

V.C.2 Dimensionally Stable Membranes (DSMs)

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Technical Targets

Progress has been made in achieving the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Program Plan. Table 1 lists the DOE's technical targets and where our research stands to date.

TABLE 1. DOE Technical Targets and GES Status

| Characteristic | Unit | 2015 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 | 95 |
| Area Resistance | Ohm*cm ² | 0.02 | 0.03 ^c |
| Cost | \$/m ² | 20 | ~100 |
| Durability with cycling <80°C | cycles | 20,000 | 20,000 |
| 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)

Fiscal Year (FY) 2011 Objectives

- Demonstrate 20,000 relative humidity (RH) cycles in a 1 mil membrane.
- Manufacture larger, more consistent membranes.
- Manufacture supported membranes that are thinner than 1 mil.
- Utilize lower equivalent weight (EW) ionomers in thin supports.

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

FY 2011 Accomplishments

- Demonstrated 20,000 RH cycles in a 1 mil membrane.
 - Membrane had higher in-plane conductivity than NRE211.
 - Stopped test at 20,000 cycles.
- Manufactured larger membranes.
 - Numerous samples sent to a third party for testing.
- Greatly decreased chemical degradation under open circuit voltage testing.
 - Greater than an order of magnitude reduction.
 - Testing confirmed by a third party for testing.
- Both commercially available polyethersulfone (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%.



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 adversely affects mechanical durability of the membrane. GES is combining 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 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 (50 micron) DSM membrane consisting of a 1/3-mil (8 micron) 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 2-3 times the conductivity of Nafion® 112, the PFSA standard, over the entire range of RH as shown in Figure 2. This conductivity

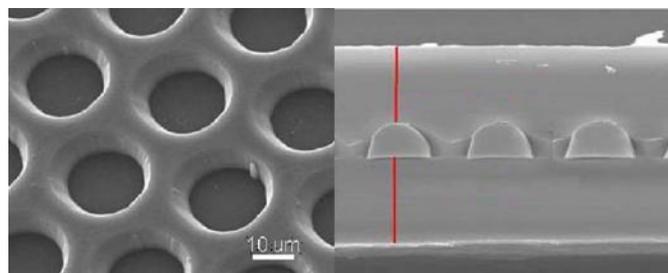


FIGURE 1. Scanning Electron Microscope Images of Laser-Drilled DSM Support (left, top view) and Support Filled with PFSA (right, cross section)

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 1100 EW and 830 EW PFSA ionomers into commercially available PES and UPE and tested the membranes under electrolysis conditions. In Figure 3, the electrolysis performance of a 3 mil (75 micron) 3DSM prepared with 830 EW ionomer and UPE support is compared to the 1100 EW electrolysis membrane electrode assembly with comparable thickness. Electrolysis 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 (100 micron) thick. We are currently working with Millipore on thinner supports, and they have supplied us with 1- and 2-mil-thick (25 and 50 micron) UPE and 3-mil (75 micron) thick PES.

3DSMs were prepared from low EW ionomer solution and the thin support materials supplied by Millipore. Mechanical durability tests were performed on these 3DSMs at 80°C. In the first RH-cycling test, cast Nafion®, NR211, failed around 4,500 cycles as seen in Figure 4. Two 3DSMs that were sintered to 140°C did not fail in the first 5,000 cycles of the first test. A 3DSM that was sintered to 200°C, which is above the melting temperature of the support, failed around 3,500 cycles. The samples were taken off test at 5,000 cycles because the test stand was needed for another project. A second RH-cycling performance test was initiated this spring to test the mechanical durability of 3DSMs. A 1-mil 3DSM sintered to 140°C successfully completed 20,000 cycles (Figure 4) and was removed from the test stand. The RH-cycling test consists of 2 minutes bone dry, 2 minutes at 95% RH at 80°C. The gas flowrate is 1 SLPM, rather than the 2 SLPM industry standard due to test stand limitations.

To improve performance, we tried to impregnate 3DSM supports with 660 and 700 EW material. Ionomer solution concentrations of 30 wt% or greater are needed to adequately fill the porous supports, but increasing the concentration of an alcohol-based ionomer concentration above 10 wt% causes the solution to become too viscous and collapse the UPE 3DSM support. Aqueous-based solutions are less viscous at higher concentrations, but these solutions are incompatible with the hydrophobic supports. Efforts centered on pretreating the 3DSM supports with a hydrophobic solution prior to casting. 3DSMs were successfully cast with pretreatment and PES supports,

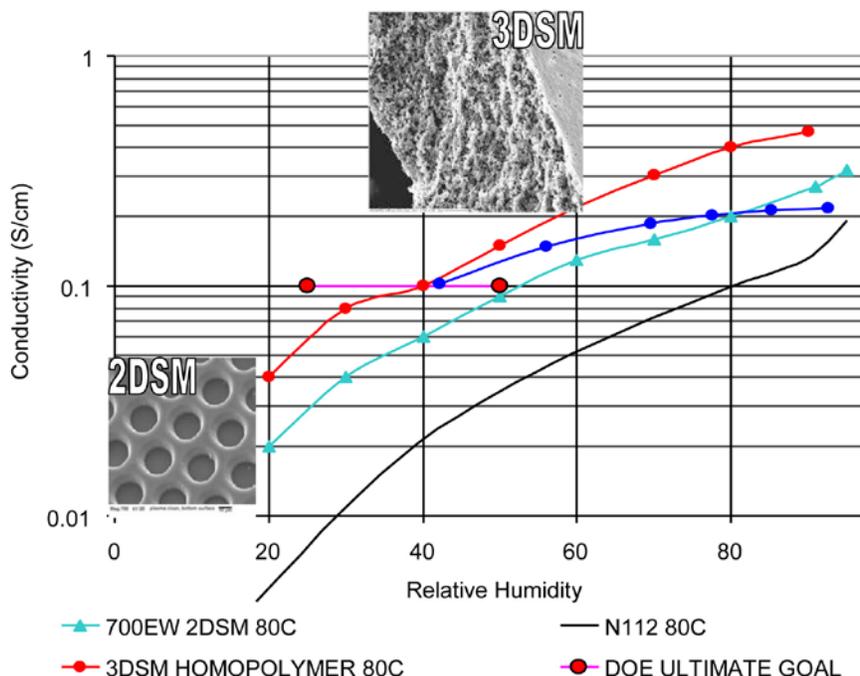


FIGURE 2. Conductivity of 2DSM membrane consisting of 700 EW PFSA in a polyimide support as well as two 3DSMs: one with the SUNY homopolymer at 80°C and a second with highly cross-linked PVEPVE. Insets of the 2DSM and 3DSM membranes are shown.

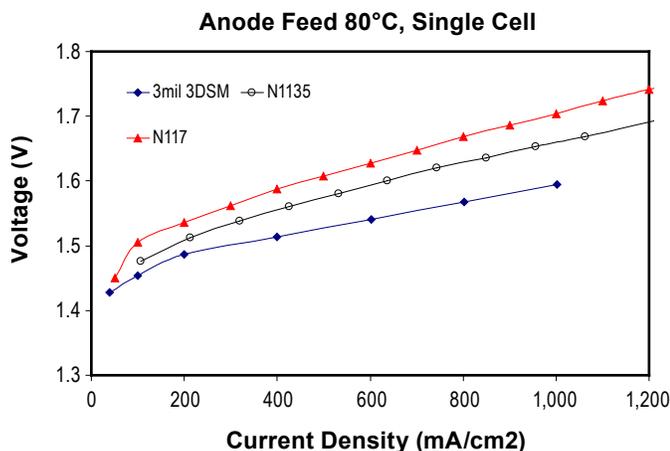


FIGURE 3. Electrolyzer Performance of N1135, N117 and a 3-mil-thick UPE 3DSM Membrane with 820 EW

although the resultant 3DSM was 65 microns thick. Surface oxidation and chlorosulfonation treatment showed dramatic increase in hydrophilicity, but failed to adequately incorporate the 660 and 700EW aqueous dispersions into the supports.

To further increase conductivity PFSA's with even higher acid content are being synthesized at SUNY under the direction of Israel Cabasso. A large number of materials have been synthesized, including the homopolymer of just

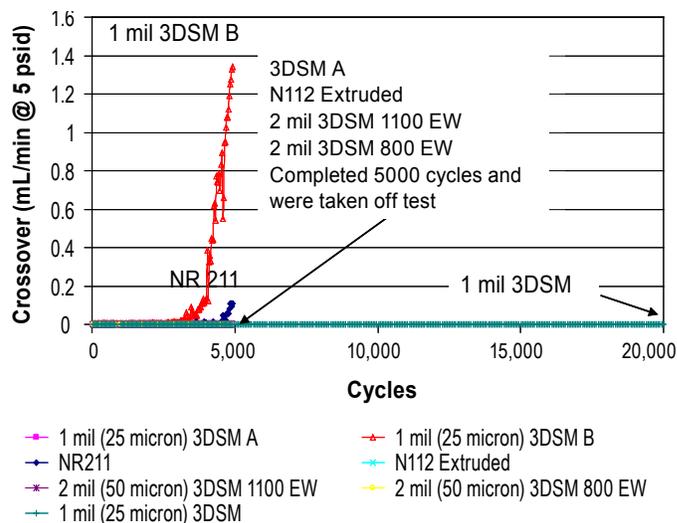


FIGURE 4. RH-Cycling Performance at 80°C for 1- and 2-mil 3DSM and Nafion® Membranes

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 (PSEPVE)-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 has been shown to successfully reduce 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 5,000-19,000 cycles, including a 1-mil 830 EW membrane. We are currently focusing on preparing even thinner (~15 µm) 3DSM's for fuel cell testing. Millipore and the Solar Energy Research Center in Florida are assisting in this effort.

FY 2011 Publications/Presentations

1. Mittelsteadt, C.M., VanBlarcom, S. Liu, H., Wie, X., Johnson, F., Cabasso, I. "Dimensionally Stable Membranes" Presentation at Washington, D.C. 2011 U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting" May 2011, Arlington, VA.