

V.C.1 Membranes and MEAs for Dry, Hot Operating Conditions

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Contract Number: DE-FG36-07GO17006

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Project Start Date: April 1, 2007

Project End Date: March 31, 2011

(A) Durability

(C) Performance

Technical Targets

TABLE 1. Progress towards Meeting Membrane Technical Targets

All membranes are 15 micron mechanically stabilized 625 EW PFIA or 20 micron unstabilized	Units	3M 2011 Status	2015 target
ASR at 120°C (H ₂ O pp 40-80 kPa)	Ohm cm ²	0.023 (40 kPa) 0.012 (80 kPa)	<0.02
Cond. at 120°C	S/cm	0.087 (25% RH) 0.167 (40% RH)	
ASR at 80°C (H ₂ O pp 25-45 kPa)	Ohm cm ²	0.017 (25 kPa) 0.006 (44 kPa)	<0.02
Cond. at 80°C	S/cm	0.115 (50% RH) 0.3 (95% RH)	
ASR at 30°C (H ₂ O pp 4 kPa)	Ohm cm ²	0.02 (3.8 kPa)	<0.03
Cond. at 30°C	S/cm	0.09 (90% RH)	
ASR at -20°C	Ohm cm ²	0.10	<0.2
Cond. at -20°C	S/cm	0.02	
O ₂ cross-over	mA/cm ²	≤1.0	<2
H ₂ cross-over	mA/cm ²	≤1.8	<2
Durability			
Mechanical (%RH Cycle)	Cycles	>20,000	>20,000
Chemical (OCV)	Hours	>2,300	>500

PFIA – perfluoro imide acid; EW – equivalent weight; RH – relative humidity; ASR – area specific resistance; OCV – open circuit voltage

Fiscal Year (FY) 2011 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 Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan 2010/2015 commercialization targets for automotive fuel cells.
- Test new membrane in fuel cell membrane electrode assemblies.

Technical Barriers

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

FY 2011 Accomplishments

- We have developed a new PEM for PEM fuel cells. This new membrane comprises a new multi-acid side-chain (MASC) ionomer, stabilizing additives for improved chemical stability and polymer nanofibers for improved mechanical stability.
- In out-of-cell tests this new membrane has shown superior mechanical stability, chemical stability and conductivity compared other available membranes. It has met DOE 2015 targets for conductivity and other physical properties, except for the conductivity under the most aggressive condition, 120°C, 40 kPa H₂O (about 25% RH at 1 atm).
- Membrane electrode assemblies (MEAs) with this new membrane provide increased performance, lower cell resistance and have met all DOE 2015 durability targets (Table 1).



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.

Approach

The focus of this project is to develop a new proton exchange membrane 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 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 that can meet the industry target.

Results

In the course of this four-year project we developed a new PEM with improved proton conductivity, chemical

stability and mechanical stability. We incorporated this new membrane into MEAs and evaluated performance and durability. The development of this new membrane involved synthesizing and evaluating new ion-containing polymers, new stabilizing additives and polymer nanofibers for mechanical stabilization. Process development work included developing and/or optimizing methods of making stable dispersions with ionomers and additives as well as coating and post processing nanofiber stabilized membranes. MEA constructions were optimized to allow effective evaluation of the membrane performance and durability in a fuel cell.

In the past we have shown that lower EW ionomers, based on our 3M perfluorinated sulfonic acid (Figure 1, PFSA), 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 low EW 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 is nearly zero. Even lower EW, non-soluble membranes (i.e. 700 EW) swell excessively. Figure 2 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 . Membranes from ionomers with EWs lower than this 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 [5]. Towards this end, we have used the bis sulfonyl imide acid as a protogenic group and linking moiety to prepare several MASC 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 [6]. Fuel cell membranes from polymers containing this functional group have been prepared in the past through the polymerization of imide functional monomers with TFE [7]. We have prepared low EW ionomers starting sulfonyl fluoride polymers which have EWs high enough to provide sufficient backbone crystallinity in the resulting ionomer to control swelling. Swelling data for examples of low EW ionomer prepared by this method are shown in Figure 2. 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

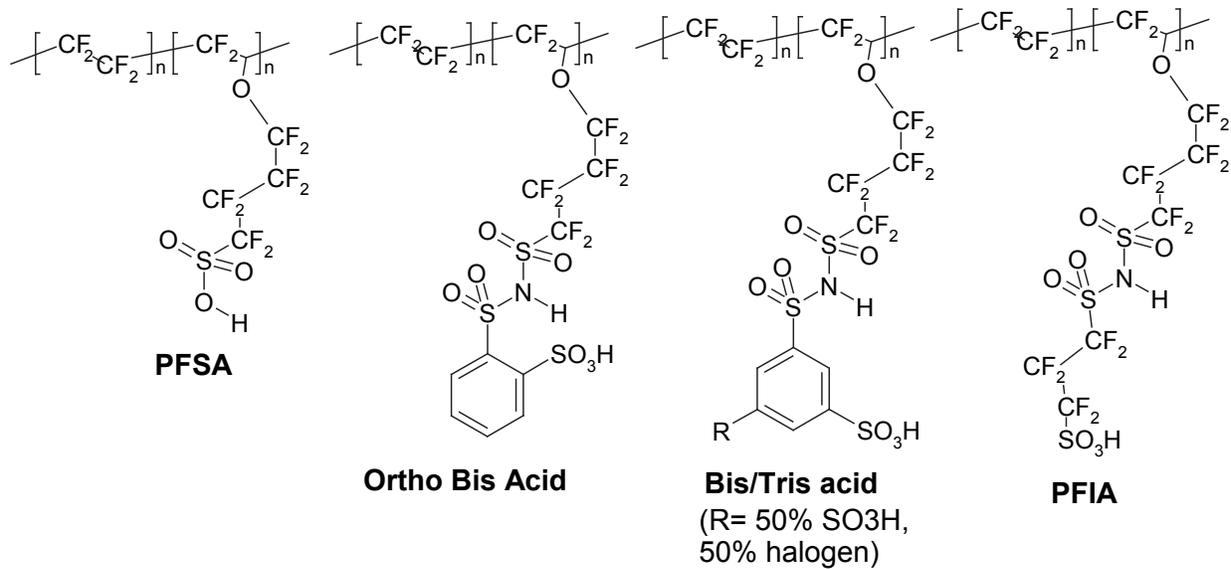


FIGURE 1. Structure of Selected Ionomers Based on the 3M Ionomer Backbone

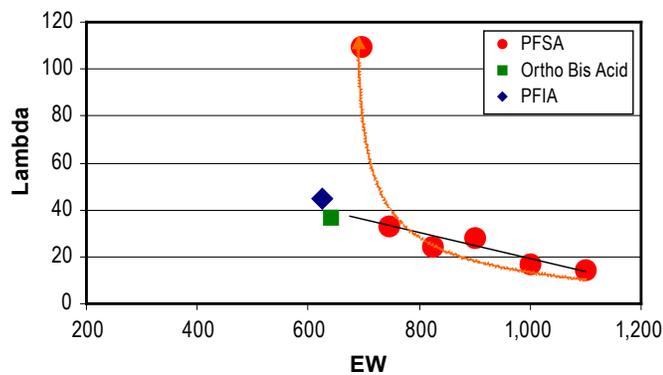
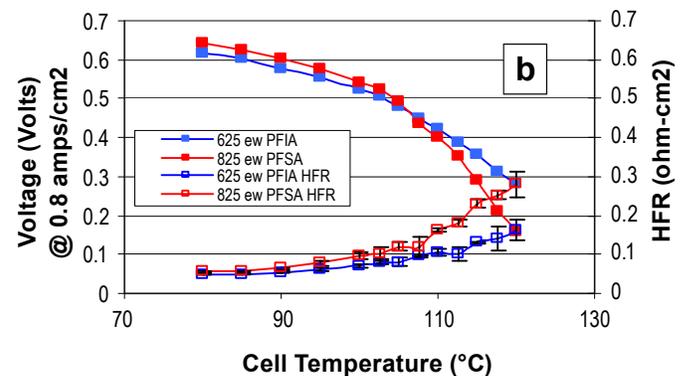
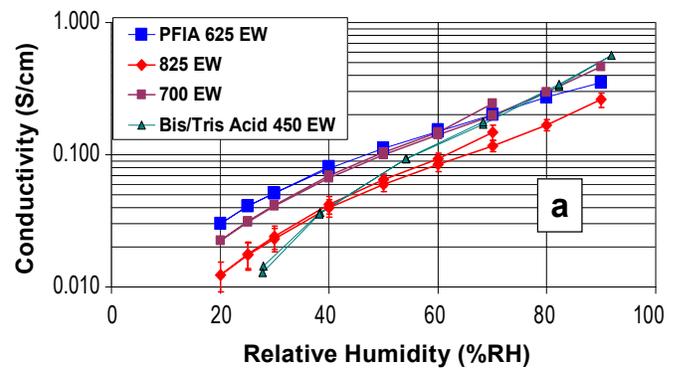


FIGURE 2. Water Absorption in Boiling Water as a Function of EW (Absorption is given as lambda (λ), or the number of water molecules per acid group.)

membranes which have provided up to 18,000 hours in accelerated durability tests in 50 cm² MEAs [2].

The ionomer selected for the final evaluation and testing is a 625 EW PFIA ionomer membrane (Figure 3). This membrane is reinforced with polymer nanofibers and also comprised a stabilizing additive package described in previous reports. The durability improvements that this additive package provides, including providing MEAs which lasted up to 18,000 hours in our accelerated durability test, were presented at the 2009 and 2010 Annual Merit Review meetings. A micrograph of the nanofiber reinforced membrane is shown in Figure 4. MEAs prepared from this membrane have also lasted over 2,300 hours in the chemical durability (OCV) test and over 20,000 cycles in the mechanical durability (RH Cycle) test (Table 1) [8]. Based



HFR - high-frequency resistance

FIGURE 3. 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 H₂/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%.

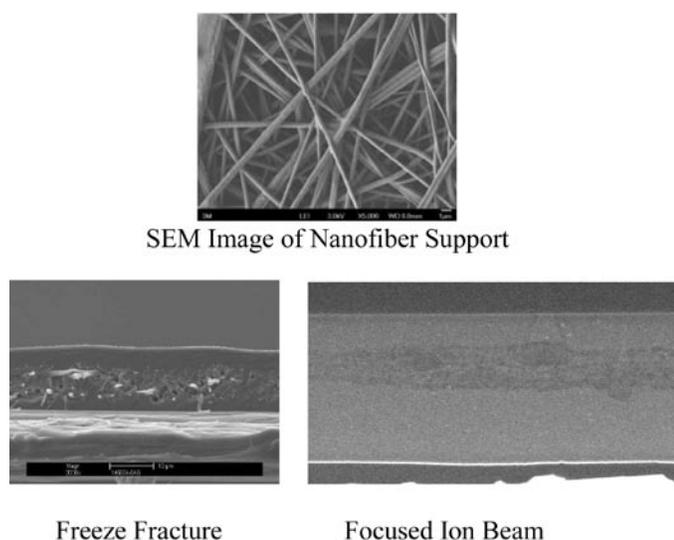


FIGURE 4. Scanning electrode micrographs (SEMs) of the nanofibers and cross-sections showing similar membranes with nanofiber support. Samples were prepared while still on carrier liner (bottom layer in images).

on this and other testing, we down-selected the PFIA as the ionomer which was used in the remainder of this project and focused on further improvements in the chemical and mechanical durability of membranes made from this ionomer to allow them to meet these durability requirements. During the course of this year we have also developed and optimized electrode and MEA construction. We have evaluated 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 reduction of catalyst loadings 38% over 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 provided further gains in both performance and catalyst stability. A summary of performance and durability data collected, including data from the FreedomCAR & Fuel Partnership Fuel Cell Tech Team Cell Component Accelerated Stress Test Protocols for PEM Fuel Cell Membranes, is shown in Table 1 [9].

Conclusions and Future Directions

This project ended March 31, 2011. As stated above, we developed a new ionomer membrane with improved performance and durability. Going forward we intend to build on this new technology to gain further understanding of the factors influencing conductivity and durability in this membranes and develop new materials based on this understanding.

FY 2011 Publications/Presentations

- Ghassemi, H.; Zawodzinski T.A. jr.; Schiraldi, D.A.; Hamrock S.J.** “Perfluoro ionomers with crosslinked structure for fuel cell application” Presented at the 241st ACS National Meeting, March 30, 2011, Anaheim CA.
- Hamrock, S.J.; Schaberg, M.S. Abulu, J.E.; Haugen, G.M.; Emery, M.M.; Yandrasits, M.A.; Xiong P.** “New proton exchange membrane development at 3M” Presented at the 241st ACS National Meeting, March 30, 2011, Anaheim CA.
- Janarthanan, R.; Haugen, G.M.; Hamrock, S.J.; Herring A.M.** “Application of zirconia and ion exchanged heteropolyacid nanocomposite modified PFSA ionomers for proton exchange membrane fuel cells” Presented at the 241st ACS National Meeting, March 30, 2011, Anaheim CA.
- Hamrock S.J.** “New fluorinated ionomers for proton exchange membrane fuel cells” Presented at the Sustainable Technology through Advanced Interdisciplinary Research Seminar, University of Tennessee, March 21, 2011, Knoxville, TN.
- Schiraldi, D.A.** “Durability in PEM Polymers” Presented at the Advances in Materials for Proton Exchange Membrane Fuel Cells Systems, February 21, 2011, Pacific Grove CA.
- Yandrasits, M.A.** “New fluorinated ionomers for proton exchange membranes” Presented at the Advances in Materials for Proton Exchange Membrane Fuel Cells Systems, February 20, 2011, Pacific Grove CA.
- Ghassemi, H.; Schiraldi, D.A.; Zawodzinski, T.A.; Hamrock, S.J.** “Poly(arylene ether)s with Pendant Perfluoroalkyl Sulfonic Acid Groups as Proton-Exchange Membrane Materials” *Macromolecular Chemistry and Physics*, **212(11)**, 673–678, 2011.
- Wu, D.; Paddison, S.J.; Elliott, J.A.; Hamrock, S.J.** “Mesoscale Modeling of Hydrated Morphologies of 3M Perfluorosulfonic Acid-Based Fuel Cell Electrolytes” *Langmuir*, **26(17)**, 14308–14315, 2010.
- Schlick, S.** “Fragmentation and Stabilization of Proton Exchange Membranes Used in Fuel Cells: Direct ESR and Spin Trapping Methods, Faculty of Chemistry” Jagiellonian University, December 10, 2010, Krakow, Poland.
- Schlick, S.** “A Dream of Hydrogen. Degradation of Fuel Cell Membranes Using ESR Methods: Ex Situ and In Situ Experiments, Institute of Nuclear Chemistry and Technology” December 8, 2010, Warsaw, Poland.
- Steven Hamrock**, “New Fluorinated Ionomers for Proton Exchange Membrane Fuel Cells, Department of Polymer Science” University of Southern Mississippi, December 1, 2010, Hattiesburg, MS.
- Schlick, S.** “Fuel Cells for Automotive, Stationary and Portable Applications: Challenges and Potential” Solvay Science for Innovation Congress, October 12–14, 2010, Brussels, Belgium.
- Danilczuk, M.; Perkowski, A.J.; Schlick, S.** “Ranking the Stability of Perfluorinated Membranes to Attack by Hydroxyl Radicals” *Macromolecules* **2010**, *43*, 3352–3358.

- 14. Wu, D.; Paddison, S.J.; Elliott, J.A.; Hamrock, S.J.**, Mesoscale Modeling of Hydrated Morphologies of 3M Perfluorosulfonic Acid-Based Fuel Cell Electrolytes, *Langmuir*, **2010**, *26* (17), 14308–14315.
- 15. Schaberg, M.S.; Abulu, A.E.; Haugen, G.M.; Emery, M.A.; O’Conner, S.J.; Xiong, P.N.; Hamrock, S.J.**, “New Multi Acid Side-Chain Ionomers for Proton Exchange Membrane Fuel Cells” *ECS Trans.* **2010**, *33* (1), 627.
- 16. Maalouf, M.; Bai, Y.; Paddison, S.; Schaberg, M.; Emery, M.; Hamrock, S.; Ghassemi, H.; Zawodzinski, T.**, “New Ionomeric Membranes for High Temperature Proton Exchange Membrane Fuel Cells: Effects of Different Side Chains’ Acidity on Conductivity” Presented at the 218th ECS Meeting, October 10–15, **2010** in Las Vegas, NV.
- 17. Kumar M.; Paddison S.**, “Chemical Degradation of the Side Chains of PFSA Membranes: An Ab Initio Study” Presented at the 218th ECS Meeting, October 10–15, **2010** in Las Vegas, NV.
- 18. Hamrock, S.J.; Schaberg, M.S.; Abulu, A.E.; Haugen, G.M.; Emery, M.A.; O’Conner, S.J.; Xiong, P.N.**, New Proton Exchange Membrane Development, Presented at the 218th ECS Meeting, October 10–15, **2010** in Las Vegas, NV.
- 19. Liu, Y.; Horan, J.L.; Schlichting, G.J.; Hamrock, S.J.; Haugen, G.M.; Herring, A.M.**, Morphology Study of Perfluorosulfonic Acid Ionomer for PEM Fuel Cell Application, Presented at 218th ECS Meeting, October 10–15, **2010** in Las Vegas, NV.
- 2. S.J. Hamrock**, U.S. Department of Energy Hydrogen Program 2010 Annual Merit Review Proceedings, http://www.hydrogen.energy.gov/pdfs/review10/fc034_hamrock_2010_o_web.pdf.
- 3. M.A. Yandrasits and S.J. Hamrock** in *Fuel Cell Chemistry and Operation*, A.M. Herring, T.A. Zawodzinski Jr., S.J. Hamrock, Editors, p. 15, ACS Symposium Series; American Chemical Society: Washington, DC, (2010).
- 4. Y.H. Lai, C.K. Mittelsteadt, C.S. Gittleman, and D.A. Dillard**, *J. Fuel Cell Sci. Technol.* **6**, 021002 (2009).
- 5. M.S. Schaberg, A.E. Abulu, G.M. Haugen, M.M. Emery, S.J. O’Conner, P.N. Xiong, S.J. Hamrock**, *ECS Trans.* **33** (1), 627 (2010).
- 6. I.A. Koppel, R.W. Taft, F. Anvia, S.Z. Zhu, L.Q. Hu, K.S. Sung, D.D. DesMarteau, L.M. Yagupolskii, Y.L. Yagupolski, N.V. Ignat’ev, N.V. Kondratenko, A.Y. Volkonskii, V.M. Slasov, R. Notario and P.C. Maria**, *J. Am. Chem. Soc.*, **116**, 3047-3057 (1994).
- 7. S.C. Savett, J.R. Atkins, C.R. Sides, J.L. Harris, B.H. Thomas, S.E. Creager, W.T. Pennington and D.D.J. DesMarteau**, *J. Electrochem. Soc.* **2002**, **149**, A1527 (2002).
- 8.** http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/htmwg_benjamin.pdf.
- 9.** Cell Component Accelerated Stress Test and Polarization Curve Protocols for Polymer Electrolyte Membrane Fuel Cells; http://www.uscar.org/commands/files_download.php?files_id=267.

References

- 1. S.J. Hamrock and M.A Yandrasits**, *Journal of Macromolecular Science, Part C: Polymer Reviews*, **46**, 219 (2006).