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

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Subcontractors:

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- Peter Pintauro, Vanderbilt University, Nashville, TN

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Project End Date: December 31, 2016

Overall Objectives

- Meet all of the Department of Energy (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 (MEAs) and evaluated in single fuel cells and finally fuel cell stacks.

Fiscal Year (FY) 2016 Objectives

- Produce enough perfluoroimide acid (PFIA) ionomer at pilot scale to fabricate membranes for Milestones 7 and 8.
- Optimize peroxide scavenging additive type and amount for PFIA-based membranes to maximize durability in the open circuit voltage (OCV) accelerated stress test.
- Produce membrane comprising a MASC ionomer, a nanofiber support, and a stabilizing additive which meets all of the 2020 membrane milestones in Table 3.4.12 (Technical Targets: Membranes for Transportation Applications) in the DOE FCTO MYRDD Plan, Section 3.4, update July 2013. This represents project go/no-go Milestone 8.
- Develop a process for producing the membrane described in Milestone Q8 in quantities large enough to produce membranes for use in Milestone Q10 (at least 20 linear meters)
- Manufacture for stack testing at least 30 MEAs with a minimum cell area of 250 cm^2. Evaluate in fuel cells and ex situ tests. Begin stack testing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the FCTO MYRDD Plan.

(A) Durability

(B) Cost

(C) Performance

Technical Targets

The DOE 2020 technical targets for the membrane are shown in Table 1 along with the data for the membrane developed in this program (Milestone 8). This membrane consists of ionomer and nanofiber developed in this project and optimized peroxide stabilizing additives.

FY 2016 Accomplishments

- Pilot scale quantities of PFIA ionomer were produced for membrane development.
- Peroxide scavenging additive levels were optimized for membranes developed in this project.
- Go/no-go project Milestone 8 was met for all DOE 2020 targets except area specific resistance (ASR) at 120°C and 40 kPa water vapor pressure.
- Suitable quantities of membrane have been fabricated for stack testing.
- Stack testing initiated at GM.

TABLE 1. Fuel Cell Membrane Targets from DOE FCTO MYRDD Plan and Results for Project Milestone 8 Membrane

Characteristic	Units	2017 & 2020 Targets	MS#8 PFIA-S (10 µm)
Maximum oxygen cross-over	mA/cm^2	2	0.6[a], 3.5[b]
Maximum hydrogen cross-over	mA/cm^2	2	1.9[c]
Area specific proton resistance at:			
120°C, P_{H2O} 40 kPa	Ohm cm^2	0.02	0.054
120°C P_{H2O} 80 kPa	Ohm cm^2	0.02	0.019
80°C P_{H2O} 25 kPa	Ohm cm^2	0.02	0.020
80°C P_{H2O} 45 kPa	Ohm cm^2	0.02	0.008
30°C P_{H2O} up to 4 kPa	Ohm cm^2	0.03	0.018
-20°C	Ohm cm^2	0.2	0.2[d]
Minimum electrical resistance	Ohm cm^2	1,000	1,635[e]
Cost	$\$/m^2$	20	Not available
Durability			
Mechanical	Cycles with <10 sccm crossover	20,000	>24,000
Chemical	Hrs	>500	614

a. O_2 crossover based on DOE Table 3.4.12 indicating measurement at 0.5 V
b. Calculated from GM O_2 permeability data at 80°C, 100% relative humidity (RH), 1 atm.
c. In cell measurements at 3M 70°C, 100% RH, 1 atm.
d. Calculated from in-plan data
e. Data provided by GM
sccm – standard cubic centimeters per minute; MS - Milestone

- Electrospinning nanofiber ionomer and support fibers has led to unique membrane constructions for evaluation.

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INTRODUCTION

Fuel cell membranes with low resistance are highly desirable in order to maximize system power and efficiency. This objective is especially difficult under low humidity conditions, where the proton resistance of the membrane is the highest. Increasing the number of charge carriers and decreasing the thickness can both be effective in reducing resistance, however, they can compromise the membrane durability if not designed properly. Proton conductivity can be increased by simply adding charge carriers, such as sulfonic acid groups, to a polymer backbone, however, it will ultimately become a water soluble polymer and not be effective as a membrane. Likewise, reducing the thickness of a membrane can result in poor durability in both accelerated testing and actual use conditions. Because of these reasons, a membrane is needed that has increased conductivity, is water insoluble, and is stable to chemical and mechanical degradation. This project aims to develop a new membrane based on a perfluorinated ion conducting polymer and nanofiber support that is able to meet the DOE targets for membrane performance, durability, and cost.

APPROACH

The approach for this project is to develop a new ionomer based on a perfluorinated polymer that contains MASC in order to provide improved conductivity at dry conditions. This strategy has the advantage of creating a polymer with a large number of charge carriers, high ion exchange capacity, while maintaining a polytetrafluoroethylene backbone that prevents the polymer from dissolving in water. Both perfluorosulfonic acid (PFSA) and perfluoro bis(sulfonyl) imides are strong acids and have excellent conductivity characteristics. The bis(sulfonyl)imide functionality also serves as a chain extender, allowing for multiple acid groups per side chain. When the side chain contains one imide and one sulfonic acid group it is designated a PFIA ionomer (Figure 1). In the case where multiple imides are used per side chain, the ionomer is considered perfluoro ionene chain extended (PFICE). In combination with the new ionomer, mechanical support will be provided by electrospun nanofibers. Work at both 3M and Vanderbilt University will determine an optimum architecture for the fiber supported membrane based on filling an existing nanofiber mat with ionomer (3M) or spinning both ionomer fibers and support fiber simultaneously followed by consolidating the ionomer fibers into a continuous matrix (Vanderbilt).

Membranes developed in this project are evaluated against the DOE 2020 targets using a variety methods with the ultimate program objective of demonstrating 2,000 h of durability in a small stack, tested at GM. Additional information regarding the failure modes and insight into improved durability will be obtained by post-mortem analysis at the end of this test.

RESULTS

This year we successfully passed the second project go/no-go milestone (#8) to meet all of the DOE 2020 targets for membrane performance, durability, and cost simultaneously with one membrane. The membrane designed for this

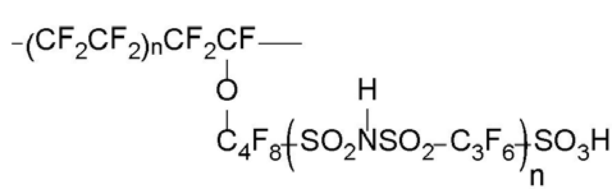


FIGURE 1. Ionomer with bis(sulfonyl)imide and sulfonic acid side chain. The ionomer is designated PFIA when n = 1 and PFICE when n > 1.

milestone was produced using a pilot scale PFIA ionomer with an equivalent weight of 650 g/mol and electrospun fluoropolymer (FC1) nanofiber support. The details of the Milestone 8 membrane construction are shown in Table 2 along with a PFSA-based control and Milestones 4 and 7 membranes for comparison. The specific results for the Milestone 8 membrane, for each target, are shown in Table 1. This membrane has met most of the DOE targets with the exception of area specific resistance at 120°C and low humidity and, depending on test conditions, the oxygen cross over target.

TABLE 2. Membrane Construction for Membranes Developed in this Project and Control

Milestone	Ionomer	Fiber Type	Additive	Fiber (vol%)	Thickness (µm)
Control	3M 725 EW	B1	Type A	20.6	14
#4	PFIA – Lab	FC1	Type A	17.2	14
#7	PFIA – Lot #1	FC1	Type A	17.3	14
#8	PFIA – Lot #1	FC1	Type A	18.0	10

EW – Equivalent weight

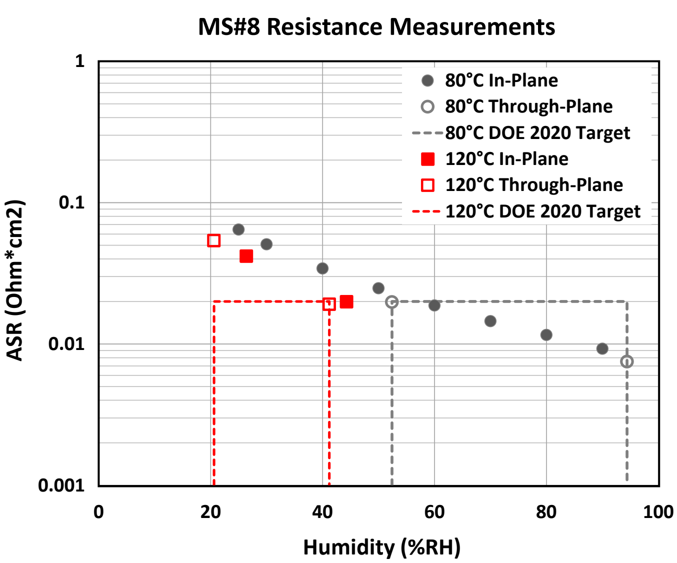
In order to assess the potential for the MASC approach to meet the most aggressive resistance target, we plotted both the through-plan and in-plane resistance for the Milestone 8 membrane versus relative humidity at 80°C and 120°C (Figure 2). Clearly the data falls within the DOE target range for the 80°C data but only at the highest humidity for the 120°C data. Analysis of this data suggests that, in order for a 10-micron membrane with typical levels of peroxide scavenging additives and supporting fiber content to meet the 120° resistance targets at all specified humidities, an ionomer with an equivalent weight of about 450 g/mol would be needed. This value is not achievable with the PFIA system and would require further development of the PFICE ionomers with between three and four acidic groups per side chain.

Despite the difficulty in meeting the most aggressive resistance target, the membrane developed in this project have demonstrated significant improvements in fuel cell performance, especially under low humidity conditions. Figure 3 shows typical performance for the Milestone 8 membrane when measured at 1.5 A/cm^2, as a function of inlet gas relative humidity. The cell voltage is over 100 mV higher at the lowest humidity when compared to the traditional PFSA-based membrane.

In addition to performance testing, durability is measured under the OCV accelerated stress test. The membranes developed under this program have routinely exceed the 500-hour target when fabricated with peroxide scavenging additives similar to those used in PFSA-based membranes. However, an unusual decrease in OCV has been observed in the first 200 h of testing for the PFIA-based membranes (Figure 4). Diagnostic testing has shown that this decrease is not due to hydrogen cross over or shorting, and the origin of this behavior is under investigation.

Larger quantities of the Milestone 8 and similar membranes were fabricated with different levels of peroxide scavenging additives. These membranes were assembled into MEAs for stack testing by GM.

Electrospinning developments at Vanderbilt University have shown that a variety of novel constructions are possible



RH – Relative humidity

FIGURE 2. Area specific resistance vs. relative humidity measured through-plane (open symbols) or calculated from in-plane conductivity (filled symbols) for Milestone 8 membrane measured at 80°C and 120°C. DOE targets are shown in dashed lines.

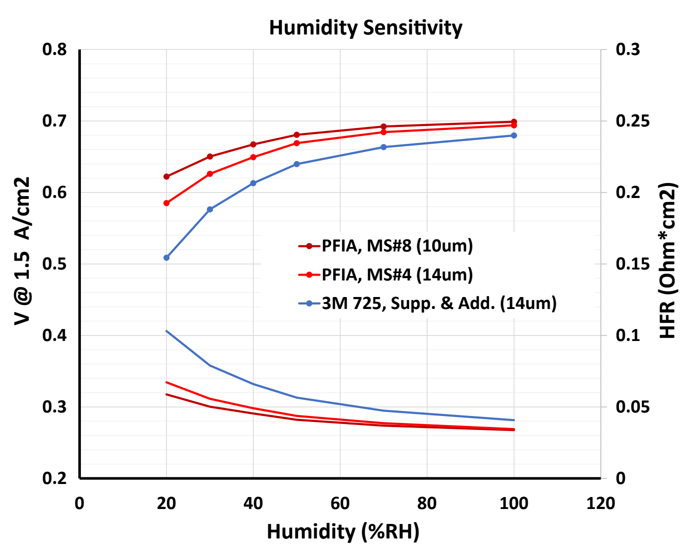


FIGURE 3. Voltage and high frequency resistance (HFR) for Milestone 4 and 8 membranes, as a function of humidity at 1.5 A/cm^2.

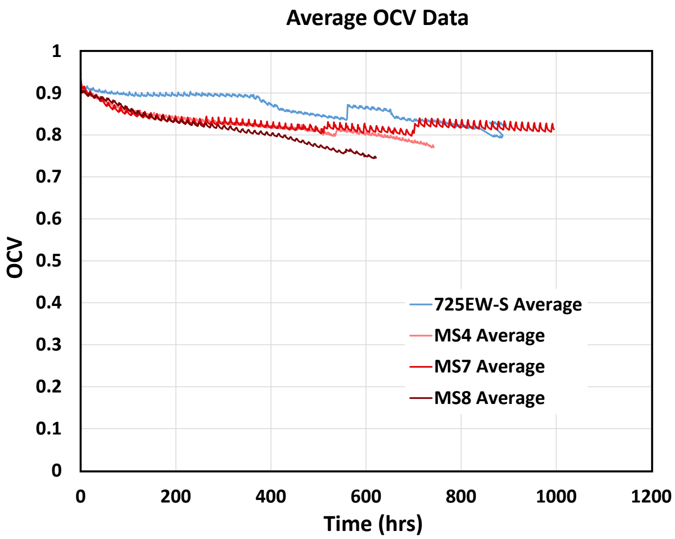


FIGURE 4. Average OCV vs. time for three PFIA-based membranes (MS4, MS7, and MS8) compared to a PFSA control (725 EW-S).

for distributing a mechanical support polymer within an ion conducting matrix.

CONCLUSIONS AND FUTURE DIRECTIONS

- Nearly all of the DOE 2020 targets for membrane performance and durability have been met with one membrane based on a pilot scale PFIA ionomer and electrospun nanofiber support.
- Peroxide scavenging additive levels were optimized for this membrane, based on the OCV accelerated stress test.
- Over 30 m of membrane were produced for use in stack testing at GM.
- Analysis of the resistance targets at 120°C and 40 kPa water vapor pressure suggests an ionomer with equivalent weight of 450 g/mol or less is necessary to meet this target with a 10-micron supported membrane.
- Accelerated OCV stress tests show a reduction in voltage within the first 200 h. The origin of this loss will be further investigated.
- Stack testing has been initiated at GM with a target run time of 2,000 h.
- Post mortem analysis is planned for MEAs run in the stack to better understand failure modes for membranes developed under this project.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. FC109 at DOE's Annual Merit Review in Washington, D.C. on June 9, 2015.

2. USCAR Fuel Cell Tech Team Presentation; "New Fuel Cell Membranes with Improved Durability and Performance," October 7, 2015, Southfield, MI.

3. "V.C.1 New Fuel Cell Membranes with Improved Durability and Performance," 2015 DOE Hydrogen and Fuel Cells Annual Progress Report.

4. D.M. Peppin, M.A. Yandrasits, A.S. Fochs, "Resistance Measurements for Multilayer Supported Membranes," Fall ECS meeting Phoenix, AZ, October 2015.

5. D.M. Peppin, M.A. Yandrasits, A.S. Fochs, "Resistance Measurements for Multilayer Supported Membranes," ECS Transactions, 69 (17) 1105–1110 (2015).

6. Leslie Dos Santos, Jun Woo Park, Ryszard Wycisk, Peter N. Pintauro, Graeme Nawn, Keti Vezzù, Enrico Negro, Federico Bertasi, Vito Di Noto, "Membranes from Blended Ionomer/PVDF Nanofibers: 1. PFSA/PVDF and PFIA/PVDF Fiber Spinning and Membrane Fabrication," Fall ECS meeting Phoenix AZ, October 2015.