize more cost effective non-precious metal catalysts. AAEMs negate many of the issues experienced with the aqueous AFC such as carbonate salt precipitation when operated in low levels of CO2 and also issues pertaining to transport and the use of a caustic electrolyte.

AAEMs are in an early stage of development and face specific technological challenges compared to their proton exchange analogues. This work employs a composite quartz crystal microbalance (QCM) to characterise a commercially available AAEM under various conditions including CO_2-containing gas that can induce carbonate formation in the membrane. Investigation into how carbonate immobilisation affects the AAEMs performance degradation and the subsequent effect this has on the ionomer’s morphology is presented. Additional cationic groups (often quaternary ammonium groups, R_4N^+) are introduced to the AAEM to compensate for a shortfall in conductivity compared to PEMs which has reportedly led to reduced mechanical strength and chemical stability of the membrane. How the presence of hydration affects both the ionomer’s water uptake and loading mechanisms as well as the susceptibility of the cationic groups to resist cleavage in the presence of hydroxide ions leading to E2 (Hofmann) elimination is also presented.

The QCM is a mass monitoring device with nanogram resolution that can be operated *in-situ* in a range of environments. It is used in this investigation as a composite (ionomer) resonator, in which a range of AAEM electrolyte thicknesses are cast directly to the electrode surface. The composite resonator along with crystal admittance spectroscopy (CAS) is used to explore interfacial characterisation of commercially available thin film AAEM ionomer dispersions from Tokuyama Co (Japan).

Electrocatalysts and Anion Exchange Composite Membranes for Alcohol Alkaline Fuel Cells

Patrick Nonjola[a]*, Mmalewane Modibedi[a], Nomthandazo Mutangwa[a], Kenneth Ozoemena[a], Mkhulu Mathe[a], Haitao Zeng[a]

*a, CSIR, Material Science and Manufacturing, PO Box 395, Pretoria, 0001 *snonjola@csir.co.za*

The high methanol crossover through Nafion and inorganic- or organic-Nafion composite membranes reduces the efficiency of DMFC in comparison with hydrogen fed PEM fuel cells[1], thus triggering the search for novel proton exchange membranes with reduced alcohol permeability[2]. Nevertheless, anion exchange membrane (AEM) direct methanol fuel cells have numerous advantages over proton exchange membrane DMFC. For example, non-noble and low cost metal, such as silver and nickel, can be used as electro-catalysts due to the inherently faster kinetics of oxygen reduction reaction in alkaline media. Furthermore, methanol oxidation is more facile in alkaline media than in acidic one. Several types of AEM have been developed during the last decade aiming to improve the performance of H_2/O_2 AEM fuel cells running with aqueous KOH electrolyte. The polymeric materials currently under investigation for H_2/O_2 solid AEM fuel cells have been recently reviewed by Couture *et al*.[3], while their performance in direct alcohol AEM fuel cells was also analyzed. Varcoe and co-workers were pioneers in synthesizing AEM with quaternized ammonium groups for DMFC by radiation grafting vinylbenzyl chloride (VBC) onto stable materials such as poly (ethylene-co-tetrafluoroethylene) (ETFE)[4]. The successful replacements of Nafion by quaternized AEM in DMFC strongly depend on the possibility to compensate the lower ion conductivity of the AEM with lower methanol permeability.

Alcohol alkaline fuel cells with anion exchange nanocomposite membranes get immense attention due to very attractive opportunity of using non-noble metal catalyst materials. In the present study, anion exchange composite membranes, anode and cathode materials were prepared and investigated for alkaline membrane fuel cells for oxygen reduction and performance studies. Membrane Electrode Assemblies (MEAs) were fabricated using in-house prepared anion exchange composite membranes, commercial anion membranes with commercial cathodes and Pt/C anodes. Fuel cell performance of the MEAs was examined.

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3rd Zing Hydrogen & Fuel Cells Conference

Day 2 Oral Presentations

Session 3

Techniques

Thermal conductivity of different PEMFC regions and impacts on numerical modelling.

O. S. Burheim, PhD
Sør-Trøndelag University College, Post Box 2320, N-7004 Trondheim

Over the last ten years the thermal conductivity of most of the PEMFC components have been reported. The property changes with material type, i.e. gas diffusion layer (GDL), micro porous layers (MPL), catalyst layers (CL), and in the membrane – and actually it also changes in the the region where the MPL and GDL bridges and forms a composite region. Moreover the thermal conductivity of all these layer changes with the temperature, compaction pressure, additives like PTFE, ageing/degradation, water content and the state of water. The thermal conductivity also changes with fabrication type and with the different series from single manufacturers.

The talk will present an overview over the thermal conductivity for all these conditions and materials and discuss the some potential impacts on a model when including local temperature gradients.

About the author:
The author finished his Ph.D. in 2009 with a focus on thermal conductivity measurements of PEMFC components and PEMFC calorimetric measurements. He has published more than ten papers focusing on thermal aspects of the PEMFC over the last five years and also published several papers on similar aspects for Li-ion secondary batteries and super capacitors. He currently lectures for engineering students within the fields of energy storage, renewable energy and thermodynamics.

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Electro-thermal impedance spectroscopy applied to an open-cathode polymer electrolyte fuel cell

Erik Engebretsen,[a] James B. Robinson,[a] Oluwamayowa Obeisun,[a] Tom Mason,[a] Donal Finegan,[a] Gareth Hinds,[b] Paul R. Shearing,[a] and Daniel J. L. Brett [a]*

a, Electrochemical Innovation Lab, Department of Chemical Engineering, UCL, London, WC1E 7JE, United Kingdom.

b, National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, United Kingdom.

Fuel cells are a key technology in power production for the transition from a carbon-based economy to a sustainable, low carbon future. The development of *in-situ* diagnostic techniques is critical to ensure safe and effective operation of polymer electrolyte fuel cell systems. Electrochemical Impedance Spectroscopy is a widely-used diagnostic technique, which relates a current stimulus to the voltage response of the system (or vice-versa). The relative phase and amplitude ratio between the stimulus and response over a range of frequencies can identify physical phenomena due to the fact that the phenomena have varying time constants. Transfer function analysis applies the same principle to other cause-effect relationships in order to determine other physical properties during fuel cell operation.

Infrared thermal imaging is an established technique which has been extensively applied to fuel cells; however, the technique is limited to measuring surface temperatures and is prone to errors arising from emissivity variations and reflections. Electro-thermal Impedance Spectroscopy can be applied to enhance infrared thermal imaging and mitigate its limitations, using an open-cathode polymer electrolyte fuel cell as a case study.

The technique operates by imposing a periodic electrical stimulus to the fuel cell and measuring the consequent surface temperature response (phase and amplitude). In this way, the location of heat generation from within the component can be determined and the thermal conduction properties of the materials and structure between the point of heat generation and the point of measurement can be determined. By selectively ‘locking-in’ to a suitable modulation frequency, spatially resolved images of the relative amplitude between the current stimulus and temperature can be generated that provide complementary information to conventional temporal domain thermograms.

The presence of H on the Zr(0001)-1x1 surface analysed with Photoemission and STM.

Katerina Horakova[a] *, Jan Lancok[a], Petr Sajdl[b], Alexander Tarasenko[a] and Vladimir Chab[a]

a, Institute of Physics, Academy of Sciences of the Czech Republic, 182 21 Prague 8, Czech Republic.
b, Institute of Chemical Technology Prague, 166 28 Prague 6, Czech Republic.

Different elements like O, H, F, Fe or Hf form a solid solution in the bulk of Zr crystal. It is extremely difficult to separate them during the purification process. They are very often found segregated at a surface during particular technological steps connected with heating and cooling that is important in industrial applications[1]. We have studied the possibility to detect the presence of H on the Zr (0001)-1x1 surface at the UHV conditions and different temperatures with photoemission, LEED and STM techniques. Two chemical states were identified at the clean surface, see Fig.1. Peak A corresponds to the metallic contribution to the Zr3d photoemission and we found a new peak B that we prescribed to the Zr-H bonding. It results from our experiments with adsorption and segregation of Si and Fe at the sub-monolayer coverage region. The deposited elements eliminate the presence of H at the surface and create a new structure. The $(2\sqrt{3}x\ 2\sqrt{3})R30^\circ$ structure is stable up to 750º C and it could be considered as an alternative way to passivate zirconium surface at extreme working conditions as in the nuclear power industry. STM experiment at clean surface was very difficult as we found plenty of fast moving species. The unstable surface shows destroyed trigonal symmetry with many defects due to bonded H atoms, (fig.2, $U_{bias}=0.1V$, I=1 nA). A small dose of O fastens moving species and produces short chains (up to 10 atoms). Hydrogen either desorbs or dissolves in the bulk that was proposed in the interpretation of the Zr corrosion process. We estimated the upper limit of H diffusion on this surface using STM current images and theoretical evaluation of the current changes in time at an identical position of the surface[2].

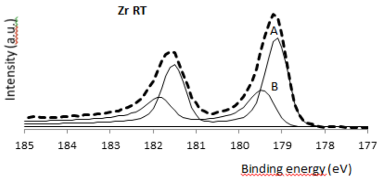

Figure 1.

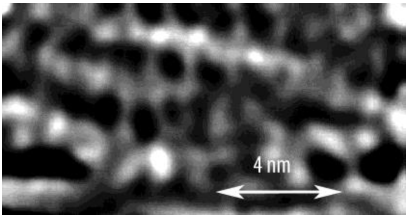

Figure 2.

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Preliminary evaluation of Co, Cu, Ru and Ni dye-sensitized-TiO_2 substrates as photocatalysts for water-splitting hydrogen production

J.E. Duran[(a) *], **L.W. Pineda** [(b)], **C. Rivera**[(b)], **D. Camacho** [(a)], **N. Montero**[(a)], **A. Jara**[(a)], **E. Gamboa**[(a)]

[(a)] *School of Chemical Engineering & CELEQ, University of Costa Rica, San José, Costa Rica, email: esteban.duranherrera@ucr.ac.cr*

[(b)] *School of Chemistry & CELEQ, University of Costa Rica, San José, Costa Rica*

Introduction

One of the big challenges in the use of renewable energies is finding efficient ways to store energy. In this sense, hydrogen is considered an excellent and environmental-friendly energy carrier, and solar water splitting the most desirable and promising process to produce it. A particularly emerging and promising technology for this process is heterogeneous photocatalysis. In this investigation, TiO_2 particles were modified with different anchor molecules and Co, Cu, Ru and Ni trimers as dye-sensitizers with the intention of extending the catalyst photon capture capacity. The effects of the catalyst modification and its preparation method on hydrogen production performance were assessed.

Experimental

For the synthesis of the photocatalysts, the trimers of different metals were prepared in first place. For this, reactions at different temperatures between 2,2 dipyridylamine, THF, n-Buli and metal chlorides were carried out. In parallel, the modification of the TiO_2 particle surface was done with different organic molecules (6-aminocaproic acid, glycine and p-aminobenzoic acid). These modifications were performed using two different heating methods, by microwave and under reflux. Finally, the metal dyes were anchored to the TiO_2-organic molecules. Hydrogen production experiments were carried out in a glass photoreactor equipped with a medium pressure lamp (365 W) at room temperature and pressure. Methanol was added as sacrificing agent (10% v/v).

Results and Discussion

The results indicate that the heating method utilized in the preparation of the photocatalysts does have an effect on their performance. Microwave heating produced more efficient photocatalysts. In a similar manner, the length and nature of the organic molecule used for anchoring the metal-dyes to the TiO_2 surface influenced the catalyst activity. Glycine, which had the shortest carbon chain, contributed to the development of better catalysts; however, p-aminobenzoic acid presented the best performance attributed to dislocated electrons of the aromatic ring. Photocatalists prepared using Cu and Co dye-sinsitizers presented the best results in terms of hydrogen production rates. For example, Co Trimer-Glycine-TiO_2 and Cu Trimer- p-aminobenzoic acid-TiO_2 catalysts prepared using microwave heating, presented specific production rates of 1887 and 2435 μmol h^{-1} g^{-1}, respectively. When Pt was added as co-catalyst, production rates up to 8250 μmol h^{-1} g^{-1} were registered. These results are remarkable if compared to the performance obtained by a CuO modified TiO_2 (155 μmol h^{-1} g^{-1}) prepared under the method reported by Xu & Sun[1].

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3rd Zing Hydrogen & Fuel Cells Conference

Day 2 Oral Presentations

Session 4

Nanomaterials

ZING CONFERENCES

Multifunctional materials for electronics and photonics

Federico Rosei
UNESCO Chair in Materials and Technologies for Energy Conversion, Saving and Storage
Centre for Energy, Materials and Telecommunications, INRS, 1650 Boul. Lionel Boulet, J3X 1S2 Varennes (QC), Canada

The bottom–up approach is considered a potential alternative for low cost manufacturing of nanostructured materials [1]. It is based on the concept of self–assembly of nanostructures on a substrate, and is emerging as an alternative paradigm for traditional top down fabrication used in the semiconductor industry. We demonstrate various strategies to control nanostructure assembly (both organic and inorganic) at the nanoscale. We study, in particular, multifunctional materials, namely materials that exhibit more than one functionality, and structure/property relationships in such systems, including for example: (i) control of size and luminescence properties of semiconductor nanostructures, synthesized by reactive laser ablation [2]; (ii) we developed new experimental tools and comparison with simulations are presented to gain atomic scale insight into the surface processes that govern nucleation, growth and assembly [3-7]; (iii) we devised new strategies for synthesizing multifunctional nanoscale materials to be used for electronics and photovoltaics [8-25]. Recent emphasis is on composite materials for water splitting / solar hydrogen [22, 26].

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Bimetallic catalysts for ethanol steam reforming: effect of operative conditions and bioethanol impurities

Vincenzo Palma, Concetta Ruocco* and Antonio Ricca
a, Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084, Fisciano (SA) Italy

Concerning ethanol steam reforming (ESR) process, the selection of proper operative conditions for coke formation minimization as well as the use of crude bioethanol streams appears crucial for costly and energetically effective H_2 production via reforming. Bioethanol is an aqueous solution which may contain some by-products (i.e. organic alcohols), capable of negatively affecting catalyst stability.

This work was focused on the study of bimetallic Pt-Ni/CeO_2-ZrO_2 catalysts for low-temperature ESR. The effect of different operative conditions (temperature, space velocity and water/ethanol molar ratio) on the stability of the catalytic formulation for steam reforming of a pure ethanol/water mixture was preliminary evaluated. Before every test, catalyst (V_{cat} = 4 cm^3) was activated under a 5vol. % H_2 in N_2 stream (1000 Ncm^3/min) at 600°C for 1 hour at an heating rate of 20°C/min. In order to analyse the influence of temperature (400-500°C), space velocity (GHSV ranging between 7500 and 30000 h^{-1}) and water/ethanol molar ratio (r.a. from 3 to 9) on carbon formation tendency, time on stream tests were carried out by keeping constant the ethanol concentration in the feeding stream (5vol. %). Temperature Programmed Oxidation (TPO) measurements were carried out in situ on the exhausts catalyst at 600 °C for 1 h at 10°C/min heating rate under 1000 Ncm^3/min flow rate of a gas mixture containing 5 vol. % of O_2 in N_2 and the carbon formation rate was evaluated starting from the area under TPO curve. It was firstly observed that the most favourable conditions for carbonaceous deposits formation are high temperatures and space velocities and low water contents in the feeding stream. Moreover, the formation of carbonaceous species, which occurred within the catalytic bed, caused the reactor plugging: pressure drops increased with temperature and space velocity with a quasi-exponential trend.

The study of the main bioethanol impurities was also performed by highlighting their influence on products distribution and hydrogen yields. The present work was focused on the analysis of the following contaminants: acetaldehyde (C_2H_4O), isopropyl alcohol (C_3H_7OH) iso-butanol (C_4H_9OH) and isoamyl alcohol ($C_5H_{11}OH$). These species were selected on the basis of the typical composition of a lignocellulosic bioethanol [1]. The results of catalytic tests performed at different operative conditions under pure mixtures suggested to evaluate the influence of raw bioethanol impurities (1 mol % with respect to ethanol) at 450°C, GHSV = 15000 h-1 and r.a. = 6. While acetaldehyde and isoamyl alcohol didn't sensibly affect carbon formation rate, C3 and C4 alcohol addition resulted in a faster reactor plugging due to coke formation. Nevertheless, the results obtained during the whole experimental campaign showed no evidence of catalyst deactivation, as ethanol was completely converted during time on stream. Therefore, the catalytic formulation may be suitable for industrial scale application, as the chance of feeding crude ethanol appears a critical issue for the overall process economy.

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Non-Noble Oxygen Reduction Catalysts by Means of Encapsulated Iron Carbide

Jens Oluf Jensen*, Yang Hu, Lijie Zhong, Chao Pan, Lars N. Cleemann and Qingfeng Li

Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark, jojen@dtu.dk

The most successful electro-catalysts for oxygen reduction in acidic environment, like in a PEM fuel cell, are based on noble metals, especially platinum. Due to cost and availability, it is highly desired to find alternatives without compromising activity or stability. In alkaline systems, a large number of metal oxides are known to be active and stable but so far, they are all unstable in acid. However, significant progress has been made in recent years with structures involving carbon and nitrogen and often transition metals.

The presentation will briefly outline the status for non-noble metal catalysts and present the activities at Technical University of Denmark on carbon encapsulated iron carbide for oxygen reduction.

The catalyst is prepared by a simple autoclave batch process in which the components self-assemble into spheres of about 500 nm. The crust of the spheres contains nanoparticles of Fe_3C somehow encapsulated by a carbon structure. The material exhibits high electrocatalytic activity for the oxygen reduction reaction and this is demonstrated in both acidic and alkaline media.[1-3]

Surprisingly, and in contrast to most other non-noble oxygen catalysts for acidic media, the present catalyst appears to function without nitrogen in the surface. It has been suggested that this may be a new catalytic site.[4] We believe the Fe_3C particles cause the activity, and since they are not normally stable in acid, it is likely that the carbon structure forms a protection against corrosion without eliminating the catalytic properties. The question is then how catalysis as a surface property can be expressed through the wrapping.

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Reverse microemulsion method for Fabrication of Nano-Nickel electrode: Electrolytic oxidation of Ethanol in direct ethanol fuel cell

Muhammad Imran Din

Institute of Chemistry, University of the Punjab, Lahore-54590, Lahore, Pakistan

Ni-nanoparticles plating has been prepared using Polysorbate 80/ *n*-hexane/ *n*-hexanol/ water microemulsion as electrolyte. The prepared micro emulsions were crystal clear and very stable at room temperature for more than 5 days. The microemulsion was used for electrochemical deposition of Nickel nanoparticles onto Nickel electrode through Brownian movement of water pools in micro emulsions to fabricate Ni-nano electrode. These electro-deposited Ni-nanoparticles were characterized by SEM, which revealed that uniform spherical nanoparticles of mean diameter 100 nm were deposited on electrode surface. The catalytic efficiency of synthesized material was investigated by using it as electrode for electro-oxidation of ethanol. The experimental data revealed that the efficiency of nano electrodes was much greater than bulk nickel electrode. Thus, the synthesized nano electrodes may be used to increase the efficiency of direct methanol fuel cell DMFC and direct ethanol fuel cell DEFC in future.

Oxidative steam reforming of ethanol with Pt-Ni/CeO_2-SiO_2 catalyst

Vincenzo Palma, Concetta Ruocco,Eugenio Meloni and Antonio Ricca
a, Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084, Fisciano (SA) Italy

Nowadays, the development of new technologies for clean energy generation is becoming an urgent need. In this scenario, bio-hydrogen (i.e. hydrogen from renewables) for use in fuel cells emerges as a very promising energetic vector. Among the different H_2 sources to be converted through reforming reaction, biomass-derived ethanol is gain particular attention, due to the benefit of combining a mature technology to a clean source. Moreover, when steam reforming is carried out with oxygen co-feeding, a notable reduction of operative costs can be achieved. However, in order to reach the desired performances at such operative conditions, the proper catalyst selection is crucial. Concerning this issue, the physiochemical properties of supports may significantly affect the catalyst performances. In particular, high surface area oxides allow a greater dispersion of the metal active phases.

In this paper, bimetallic Pt-Ni/CeO_2 catalysts supported over mesoporous silica were employed for ethanol reforming in the low-temperature range. The results of catalyst physiochemical characterization showed an increase of surface area as well as a reduction of both CeO_2 and NiO with respect to SiO_2-free samples [1]. Moreover, the results of XRD and Raman analyses displayed that no alloy or mixed oxides were formed between CeO_2 and SiO_2, suggesting that ceria has been forming a surface over-layer on SiO_2 substrate. In particular, catalyst behaviour was investigated under a $H_2O/C_2H_5OH/N_2$ as well as H_2O/C_2H_5OH/AIR mixture between 300 and 600 °C at different space velocities (10000-30000 h^{-1}). Ethanol conversion, for both steam (ESR) and oxidative steam reforming (OSR) reactions, was not affected by contact time decrease at T > 480°C while at lower temperatures, the space velocity growth led to reduced C_2H_5OH conversion, more pronounced when tests were performed without O_2 co-feeding. In fact, it was observed [2] that, in the presence of oxygen, the reaction rates for oxidation reactions are higher than those under ESR conditions. It's worthwhile noting also that O_2 was completely converted in the temperature interval investigated, independently from contact time applied. Moreover, the catalysts showed high resistance to deactivation during reforming tests at 500°C and 20000h^{-1}: the improvement of active species dispersion, as a consequence of catalyst formulation enrichment by SiO_2 addition, resulted in lower carbon selectivity with respect to the SiO_2-free sample. However, the higher extent of coke gasification reaction for OSR reaction further increased catalyst stability and total ethanol conversion was recorded for almost 3500 min, 1000 min more than ESR case. Moreover, O_2 addition promoted carbon monoxide oxidation to CO_2, coupled to a much less evident reduction of hydrogen selectivity. Further investigations will be focused on catalyst performances evaluation at different water/ethanol as well as oxygen/ethanol ratios.

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3rd Zing Hydrogen & Fuel Cells Conference

Day 3 Oral Presentations

Session 6

Systems

ZING CONFERENCES

Hydrogen Safety Engineering for Indoor Systems

Vladimir Molkov
Hydrogen Safety Engineering and Research Centre (HySAFER), University of Ulster, Newtownabbey, Shore Road, BT37 0B, Northern Ireland, UK

This plenary gives an overview of the state-of-the-art in hydrogen safety engineering of indoor systems achieved within the HyIndoor project (www.hyindoor.eu) funded by Fuel Cell and Hydrogen Joint Undertaking. Physical phenomena, associated hazards and consequences relevant to indoor use of hydrogen and fuel cell systems are discussed.

The predictability of the original model of passive ventilation of unignited releases is compared against experimental data by CEA[1]. The passive ventilation model predictions are closer to experimental data than calculations by former natural ventilation models. Computational Fluid Dynamics (CFD) is considered as a contemporary and the most promising tool for hydrogen safety engineering. The Large Eddy Simulation (LES) model demonstrated a better reproducibility of experiments in an enclosure with different vents and release conditions compared to laminar and standard k-epsilon models[2].

The results of numerical studies of indoor jet fires in a passively ventilated enclosure are presented[3]. The dynamics of both well-ventilated and under-ventilated hydrogen fires in fuel-cell-like enclosure are simulated by the CFD model that includes detailed chemistry. Different regimes of indoor fire are identified. Phenomena of hydrogen indoor fire self-extinction and external flame are simulated for the first time. The simulations demonstrated a complex flow dynamics of reacting mixture in the enclosure during self-extinction and external flame regimes.

The increase of fire resistance of on-board hydrogen storage is identified as the main safety strategy for hydrogen-powered vehicles to exclude the so-called pressure peaking phenomenon[4] that can destroy a garage in a second if existing release rates from TPRD of about 400 g/s will be accepted further. The increase of fire resistance of on-board storage from about 10 to 1-2 hours would allow the essential decrease of TPRD diameter. This in turn would reduce flame length by orders of magnitude to let passengers to perform self-evacuation and first responders to carry out rescue operations. Reduction of TPRD diameter would exclude the pressure peaking phenomenon in a garage at all.

Safety strategies and technique to mitigate localized deflagrations in enclosures are presented.

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Hydrogen and fuel cells in the context of Closed Loop Mobility

John Jostins, (Microcab), Christophe Quillivic, (Coventry University)
Coventry University, Priory Street, Coventry, United Kingdom. CV1 5FB

Cities and citizens need mobility of various types. Getting around cities requires a wide range of public transport, as well as opportunities for cycling and walking, all optimised and integrated using digital information systems. Congestion and air quality are serious problems in cities, exacerbated by slow moving traffic dominated by internal combustion engines. Human health is put at risk and frustration and lower productivity are the results. This paper discusses a model whereby a fleet of compact fuel electric vehicles are employed in a car sharing scheme in an urban context. The vehicles are owned and operated by a car sharing entity for the purpose. Alternative business models such as car sharing clubs are growing as citizens realise that private car ownership is not necessarily the optimum way to access personal mobility in these environments. 'London has one of the largest car club markets in Europe, with over 135,000 members in January 2015' http://content.tfl.gov.uk/tfl-car-club-strategy.pdf

Hydrogen for refuelling the fleet is generated from water using peak renewable energy available in the region where the fleet is to be deployed. Renewable energy such as wind power is variable and often peak power is wasted if the grid is congested. As renewable energy systems increase, energy storage becomes a more pressing issue in order to maximise the use of these resources. At peak times energy can be used to electrolyse water to produce hydrogen for use later, giving a very low carbon fuel. Fuel cell vehicles using hydrogen in urban mobility offer zero emissions, quick fill and longer range than their EV counterparts. With electric drive, these vehicles are clean at point of use but can be refuelled in minutes.

The vehicles themselves will be designed, built and maintained in the context of a circular economy where the underlying base vehicle has an extended life and sub-systems are remanufactured at appropriate intervals within that lifespan. Vehicles operated and maintained in a circular economy make better use of valuable resources. As the vehicles are not owned by the end users, this is an ideal scenario to enact a circular economic model, as the controlling entity wants to maximise the use of resources, where the private owner could dispose of the car in an unregulated way, leading to eventual scrappage. In the car sharing scenario, the user does not own the vehicle but simply uses it for a period of time for their mobility needs. This car sharing model optimises vehicle use, minimises congestion by reducing vehicle numbers, gives clean air at point of use and uses green hydrogen, produced by excess renewable energy, as a vehicle fuel.

Microcab is currently engaged on two InnovateUK funded projects, 'Fuel Cell Recovery' (2014-2016) about the remanufacture of fuel cells and 'Closed Loop Mobility' (2015-2016) which investigates the feasibility of car sharing, hydrogen fuel cell powertrains and the circular economy. These projects will be discussed in the paper.

Key words: Hydrogen, fuel cells, fuel cell electric vehicles, car sharing, mobility, cities, circular economy, air quality.

Effect of non-regulated pH on the dynamics of dark fermentative biohydrogen production with suspended and immobilized cell culture systems

Joelle Penniston, E.B. Gueguim Kana*
University of KwaZulu-Natal, School of Life Sciences, Pietermaritzburg, South Africa

Biohydrogen has been identified as a promising alternative to the use of non-renewable fossil reserves, owing to its sustainability and non-polluting nature. pH is considered as a key parameter in fermentative biohydrogen production processes, due to its effect on the hydrogenase activity, metabolic activity as well as substrate hydrolysis. The present study assesses the influence of regulating pH on dark fermentative biohydrogen production. Four experimental hydrogen production schemes were evaluated. Two were implemented using suspended cells under regulated pH growth conditions (Sus_R) and suspended and non-regulated pH (Sus_N). The two others regimes consisted of alginate immobilized cells under pH regulated growth conditions (Imm_R) and immobilized and non-pH regulated conditions (Imm_N). All experiments were carried out at 37.5°C with glucose as sole source of carbon. Sus_R showed a lag time of 5 hours and a peak hydrogen fraction of 36% and a glucose degradation of 37%, compared to Sus_N which showed a peak hydrogen fraction of 44% and complete glucose degradation. Both suspended culture systems showed a higher peak biohydrogen fraction compared to the immobilized cell system. Imm_R experiments showed a lag phase of 8 hours, a peak biohydrogen fraction of 35%, while Imm_N showed a lag phase of 5 hours, a peak biohydrogen fraction of 22%. 100% glucose degradation was observed in both pH regulated and non-regulated processes. This study showed that biohydrogen production in batch mode with suspended cells in a non-regulated pH environment results in a partial degradation of substrate, with lower yield. This scheme has been the culture mode of choice for most reported studies in biohydrogen research. The relatively lower slope in pH trend of the non-regulated pH experiment with immobilized cells (Imm_N) compared to Sus_N revealed that that immobilized systems have a better buffering capacity compared to suspended systems, which allows for the extended production of biohydrogen even under non-regulated pH conditions. However, alginate immobilized cultures in flask systems showed some drawbacks associated to high rate of gas production that leads to increased buoyancy of the immobilization beads. This ultimately impedes the release of gas out of the flask.

Process intensification in Methane Steam Reforming for H_2 production: an innovative catalytic configuration

Vincenzo Palma, Antonio Ricca*, Marco Martino, Eugenio Meloni
*Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy - *e-mail: aricca@unisa.it*

Nowadays, H_2 employment in fuel cell was pointed as the most viable route towards green energy solution. The main technique to produce hydrogen is catalytic methane steam reforming (MSR), a highly endothermic reaction carried out at very high temperature. The process intensification in this sense was focused on the improved heat and mass transfer management in the catalytic volume. Previous studies[1] demonstrated that structured catalysts characterized by a allowing a flatter thermal profile along the catalytic bed, reducing also hot-spot phenomena. This results in a higher average temperature at the outlet section of the catalytic bed and consequently in higher conversion. This study focused on the Steam Reforming (SR) process intensification obtained in one hand by optimizing the chemical formulation of SR catalyst, in the other hand by deposing the catalyst on a Silicon Carbide (SiC) monolith (porous walls, honeycomb shape), characterized by excellent thermal conductivity and mechanical resistance. High thermal conductivity greatly affected the non-adiabatic processes performances,

Ni / (CeO_2-Al_2O_3) based catalysts were prepared and tested in order to investigate the role of Ceria and Alumina on the catalytic performances. The oxygen-storage capacity ascribed to Ceria increased catalyst reducibility, and in turn improved catalytic performances in reforming reactions. On the other hand, the alumina presence increased the thermal stability to the sample, affecting on hydrocarbon conversion.

Once optimized the catalytic formulation, experimental tests carried out on SiC catalytic honeycomb monolith demonstrated that the physical properties of the support resulted in a marked system performances enhancement. One of the most relevant limitation in SR processes is the difficulty in provide heat to the catalytic system in the operating high temperatures. The high thermal conductivity of the SiC allows to minimize heat transfer resistance from the heating medium to the catalytic volume and optimize the thermal management along the catalyst, so increasing the heat flux toward the reaction volume and in turn maximizing the reforming reactions rate. A further investigation was carried out by alternately plugging the channels of the catalysed monolith, so forcing gas to cross the porous walls of the catalyst. Such arrangement (named Wall-Flow (WF)) was responsible to a deeper contact between the gas (reactants) and solid (catalyst) phase that in turn maximized the mass transfer rate, crucial in the homogeneous catalysis. As a result, an evident performances increasing was achieved in WF configuration with respect to the common FT (Flow-Through) channels monoliths, both in terms of methane conversion and hydrogen production; the benefit was more evident at lower temperature, in which mass transfer of gas stream in catalysts porosity were less promoted.

Therefore, the catalyst optimization in chemical and engineering point of view appeared able to enlarge the steam reforming operating window. In particular, the high conductive structured catalyst allowed to obtain appreciable performances for high reactants rate and relatively low temperature, without employing noble metals based formulations.

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Sorption-enhanced Reaction for High-purity Hydrogen Production

Chan Hyun Lee, Ki Bong Lee*

Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 136-713, Republic of Korea.

Hydrogen is receiving attention because of its possibility as a new clean energy carrier. For mass production of hydrogen, synthesis gas produced from coal gasification and/or methane in natural gas are converted to hydrogen through shift and/or reforming reactions. The thermodynamic limitation of the conventional hydrogen production reaction can be circumvented by applying the sorption-enhanced reaction (SER) concept. SER has outstanding advantage of producing high-purity hydrogen directly without further purification processes, because by-product CO_2 is removed by sorption simultaneously with reaction in a single reactor. As a method for further improving SER, a multi-section column packing concept was recently proposed, and it was shown that high-purity hydrogen productivity could be improved. In this talk, the SER concept for high-purity hydrogen production is introduced and recent studies on the application of multi-section column packing concept are explained. The experimental results showed that more high-purity hydrogen could be produced by applying multi-section column packing concept with one-body hybrid solid pellets to SER.

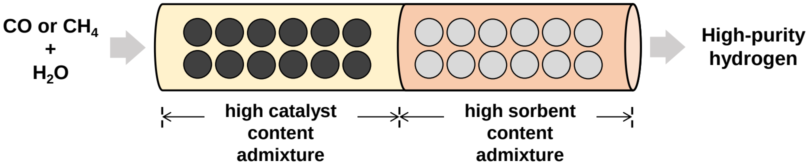

Figure 1.

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3rd Zing Hydrogen & Fuel Cells Conference

Day 3 Oral Presentations

Session 7

Applications

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Polymer Electrolyte Electrolyser versus Solid Oxide Electrolyser Technology: A Comparison of How to Make Hydrogen

Brant A. Peppley

Queen's University, Kingston, ON, CANADA

There is an urgent need for energy storage technologies to couple with the rapidly expanding generation capacity of wind and solar renewables. A major issue is fast response and the ability to react to the dramatic fluctuations in renewable power generation. Although the alkaline electrolyser is the most widely used industrial scale electrolysis technology it suffers dramatic losses in efficiency in transient operation. The PEEC on the other hand has very fast response to current fluctuations but is much more costly in terms of capital cost.

This presentation will examine the broader applications of each technology with a perspective on moving toward a zero-carbon fuel infrastructure. The benefits of each technology will be examined both in the near term scenario and for the longer term transition to a broader utilization of hydrogen as a transportation fuel.

Disrupting the Business Case Around Solid State Hydrogen Storage

Chris Reid
Hydrexia; Disrupting The Business Case Around Solid State Hydrogen Storage

The paper presents three case studies that evaluate the performance and economics of solid state Hydrogen storage systems based on metal hydride technology against incumbent solutions:

1. Hydrogen storage and delivery for industrial markets
2. Hydrogen storage and delivery for FCEV refueling applications
3. Hydrogen storage and supply for steam methane reformer backup applications

Each case study presents both the market requirements and product configuration for the intended solution. The analysis compares the total cost of ownership of contemporary solid-state product against incumbent solutions, including bulk tube trailers, liquid hydrogen supply and onsite generation. The paper also illustrates real-world project examples of hydride based storage products in operation around the world.

The analysis of the business case shows that the latest generation of hydrogen storage systems based on metal hydrides offer significant commercial advantage over not only traditional storage methods, but previous hydride-based systems, and illustrates a pathway for adoption in applications traditionally considered uneconomical for this technology.

Metal Hydrides for Hydrogen Storage

Metal hydrides have been researched for many years as a compact solution for hydrogen storage and delivery. Hydrogen is absorbed into the metal powder and stored at low pressure inside a containment vessel and heat input is needed to release the hydrogen from the vessel. Magnesium hydride (MgH2) systems have seen considerable interest for their high gravimetric and volumetric storage density.

Metal hydride storage and delivery products can address many of the challenges currently faced by today’s hydrogen infrastructure.

1. Industrial Hydrogen Delivery - Hydrogen is an expensive commodity for fuel because it is difficult to store and transport in high density. Compressed hydrogen customers can pay up to 10X the feedstock cost because of the expensive logistics costs associated with compressed gas delivery. Liquid hydrogen (LH2) presents a lower cost storage and delivery method for high-volume supply, but LH2 systems require substantial upfront capital investment.

2. Hydrogen Energy Infrastructure - Hydrogen re-fuelling customers, such as energy companies and fleet operators, are often challenged by siting and regulatory requirements for compressed and liquid hydrogen systems particularly in urban or retail environments, where space is a constraint and at a premium for station operators.

3. Renewable Energy Infrastructure - Harnessing renewable sources of hydrogen, such as wind, solar biomass, as well as waste hydrogen sources from chemical plants and industrial processes, is challenging because of the low-pressure and sometimes intermittent nature of supply. Conventional hydrogen storage and delivery solutions are not well matched to these low-pressure renewable sources, requiring substantial capital infrastructure investment for compression or liquefaction plants.

Disrupting the Business Case Around Solid State Hydrogen Storage

Chris Reid continued

Magnesium-hydride storage systems can store or deliver hydrogen at higher densities, lower pressures and lower costs in all of the above application spaces. They offer a safe, low-pressure and small footprint storage solution for urban and retail hydrogen refuelling stations and solid-state products pair well with low-pressure renewable hydrogen sources, requiring only simple and low-cost integration. Notwithstanding these technical advantages, with no compelling business case, commercial take-up of these systems will be somewhat limited.

New hydride materials based around a proprietary alloy have been developed which produce a refined metallic grain structure that enables fast kinetics for absorbing and desorbing hydrogen, without requiring specialized milling or handling processes.

Eliminating these costs fundamentally changes the business case around the adoption of this storage technology in traditional and emerging markets including:

- Industrial Merchant Hydrogen Storage and Delivery
- Hydrogen Energy Infrastructure
- Renewable Energy Storage

The paper describes two nominal product configurations, including storage and delivery architecture as well as balance of plant system requirements for filling and discharging hydrogen at the customer site:

- Electric Stationary Platform (ESP) - a portable and scalable solution designed for deployment at industrial and energy customer sites that currently use multi-cylinder packs or bulk tube trailers for ground storage. Standard electric packs store 100kg of hydrogen and provide a compact, safe and low cost bulk storage solution. Packs can be easily delivered to customer sites using a truck and crane system
- Oil Trailer Platform (OTP) - a mobile solid-state trailer that is designed to maximize hydrogen delivery density and minimize hydrogen delivery cost. The intended application is bulk tube trailer replacement for industrial and emerging energy markets. In this configuration a solid-state trailer can store and deliver 900kg H2, over 3 time the capacity of a standard bulk tube trailer.

Also described are the design configurations, system specifications and performance data which form the basis of the three case studies.

Case Studies

Three case studies are presented in the paper that evaluate the performance and economics of solid state Hydrogen storage systems based on metal hydride technology against the incumbent solutions:

1. Hydrogen storage and delivery for industrial markets
2. Hydrogen storage and delivery for FCEV refuelling applications
3. Hydrogen storage and supply for steam methane reformer backup applications

Each case study presents both the market requirements and product configuration for the intended solution. The analysis compares the total cost of ownership of contemporary solid-state product against incumbent solutions, including bulk tube trailers, liquid hydrogen supply and onsite generation. The paper also illustrates real-world project examples of hydride based storage products in operation around the world.

Effect of GDL Structure on the Performance of Air-Cooled, Open-Cathode Fuel Cells Using Hydro-Electro-Thermal Analysis.

Q. Meyer,[a] S. Ashton[b], D. Finegan[a], E. Engebretsen[a], Pierre Boillat[c,d], Magali Cochet[c], Paul Adcock[b], P.R Shearing[a,e], D. J.L. Brett[a]*

[a]*Electrochemical Innovation Lab, Department of Chemical Engineering, UCL, London, WC1E 7JE, UK,*
[b]*Intelligent Energy, Ashby Road, Loughborough, LE11 3GB, UK.*
[c]*Electrochemistry Laboratory (LEC), PSI, 5232 Villigen, Switzerland.*
[d]*Neutron Imaging and Activation Group (NIAG), PSI, 5232 Villigen, Switzerland*
[e]*UCL/Zeiss Centre for Correlative X-ray Microscopy, UCL, London, WC1E 7JE, UK*

Polymer electrolyte fuel cells (PEFCs) fuelled with hydrogen is among the most promising energy conversion technologies for a broad range of applications. *In situ* diagnostic techniques provide a means of understanding the internal workings of fuel cells so that improved designs and operating regimes can be identified. Therefore, the combination of existing metrologies and development of novel methods is crucial to enable the next breakthrough in fuel cell performances. Investigations of the dead-ended anode[1], current of lowest resistance[2], current and temperature mapping via a single PCB sensor plate[3], combined with water mapping in through-plane using neutron imaging[4], and hydro-electro-thermal analysis, has enabled optimum operating regimes to be identified, at the cell and stack level.
Here, the effect of two commercial cathode gas diffusion layers with high/low porosity is characterised using these novel diagnostic techniques. Firstly, their porosity was extracted *ex-situ* using X-ray CT tomography (VERSA, ZEISS). Then these two GDL were analysed *in-situ,* inserted in two, otherwise identical, air-cooled open-cathode stacks to study how the structure influences the hydro-electro-thermal profile in steady-state and transient operation. The stacks were imaged in in-plane and through-plane orientation in order to separate cathodic and anodic water and characterise the water transients across the cell (NEUTRA, Paul Scherrer Institute), meanwhile the current and temperature profiles have been monitored to investigate the effect of the water gradients on the performance.

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Fire Resistance of Onboard Hydrogen Storage: Recent Developments in Thermal Protection

Dmitriy MAKAROV, Vladimir MOLKOV, Yangkyun KIM, Sergii KASHKAROV
Fire Safety Engineering and Research Centre (HySAFER), Ulster University, Shore Road, Newtownabbey, Co.Antrim, BT370ZA, UK
dv.makarov@ulster.ac.uk

Hydrogen-powered fuel-cell vehicles (FCV) are hitting roads and refuelling stations are operating in different countries around the world. Full-scale commercialisation of hydrogen and fuel-cell systems brings safety on the forestage of research and development in associated technological areas. The fire resistance of onboard hydrogen storage remains one of the main unresolved technological safety issues for hydrogen-powered vehicles.

The most widespread for FCV use Type 4 tanks are made of carbon-fibre reinforced polymer (CFRP) with plastic liner and can stand in fire up to about 6-8 minutes before catastrophic failure. Review of available car fire statistics (15,500 accidental car fires annually in the Great Britain alone) suggests that a FCV fire is a realistic scenario, which is addressed in regulations, codes and standards (RCS) by the requirement to conduct a bonfire testing of on-board high-pressure hydrogen storage tank. Standards do not specify fire resistance or requirements to safety of TPRD operation, which silently assumes “as fast as possible” blowdown strategy creating unacceptably large hydrogen jet fires, compromising evacuation and intervention of first responders, general public safety and property protection. However higher fire resistance rating (FRR) would allow longer hydrogen release from TPRD, smaller hydrogen flow rate and shorter jet flame, inherently safer rescue operations by first responders and self-evacuation, public acceptance of the technology, etc.

The talk will give overview of ongoing research programme conducted at Ulster University to improve fire resistance of Type 4 tanks. The programme combines modelling and experimental research. Pre-test numerical simulations indicated that use of thermal protection has a potential to increase FRR of Type 4 tanks beyond car fire duration. It was also demonstrated that specification of temperature dynamics in bonfire protocol does not guarantee unique test outcomes: fire resistance may depend on the burner type and the bonfire heat release rate (HRR), yet fully complying with RCS requirements on temperature.

For the experimental programme the research team collaborated with Karlsruhe Institute of Technology (Germany), where a series of experiments to test bare and thermally protected Type 4 hydrogen tanks was conducted. The experiments were performed in a closed 220 m^3 vessel with a premixed methane-air burner according to the requirements of “Engulfing fire test” section of the Global Technical Regulation on hydrogen and fuel cell vehicles 2013 (GTR#13). The experimental bonfire programme included testing effect of thermal protection of the tank, bonfire HRR, etc. Thermal protection solutions included different thicknesses of intumescent paint coating (as a typical industrial fire protection technique) and dual shell tank design with in-between thermal insulation material.

The major achieved outcome of the research programme is a practical realisation of the order of magnitude longer FRR: while FRR of bare tanks was 8-9 minutes, i.e. similar to the available from literature data, the tank coated by 20 mm intumescent paint layer withstood fire test for 1 hour 50 minutes until the test was terminated due to fully consumed fuel for the burner. The bonfire tests also confirmed predicted in simulations effect of bonfire HRR on FRR: fire tests with HRR 170 and 78 kW

Fire Resistance of Onboard Hydrogen Storage: Recent Developments in Thermal Protection

Dmitriy MAKAROV continued

lead to fire resistance of bare unprotected tanks 8 and 16 minutes respectively, though both complied with the GTR#13.

The research results highlighted a gap addressing public safety in current RCS, and the project team is working on bringing this information to standard developing organisations, regulators, and health and safety officials.

Hybridization of PEM Fuel Cell using Genetic Optimization

Marco A. Rodríguez[a]

a, Electrical and Computer Engineering Department, Binghamton University, 4400 Vestal Parkway East, Binghamton, NY 13902, USA.

Hydrogen fuel cells such as proton exchange membrane fuel cells (PEMFCs) convert chemical energy into electrical energy without producing air pollutants. PEM fuel cells are better operated in steady state. Sudden changes in power demand cause mechanical stress and deterioration of fuel cell components. Fuel cell hybridization with high power density devices such as batteries or supercapacitors is usually implemented to augment the fuel cell's power during sudden spikes in power demand. Hybridization with batteries or supercapacitors has the additional benefit of allowing the recovery of energy during periods when the load acts as a generator.

This study developed a genetic optimization program to determine key switching rules for the optimum operation of a DC motor to which sudden changes in power demand are introduced. These power demand changes can be in the form of higher or lower power requirements. Making an analogy to driving cycles, three operating modes are investigated: ‘flat' mode, ‘uphill' mode and ‘downhill' mode. A PEM fuel cell model is also developed. This study not only demonstrated the effectiveness of genetic optimization in the modeling of PEMFCs and the definition of optimum hybridization switching rules, but it assisted in the discovery of new possibilities than translated into better `AND' and 'OR' logical statements for the three operating modes. We also witnessed the importance of accurate fuel cell and supercapacitors modeling.

3rd Zing Hydrogen & Fuel Cells Conference

Day 3 Oral Presentations

Session 8

SOFC/SOE/PEMWE

ZING CONFERENCES

SOFCs on the move from high to low temperature operation

Søren Linderoth
DTU Energy, Technical University of Denmark (DTU)

SOFCs (Solid Oxide Fuels Cell) typically works at rather high temperatures which in particular stems from the need thermal activation of the ionic conduction in the solid oxide electrolyte. In some cases the operating temperature is app. 1000oC, however, in order to lower the overall system costs, incl. choice of materials, the development is towards lower operating temperatures. This has required new designs of SOFCs and much improved functional materials (electrolyte and electrodes). The operating temperature is now approaching 400-600 oC, which in the context is considered low temperature. This development is achieved by, and allows for, new materials choices. Here the development of metal-supported SOFCs will be presented and discussed, utilizing both traditional thick film techniques, such as e.g. tape casting, screen printing, infiltration techniques, - and thin film techniques, such a pulsed laser deposition (PLD) techniques.

3rd Zing Hydrogen & Fuel Cells Conference

Day 3 Oral Presentations

Session 9

Fuel Cell Materials

ZING CONFERENCES

Determination of Permeability of Gas Diffusion Layer of Proton Exchange Membrane Fuel Cells

Sadegh Hasanpour, A.B. Phillion and Mina Hoorfar
School of Engineering, the University of British Columbia, Kelowna, BC, V1V1V7, Canada.

One vital component of proton exchange membrane fuel cells (PEMFCs) is the gas diffusion layer (GDL), which provides a pathway for the reactants to reach the reaction sites and for the by-products to be removed. Different transport properties (including permeability) of this layer have been investigated experimentally and numerically[1]. For the latter involving modelling species transport through this highly porous structure, identifying a geometry that best resembles the GDL is very important. In this study, 3D images of a GDL sample have been obtained with high resolution imaging, X-ray microtomography, and used as a model to simulate flow through this layer. This layer is typically treated with micro-porous layer (MPL). In this paper, MPL was separated and permeability through the MPL is investigated separately using an image-processing method developed in-house. The results indicate that MPL reduces the permeability of GDL considerably. This work facilitates the study of the effect of MPL on the permeability of the GDL, which is impossible to be determined using experimental approaches alone.

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Electrical and thermal bulk resistance of non-uniformly compressed Gas Diffusion Layer

Ajit Vikram, Prabudhya Roy Chowdhury, Ryan Philips, Sadegh Hasanpour, Mina Hoorfar,*

School of Engineering, University of British Columbia, Kelowna, V1V 1V7, Canada.

Optimization of gas diffusion layer (GDL) properties, including electrical and thermal conductivity, is very crucial for enhancing the performance of proton exchange membrane (PEM) fuel cells. In an actual fuel cell assembly, the GDL is compressed between a channelled bipolar plate (BPP) and a nearly flat membrane. Increasing compression of the fuel assembly not only decreases the thermal and electrical resistance of the GDL, but also provides higher resistance to the gas flow, due to decreased porosity of GDL. Due to the channel and rib structure of the bipolar plates at the GDL-BPP interface, the compression over the GDL is not uniform. As a result, the electrical and thermal bulk properties of the GDL changes from those occurred for uniform compression. Most experimental methods reported in the literature for the measurement of the thermal and electrical resistance of the GDL have either not taken the effect of non-uniform compression of the GDL into account[1] or have not separated the effective bulk resistance of the GDL from the overall assembly resistance[2]. In this work, an experimental setup was developed to estimate accurately both electrical and thermal effective bulk resistances of the GDL for both cases of uniform and non-uniform compression. The contributions of the BPP bulk resistance, contact resistance at all interfaces, and any external circuit resistance were eliminated to obtain the effective bulk resistance of the compressed GDL. The experimental results for both thermal and electrical resistance as a function of compression pressure showed a significant variation in the GDL bulk resistance for the case of the non-uniformly compressed GDL compared to that of the uniformly compressed GDL (see Figure 1). The electrical bulk resistance of the GDL (Figure 1(b)) is lower for non-uniformly compressed GDL compared to the uniform compression (for the majority of the compression pressure studied here). However, the thermal bulk resistance of non-uniformly compressed GDL came out to be higher than the uniformly compressed GDL.

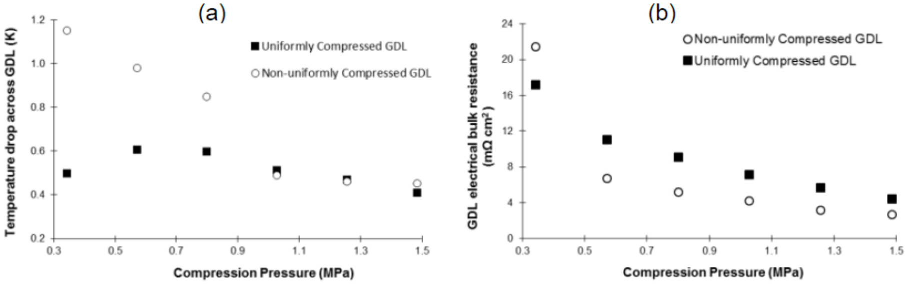

Figure 1. (a) Thermal and (b) electrical bulk resistances of the uniformly and non-uniformly compressed GDLs as a function of the compression pressure

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TBC

Walter Merida
Clean Energy Research Centre, 2360 East Mall, Vancouver, BC, V6T 1Z3 Canada

No abstract submitted

3rd Zing Hydrogen & Fuel Cells Conference

Day 4 Oral Presentations

Session 10

Hydrogen

ZING CONFERENCES

Electrochemical Conversion of Biomass for Clean Hydrogen Production

C. Coutanceau

Université de Poitiers, IC2MP, 4 rue Michel Brunet, 86000 Poitiers, France

Facing the depletion of fossil resources and the environmental issues related to their use, the modern society has to develop eco-processes for energy production, conversion and storage. In this context, the hydrogen economy has emerged as a solution by proposing the production of electricity using polymer electrolyte membrane fuel cells (PEMFC) particularly for transport applications. However, the success of this approach leans on the broad availability of molecular hydrogen.

Hydrogen is one of the most abundant elements in the universe, but on earth it does not exist as dihydrogen molecules, or in non-significant amount. It is almost always combined with carbon (in hydrocarbons), oxygen (in water) or both in biomass (carbohydrates, alcohols, etc.), so that it has to be produced prior to its use in a fuel cell. Currently, more than 95 % of hydrogen produced in the world (ca. 50 million tons per year) comes from fossil resources, particularly from natural gas reforming. About 4 % of hydrogen production comes from water electrolysis, which can be a renewable method according to the primary energy sources (use of renewable energy such as solar, wind and tidal energies), but this technology remains still expensive due to material costs and/or low energy efficiency.

As alternative, it has been proposed to produce hydrogen by reforming of biomass. However, the processes are relatively complex and need flash pyrolysis or gasification steps to produce syngas, a mixture of dihydrogen, carbon monoxide, carbon dioxide, water, methane, etc. Moreover, the reforming of carbon-containing compounds (e.g., hydrocarbons and biomass) produces hydrogen streams containing significant amounts of carbon monoxide (CO), which is a poison for platinum-based catalysts in low temperature fuel cells, leading to poor electrical performances. Hence, time and energy consuming processes, not to mention cost, have to be implemented to produce hydrogen streams containing less than 20 ppm CO, thus suitable for use in PEMFC.

Following the example of the water electrolysis process, which leads to extremely high-purity hydrogen, the electrolysis of compounds from biomass (alcohols, polyols, sugars, etc.) can be a very good alternative for the production of clean hydrogen. The conversion of biomass by electrochemical methods can be performed in aqueous media or deep eutectic solvents at low temperatures and pressures. The control of the electrode potential, electrolyte pH and nature, concentration, and the adequate formulation of catalysts lead to improve the conversion rate and the selectivity of the reaction towards desired products. Moreover, the biomass conversion at the anode of an electrolysis cell is performed simultaneously with the production of pure hydrogen at the cathode. Hydrogen may be stored for further energy conversion in a fuel cell, or used as chemical reagent for further chemical hydrogenation reactions.

Hydrogen and added value chemicals cogeneration may allow increasing economical and industrial interests towards electrochemical technologies. Indeed, such technology leads to decrease the electrolysis cell potential (energy saving) for hydrogen production in comparison with water electrolysis and generation of value added or industrially interesting compounds.

A Summary of Canada's Program on Hydrogen Production using the Thermo-chemical Cu-Cl Cycle

Kamiel S. Gabriel[1] (Kamiel.gabriel@uoit.ca), **and Greg F. Naterer**[2] (gnaterer@mun.ca)

1. Professor, Automotive, Manufacturing and Mechanical Engineering, University of Ontario Institute of Technology (UOIT), 2000 Simcoe Street N., Oshawa, Ontario, L1H 7K4, Canada
2. Professor and Dean, Faculty of Engineering & Applied Science, Memorial University of Newfoundland, St. John's, NL, A1B 3Y1, Canada

Thermochemical hydrogen production cycles utilize heat as the main energy input to split water through a series of reactions in a closed cycle for hydrogen production. One of the promising energy sources is a Generation IV (Gen IV) nuclear reactor that could provide the high temperature requirement of the thermochemical hydrogen production cycles. Heat must be extracted from the Gen IV reactors and transported to the hydrogen production plant, then transferred to the endothermic reactors in the cycle. The University of Ontario Institute of Technology (UOIT), Canadian Nuclear Labs (subsidiary of Atomic Energy of Canada Limited), Argonne National Laboratory (ANL) and several other partner institutions in Canada, US, and Europe are currently collaborating on the development of enabling technologies for the Cu-Cl cycle. The Cu-Cl cycle is a sequence of thermochemical and physical processes, which include electrolysis, hydrolysis, thermolysis, and evaporative drying. In the 4-step cycle, the water splitting process begins in the hydrolysis reactor where steam reacts with cupric chloride (solid) to form copper oxychloride (solid) and hydrochloric gas (see Fig. 1).

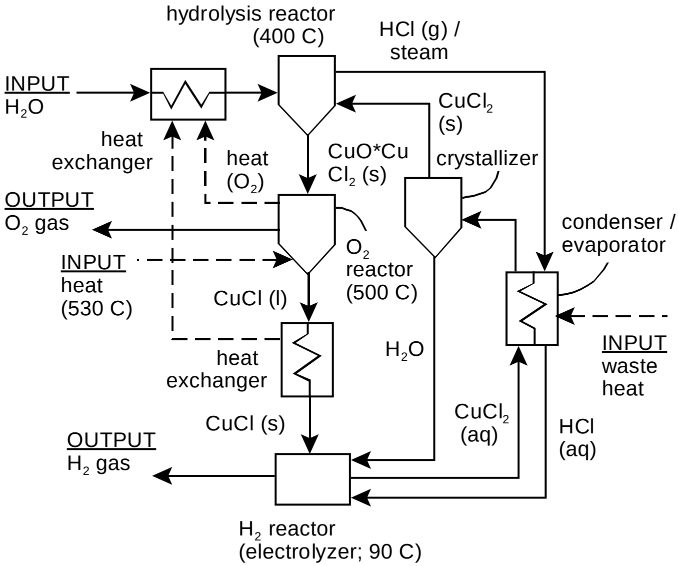

Fig. 1. Schematic of a thermochemical copper-chlorine cycle

For successful operation of the Cu-Cl cycle for hydrogen production, it is important to efficiently design intermediate processes of integration of the main steps. As depicted in Fig. 1, molten CuCl leaves the oxygen reactor, enters an intermediate step which recovers heat, thus changing phase to solid, and

A Summary of Canada's Program on Hydrogen Production using the Thermo-chemical Cu-Cl Cycle

Kamiel S. Gabriel continued

then reaches the electrolysis reactor for the production of hydrogen. Similarly, moist HCl gas leaves the hydrolysis reactor and condenses and enters the electrolysis reactor. The performance of the cycle is improved by dissolving the solid CuCl particles in aqueous HCl before reaching the electrolysis cell. A detailed understanding of the dynamics of the particles and the dissolution rates aids in the design of the mixing step and effective integration of the cycle.

This presentation provides an overview of the status of Canada's program in hydrogen production[1] using the thermochemical copper-chlorine (Cu-Cl) cycle. Enabling technologies for the Cu-Cl cycle are being developed by a Canadian consortium, as part of the Generation IV International Forum (GIF) for hydrogen production with potential link to the next generation of nuclear reactors. Recent advances towards an integrated lab-scale Cu-Cl cycle are discussed, including experimentation, modeling, simulation, advanced materials, thermo-chemistry, safety, reliability and economics.

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Electrical and Structure Response of The Sample $La_{0.5}Ca_{0.5}Fe_{1-x}Mn_xO_3$ With Potencial Aplications in Solid Oxide Fuel Cells SOFC

H.A Martinez-Rodriguez,[a *] **J.F Jurado**[b]

a, Laboratorio de Física del Plasma, Universidad Nacional de Colombia sede Manizales, Km 9 vía al Aeropuerto la Nubia A.A 127 Manizales, Colombia.

b, Propiedades Térmicas-Dieléctricas de Compositos: TDPC-Group, Universidad Nacional de Colombia sede Manizales, Km 9 vía al Aeropuerto la Nubia A.A 127 Manizales , Colombia.

In the literature, there are many designs and fuel cells structures; however, the solid oxide fuel cells (SOFC) has achieved high interest in the scientific community due to they are the most efficient, in the order of 50% and 80%, converting fuel to electricity. These fuel cells can present a high potential applications be important for applications, because the energy is used to generate the electrochemical reaction between hydrogen as well as oxygen from air, to produce electricity, water and heat [1].

A material employed as electrode prototype for being used in SOFC was $La_{0.5}\ Ca_{0.5}\ Fe_{1-x}\ Mn_xO_3$. This material was synthetized by conventional solid state reaction [2], from binary oxides such as La_2O_3, CaO_2, Fe_2O_3 and MnO_2. For the material production two processes were carried out. Initially, a ball mill was employed in order to summit the material to mechanical treatment of macerated and a thermal treatment was applied producing temperature ramps up to 900°C during 12 hr. After that, the material was milled again and submitted to a temperature ramp of 1200 °C during 24 hr. The X-RAY diffraction analysis was obtaining at room temperature, showed that the bulk material has a perovskite single phase. Resistance measurements as a function of temperature showed a semiconducting behavior. The impedance measurements at room temperature presented a high degree of material diffusion, and by the equivalent circuit parameters, an electrical response was obtained as can be find in the literature. From the results analysis, we can conclude that the material synthesis process is suitable.

Figure 1.

These materials presented the tendency to decrease the resistance as the temperature was increases, because of the difficulty of changing the structure that It is evidenced during the XRD characterization. The activation energy changes are related with the possible states present by the material depending on the temperature.

Electrical and Structure Response of The Sample $La_{0.5}Ca_{0.5}Fe_{1-x}Mn_xO_3$ With Potencial Aplications in Solid Oxide Fuel Cells SOFC

H.A Martinez-Rodriguez **continued**

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H_2 Production in a Compact Thermal Integrated Fuel Processor based on Auto-Thermal Reforming

Vincenzo Palma[a], Antonio Ricca[a,*], Maurizio Rea[b], Gaetano Paolillo[b]

*a, Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy - *e-mail: aricca@unisa.it*

b, R&D, SOL S.p.a., Via Borgazzi, 27, 20900 Monza (MB), Italy

Nowadays, the combination hydrogen-fuel cell is identified as the most viable solution to counter the problems of energy growing demand and environmental pollution. The high difficulties in H_2 transport and storage make the distributed production as a very interesting solution. H_2 production by auto-thermal reforming of hydrocarbons results as the optimal solution for the coupling with a fuel cell system. Auto-thermal Reforming (ATR) is a catalytic process, in which hydrocarbon reacts with oxygen (or air) and steam to produce syngas. In the typical process arrangement, the high carbon monoxide content in the produced syngas requires a further catalytic stage for the Water-Gas Shift (WGS), in which carbon monoxide reacts with steam to produce further hydrogen. In this paper, a compact kW-scale fuel processor, able to produce a H_2-rich stream by methane auto-thermal reforming, was proposed. The system consists in two catalytic stages for the ATR and WGS reactions. Particular attention was paid to the system thermal integration: a special heat exchanger system was designed and mounted between the ATR and WGS modules, in order to preheat reactants feeding the system by exploiting the sensible heat of exhaust gas from the ATR stage, and at the same time cooling the process stream up to a temperature consistent to the WGS stage. Such configuration was able to self-sustain the process, by allowing to pre-heat reactants from room temperature up to ATR inlet conditions without any external heat exchangers. Only for the start-up procedure, a spark generator was used to trigger the reaction.

Experimental results demonstrated that the integrated configuration allowed short start-up time, since the system reached the thermal regime in less than 3 minutes, and assuring a hydrogen concentration of about $30\%_{vol}$ in less than 5 minutes. Preliminary tests showed very impressive performances of the system, able to produce up to 10 Nm^3/h of hydrogen by methane processing. The high reactants flow rate seemed to enhance system performances, by reducing heat losses and improving solid-gas mass transfer mechanisms. Appreciable performances were also achieved by replacing methane with natural gas, despite a non-negligible inhibition effect on ATR catalyst. The ATR stage was able to reach the thermodynamic equilibrium in all investigated operating conditions; on the other hand, the low steam content, required to the system thermal integration, led to an incomplete CO conversion, due to thermodynamic limitations. The system computational analysis evidenced that a further heat exchanger to be placed downstream the WGS module may improve the carbon monoxide conversion, and in turn, the overall system efficiency. Anyway, despite the low CO conversion, the system was able to produce up to 10 Nm3/h of hydrogen, assuring a thermal efficiency of 68% (that could increase up to 71% by optimizing WGS catalyst), significantly higher than reported efficiency (63%) of conventional distributed hydrogen production plants [1].

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Hydrogen Safety – Lessons learnt from Nuclear Safety

Thomas Jordan
Hydrogen Group of IKET, Karlsruhe Institute of Technology, PO Box 3630, 76021, Germany

Severe accidents of nuclear installations in general and even normal operations of boiling water reactors imply the generation of considerable inventories of hydrogen. Inappropriate design and operations of these nuclear facilities may then promote severe accident scenarios. The major nuclear accidents, like Three Miles Island, Tchernobyl or Fukushima, have been accompanied by strong hydrogen explosions destroying at least sensitive parts or enclosures of the reactors. The accidents initiated new research for hydrogen safety, safety re-assessments and partially changes in design and management.

The application of hydrogen as an energy carrier is relying on quite different operational conditions, implying different phenomena, hazards and risks. However, it is worthwhile to exploit the longterm experience on the nuclear side by identifying communalities and sharing the associated learnings with the non-nuclear community.

So the author characterises prototypical accidental conditions for both “worlds”, then identifies communalities and finally highlights those aspects, which are worthwhile to be considered for in the risk management of the new hydrogen technologies.

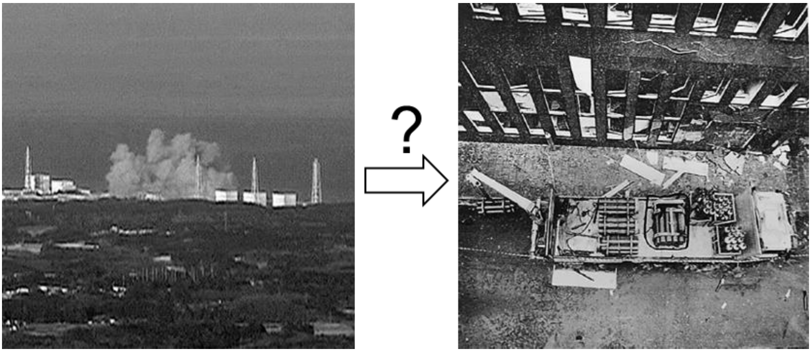

Figure 1. What can be learnt from nuclear accidents with respect to hydrogen safety?

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3rd Zing Hydrogen & Fuel Cells Conference

Poster Presentations

Mathematical model of cryogenic system for condensing of anode off gases

Jarosław Milewski*, Rafał Bernat

a, Institute of Heat Engineering, Warsaw University of Technology, 21/25 Nowowiejska Street, 00-665, Warsaw.

An integrated cryogenic system to separate carbon dioxide and water and produce hydrogen reach gas is investigated and modeled. The main objective of this model is to eliminate the requirement of a standard H_2O/CO_2 removal process in the liquefaction system to directly separate water and carbon dioxide. A few sets of heat exchangers are modeled to obtain the most favorable energy savings. A thermal regeneration scheme is presented for the purpose of saving energy.

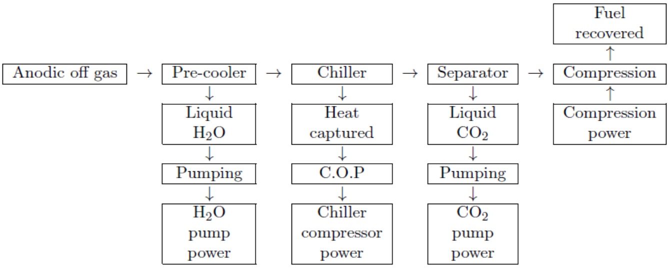

Figure 1. Schematic diagram of the cryogenic anode off gas separation unit

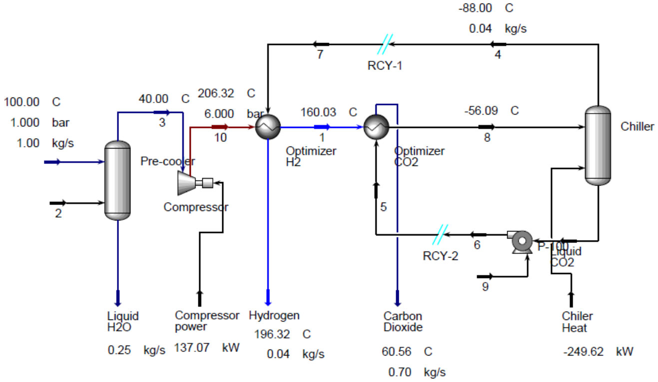

Figure 2. The concept of cryogenic separation system for MCFC

The activity and stability of Pd catalysts supported on TiO_2/MWCNTs surface for DFAFC

A. Malolepszy[a,b*], M. Mazurkiewicz[b,c], L. Stobinski[b,c,d]
a, Faculty of Materials Science and Engineering Warsaw University of Technology
Woloska 141, 02-507 Warsaw, Poland
b, Department of Chemical and Process Engineering, Warsaw University of Technology,
Warynskiego 1, 00-645 Warsaw, Poland
c, University Research Centre "Functional Materials", Warsaw University of Technology,
Woloska 141, 02-507 Warsaw, Poland
d, Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 48/52, 01-224 Warsaw, Poland

The aim of this research was to develop a new type of high activity and stability palladium catalysts for direct formic acid fuel cells (DFAFC). The new catalyst was obtained using functionalized multiwall carbon nanotubes (MWCNTs-$COONH_4$) decorated with titanium dioxide nanoparticles. Metal oxide nanoparticles were obtained using the solvothermal method. Palladium nanoparticles were deposited on the surface of the TiO_2/MWCNTs-$COONH_4$ nanocomposites during reduction of palladium (II) chloride using sodium borohydride. The fabricated composite catalysts were characterized: *i)* X-ray diffraction (XRD) – to determine the average size of crystallites and the phase composition, *ii)* electron microscopy (SEM/STEM) – for imaging the distribution of metal oxide and palladium nanoparticles, *iii)* thermo-gravimetric analysis (TGA) – for determining the thermal stability and percentage content of carbon nanotubes, metal oxides and palladium. The activity and stability of the palladium catalysts was tested with a prototype formic acid fuel cell. The results provide a technological basis for development of commercial catalysts to be used for electro oxidation of formic acid.

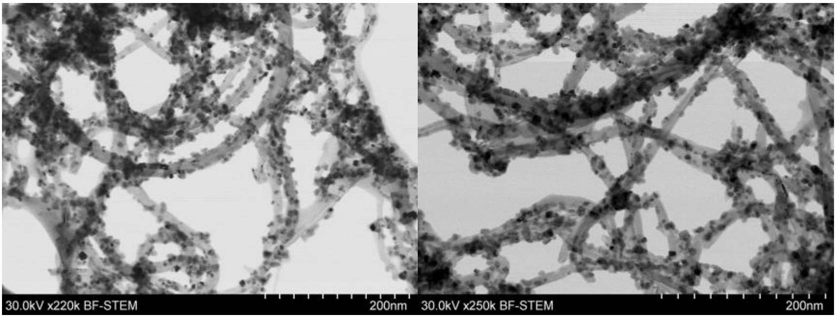

Figure 1. The STEM images of 20% TiO_2/MWCNTs-$COONH_4$ support

Hydrogen Production by Microorganisms in Bioreactors

Sergei A Markov*
Biology Department, Austin Peay State University, 601 College Street, Clarksville, TN, 37044, USA.

Some microorganisms can produce H_2 either from reduced organic materials (*i.e.*, biomass) or from water in reactions catalyzed by nitrogenase or hydrogenase enzymes. It is possible to design bioreactors for large-scale H_2 production using these microorganisms as biocatalysts. Bioreactors can be distinguished based on the nature of H_2 production: bioreactors with H_2 production in the darkness by bacteria via water-gas shift reaction or fermentation and photobioreactors with H_2 production from H_2O using solar light by cyanobacteria or green algae.

"Water-gas shift reaction" bioreactors are based on unique type of H_2-producing activity originally found in a strain of purple bacteria by Uffen [1]. Water-gas shift reaction proceeds according to the equation:

$CO + H_2O \rightarrow H_2 + CO_2$

Hydrogen production from glycerol by fermentation is based on following reaction:

$\text{Glycerol} \rightarrow H_2 + CO_2 + C_2H_5OH$

Hydrogen produced by bacteria in the “water-gas shift reaction” or from glycerol by fermentation is sufficiently clean for direct injection into hydrogen fuel cells. Traditional fermenters (stirred tank bioreactor) or bioreactors with immobilized cells can be used for H_2 production by bacteria in the darkness.

In cyanobacteria and green algae H_2 production is tied to photosynthetic water splitting reactions according to reaction: $H_2O \rightarrow H_2 + O_2$

Thus, it is possible to use solar (light) energy for the production of H_2 from water. The main challenge in photobioreactor design is to create a simple, inexpensive, with high volumetric productivity energy efficient photobioreactor, which is scalable to industrial capabilities. Photobioreactors should also provide the most efficient utilization of the solar energy, and allow monitoring culture purity and basic process parameters. To be used outdoors, such photobioreactor requires a cooling system (water sprinkler, heat exchange, or photobioreactor can be simply submerged into the ground) during summer and early fall periods, and the mixing of algal culture to achieve uniform illumination of all cells. Current research and development efforts are concentrated on designing tubular PVC or plastic bag photobioreactors incorporating cyanobacteria and green algae.

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Noncovalent modification of carbon nanotubes used as a support for Pd catalysts in direct formic acid fuel cells

M. Mazurkiewicz[a,b],* , **A. Malolepszy**[b,c], **L. Stobinski**[a,b,d]
a, University Research Centre "Functional Materials", Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland
b, Department of Chemical and Process Engineering, Warsaw University of Technology, Warynskiego 1, 00-645 Warsaw, Poland
c, Faculty of Materials Science and Engineering Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland
d, Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 48/52, 01-224 Warsaw, Poland

Direct formic acid fuel cells (DFAFCs) belong to low-temperature proton exchange membrane (PEM) type of fuel cells. Due to lower toxicity than methanol and the possibility of easier storage than hydrogen, formic acid can be a good alternative fuel, especially for small and portable devices. Palladium nanoparticles used for oxidation of formic acid in DFAFC can provide higher power densities than platinum[1]. Carbon materials are used as a support for the precious metal nanoparticles because of their high surface area, chemical inertness in the fuel cell environment and good electrical conductivity[2]. Carbon nanotubes (CNTs) among other carbon materials possess unique tubular structure which affects their properties and makes them a good candidate for a catalyst support used in a low temperature fuel cell[3,4]. There are two major methods to functionalize carbon nanotubes: covalent and noncovalent modifications[5]. The covalent modification usually involves oxidizing carbon nanotubes with different chemicals (e.g. HNO_3, H_2O_2, $KMnO_4$). This treatment is responsible for the degradation of the CNTs structure leading to a decrease in their conductivity. The noncovalent modification (by π-π interaction) can introduce functional groups in CNTs without damaging their structure.

In this work we present multiwall carbon nanotubes (MWCNTs) modified with different amounts of benzoic acid (1:1, 1:10, 1:100 benzoic acid:MWCNTs weight ratio). We study the influence of these modifications on the catalytic properties of Pd/MWCNTs for formic acid oxidation used in DFAFC. The Pd catalysts were synthesized using a chemical reduction method (with $NaBH_4$).The obtained catalysts were characterized using scanning and transmission electron microscopy (SEM, TEM), TGA analysis, Raman spectroscopy, X-Ray diffraction (XRD) and were tested in a prototype Direct Formic Acid Fuel Cell for their catalytic activity.

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Effect of GDL Structure on the Performance of Air-Cooled, Open-Cathode Fuel Cells Using Hydro-Electro-Thermal Analysis.

Q. Meyer,[a] S. Ashton[b], D. Finegan[a], E. Engebretsen[a], Pierre Boillat[c,d], Magali Cochet[c], Paul Adcock[b], P.R Shearing[a,e], D. J.L. Brett[a]*
[a]*Electrochemical Innovation Lab, Department of Chemical Engineering, UCL, London, WC1E 7JE, UK,*
[b]*Intelligent Energy, Ashby Road, Loughborough, LE11 3GB, UK.*
[c]*Electrochemistry Laboratory (LEC), PSI, 5232 Villigen, Switzerland.*
[d]*Neutron Imaging and Activation Group (NIAG), PSI, 5232 Villigen, Switzerland*
[e]*UCL/Zeiss Centre for Correlative X-ray Microscopy, UCL, London, WC1E 7JE, UK*

Polymer electrolyte fuel cells (PEFCs) fuelled with hydrogen is among the most promising energy conversion technologies for a broad range of applications. *In situ* diagnostic techniques provide a means of understanding the internal workings of fuel cells so that improved designs and operating regimes can be identified. Therefore, the combination of existing metrologies and development of novel methods is crucial to enable the next breakthrough in fuel cell performances. Investigations of the dead-ended anode[1], current of lowest resistance[2], current and temperature mapping via a single PCB sensor plate[3], combined with water mapping in through-plane using neutron imaging[4], and hydro-electro-thermal analysis, has enabled optimum operating regimes to be identified, at the cell and stack level.
Here, the effect of two commercial cathode gas diffusion layers with high/low porosity is characterised using these novel diagnostic techniques. Firstly, their porosity was extracted *ex-situ* using X-ray CT tomography (VERSA, ZEISS). Then these two GDL were analysed *in-situ,* inserted in two, otherwise identical, air-cooled open-cathode stacks to study how the structure influences the hydro-electro-thermal profile in steady-state and transient operation. The stacks were imaged in in-plane and through-plane orientation in order to separate cathodic and anodic water and characterise the water transients across the cell (NEUTRA, Paul Scherrer Institute), meanwhile the current and temperature profiles have been monitored to investigate the effect of the water gradients on the performance.

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Charge-storing biofuel cells based on nanobiocomposite materials

Dmitry Pankratov,[a,b] Zoltan Blum[a], Yulia Parunova,[b] Alexey V. Lipkin,[b] and Sergey Shleev[a,b]*

a, Biomedical Sciences, Faculty of Health and Society, Malmö University, Jan Waldenströms gata, 25, SE-21428, Malmö, Sweden

b, NBICS Centre, National Research Centre "Kurchatov Institute", Akademika Kurchatova Sq., 1, 123182, Moscow, Russia

Within our modern society there are serious problems with generation of electric power and storage of electric energy. The problems include detrimental environmental consequences and inadequate efficiency in the conversion steps, and unfavourable time-constants together with losses at the storage step. Moreover, the two steps are always separated and additional technical units are required to connect them. The complexity of the setup will add to the efficiency problems and increase not only the financial but also the environmental costs of electric energy.

Owing to the increased interest in alternative fuels in the last few decades, biofuel cells (BFCs) have become a hot research topic and have shown great potential in certain niche applications. BFCs possess various advantageous, but also less-advantageous, properties as a consequence of the features of biocatalysts. On the one hand, BFCs are "green" renewable electric power devices, which, hypothetically, can be produced at low cost. On the other hand, the critical parameters achieved, for example, current and power densities are far from those realised in commercially available fuel cells (FCs).

The combination of capacitors and BFCs results in hybrid biodevices, which can operate in both steady-state and pulse modes, and can be used for long-time, low-current and short-time, high-current practical applications, respectively.

Very recently a new method for concomitant electric power generation and storage has been offered and verified by the fabrication and characterisation of an appropriate hybrid electric biodevices[1,2]. The devices could be referred to as charge-storing BFCs (CSBFCs) or, alternatively, self-charging biocapacitors.

Both energy generating and charge storing parts of biodevices were built from 3D nano-biostructures based on a nanocomposite consisting of carbon nanotubes and the poly (3,4-ethylenedioxythiophene) with immobilized anodic and cathodic biocatalysts, cellobiose dehydrogenase and bilirubin oxidase, respectively. The membrane-, separator-, cofactor-, and, mediator-less charge-storing CSBFCs were evaluated in a glucose-containing, air-saturated, phosphate-buffered saline. Operating in a pulsed mode, the power output was improved by a factor of about 200 in comparison to conventional BFCs based on the same catalysts.

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Assessment of hydrogen rate production by photolytic oxidation of aqueous sulfite solutions under pH control

R. Orozco-Mena[a], E. Herrera-Peraza[a], D. Chavez-Flores[b], J. J. Alvarado-Gil[c], V. H. Ramos-Sánchez[b]*

*vramos@uach.mx

a, Centro de Investigación en Materiales Avanzados S.C. Chihuahua Chih. México.
b, Universidad Autónoma de Chihuahua, Chihuahua Chih. México.
c, Centro de Investigación y Estudios Avanzados del I.P.N., Mérida, Yuc., México.

Hydrogen is an energy carrier capable to replace fossil fuels and provide energy for transportation, industry, and households. The sulfur-ammonia (S-NH_3) phototermochemical cycle exploits entirely the solar radiation spectrum to split water. This sustainable approach uses the UV radiation to promote the photolytic oxidation of ammonium sulfite to produce hydrogen and ammonium sulfate, an energy carrier, and a potential fertilizer respectively. An alternative pathway of this process is the photooxidation of sodium sulfite instead[1]. Photolytic oxidation rates are under control of pH. This moves from 8 to 3 during hydrogen production, showing a clear reaction rate reduction as the system approaches an acidic media[2]. In spite of the fact that, the best rates have been obtained at 7.8 because equimolar quantities of HSO_3^- and SO_3^{2-} ions occur, buffer addition has not been attempted to assess its effect in reaction kinetics. Therefore, in this work, our main objective was to evaluate reaction rates on the photolytic oxidation, exclusively at 254 nm, of both: Na_2SO_3 and $(NH_4)_2SO_3$ adding a buffer of phosphates to keep pH around 8. Measurements were carried out in a UV photoreactor (40 W), and reaction rates were monitored by gas chromatography with a thermal conductivity detector, UV Raman spectroscopy and HPLC with a diode array detector. The assessment revealed that a buffer maintained pH close to 8 preventing significantly the abovementioned reaction rate decrease, inhibiting undesired reverse reactions. Under these conditions, ammonium sulfite exhibited a superior rate of hydrogen production. Based on these observations, it would be natural evaluating also hydrogen production *via* ammonium sulfite electrooxidation under pH control.

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Design of materials for Molten Carbonate Fuel Cell

T. Wejrzanowski, K. Cwieka, K.J. Kurzydlowski

Faculty of Materials Engineering, Warsaw University of Technology, Woloska 141. 02-507 Warsaw

Development of Molten Carbonate Fuel Cells (MCFC) is strongly associated to improvement of durability and efficiency of its components. This can be only achieved by determination of relationships between structure and properties of materials for MCFC. In the present study the tape-casting technique has been used. In this method green tapes are formed from slurry with strictly defined composition and properties. Proper combination of ingredients allows to achieve optimal structural characteristics of final products.

Porosity, as a crucial feature for each of main MCFC components: anode, cathode and matrix, can be obtained by combination of the slurry composition. Necessary porosity level is strictly determined by kinetics of chemical reactions and electrolyte upholding by capillary forces as well as ion transport in case of the electrodes and matrix respectively.
Present work is aimed to obtain materials, which may improve efficiency and durability of MCFC. In order to achieve this goal, the subsequent stages like: slurry composition optimization, tape-casting process set-up and heat treatment parameters have been carried out.

Present work introduces the results of optimization of the manufacturing process parameters and characterization of materials obtained herewith. The influence of slurry composition and heat treatment conditions are correlated with structural parameters such as porosity, pore size and pore morphology in final products. Testing of materials in MCFC assembly were performed and the results are presented.

Highly efficient H_2 generation by oxide nanostructures

M. Miki-Yoshida*, P. Amézaga-Madrid, P. Pizá-Ruiz, W. Antúnez-Flores, Jesús Salinas-Gutiérrez, V. Collins-Martínez.

Centro de Investigación en Materiales Avanzados S.C., Miguel de Cervantes 120, Chihuahua, Chih, CP 31136, Mexico.

Oxide based nanostructures were grown by aerosol assisted chemical vapour deposition onto borosilicate glass substrates covered by a TiO2 thin film as a buffer. Details of the experimental setup and general synthesis conditions were reported elsewhere[1,2]. Nanostructures were a multilayered coating composed by: oxides of Ti, Ti-Fe, Ti-Ni, and TiOx-FeOx. All the nanostructures were covered by a continuous layer of Pt nanoparticles. Microstructure of the samples were analysed by electron microscopy and x-ray diffraction. Optical properties were also determined in the UV-visible-near IR interval. Finally photocatalytic generation of H_2 was evaluated in a batch reactor under visible light irradiation, using a filtered low vapour pressure Hg lamp of 250 W. H_2 evolution was tested every hour by gas chromatography. Table 1 resumes the principal characteristics of the different coatings and generated H_2 in $\mu mol.h^{-1}.g^{-1}$, taking into account their mass.

Sample	A – Ti oxide	B – Ti-Ni oxide	C – Ti-Fe oxide	D – TiO_x-FeO_x-TiO_x
1st layer	TiO_2	TiO_2	TiO_x-FeO_x Ti/Fe at. ratio: ~ 1	TiO_2
2nd layer	Nano Pt	TiO_x-NiO_x Ti/Ni at. ratio: ~ 1	Nano Pt	FeO_x
3rd layer		Nano Pt		TiO_2
4rd layer				Nano Pt Ti/Pt at. ratio: ~ 7
H_2 generation [$\mu mol\ h^{-1}\ g^{-1}$]	4	17	59	128

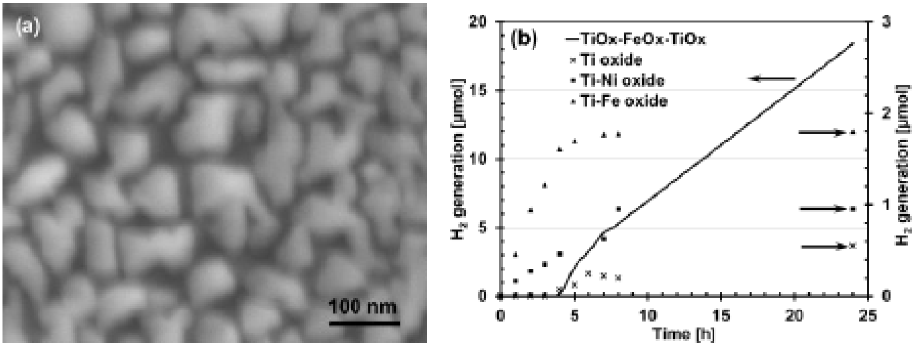

Figure 1. a) Backscattered electron SEM image of Pt nanoparticles on the surface of sample D. b) H2 generation as a function of time

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The Carbon Monoxide Poisoning on a PBI/H_3PO_4 High Temperature Polymer Electrolyte Membrane Fuel Cell

Fan Zhou [a]*, Søren Juhl Andreasen [a] and Søren Knudsen Kær [a]

a, Department of Energy Technology, Aalborg University, Aalborg East, 9220, Denmark.

The PBI/H_3PO_4 high temperature polymer electrolyte membrane (HT-PEM) fuel cell enables operation in the range of 120 °C and 200 °C, which provides high impurity tolerance than its low temperature counterpart. Therefore the H_2-rich reformate gas produced from light fuel such as methanol, ethanol and methane is usually adopted as the fuel gas for PBI/H_3PO_4 HT-PEM fuel cell to increase the fuel flexibility. The carbon monoxide (CO) is a typical impurity contained in the reformate gas which can be harmful to the performance of the PEM fuel cell. In this work, the performance of a PBI/H_3PO_4 high temperature PEM fuel cell was characterized with the presence of CO in anode fuel stream under different CO concentrations and different operating temperatures. The performance loss caused by CO poisoning was evaluated by polarization curve under different operating conditions. In addition, the electrochemical impedance spectroscopy (EIS) and current density distribution were measured as well to gain insight into the CO poisoning effect on the HT-PEM fuel cell.

The experimental results show that the cell voltage drops at all current density ranges with the presence of CO, and the cell voltage loss becomes higher at higher current density. With higher CO concentration and lower operating temperature, the cell voltage caused by CO poisoning become higher. The EIS measurements reveal that higher CO concentration brings about higher charge transfer resistance which is the main reason for the lower cell performance with higher CO concentration. With higher operating temperature, the charge transfer resistance and the mass transfer resistance become lower while the ohmic resistance remains almost unchanged. The current density distribution is changed by the presence of CO in the anode stream. The increase in current density in upstream regions and the decrease in current density in downstream regions can be observed with the presence of CO. The results from this work can help to optimize the operating conditions and control strategies of the HT-PEM fuel cell.

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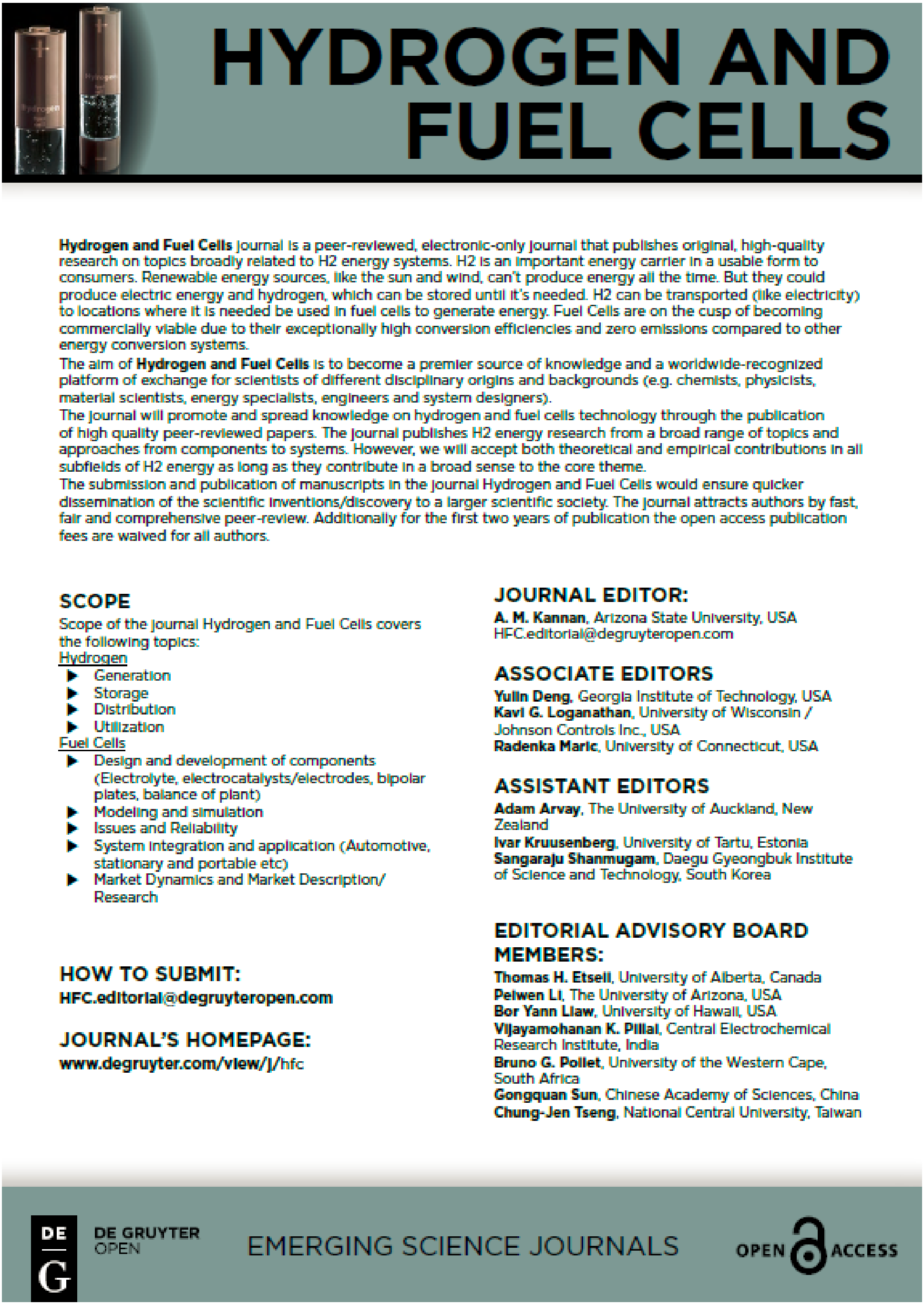

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