



**The Abdus Salam  
International Centre for Theoretical Physics**



**SMR.1841**

**CONFERENCE on  
*FROM PHYSICAL UNDERSTANDING TO  
NOVEL ARCHITECTURES OF FUEL CELLS***

**May 21 - 25, 2007**

**Miramare - Trieste, Italy**

**BOOK OF ABSTRACTS**

WEB page: <http://agenda.ictp.it/smr.php?1841>

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## PREFACE

This Conference will focus on the properties of complex media in fuel cells and the relevant physical processes, as well as on nonlinear science of operation of the cell as a whole. Its interdisciplinary scope will bring together scientists from the cutting edge of fuel cell research as well as experts from related disciplines in order to stimulate further advances in rational design of fuel cells.

Topics addressed will encompass:

- \* **energy conversion for a hydrogen economy**
- \* **frontiers in fuel-cell-relevant materials research**
- \* **physical processes in fuel cell components (theory and experiment)**
- \* ***in-situ* diagnostics vs. performance modelling of fuel cells and stacks**
- \* **from novel materials and architectures to competitive fuel cells**

### **ORGANIZING COMMITTEE:**

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NRC Institute for Fuel Cell Innovation, Vancouver*)

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This book is also available in electronic format at the WEB site:

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**The Abdus Salam  
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**Conference on**

***From Physical Understanding to  
Novel Architectures of Fuel Cells***

**May 21 – 25, 2007**

**Miramare-Trieste, Italy**

**Venue: Adriatico Building, Kastler Lecture Hall**

**Final Program**

***SOCIAL ACTIVITIES KINDLY SPONSORED BY***



***GENERAL MOTORS CORPORATION - FUEL CELL ACTIVITIES***

Monday, May 21, 2007, 8:30 – 18:15

**8.30 - 10.00 REGISTRATION AND ADMINISTRATIVE FORMALITIES**

**10:30 OPENING**

*Welcoming address on behalf of the ICTP*

*Erio Tosatti - ICTP and SISSA, Trieste*

*From Physical Understanding to New Design. Introduction*

*Alexei A. Kornyshev - Imperial College, London, U.K.*

**Session 1: Fuel Cells – Challenges for Materials, Operation and Design**

*Chair: Michael Eikerling - Simon Fraser University and NRC-IFCI*

**11:00 Shimson Gottesfeld - MTI Microfuel Cells Inc., Albany, U.S.A.**

*Addressing Materials and Electrocatalysis Challenges in DMFCs with Combined Engineering and Science Tools*

**11:30 Rainer Bussar - Technical University Munich, Germany**

*Challenges and Directions in Electrocatalyst Research for PEFCs*

**12:00 Thomas A. Zawodzinski - CWRU, Cleveland, U.S.A.**

*Beyond Conductivity! The Interplay between Electrolyte Performance Characteristics and Other Features*

**12:30 – 14:00 Lunch-break**

**14:00 Günther G. Scherer - Paul Scherrer Institute, Villigen, Switzerland**

*Performance Evaluation in Fuel Cells – Combined Locally Resolved In-situ Diagnostic Methods*

**14:30 Jürgen Stumper - Ballard Power Systems, Burnaby, Canada**

*PEM Fuel Cells for Automotive Applications: Prospects and Challenges*

**15:00 – 15:30 Coffee-break**

## Session 2: Fundamentals of Proton Transport

Chair: Alexei A. Kornyshev - *Imperial College, London, U.K.*

- 15:30 Alexander M. Kuznetsov - *Russian Academy of Sciences, Frumkin Institute, Moscow*  
***Theoretical Models of Proton Transfer in Condensed Media***
- 16:00 Dominik Marx - *Rhur-Universitaet Bochum, Germany*  
***Understanding Charge Migration Mechanisms in Aqueous Environments***
- 16:30 Detlef W.M. Hofmann - *CRS4, Pula, Italy*  
***New Reactive Force Field for Proton Transport in Water, Acid Solutions and Polymeric Electrolyte Membranes***
- 17:00 – 17:15 **Break**
- 17:15 Arieh Warshel - *University of Southern California, Los Angeles, U.S.A.*  
***Effective Strategies for Unraveling Microscopic Energetics and Dynamics of Proton Transport in Complex Systems: From QM/MM to Monte Carlo EVB Based Models***
- 17:45 Joachim Heberle - *Bielefeld University, Germany*  
***Bioenergetic Protons and BioH<sub>2</sub> Production***
- 19:00 **Reception**

**Tuesday, May 22, 2007, 9:00-17:30**

## Session 3: Theory and Molecular Modeling of Structure Formation and Transport in Hydrated Ionomers

Chair: Steven Holdcroft - *Simon Fraser University*

- 9:00 Gerard Gebel - *CEA, Grenoble, France*  
***Multiscale Transport Properties in Hydrated Ionomers***
- 9:30 Alexei R. Khokhlov - *Moscow State University, Russia*  
***Statistical Physics and Computer Modeling of Ionomers: Fundamentals and Application to Proton-conducting Membranes***
- 10:00 T. Weston Capehart - *General Motors R&D Center, Warren, U.S.A.*  
***Molecular and Mesoscale Modeling of Hydrated Ionomers***

**10:30 – 11:00**

**Coffee-break**

**11:00** Eckhard Spohr - *Forschungszentrum Jülich, Germany*

***Atomistic Simulations of Proton Transport in Model PEM Pores***

**11:30** Nico van der Vegt - *Max Planck Institute, Mainz, Germany*

***Dual scale modeling of mobility of additives in a polymer matrix***

**12:00 – 14:00**

**Lunch-break**

#### **Session 4: Fuel Cell Membranes – Fabrication, Structure, Properties and Performance**

**Chair: Thomas A. Zawodzinski -CWRU, Cleveland**

**14:00** Sossina M. Haile - *California Insitute of Technology, Pasadena, U.S.A.*

***Design of Fuel Cells with Solid Acid Proton Conductors***

**14:30** Steven Holdcroft - *Simon Fraser University, Burnaby, Canada*

***Fluorous, Ion-containing Block Copolymers: Model Polymers for Investigating the Role of Morphology on Proton Conduction***

**15:00** Brian C. Benicewicz - *Rensselaer Polytechnic Institute, Troy, U.S.A.*

***Status and Challenges of High Temperature PBI Fuel Cell Membranes***

**15:30** V. Baglio - *Istituto di Tecnologie Avanzate, Messina, Italy*

***Composite membranes***

**16:00 – 16:30**

**Coffee-break**

#### **Session 5: Electrocatalysis for Fuel Cells**

**Co-Chairs: Ulrich Stimming - Technical University Munich  
and Göran Lindbergh - Royal Institute of Technology, Sweden**

**16:30** Axel Gross - *University of Ulm, Germany*

***Structure-Reactivity Relationship and Elementary Reaction Steps in Electrocatalysis***

**17:00** M.T.M. Koper - *Leiden University, Netherlands*

***Structure sensitivity of fuel cell anode reactions***

**Wednesday, May 23, 2007, 9:00-18:00**

- 9:00 Jan Rossmeisl - *Technical University of Denmark, Lyngby*  
***Activity Descriptor for Oxygen Reduction Catalysts***
- 9:30 Elena R. Savinova - *Russian Academy of Sciences Novosibirsk and CNRS-ULP-ECPM Strasbourg*  
***On the Role of Structural Defects in Electrocatalysis by Supported Metals***
- 10:00 Nenad Markovic - *Argonne National Laboratory, U.S.A.*  
***Surface Science Studies of Model Electrocatalysts***
- 10:30 – 11:00 Coffee-break**
- 11:00 Katharina Krischer - *Technical University Munich, Germany*  
***Dynamic Instabilities in Electrocatalysis and their Impact on Reaction Efficiencies***
- 11:30 Anthony Kucernak - *Imperial College London, U.K.*  
***Is CO oxidation a useful reaction for studying fuel cell electrocatalysts?***

**12:00 – 14:00 Lunch-break**

### **Session 6: Poster Session**

Chair: Anthony Kucernak - *Imperial College London, U.K.*

- 14:00 – 15:00 Oral presentations by selected poster presenters
- 15:00 – 18:00 Discussions at posters
- 19:00 Conference dinner**



Thursday, May 24, 2007, 9:00-17:45

## Session 7: Random Heterogeneous Media and Electrode Operation

Co-chairs: Nico van der Vegt - *Max Planck Institute*  
and Günther G. Scherer - *Paul Scherrer Institute*

- 9:00 Markus Bier - *Utrecht University, Netherlands*  
***Colloid Based Crystalline and Amorphous Structures***
- 9:30 Klaus Mecke - *University Erlangen-Nürnberg, Germany*  
***Fluids in Porous Media: A Morphometric Approach to Structure-Property Relations***
- 10:00 Alexei S. Ioselevich - *Russian Academy of Sciences, Landau Institute*  
***Modelling of Porous Materials: From Topology to Physical Properties***
- 10:30 – 11:00 **Coffee-break**
- 11:00 Michael Eikerling - *Simon Fraser University and NRC Institute for Fuel Cell Innovation*  
***From Microstructure Formation to Performance of PEFC Cathode Catalyst Layers: Insights for Advanced Design***
- 11:30 Nenad Markovic - *Argonne National Laboratory, U.S.A.*  
***Advanced Electrode Structures***
- 12:00 – 14:00 **Lunch-break**
- 14:00 Göran Lindbergh - *Royal Institute of Technology, Stockholm, Sweden*  
***Investigation PEMFC electrodes and MEAs using electrochemical techniques***
- 14:30 Daniel R. Baker - *General Motors R&D Center, Warren, U.S.A.*  
***Measurement of proton resistance in cathode catalyst layers and its correlation with the ionomer-to-carbon ratio***
- 15:00 – 15:30 **Coffee-break**

## Session 8: Fuel Cell Modeling and Diagnostics

Chair: Shimson Gottesfeld - *MTI Microfuel Cells Inc.*

15:30 **Sergei F. Burlatsky** - *United Technologies Research Center, East Hartford, U.S.A.*

***Mutiscale Modeling for PEM: From Atomistic Modeling to Improved Durability and Power Density, and Cost Reduction***

16:00 **Andrei Kulikovsky** - *Forschungszentrum Jülich, Germany*

***Physical Modeling of Direct Methanol Fuel Cells and Stacks***

**16:30 – 16:45** **Break**

16:45 **Alexei A. Kornyshev** - *Imperial College London, U.K.*

***Hungry Fuel Cell***

17:15 **Felix N. Büchi** - *Paul Scherrer Institute, Villigen, Switzerland*

***Fuel Cell Stack Operation: Exploring Inhomogeneous Cell Polarization***

**Friday, May 25, 2007, 9:00-12:00**

**9:00 – 11:30** **Workshop: Where Theory and Fundamental Experiments Can Help to Improve Fuel Cells?**

**Panel: E. Savinova\*, G. Gebel\*\*, G. Lindbergh\*\*\*, S. Gottesfeld\*\*\*\***

\* Electrocatalysis

\*\* Proton conducting materials

\*\*\* Electrodes

\*\*\*\* Cells and stacks

Each panellist sets a list of five min statement presenters in indicated areas, with subsequent spontaneous discussion of their statements that each panellist will run.

**11:30-11:45** **Summary and closing the conference**

**M. Eikerling** - *Simon Fraser University and NRC-IFCI*



*The Abdus Salam*  
**International Centre for Theoretical Physics**



Activity SMR: **1841**

# **Conference on "From Physical Understanding to Novel Architectures of Fuel Cells"**

21 May 2007 - 25 May 2007  
Trieste - ITALY

**Total Number of Visitors: 84**

**Final List of Participants**

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# **ABSTRACTS OF POSTERS**

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## **Novel Ionogels encompassing of ionic liquid with liquid like performance**

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### **Abstract**

Synthesis of high performance electrolytes which are ubiquitous in all electrochemical devices is a daunting challenge and acts to curtail the progress of many of our technologies that cater to the need of our society. The earlier issues such as low ionic conductivity, electrochemical stability, corrosion, thermal stability and low vapor pressure have been resolved by ionic liquids which holds attraction for both academia and industries. Room temperature ionic liquids which have recently generated a surge of interest as electrolytes are in the forefront area of chemical research. The recent years have witnessed the revival of commercial interest in the development of alternate energy sources and on renewable and greener sources of energy, such as high performance batteries and fuel cells, the latter being most promising technologies under exploration. These devices are of tremendous practical utility in view of our energy and environmental needs.

An alternative method based on sol-gel chemistry wherein an ionic liquid is ensconced in a solid matrix composed of inorganic materials, without compromising on its electrochemical and thermal properties has been developed by us. The ensuing ionogels or electrolytes are full of ions have been prepared by a simple non-hydrolytic sol-gel route. The ability of these highly conducting ionogels ( $\sim 10^{-2}$  S cm<sup>-1</sup> at 25 °C) to act as liquid electrolytes inspite of their solid form have been investigated

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# BaCe<sub>1-x</sub>Y<sub>x</sub>O<sub>3</sub> PROTON CONDUCTORS: THE ROLE OF SYNTHETIC ROUTE ON THE CONDUCTIVITY

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Solid oxide fuel cells (SOFCs) have gained many attentions as a promising energy conversion system due to their high thermodynamic efficiency and low impact to the environment. Nevertheless, the lowering of SOFCs operating temperatures (usually in the range 800-1000°C) is a key factor for their commercialization. In the view of developing intermediate temperature SOFCs, proton conducting ceramics are promising candidates as electrolytes, because of their significant electrical conductivity under humidified H<sub>2</sub> atmosphere, over the wide 300°C÷1000°C temperature range. Among these, various doped barium cerates, such as BaCe<sub>1-x</sub>A<sub>x</sub>O<sub>3-δ</sub> (with A = Y, Gd, Yb, Nd, Sm), have been intensively investigated. In particular, BaCeO<sub>3</sub> has been reported to have high conductivities when doped with Y.<sup>[1]</sup>

The main purpose of this work was to evaluate and compare the electrical properties of the sintered BaCe<sub>1-x</sub>Y<sub>x</sub>O<sub>3-δ</sub> (x=0, 0.1, 0.15 and 0.2) powders prepared by either solid state reaction or a modified sol-gel Pechini method. In fact, the usual solid-state process for the preparation of ceramic oxides requires high temperature treatments at 1400÷1600°C, causing a barium deficiency due to BaO vaporization.<sup>[2]</sup> A few wet chemical methodologies, as oxalate co-precipitation, citrate and Pechini processes<sup>[3]</sup> have been developed to prepare BCY compounds, in order to produce nanostructured powders and to reduce sintering temperatures.

In order to underline the protonic contribution to the total conductivity, the electrical measurements were carried out in wet and dry atmosphere by means of Electrochemical Impedance Spectroscopy (EIS). An extensive structural and morphological investigation was performed by means of X-Ray Diffraction and Scanning Electron Microscopy (SEM). Moreover, simultaneous differential thermal analysis and thermogravimetry were done in dry and wet air atmosphere to evaluate the water uptake of the Y-doped cerates.

Single phase compounds were obtained in the whole range of stoichiometry by both synthetic procedures, and by using sol-gel synthesis method, the obtained nanopowders exhibited single orthorhombic structure after heating at 1100 °C for 2 hours. In this case, dense pellets (higher than 90% of bulk materials) were prepared by sintering at 1250 °C. On the contrary, lower density materials were obtained by solid state reaction microsized powders, even if sintered at 1400°C.

In H<sub>2</sub>/H<sub>2</sub>O atmosphere, BCY pellets prepared by sol-gel synthesis exhibited total conductivity close to 10<sup>-2</sup> Ω<sup>-1</sup>cm<sup>-1</sup> at 500 °C when 15%Y-doped. In isothermal conditions this stoichiometry exhibited the highest conductivity values among the considered compositions in the 500÷700°C range.

Because of the promising data obtained for BCY (15%Y), the optimization of screen printing process on Ni-GDC cermet is being to be carried out for this stoichiometry, in order to fabricate the anode-supported half cell.

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## NMR and conductivity studies on proton conducting PVAc based electrolytes

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### Abstract

The development of novel proton conducting polymer electrolytes attracted considerable interest due to their prominent applications in various electrochemical devices such as fuel cells, humidity and gas sensors and electrochromic displays [1-2]. When a hybrid polymer electrolyte is prepared for practical applications, the need for understanding favorable physical properties such as microscopic ion dynamics and ion-polymer interactions must also be considered. Nuclear magnetic resonance (NMR) is one of the powerful probes in microscopic dynamics and clarifying ion environments in polymer electrolyte materials [3]. In the present investigation, the microscopic ion environment and conductivity measurements of PVAc:NH<sub>4</sub>SCN proton conducting polymer matrices have been carried out by using <sup>1</sup>H NMR and complex ac impedance spectroscopy analyses.

The polymer electrolytes composed of Poly (vinyl acetate) (PVAc) with various stoichiometric ratios of ammonium thiocyanate (NH<sub>4</sub>SCN) have been prepared by solution casting method. XRD analysis of the PVAc:NH<sub>4</sub>SCN matrices reveals the complex formation. <sup>1</sup>H NMR results reveal the existence of different H<sup>+</sup> environments present in the PVAc matrix. The linewidth measurements indicate the conductivity enhancement with temperature. Ionic conductivity results show increase in proton conductivity from 5.5x10<sup>-4</sup> Scm<sup>-1</sup> (303K) to 1.2x10<sup>-2</sup>Scm<sup>-1</sup> (373K) with temperature is in good agreement with <sup>1</sup>H NMR measurements.

**Keywords:** Proton conductivity, <sup>1</sup>H NMR measurements, Impedance spectroscopy, XRD analysis

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## Size-confinement of CsH<sub>2</sub>PO<sub>4</sub> in anodic alumina membranes for thin film electrolyte solid acid fuel cell

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Recent advances have made solid acids a potential alternative to perfluorosulphonic polymeric membranes commonly used in fuel cell [1]. We have recently suggested [2] a different membrane conception for fuel cell application: porous anodic alumina membranes filled with solid proton conductor. Anodic Alumina Membranes (AAM) are characterized by many unique properties that make the fuel cell described in this work interesting by different point of views:

(1) AAMs are well known for the extremely ordered porous structure made of parallel cylindrical pores, located into a hexagonally packed arrangement. They can be easily electrochemically grown in a rather wide range of thickness (from few micron to hundreds micron) and porosity (from 10 to 30 %) with pores diameter ranging from 20 nm to 200 nm depending on anodizing parameters through a self-ordering process [3,4]. Thus, through an optimal filling technique of AAMs, a nanowire-type structure of the proton conductor is obtained and a highly precise control of its size (thickness and diameter) should be possible.

(2) Since the kinetic of solid acid fuel cells [1, 2] appears mainly controlled by the ohmic drop into the electrolyte, very low membrane thickness should enhance the performance of the fuel cell, preventing also possible powdering of the salt.

(3) The easy handling of porous anodic alumina in micro-machining operations suggesting also possible realization of novel AAM/solid acid based micro fuel cell.

(4) In addition, it could be expected possible increase of the proton conductivity by the ordered size confinement of cesium dihydrogen phosphate into inert porous aluminum oxide.

In this frame, we have valued a possible use of CsH<sub>2</sub>PO<sub>4</sub> in room temperature SAFC by embedding the salt into an inorganic highly ordered porous alumina matrix. The morphological and structural characteristics of the composite membranes porous alumina/Cesium dihydrogen Phosphate has been examined and their electrochemical behaviour studied in a hydrogen-oxygen fuel cell working at room temperature and low humidity in order to value if an improvement of performance by means of ordered nano-sizing of the solid acid into AAM can be possible.

Short circuit current densities of about 280 mA cm<sup>-2</sup> and peaks power of 50 mW cm<sup>-2</sup>, calculated on the real active surface of CsH<sub>2</sub>PO<sub>4</sub> (considering a AAM porosity of 30%) are achieved at room temperature and low humidity (25 °C). These results are sensibly higher of the expected values considering the proton conductivity data of CsH<sub>2</sub>PO<sub>4</sub> at room temperature. These encouraging results accompanied also by a decreasing of fuel cell performance with time, will be discussed in the light of possible conduction mechanism together with evaluation of the causes of membrane degradation.

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## Application of High Resolution Neutron Imaging in PEFC Diagnostics

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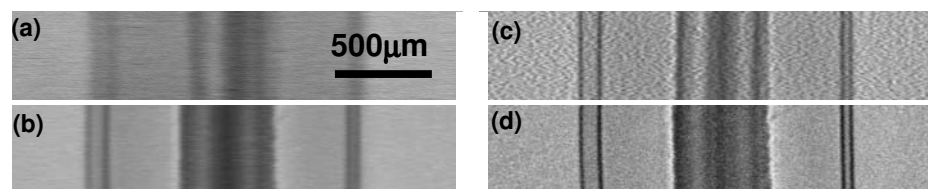
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Neutron radiography is a powerful tool to detect the presence and distribution of liquid water inside polymer electrolyte fuel cells (PEFC)<sup>[1-4]</sup>. The key characteristics of this method are: (1) non intrusive, (2) quantitative, and (3) locally resolved.

Usually, cells are imaged in *through plane* direction (cell perpendicular to the beam). This allows measuring the water distribution over the cell area, but not distinguishing between water within membrane, anode, and cathode. This information, though, can be obtained by *in plane* imaging (cell irradiated from the side). This configuration sets very demanding requirements on spatial resolution, because the typical thickness of gas diffusion layers is 200  $\mu\text{m}$ , and the whole MEA is hardly one millimeter thick.

The new CCD based high resolution detector available at the Swiss continuous spallation neutron source SINQ<sup>[5]</sup> constituted an important step towards high resolution in-plane imaging. Additional improvements could be obtained taking into account the fact that a high spatial resolution is required in one direction only, i.e. the direction across the membrane<sup>[6]</sup>: for example, placing the detector in a tilted position magnifies the image in the horizontal direction and results in a clearly improved spatial resolution. These developments were successfully applied to allow unprecedented insight into fuel cells.



**Figure 1 – *In plane* images of dry fuel cells, illustrating the recent improvements in spatial resolution. The images were taken with different detectors: (a) imaging plate (b) new CCD based high resolution detector (c,d) respectively the same detectors, placed in a tilted position. The horizontal and vertical scales are not identical.**

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## **Structural Studies of Proton-Conducting Fluorous Block Copolymer Membranes**

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We use diblock copolymers as a model system to investigate the correlation between morphology and transport properties in ionomer materials. Diblock copolymers with a fluorinated block and a sulfonated polystyrene block allow control of the ionic exchange capacity by adjusting either the length of the sulfonated polystyrene chains or their degree of sulfonation. We have studied the structure of membranes made from various polymer configurations by small angle neutron scattering using contrast variation. Analysis shows that there is phase separation at length scales of the order of a few tens of nanometers due to the immiscibility of the two polymer blocks; and that there is substructure within the sulfonated polystyrene domains due to separation between the hydrated ionic groups and the hydrophobic polystyrene. We compare these results to transmission electron microscopy images and with proton conductivity and water content measurements.

## Numerical models of electrochemical devices

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We describe an approach for the numerical solution of coupled nonlinear reaction-diffusion-convection systems which uses the Voronoi box based finite volume method in one-, two- and three-dimensional domains [2, 3, 5]. It is applied to the modeling of direct methanol fuel cells and electrochemical flow cells.

The comprehensive model of the processes in the MEA of a direct methanol fuel cell, jointly developed with Forschungszentrum Jülich [1] includes

- Two phase flow of fluid and gas in the porous transport layers, including mixed wettability effects
- Charge transport in porous matrix and membrane
- Detailed catalytic reaction kinetics including catalyst coverings
- Phase change reactions (evaporation, condensation, dissolution)
- Stefan Maxwell model for the flow of a gas mixture
- Solute transport
- Energy balance

In order to gain more precise information on the anodic reaction kinetics, using the same numerical method, a model for electrochemical flow cells [4] is developed in cooperation with the group of R.J.Behm in Ulm. Simplified assumptions on the flow process allow here the coupling of transport processes in the channel to transport and reaction processes in the porous catalyst layer. The model is verified against known expressions for the limiting current, first comparisons with limiting current measurements have been performed. The model is coupled to a Levenberg-Marquardt method, with the aim to fit some of its parameters to measurements.

Several open questions arise which will be discussed in some detail

- Coupling of flow in channels and porous layers including mass transfer and creation of  $CO_2$  bubbles
- Paths and parametrizations of catalytic reactions
- Two phase flow parametrization
- Which ansatz to choose: Ideal conductivity, Ohms law or Nernst Planck-Poisson ?

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## Mesoporous Pt/Ru electrodes for direct methanol micro-fuel cells

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Direct methanol fuel cells are very promising devices for applications as power supply for portable electronic systems, medicine, communication and transport. High performance electrochemically obtained anodes and cathodes are especially interesting because their *in-situ* construction capability, aiming to applications in micro watt fuel cells (μFCs) [1]. As recently demonstrated, adjacent electroplated anode-cathode [2], silicon based [3] and commercial membrane electrode assembly based [4], μFCs can operate successfully in a compact design for *on-board* applications. However, no special efforts have been made to optimize the catalyst characteristics in this type of design. During the past years, new all-metallic mesoporous (MP) structures were synthesized by chemical [5] and electrochemical reduction [6] of metallic salts dissolved in the aqueous domains of a liquid crystal solution. Likewise, MP particles of Pt/Ru alloys [7] were obtained by chemical co-reduction (*ex-situ*). On the other hand, the Pt surface has been broadly modified by spontaneous deposition of Ru and results show that these electrodes improve twice the catalytic activity against conventional Pt/Ru alloys [8].

In this work, we propose a whole *in-situ* process for the production of greatly active Pt-Ru electrodes for practical *on-board* applications. These electrodes were obtained from electrochemical reduction of metallic salts dissolved in the aqueous domains of a liquid crystal solution by means of a potential step. Surface modification with Ru adatoms was carried out by spontaneous deposition from an aged solution of Ru<sup>+3</sup>.

The electrochemical characterization of these Pt electrodes reveals a high efficiency for methanol electrooxidation, with a mass activity of 41 Ag<sup>-1</sup>, which is improved up to 110 Ag<sup>-1</sup> when Ru adatoms are present as surface modifiers. These results support the viability of an *in-situ* building up for applications *on-board* fuel cell devices. The high current densities are related to low CO<sub>2</sub> conversion efficiencies, as it was established by using differential electrochemical mass spectrometry in a thin layer flow cell configuration (TLFC-DEMS).

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## The Use Of Simulation as a Design Tool In MEA Development

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Computer simulation of the varied processes occurring in the Membrane Electrode Assembly (MEA) of proton exchange fuel cells (PEMFC) is a well-established field. Whilst reasonable models exist for most of the processes, the complexity of a complete model has now made validation extremely difficult. In the literature, it is usual for models to be fitted to a relatively limited dataset, sometimes a single polarization curve. This means that the models are of limited validity and cannot be reasonably used to make predictions of MEA performance under conditions other than those used for validation. It is also difficult to use the models as predictive tools to improve MEA design. An alternative approach has therefore been adopted in Johnson Matthey. It has been found that the combination of relatively straightforward finite element models with appropriate experimental data can be more valuable in improving the understanding of MEA performance and in predicting fruitful areas for MEA improvement.

It has been shown that Tafel slopes reported in the literature as being representative of the kinetics of the electrochemical reaction are in fact heavily influenced by catalyst layer properties and that the true Tafel slope of the oxygen reduction reaction is likely to be at the lower end of the range of values reported in the literature.

The combination of experimental data and simple models has also been used to make suggestions of novel MEA designs with improved performance.

It has been demonstrated that performance losses that would conventionally be assigned to mass transport limitations could be a result of poor GDL conductivity. The correct way to address these losses is through changes in conductivity rather than water handling properties.

The requirements for a model to accurately predict the performance of an MEA under operating conditions will be discussed. It will be proposed that in order to be of value as a predictive tool, a model must contain a level of structural realism not currently present. Possible approaches towards this will be outlined and their feasibility discussed.



## Magnetic properties of Sr and Vacancy doped Nano-Crystalline (La,Sr/□)(Mn,Fe)O<sub>3±δ</sub> Manganites

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We report here the DC magnetic measurements of nano-crystalline perovskite systems La<sub>0.8</sub>Sr<sub>0.2</sub>Fe<sub>x</sub>Mn<sub>1-x</sub>O<sub>3±δ</sub> ( $x = 0.02, 0.20$ ), La<sub>1-y</sub>□<sub>y</sub>Mn<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3±δ</sub> ( $y = 0.1, 0.2$ ) in the temperature range 300K-20K. Samples synthesized by sol-gel technique show single-phase crystal structure with particle size 150-200Å ±20 Å. The magnetic moment increases initially with decrease in temperature showing a paramagnetic to ferromagnetic transition for all the samples. Further decrease in the temperature decreases the magnetic moment below 100K. The broad slope in FC curves could be attributed to nano particle size and with increase in Fe content the transition from Paramagnetic-Ferromagnetic-Antiferromagnetic becomes sharper. Mössbauer spectrums for all the samples show paramagnetic character at room temperature exhibiting a paramagnetic doublet. Mössbauer measurements at 80 K show magnetic ordering along with a central doublet for the Sr doped sample while there is no magnetic ordering seen for the vacancy doped samples. Occurrence of doublet in Mössbauer patterns at low temperature confirms the nanocrystalline nature of the samples indicating a superparamagnetic nature. Absence of metal-insulator transition and insulating nature observed in our temperature dependent resistivity studies in the temperature range 300-80K may be attributed to Fe doping and nanocrystalline nature of the samples.

**KEY WORDS:** Nano-Crystalline, Mössbauer Spectroscopy, Vacancy doping.

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## Highly Selective ORR Electrocatalysts for Mixed Reactant Direct Methanol Fuel Cells

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CMR Fuel Cells is a UK developer of fuel cell stacks for portable and small stationary power generation systems. Its unique and broadly patented mixed-reactant flowthrough fuel cell stack architecture has been demonstrated as early as 2001. Since then, further improvements in the technology for DMFC stacks enabled power densities of several hundred watts per liter. To allow flow-through of a mixture of fuel and air, CMR fuel cells utilize perforated MEAs and for efficient operation require the use of highly selective anode and cathode electrocatalysts. For the cathode, methanol tolerance is a prerequisite in a mixedreactant DMFC. While Pt is the most widely used ORR electrocatalyst in DMFCs, it suffers from its extreme susceptibility to methanol poisoning. Platinum-free precious metal chalcogenides have been suggested as alternatives with comparable oxygen reduction activity in the presence of methanol [1].

In a detailed study [2] of a developmental RuSe/C from the Hahn-Meitner Institute we were able to confirm that the selenium species on the catalyst was subject to oxidative dissolution if the catalyst was exposed to potentials exceeding 0.85V versus RHE in acidic electrolyte. In the same study a commercially available RhxSy/C from E-TEK was shown to be stable.

In this presentation we wish to report our results on a recently developed RuSex/C catalyst. The novel preparation method resulted in stabilization against electrochemical corrosion at potentials expected under direct methanol fuel cell operating conditions, while maintaining the ORR activity and selectivity in the presence of methanol of its predecessors.

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## Structure Formation in Catalyst Layers for PEFC Studied by Meso-scale Computing Simulations

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Synthesis and design of novel multistructured catalyst layers (CL) for Polymer Electrolyte Fuel Cells (PEFC) is of vital importance for improving the operation of these cells [1-3]. A conventional CL consists of Pt nanoparticles dispersed on carbon black and Nafion as the proton conducting ionomer. Appropriate distributions of these components together with sufficient gas porosity ensure a uniform distribution of reactants and reaction rates in the catalyst layer [3,4]. In order to guarantee high catalyst utilization, a rational design strategy is necessary to obtain an optimized composition and porous structure with well-attuned pore size distribution and wetting properties.

Due to the lack of systematic fabrication techniques with controlled microstructures [5,6], advanced computational tools are demanded to directly correlate the geometrical complexity of the catalyst layer to physico-chemical processes in PEFC. Here, we apply a versatile meso-scale simulation technique to rationalize the effect of fabrication processes and evaluate the microstructures formed with respect to the type and composition of ingredients, agglomerated structure, agglomerate size/composition, pore size distribution, pore network formation and transport processes. This versatile computational study aims to establish a relation between the electrochemical heterogeneity and geometrical disorder of the porous catalyst layer and its performance. Such studies in combination with experimental information provide valuable insights for optimization of performance and stability of CL operation and advanced CL design.

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## Pt Utilization Analysis Using CO Adsorption

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### Introduction

It is essential to utilize Pt as efficiently as possible for reducing the cost of PEFCs. Pt utilization ( $u_{Pt}$ ) defined as follows:

$$u_{Pt} = \frac{\text{ECSA}^* \text{ of Pt in an MEA}}{\text{SA}^* \text{ of a Pt/C catalyst}}$$

is generally used as an indicator how efficiently Pt is used in an MEA, but various methods have been proposed to determine the numerator and denominator and their results were widely spread[1]. In this paper, a reliable method for determine  $u_{Pt}$  is proposed and its result and implication are presented.

\*1 electrochemically active surface area, \*2 surface area

### Concept

The numerator, ECSA, and the denominator, SA, have been customarily determined by H adsorption voltammetry, and TEM, XRD, or CO pulse measurement, respectively. However, the absolute values obtained by these methods are not reliable because they need conversion factors from the measured values to the surface areas, which are not necessarily proven reliable. The method we propose here uses CO as the common probe for both the numerator and denominator, and  $u_{Pt}$  is described as follows:

$$u_{Pt} = \frac{\text{amount of CO adsorbed on EC}^* \text{ Pt in an MEA}}{\text{amount of CO adsorbed on a Pt/C catalyst powder}}$$

Since no conversion factors are necessary, the absolute value of  $u_{Pt}$  is expected to be more reliable.

\*3 electrochemically active

### Experimental

MEAs were fabricated in a decal method using 45%Pt/Ketjen catalyst prepared in a conventional procedure. The Nafion/carbon weight ratio was 0.75.

The CO adsorption amount of the Pt/C catalyst was measured by CO pulse measurement. The catalyst was pretreated in H<sub>2</sub>, or in H<sub>2</sub> followed by O<sub>2</sub> and H<sub>2</sub> at 80°C. The measurement temperature was between 30°C and 80 °C.

The amount of CO adsorbed on electrochemically active Pt in the MEA was estimated from CO stripping voltammogram assuming two electron oxidation. CO(100ppm)/N<sub>2</sub> was supplied to the MEA whose cathode potential was held at 0.05-0.40V vs. RHE for 15-30min under fully humidified atmosphere (cell temperature was 30-80°C).

### Results and discussion

#### Amount of CO adsorbed on catalyst powder

CO adsorption amount of the Pt/C catalyst increased 3% by adding the O<sub>2</sub> pretreatment. It also increased 6% by lowering sample temperature from 80 to 30°C, and became stable at 1.87 mmol/g<sub>Pt</sub> below 30°C.

#### Amount of CO adsorbed on electrochemically active Pt

Figure 1 shows H<sub>2</sub> generation current change over time at 50mV during the gas-change procedure. Below 40°C, once CO fully covered Pt, CO remained adsorbed even after the N<sub>2</sub> purge. This result shows that 40°C is low enough to obtain reliable CO stripping value. The CO stripping measurement showed that neither the set potential during CO adsorption nor the sweep rate affects the CO desorption amount under these conditions. The obtained value for our sample was 1.65 mmol/g<sub>Pt</sub> and  $u_{Pt}$  was 88%, which is much higher than the values estimated by other conventional methods as in Fig.2.

Therefore, we can conclude that Pt utilization is already high for today's MEA and that there is not much room for its improvement. The high value of  $u_{Pt}$  suggests that, for the reduction of precious metal loadings, further improvement is required in the activity of the catalyst, not just in its utilization.

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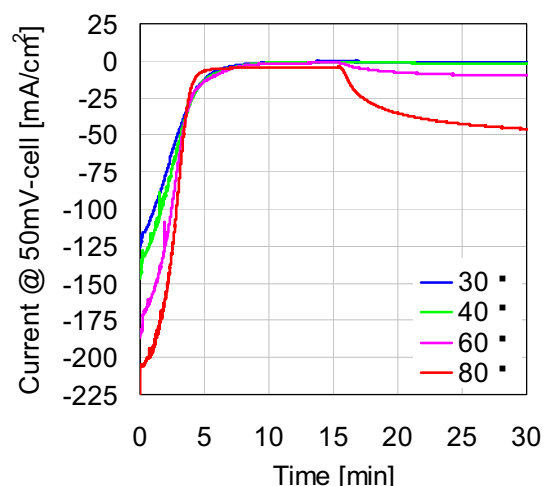


Fig.1 CO adsorption change monitored by H<sub>2</sub> generation current change at 50mV over time.

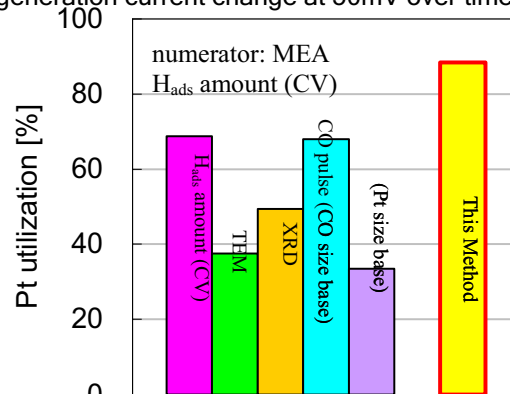


Fig.2 Comparison of  $u_{Pt}$  by surface area and  $u_{Pt}$  by CO adsorption amount.

## Formation of High Ionic Conducting $\gamma$ -BICUVOX at Moderate Synthesis Temperature

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In the present investigation the low temperature oxide ion conducting material for fuel cell application is derived from bismuth vanadate ( $\text{Bi}_4\text{V}_2\text{O}_{11}$ ). It exhibits three structural phases ( $\alpha$ ,  $\beta$  and  $\gamma$ ) between room temperature and  $800^\circ\text{C}$ . The high temperature  $\gamma$ -phase existing in the temperature range between  $570^\circ\text{C}$  and  $800^\circ\text{C}$  is tetragonal and exhibits good ionic conductivity. In present investigation, we have succeeded in stabilizing this high temperature disordered  $\gamma$ -phase at room temperature by partial substitution of copper for vanadium, with enhanced ionic conductivity even at low temperature. Many research groups have synthesized BICUVOX material using solid state reaction method. This method, however, is not suitable for fabrication of heterostructure planar single chamber solid oxide fuel cell. We have developed a simple, cost effective and moderate temperature spray pyrolysis technique to synthesize thin films of copper substituted bismuth vanadate with composition  $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ . These films can be used as an electrolyte in low temperature solid oxide fuel cells. The basic requirements of electrolyte material to be used in SOFC are high ionic conductivity and good chemical and thermal stability. These requirements are met by forming the thin films of  $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$  at moderate temperature.

Pinhole free and adherent thin films of  $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$  have been synthesized on alumina substrates by optimizing various spray parameters such as substrate temperature, spray rate, concentration of solution and distance between tip of the nozzle and the substrates. These films have been characterized for structural and electrical studies by various techniques. Spray deposited  $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$  films showed single phase nature with tetragonal crystal structure. The detailed results on structural and transport properties of  $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$  are discussed and reported in paper.

## Laccase - syringaldazine modified carbon - silicate composite electrode as cathode for biofuel cell

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Laccase catalyses four electron reduction of dioxygen to water [1]. This property makes this enzyme one of the possible candidates as biocatalyst on cathode for membraneless biofuel cell [2]. Syringaldazine (3,5-dimethoxy-4-hydroxybenzaldehydazin) is the compound used for determination of laccase activity [3]. It is one of the possible mediators for this enzyme.

Voltammetrically stable syringaldazine modified ceramic carbon electrode (CCE) was obtained by sol-gel processing of hydrophobic methyltrimethoxysilane based sol with dissolved syringaldazine together with dispersed graphite particles [4]. Laccase from *Cerrena unicolor* was encapsulated within thin hydrophilic tetramethoxysilane-based silicate film on the CCEs surface [5].

The electrochemical behaviour of electrode without laccase was monitored using cyclic and differential pulse voltammetry. The redox potential of syringaldazine depends on *pH*. Laccase - syringaldazine modified electrode exhibits catalytic activity towards dioxygen. Obviously, water insoluble syringaldazine immobilized within hydrophobic matrix of CCE shuttles electrons between carbon particles and enzyme.

Maximal current densities of electrocatalytic dioxygen reduction are observed in lower *pH* range (ca. 4.8), however in physiological *pH* range electrode is also active and exhibits better stability than ABTS modified electrode [6].

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## Development of electrocatalysts supported on non-conventional carbon materials for PEMFCs

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Recently, novel non-conventional carbon materials have attracted much interest as electrocatalyst support because of their good electrical and mechanical properties. The examples are supports produced from carbon nanofibers, carbon nanotubes, carbon aerogels or ordered mesoporous carbons (OMC). The electrocatalysts prepared with these materials have a better performance in methanol electrooxidation than commercial ones. The ordered mesoporous carbons have received great attention because of their potential use as catalytic supports in fuel cell electrodes since the discovery of the mesoporous silica materials. They have controllable pore sizes, high surface areas, and large pore volumes. However, they contain a small amount of oxygenated surface groups, which is disadvantageous for many applications. The relevance of the functionalization of carbon supports on the dispersion and anchoring of platinum particles on the support [1-4] has been reported in the literature. However, the functionalization of OMC has not been studied in a large extend because their ordered structure could collapse during the process.

The objectives of the present research are to modify different carbon materials (OMC, nanofibers as well as common Vulcan) by chemical treatment maintaining their ordered structure and to determine their effect on the dispersion and catalytic performance of platinum electrocatalysts supported on the functionalized materials. In this work, we pay attention on ordered mesoporous carbons synthesized using SBA-15 silica as template. Their texture and surface chemistry were modified by oxidation treatments in liquid phase using nitric acid at different concentrations as oxidative agent. OMC were used as platinum catalyst supports using the method of reduction with NaBH<sub>4</sub>, formic acid and glycols. Carbon materials were characterized by means of N<sub>2</sub>-physisorption, X-ray diffraction (XRD), high resolution transmission electronic microscopy (HR-TEM) and temperature programmed desorption (TPD). Methanol and carbon monoxide oxidation at platinum supported electrocatalysts were studied electrochemically by cyclic voltammetry, differential electrochemical mass spectrometry (DEMS) and Fourier transform infrared spectroscopy. Current-time curves were recorded in order to establish the activity towards these reactions.

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The authors gratefully acknowledge financial support given by the spanish MEC under the projects NAN2004-09333-C05 and MAT2005-06699-C03 (FEDER). The authors are also indebted to the SCT-UB technical services for the TEM facilities. J.R.C.S. thanks MEC for the research contract.

## Interfacial Structure and Dynamics in Fuel Cell Membranes

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Understanding the effect of chemical architecture, phase separation, and random morphology on proton transport and stability is vital for the advanced design of polymer electrolyte membranes (PEM). We explore the concerted dynamics of flexible charged sidechains, water molecules, and protons at hydrated polymeric aggregates inside PEM. We perform ab-initio calculations based on DFT for a primitive model of this interface. It consists of a two-dimensional hexagonal array of flexible acidic surface groups with fixed endpoints and one water molecule per group. We vary separations of surface groups and found strong dependency of sidechain correlations on the separation between surface groups. At a critical surface group separation of  $\sim 7\text{\AA}$  we observed a transition between highly correlated and cluster-like conformations of surface groups. Transitions between these conformations include proton transfer. We have identified hydronium translation, surface group rotation  $\phi$ , and surface group tilting  $\theta$  as collective coordinates that trigger this transition. We explored transition paths by calculating contour plots of the total energy as a function of these collective coordinates. For the lowest energy path we obtain a barrier-energy of 0.5 eV. This reaction path will be used to initiate dynamical simulations such as umbrella sampling. Furthermore we have calculated frequency of normal modes of these collective coordinates using harmonic approximation to the surface energy. Overall, results of our calculations provide valuable fundamental insights into proton transport mechanisms in PEMs at elevated temperature and minimal hydration that we will later on exploit in view of advanced membrane design.



## Nanotubes of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ for high performance cathodes of solid oxide fuel cells

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Perovskite-type mixed oxides, such as  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$  compounds, are at the present time one of the most widely used materials for cathode of intermediate temperature solid-oxide fuel cells. A significant increase of the specific area of the cathode can be achieved by preparing structures on the nanometric scale.

We have synthesized nanocrystalline tubular structures of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  by denitration, using polycarbonate porous templates, microwave irradiation and a further calcination at different temperatures. The shape and size of the tubes are determined by the characteristics of the template pores. The final thermal treatment is needed to obtain the desired perovskite-type crystal structure. The resulting products were studied by means of X ray diffraction and electron microscopy techniques.

We developed a very fast and simple method to attach them to ceria-based solid electrolytes, which allows the retention of its original hollow nanostructure. This procedure is based on a fast sintering treatment of an ink prepared with the cobaltite nanotubes, with relatively low dwell temperatures. In this way, we were able to investigate the performance of these novel nanostructured cathodes. We have observed that the obtained cathodes display lower polarization resistance than conventional microstructures reported in the literature.

We have studied the influence of the template pores diameter, microwave irradiation time and final thermal treatment temperature in order to optimize the electrical properties of the cathodes.

## Performance of Cobaltite Solid-Oxide Fuel Cell Cathodes with different nano/microstructure

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The  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (cobaltite) are good candidates for solid oxide fuel cell (SOFC) cathodes because these materials present high ionic and electronic conductivity, and compatibility with Cerium Gadolinium Oxide (CGO) electrolytes allowing a lower temperature of operation [1,2]. Most of reported cobaltite films have been deposited by slurry deposition techniques such as spraying [3], painting [4], or spin coating [5]. In order to further increase SOFC performance, it is necessary to understand how the microstructure of the composites electrodes affects the performance of the system. The aim of this work is to study the microstructure and electrode resistance of porous electrodes of the same composition films, i.e.  $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (LSCFO), deposited by different methods and to identify the sintering conditions to obtain low cathode overpotential values.

LSCFO have been prepared by an acetic acid-based gel and hexamethylenetetramine (HTMA) routes to obtain powders with grain sizes ranging from 10 to 800 nm depending on sintering conditions. Then, cathodes films were deposited onto CGO ceramic substrates (pressed  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  disks) by serigraphy, spin coating, dip-coating [6], and electrophoresis deposition technique. On the other hand, nanostructured cathode thin films with vertically-aligned nanopores (VANP) were processed using a pulsed laser deposition technique (PLD). These VANP structures enhance oxygen-gas phase diffusivity, thus improve thin film SOFC performance.  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (LSCO) and LSCFO were deposited on various substrates (YSZ, Si and CGO) [7].

The structure, morphology and composition of the powders and films were characterized by X-ray diffraction, transmission and scanning microscopy, and energy dispersive spectroscopy, respectively. The grain size and strain of initial powders and films prepared through different routes is analyzed by Rietveld analysis. The influence of the microstructure on the transport properties (ionic and electronic conductivity) is evaluated by means of impedance spectroscopy. We found that the electrochemical properties of LSFC cathodes films strongly depend on the microstructure that is mainly determined by synthesis parameters and technique used for the deposition of the films.

I will also present the initial structural characterization of LSCFO nanotubes that may be used for obtaining highly porous nanostructured cathodes.

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## $\mu$ -PEFCs - A novel concept with less particular parts

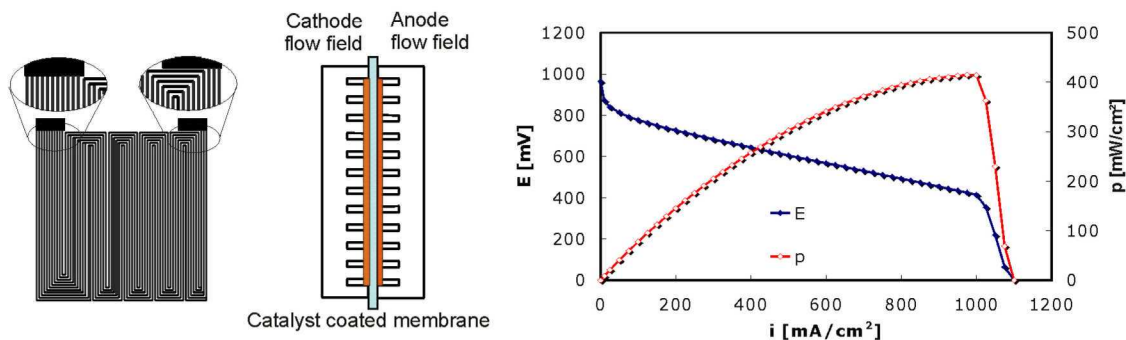
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Micro fuel cells are, due to their potentially high energy density, considered to be a suitable energy source for hand-held devices, such as laptops or cell phones.

In our work, a novel, simplified concept for micro polymer electrolyte fuel cells is introduced that combines the necessary functions in only three parts: Two Glassy Carbon based plates containing micro-structured flow fields and a catalyst coated membrane. The micro-structures are prepared in a sequence of three processes, i.e. sputtering, laser ablation, and Reactive Ion Etching in oxygen plasma [1-3].

With a fuel cell employing flow fields with merging channels we obtained a maximum power density of  $415 \text{ mW/cm}^2$  at a cell voltage of  $425 \text{ mV}$  ( $T_{cell} = 50^\circ\text{C}$ ,  $\lambda(\text{H}_2) = 1.3 @ 1\text{A/cm}^2$ ,  $\lambda(\text{O}_2) = 1.7 @ 1\text{A/cm}^2$ , 80% relative humidity). The micro fuel cell showed remarkable effects like an optimal operation temperature of  $45 - 50^\circ\text{C}$  or a strong influence of the flow field structure onto the performance [4,5]. Nevertheless, this micro fuel cell, due to its rather simple principle, can also be used as a powerful tool to examine processes occurring in technical PEFCs, like reaction kinetics, or mass transport limitations caused by a rather complex architecture.



*Top view scheme of a flow field with merged channels; Sketch of the simplified micro-fabricated PEFC; Polarization and power density curve, recorded under the conditions given in the text*

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## **Sputtered electrocatalysts for hydrogen energy conversion**

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### **ABSTRACT**

The active materials utilized in the contemporary hydrogen – oxygen polymer electrolyte electrochemical energy converters (PEMEEC) are still rather expensive. The catalysts are predominantly noble metals, typically platinum or platinum alloys with loading of about 1-2 mg.cm<sup>-2</sup>, interfaced with costly polymer electrolytes, typically Nafion. Significant cost savings can be gained through development of cheaper electrocatalysts and reduction of the loadings. These approaches depend essentially on the selected method for catalysts preparation which not only affects the activity of the catalytic material but often imposes limitations upon the minimal threshold loading required for the stability of the catalyst. The method of plasma enhanced physical vapour deposition (magnetron sputtering) is a feasible technique broadly used in microsystem technology for preparation of thin films with controllable thickness and tailored properties (composition, density, porosity, etc.) which can be easily adopted for direct incorporation of the catalytic material into the matrix of the membrane electrode assembly (MEA). The research reports on preparation of series of thin films (metals, metal oxides, alloys, and multilayer structures) by reactive DC magnetron sputtering. The sputtering process was optimised to achieve films with highly extended fractal surface. The composition, morphology and surface state of the sputtered films were characterised using X-ray diffraction, SEM, EDX, and AFM analysis. The catalytic activity was assessed by cyclic voltammetry and steady state polarization techniques. The selected materials demonstrated high catalytic activity, long-term mechanical stability and corrosion resistance. The results give credence to recommend the method as a reliable and cost effective alternative for PEMEEC catalyst preparation.

**Keywords:** electrocatalysis, PEM, hydrogen energy conversion

# A multi-scale model for the catalyst layer of a PEM fuel cell

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The catalyst layer of a proton exchange membrane (or PEM) fuel cell is a composite, multi-scale structure consisting of a polymer membrane, platinum catalyst, and carbon grains as support. We develop a model for mass and charge transport within the catalyst layer which separates phenomena taking place on two distinct scales: the rapid transport of reactants gas species through macropores, and the relatively slow diffusion of dissolved species through the polymer electrolyte. The resulting “1+1D” model takes advantage of this scale separation to obtain a fast numerical solution algorithm. Since the catalyst layer plays such a critical role in the overall operation of a fuel cell, we demonstrate how this model can be used to make predictions about the effect of changes in catalyst layer microstructure on fuel cell performance.

## Internal reference electrode systems for PEM fuel cells

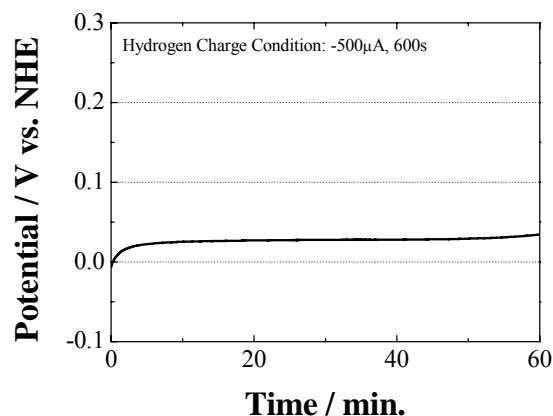
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In this poster we describe a range of different reference electrode systems for use within the polymer electrolyte of a solid polymer electrolyte fuel cell. Such reference electrodes need to be physically thin and must not be unduly influenced by the operating conditions of the fuel cell system. We have examined reference electrode systems based around a Pd/PdH reference electrode system. Porous palladium<sup>[1]</sup> is deposited on either a thin gold wire ( $\varnothing=50\mu\text{m}$ ) or carbon fiber ( $\varnothing=7\mu\text{m}$ ), and this palladium is charged with hydrogen. This reference electrode shows a stable electrode potential for 4 hours. However, it was found that this structure was somewhat fragile. An alternative approach as been sought utilizing porous palladium deposited onto a gold layer which is segregated onto Nafion®112 surface<sup>[2]</sup>. Such a Pd/PdH/Au/Nafion composite reference electrode has shown stable operation over a period of 40 minutes, somewhat shorter than the wire electrodes, but with much greater structural stability.

Pt/Au/Nafion composite electrode is used as DHE will report in this poster.



**Fig. 1** Pd/PdH/Au/Nafion electrode performance

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**The Development of Direct Methanol Fuel Cell at the School of Chemical Engineering and Analytical Science, The University of Manchester**

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The recent works in the development of direct methanol fuel cells (DMFCs) technology at the School of Chemical Engineering and Analytical Science (CEAS), at the University of Manchester is reported. The effort on the DMFC in CEAS is mainly on the development of DMFC based on the technology of proton exchanged membrane fuel cells (PEMFCs) in which polymer electrolyte and carbon supported platinum catalyst are employed in the membrane electrode assembly (MEA). The development of novel composite membranes, Nafion<sup>®</sup>-Zeolite, has been studied. These composite membranes are synthesized and employed as electrolyte in MEAs, which are tested in the DMFC testing unit manufactured in-house. The results achieved are compared with those obtained from MEAs fabricated with commercially available electrolyte membrane, Nafion-117. In term of the development of carbon supported platinum catalysts, novel mesoporous carbon with high surface area has been synthesized and incorporated with platinum catalyst. This novel material is aimed to be employed in the electrode of MEAs. These MEAs will be tested and the results will be evaluated and compared with those from commercially available materials such as platinum catalyst supported by Vulcan XC-72. Apart from the development of those materials, the experimental study on the effect of flow field configurations on the performance of DMFC is also reported.

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## **ABSTRACTS OF TALKS**



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Membrane development: from low to high temperatures (PEFC), from high to low temperatures (DAFC).

## Measurement of proton resistance in cathode catalyst layers and its correlation with the ionomer-to-carbon ratio

Daniel R. Baker, Michael W. Murphy, Wenbin Gu, Yuxiu Liu, Hubert Gasteiger

Ohmic resistance to proton transport in the cathode electrode can be a major source of voltage loss in PEM fuel cells, especially under dry operating conditions. An experimental method for measuring the proton sheet resistance in the cathode, using either H<sub>2</sub>/N<sub>2</sub> or H<sub>2</sub>/O<sub>2</sub> on the anode/cathode, was developed in reference [1], based on impedance modeling developed in reference [2]. In this talk, we focus on the system using H<sub>2</sub>/N<sub>2</sub>, and refine the measurements and modeling to improve the accuracy and versatility of the method. Special electrodes were prepared from ≈ 50% Pt/Vulcan and 1100 Equivalent Weight ionomer (Dupont), with uniform ionomer distributions and ionomer-to-carbon (I/C) ratios ranging from approximately 1.2 down to 0.3. The proton sheet resistances were measured at four different values of relative humidity (RH). The dependence of sheet resistance on I/C and humidity will be discussed, and evidence will be shown for a critical percolation threshold near I/C=0.3, below which proton conductivity vanishes. A brief discussion of impedance spectra for electrodes with non-uniform ionomer distributions will illustrate via simulation how to interpret such spectra.

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## PBI Polymers for High Temperature PEM Fuel Cells

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### Abstract

Polybenzimidazole (PBI) polymers are excellent candidates for PEM fuel cell membranes capable of operating at temperatures up to 200°C. The ability to operate at high temperatures provides benefits such as faster electrode kinetics and greater tolerance to impurities in the fuel stream. In addition, PBI membranes doped with phosphoric acid can operate efficiently without the need for external humidification and the related engineering hardware to monitor and control the hydration levels in the membrane. PBI membranes are currently being investigated as candidates for portable, stationary, and transportation PEM fuel cell applications.

A new sol-gel process was developed to produce PBI membranes loaded with high levels of phosphoric acid.<sup>1,2</sup> This process, termed the PPA process, uses polyphosphoric acid as the condensing agent for the polymerization and the membrane casting solvent. After casting, absorption of water from the atmosphere causes hydrolysis of the polyphosphoric acid to phosphoric acid. The change in the nature of the solvent induces a sol-gel transition that produces membranes with high loadings of phosphoric acid and a desirable suite of physical and mechanical properties. The new membranes were characterized through measurements of acid doping levels, ionic conductivity, NMR, mechanical properties and fuel cell testing.<sup>3</sup> The durability of these new membranes in multiple operating environments is of particular importance for the further development of practical fuel cell devices. Testing protocols have been developed to examine the behavior of PBI membranes under both static and cyclic conditions. The results of long-term testing under these conditions as well as long term static testing will be presented.

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## **Colloid Based Crystalline and Amorphous Structures**

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### **Abstract**

A few basic concepts of colloidal science and the simple DLVO theory are introduced in order to provide the participant with a crude understanding of colloidal interactions. Without going into numerical details, this insight leads directly to a generic phase diagram of colloids in terms of which processes of structure formation can be illustrated.

A few real examples of synthesised colloid based crystalline and amorphous structures will be shown in the presentation. The highlight will be a recently fabricated porous amorphous structure designed for the application in fuel cell electrodes. It is the authors intention not to give detailed explanations on recent improvements in colloidal science but to qualitatively illustrate how principles of colloidal science can be applied in the development of, e.g., novel fuel cell architectures.

# Fuel Cell Stack Operation: Exploring Inhomogeneous Cell Polarization

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## Abstract

Cell interaction phenomena in fuel cell stacks that arise from inequalities between adjacent cells are investigated in detail experimentally. For that, a specialized 2-cell stack with advanced localized diagnostics was developed. The results show that inequalities propagate by electrical coupling, inhomogeneous cell polarization and inducing in-plane current in the common bipolar plate. The effects of the different loss-mechanisms are analyzed on a theoretical [1] and experimental basis [2].

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## Structure-reactivity relationship and elementary reaction steps in electrocatalysis

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The systematic modification of the reactivity of metal surfaces is of strong current interest since it might lead to the design of better catalysts in electrocatalysis. This requires a detailed knowledge of the fundamental factors that determine the reactivity. We have addressed this issue by performing periodic density functional theory (DFT) calculations of simple molecules interacting with typical electrode metal surfaces. We have in particular focused on bimetallic surfaces since they are well-suited for tailoring the reactivity by preparing specific surface compositions and structures.

Bimetallic systems can show chemical properties that either correspond to an average over both constituents or they exhibit properties that are beyond those of the single constituents [1]. We have studied the local reactivity by determining the adsorption energies of probe molecules such as CO. Besides the effect of strain we have focused on the ligand effect caused by the electronic interaction between the components of a bimetallic system and the ensemble effect related to the availability of higher coordinated adsorption sites. In PtAu [2] and PdCu [3] systems, both effects can show opposite trends as a function of the composition. In addition, we have addressed the influence of the presence of water and of an external electric field on the chemisorption properties [4].

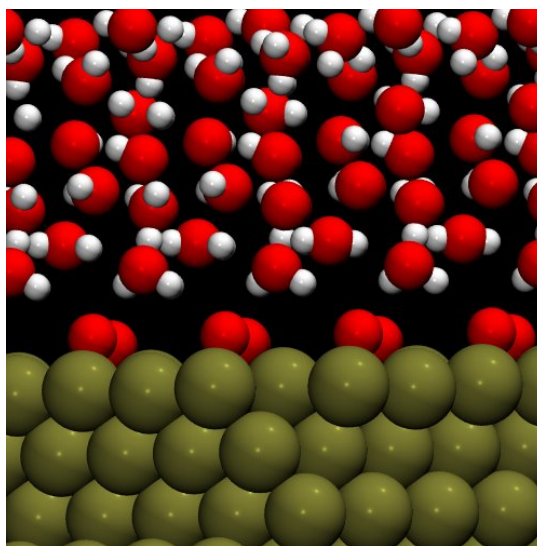


Fig. 1 Adsorption geometry of O<sub>2</sub> on Pt(111) in the presence of water and one Zundel ion, considered as an initial step in the oxygen reduction reaction.

Furthermore, first results will be reported with respect to the determination of the elementary reaction steps in electrocatalysis such as the oxygen reduction reaction on Pt(111) (see Fig. 1).

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## Design of Fuel Cells with Solid Acid Proton Conductors

Sossina M. Haile, California Institute of Technology

The compound  $\text{CsH}_2\text{PO}_4$  has emerged as a viable electrolyte for intermediate temperature fuel cells. This material is a member of the general class of compounds known as solid acids or acid salts, in which polyanion groups are linked together via hydrogen bonds and monatomic cations provide overall charge balance. Within this class, several solid acids display a so-called superprotonic transition, at which the compound transforms to a structurally disordered phase of high conductivity. At the transition the conductivity jumps by 3-5 orders of magnitude and the activation energy for proton transport drops to a value of  $\sim 0.35$  eV. The rapid proton transport in the superprotonic phase results from the high degree of polyanion rotational disorder. In the case of  $\text{CsH}_2\text{PO}_4$  the transition occurs at 230 °C (with the conductivity rising to  $2.2 \times 10^{-2}$  S/cm at 240 °C), enabling fuel cell operation at temperatures between 230 and 260 °C.

Solid acids, and  $\text{CsH}_2\text{PO}_4$  in particular, offer a number of realized and potential advantages for fuel cell operation relative to polymer, solid oxide, and liquid electrolyte alternatives. Fuel cell development based on this material, however, is still very much in its infancy. Fabrication methodologies have progressed to the stage that thin ( $\sim 25$   $\mu\text{m}$ ) electrolyte cells supported on porous gas diffusion electrodes, can be reproducibly prepared. In such cells, which yield peak power densities of over 400  $\text{mW}/\text{cm}^2$ , oxygen electro-reduction is rate-limiting, much as it is in conventional polymer electrolyte membrane fuel cells. In this work we present recent results aimed at quantifying electrocatalytic activity of Pt in  $\text{CsH}_2\text{PO}_4$  based fuel cells.

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**New reactive force field allowing bond breaking/formation in classical simulation of proton transport in water, acid solutions and polymeric electrolyte membranes**

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We present a new effective classical force field for the simulation of the conductivity in fuel cell membranes. The force field is based on the central force model for water, i. e. the interactions between the atoms are defined by three atom pair potentials. The force field integrates the inter- and intramolecular part into a single potential. This approach has two special features: Firstly, it allows to model on the classical level bond breaking and formation, secondly, integral equation theory of liquids becomes applicable. These properties make the force field very attractive for computer simulations of proton transport and proton conductivity in water and acid solutions. It enables us to perform simulations for large systems with long simulation times, which is required for the derivation of conductivity from molecular dynamics. The potentials of the force field were optimized to reproduce the experimental radial distribution functions of water in a wide range of temperatures and pressures exactly. We show, that the force field reproduces correctly not only the RDF, but also other properties of water, e.g. density, selfdiffusion, and lifetimes of hydroniums. Finally we compare simulated properties of hydrated Nafion membranes, dissoziation degree, selfdiffusion, and conductivity with experimental data.

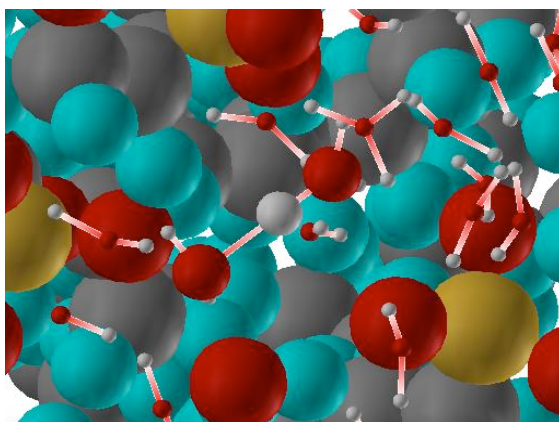


Figure 1. The transition state of hydrogen transfer between two waters in hydrated Nafion. A

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**Fluorous, Ion-containing Block Copolymers: Model Polymers for Investigating the Role of Morphology on Proton Conduction**

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In order to predict the performance of a proton exchange membranes in a fuel cell and to design application-specific materials it is necessary to develop a fuller understanding the physico-chemical attributes of the solid polymer electrolyte. This necessarily requires the undertaking of rigorous, systematic studies on representative materials that possess known and controllable structures and morphologies. In this presentation the synthesis and properties of several series of novel ionic, block copolymers are described.

# Statistical Physics and Computer Modeling of Ionomers: Fundamentals and Application to Proton-conducting Membranes

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Although recent years have witnessed an impressive confluence of experiments and theories, there are controversial opinions concerning the morphology of ionomer membranes used in polymer electrolyte fuel cells. For this problem, numerical mesoscopic simulations in conjunction with simple models provide a rather detailed answer. We discuss, with examples from our own and other studies, some applications of the analytical approaches and mesoscopic simulation techniques, including dissipative particle dynamics (DPD), cellular-automaton-based (CA) method,<sup>1</sup> integral-equation (RISM)<sup>2</sup> and field-theoretic (SCMF)<sup>3</sup> methods, and integrated multiscale modeling strategies. The main question addressed in this talk is what role do the competing hydrophobic/polar interactions play for the structural properties and behavior of hydrated Nafion membranes. The results demonstrate the important predictive capability of the mesoscopic simulations to Nafion membranes with different hydrated morphologies. We check against simulation data the existing phenomenological models used in the literature to describe the structural features of water-swollen ionomer membranes. In particular, our SCMF calculations predict distinct morphological changes in the material upon alteration of temperature and water content.<sup>3</sup> We find that the hydration level corresponding to the microphase segregation depends on the temperature of the system. Spherical clusters constituting the hydrophilic microphase of the membrane at relatively low water content (but above the transition point) grow in size, coalesce and form a network of channels responsible for the ionic transport at higher hydration levels. This hydrophilic phase is shielded from the hydrophobic matrix by the sidechains of Nafion, their end-groups being turned towards the water clusters. The results obtained are similar to those reported from RISM and CA studies and support the "cluster-network" model for the low hydration levels and the "sponge" model at higher hydration levels.

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## Structure sensitivity of fuel cell anode reactions

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This talk discusses the structure sensitivity of fuel cell anode reactions such carbon monoxide oxidation, methanol oxidation, and ethanol oxidation on stepped single-crystal platinum electrodes. Electrochemistry experiments are complemented with in situ infrared spectroscopy and on-line mass spectrometry, and compared to experimental results obtained in ultra-high vacuum and density functional theory calculations. Mechanistic implications of our results will be discussed.

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# Physical modeling of direct methanol fuel cells

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Our basic model of a DMFC describes the through-plane transport of reactants and charges and the consumption of feed molecules along the channel. Large ratio of channel length to the MEA thickness makes it possible to split the fully 2D problem into a 1D through-plane problem and a 1D problem in channels. This idea was utilized some 20 years ago by Fuller and Newman in numerical modeling [1]; we employ this approach to construct analytical models.

The idea of spitting will be illustrated with the model of the cathode side of a hydrogen cell and compared to experiments [2]. Then we will discuss the quasi-2D model of a DMFC; using this model the effect of gaseous bubbles in the anode channel on cell performance will be rationalized [3].

At low oxygen flow rates the model gives unexpected solution: current density appears to be localized close to the oxygen channel inlet. Furthermore, even at vanishingly small current in the load, local current density at the oxygen channel inlet remains constant. This explains lowering of cell open-circuit voltage (mixed potential) [3].

In order to verify this effect we have designed a linear cell with the straight channels and segmented electrodes. The results of experiment with this cell confirm the model predictions discussed above. Moreover, we have found that the oxygen-depleted part of the cell turns into electrolysis mode and it serves as a “load” for the galvanic (oxygen-rich) domain [4].

Further studies have shown that operation in electrolysis mode improves galvanic performance of the cell. Periodical “activation” of cell by running it for several seconds in electrolysis mode improves galvanic performance by 10–30% [5].

Under certain conditions hydrogen produced in the electrolytic domain is utilized within the cell as a fuel. Finally, we discuss this *direct methanol-hydrogen fuel cell* [6].

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## THEORETICAL MODELS OF PROTON TRANSFER IN CONDENSED MEDIA.

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A short overview of main physical models for the elementary acts of proton transfer in condensed media is presented. The physical mechanisms of the transitions are discussed and major results for the rate constants are given. Especial attention is paid to the proton transfer in the systems with hydrogen bonds one of the most important of which is represented by water. An approach for the elucidation of the mechanism of proton transfer in the surface layers of narrow pores of the membranes of the fuel cells is suggested.

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# Fluids in porous media: a morphometric approach to structure-property relations

Klaus Mecke (Universität Erlangen)

Predicting the relationship between the morphology of porous media and their physical properties, e.g. the conductivity, elasticity and permeability, is a long-standing problem and important to a range of applications from geophysics to materials science [1]. Here, a set of four morphological measures, so-called Minkowski functionals, is defined which allows one to quantitatively characterize the shape of spatial structures, to optimally reconstruct porous media, and to accurately predict material properties [2]. The method is based on integral geometry and Kac's theorem which relates the spectrum of the Laplace operator to the four Minkowski functionals. Analytic expressions for mean values of Minkowski functionals in Boolean models lead to the definition of an effective shape of a grain in a system made up of a distribution of arbitrarily shaped constituents. Reconstructing the microstructure using this effective grain shape yields an excellent match to the percolation thresholds and to the mechanical and transport properties across all phase fractions [3]. Additionally, the use of the effective shape in effective medium formulations leads to good explicit predictions of bulk moduli. The method is verified for several model systems and sedimentary rock samples, demonstrating that a single tomographic image is sufficient to estimate the morphology and physical properties such as permeabilities and elastic moduli for a range of porosities.

Also the thermodynamic behavior of fluids in porous media, i.e., the shape dependence of the grand canonical potential and of surface energies of a fluid bounded by an arbitrarily shaped convex pore can be calculated in the thermodynamic limit fully from the knowledge of the Minkowski functionals, i.e., of only four morphometric measures [4]. This remarkable result is based on Hadwiger's theorem on the completeness of the additive Minkowski functionals and the assumption that a thermodynamic potential is an additive functional which can be understood as a more precise definition for the conventional term extensive. As a consequence, the surface energy and other thermodynamic quantities contain in the thermodynamic limit, beside a constant term, only contributions linear in the mean and Gaussian curvature of the pore and not an infinite number of curvature terms. Finally, starting from a microscopic density functional for an inhomogeneous fluid in a porous medium the phase coexistence (capillary condensation) and the critical point of the fluid is determined in terms of structure functions and morphological measures of the pore space and calculated explicitly for specific random porous structures using results from integral geometry.

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## On the role of structural defects in electrocatalysis by supported metals

Alexei M. Kuznetsov<sup>a</sup>, Alexei N. Gavrilov<sup>b</sup>, Pavel A. Simonov<sup>a</sup>, Vladimir I. Zaikovskii<sup>a</sup>,  
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Structural defects play major role in catalysis and electrocatalysis. In this talk we will discuss the role of structural defects in electrocatalysis by mono- (Pt) and bimetallic (PtRu) supported catalysts in model reactions of CO and methanol oxidation. The advantages and disadvantages of various types of supported noble metal catalysts for fuel cell applications will be analyzed.

### Acknowledgements

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# Atomistic Simulation of Proton Transport in Model PEM Pores

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Proton transport in fuel cell membranes such as Nafion or PEEK takes place in a strongly inhomogeneous aqueous environment. Local proton motion, both the magnitude of the transport coefficients and the nature of the transport (vehicle vs. structural diffusion), is influenced strongly by key system properties such as

- the chemical and electrostatic nature of sulfonate groups, and their arrangement on the polymer chains,
- high proton concentration,
- the amount of water in the membrane and thus the nature, size and connectivity of aqueous domains.

Transport coefficients and mechanistic insight obtained from classical molecular dynamics studies employing a simplified empirical valence bond model in simple model pores will be discussed [1-3]. In particular the question will be addressed how the relative importance of Grotthuss (structural diffusion) changes with water content, temperature and sulfonate density.

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# **PEM fuel cells for automotive applications: prospects and challenges**

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## **Abstract**

One of the main obstacles impacting fuel cell development progress is the fact that many of the fundamental processes still are only partially understood. Therefore, an overview over some of the fundamental processes that determine the functionality of the main components of a PEM fuel cell will be provided together with illustrative examples on how advanced diagnostic measurement tools can help advance understanding. Also, some of the key challenges and issues that need to be overcome in order to achieve commercially-viable PEM fuel cell technology will be discussed.

## Dual scale modeling of mobility of additives in a polymer matrix

Authors: Nico F.A. van der Vegt, Kurt Kremer

Max Planck Institute, Mainz, Germany

### Abstract:

In my talk I will discuss the development and use of (high-resolution) classical atomistic and (low-resolution) coarse grained models in computer simulations of polymer materials. I will illustrate how coarse grained models can be used to study materials in which all length scales are equilibrated [1] and how by virtue of "inverse mapping of chemical details" [2,3] permeation of small solute molecules can be addressed. I will moreover show an example in which diffusion of small solutes inside a polymeric matrix is predictively modelled with a coarse grained model.

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# Effective strategies for unraveling microscopic energetics and dynamics of proton transport in complex systems: From QM/MM to Monte Carlo EVB based models

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Proton transport (PTR) plays a major role in many biological processes. The control of PTR by biological systems became a popular issue after the discovery of aquaporin and subsequent works. These studies illustrated that aquaporin transports water while preventing PTR. Most workers in the field have argued that PTR in proteins is controlled by the so-called Grothuss mechanism, where the orientation of the water molecules plays a crucial role. Furthermore, simulation studies of the transport of neutral water through aquaporin were used to postulate how the PTR is controlled. However, it is not clear why simulations of neutral water molecules should be useful in studies of charge transport processes. Obviously, this and other related issues can only be explored by simulating the relevant PTR process.

This lecture will introduce reliable and effective methods for actual simulations of PTR in solutions and proteins. This will include QM/MM methods, the EVB method [1] and a simplified version of the EVB that will be used as our main tool in studies of multistep PTR. It will be demonstrated that PTR in proteins is controlled by the electrostatic free energy of the proton rather than the effect of water orientation. This point will be illustrated by studies using different levels of our model, ranging from the simplified modified Marcus' equation [2-4] to simplified EVB with Brownian Dynamics and / or Monte Carlo and finally fully atomistic EVB [3]. The use of our approach in probing key problems (such as the action of cytochrome c oxidase [3-7]) will be illustrated, emphasizing its ability to provide a molecular unpretending of fundamental pumping process

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## **Dynamic instabilities in electrocatalysis and their impact on reaction efficiencies**

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CO is a well known poison for electrocatalytic reactions on Pt electrodes. It might be present as contamination of the educt feed, as e.g. in the H<sub>2</sub>-feed to a fuel cell, or form as a reaction intermediate during the electrooxidation of organic species, such as methanol. The presence of CO also promotes dynamic instabilities and thus renders homogeneous, stationary operation conditions unstable.

We present theoretical and experimental results on instabilities and pattern formation in CO|Pt and H<sub>2</sub>,CO|Pt-systems and discuss strategies how the dynamic instabilities can be exploited to minimize the poisoning effect of CO, in particular, how to minimize the voltage loss at the anode of a fuel cell when fed with CO contaminated H<sub>2</sub> gas.

## BIOENERGETIC PROTONS AND BIO-H<sub>2</sub> PRODUCTION

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### **Abstract**

Understanding of proton transfer reactions along the cellular membrane is of fundamental importance for bioenergetics. The purple membrane of Halobacteria represents a sufficiently simple system to study lateral proton transfer with the help of judiciously placed pH-indicators along the surface of bacteriorhodopsin. Active proton transfer across bacteriorhodopsin is observable by time-resolved FT-IR spectroscopy. Examples will be provided that illustrate how single proton transfer events can be traced in time and space<sup>1,2</sup>.

As a methodological advance, we have recently developed Surface Enhanced Infrared Difference Absorption Spectroscopy (SEIDAS)<sup>3</sup> to probe potential-induced structural changes of a protein on the level of a monolayer. A novel concept is introduced to incorporate membrane proteins into solid supported lipid bilayers in an orientated way via the affinity of the His-tag to the Ni-NTA terminated gold surface<sup>4</sup>. Full functionality of the surface tethered cytochrome c oxidase is demonstrated by cyclic voltammetry after binding of the natural electron donor cytochrome c. General applicability of the methodological approach is shown by tethering photosystem II to the gold surface<sup>5</sup>. In conjunction with hydrogenase, the basis is set towards a biomimetic system for H<sub>2</sub>-production.

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## Modelling of porous materials: From topology to physical properties.

Alexey S. Ioselevich and Dmitry S. Lyubshin, Landau Institute of Russian Academy of Sciences

We introduce and study several kinetic models for the porous material fabrication process. All these models involve consecutive removing of pore-former particles, randomly embedded in the initially solid network. After each step of this process the system is locally adjusted to secure the connectivity: clearly, disconnected clusters can not be mechanically stable without support from the "mainland". Depending on the details of the adjustment procedure different scenarios are possible. The properties of the system can either change smoothly with the increase of porosity, or experience a second order topological phase transition to the "tree-like phase" with dramatic physical consequences. In the tree-like phase the system does not have a backbone, and, therefore, it should be non-conducting and extremely fragile. In more realistic models for the adjustment procedure the phase transition is smoothed and the high-porosity state pertains finite (though, extremely poor) conductivity and elasticity. Some principal results (e.g., the existence and characteristics of the phase transition in the simplest model) were obtained analytically, but the main instrument of our study for more sophisticated models was based on numerical simulations. Our results may give an insight for the problems, which technologists encounter, when dealing with highly porous materials.

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# Investigation PEMFC electrodes and MEAs using electrochemical techniques

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The performance of porous electrodes and Membrane Electrode Assemblies (MEAs) in a fuel cell depends on a combination of intrinsic material properties, electrode and MEA design and operating conditions. Intrinsic properties include for example catalytic activity for a given composition of a catalyst, while electrode porosity, surface area of the catalyst or effective transport properties in the gas phase or ionomer can be affected by the design. Operating conditions will in the end influence all these parameters.

We have for a long time developed techniques that can be used to evaluate electrodes and MEAs at well-controlled fuel cell working conditions [1-8]. By using a combination of mathematical modelling, electrochemical measurements and ex-situ techniques for determination of the electrode morphology it is possible to discriminate between intrinsic properties and the influence of design and operating conditions. This makes it possible to extract parameters and identify rate-limiting processes for different materials, designs and operating conditions. Some example of this for the oxygen reduction reaction and the hydrogen oxidation reaction will be given in this presentation.

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# Challenges and Directions in Electrocatalyst Research for PEMFCs

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A present challenge in the development of polymer electrolyte fuel cells is to achieve sufficiently high power densities  $>1\text{W}/\text{cm}^2$  at voltages  $>0.8\text{ V}$ . Under such operation conditions the ratio of electrical power ( $P_{\text{el}}$ ) and co-generated heat ( $P_{\text{th}}$ ) is  $P_{\text{el}}/P_{\text{th}}>2$ . Thus, on one hand a higher energy conversion efficiency of the fuel cells would be achieved; on the other hand, the heat management of the fuel cell stack and system requires a less complicated design and hence decrease costs. In order to tackle these targets the following aspects need further development:

- In  $\text{H}_2/\text{O}_2$ -cells the catalyst of the cathode has to be improved. In alcohol/  $\text{O}_2$ -cells the anode and cathode reaction rates have to be enhanced;
- Supports other than carbon based materials should be taken into account;
- The overall resistance of the catalyst layer needs to be decreased with respect to the electron and proton conductivity;
- The mass transport in the catalyst layer has to be optimized in order to limit transport problems of reactants and products at high current densities.

In catalyst development nowadays it is possible to identify promising candidates using density functional theory (DFT), as was shown for example by Nørskov et al.<sup>[1,2]</sup> Especially non-noble, possibly bimetallic materials should be considered. For such materials the electrocatalytic activity can be influenced by alloy formation.<sup>[1]</sup> It is known that the activity of electrocatalysts is furthermore determined by particle size.<sup>[3, 4, 5]</sup> Consequently a major aspect will be to identify the optimal particle size and particle distribution in order to achieve the maximum utilization of catalyst material.

Also, novel non-carbon based support materials with higher corrosion stability and improved conductivity can be of importance. For example, ruthenium oxide ( $\text{RuO}_x(\text{H}_2\text{O})_y$ ) was shown to be a promising material because it provides both, electron and proton conductivity.<sup>[6]</sup> This helps to increase the utilization of the catalyst. Shortly summarized, in addition to the obvious “quest” for novel catalyst material, we need to understand the major factors that influence the specific activity of a catalyst material: Among these, we have to clarify how the interactions of the catalyst with the support material determine reactivity. This includes further an understanding of individual particle reactivity. Furthermore, we have to understand the structure- and size reactivity correlation in greater detail.

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Molecular and Mesoscale Modeling of Hydrated Ionomers  
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Proton exchange membrane fuel cells are the primary fuel cell system being developed for use in automotive applications due to their power densities approaching one watt/cm<sup>2</sup> and suitable range of operating temperatures. The performance of the ionomers used as proton exchange membranes, however, needs substantial improvement to make fuel cells economically competitive with alternative approaches. Chemically and mechanically robust ionomers that operate at higher temperature and lower relative humidity would simplify stack control and improve overall fuel cell efficiency. The principal goal of this work has been to provide guidance to the synthesis and processing of high performance organic triblock copolymer membranes using *ab initio*, molecular dynamics (MD), and mesoscale modeling, while using perfluorinated sulfonic acid ionomers (PFSAI), like Nafion, to develop the methodology at each length scale and as a basis for comparison. The dependence of acid hydration and ionization on water content and local electric fields were modeled with *ab initio* calculations of small acid-water nanoclusters using the B3LYP//6-311G(d,p) model chemistry<sup>1</sup> for both perfluorinated and aromatic sulfonic acids. Model predictions of the water absorption isotherm of PFSAI membranes were obtained by combining these *ab initio* results with the James-Guth continuum relation<sup>2</sup> for the mechanical response of the membrane. At an intermediate length-scale, MD simulations were used to extract Flory-Huggins parameters ( $\chi_{HF}$ ) using the conventional approach based on the Hildebrand solubility parameters,<sup>3</sup> as well as through a series of MD simulations at various compositions that utilize the fundamental definition of  $\chi_{FH}$ . The latter calculation reveals a strong dependence of  $\chi_{HF}$  on composition. The mesoscale morphologies of both PFSAI and triblock membranes were investigated using self-consistent mean field theories (SC-MFT) derived from the Edwards equation and the random phase approximation (RPA).<sup>3,4</sup> Due to the lower value of  $\chi_{HF}$  between the hydrophobic and hydrophilic blocks of the organic triblock membranes compared to PFSAI, polydispersity was found to have a substantial effect on the level of phase separation in the triblock membranes and the retention of water within their hydrophilic phase. Although PFSAI remains the benchmark for performance, progress has been made in utilizing the favorable lamellar morphology of the triblock ionomers to increase the volume fraction of the conducting phase and reduce its tortuosity. Continuing iterations between synthesis and modeling, the development of a robust organic membrane that exceeds the performance of PFSAI at high temperature and low relative humidity appears to be tractable.

\* This work was done in collaboration with Armand Soldera (University of Sherbrooke), Gerhard Maier (polyMaterials A.G.), James Wescott and Lalitha Subramanian (Accelrys), and Yue Qi (General Motors R&D Center).

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## Cathode Catalyst Layers in PEFC: The Major Competitive Ground

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The cathode catalyst layer (CCL) is the major competitive ground for electrochemical reaction, reactant transport, and water and heat exchange in a Polymer Electrolyte Fuel Cell (PEFC) [1]. The complex porous structure and partial liquid saturation have a strong impact on the current generation during oxygen reduction [2]. In addition, the CCL controls water fluxes and converts liquid water into water vapor. Understanding these complex coupled functions in relation to fabrication procedures and physical characterization of effective properties is a multiscale problem. It demands hierarchical approaches in modeling. Correspondingly, our theoretical studies proceed in several steps, two of which will be considered in this presentation. At the mesoscopic scale, we employ coarse-grained molecular dynamics simulations to explore self-organization upon catalyst layer formation from colloidal dispersion [3]. These simulations provide insights into structural correlations and dynamical behavior of different phases in the catalyst layer composite. We explore the emerging structural picture to develop theoretical approaches that link spatial distributions of reactants, electrostatic potentials, and reaction rates with catalyst utilization, water handling capabilities, and voltage efficiency [2,4]. Results demonstrate that the CCL acts like a watershed in the fuel cell, regulating the balance of opposite water fluxes towards membrane and cathode outlet. Due to a benign porous structure, the CCL represents the prime component for vaporization of liquid water in PEFC. The non-linear spatial coupling between liquid water accumulation and oxygen depletion gives rise to critical effects and bistability in catalyst layer operation. Overall, these studies emphasize the importance of both morphology and operating conditions for the successful design of CCL.

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## Addressing Materials and Electrocatalysis Challenges in DMFCs with Combined Engineering and Science Tools

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### Abstract

This talk opens with review of recent development of direct methanol fuel cells (DMFCs) for portable electronic devices, including multi-functional handsets, laptops and more. Methanol fuel has substantial advantages for such applications, being a liquid under ambient conditions associated with relatively high theoretical energy density and with relatively high rates of anodic oxidation when considering it is a carbonaceous fuel. However, the miniaturization required for consumer electronics applications sets a high bar for DMFC technology developers. An innovative approach to DMFC system simplification, applied starting in 2003 at MTI MicroFuel Cells (Albany, NY), has contributed significantly to system miniaturization capability and is, in fact, an example for the theme of this meeting: "Physical Understanding leading to a Novel Fuel Cell Architecture"

It will be further shown that the only way to define a target performance for some micro fuel cell application, is to consider the specific *combined* demands of power output, energy conversion efficiency and use time. Once these combined demand parameters are defined, system optimization is required to achieve the minimum possible volume, or weight of the power source. Main adjustable parameter in such optimization are the cell voltage and cell temperature and the input required for the optimization includes the dependence of the polarization curve on temperature and the thermal properties of the packaged power system. An example for such optimization will be given for a 1w; 30Wh target DMFC power source.

Finally, the remaining gap between present DMFC micro-fuel performance and that required for smallest handset applications will be diagnosed. It will be shown that future, advanced electrocatalysts are probably the most important tool for closing this performance gap. Recent theory (DFT) and novel catalyst synthesis developments (shell on core) provide a basis for optimism in this regard.

## Introductory notes

### Alexei A. Kornyshev

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In this talk I will overview a brief history of fuel cells and pressing questions that we need to answer to understand their work in depth. I will focus on what various disciplines, including physics, can do to help to improve fuel cells. Some material and ideas I will be talking about can be found in review articles:

Eikerling M., Kornyshev A.A., Kulikovskiy A.A.  
Physical modeling of fuel cells and their components  
in: *Encyclopedia of Electrochemistry*, 5, A. Bard et al. (eds.), Wiley-VCH, New York (2007), Chapter 8, 1-90.

Eikerling M., Kornyshev A.A., Kucernak A.R.  
Water in polymer electrolyte fuel cells: Friend or foe?  
*Phys. Today* **59**, 38-44 (2006).

Eikerling M., Kornyshev A.A., and Kulikovskiy A.A.  
"Can theory help to improve fuel cells?"  
*Fuel Cell Review*, **1**, 15-24 (2005).

# “Hungry” fuel cell

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This talk discusses the laws of the fuel consumption in a polymer electrolyte fuel cell and its related performance. These laws are presented in an analytical form and are particularly useful for comparison with experimental data and gaining new information from this comparison. First we verify these laws with space resolved current voltage measurements in a *single channel fuel cell*. Next, we compare them with three dimensional computer simulations based on numerical solutions of the nonlinear equations that characterize key transport phenomena and reactions; we see that the theory is basically reproduced by the simulations.

The results give a picture of the inside-the-cell distribution of performance associated with fuelling and the regimes of the fuel cell starvation when fuelling and/or flow field design are not optimized. This picture helps to understand the modes of *smart fuelling* and is lessening for developing alternative designs of the feeding flow fields.

One bit of information to write home about is that we show that in quite a number of cases and flow field architectures a substantial part of the cell does not generate current at all! Smart, stoichiometry-optimized fuelling is needed to extract from cells and stacks the maximum of what they can deliver.

*Sharing information about important elements of the cell performance, otherwise not openly discussed,* brings us closer to a complete functional map of a fuel cell without which R&D in this area would be, to a high degree, a subject of trial and error. This is essentially the main target of the talk. Another aspect that is worth of mentioning is the importance of simple analytical theory, which –as will be shown in the talk – works amazingly well for description of fuelling, practically without any adjustable parameters. In combination with specially designed experiments the theory can illuminate the performance of the fuel cell; this helps a lot in focusing the time-consuming numerical modelling, instead of simulating the system behaviour ad hoc.

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5. A.A.Kulikovsky, *Electrochem. Comm.* **6** (2005) 1259.

**Key words:** Polymer Electrolyte Fuel Cells, fuelling, oxygen utilisation, flow fields

## Understanding Charge Migration Mechanisms in Aqueous Environments

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This talk reviews what ab initio computer simulations uncovered concerning the structure and dynamics of charge defects in bulk water. First, the solvated proton is discussed, which is essentially understood, followed by a discussion of the behavior of the solvated hydroxide, which is controversial. Finally, a glimpse is given to recent advances in understanding protonated water networks inside channel proteins.

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# Performance evaluation in fuel cells – combined locally resolved in-situ diagnostic methods

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Recent demonstration projects have clearly indicated that the performance as well as the longevity of polymer electrolyte fuel cells (PEFCs) has to be improved to be competitive to conventional energy conversion devices. This requires a better understanding of the fundamental processes as well as their losses occurring in these cells, i.e., mass transport and electrochemical losses have to be minimized. Investigations have to be performed on cells having a size (active area) of technical relevance.

Electrochemical impedance spectroscopy yields information on elementary processes, e.g. charge transfer at interfaces as well as transport processes within the membrane-electrode-assembly and measures to minimize losses can be discussed [1]. Single electrode behavior at these particular interfaces in 1-dimensional cells can be investigated by the concept of a *pseudo reference electrode* into the "solid" electrolyte. These measurements allow the individual optimization of anode- and cathode/solid polymer electrolyte interface [2, 3]. Locally resolved impedance spectroscopy yields information on DC current distribution and the respective contributions to over-voltage losses in dependence of the mass flow direction of the reactants under varying humidification conditions [4, 5, 6].

The liquid water distribution in components of PEFCs can be visualized by Neutron Radiography [7, 8, 9]. In combination with locally resolved impedance measurements, the influence of mass flow onto the "local electrochemical activity" across the active area can be studied in dependence of the local (segmental) humidification conditions. Results from the application of these *in situ* diagnostic tools and combinations thereof to PEFCs [10] will be presented in this lecture.

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## **Beyond Conductivity! The Interplay between Electrolyte Performance Characteristics and Other Features**

**Tom Zawodzinski**  
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Polymer electrolytes are the central feature of the eponymous PEM fuel cells. However, a variety of system and other aspects play into what is required of these materials. In this talk, we will provide an overview of the features of several available electrolyte types together with a critical discussion of their chemistry and physics. These will be put into the context of the requirements of the cell and system to provide additional guidance on electrolyte choices.



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