

V.G.16 Dimensionally Stable Membranes

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

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Project End Date: April 1, 2011

Objectives

- Determine the effect of pore size and substrate thickness on conductivity and water uptake of dimensionally stable membranes (DSMs).
- 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 (RH), at room temperature, 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 Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

Progress has been made in achieving the DOE 2010 Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan technical targets. 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 Dimensionally Stable Membrane (DSM) Status
Inlet Water Vapor Partial Pressure	kPa	1.5	20 ^a
Oxygen Cross-Over	mA/cm ²	2	1.5 ^b
Hydrogen Cross-Over	mA/cm ²	2	1.8 ^b
Membrane Conductivity Operating Temperature	S/cm	0.10 0.07 0.01	0.093 ^a 0.083 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	Testing just initiated
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 stoich 1.1/2.0.

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

^cFor 18 um 2DSM material operating at conditions listed above in (°)

Accomplishments

- Successfully demonstrated that DSMs based on laser drilling pores restrain x-y swelling (<5%) with a wide range of pore size and thickness.
- Polyimide and polysulfone both shown to be effective supports for the laser-drilled supports (limit in-plane swelling below 5%).

- 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.
- PFSA monomer homopolymerized. Generally a copolymerization of the acid-functionalized monomer with another perfluorinated ionomer is reported in the literature. This allows us to truly generate PFSA's with any acid content we choose. Though patent literature covers the homopolymer, we believe that this is the first time that this has been achieved. This polymer has been incorporated in the DSM structure.
- Short-term (DOE 2008 High Temperature Membrane) conductivity targets have been met for room temperature conductivity. Promising results confirmed by independent lab (Bekktech) using a two-dimensional laser-drilled (2DSM) support material:
 - 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-ESF and incorporated in three-dimensional (3DSM) support material:
 - Demonstrates 0.08 S/cm conductivity at 30% RH, approaching DOE ultimate target of 0.10 S/cm at 25% RH.
- Demonstrated improved fuel cell performance at 95°C and 25% RH, 7 psig H₂/air (0.68 V at 500 mA/cm²).



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's 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 generating the PFSA

polymers which is being done with our partners at SUNY-ESF, 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.

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 RH 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.

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. A cross-section of a 3DSM composite constructed with this new ionomer is shown in Figure 3. This material has demonstrated 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. Though water soluble,

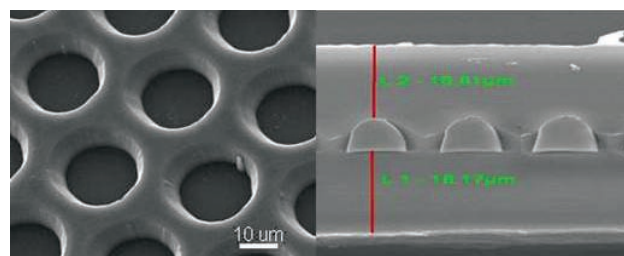


FIGURE 1. SEM Images of Laser-Drilled DSM support (left) and Support Filled with PFSA (right)

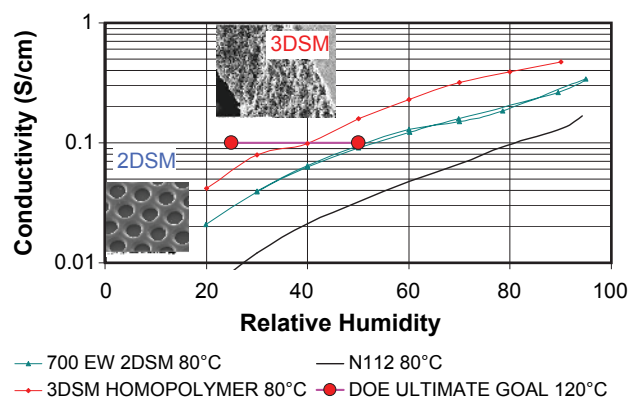


FIGURE 2. Conductivity of 2DSM membrane consisting of 700 EW PFSA in a polyimide support as well as that of the 3DSM with the SUNY-ESF homopolymer at 80°C. Insets of the 2DSM and 3DSM membranes are shown.

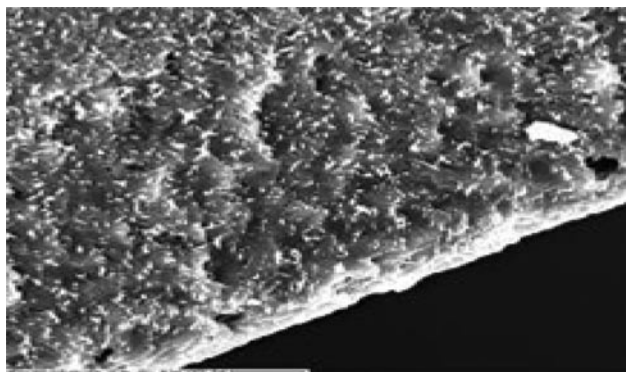


FIGURE 3. 3DSM Support Filled with Ionomer from SUNY-ESF

efforts are underway to cross-link the material in situ of the 3DSM support to prevent leaching.

Preliminary 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. In our first DSM membrane electrode assemblies (MEAs) the DSM MEA performed much better than Nafion® 112 at 95°C when fully humidified. However, the DSM and Nafion® 112 performances were not much different at 25% RH. This was unexpected; both the ex situ conductivity test, as well as an in situ impedance test, showed the DSM membrane to have much lower resistance. We attributed this to poor electrode design. With improved electrode structures the DSM performance is greatly improved, and far out-performs Nafion® 112 as also seen in Figure 4.

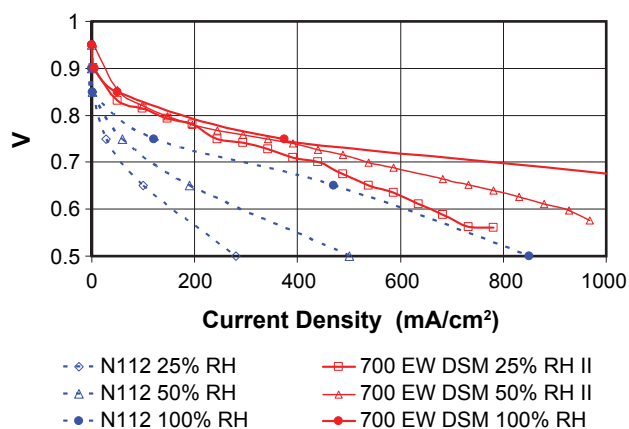


FIGURE 4. Comparison of fuel cell performance of a 2-mil Nafion® 1,100 EW material with that of a 2 mil DSM membrane. Cell is operated at 95°C, 7 psig balanced pressure and 4.0/4.0 stoichiometry H₂/air.

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. Finally, RH cycling of the 2DSM and 3DSM materials has been initiated to demonstrate these materials superior mechanical attributes.