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

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

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Project End Date: September 30, 2016

Overall Objectives

- This project seeks to meet all of the DOE Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration (MYRDD) 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) 2015 Objectives

- Produce a supported membrane based on 3M's MASC polymer technology to meet project milestone 4 targets for durability and performance
- Meet project milestone 5 to demonstrate ionomer proton conductivity at 80°C and 40% relative humidity of 0.1 S/cm using ionomers containing more than two acid groups per side chain
- Produce larger scale quantities (1–5 kg) of perfluoroimide acid (PFIA) ionomer
- Develop new nanofibers and nanofiber supported composite membranes
- Investigate surface treatments for nanofiber supports

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office MYRDD Plan:

(A) Durability

(B) Cost

(C) Performance

Technical Targets

Technical targets for the PFIA-based project milestone 4 membrane are shown in Table 1 along with the comparative data for a perfluorosulfonic acid (PFSA) control. Both membranes contain a nanofiber support material and peroxide stabilizing additives.

FY 2015 Accomplishments

- Go/no-go milestone 4 consisting of both performance and durability targets was met with a 14 micron membrane made with lab-scale PFIA ionomer and experimental nanofibers.
- Perfluoro ionene chain extended (PFICE) ionomers with two, three, or four acid groups per side chain have shown exceptional proton conductivity with PFICE-4 meeting the conductivity target for project milestone 5.
- One pilot-scale run of PFIA ionomer has been completed.
- A simple model based on nanofiber and ionomer properties has been developed that predicts membrane swell after boiling in water.

TABLE 1. Technical Targets for PFIA-Based Membranes

Characteristic	Units	2017 & 2020 Targets	725 EW-S (14 µm)	Project milestone 4 PFIA-S (14 µm)
Maximum oxygen cross-over	mA/cm^2	2	n/a	n/a
Maximum hydrogen cross-over	mA/cm^2	2	1.1	1.4
Area specific proton resistance at:				
120°C, P_{H2O} = 40 kPa	Ohm cm^2	0.02	0.153	0.072
80°C, P_{H2O} = 25 kPa	Ohm cm^2	0.02	0.040	0.027
30°C, P_{H2O} = 4 kPa	Ohm cm^2	0.03	0.028	0.027
-20°C	Ohm cm^2	0.2	n/a	n/a
Minimum electrical resistance	Ohm cm^2	1,000	5,600[a]	5,700[a]
Cost	$\$/m^2$	20	n/a	n/a
Durability				
Mechanical	Cycles with <10 sccm crossover hours	20,000	>20,000	>23,000
Chemical	hr	>500	894	742

[a]Data provided by GM
sccm: standard cubic centimeter per minute
S: Siemens

- Blister test data has shown that experimental nanofibers developed in this project have similar strength properties as expanded polytetrafluoroethylene (ePTFE).
- Surface treatments for nanofiber have been investigated.
- Lab membranes made by electrospinning a support fiber and an ionomer fiber simultaneously followed by pressing ionomer fibers into continuous phase.

INTRODUCTION

Membrane resistance remains a challenge for automotive applications where fuel cells are operated under hot or dry conditions. The focus of this program is to reduce this resistance while maintaining good durability and acceptable cost. Increasing the number of proton charge carriers through increased acid content of the membrane is one way to reduce membrane resistance. Unfortunately membranes based on PFSA polymers become water soluble when the acid content exceeds about 1.4 mmol/g or an equivalent weight (EW) of about 700 g/mol. By using MASC polymers, we are able to increase proton conductivity and lower membrane resistance while retaining a water insoluble polymer. However, membranes made using these polymers typically fall short of durability targets thereby requiring a mechanical support. Electrospun nanofibers offer one way to provide support resulting in durable membranes. It is the goal of this program to develop new ionomers and new nanofiber supports in order to meet all of the DOE targets for resistance, durability, and cost in a single membrane.

APPROACH

The new materials part of this project include both ionomer and nanofiber support development. Ionomers are based on 3M PFSA backbone polymer where the side chain is extended to include one, two, or three imide groups and terminated with the traditional sulfonic acid (Figure 1). 3M's PFIA polymer is the case where n = 1 and the PFICE polymers describe the more general case where n = 1, 2, or 3. For this class of materials, the nitrogen proton is highly acidic and functions as a proton charge carrier while the number of tetrafluoroethylene units in the backbone remain high, preventing the polymer from dissolving in water.

Electrospun nanofiber development is shared between the labs at 3M and Vanderbilt University. Nanofiber materials developed at 3M can be used in a traditional cast

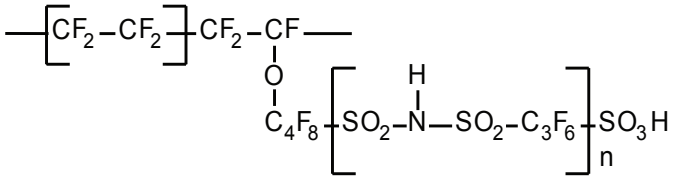

FIGURE 1. Chemical structure for 3M's PFICE polymers. The number of imide containing repeat units is designated by n where the special case of n = 1 is PFIA.

and fill process to make a composite membrane where Vanderbilt is pursuing membrane fabrication methods based on electrospinning both a support fiber and an ionomer fiber. This dual fiber approach allows the ionomer fibers to be pressed into a continuous matrix while leaving the reinforcing support fibers intact. A wide range of fiber distribution throughout the membrane are possible with this method.

Experimental membranes are characterized at Vanderbilt, 3M, and General Motors (GM) with 3M and GM performing most of the fuel cell testing. Final stack testing will be competed in the GM labs.

RESULTS

This last year we successfully passed our project's first go/no-go milestone 4, using lab-made PFIA ionomer and experimental nanofiber support materials. This milestone required that the performance of the new membrane exceed that of a similar thickness state-of-the-art 3M 725 EW-based membrane and pass the chemical (open-circuit voltage) and the mechanical (relative humidity [RH] cycle) accelerated stress tests. Table 1 shows that the durability target has been met and that we have improved upon the resistance values but still fall short of the DOE established targets.

A pilot-scale batch of PFIA was completed this last year in order to supply material for membrane development. This batch was determined to have an equivalent weight of about 660 g/mol by titration and will be used as one of the ionomer options for the next project's go/no-go milestone 8 requiring that all of the DOE targets be meet with a single membrane. See Table 2 for in-plane swell and solubility values.

Laboratory quantities of the PFICE polymer have been made and tested for conductivity, swell, and water solubility. Table 2 shows the expected equivalent weight and the titrated values for a series of polymers made from the same, 700 EW, backbone polymer.

As expected, these polymers had very high swell but were largely insoluble in water. The conductivity of the unsupported membrane, however, was measured to be very high at all humidities, and the PFICE-4 met the project milestone 5 target of 0.1 S/cm^3 at 80°C and 40% RH (Figure 2).

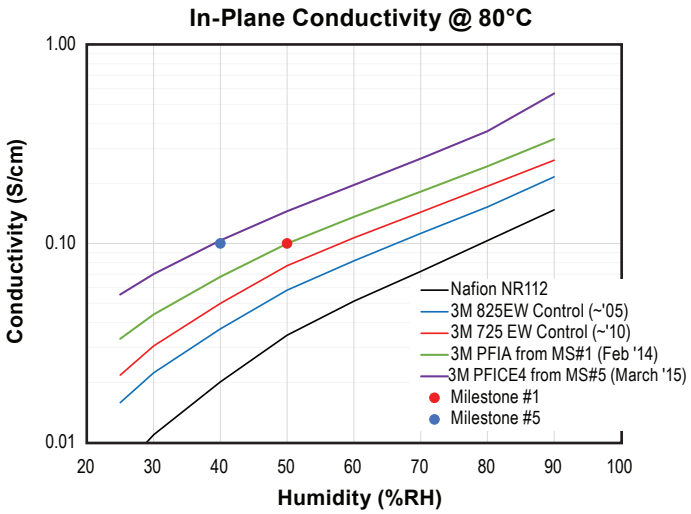

FIGURE 2. In-plane proton conductivity for PFIA and PFICE-4 (4 acid groups per side chain) at 80°C as a function of relative humidity. 3M's 825 and 725 EW membranes along with Nafion® 112 are shown for reference.

Controlling in-plane swell of these membranes is an important function of the nanofiber support material. A method of predicting the swell of a composite membrane (ε_c) was developed based on a rule of mixing approach using the modulus of the supporting nanofiber (E_s), the fiber fraction (f), the modulus of the unsupported swollen ionomer (E_i) and the swell of the ionomer (ε_i).

$$\varepsilon_c = \frac{E_i * (1-f) * \varepsilon_i}{E_i * (1-f) + E_s * f} \quad (1)$$

This analysis was applied to a variety of experimental support materials and an ePTFE support and shown in Figure 3. By plotting swell versus the product of the fiber modulus and fraction, in other words a stiffness factor, we can estimate the swell for new nanofiber candidates at a variety of fiber fractions.

The supports developed under this program have also been evaluated for strength using GM's blister test method [1,2]. A series of membranes were made with a variety of fiber fractions using a fluoropolymer nanofiber (FC1) or a comparative ePTFE support. The normalized pressure

TABLE 2. Swell, Solubility, EW, and Titrated Values for a Series of PFIA-Based Polymers

Ionomer	Starting polymer EW	Number of Imides (n)	Theoretical EW (g/mol)	Titrated EW (g/mol)	In-plane Swell after Boing in Water (%)	Water Solubility (%)
Pilot-Scale PFIA	825	1	560	660	48	4.8
PFICE-2	700	1	501	534	95	9.2
PFICE-3	700	2	431	475	113	10.2
PFICE-4	700	3	397	438	204	14

needed to burst the membrane is plotted versus fiber fraction for two different blister fill rates (Figure 4). In the case of the rapid fill rate (200 s) the burst strength is higher for the more compliant ePFTE but at slower fill rate (2,000 s) there is no difference in strength between the FC1 nanofiber and the ePTFE comparison. It is our belief that the longer fill times are more relevant for predicating membrane durability in a fuel cell.

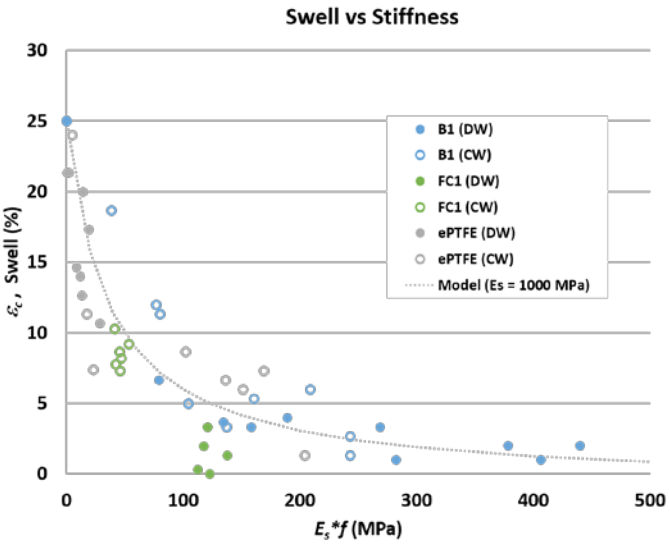

FIGURE 3. Swell versus the product of fiber modulus (*Es*) and fiber fraction (*f*). Symbols represent measured data points and the dotted line represents the values predicted by the rule of mixing model.

Work at Vanderbilt University focused on developing new nanofiber systems, multiple fiber composites, and fibers made from ionomer and inter polymer blends. Also investigated was the used of plasma treating fibers in an effort to improve the fiber-ionomer interface. To date surface treatments have not resulted in improved membrane properties.

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions from FY 2015:

- PFIA-based membranes have very high proton conductivity values. However, the 14 micron supported membrane used in project milestone 4 still does not meet the DOE's targets for area specific resistance.
- Experimental PFICE ionomers have exceptional proton conductivity while remaining largely insoluble in water.
- Characterization of membrane swell and blister strength as a function of fiber and ionomer properties can provide guidance for developing new nanofiber supports and subsequent membranes.

Future work for FY 2016:

- Pilot-scale PFIA ionomer will be used to fabricate membrane for the project's next go/no-go milestone 8. A target thickness of 10 microns has been selected in order to meet the area specific resistance targets set out by the DOE FCTO MYRDD Plan.

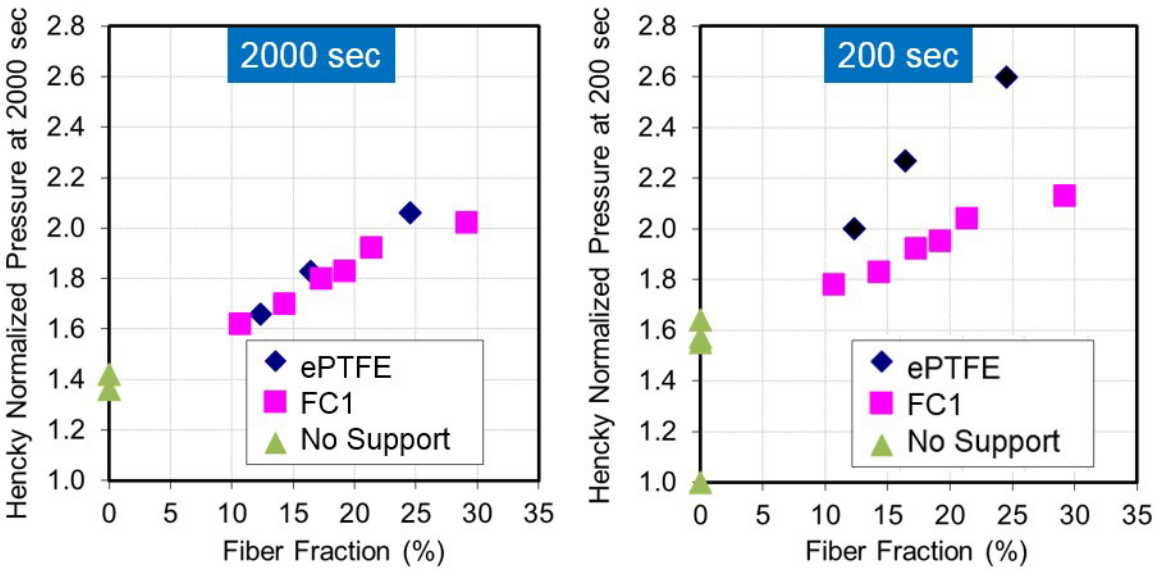

FIGURE 4. Hencky normalized pressure at burst for membranes made with experimental nanofiber supports, FC1 (■), ePTFE (♦) or no support (▲). Data on the right represents fast fill rates (200 seconds) and the graph on the right represents slow fill rates (2,000 seconds).

- Sufficient quantities of the project milestone 8 membrane will be fabricated for single cell durability testing and, ultimately, stack testing at GM.
- Postmortem analysis will begin to better understand degradation mechanisms for the PFIA and PFICE systems.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. USCAR Fuel Cell Tech Team Presentation; "New Fuel Cell Membranes with Improved Durability and Performance," August 13, 2014, Southfield, MI.

2. "V.C.1 New Fuel Cell Membranes with Improved Durability and Performance," 2014 DOE Hydrogen and Fuel Cells Annual Progress Report.

3. "Electrospinning PFSA + PVDF Nanofibers for Fuel Cell Membrane Fabrication," R. Wycisk, J.W. Park, D. Powers, and P.N Pintauro, 226th meeting of the Electrochemical Society, October 8, 2014, Cancun, Mexico.

4. Project Review Meeting with DOE Staff on November 4, 2014, St. Paul, MN.

5. Peter N. Pintauro, Ryszard Wycisk, and Jun Woo Park, "New Membrane Morphologies for PEM Fuel Cells," American Institute of Chemical Engineers Annual Meeting, Atlanta, GA, November 2014 (invited talk).

6. "Engineering a Proton Exchange Membrane for Automotive Fuel Cell Applications," Craig Gittleman, Advances in Polymers for Fuel Cells and Energy Devices Asilomar Conference Grounds Pacific Grove, California, February 8, 2015.

7. M. Yandrasits, "New Fuel Cell Membranes with Improved Durability and Performance," FC109 at DOE's Annual Merit Review in Washington, DC, on June 9, 2015 http://www.hydrogen.energy.gov/annual_review15_fuelcells.html#membranes.

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1. Li, Y., Grohs, J., Pestrak, M.T., Dillard, D.A., Case, S.W., Ellis, M.W., Lai, Y.H., Gittleman, C.S., and Miller, D.P., "Fatigue and Creep to Leaking Tests of Proton Exchange Membrane Using Pressure-Loaded Blisters," *J. Power Sources,* Vol 194, pp. 873–879, 2009.

2. Dillard, D.A., Li, Y., Grohs, J., Case, S.W., Ellis, M.W., Lai, Y.H., Budinski, M.K., and Gittleman, C.S., "On the Use of Pressure-Loaded Blister Tests to Characterize the Strength and Durability of Proton Exchange Membranes." *Journal of Fuel Cell Science and Technology*, Vol 6 (3), pp. 031014-1 – 031014-8, 2009.