

V.D.13 Membranes and MEAs for Dry, Hot Operating Conditions

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Technical Targets

Table 1. Progress towards Meeting Membrane Technical Targets

		3M	2010 Target	2015 Target
		2009 Status		
Conductivity at 120°C	S/cm	0.146 (46% RH)	0.1	0.1
		580 EW PFSA		
Conductivity at 80°C	S/cm	0.1 (39% RH)	0.1	0.1
		0.13 (50% RH)		
		0.50 (92% RH)		
		580 EW PFSA		
Conductivity at 30°C	S/cm	0.1 (80% RH)	0.07	0.07
		580 EW PFSA		
Conductivity at -20°C	S/cm	0.014 S/cm	0.01	0.01
		700 EW PFSA		
O ₂ cross-over	mA/cm ²	<0.5	2	2
		20 μM Membrane		
H ₂ cross-over	mA/cm ²	<2	2	2
		20 μM Membrane		
Durability w/ cycling	Hours	12,000 (80°C)	5,000 (80°C)	5,000 (80°C)
		1,000 (120°C)		
		825 EW PFSA		
OCV Lifetime	Hours	500	200	200
Humidity cycles	Cycles	> 20,000 Un-reinforced Membrane	20,000	20,000

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

Objectives

To develop a new proton exchange membrane 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 commercialization targets for automotive fuel cells.

Technical Barriers

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

- (A) Durability
- (C) Performance

Accomplishments

- Conductivity, fuel cell and diffusion measurements on a broad range of EWs and varied side-chains have provided insight into structure/conductivity relationships.
- We have synthesized new two and three acid-per-sidechain ionomers. These show:
 - Enhanced conductivity vs. starting PFSA.
 - High hydrolytic stability (no hydrolysis > 1 week in hot H₂SO₄ or in 250°C H₂O).
- Hetero poly acids (HPAs) have provided enhanced conductivity and chemical resistance. Model compounds show we can form a stable linkage

which may allow water stable HPA containing ionomer membranes.

- 825 EW 3M ionomer with new additives and optimized fabrication process provides:
 - >20,000 cycles in %RH cycle test.
 - >500 hours in OCV test.
 - >12,000-hour membrane electrode assembly (MEA) lifetimes in accelerated tests.
- Dissipative particle dynamics (DPD) simulations show morphologies consistent with clipped random wave (CRW) analysis of small angle X-ray scattering (SAXS) data and conductivity measurements.
- Polymer and model compound stability studies are providing insight into degradation pathways and relative stability.



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 proton exchange membranes (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 performance and durability. 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

Membranes based on the 3M Ionomer (Figure 1a) have been prepared with a variety of EWs (grams polymer/moles acid). Figure 2 shows the conductivity of some of these PFSAAs as a function of EW at 80°C, and at a number of different hydration, or λ values (λ represents the number of water molecules absorbed per sulfonic acid group, determined gravimetrically). It can be seen that at lower humidification levels, the impact of EW on conductivity is greater than at higher humidification. This suggests that the hydrated acid groups may be more accessible to one another in the lower EW ionomer, allowing proton transport even with little or no “free” water. Another observation consistent with this is that pulsed-field gradient spin-echo nuclear magnetic resonance (NMR) measurements of proton diffusion coefficients show that for the lowest EW ionomers, the diffusivity decreases by a smaller amount as the water content decreases, compared to higher EW membranes. It is worth noting that the low EW ionomers have higher conductivity than the model compound perfluorobutane sulfonic acid, indicating the importance of the phase separated structure of the PFSAAs.

New membrane fabrication processes have allowed the fabrication of ionomer membranes with EWs of about 800 which can meet the %RH cycle target of 20,000 cycles without any mechanical stabilization or reinforcement.

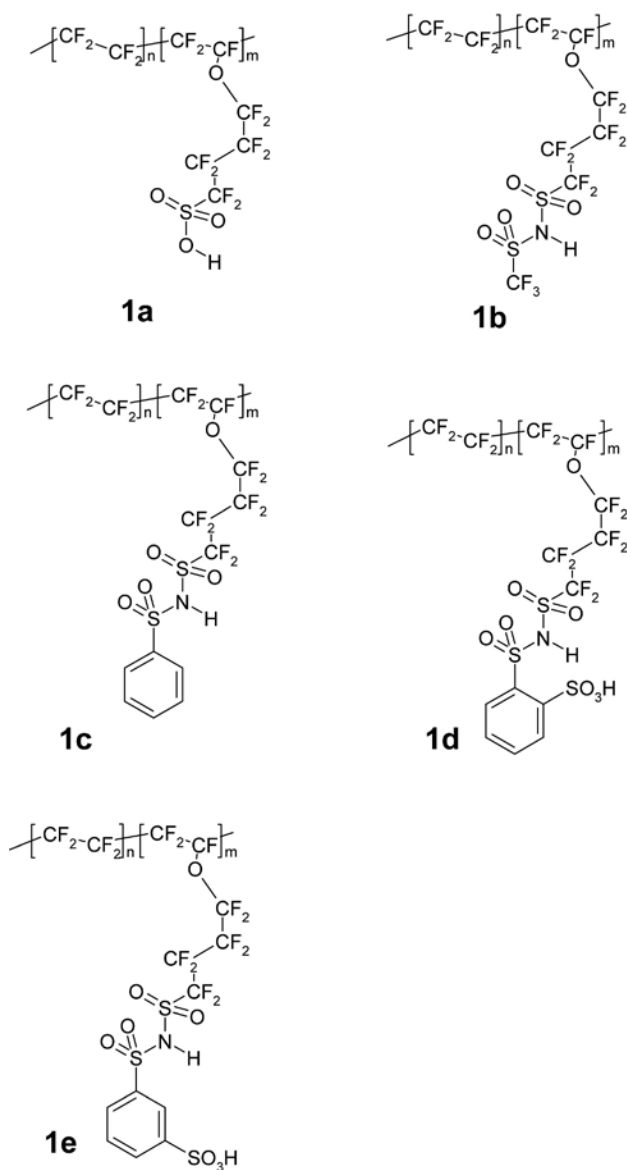


FIGURE 1. Structure of selected ionomers based on the 3M Ionomer. 1a: PFSA, 1b: Trifluoromethyl Imide, 1c: Phenyl Imide, 1d: Ortho Bis Acid, 1e: 1D Meta Bis Acid.

While lower EW ionomers provide higher proton conductivity under drier conditions, the mechanical integrity of these membranes is poor. The 3M ionomer swells excessively at EWs below about 750 and becomes water soluble at EWs below about 650. This is near the EW at which the tetrafluoroethylene (TFE) segments in the polymer backbone are too short to crystallize, as measured by wide angle X-ray scattering. 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 sidechain.

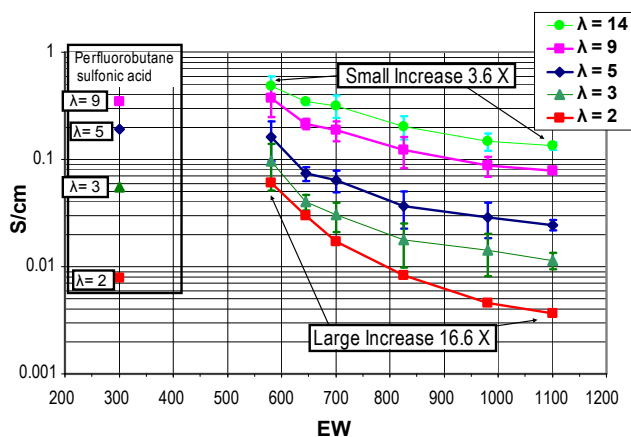


FIGURE 2. Conductivity of 3M PFSA ionomers as a function of EW for assorted humidification (λ) values.

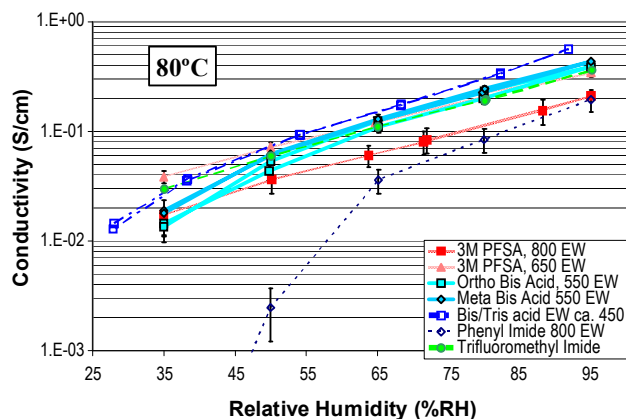


FIGURE 3. Conductivity of selected ionomer membranes as a function of %RH at 80°C.

Towards that end, we have prepared several bis sulfonyl imide polymers, some of which are shown in Figures 1b-e.

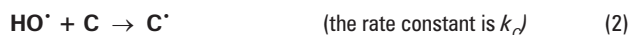
PFSA's with the sulfonic acid group replaced with a bis sulfonyl imide group have been described before [2]. They benefit from increased conductivity due to increased acidity. Figure 3 shows that a bis-trifluoromethyl imide with an EW of about 800 (1b) has conductivity much higher than an 800 EW PFSA, and has conductivity close to that of a 650 EW PFSA. However, the sidechain of this imide has a higher MW than the sulfonic acid sidechain in a PFSA. To prepare this ionomer, a polymer precursor (that is the sulfonyl fluoride form of the polymer) with an EW of 650 was used. The ultimate result is a trade-off, where the increase in EW due to the increase in sidechain MW is offset by the higher conductivity from the increase in acidity, and there is no net gain in conductivity. In other words, a 650 EW polymer precursor has been converted to an 800 EW ionomer with the conductivity of a 650 EW PFSA. The

use of an imide having multiple protogenic hydrogen overcomes this dilemma. Our approach is to prepare ionomers based on the phenyl imide (1c). This parent compound suffers from the same drawback as the perfluorinated analog, 1b, in that we are increasing the MW of the sidechain. Further, this imide does not have the enhancement in conductivity due to increased acidity, as this mixed fluorocarbon/hydrocarbon imide acid has a pKa similar to a PFSA. Figure 3 shows that the 800 EW phenyl imide has conductivity which is similar to the 800 EW PFSA at high %RH, but the conductivity drops off precipitously at lower %RH, and the conductivity of this material is more than 1,000 times lower than the PFSA at 35% RH. This is due to a large degree from significant drying out of this ionomer at low humidity, and at 35% RH the value of lambda for this material is about 0.5, compared to 2 for the 800 EW PFSA. Attachment of additional sulfonic acid groups to the benzene ring improves the conductivity of this type of imide dramatically. Figure 3 shows conductivity for compounds 1d, 1e. These bis acid compounds were prepared from an 800 EW starting polymer, but have an EW of about 550, as the EW of the polymer is “cut in half” when the sidechain is modified to have two protogenic groups. These polymers do have higher conductivity than their precursor at RH above about 40%. They do show a small downward curvature in the low RH region, possible due to morphological differences between this polymer and the PFSA. Since these polymers were prepared with an 800 EW precursor polymer, the backbone crystallinity provides lower swelling and better mechanical properties at higher humidification. We have recently prepared a 450 EW ionomer with an average of about 2.5 protogenic hydrogens per sidechain which has shown an additional increase in conductivity.

DPD simulations [3] have been used to investigate the effects that these different protogenic groups may have on the hydrated morphology of membranes with the same backbone chemistry. This is done to gain a better understanding of the relationship between proton transport and the polymer structure. Initial investigations of the hydrated morphologies of the three different ionomers shown in Figures 1a, 1c and 1d show that there are significant differences between these materials in the size and shape of the water clusters at several different hydration levels. In the case of the PFSA polymers, the morphologies from these simulations are in good agreement with morphologies derived from CRW analysis of SAXS experiments done on the ionomer at different hydration levels [4]. Similar experiments on the other ionomer structures are currently being carried out.

We have investigated the degradation pathways for these PFSA and ionomers by studying the ex situ degradation of ionomers and model compounds using electron spin resonance (ESR) spectroscopy and high pressure liquid chromatography/mass spectroscopy. A

kinetic approach, using ESR spectroscopy, has been used to compare the stability of Nafion® and 3M Ionomer as aqueous dispersions to attack by hydroxyl radicals generated by ultraviolet (UV)-irradiation of H₂O₂ solutions [5]. Hydroxyl radicals and carbon-centered radicals derived from the membranes were detected as adducts of 5,5-dimethylpyrroline-N-oxide (DMPO) as the spin trap [6,7]. Once generated by UV-irradiation of H₂O₂, HO• radicals can be trapped by the spin trap (reaction 1 below), or react with membranes or other competitors (C in reaction 2 below). The concentration of HO• radicals depends on the reaction rates of these parallel reactions, and can be measured by tracking the intensity of the ESR spectrum of the DMPO/OH adduct as a function of time during UV-irradiation of a solution containing the spin trap and the competitor.



The reaction rate constant for the reaction of HO• radicals with the competitor can be deduced from equation 3 below [8,9]

$$V/v - 1 = k_c[C]/k_{\text{DMPO}}[\text{DMPO}] \quad (3)$$

where V and v are initial reaction rates of DMPO/OH adduct formation in the absence and presence of competitor (membrane), and $[C]$ and $[\text{DMPO}]$ are the competitor and DMPO concentrations, respectively. Therefore, by plotting $V/v - 1$ vs. $[C]/[\text{DMPO}]$ we can determine k_c/k_{DMPO} . The results, shown in Figure 4, have indicated that the rate constant for the reaction of

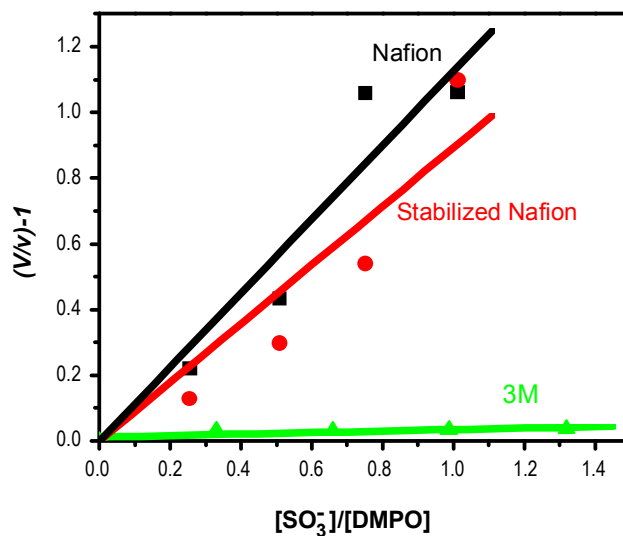


FIGURE 4. Membranes as competitors for HO• radicals. Membrane concentrations were expressed as the concentrations of sulfonic groups. The 3M Ionomer and the ionomer labeled “Stabilized Nafion®” have been stabilized via carboxylate end-group removal.

hydroxyl radicals with the 3M membranes is significantly slower compared to that for Nafion®.

New inorganic membrane/MEA components have also shown promise in stabilizing membranes both in ex situ tests and in fuel cell tests. MEAs prepared with these new membranes have archived lifetimes in accelerated tests in excess of 12,000 hours.

Conclusions and Future Directions

Our focus in the first portion of this project has been on new polymers and new stabilizing or conductivity enhancing membrane components. We have also focused on gaining a better understanding of structure property relationships relevant to conductivity and durability. We have met all of the DOE membrane targets with at least one of the materials tested, and we have a clear path toward materials which can meet all of the targets. While low EW ionomers have inadequate stability with liquid water, multi acid sidechains show promise as a pathway towards membranes which can meet both conductivity and durability targets. Future activities include:

- Continue preparation and evaluation of the conductivity and durability of low EW PFSA, new imide containing polymers and membrane additives.
- Continue to probe factors in transport using NMR 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. Investigate the structural basis for the higher stability of 3M membranes compared to Nafion® in ESR experiments.
- Evaluate membranes crosslinked in both the hydrophilic and hydrophobic regions.
- Provide water stable membranes comprising HPAs.
- Develop a better understanding of role of crystallinity on swelling in new polymers using X-ray scattering, mechanical properties testing and modeling.
- Evaluate additional stabilizers (including new HPA based stabilizers).
- Describe degradation pathways and rates for current group of model compounds and correlate with membrane stability.

FY 2009 Publications/Presentations

1. Niccolo V. Aieta, Ronald J. Stanis, James L. Horan, Michael A. Yandrasits, David J. Cookson, Bridget Ingham, Steven J. Hamrock, and Andrew M. Herring “*Clipped Random Wave Morphologies and the Analysis of the SAXS of an Ionomer Formed by Co-Polymerization of Tetrafluoroethylene and CF₂=CFO(CF₂)₄SO₃H.*” *Macromol., in press.*
2. Michael A. Yandrasits and Steven J. Hamrock “*Membranes for PEM Fuel Cells*” in “ACS Symposium Series: Fuel Cell Chemistry and Operation I”, *in press.*
3. Gregory Haugen, Michael Emery, Steven Hamrock, Michael Yandrasits, and Sara Barta “*Open Circuit Voltage Fuel Cell Durability Testing using Multiple PEM MEAs*” in “ACS Symposium Series: Fuel Cell Chemistry and Operation I”, *in press.*
4. Niccolo V. Aieta, Ronald J. Stanis, James L. Horan, Michael A. Yandrasits, David J. Cookson, Bridget Ingham, Steven J. Hamrock, and Andrew M. Herring “*Clipped Random Wave Morphologies Derived From SAXS Of Differing Equivalent Weights Of The 3M Ionomer : A New Way To Visualize Copolymers*” *Advances in Materials for Proton Exchange Membrane Fuel Cell Systems*; Pacific Grove: California, February 17, 2009.
5. Sonny Sachdeva, Neeraj Sharma, Steven J. Hamrock, and Andrew M. Herring, “*Characterization Of Heteropolyacid Immobilized Proton Exchange Membranes*” *Advances in Materials for Proton Exchange Membrane Fuel Cell Systems*; Pacific Grove: California, February 17, 2009.
6. Steven J. Hamrock, “*Proton Exchange Membrane Development at 3M*”, *Advances in Materials for Proton Exchange Membrane Fuel Cell Systems*; Pacific Grove: California, February 16, 2009.
7. David Schiraldi, “*Durability of Non-perfluorinated Membrane Materials for Fuel Cells*” *Advances in Materials for Proton Exchange Membrane Fuel Cell Systems*; Pacific Grove: California, February 16, 2009.
8. Shulamith Schlick “*Fragmentation of Proton Exchange Membranes Used in Fuel Cells: Direct ESR and Spin Trapping Methods*” *Commissariat a l’Energie Atomique (CEA), Grenoble, France, October 23, 2008.*
9. Niccolo V. Aieta, Mike A. Yandrasits, Steven J. Hamrock, Ronald J. Stanis, James L. Horan, and Andrew M. Herring “*Representative Morphologies of Nafion™ and Other PFSA Membranes Using a Fourier Transform Approach to the Reduction of SAXS Data at Different Levels of Hydration*” 214th ECS National Meeting, Honolulu, HI, October 12, 2008.
10. David Schiraldi, “*Chemical Durability Studies Of PFSA And Nonfluorinated PEM Materials*”, 236th ACS National Meeting, August 20, 2008, Philadelphia, PA.
11. Stephen J. Paddison “*Mesoscopic Modeling Of The Morphology And State Of Water In Hydrated PFSA Fuel Cell Membranes*”, 236th ACS National Meeting, August 18, 2008, Philadelphia, PA.
12. Michael Yandrasits, “*PEMFC Membrane Development At 3M*”, 236th ACS National Meeting, August 18, 2008, Philadelphia, PA.

1. Niccolo V. Aieta, Ronald J. Stanis, James L. Horan, Michael A. Yandrasits, David J. Cookson, Bridget Ingham,

13. Steven Hamrock, "Membranes for PEM Fuel Cells", Gordon Research Conference - Membranes: Materials & Processes, August 11, 2008, Colby-Sawyer College, NH.

14. D. Wu, S. J. Paddison, and J. A. Elliott, "A Comparative Study Of The Hydrated Morphologies Of Perfluorosulfonic Acid Fuel Cell Membranes", *Energy and Environmental Science*, 2008, 1, 284-293.

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