V.M.3 New Polyelectrolyte Materials for High Temperature Fuel Cells

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Collaborators:
- Los Alamos National Laboratory (LANL)
- Minnesota, Mining and Manufacturing Company (3M)

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Objectives

- Investigate the use of solid polyelectrolytes for high temperature fuel cell operation that do not require the presence of water.
- Prepare solid polymer electrolytes where only the proton moves across the membrane during operation (no mobile solvent such as water).
    - Significant system simplifications for fuel cells (heat and water management).
    - Significant increase in mechanical durability due to absence of water-swelling and freezing in the membranes.
- Incorporate polyelectrolyte materials into gas diffusion electrodes, build and test membrane electrode assemblies (MEAs) that operate without humidification at temperatures up to 120°C.
- Improve transport, mechanical and chemical properties to meet DOE goals.

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) Durability
(B) Cost
(C) Performance
(E) System Thermal and Water Management

Technical Targets

1. Dry membrane conductivity (no humidification) = 0.1 S/cm at 120°C, 0.07 S/cm at ambient temperature, 0.01 S/Cm at -20°C.
2. Hydrogen and oxygen cross-over <2 mA/cm^2 equivalent.
3. Area specific impedance in practical MEAs <0.02 ohm-cm^2.
4. Cost <$25/m^2 for membrane and <$60/kWh.
5. Durability 5,000 hours.

Accomplishments

- Demonstrated the feasibility of a polymeric solid-state proton conducting membrane with no mobile solvent where the proton conductivity loss due to immobilization of the solvent molecule is negligible (LBNL).
- Demonstrated that the structure-diffusion (Grotthuss) mechanism of proton transport is necessary to achieve the conductivity goals. This is promoted by phase separation that is favored by the use of block co-polymer backbones (LBNL/LANL).
- Water-uptake measurements indicate that perfluorinated sulfonic acids (PFSA) when combined with imidazole solvents reject water. This is very attractive for avoidance of mechanical stress due to water swelling and for sub-zero temperature operation and start-up (LBNL).
- Developed capability to build and test non-PFSA MEAs (LANL)
- Developed capabilities to investigate, understand and prevent aging phenomena (LANL/3M).

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Approach

Polymer electrolyte membrane (PEM) fuel cells are a major focus of the DOE effort for alternatives to the internal combustion engine for transportation purposes. Unfortunately, despite many decades of effort fuel cells are still relatively inefficient in converting the fuel (hydrogen or methanol) to electrical energy. A typical fuel cell operating at 1 A/cm^2 only achieves about 50%

efficient conversion to electrical energy, the remainder converting to heat which must be removed by means of a heat exchanger or radiator. For PEM fuel cells, the heat and water management requirements for a typical light vehicle need too much volume to be competitive. This problem could be solved by the development of more efficient electrocatalysts for the oxygen reduction reaction. However, despite much excellent research, the goal of a better catalyst remains elusive and as a result attention has turned to the membrane material to provide a solution.

PFSA polymers such as Nafion® have been used as the membrane material for PEM fuel cells for many years. However, in order to provide the required conductivity the PFSA must be swollen with liquid water which solvates the protons and allows dissociation of the sulfonic acid groups. However, the need to control the water content of the membrane requires a complicated heat and water management system which is undesirable in a vehicular application where space and weight are at a premium. Therefore, there is a compelling need to develop new membrane materials that do not require water in order to conduct protons.

Heterocyclic bases such as imidazole have been known for many years to be capable of proton solvation and to support proton conduction. These bases can be used as a mobile solvent to replace water or they may be covalently tethered to the polymer structure to prevent losses due to evaporation, electro-osmosis or dissolution in water formed at the fuel cell cathode. In the latter case, a completely solid-state membrane would result in which only the proton moves. Figure 1 shows a generalized molecular structure of a polymer material that should act in this manner. The ideal structure of the
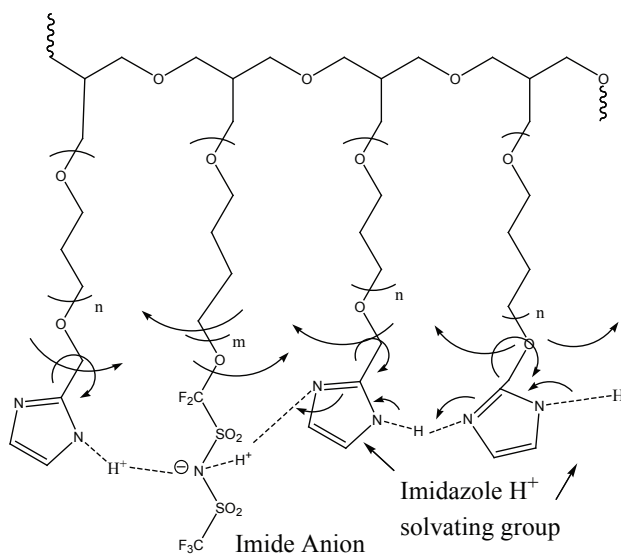
polymer that the acid and base groups would be tethered to needs to be elucidated and this is the subject of this project. Structural parameters to be varied are:

- The nature of the backbone – should it be flexible or stiff, hydrocarbon or perfluorinated?
- The length and flexibility of the side chains that tether the acids and bases.
- The concentrations of the acids and bases both absolutely and relative to each other.
- How are the bases tethered in order to promote structure diffusion?
- What degree of phase separation is required between the ionic groups and the backbone to promote structure diffusion proton transfer?

These are parameters that are considered to influence the proton conductivity which is the primary property of interest. They also influence the other properties such as gas permeability, morphology, mechanical strength and interfacial behavior.

In order to vary these structural parameters and study the effects, the project involves:

- The synthesis of random and block co-polymer backbones;
- Attachment of acid groups (alkylsulfonate, fluoroalkylsulfonate, fluoroalkylsulfonylimide) to the backbones by means of variable tethers;
- Attachment of imidazole and imidazolium groups;
- Measurement of conductivity of membranes;
- Preparation and testing of MEAs with the new polymers; and
- Determination of the chemical and mechanical stabilities of the membrane materials.

The primary goal for the first two years is to determine whether a conductivity of 0.1 S/cm is attainable and what structural factors of the polymers favor this. Morphological studies including atomic force microscopy (AFM), small angle X-ray scattering (SAXS), and small angle neutron scattering (SANS) will be important in providing insight.

Preliminary Results

Although the project has just begun some preliminary results have been obtained primarily at LANL which illustrate some of the approaches to be taken. Table 1 shows results that detail observed physical changes in Nafion® PFSA and a sulfonated hydrocarbon polyelectrolyte (BPSH) upon aging at 120°C. Figure 2 shows the AFM pictures of the aging of BPSH-40 which illustrates the need for detailed morphological and mechanical measurements as well as classical conductivity measurements. More detailed

FIGURE 1. Schematic of Polymer Structure Designed to Facilitate Proton Conduction without the Need for Mobile Solvents such as Water

TABLE 1. Changes in Water Uptake (WU) and Ion Exchange Capacity (IEC) due to Physical Aging

Membrane	WU_v (Before Aging)	WU_v (After Aging)	% Increase	IEC_v (wet) (Before Aging)	IEC_v (wet) (After Aging)	% Decrease
Nafion 112 (120°C)	40	83	108%	1.17	0.92	21%
Nafion 212 (120°C)	48	151	215%	1.15	0.77	33%
Nafion 1135 (120°C)	36	89	147%	1.33	0.89	33%
BPSH-40 (120°C)	76	135	78%	1.15	0.75	35%
BPSH-40 (80°C)	76	74	no change	1.15	1.18	no change
BPSH-35 (120°C)	52	96	85%	1.33	1.10	17%
BPSH-35 (80°C)	52	51	no change	1.33	1.37	no change
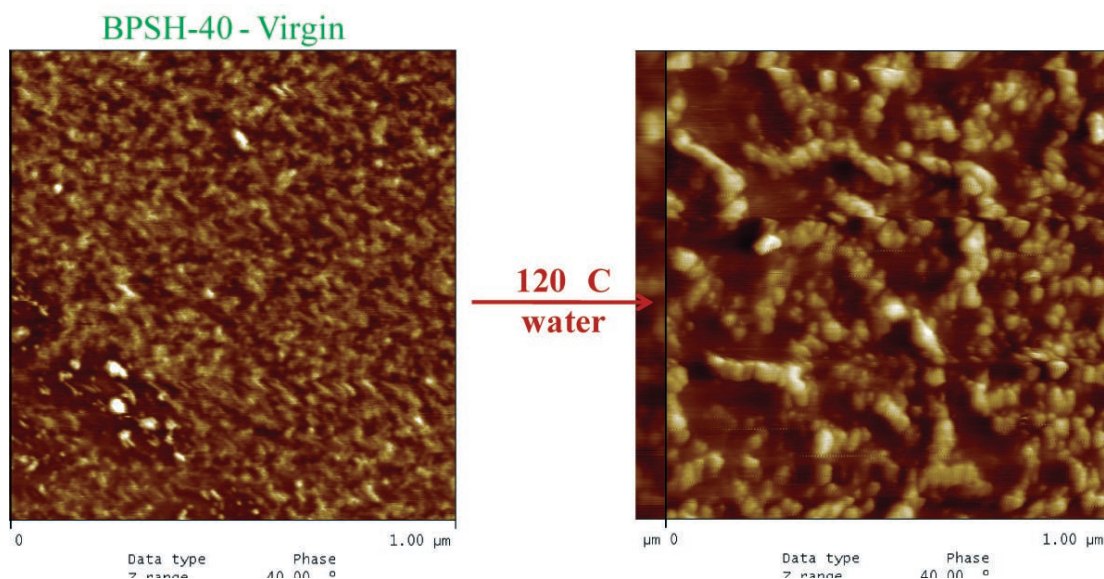
**FIGURE 2.** Tapping-Mode AFM Images of BPSH-40 before (left) and after (right) Aging at 120°C

water uptake measurements at LBNL have shown that the water uptake of Nafion® doped with imidazole is very small (<5% of undoped PFSA), indicating that the perfluorinated structures will be desirable to prevent swelling of the membranes. Chemical degradation measurements of Nafion® show that low relative humidity conditions lead to increased degradation rates in MEAs. Similar experiments will be carried out with the 3M PFSA material which is prepared under a separate DOE project ("Membranes and MEAs for Dry, Hot Operating Conditions", Contract Number DE-FG36-07GO17006).

Further preliminary results obtained at LANL have shown the beneficial effects of morphology control for improved performance. Figure 3 shows the polarization behavior of MEAs using random and multiblock copolymers of polyethersulfone-polyimide copolymer PES-PI at 100°C and different relative humidity levels. It can be seen that the multiblock copolymer performs significantly better at lower relative humidity than the random copolymer, clearly illustrating the value of the morphological investigations planned for this project.

Future Plans

- Characterization of PFSA materials (Nafion®, 3M) doped with heterocylic bases.
- Preparation and characterization of polyelectrolytes with C-tethered imidazole and imidazolium ions, as both random and block co-polymers.
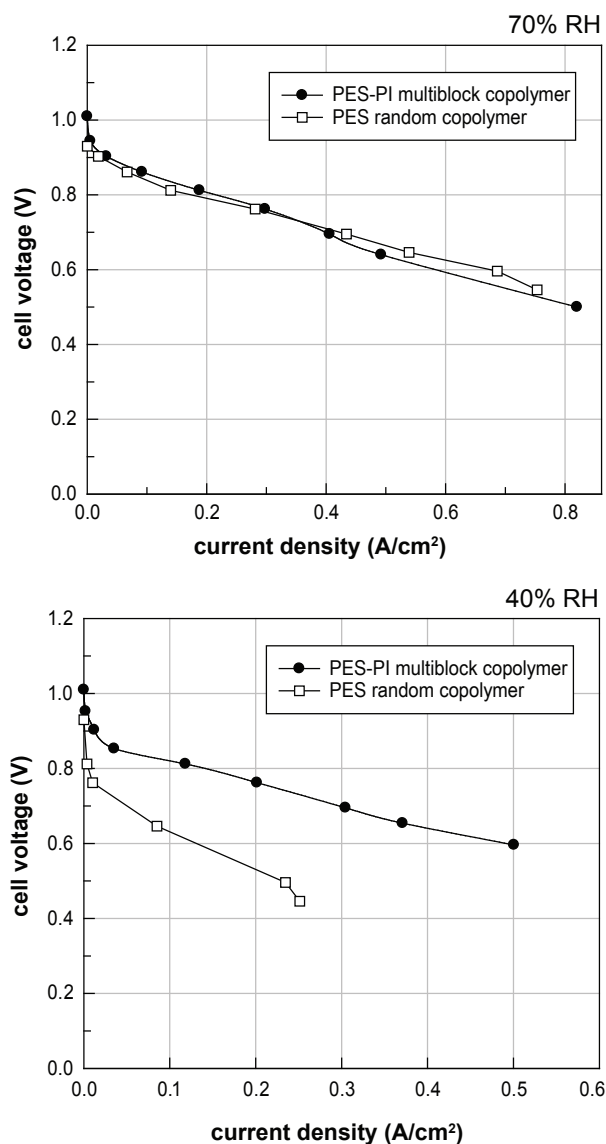
FIGURE 3. PEMFC Performance of a Multiblock Copolymer Versus a Random Copolymer at 100°C and varied Relative Humidity (RH)

- Studies of chemical and mechanical stability of imidazole-containing polymers.
- Preparation and testing of MEAs with new polymers.

Expected Major Milestone FY 2008

Determination of the feasibility of a conductivity of 0.1 S/cm at 120°C with no humidification. As part of the activities towards this decision point, a modeling effort will be undertaken to determine the trade-offs between lower conductivity and system simplifications. This work will be undertaken in concert with the Fuel Cell Systems Analysis work being carried out at Argonne National Lab (Ahluwalia et al.).

FY 2007 Publications/Presentations

1. "New Polyelectrolyte Materials for High Temperature Fuel Cells", John B. Kerr, Poster Presentation FCP-33, DOE Office of Hydrogen, Fuel Cells and Infrastructure Technologies Review Meeting, Arlington, VA, May 17, 2007.

2. Non-Nafion Catalyst Binders for Proton Exchange Membrane Fuel Cells, Y.S. Kim, J. Chlistunoff, B. Pivovar, M. Sankir, J. E. McGrath, 209th Electrochemical Society Meeting, Denver, CO, May 11, (2006).

3. Performance and durability of Sulfonated Poly(arylene Ether) Membranes, Y. S. Kim, Advances in materials for Proton Exchange Membrane Fuel Cell Systems, Asilomar conference Grounds Pacific Grove, California, Feb. 18–21 (2007).

4. Accelerated Pysical Aging of Proton Exchange Membranes, M. L. Hill, Y.S. Kim and B. Pivovar, Abs. No 928 211th ECS Meeting –Chicago, Illinois, May 6–10, 2007.