V.C.1 New Fuel Cell Membranes with Improved Durability and Performance

Michael Yandrasits
3M Company
3M Center, Building 201-1W-28
St. Paul, MN 55144
Phone: (651) 736-5719
Email: mayandrasits@mmm.com

DOE Managers
Jacob Spendelow
Phone: (202) 586-4796
Email: Jacob.Spendelow@ee.doe.gov
David Peterson
Phone: (720) 356-1747
Email: David.Peterson@ee.doe.gov

Contract Number: DE - EE0006362

Subcontractors:
- General Motors Fuel Cell Activities, Pontiac MI – Craig Gittleman
- Vanderbilt University, Nashville, TN – Peter Pintauro

Project Start Date: October 1, 2013
Project End Date: September 30, 2016

Overall Objectives

- Meet all of the DOE Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan membrane performance, durability, and cost targets simultaneously with a single membrane.
- Membranes will be based on multi-acid side chain (MASC) ionomers.
- Electrospun nanofiber structures will be developed to reinforce membranes.
- Peroxide scavenging additives will be used to enhance chemical stability.
- New membranes will have improved mechanical properties, low area specific resistance and excellent chemical stability compared to current state of the art.
- Experimental membranes will be integrated into membrane electrode assemblies and evaluated in single fuel cells and finally fuel cell stacks.

Fiscal Year (FY) 2014 Objectives

- Baseline performance of conventional membranes and demonstrate MASC ionomer conductivity of 0.1 S/cm at 80°C and 50% relative humidity (RH).
- Identify one or more polymer systems for use as reinforcing fibers made by electrospinning.
- Develop methods for making perfluoroimide acid (PFIA) electrospun fibers.
- Make a membrane in the lab that has improved performance over state-of-the-art membranes and meets DOE accelerated durability targets.

Technical Barriers

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

(A) Durability

(B) Cost

(C) Performance

Technical Targets

Technical targets are shown in Table 1 along with the comparative data to date. The conventional membranes listed are perfluorosulfonic acid-based membranes that are either unsupported (725 equivalent weight [EW]-20 μm) or supported with 3M's standard nanofiber material (725 EW-S-14 μm). The experimental PFIA is shown in both the unsupported (PFIA-20 μm) and supported (PFIA-S-14 μm) forms.

FY 2014 Accomplishments

- Successfully synthesized three lots of PFIA ionomer in the lab and demonstrated conductivity of 0.1 S/cm at 80°C and 50% RH.
- Initiate scale up efforts for PFIA ionomer.
- Fabricated 20 nanofiber support candidates and evaluated composite membranes for mechanical properties including swell in hot water.
- Developed a method for decoupling conductivity of the center composite layer from the pure ionomer skin layers of a supported membrane.
- Developed a method to electrospin PFIA ionomer.

INTRODUCTION

One of the key challenges for fuel cell membranes is the ability to meet the automotive industry targets for

TABLE 1. DOE Targets and Measured Data to Date

Characteristic	Units	2017 & 2020 Targets	725 EW (20 µm)	725 EW-S (14 µm)	PFIA (20 µm)	PFIA-S (14 µm)
Area specific proton resistance at:						
80°C and water partial pressures from 25 Kpa	Ohm cm^2	0.02	0.026	0.034	0.017	0.025
Durability						
Mechanical	Cycles with <10 sccm crossover hours	20,000	8,300	>20,000	12,000	26,300*
Chemical	hrs	>500				2,170*

*Durability samples made with 80/20 blend of PFIA and 825EW PFSA

area specific resistance, durability, and cost. One way to reduce membrane resistance is to use low EW ionomers. Unfortunately, membranes based on perfluorosulfonic acid polymers with equivalent weights of about 700 g/mol or lower have significant water soluble fractions and are not stable for long times in an operating fuel cell. New ionomers are needed that have improved conductivity, especially under hot and dry operating conditions, that are not water soluble. By increasing the number of acid groups per side chain, the proton conductivity can be increased while retaining the polymer backbone to resist solubility. However, increasing the bulk proton conductivity alone is likely not enough to meet the area specific resistance targets. Thinner membranes will also improve the resistance but they will compromise durability. In this case polymer fiber supports are needed to improve the mechanical strength, resist swelling in the x-y plane, and increase durability.

Previous projects have made significant advances in meeting many of the membrane targets but often the samples used to meet one milestone were different than those used to meet another. For example, a thin, unsupported, low EW ionomer membrane can meet many of the performance targets while falling short of the durability goals. Likewise, a fiber supported membrane can often meet the accelerated durability targets while having relatively poor performance. This project is focused on meeting all of the DOE goals with one membrane.

APPROACH

The goal of this project is to make a fuel cell membrane that meets all of the Department of Energy Fuel Cell Technologies Office targets for performance, durability and cost. The materials part of this project is split into two parts; ionomer development and nanofiber support development. The basis of the ionomer development is 3M's MASC polymers. The main candidate in this category is an ionomer that has two side-chain acid groups, a perfluoroimide and a sulfonic acid. Work is also underway to increase the number of acid groups per side chain to three or more by increasing the number of imide groups per side chain. The mechanical support part of the project relies on fibers made by an electrospinning process. These fibers will be made from fluoropolymers, aromatic polymers, or blends. Work at Vanderbilt University will also evaluate electropsun ionomer fibers and dual spun (ionomer with support fibers) membranes. The final membrane developed in this project will combine both new ionomer and nanofiber technology.

Membranes developed under this project are evaluated with both in-cell and out-of-cell testing. Mechanical properties testing are conducted at both 3M and General Motors (GM) laboratories with particular emphases placed on GM's blister test. Accelerated tests are underway to evaluate the mechanical failure mechanism based on a humidity cycle test [1] and chemical stability based on an open-circuit voltage hold test [2]. Fuel cell performance testing is being conducted with single-cell test stations and ultimately the new membrane will be demonstrated in a small stack.

RESULTS

The ionomers under development in this project are shown in Figure 1. The structure in Figure 1a is 3M's PFIA and has a calculated EW of 620 g/mol. This polymer was initially developed under a previous DOE-funded project [3] in small lab quantities (~100g) and will be made in pilot-scale quantities (~1-5 kg) as part of the current project. In the past three quarters preliminary work to establish reaction conditions, efficiency, safety, and quality control has been initiated. It is expected the first pilot-scale reaction will be run in the fourth quarter of this project.

Methods to increase the number of acid groups per side chain to three or more are under development. The structure shown in Figure 1b is an example of an ionene chain extended polymer with two imide groups and one acid group. Small quantities of this polymer have been made in the lab and are under evaluation.

Conductivity milestones have been established for this work of 100 mS/cm at 80°C and 50% RH at the end of the first quarter and 100 mS/cm at 80°C and 40% RH at the end of the fifth quarter. These milestones are shown in Figure 2 along with three lots of PFIA ionomer tested to date. It can be seen that the first milestone is within the 95% confidence

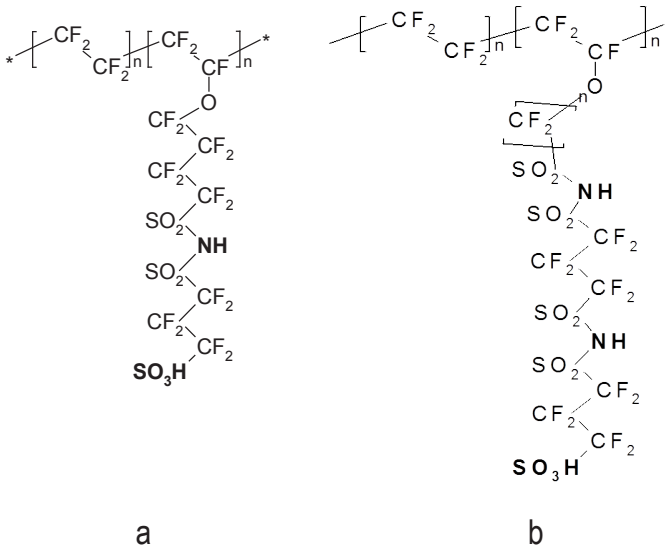

FIGURE 1. Multiacid side chain structures; a) PFIA and b) Perfluoroionene chain extended ionomers.

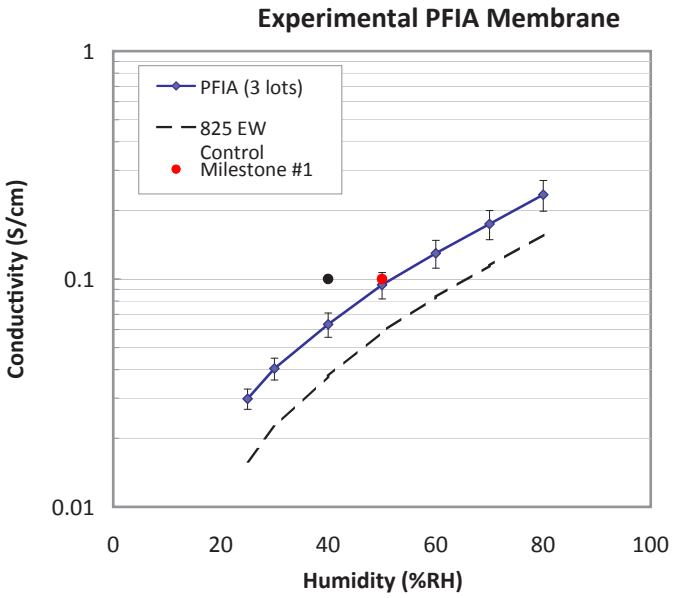

FIGURE 2. Conductivity versus RH for three lots of PFIA membrane with 95% confidence intervals. Standard 825 EW membrane indicted by dashed line. Project milestones indicated with circles.

range of three PFIA lots but the fifth milestone has not yet been met. It is our expectation that the perfluoroinonene chain extended polymers will be able to achieve the conductivity targets set out in milestone number five.

Several new nanofiber materials have been generated under this project. All of the materials have been made using electrospinning process and conventional fluoropolymers, aromatic hydrocarbon polymers, or blends. A key metric is the ability for the support to restrict the swell of the ionomer

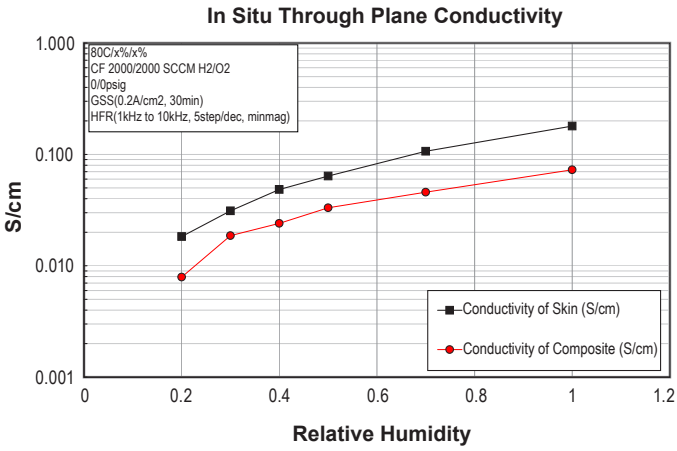

FIGURE 3. Through plane conductivity versus RH measured in-cell with contributions from the center composite layer decoupled from pure ionomer skin layer.

in the x-y plane to less than 5% in each direction. There have been 20 nanofiber samples generated in the first three quarters and the average fiber content required in a composite membrane to meet the 5% swell target is about 20% by volume in the down-web direction and about 35% in the cross-web direction.

A consequence of adding supporting fibers to an ionomer membrane is a reduction in the proton conductivity of the membrane. In order to better understand this impact, methods have been developed to measure the in-cell membrane resistance and to decouple the contribution of the center composite layer from the unsupported skin layers. This approach involves testing a series different thickness supported and unsupported membranes and extrapolating values to zero membrane thickness to obtain the non-membrane related resistance. Figure 3 shows the results of one of these experiments where the center composite layer has about half the conductivity of the pure ionomer. This is an encouraging result since the fiber content is about 50% by volume in this layer. It is expected that stiffer, stronger fibers could be developed that meet the mechanical property requirements at lower total fiber content and therefore, lower resistance loses.

In addition to new support fiber development, Vanderbilt University has developed methods to electrospin 3M ionomers including the PFIA ionomer. Figure 4 shows electron microscope images for one set of experiments. In order to make high quality fibers a spinning aid such as polyethylene oxide needs to be used. The series of images demonstrates the effect of increasing the polyethylene oxide content from 0 to 4 weight percent with 1% being the optimum. These conditions can be used to make dual-spun fiber membranes where the ionomer and a support fiber are spun at the same time resulting in a mixed fiber membrane. The ionomer can then be fused into a continuous phase

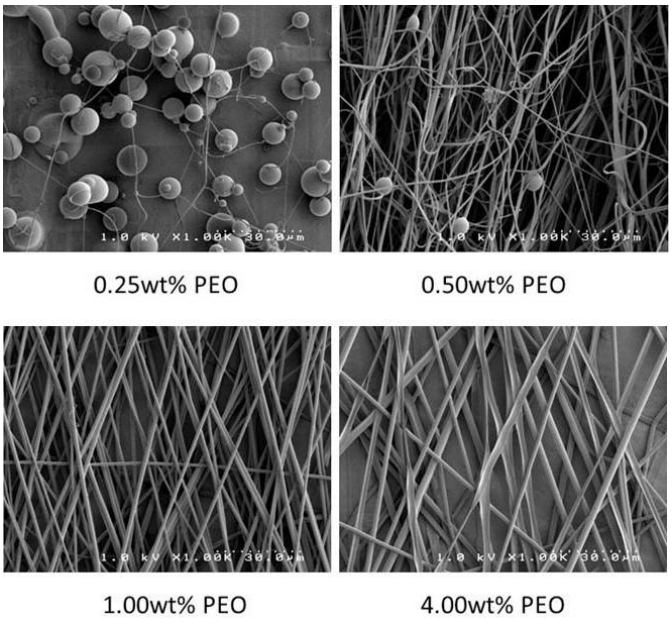

FIGURE 4. Electron microscope images of PFIA electrospinning experiments showing the effect of added polyethylene oxide (contribution from Vanderbilt University).

leaving the fiber support evenly distributed throughout the membrane.

CONCLUSIONS AND FUTURE DIRECTIONS

- 3M's PFIA shows good conductivity at 80°C and 50% RH and meets milestone #1 but falls short of milestone #5 (0.1 S/cm @ 80°C, 40% RH).
- Synthetic routes to ionene chain extended polymers are being developed. These polymers will have three or more acid groups per side chain.
- Fiber contents of about 20-35% by volume are needed to reduce swell in hot water of composite membranes to less than 5%.
- Experiments to decouple the resistance of the fiber composite center layer from the pure ionomer skin have shown that the conductivity is approximately proportional to the ionomer content.
- Work to scale up PFIA ionomer to 1-5 kg batches has been started.
- Membranes will be made in the second year of this project that incorporate PFIA ionomer and new nanofiber technology.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. http://www.hydrogen.energy.gov/pdfs/review14/fc109_yandrasits_2014_o.pdf (M. Yandrasits 2014 Annual Merit Review Proceedings Fuel Cells).

REFERENCES

1. FOA DE-FOA-0000360 Appendix Table D-3: MEA Chemical Stability and Metrics.

2. FOA DE-FOA-0000360 Appendix Table D-4: Membrane Mechanical Cycle and Metrics.

3. http://www.hydrogen.energy.gov/pdfs/progress11/v_c_1_hamrock_2011.pdf). Status represents 3M PFIA membrane (S. Hamrock, U.S. Department of Energy Hydrogen and Fuel Cells Program 2011 Annual Progress Report).