

## IV.B Membranes and MEAs

### IV.B.1 High-Temperature Membranes

*Thomas A. Zawodzinski (Primary Contact), Hossein Ghassemi, Hayley Every, Chockalingam Karuppaiah, Berryinne Chou, Thomas Kalapos, Michael Pelsozy, Ramachandran Subaraman, Bryan Pivovar<sup>1</sup>, John Kerr<sup>2</sup>, and Robert Weiss<sup>3</sup>.*

*Department of Chemical Engineering and Case Advanced Power Institute*

*Case Western Reserve University*

*Cleveland, OH 44106*

*Phone: (216) 368-5547; Fax: (216) 368-3016; E-mail: taz5@po.cwru.edu*

<sup>1</sup>*Los Alamos National Laboratory*

<sup>2</sup>*Lawrence Berkeley National Laboratory*

<sup>3</sup>*University of Connecticut*

*DOE Technology Development Manager: Nancy Garland*

*Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov*

#### Objective

- To develop new membranes and membrane electrode assemblies (MEAs) for operation at low relative humidity and at temperatures approaching 120°C

#### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

#### Approach

- Simultaneously carry out R&D on
  - Physical chemistry of polymer electrolytes
  - New polymeric electrolytes
  - New approaches to proton transport in polymer electrolytes
  - Development of MEAs based on new polymer electrolytes

#### Accomplishments

- New Membranes
  - Implemented new chemistry for attaching sulfonic acid groups to silica
  - Synthesized new multiblock membranes with high proton conductivity
  - Developed ability to separate local chemical interactions from long-range transport effects influenced by polymer morphology

- Showed fundamental limitation of sulfonated aromatics for low hydration conditions
- Investigated effects of substituents on imidazole proton affinity, adsorption
- Catalyst-Coated Membranes (CCMs)/Electrodes
  - Developed new, generic approach to MEA preparation
- Industrial and Other Collaborative Interactions
  - Began discussion on testing methods for high-temperature polymer membranes
  - High-Temperature Polymer Membrane Working Group continues to expand with increased industrial interaction

## Future Directions

- Computational Studies: Conduct more extensive work on novel systems designed to identify approaches to maintain water content at 120°C
- Membrane Development:
  - Balance of High-Temperature Membrane Working Group: Provide new materials from each partner
  - Implement battery of methods for screening membranes; new electrolytes to be tested in 4-month cycle starting in fall
  - Continue development of phase-separated multiblocks and inorganic/organic composites
  - Introduce stronger acid functionality
  - Assess membrane stability for some classes of materials
- CCMs/Electrodes:
  - Continue to develop MEAs from new materials (Case Western Reserve University)
  - Expand initial tests on oxygen reduction reaction at high temperature/low humidity with intent to provide solutions to performance limitations
  - Provide means for scale-up of polymers, film-making and CCM production to modest scale
- High-Temperature Membrane Working Group:
  - Foster ever broader industry participation
  - Begin to share materials throughout group
- Industry and Other Collaborations:
  - Next round of new-start funding: Increase emphasis on 120°C and low RH solutions
  - Begin to distribute ‘lessons learned’ info via website

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## Introduction

The need to operate at temperatures exceeding 100°C at low relative humidity presents difficult new challenges for the proton conductors used in fuel cells. This difficulty stems from the decrease in water content of the polymer electrolytes in the desired temperature range. There is a need for detailed understanding of the impact of poor or zero hydration on membrane and electrode processes in the fuel cell. Water plays a facilitating role in proton transport. Thus, lower water content leads to lower

conductivity. Lack of water also has important negative consequences for electrode behavior.

This project involves

1. Membrane development efforts, including investigation of novel composite and block copolymer structures that can function at low relative humidity;
2. A study of proton transfer and water dynamics to inform the synthetic efforts; and
3. Development of CCMs for high-temperature/low-humidity operation.

We are using theory to explore specific possibilities for new acid group types or for acid-base interactions that could lead to progress in identifying new proton transfer media and to assess the possibility of holding useful water in electrolytes at high temperature. We are increasing our understanding of the energetics of proton transfer to inform synthetic efforts. We are working to incorporate new polymers in fuel cells by developing CCMs from the new materials. Finally, we also have extended our range of polymer electrolyte development efforts by including several different universities and obtaining significant industrial input. Our goal is to engage the polymer community to the maximum extent possible, harvesting the best new ideas for development.

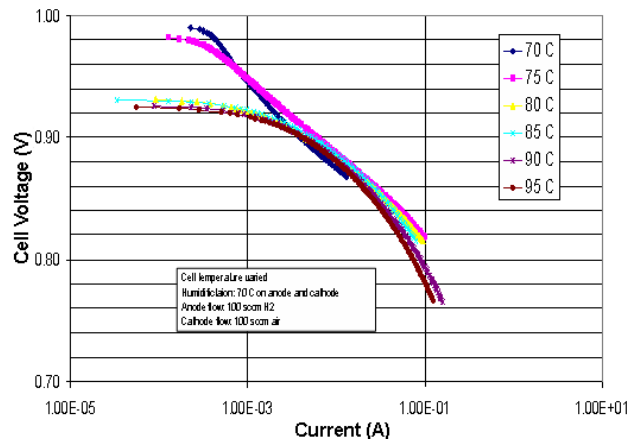
## Results

### Physical Chemistry

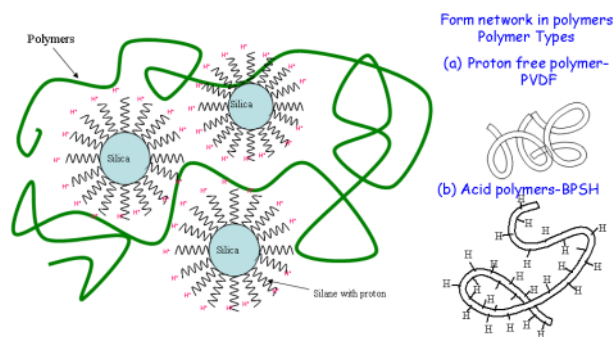
We have developed a new approach using nuclear magnetic resonance signatures at multiple length scales to probe the behavior of water and charge carriers in membranes. Results obtained upon application of this approach to a series of hydrated sulfonated poly(sulfones) with varying sulfonation levels strongly suggests that direct sulfonation of simple aromatics, to the limit of extent of sulfonation sufficient to lead to polymer dissolution, is a fundamentally limited approach to obtaining conduction at low relative humidity (see Figure 1). This leads us to suggest that multi-component systems (composites, blends, etc.) or systems with special controlled morphologies are needed.

### New Membranes

Many new materials are presently in preparation and testing. Our work has focused on (i) polymer matrices filled with surface-modified inorganic particles (see Figure 2); (ii) polymeric systems with intrinsically stronger or more stable acid groups (see Figure 3); and (iii) multiblock polymer systems with phase separation that stabilizes the polymer to allow enhanced stability (see Figure 4). We are investigating these materials via a battery of physical chemistry tests. These are useful both intrinsically



**Figure 1.** Changes in Open Circuit Voltage Observed with Sub-Saturation between 70°C and 95°C



**Figure 2.** Building Silica/Polymer Composite Membranes

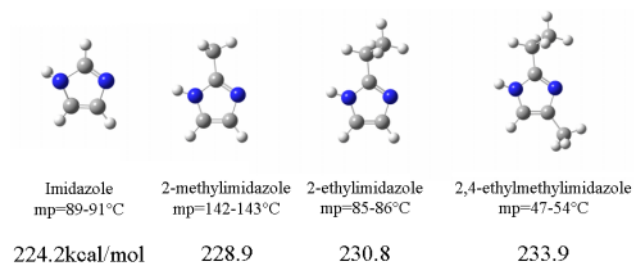
and as test or model systems. We have also investigated some useful processing approaches to improving conductivity, particularly in composite systems.

### CCMs

We have developed a multi-layer CCM formation approach that enables us to prepare useful CCMs from many (soluble) polymers.

### Industrial and Other Collaborative Interactions

We have organized the High-Temperature Polymer Membrane Working Group, which has met bi-annually to allow us to assess progress, to develop standard approaches to problems and to



**Figure 3.** Computational Studies of Substituent Effects on Imidazole Proton Affinity

communicate issues and needs to the HTM community at large.

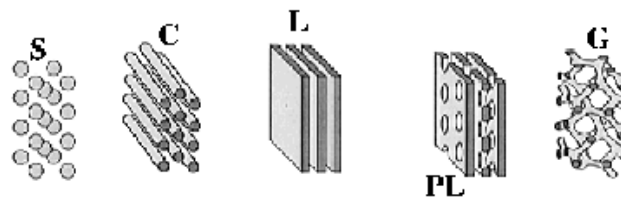
This project consists of a series of collaborative efforts with industry, national laboratories, and universities to facilitate efforts to achieve the targets for high-temperature polymer membranes. Participants in this effort include researchers from Foster-Miller, the University of Connecticut, Lawrence Berkeley and Los Alamos National Laboratories, the Naval Surface Warfare Center, Mitsubishi Corporation, the University of Massachusetts-Amherst and Virginia Tech. This group is investigating a series of approaches including:

- Synthesis of materials with high-acidity functional groups,
- Polymer blends for enhanced conductivity,
- Tailored nano-structures for incorporation of highly sulfonated polymers in polymer composites,
- Ionic liquids as proton conduction media, and
- Novel proton carriers for use in polymers.

We have organized the High-Temperature Polymer Membrane Working Group, which has met bi-annually to assess progress, to develop standard approaches to problems and to communicate issues and needs to the high-temperature membrane community at large. Here are brief summaries of several of the specific projects, with points of contact.

*1. Los Alamos National Laboratory, PI: Bryan Pivovar pivovar@lanl.gov*

LANL's approach to exploring this problem is to investigate 'free' protons containing ionic liquids. These 'free' proton ionic liquids are based on imidazole cations and dihydrogen phosphate



**Figure 4.** Schemes for different multiblock copolymer morphologies : spheres (S), columns (C), lamellae (L), perforated layers (PL), gyroid (G).

( $\text{H}_2\text{PO}_4^-$ ) or bisulfate ( $\text{HSO}_4^-$ ) anions capable of proton conduction (hopping candidates). While these substances have the ability to act as anhydrous proton conductors, they are extremely hygroscopic and may exhibit greatly increased conductivity even at low RH. Candidate materials have been evaluated in terms of conductivity, water uptake and thermal stability in the ionic liquid form. The most promising of these materials have been tethered to a polymer architecture based on polynorbornene. While, the reported conductivity for the first generation polymer was somewhat low, 5-12 mS/cm, it was still promising considering the presence of only a weakly ionic imidazole group. The addition of an acidic group, dihydrogen phosphate, greatly increased the conductivity of the membrane even under dry conditions.

*2. Lawrence Berkeley National Laboratory, PI: John Kerr jbkerr@lbl.gov*

Conductivity, thermal and mechanical measurements have been used to investigate the use of imidazoles as solvation groups in polymeric proton conductors where the acid groups are tethered to the polymer. Acid forms of commercially available Nafion and polyether polyelectrolytes designed for use in lithium-polymer batteries have been used as the polymer matrix and have been doped with varying amounts of imidazole and N-methylimidazole to provide an easily prepared water-free proton-conducting gel:

- The conductivity results show distinct temperature dependences that are consistent with the operation of the Grotthuss mechanism of proton conduction with the imidazole-doped polyelectrolytes. Conductivity at 120-150°C  $>10^{-2}$  S/cm.
- The N-methylimidazole-doped polyelectrolytes cannot support the Grotthuss mechanism and

- show a distinctly steeper temperature dependence of conductivity.
- Imidazole-doped polyether polyelectrolytes with alkylsulfonate and fluoroalkylsulfonate acid groups:
    - Do not show Grothhuss-type temperature dependence. This is believed to be due to the miscibility of the rubbery polyether polyelectrolytes with the imidazole that do not phase separate as strongly as Nafion resulting in interruptions to the Grothhuss pathway. This strongly indicates that the morphology of the polymer is critical to promotion of Grothhuss-type conduction.
    - Conductivity is enhanced by stronger acid groups. Therefore, the use of fluoroalkylsulfonyl imides is almost certainly required to achieve the highest conductivities.

Attachment of N-alkyl tethered imidazoles to polyether polyelectrolytes by covalent bonds results in almost no loss of conductivity provided the concentration of imidazole is greater than that of the acid group. This has been observed for imidazoles attached along with alkylsulfonate anions and the conductivity at 120°C is less than  $10^{-4}$  S/cm. However, use of fluoroalkylsulfonate and imide acid groups are expected to lead to an increase of conductivity by an order of magnitude. Promotion of the Grothhuss-type conduction is possible by use of the C-tethered imidazole and by appropriate control of morphology. Polyelectrolytes that include these features are currently under construction. It is anticipated that all solid-state, water-free membranes are possible with conductivities greater than  $10^{-2}$  S/cm at 120-150°C. The stability of such membranes is the next issue to be addressed.

3. *University of Connecticut, PI: Robert Weiss  
rweiss@mail.ims.uconn.edu*

The microstructure of composite proton-exchange membranes (PEMs) determines factors like proton conductivity, reactant cross-over and structural stability in the fuel cell environment. Sulfonated poly(ether ketone ketone) (SPEKK) was selected as a proton conducting component with high temperature stability, excellent chemical and solvent

resistance and good mechanical properties. Fuel cell performance comparable to Nafion<sup>®</sup> was obtained with SPEKK, but the long-term stability in an MEA was limited due to fatigue at the membrane/gasket interface. Polymer blends with engineering thermoplastics like poly(ether imide) (PEI) and poly(ether sulfone) (PES) are being developed and show some promise in alleviating that issue and to reduce reactant cross-over and provide high-temperature fuel cell operation. The solution casting procedure, e.g. the ternary phase behavior, has been studied in order to design and control the final PEM morphology. In this way, membranes with dispersed droplet phase morphologies, co-continuous, dual phase morphologies and single-phase homogeneous morphologies have been prepared. That allows us to study the impact of the PEM microstructure on membrane properties. The most promising membranes so far have been SPEKK/PES blends with single phase morphology, which exhibit excellent membrane integrity in high temperature conditions, and co-continuous SPEKK/SPEKK blends, in which an acidic highly proton-conducting matrix is interconnected with a less acidic matrix. These materials achieved high proton conductivity and long-term mechanical and chemical membrane stability. Moreover, anisotropic microstructures with channels of the conductive component SPEKK in a matrix of PEI were obtained by applying an electric field during solution casting or directly to a melt of the blend. The anisotropy of conductive polymer channels through the membrane thickness provided enhanced through-plane conductivity. Another strategy for obtaining high proton conductivity, with potentially lower water content and low membrane swelling, consists of dispersing highly sulfonated crosslinked polystyrene particles in a relatively low sulfonated SPEKK matrix. Conductive SPS nanoparticles may be prepared by emulsion polymerization, and electrical field alignment provides additional performance enhancement by aligning the particles.

### **Conclusions**

The development of new polymer electrolytes for operation at elevated temperature is underway. However, this is a long-term project. Replacement of water is the most difficult problem, but adequate stability and cathode activity are not trivial objectives

to achieve. We have developed several different approaches to address this problem. Fundamental work, including computational and experimental studies of new acid-functionalized materials, can provide useful insights into the conduction process to guide synthetic efforts. The first polymers geared for temperatures in excess of 100°C are emerging, and testing is showing that, although promising, there are definite shortcomings. Work on making viable new materials continues and has expanded to include new participants from the polymer community.