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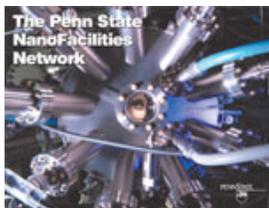
Materials for High Temperature PEM Fuel Cells

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The Penn State NanoFacilities Network 2005 Calendar

Sponsored by:

The Pennsylvania State University
[Materials Research Institute](#)
 &
[The Energy Institute](#)



December 11, 2003
8:30 a.m - 5:00 p.m.

[C213 Coal Utilization Laboratory, University Park PA 16802](#)

Objectives:

- Review the current R&D on HT PEM fuel cells at Penn State
- Identify avenues for enhancing on-campus collaborations in the area of new materials for HT PEM fuel cells
- Consider further opportunities to collaborate with other research institutions and industry
- Identify possible sources of funding and support for further development of new materials for HT PEM fuel cells at Penn State

Penn State Speakers:

[Harry R. Allcock](#) - [Download Presentation \(PDF, 656KB\)](#)
[John M. Andresen](#) - [Download Presentation \(PDF, 12.8MB\)](#)
[Serguei N. Lvov](#) - [Download Presentation \(PDF, 304KB\)](#)
[Thomas E. Mallouk](#)
[Digby D. Macdonald](#) - [Download Presentation \(PDF, 6MB\)](#)
[Evangelos Manias](#) - [Download Presentation \(PDF, 1.4MB\)](#)

Invited Speakers:

[James M. Fenton](#) - University of Connecticut - [Download Presentation \(PDF, 2.7MB\)](#)
[Mark F. Mathias](#) - General Motors - [Download Supporting Paper \(PDF, 435KB\)](#)
[David J. Wesolowski](#) - Oak Ridge National Laboratory - [Download Presentation \(PDF, 7.8MB\)](#)
[Rosemarie D. Wesson](#) - NSF (tentative)

Industrial Participants:

[Anca Ghenciu](#) - Johnson Matthey
[J. Xu](#) - Air Products and Chemicals Inc.

Working Lunch (supported by [Johnson Matthey](#)): 12:00 - 13:00

Workshop Organizer: [Serguei N. Lvov](#)

Harry R. Allcock

New Polymer Membranes for Proton Conduction Fuel Cells

Improvements to the membrane component of polymer electrolyte-based fuel cells is a crucial requirement for

advances in this technology. This talk will give a brief overview of some of the options being investigated in different laboratories including the approach based on polyphosphazenes being developed in our program at Penn State.

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John M. Andresen

Carbon Materials for High Temperature PEM Fuel Cells

High temperature PEM fuel cell technology is currently the best option for achieving near emission-free power for both stationary and automotive needs. While tremendous progress has been achieved for PEM fuel cells in the past decade some major barriers remain before the technology can become commercially viable, including reduced cost of the PEM fuel cells, increased durability of its components, and development of high-performance thermal systems. Carbon materials carry the potential to address some of these obstacles for high temperature PEM fuel cells. Firstly, the carbon-based bipolar plates of the fuel cell present several challenges. Although the performance of pure graphite bipolar plates is generally viewed as the bench-mark against which alternative plate materials are measured, their mechanical strength and ductility are critical issues. The use of graphite/polymer composites represents several opportunities in this area if thermal and mechanical stability issues can be resolved. Secondly, carbon acts as an excellent support for catalysts due to its high surface area where the catalyst is easy to disperse and agglomeration is prevented, as well as sufficient electron conductivity and chemical stability under fuel cell operation. Still there are challenges towards the carbon-supported catalyst especially towards increased CO tolerance. Thirdly, carbon cloth has been widely used as a gas-diffusion media in the PEM fuel cell due to its high reactant and product permeability, high electronic and heat conductivity, and good mechanical strength. However, durability issues and cost considerations are still issues of concern. The presentation will review the use of carbon materials for high temperature PEM fuel cells in terms of challenges and opportunities.

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Serguei N. Lvov

Surface Chemistry of Solid Oxide Materials for High Temperature PEMFCs

Proton exchange membrane fuel cells (PEMFCs) are considered to be one of the most promising sources of electrical energy, and proton conducting polymers such as Nafion have been extensively studied for use in PEMFCs. However, Nafion is limited to operating temperatures below 100 °C due to the tendency of the membrane to dehydrate. One of the approaches for elevating the operational temperature of a PEMFC above 100°C is to use a solid oxide inside of a composite solid oxide/polymer membrane. It is believed that a solid oxide enhances water retention at high temperatures extending the operating temperature range and also could reduce the undesirable cross-over processes. We believe that the solid oxide/water interface chemistry and structure of the electrical double layer (EDL) should be studied in greater detail to understand the function of an inorganic filler in preparing a composite solid oxide/polymer membrane for high temperature PEMFCs. Previously obtained high-temperature surface chemistry data and modeling results for the metal oxide/water interfaces were used to analyze possible performance of metal oxide microparticles in composite proton exchange membranes. It was experimentally found that the composite membranes can exhibit higher proton conductivity compared to pure Nafion in a wide temperature range from 20 to 140 oC and this observation correlates with the experimentally measured water uptake.

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Thomas E. Mallouk

Searching the Periodic Table for Better Anode and Cathode Electrocatalysts

Combinatorial chemistry offers the advantage of high throughput in searching for new and improved materials for many applications. In the case of heterogeneous catalysis, the combinatorial approach has been used for almost a century, but there are still relatively few success stories to tell. This is because catalysis presents some unique and difficult problems to combinatorial chemistry. There is often a trade-off between the speed of a screening method and its reliability in identifying catalysts that perform well under real world conditions. Also, because catalyst preparative methods vary with composition, it is difficult to devise a combinatorial library synthesis that

can effectively explore a broad range of compositions. We consider these interrelated problems for combinatorial libraries of PEM fuel cell and electrolyzer catalysts. We compare the reliability of different screening methods and also discuss synthetic methods that can be applied to a range of electrocatalyst compositions.

Digby D. Macdonald

Balancing Hydrophobicity and Hydrophilicity in Proton Conducting Membranes

The development of new proton conducting membranes for PEM fuel cell applications has been largely an empirical exercise, in which new polymers are synthesized and tested. While this approach has resulted in a large number of interesting polymers, the cold, hard fact is that none surpass some forms of Nafion in performance. We postulate that the principal problem is that the mechanistic details of proton conduction in these materials is not sufficiently well understood that enhanced conductivity, particularly at elevated temperature, cannot be engineered into the system at the molecular level. It is apparent, however, that the conductivity, and many other properties of the membrane (e.g., mechanical strength and water retention), is a delicate balance between hydrophobicity and hydrophilicity and, in particular for conductivity, the molecular state of water in the polymer. These factors are readily controlled by molecular design and hence their impact on conductivity must be understood if we are to develop rational molecular design strategies for new membrane materials. This talk will review our work in this area, which has the ultimate goal of establishing the mechanism of proton conduction in PEMs (e.g. polyether sulfones) and of identifying and prioritizing those factors that give rise to enhanced performance.

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Evangelos Manias

Routes to Increasing the Temperature of Operation for Polymer PEMs

Our approaches to synthesize and characterize polymer PEMs for fuel cells capable of operating at high-temperatures (120-140 °C) will be discussed. The emphasis will be on the principles guiding the design of the polymers, our approaches to connect their conductivity to the physical properties of the films, and promising methods to overcome the challenges of fuel cell operation at high temperatures. Examples include: the application of AFM techniques to investigate the phase-separation in segmented hydrophilic/hydrophobic polymers (as related to their proton conductivity), nanocomposite polymer/multi-proton layered silicate PEMs, and the potential of ceramic foams based on preceramic polymers.

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James M. Fenton

High Temperature Membrane Electrode Assemblies for Development for Proton Exchange Membrane Fuel Cells

The University of Connecticut and Ionomem Corp., a Connecticut company formed on September 19, 2000, have developed high-temperature membrane-electrode assemblies (MEAs) for proton-exchange membrane fuel cell (PEMFC) applications. The MEA is the key component of the PEMFC, making up a substantial fraction of the fuel cell power plant cost. The unique feature of the Ionomem MEA is its ability to operate at higher temperatures and under drier environments than the present commercial membranes. This ability can result in higher fuel cell system efficiency and lower cost. Higher temperature operation allows the use of smaller radiators in automobiles and more useful waste heat for stationary applications. In contrast with commercial MEAs, Ionomem's product can be used under dry reactant feed conditions for portable applications.

These MEAs have been evaluated with a reference operating condition of 120 oC cell temperature and one atmosphere reactant pressure. These MEAs are currently being evaluated for various fuel cell applications that operate on hydrogen fuel containing carbon monoxide or on pure hydrogen in the absence of reactant humidification. The favorable MEA properties are obtained by the incorporation of solid proton conductors, such as phosphotungstic acid or zirconium hydrogen phosphate, into the Nafion? ionomeric electrolyte to provide protonic conductivity at reduced water vapor pressure and assist in water retention.

Ionomem, in collaboration with the University of Connecticut, has increased the voltage performance of the MEA by 28% (0.2 W/cm² at 0.50V (400mA/cm²) to 0.24 W/cm² at 0.60V (400mA/cm²) at 120 oC and 1 atmosphere pressure) and currently manufactures the MEA at full-scale commercial size (300 cm² active area) in facilities at

the University of Connecticut. Under conventional lower-temperature, humidified conditions Ionomem's MEA performance is equivalent to that of commercial MEAs. At elevated temperature Ionomem's MEA performance greatly exceeds that of commercial MEAs. A four-cell full-scale stack that provides 288 watts at a current of 120 amperes while providing 116 °C hot water has been demonstrated.

Discussion will be presented on: (1) Development of highly conductive stabilized proton exchange membranes (PEMs) for high temperature /low relative humidity (atmospheric pressure) operation; (2) Understanding the oxygen reduction reaction (ORR) kinetics in proton exchange membrane fuel cells (PEMFCs), especially at elevated temperatures (>100°C), as a function of partial pressures, temperatures and relative humidity. Optimization of the structure of the cathode to improve the performance; (3) Improving the oxygen transport characteristics of the gas diffusion layer (GDL) by first determining the limiting transport mechanism, and then using it to guide the optimization strategy; (4) Carbon monoxide tolerance properties of hydrogen PEMFC at elevated temperature (>100°C) and low relative humidity.

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Mark F. Mathias

Membrane and Catalyst Research Needs for Higher Temperature PEM Fuel Cells

The automotive drivers behind the need for higher temperature operation (120°C vs 80°C) will be described. For the membrane, this translates to a requirement of high proton conductivity at lower (<75%) relative humidity than what is provided by perfluorosulfonic acid materials. This should be achieved without excessive (>50%) water uptake when exposed to liquid water because of mechanical issues associated with membrane dimensional stability. For the catalyst, whereas there appears to be a path to sufficiently active Pt-based catalysts that can meet automotive cost targets, support corrosion and dispersion stability at higher temperatures are critical issues that need further research attention.

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David J. Wesolowski

Temperature dependence of surface charge and ion adsorption characteristics of metal oxides in aqueous electrolytes

Incorporation of metal oxides into proton exchange membranes appears to improve their operational characteristics, particularly their thermal stability and proton conduction efficiency at elevated temperatures. In this talk, I will present a brief overview of our current state of knowledge of the surface charging and ion adsorption characteristics of metal oxides in contact with aqueous solutions at elevated temperatures. Surface charge density and cation sorption affinities increase strongly with increasing temperature for a given pH (relative to the oxide point of zero charge) for rutile (TiO₂) and magnetite (Fe₃O₄). Results from pH-titrations at elevated temperature are in excellent agreement with electrophoretic mobility studies of oxide suspensions conducted by Dr. Lvov's group at Penn State, indicating that the pH of zero surface charge of all oxides studied to date decreases with increasing temperature, similar to the temperature dependence of the neutral pH (1/2pK_w). These oxide surface properties, as well as the structure and reactivity of the electrical double layer at wet oxide surfaces, may be relevant to PEM performance enhancement. Dr. Lvov and I are also involved in a multi-institutional effort to fully characterize the oxide-water interface at the molecular level, using synchrotron X-ray studies as well as ab initio, molecular dynamics (MD) simulations and Gouy-Chapman-Stern site complexation modeling (SCM) in conjunction with our pH titration and electrophoresis studies. Recent MD and SCM results on the rutile (110)-water interface will be presented.

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