VII.B Membranes & MEAs

VII.B.1 High-Temperature Membranes

Thomas A. Zawodzinski (Primary Contact), Hossein Ghassemi, Berryinne Chou, Thomas Kalapos, Michael Pelsozy and Ramachandran Subaraman
Department of Chemical Engineering and Case Advanced Power Institute
Case Western Reserve University (CWRU)
Cleveland, OH 44106
Phone: (216) 368-5547; Fax: (216) 368-3016; E-mail: taz5@po.cwru.edu

Other Investigators: Brian Coughlin, UMass-Amherst; James McGrath, Virginia Tech; Ken Tasaki, Mitsubishi Chemical; Jennifer Irvin, Naval Air Warfare Center (NAWC); Bryan Pivovar, Los Alamos National Laboratory (LANL); and John Kerr, Lawrence Berkeley National Laboratory (LBNL)

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

Start Date: FY 2002
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

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

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:

- A. Cost
- B. Durability
- C. Electrode Performance
- D. Thermal and Water Management

Technical Targets

- DOE Technical Targets for Fuel Cell Stack System for 2010
- Cost: $35/kW
- Durability: 5000 hours

Approach

- Synthesize and characterize new membranes that provide a path to high conductivity under low-RH, high-temperature conditions.
- Simultaneously carry out R&D on:
    - Physical chemistry of polymer electrolytes

  - New approaches to proton transport in polymer electrolytes
  - Development of MEAs based on new polymer electrolytes

Accomplishments

- Improvement of >1 order of magnitude in conductivity of network structures, multiblocks, with decent low-RH performance (Case)
- First fuel cell tests of multiblock polymers (Case)
- Demonstration of good performance of C_{60}-doped polymers (Mitsubishi)
- Synthesis, testing of 'strong acid' systems (NAWC, Case)
- Development of new materials based on polymer versions of ionic liquids, multi-site bases (LBNL, LANL)
- New fast proton conduction mechanism under study, implemented in first materials (Case)
- Transport limitations separated: morphology vs. basic interactions, leading to elimination of class of materials

Future Directions

- Continue multi-faceted synthesis effort with increased sample 'circulation,' feedback on physical properties, etc.
- Culminate synthetic efforts in MEA preparation, fuel cell testing as appropriate.
- Membrane Development:
  - Implement battery of methods for screening membranes; new electrolytes to be tested in 4-month cycle starting in fall.
  - Assess membrane stability for promising classes of materials.
- Catalyst-Coated Membranes/Electrodes:
  - Prepare MEAs from new materials (CWRU).
  - Carry out fuel cell tests on the oxygen reduction reaction (ORR) at high temperature/low humidity with intent to provide solutions to performance limitations.
  - Provide means for scale-up of polymer, film-making and catalyst-coated membrane (CCM) production to modest scale.
- Collaborations and High Temperature Membrane Working Group:
  - Foster ever broader industry participation.
  - Begin to share materials throughout group.
  - Distribute 'lessons learned' info via website.

Introduction

The need to operate at temperatures exceeding 100°C and 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.

The basic approach of this project is to develop a series of polymers that contain key features for conduction at low RH and elevated temperature. These polymers are developed to a 'proof-of-concept' stage. Some exploratory activities focus on functionality (i.e., conductivity), perhaps at the short-term expense of mechanical properties or durability.

A series of new membranes is being developed and tested to advance the state of the art in both knowledge of key components leading to conduction and in available materials.

Testing of key properties of these membranes provides a feedback loop for rational development. Key focus areas of testing include transport (conductivity, water diffusion), physical properties of the polymers and durability of the polymers. In a few cases, specific model compounds are studied to provide insight into a specific feature. Finally, for some materials, MEAs are prepared and tested in fuel cells.

Synthesis of New Materials

Zawodzinski: Several classes of materials are under study. The goal of our synthetic materials effort is to develop 'building blocks' that provide information on key elements needed for an appropriate electrolyte. Elements considered and controlled in our work include the acid strength of protogenic groups; the spacing, organization and loading of such groups; the polymer morphology (pore or channel formation, crystallization); and the use of composite or other additives with various binders as well as processing conditions. The synthesis is followed up by characterization under various conditions of temperature and humidity. Elementary studies include water uptake and conductivity as a function of water content and temperature.

In one thrust, multi-block copolymers, in which one block is hydrophobic (fluorinated) and the other is sulfonated, were synthesized. The chemical structure of these polymers is shown in Figure 1. These materials phase segregate to form channels through which conduction takes place. By controlling the block size and the ratio of the two blocks, the degree of phase segregation and the ion exchange capacity (equivalent weight) of the polymer are controlled. Extremely promising results were obtained during the last year, with conductivity approaching 80 mS/cm at 30% RH and 60°C for one composition. Furthermore, the morphology control seems to allow for less decrease in conductivity as the water content is decreased vs. that observed in Nafion. The latter result is shown in Figure 2.

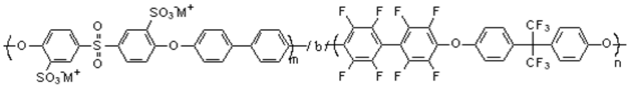

Figure 1. Chemical Structure of Multi-Block Copolymers

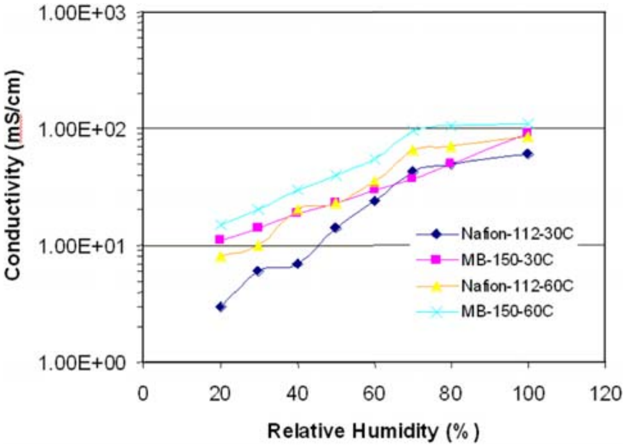

Figure 2. Plot of Conductivity vs. RH for Two Multiblock Polymers and for Nafion

In another thrust, composite electrolytes were prepared by mixing organically modified nanoparticulate silica with various binders. Through improvements in processing methods, binder composition, and particle dispersion, we increased the conductivity by more than an order of magnitude during the previous year, again exceeding 10 mS/cm at 20% RH and 90°C.

To increase the acid strength relative to that provided by a sulfonic acid substituted onto an aromatic ring, sulfonimide-substituted materials represent possible candidates. Because of concerns raised regarding hydrolytic stability of aryl sulfonimides, model compounds were prepared and their stability studied. These materials proved to be stable after hundreds of hours of exposure to acid solutions. New polymers have been prepared using this acid group and are under investigation.

Finally, another mode of water-free proton conduction was explored during the past year. In initial studies, new materials using this approach yield conductivity in excess of 10 mS/cm under dry conditions at 150°C.

Coughlin: In this work, a series of block copolymers with controlled morphology are being synthesized. Recent progress has been made in preparing the acrylate monomers. Insight into the role of morphology in conduction is expected.

McGrath: In this work, a series of copolymers and blends are being synthesized with the specific goal of compatibilizing the polymer with inorganic additives. High-conductivity zirconium phosphate/ phosphonate additives are being combined with a series of poly (arylene etherbenzimidazole)/ polysulfone materials to provide a route to low-RH conduction.

Tasaki: This effort has focused on the use of fullerene additives with Nafion to achieve improved conduction. Preliminary results appear promising. High degrees of dispersion of the fullerene have been achieved. At 20% RH, conductivity of a fullerene-Nafion composite is higher than that of Nafion by nearly an order of magnitude.

Irvin: Most of the alternative polymers being synthesized have sulfonated aromatic moieties as acid groups. In this activity, methods to introduce fluoro-sulfonic acid groups are being explored.

Pivovar: Water-free conduction using polymeric analogs of ionic liquids is the goal of this work. Polymers with imidazole pendant chains doped with phosphoric acid and sulfuric acid were prepared. These materials exhibited conductivity approaching 40 mS/cm at 80°C under dry conditions. It remains to be seen how much charge is carried by protons in these electrolytes.

Kerr: The limits of conduction using imidazole acceptors are under investigation in this study. During this year, a series of grafted polymers, with imidazole and acid group termini to side chains, was prepared. Conductivity of N-tethered imidazole polymers approached that of the parent polymer doped with free imidazole.

Industrial and Other Collaborative Interactions

In addition to the highly collaborative research effort described above, 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 communicate issues and needs to the high-temperature membrane community at large.

Conclusions

The development of new polymer electrolytes for operation under low RH and at elevated temperature is underway. However, this is a long-term project. Replacement of water while retaining conductivity is the most difficult problem. Several different approaches are under investigation to address this issue. 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 tailored for these conditions and testing are showing several promising avenues. Work on making viable new materials continues and has expanded to include new participants from the polymer community.