

V.D.2 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 and improved durability under hotter and drier conditions, in order to meet DOE Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan 2010 commercialization targets for automotive fuel cells.
- Test new membrane in fuel cell membrane electrode assemblies (MEAs).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.3) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(C) Performance

Technical Targets

TABLE 1. Progress towards Meeting Membrane Technical Targets

All membranes are 20 micron	Units	3M 2010 Status	2010 target	2015 target
Area Specific Resistance at 120°C (H ₂ O pp 40-80 kPa)	Ohm cm ²	0.038 (50 kPa) 0.02 (80 kPa) 625 EW PFIA	≤0.02	≤0.02
Area Specific Resistance at 80°C (H ₂ O pp 25-45 kPa)	Ohm cm ²	0.017 (25 kPa) 0.006 (44 kPa) 625 EW PFIA	≤0.02	≤0.02
Area Specific Resistance at 30°C (H ₂ O pp 4 kPa)	Ohm cm ²	0.03 (3.8 kPa) 625 EW PFIA	≤0.03	≤0.03
Area Specific Resistance at -20°C	Ohm cm ²	0.14 700 EW PFSA	≤0.2	≤0.2
O ₂ cross-over	mA/cm ²	<0.5	≤5	≤2
H ₂ cross-over	mA/cm ²	<2	≤5	≤2
Durability Mechanical (%RH Cycle)	Cycles	10,000 625 EW PFIA	≥20,000	≥20,000
Chemical (OCV)	Hours	450 625 EW PFIA	≥500	≥500

EW – equivalent weight; PFIA – perfluoro imide acid; PFSA – perfluoro sulfonic acid; RH – relative humidity; OCV – open circuit voltage

Accomplishments

- Conductivity, fuel cell and diffusion measurements on a broad range of EWs and varied side-chains have provided insight into structure/conductivity relationship.
- We have synthesized new two and three acid-per-sidechain ionomers. These show:
 - Enhanced conductivity vs. starting PFSA.
 - Lower swelling in boiling water compared to PFSA with the same EW.
 - High hydrolytic stability (no hydrolysis >1 week in hot H₂SO₄ or in 250°C H₂O).
 - One of these, the PFIA ionomer allows us to make membranes which have conductivity in excess of 100 mS/cm below 40% RH at 120°C.
- Hetero poly acids (HPAs) have provided enhanced conductivity and chemical resistance. Inorganic

- oxide/HPA composites have shown partial stability to boiling water.
- We have shown that 825 EW 3M ionomer with new additives and optimized fabrication process provides:
 - >20,000 cycles in %RH cycle test.
 - >800 hours in OCV test.
 - >18,000 hour MEA lifetimes in accelerated tests.
 - Polymer and model compound stability studies are providing insight into degradation pathways and relative stability.
 - Dissipative particle dynamics simulations show morphologies consistent with clipped random wave analysis of small angle X-ray scattering (SAXS) data and conductivity measurements.
 - Electron spin resonance (ESR) measurements indicate that the rate constant for the reaction of hydroxyl radicals with the 3M membranes is significantly slower compared to that for Nafion®.



Introduction

Proton exchange membrane fuel cells (PEMFCs) represent a promising power source for a variety of applications. While many breakthroughs have been made over the last few years in the development of PEMFCs, 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]. Requirements of system size, efficiency, performance, start-up and cooling mean that fuel cells must be able to run robustly and exhibit adequate durability under a wide variety of operating temperatures, including temperatures up to 120°C. 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 -20°C to 120°C. 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 and other fuel cell applications.

The processes for making the new membranes, and the 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. These membranes and MEAs made from them should meet the 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 past we have shown that lower EW ionomers, based on our 3M perfluorinated sulfonic acid (PFSA, Figure 1), provide higher proton conductivity under drier conditions. PFSA membranes with EW under about 700 can meet DOE conductivity targets [2]. Unfortunately, the mechanical integrity of these membranes is poor. The 3M ionomer swells excessively at EWs below about 750 and becomes soluble in boiling water at EWs below about 650-700. At an EW of 700 the tetrafluoroethylene (TFE) segments in the polymer backbone are short, and the crystallinity index, measured by wide angle X-ray scattering (WAXS) is nearly zero, this is shown in Figure 2. Even lower EW, non-soluble membranes (about 700 EW) swell excessively. Figure 3 shows that membranes prepared from ionomers with EWs above about 750 show a gradual increase in hydration in boiling water with decreasing EW, increasing from about 14 moles of water per sulfonic acid group ($\lambda=14$) for an EW of 1100, to about 33 waters of hydration per sulfonic acid group ($\lambda=33$) for an EW of 750. Below this EW water absorption increases dramatically. The 700 EW ionomer has a λ value of >100. As shown in Figure 2, membranes from ionomers with EWs below

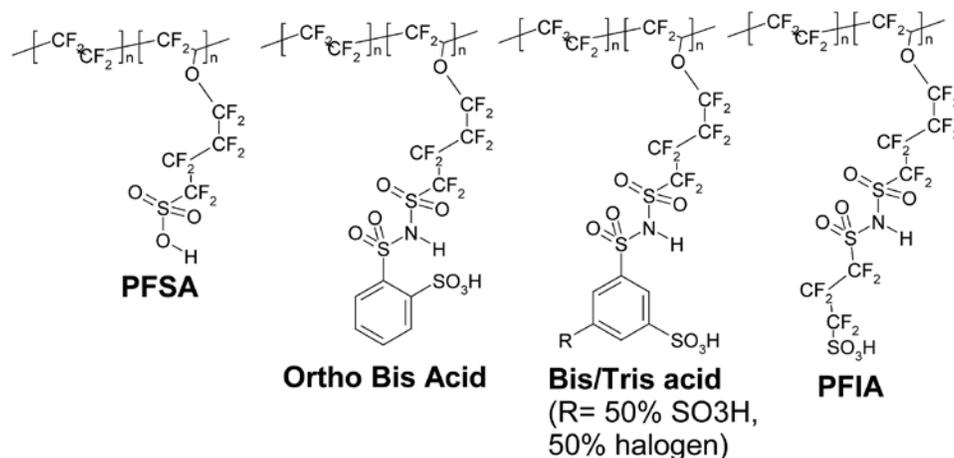


FIGURE 1. Structure of Selected Ionomers Based on the 3M Ionomer Backbone

700 partially dissolve in boiling water so this test can not be performed [3]. This excessive swelling or membrane solubility is known to lower MEA durability during fuel cell operation [4].

One way to produce polymers with long enough TFE segments in the backbone for crystallization and low enough EW to provide high conductivity is to have more than one protogenic hydrogen on each functional side-chain. Towards this end, we have used the bis sulfonyl imide acid as a protogenic group and linking moiety to prepare several multi-acid side-chain ionomers, some of which are shown in Figure 1. The bis sulfonyl imide acid is highly acidic, in some cases more acidic than a structurally similar sulfonic acid [5]. Fuel cell membranes from polymers containing this functional group have been prepared in the past through the polymerization of imide functional monomers with TFE [6]. We have prepared new, very low EW ionomers from sulfonyl fluoride ionomer precursors with sufficient

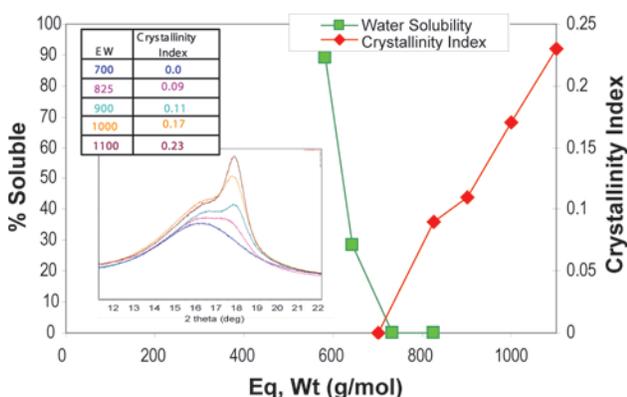


FIGURE 2. Water solubility and crystallinity index for a range of different EW 3M PFSA. Water solubility was measured after 3 hours in boiling water. The inset shows the WAXS spectra from which the crystallinity index was calculated.

backbone crystallinity to prevent excessive swelling. Swelling data for examples of low-EW ionomer prepared by this method are shown in Figure 3. Membrane samples prepared from both the ionomer labeled Ortho Bis Acid and PFIA absorb about 40 waters per acid group, much lower than the 700 EW PFSA. We have prepared samples of the 625 EW PFIA with in plane linear swelling as low as 20%, similar to what we see for 825 EW membranes which have provided up to 18,000 hours in accelerated durability tests in 50 cm² MEAs [2]. We are optimizing the membrane construction and fabrication process for this ionomer.

Figure 4a shows conductivity of two PFSA (825 and 700 EW), the same 625 EW PFIA whose water absorption is shown in Figure 3, and a 450 EW sample of the ‘Bis/Tris acid’. The Bis/Tris acid has very high conductivity at higher relative humidity compared to either PFSA, but the conductivity drops off at lower %RH and is lower than both PFSA below about 40% RH. This lower conductivity at lower %RH is similar to what is observed for sulfonated arene ionomers which show significant drop off in conductivity at lower

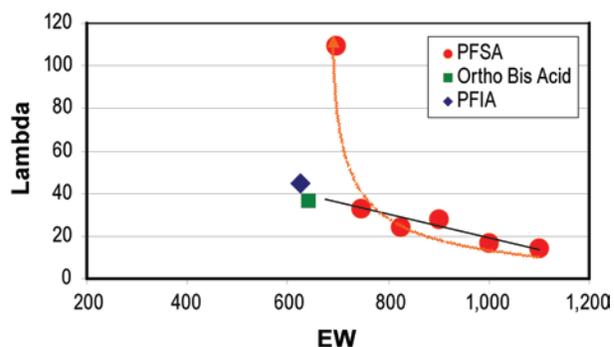


FIGURE 3. Water absorption in boiling water as a function of EW. Absorption is given as lambda (λ), or the number of water molecules per acid group.

%RH and may be due to the lower pKa of the aromatic sulfonic acid groups compared to the perfluoroalkyl sulfonic acid groups of the PFSA [7]. The 625 EW PFIA has conductivity at high %RH between the 700 and 825 EW PFSA, but shows higher conductivity than either at low EW. The higher conductivity at lower EW may be due to the higher acidity of the perfluoro bis sulfonamide (one of the most acidic acids known). Figure 4b compares the performance in a fuel cell of this 625 EW PFIA to our 825 EW PFSA. At the higher temperature and lowest humidity (120°C, 23 % RH) the fuel cell performance is over 100 mV higher and the through plane resistance is more than 0.100 Ohm-cm² lower than the 825 EW PFSA.

MEAs prepared from this ionomer have also lasted 450 hours in the DOE prescribed chemical durability (OCV) test and about 10,000 cycles in the DOE prescribed mechanical durability (RH Cycle) test (Table 1) [8]. Based on this and other testing, we have down-selected the PFIA as the ionomer to use in the remainder of this project and focus on further improvements in the chemical and mechanical durability of membranes made from this ionomer to allow them to meet these durability requirements.

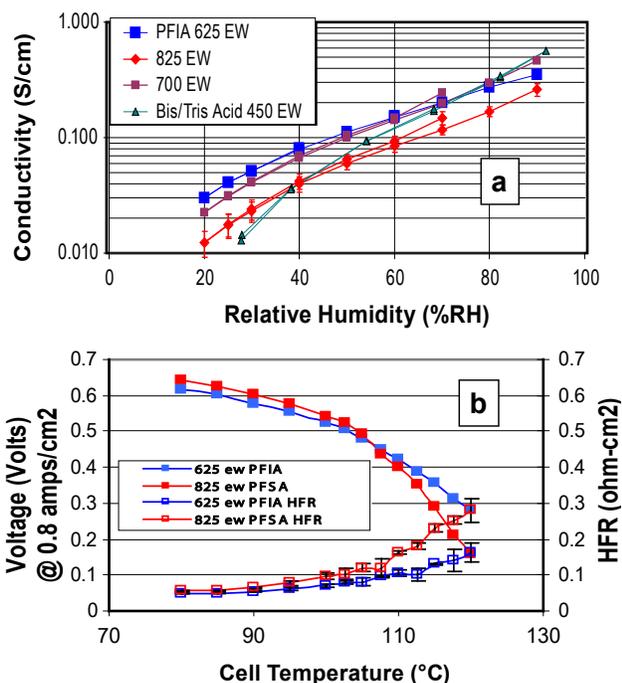


FIGURE 4. a) The conductivity at 80°C for selected ionomer membranes. Conductivity was measured using a 4-point, in-plane conductivity cell inside a constant humidity oven. b) The voltage of two 50 cm² MEAs with an 825 EW PFSA and a 625 EW PFIA membrane at 0.8 A/cm² running on hydrogen/air at ambient pressure. The cell inlet humidification is held constant with an 80°C dew point and the cell temperature is raised from 80°C to 120°C. This causes the relative humidity to drop from 100% to about 24%.

During the course of this year we have also performed work to optimize the electrode. The early work looked at different ionomer equivalent weights, ionomer to carbon ratios, catalyst types, gas diffusion layer types, and process variables. Test methods were developed that screened electrodes over a variety of test conditions to optimize performance over the whole range of automotive operating conditions – cool/wet to hot/dry and high current. Results of that work led to gains in performance and a 38% reduction of catalyst loadings compared to the initial baseline. Gains were also realized in catalyst cycling stability and in the reduction of the overall MEA fluoride release rate. New processing methods and catalyst morphologies are showing promise of further gains in both performance and catalyst stability. As we demonstrated early during this contract, an important variable in electrode performance under dry conditions is the thinness of the PEM and its ability to maximize the water management [9]. Gains have also been achieved in chemical stability through use of additives in the electrode formulation that we have observed diffusing into the PEM. We have evaluated stabilized HPAs that have reduced fluoride release rate at no cost to conductivity at levels added so far. These HPAs show partial stability to boiling water.

Conclusions and Future Directions

The focus of this project has been to develop new polymers and new stabilizing or conductivity enhancing membrane components to provide a membrane which can meet all DOE 2010 and 2015 targets including both conductivity and durability. We have also focused on gaining a better understanding of structure property relationships relevant to conductivity and durability to aid in this development. We have met all of the DOE membrane targets with at least one of the materials tested, and our new PFIA ionomer met the 30°C and 80°C conductivity targets, has nearly met the 120°C conductivity target (>100 mS/cm above 40% RH), has come very close to meeting all conductivity targets and has come very close to meeting all durability targets as well. We are confident that we will meet our goal in the final year of this project. Future activities include:

- Continue preparation and optimization of the conductivity and durability of the PFIA ionomer with membrane additives.
- Continue to probe factors in transport using nuclear magnetic resonance relaxation and diffusion, SAXS, conductivity, modeling and other spectroscopic measurements. Continue to develop a better understanding of effect of low lambda on proton transport.
- Evaluate impact of new protogenic groups, multi-acid side-chains and additives on membrane oxidative and chemical stability using ESR, ex situ tests, model compound tests and fuel cell tests.

- Develop a better understanding of role of crystallinity on swelling in new polymers using X-ray scattering, mechanical properties testing and modeling.
- Use atomistic and mesoscopic simulations to study the hydrated morphology of 3M PFSA and multi-acid side-chain membranes
- Provide completely water stable membranes comprising HPAs. Evaluate additional stabilizers.
- Describe degradation pathways and rates for current group of model compounds and correlate with membrane stability.

Special Recognition & Awards/Patents Issued

1. US Patent application 20090269644, Hamrock; Steven J. ; Schaberg; Mark S. ; Sharma; Neeraj ; Abulu; John E.; *Proton Conducting Materials*, Published October 29, 2009.

FY 2010 Publications/Presentations

1. M. Spulber, S. Schlick, "Using Cyclodextrins to Encapsulate Oxygen-Centered and Carbon-Centered Radical Adducts: The Case of DMPO, PBN, and MNP Spin Traps", *J. Phys. Chem.* 2010, Web posting 12 May 2010.
2. M.A. Yandrasits, S.J. Hamrock, "Membranes for PEM Fuel Cells" in "ACS Symposium Series: Fuel Cell Chemistry and Operation I", pp 1-13, 2010.
3. G.M. Haugen, M.A. Emery, S.J. Hamrock, M.A. Yandrasits, S. Barta, "Open Circuit Voltage Fuel Cell Durability Testing using Multiple PEM MEAs" in "ACS Symposium Series: Fuel Cell Chemistry and Operation I", pp 137-151, 2010.
4. M. Danilczuk, A.J. Perkowski, S. Schlick "Ranking the Stability of Perfluorinated Membranes Used in Fuel Cells to Attack by Hydroxyl Radicals and the Effect of Ce(III): A Competitive Kinetics Approach Based on Spin Trapping ESR", *Macromolecules*, 43, 3352-3358, 2010.
5. M. Maalouf, B. Pyle, C-N. Sun, D. Wu, S.J. Paddison, M.S. Schaberg, M.A. Emery, K.H. Lochhaas, S.J. Hamrock, H. Ghassemi, T.A. Zawodzinski Jr "Proton Exchange membranes for high temperature fuel cells: Equivalent weight and end group effects on conductivity" *ECS Transactions*, 25(1), 1473-1481, 2009.
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10. T.A. Zawodzinski, M. Maalouf, B. Pyle, C-N. Sun, M. Schaberg, and S. Hamrock, "Proton Transfer and Water Motion in Low EW PFSA's" Oral presentation at the 217th Electrochemical Society Meeting, Vancouver, BC, Canada, April 25, 2010.
11. R. Janarthanan, A.M. Herring, G.M Haugen, S.J. Hamrock, "Immobilization of composite inorganic additive on PFSA ionomers for improved performance" Oral presentation at the ACS National Meeting, San Francisco CA, March 21, 2010.
12. S. Schlick, *Polymer Degradation and Stabilization by ESR and ESR Imaging Methods: From Heterophasic Polymers to Ionomer Membranes Used in Fuel Cells*, Seminar at the Georgia Institute of Technology, Atlanta, GA, 8 March 2010.
13. M. Kumar and S.J. Paddison, "Ab initio calculations of chemical degradation of PFSA membranes", Oral presentation at the AIChE Annual Meeting, Nashville TN, Nov. 12, 2009.
14. S.J. Hamrock, "New Fuel Cell Membrane development at 3M", Oral presentation at the Fuel Cell Seminar, Palm Springs CA, November 2, 2009.
15. M. Maalouf, B. Pyle, C.N. Sun, D. Wu, S.J. Paddison, M. Schaberg, M. Emery, K.H. Lochhaas, S.J. Hamrock, H. Ghassemi and T. A. Zawodzinski Jr "Proton Exchange membranes for high temperature fuel cells: Equivalent weight effects on conductivity" Oral presentation at the 216th Electrochemical Society Meeting, Vienna, Austria, October 9, 2009.
16. S. Schlick, "Degradation of Fuel Cell Membranes Using ESR Methods: In Situ and Ex Situ Experiments", Polymer Degradation Discussion Group (PDDG), Sestri Levante, Italy, September 6-10, 2009 (Invited lecture).
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