

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

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Subcontractors:

- General Motors (GM) Fuel Cell Activities, Pontiac, MI, Craig Gittleman
- Vanderbilt University, Nashville, TN, Peter Pintauro

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Project End Date: September 30, 2017

Overall Objectives

- All of the DOE Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan membrane performance, durability, and cost targets will be met 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 the current state of the art.
- Experimental membranes will be integrated into membrane electrode assemblies (MEAs) and evaluated in single fuel cells and finally in fuel cell stacks.

Fiscal Year (FY) 2017 Objectives

- Begin stack test at General Motors, demonstrate 2,000 h durability with membranes developed in this project.
- Postmortem analysis on MEA cells from stack test.
- Investigate origin of performance decay observed in the open circuit voltage (OCV) accelerated stress test.

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

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

FY 2017 Accomplishments

- Stack testing completed at General Motors. Testing terminated at about 800 h due to several cell failures.
- Postmortem analysis of cells from stack test were completed at GM. Cross section images on failed membranes showed membrane degradation and debris in some locations.
- Degradation mechanism for perfluoroimide acid (PFIA) ionomer investigated at 3M using multi-layer membrane technique.



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

TABLE 1. Fuel Cell Membrane Targets from DOE Fuel Cell Technologies Office 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	h	>500	614

^aO₂ crossover based on DOE Table 3.4.12 indicating measurement at 0.5 V

^bCalculated from GM O₂ permeability data at 80°C, 100% relative humidity (RH), 1 atm.

^cIn cell measurements at 3M 70°C, 100% RH, 1 atm.

^dCalculated from in-plane data

^eData provided by GM

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 can 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, in other words high ion exchange capacity, while maintaining a polytetrafluoroethylene backbone that prevents the polymer from dissolving in water. Both perfluoro sulfonic acid 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 (Figure 1). When the side chain contains one imide and one sulfonic acid group it is designated as a PFIA ionomer. In the case where multiple imides are used per side chain, the ionomer is considered perfluoro ionene chain extended.

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

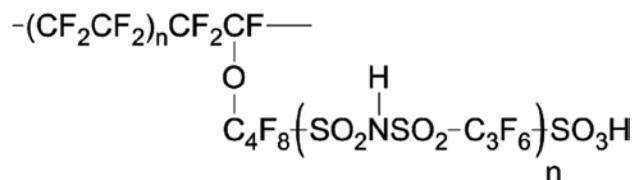


FIGURE 1. Structure for perfluoro ionene chain extended ionomers. Where n=1 the ionomer is designated PFIA.

(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 postmortem analysis at the end of this test.

RESULTS

Throughout the course of this project we have demonstrated exceptional membrane performance and durability in accelerated stress tests as shown in Table 1. In almost all cases we have been able to meet the DOE 2020 targets for automotive membranes. This year, as a

final demonstration, we initiated a stack test at GM using experimental membranes developed in this project. This stack test represents the first long term performance test that was run under non-accelerated conditions such as OCV hold or humidity cycling. Unfortunately, the experimental samples did not meet the 2,000 h target and the test was terminated at about 800 h. Failed MEAs were cross sectioned as part of the postmortem analysis. Regions of thin and missing membrane were observed in areas where leaks were detected. Images from other areas of the MEA show cracks in the membrane layer on the anode side that were arrested by the nanofiber support material. An unexpected level of debris was also observed in many of the images. Complete understanding of the origins of the premature stack failure are currently under investigation.

Accelerated stress testing such as the OCV hold has been used throughout this project as a means of comparing the stability of new membranes to those of established controls. While membranes made with the PFIA ionomer have routinely exceeded the 500 h DOE target, these samples exhibit two new behaviors. Figure 2 shows representative OCV hold data for membranes made with PFIA ionomer and a perfluorosulfonic acid (PFSA) control. Early in the test, the PFIA membrane shows a decay in the OCV potential in the first 200 h. In addition, the membrane resistance increases over the time of the test. The role of chemical stability is under investigation as a potential cause of these observations.

To better understand the chemical stability of the PFIA ionomer, we devised an experiment using three layers of membrane where, at the end of an OCV test, the center layer could be removed from the catalyst containing outer layers and analyzed for conductivity and chemical composition. Several MEAs were run in this configuration and large pieces of the center membrane were removed and analyzed. The conductivity of the PFIA membrane was lower than that for the membrane at the beginning of life (data not shown) where the traditional PFSA-based membrane showed little to no change. In addition, ^{19}F nuclear magnetic resonance (NMR) was run on the aged PFIA membrane and showed the appearance of a sulfonamide functionality during the OCV test. Figure 3 shows the ^{19}F NMR curves for the PFIA sample prior to testing (top), a sample with a known sulfonamide content of 10% (center) and the PFIA membrane after OCV testing (bottom). The aged membrane clearly shows the appearance of the sulfonamide functionality and the sulfonic acid associated with the PFSA side chain. The appearance of the sulfonic acid may be a result of decomposition or simply transfer of PFSA from the outer membrane layers, however, the amide functionality suggests the degradation of the PFIA side chain follows a somewhat more complicated pathway than that of the simpler PFSA ionomer.

A complete understanding of the degradation mechanism and kinetics is not known at this time; however, it appears as if the oxidative degradation of the PFIA polymer may

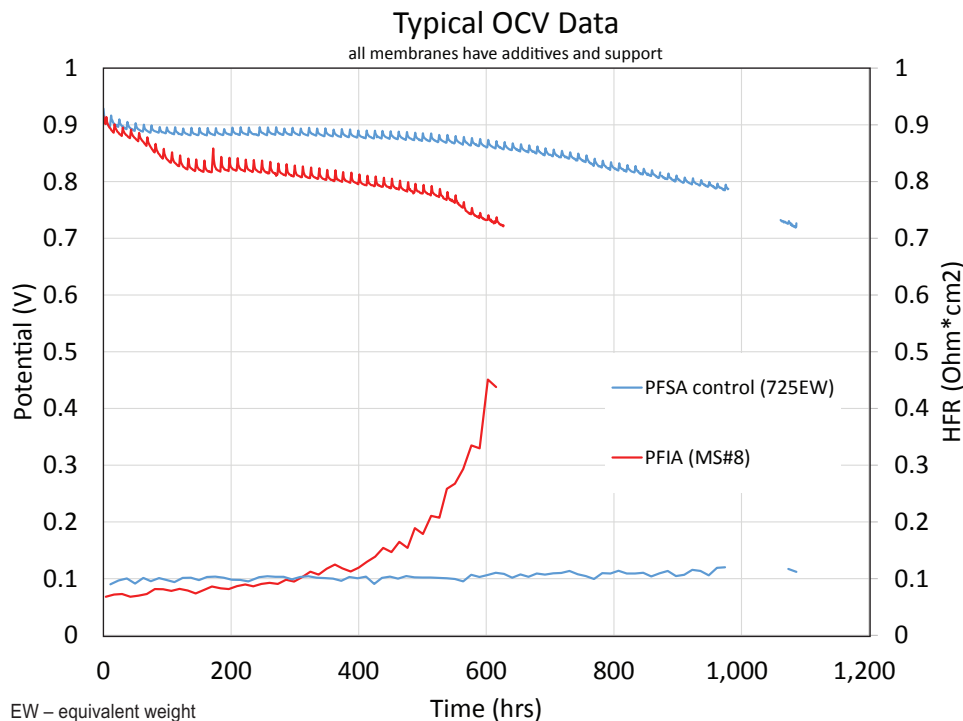


FIGURE 2. Representative accelerated stress testing at OCV. Cell potential and high frequency resistance (HFR) as shown for membranes made using a traditional PFSA ionomer (blue data) and PFIA ionomer (red data).

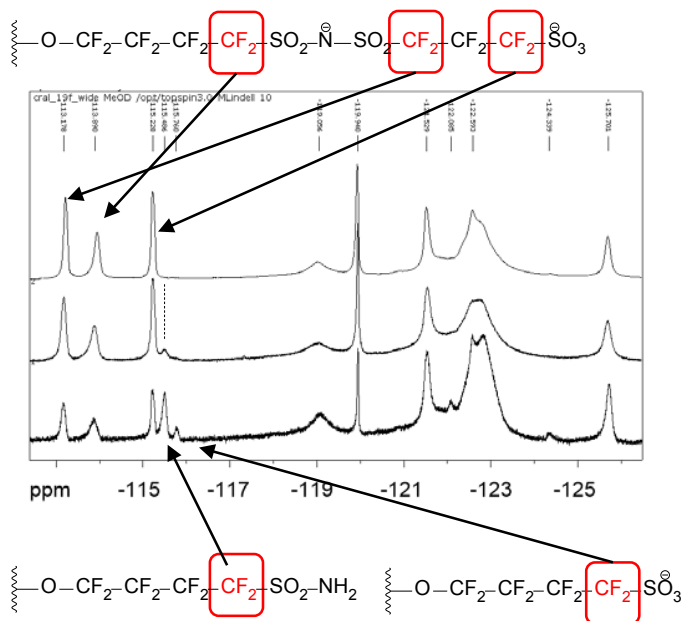


FIGURE 3. ¹⁹F NMR spectra with associated peak assignments for a new PFIA ionomer (top), a sample with known sulfonamide content (center), and a PFIA based membrane after OCV testing (bottom).

be similar to that of the more well-known PFSA systems [1]. The key difference between these two ionomers is the number of protoengic groups on the side chain. In the case of PFSA ionomers, oxidative attack on the sulfonic acid result in degradation of the sidechain and, ultimately, backbone cleavage. In the PFIA case attack at the terminal sulfonic acid or the sulfonamide group may result in the degradation of the side chain resulting in a sulfonamide structure. Or, attack at the sulfonimide may also result in the degradation of the

side chain leading to backbone chain cleavage and fragments of the side chain. While the specifics are not known, the possible decomposition pathways for the PFIA structure are shown in Figure 4. At this time, there is no evidence that the imide linkage is more subject to degradation than the sulfonic acid group, however, it appears that the consequences of this degradation may be different.

The benefits of the MASC approach with a nanofiber mechanical support and peroxide scavenging additives have been demonstrated throughout the course of this project. Understanding the degradation consequences of these new ionomers and membranes will be the remaining focus of the project.

CONCLUSIONS AND UPCOMING ACTIVITIES

- Membrane based on 3M’s PFIA ionomer and nanofiber support materials have meet nearly all the DOE 2020 targets for performance and accelerated durability.
- Stack testing at GM was terminated after 800 h of run time on four experimental membranes developed in this project.
- Conductivity and ¹⁹F NMR data shows that the PFIA degradation results in new functional groups.
- Additional investigation into PFIA stability is planned through the use of model compounds.
- Rotating disk electrode studies are planned to study the effect of ionomer decomposition products on catalyst activity.

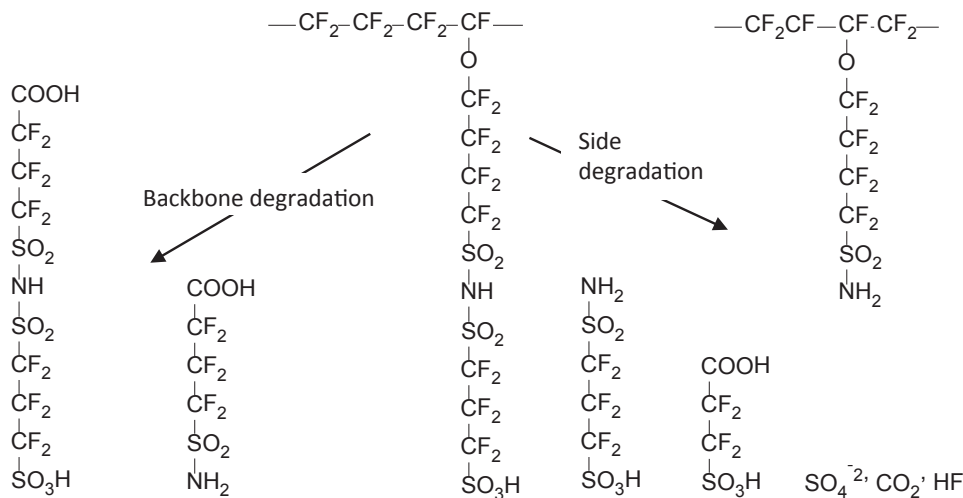


FIGURE 4. Possible degradation pathways and associated fragments for a PFIA ionomer.

FY 2017 PUBLICATIONS/PRESENTATIONS

- 1.** FC109 at DOE's Annual Merit Review in Washington, D.C., on June 8, 2017.
- 2.** USCAR Fuel Cell Tech Team Presentation, "New Fuel Cell Membranes with Improved Durability and Performance," November 16, 2016, Southfield, MI.
- 3.** "V.C.1 New Fuel Cell Membranes with Improved Durability and Performance," 2016 DOE Hydrogen and Fuel Cells Annual Progress Report.
- 4.** M. Yandrasits, M. Lindell, M. Kurkowski, M. Schaberg, "Ultra-Low EW Ionomers and Membranes for Fuel Cells," PRiME 2016, Fall ECS Conference, Honolulu, HI, October 5, 2016.
- 5.** M. Yandrasits, "Perfluoro Imide Acid (PFIA) Ionomers for Fuel Cell Membranes," Gordon Research Conference Stonehill College, Easton, MA, August 8, 2016.
- 6.** M. Yandrasits, M. Lindell, M. Kurkowski, M. Schaberg, "Increasing Fuel Cell Efficiency by Using Ultra-Low Equivalent Weight Ionomers," The Electrochemical Society Interface, Spring 2017.