

V.D.3 Dimensionally Stable Membranes (DSMs)

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Research Foundation of the State of New York – ESF,
State University of New York (SUNY), Syracuse, NY

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Project End Date: April 3, 2011

Objectives

- Determine the effect of pore size and substrate thickness on conductivity and water uptake.
- Demonstrate polymerization conditions suitable for bulk polymerization of perfluorinated sulfonic acids (PFSA's).
- Demonstrate, by the 3rd quarter 2007, membrane conductivity of 0.07 S/cm, at 80% relative humidity, at room temperature (RH), and using non-Nafion[®] materials. Samples will be prepared and delivered to the Topic 2 Awardee.
- Go/No-Go Decision: Demonstrate, by the 3rd quarter, membrane conductivity >0.1 S/cm, at 25% RH at 120°C, using non-Nafion[®] materials. Samples will be prepared and delivered to the Topic 2 Awardee.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Durability
- Cost
- Performance

Technical Targets

Progress has been made in achieving the DOE 2010 Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan. Table 1 lists the DOE's technical targets and where our research stands to date. There are two other DOE targets for membranes relating to durability, which we have not yet addressed.

TABLE 1. DOE Technical Targets and GES Status

| Characteristic | Unit | 2010 Target | GES DSM Status |
|--|---------------------|-------------|--------------------|
| Inlet Water Vapor Partial Pressure | kPa | 1.5 | 20 ^a |
| Oxygen Crossover | mA/cm ² | 2 | 1.5 ^b |
| Hydrogen Crossover | mA/cm ² | 2 | 1.8 ^b |
| Membrane Conductivity | S/cm | | |
| Operating Temperature | | 0.10 | 0.093 ^a |
| 20°C | | 0.07 | 0.083 |
| -20°C | | 0.01 | Not tested |
| Operating Temperature | °C | ≤120°C | 95°C |
| Area Resistance | Ohm*cm ² | 0.02 | 0.03 ^c |
| Cost | \$/m ² | 20 | ~\$100 |
| Durability with Cycling <80°C | hours | 5,000 | 10,000 Cycles |
| Unassisted Start from Low Temperature | °C | -40 | Untested |
| Thermal Cyclability in Presence of Condensed Water | | Yes | Yes |

^a95°C with H₂/air at 20 psia balanced pressure. H₂/air Stoichiometry 1.1/2.0.

^bCrossover measured for 1 atm of pure H₂ and pure O₂ at 95°C and 50% RH.

^cFor 18 μm two-dimensional laser-drilled (2DSM) material operating at conditions listed above in ^(a).

Accomplishments

- Successfully demonstrated that DSMs based on laser drilling pores restrain x-y swelling (<5%) with a wide range of pore size and thickness and substrate materials.
- Effective methods of generating new PFSA polymers have been generated. These have been generated via bulk polymerizations which will allow for the direct formation of the composite membrane.
- Short-term (DOE 2008 High Temperature Membrane) conductivity targets have been met for room temperature conductivity, promising results confirmed by independent lab (Bekkttech) using a 2DSM support material, resulting in passing the

- go/no-go project decision point and continuation of the project:
 - 0.0852 S/cm at 30°C and 80% RH vs. goal of 0.07.
 - 0.031 S/cm at 25% RH and 120°C is below DOE target, but getting closer.
 - 0.093 S/cm achieved at 120°C and 50% RH close to DOE upper target for RH.
- New PFSA material generated at SUNY and incorporated in three-dimensional support material (3DSM).
 - Demonstrates 0.08 S/cm conductivity at 30% RH, approaching DOE ultimate target of 0.10 S/cm at 25% RH.
 - DOE conductivity targets met with 3DSM and homopolymer; GES results significantly higher than Bekktech.
- Demonstrated improved fuel cell performance at 95°C and 25% RH 7 psig H₂/air (0.68 V at 500 mA/cm²).
- Both commercially available polyether sulfone (PES) and ultra-high molecular weight polyethylene (UPE) successfully incorporated as porous supports in 3DSM:
 - Swelling reduction similar to 2DSM.
 - Conductivity penalty of support ~33%.
- Increased mechanical durability with 2DSM and 3DSM, demonstrated through RH cycling (10,000 cycles, 2 min bone-dry, 2 min 95°C dew point).
- Collaborating with Millipore for thinner 3DSM support samples.



Introduction

PFSA materials have demonstrated promising high temperature/low RH conductivity, yet are still unsuitable for automotive applications. Increasing acid content and making the membranes thinner are two methods for lowering the resistance of these materials. However, each of these methods has a negative impact on mechanical durability of the membrane. GES is trying to combine the good conductivity properties of high acid content PFSA and improve their mechanical properties by making composite materials.

Approach

GES's approach is to use very high acid content PFSA materials and support them with high-strength non-acidic materials. This involves using commercially available PFSA materials as well as generating new

PFSA polymers, generating the supports, and finally forming and characterizing the composites.

Results

GES has successfully imbedded high acid content PFSA materials in laser-drilled supports consisting of either polysulfone or polyimide (Kapton®). Figure 1 shows the laser-drilled support, as well as the composite DSM. A matrix of support material, pore size, support thickness and equivalent weight (EW) of PFSA fill has been completed. When the supports are 10% of the total material and have no greater than 60% void space, they nearly eliminate swelling in the x-y direction. This is true regardless of hole size, acid content of the PFSA fill material, or whether polysulfone or polyimide was used as the support. Fuel cell testing has been carried out on a 2-mil DSM membrane consisting of a 1/3-mil polyimide support filled with 700 EW PFSA and the 2DSM far outperforms Nafion® 112 performance.

A sample composite material with low EW PFSA and 10% support material has demonstrated 2-3x the conductivity of Nafion® 112, the PFSA standard, over the entire range of relative humidity as shown in Figure 2. This conductivity still falls short of the DOE target however, as seen in the figure. Previously it appeared that this approach would not be able to reach the DOE's cost target, however in a separate DOE contract GES has demonstrated a successful method of micro-molding these substrates.

Commercially available porous supports offered an alternative to the cost-prohibitive 2DSM supports: an unforeseen development from the original proposal but very promising as the 3DSMs demonstrated the dimensional stability and improved mechanical properties of the 2DSM. We successfully incorporated both 1,100 EW and 830 EW PFSA ionomers into commercially available PES and UPE and tested the membranes under electrolysis conditions. Figure 3 compares the electrolysis performance of a 3-mil 3DSM prepared with 830EW ionomer and UPE support to that of an 1,100 EW electrolysis membrane electrode assembly with comparable thickness. Electrolysis

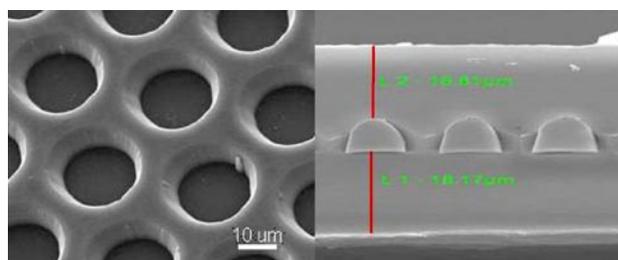


FIGURE 1. Scanning electron microscope images of laser-drilled DSM support (left) and support filled with PFSA (right).

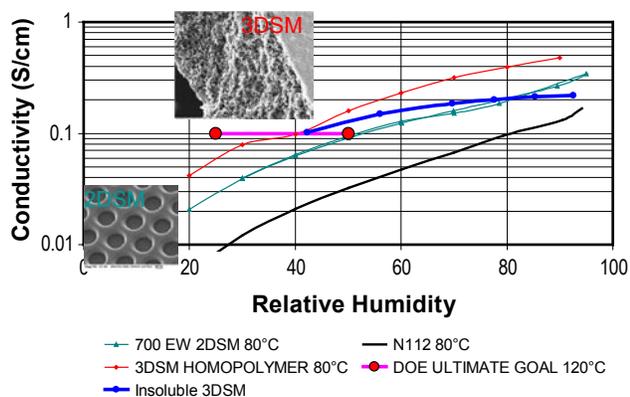


FIGURE 2. Conductivity of 2DSM membrane consisting of 700 EW PFSA in a polyimide support as well as two 3DSMs: one with the SUNY homopolymer at 80°C and a second with highly cross-linked PVEPVE. Insets of the 2DSM and 3DSM membranes are shown.

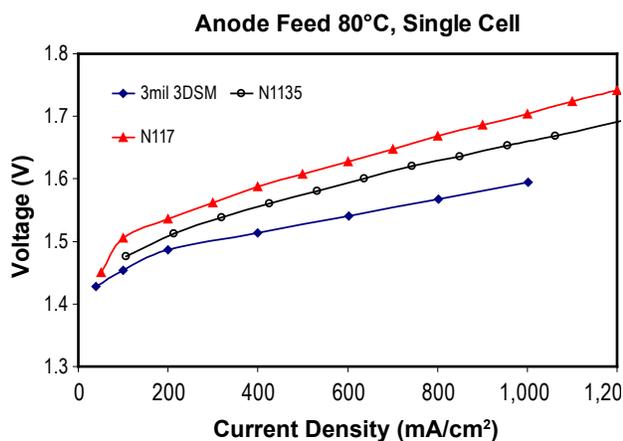


FIGURE 3. Electrolyzer performance of N1135, N117 and a 3-mil-thick UPE 3DSM membrane with 820 EW.

conditions were used as the poor membrane-electrode interface in fuel cell membranes contributes to the overall resistance and thereby decreases fuel cell performance. Electrolyzer testing allows us to test the membranes in an electrochemical cell and determine the performance penalty due to the support, even with a thick membrane. The thinnest PES porous support commercially available is 4 mils thick. We are currently working with Millipore on thinner supports, and they have supplied us with 1- and 2-mil-thick UPE. We have successfully incorporated low EW PFSA ionomers into these thinner supports and tested through plane conductivity, shown in Table 2. As seen in the table we are now able to generate very thin membranes without a large conductivity penalty. For example the 0.7 μm UPE membrane has a final thickness of 0.4 mil with only a 20% conductivity penalty compared to neat 1,100 EW PFSA.

TABLE 2. Through-Plane Conductivities of Differently Prepared Samples

| Material/ Pore Size | Ionomer | Starting Thickness (mils) | Final Thickness (mils) | Through-Plane Conductivity (S/cm) |
|------------------------|----------|---------------------------------|------------------------------|---|
| Nafion® 111 | 1,100 EW | 1 | 1 | 0.05 |
| 0.45 μm UPE | 1,100 EW | 2 | 2.1 | 0.023 |
| 0.7 μm UPE | 1,100 EW | 1 | 0.4 | 0.040 |
| 0.7 μm UPE | 850 EW | 1 | 1.5 | 0.045 |
| 0.7 μm UPE | 700 EW | 1 | 0.6 | 0.018 |

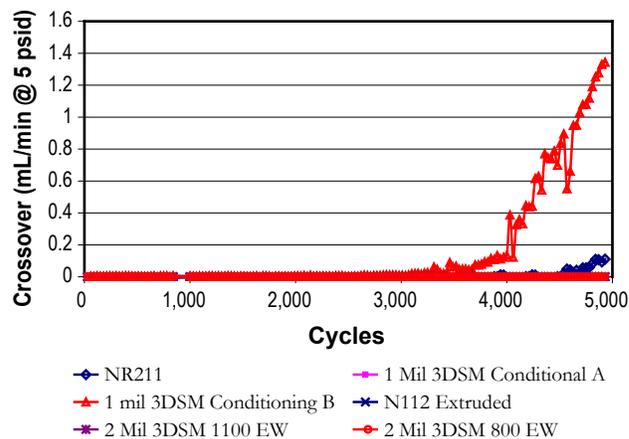


FIGURE 4. RH-cycling performance at 80°C for 1- and 2-mil 3DSM and Nafion® membranes.

The mechanical durability of the 3DSMs was tested through RH-cycling performance of the resultant thinner 3DSMs prepared with the materials from Millipore and the low EW ionomers at 80°C. Cast Nafion®, NR211, failed around 4,500 cycles, before the 1-mil 3DSM, as seen in Figure 4. The 3DSM Condition B, which failed early, was sintered to 200°C, well above the supports melting temperature. The sample (3DSM Condition A) which was sintered to 140°C, just below the support melting temperature lasted longer than NR211, the cast Nafion® reference. The 2-mil 3DSM which was also sintered to 200°C did not fail in the first 5,000 cycles. The samples were taken off test at 5,000 cycles because the test stand was needed for another project.

To further increase conductivity PFSA's with even higher acid content are being synthesized at SUNY-ESF under the direction of Israel Cabasso. A large number of materials have been synthesized, including the homopolymer of just the active monomer. Improvements in the synthesis of this polymer have led to a film-forming ionomer that can be readily incorporated in GES's 3DSM structures. In the previous years we demonstrated that this material has a conductivity that is approximately twice that of the

best 2DSM material to date and approximately five times that of Nafion[®] 112 over an entire range of RH as seen in Figure 2. Also seen in the figure is that this material comes very close to meeting the DOE target for conductivity down to 25% RH. Unfortunately this material swelled excessively in water.

Work at SUNY in this past year has centered on reducing this swelling while maintaining the high conductivity at low RH. A highly cross-linked perfluoro (4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride (PVEPVE)-based polymer was cast and characterized for conductivity at GES. The conductivity of this polymer was quite high at low levels of RH as seen in Figure 2. Surprisingly, the conductivity at higher levels of RH does not increase as quickly as the non-crosslinked materials. We believe that this is due to the lower water contents at higher RH due to the cross-linking. Water sorption isotherms of this material will be conducted to confirm this conclusion.

Conclusions and Future Directions

The DSM with laser-drilled supports successfully has been shown to restrain x-y swelling in high-acid content PFSA's over a range of composite dimensions and compositions. Though 2-3 times more conductive than Nafion[®] 112, it still is short of the DOE's conductivity targets. Work has been done to synthesize PFSA's with even higher-acid content, including the homopolymer that contains only the functional monomer. This polymer, when incorporated in the

3DSM has come very close to meeting the DOE targets. This polymer is water soluble however, and eventually leaches out of the 3DSM support. Efforts have begun to cross-link this polymer to make it insoluble and resulted in a polymer with similar low RH performance that is hydrolytically stable. RH cycling of the 2DSM and 3DSM materials has been completed to demonstrate these materials superior mechanical attributes; each of them surpassing 5,000-10,000 cycles, including a 1-mil 830 EW membrane. We are currently focusing on preparing even thinner (~15 μ m) 3DSMs with lower EW (700 EW) ionomer for fuel cell testing. Millipore and the Solar Energy Research Center in Florida are assisting in this effort.

Special Recognitions & Awards/Patents Issued

1. 2009 DOE Hydrogen Program Review R&D Award.

FY 2010 Publications/Presentations

1. Mittelsteadt, C.M., VanBlarcom, S. Liu, H., Wie, X., Johnson, F., Cabasso, I. "Dimensionally Stable Membranes" Presentation at FreedomCar, Michigan, April 2009.
2. Mittelsteadt, C.M., VanBlarcom, S. Liu, H., Wie, X., Johnson, F., Cabasso, I. "Dimensionally Stable Membranes" Presentation at Washington D.C. Semi-annual review Jun 2010.
3. Mittelsteadt, C.M, Willey, J. "Dimensionally Stable Membrane for High Pressure Electrolyzers" Presentation at IECEC Meeting Denver Colorado. August 5, 2009.