V.G.5 Membranes and MEAs for Dry, Hot Operating Conditions

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Objectives

- To develop a new proton exchange membrane (PEM) with:
    - Higher proton conductivity
    - Improved durability

under hotter and drier conditions, in order to meet DOE Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan 2010 commercialization targets for automotive fuel cells.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(C) Performance

Technical Targets

TABLE 1. Progress toward Meeting Technical Targets for Membranes for Transportation Applications

		2008 Status	2010 target	2015 target
Conductivity at 120°C*	S/cm	0.03 (25%RH)	0.1	0.1
Conductivity at 80°C*	S/cm	0.05 (50%RH) 0.29 (100%RH)	0.1	0.1
Conductivity at 30°C*	S/cm	0.08 (80% RH, 25°C)*	0.07	0.07
Conductivity at -20°C	S/cm	Not tested	0.01	0.01
O$_2$ crossover	mA/cm^2	Not tested	2	2
H$_2$ crossover	mA/cm^2	<2	2	2
Durability w/cycling**	hours	>5,000 (80°C) >4,000 (90°C) <1,000 (120°C)	5,000 (80°C) 2,000 (120°C)	5,000 (80°C) 5,000 (120°C)

* Conductivity results are for 640 equivalent weight (EW) membrane.
** Durability results are for 825 EW, 20-25 micron membrane.

Accomplishments

- Achieved durability of *ca.* 1,000 hours at 120°C with an 800 EW membrane.
- Achieved a conductivity of 30 mS/cm at 120°C, 23% relative humidity (RH).
- Achieved a conductivity of 50 mS/cm at 120°C, 50% RH.
- Achieved 80 mS/cm conductivity at 25°C, 80% RH.

✧   ✧   ✧   ✧   ✧

Introduction

PEM fuel cells represent a promising power source for transportation and other applications. While many breakthroughs have been made over the last few years in the development of PEM fuel cells, technical and economic barriers for their commercialization still exist. Key areas where improvements are still needed are in expanding the temperature range and

lowering the humidification requirements of the stack [1]. This is particularly true for automotive fuel cell applications. Requirements of system size, efficiency, performance, start-up and cooling mean that automotive fuel cells must be able to run robustly and exhibit adequate durability under a wide variety of operating temperatures, including temperatures up to 120ºC. They must also be able to do this with little or no external gas humidification (i.e., "dry"), and during start-up, shut-down, or periods of lower stack temperatures, they must run in the presence of, and be stable to, some liquid water in the gas channels. Unfortunately, operation under these hot, dry conditions seriously compromises both the conductivity and durability of the ionomer membrane.

The objectives of this collaborative effort are to develop new PEMs for fuel cells capable of providing excellent durability and performance while operating under low humidification conditions and at temperatures ranging from -20ºC to 120ºC. Success on this project should result in PEMs with the performance and durability characteristics required for the development of fuel cells which meet commercialization targets for the automotive industry. These membranes may also have improved characteristics making them useful in other fuel cell applications. The processes for making the new membranes, and the membrane electrode assemblies (MEAs) comprising them, should be scalable for manufacturing at high volumes and at costs that can meet industry targets.

Approach

The focus of this project is to develop a new PEM which can operate under hotter, drier conditions than the state-of-the-art membranes today. This membrane will then be integrated into an MEA and then finally into a fuel cell stack. These MEAs should meet the performance and durability requirements that meet 2010 DOE technical targets for membranes. Activities include:

- Synthesize and test new polymer membranes, including both fluorinated and non-fluorinated polymers as well as composite or hybrid systems, and evaluate their conductivity and chemical and mechanical stability.
- Evaluate new membrane manufacturing methods for increasing membrane mechanical properties and improving MEA lifetime.
- Develop new membrane additives aimed at increasing conductivity and improving membrane stability/durability under these dry conditions.
- Perform both experimental and theoretical studies of factors controlling proton transport and mechanisms of polymer degradation and factors affecting membrane durability in an MEA.

- Focus on materials which can be made using processes which will be scalable to commercial volumes using cost effective methods.

Results

In the first year of this project the focus was on both the development of new materials as well as the development of both in situ (in a fuel cell) and ex situ methods of characterizing these new materials.

New perfluorosulfonic acids (PFSAs) based on our 3M ionomer (1A) were prepared with very low EWs. This year, we have prepared ionomers with a wide range of EWs, the lowest below 600 g/mole. The conductivity of some of these ionomers is shown in Figure 1a. The lowest EW membrane shown, 640, has a proton conductivity of 30 mS/cm at 120°C and 23% RH. Figure 1b further shows the conductivity of two of these membranes at room temperature, with the
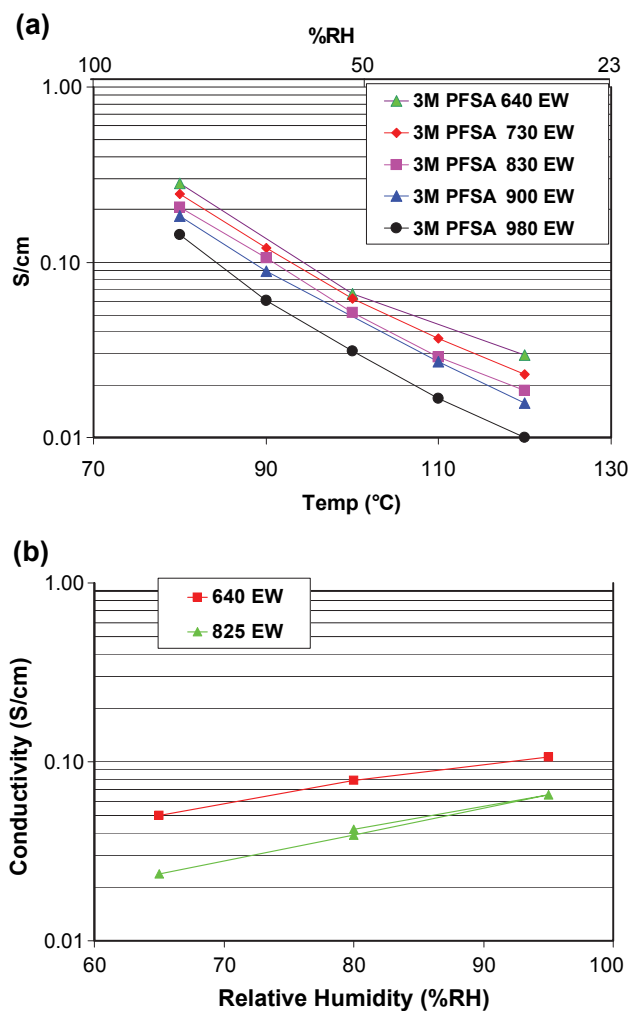

FIGURE 1. Conductivity of selected EW 3M PFSA membranes: a) conductivity vs. temperature at a constant 80ºC dew point; b) conductivity vs. %RH at 25°C.

640 EW having conductivity of 80 mS/cm at 25°C, 80% RH, exceeding the DOE target for room temperature conductivity shown in Table 1. Membranes prepared from this ionomer are stable to hot water provided they have an EW above about 700. Below this EW, the membranes will fall apart or dissolve in hot water and other solvents. This is due in part to the lower EW polymers having insufficient tetrafluoroethylene units to allow the backbone to crystallize. These backbone crystallites are an important source of mechanical stabilization in these polymers [2]. Still, studying ionomers with EWs below this threshold allows a quantitative understanding of the effects of high acid site density on proton conductivity under dry conditions. In addition, we are investigating several ways of preparing stable, very low EW ionomers, some of which are discussed below.

One approach involves preparing a series of polymers where we are changing the protogenic group. This can enable further decreasing the EW of the ionomers as well as providing sites for cross-linking and for the attachment of other conductivity enhancing groups. Figure 2 shows the structures of some of the polymers we have prepared so far (we have not yet converted all of these new polymers into membranes). While the acidity of the perfluoro bis sulfonyl imide (referred to as imide, 1D) is known to be higher than a perfluoro sulfonic acid [3], the mixed aromatic/fluorocarbon imides (1B,C and E) will be somewhat lower. However, the aromatic rings in the imide-containing polymers can be substituted with additional sulfonic acid groups (1C) to lower EW or with a linking group, such as the phosphonic acid group shown (1E), for attachment to heteropoly acids (HPAs), zirconia, or other inorganic species. These groups can also be attached to two of more side-chains via bis sulfonyl imide linkages, to provide a cross-link in the hydrophilic region of the ionomer.

Initial conductivity measurements comparing compound 1B to our standard ionomer (1A) are shown in Figure 3. We are attempting to understand the lower conductivity results for the aromatic imide at lower %RH, which may be due to their lower acid strength, different ionomer morphology, or other reasons. It is important to note that these aromatic imides are intended to be used as linking groups, cross-linking groups and/or carriers for additional protogenic groups, and not expected to provide proton conductivity higher than comparable PFSAs by themselves.

In addition to studying membranes where the ionic regions of the membrane are cross-linked, we are evaluating crosslinking the membrane by incorporating a reactive "cure site monomer" into the polymer during polymerization. This should cross-link the hydrophobic region of the ionomer and hopefully allow a direct comparison of the advantages and disadvantages of cross-linking the hydrophilic vs. hydrophobic regions of the ionomer structure.

With co-workers at Case Western we have prepared membranes which are based on hybrid structures of fluorocarbon and hydrocarbon ionomer segments for optimized conductivity, mechanical properties and durability. These materials are still being prepared and have not been tested yet.

In all of the cases discussed above, the chemical stability of the functional elements of these polymers is considered and carefully evaluated. The Case Western group is preparing and evaluating model compounds to provide an understanding of the oxidative and hydrolytic stability of these materials. This work will also provide insight into the degradation mechanisms of these materials.

University of Detroit Mercy has used electron spin resonance (ESR) spectroscopy to study the degradation pathways of these PFSA-based ionomers and to study the effect of stabilizing additives such as cerium cations on the type and amount of radicals formed during attack of oxygen radicals on PEMs and model compounds. Oxygen radicals were generated via the photo-Fenton
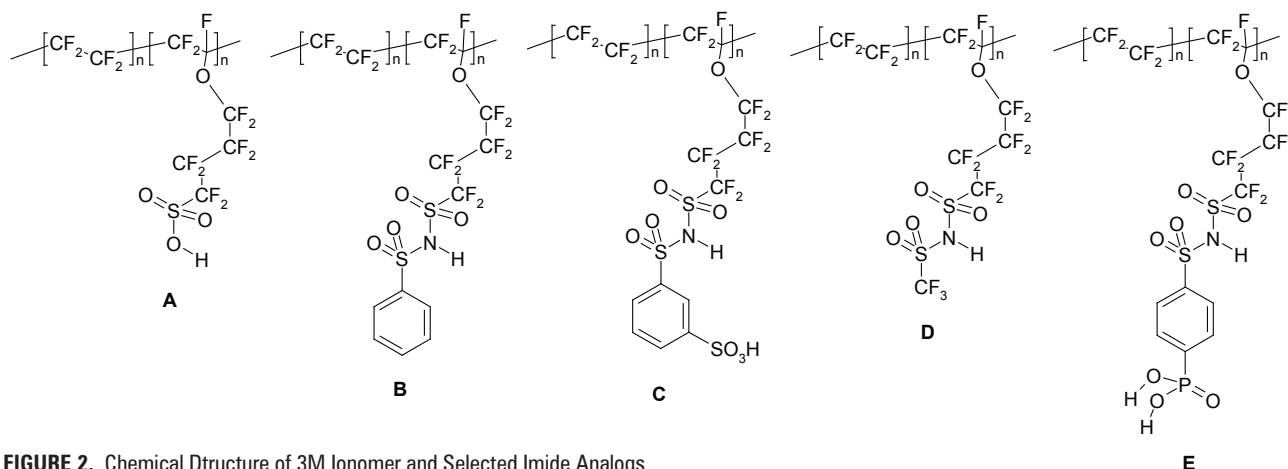

FIGURE 2. Chemical Dtructure of 3M Ionomer and Selected Imide Analogs
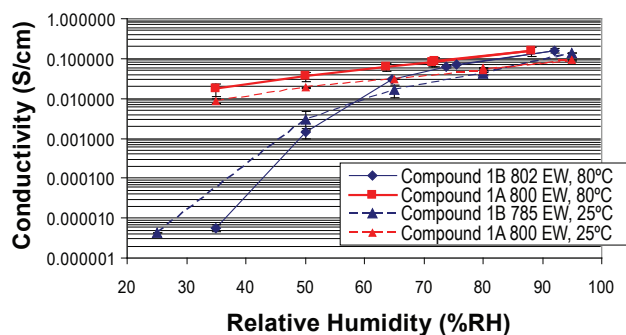
FIGURE 3. Conductivity of Compounds 1A and 1B at 80°C (solid line) and 25°C (dashed line)

FIGURE 4. a) ESR spectra of a Nafion™ membrane neutralized with 10 mole% Fe and varying amounts of Ce (III) cations. b) The integrated intensity of the ESR signal due to the carbon-centered radical as a function of Ce (III) content.

reaction. Degradation products were studied by both spin trapping and direct ESR measurements. Carbon-centered radical (CCR) and •OH radical adducts were detected by spin trapping with DMPO. The magnetic parameters for the CCR adducts in Nafion™ and 3M solutions are different, suggesting: (a) formation of different radicals, and (b) possible attack of •OH radicals on the side chain. ESR measurements on ionomer membranes with 10 mole% Fe neutralization and varying amounts of Ce neutralization (Figure 4) showed that a carbon centered radical is not generated when the membrane contains only Ce(III) and no Fe, and that with a constant 10% neutralization by Fe, Ce(III) is an effective stabilizer of the membrane towards degradation at levels above about 10%.

We are evaluating inorganic materials as components of these membranes for both increasing performance and durability, particularly HPAs. Addition of these compounds to membranes has been shown to provide enhanced conductivity and fuel cell performance [4]. We have found that this is particularly true in the presence of certain membrane stabilizing additives, such as transition metal salts and oxides. Figure 5 shows the conductivity of membranes doped with Ce cations, an additive known to stabilize membranes towards oxidative degradation, and varying amounts of an HPA. The HPA mitigates the negative effect of the added cations. While the addition of the acid form of HPAs to PFSA membranes can provide benefits, the solubility of these materials in water precludes their use in fuel cells. A major focus of our work is to immobilize the HPAs, either by linking the lacunary form to the ionomer via a linking group, linking to a dispersed inorganic particle, or other methods. The Colorado School of Mines has prepared several HPAs and their salts for investigation. Initial tests show that the linkage on one lacunary HPA to an aromatic phosphonic acid is stable under aqueous, acidic conditions. We have recently synthesized compound 1E and are working to attach this polymer to a lacunary HPA and form a membrane for evaluation.
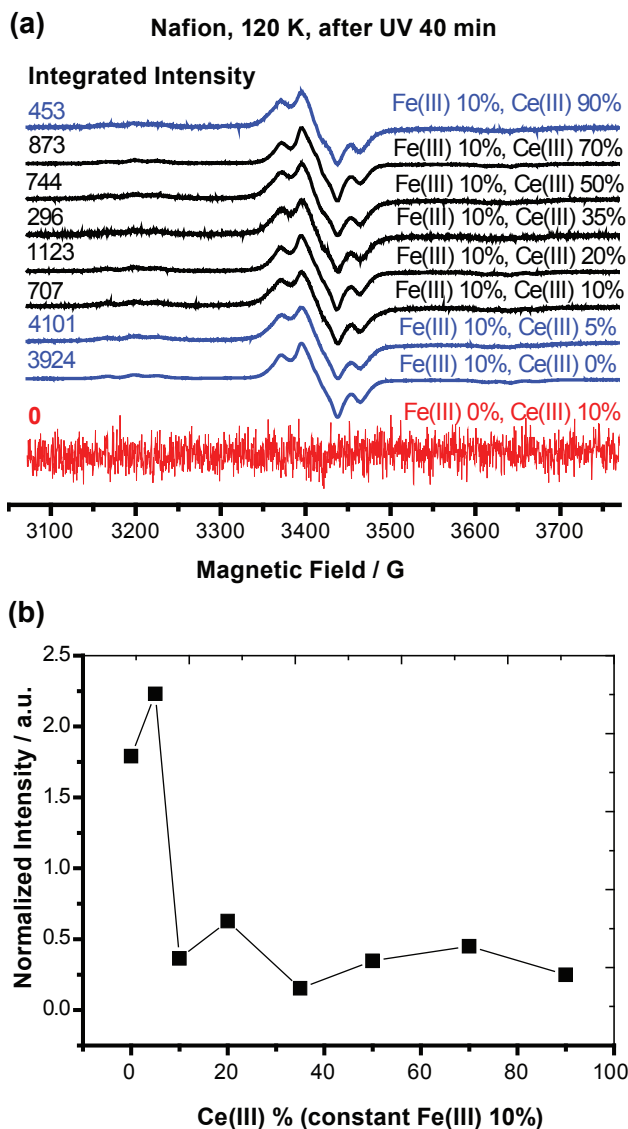
Modeling work underway at the University of Tennessee seeks to shed light on factors affecting both conductivity and the chemical stability of these membranes. Initial calculations compare the 3M ionomer to Nafion™ and to the short side-chain polymer developed at Dow. The initial phase of the theoretical work included development of a modeling protocol to determine how polymer chemistry and additives (if present) affect: (1) hydrated morphology; (2) aggregation and distribution of the sulfonic acid groups; and (3) water and proton transport. This has shown that there are differences in the hydrated morphologies of these three polymers. Parallel to this work, initial calculations
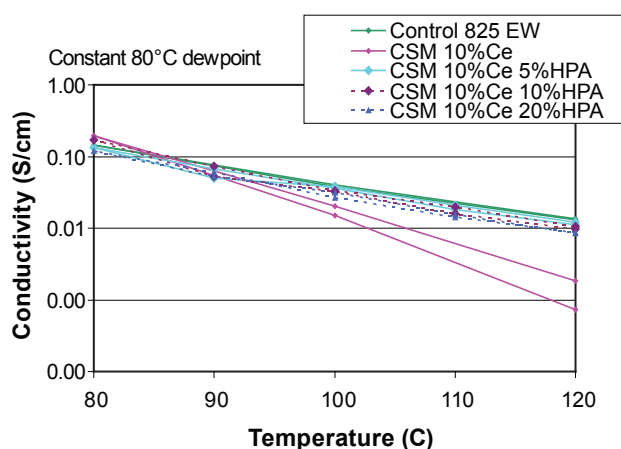
FIGURE 5. Conductivity vs. temperature at a constant 80°C dew point for PFSA/HPA membranes with 10% mole% Ce (III) cations added.

have been performed to establish a framework for assessing the relative chemical stability of the ionomer through extensive calculations of the energetics associated with the homolytic cleavage of chemical bonds by •OOH and •OH radicals. It is anticipated that this latter investigation will aid in the understanding of chemical degradation of PFSA membranes.

Conclusions and Future Directions

- We have prepared ionomers with EWs below 600 and have begun characterizing them. The lowest EWs have very good conductivity under hot, dry conditions. An ionomer membrane with an EW of 640 exceeded the DOE target for room temperature conductivity at 80% RH.

- We have prepared several new polymers and begun in situ and ex situ characterization of these materials. Initial conductivity measurements on one new aromatic imide ionomer show conductivity comparable to a PFSA at high humidity, but lower conductivity at lower humidity.

- We have begun preparation of hybrid fluorocarbon/ hydrocarbon ionomers.

- ESR studies have demonstrated that the carbon-centered radicals generated from attack by hydroxyl radicals on different PFSAs are chemically distinct, and that addition of Ce ions to the membrane dramatically lowers the concentration of carbon centered radicals formed.

- We have shown that HPAs can improve conductivity of membranes doped with Ce cations to provide membranes with high conductivity and good oxidative stability.

- Initial modeling results have shown differences in the hydrated morphologies of the 3M ionomer, Nafion™ and the short side-chain Dow polymer.

Future Directions Include:

- Continuing to study the effect of cross-linking low EW ionomers in both the hydrophilic and hydrophobic regions to help stabilize them in the presence of liquid water.

- Conversion of new imide polymers into membranes and evaluation.

- Investigate the factors affecting conductivity of sulfonic acid and imide polymers using nuclear magnetic resonance diffusion and other methods.

- Synthesis of new aromatic imide polymers with additional (up to four) acid groups on each side chain.

- Prepare HPAs attached to the ionomer, or another insoluble species (particle, etc.) for evaluation.

Special Recognitions & Awards/Patents Issued

1. 2008 DOE Hydrogen Program R&D Award, presented to Steven Hamrock in part for recognition of this project team's achievement in fuel cell R&D.

FY 2008 Publications/Presentations

1. Steven Hamrock "*Membranes for PEM Fuel Cells*" presentation at the University of St. Thomas, February 15, **2008**.

2. Andrew Herring, Niccolo Aieta, Mei-Chen Kuo, Steven Dec, Matthew Frey, Anitha Genupur, Gregory Haugen, and Steven Hamrock "*Improving the effect on proton conduction in PFSA polymers by the smart addition of Heteropoly Acids*" 213th ECS National Meeting, Phoenix, AZ, May 18, **2008**, Presentation 448.

3. Michael Emery, Matthew Frey, Mike Guerra, Gregory Haugen, Klaus Hintzer, Kai Helmut Lochhaas, Phat Pham, Daniel Pierpont, Mark Schaberg, Arne Thaler, Michael Yandrasits, and Steven Hamrock "*The Development of New Membranes for Proton Exchange Membrane Fuel Cells*", in Proton Exchange Membrane Fuel Cells 7, *ECS Transactions*, *11 (1),* pp. 3-14, **2007**.

4. Niccolo Aieta, Jennifer Leisch, Monica Santos, Michael Yandrasits, Steven Hamrock, and Andrew Herring, "*Tracking Crystallinity Changes in PFSA Polymers During Ex-Situ Peroxide Degradation*" in Proton Exchange Membrane Fuel Cells 7, *ECS Transactions*, *11 (1)*, pp. 1157-1164, **2007**.

5. Steven Hamrock, "*New Membranes for PEM Fuel Cells*", 212th ECS National Meeting, Washington D.C., October 8, **2007**, Presentation 384.

6. Niccolo Aieta, Michael Yandrasits , Monica Santos, Andrew Herring, "*Crystallinity effects correlated to degraded PFSA membrane performance*" 212th ECS National Meeting, Washington D.C., October 8, **2007**, Presentation 532.

7. Gregory Haugen, Michael Emery, Steven Hamrock, Mike Hicks, Stephen Roscoe, Mark Schaberg, and Michael Yandrasits, "*Spatially Resolved Degradation*", 212th ECS National Meeting, Washington D.C., October 8, **2007**, Presentation 533.

8. Michael Yandrasits "*Membrane and MEA Durability*" presented at the Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, RI, July 23, **2007.**

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4. A) A.M. Herring, *Journal of Macromolecular Science, Part C: Polymer Reviews* **46**, 245, **2007.** B) Andrew Herring, Niccolo Aieta, Mei-Chen Kuo, Steven Dec, Matthew Frey, Anitha Genupur, Gregory Haugen, and Steven Hamrock "*Improving the effect on proton conduction in PFSA polymers by the smart addition of Heteropoly Acids*" 213th ECS National Meeting, Phoenix, AZ, May 18, **2008**, Presentation 448.