

## V.M.17 Dimensionally Stable Membranes

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Subcontractor:

The Research Foundation  
State University of New York College of  
Environmental Science and Forestry (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.
- Demonstrate polymerization conditions suitable for bulk polymerization of perfluorinated sulfonic acids (PFSA's).
- Demonstrate, by the 3<sup>rd</sup> Quarter 2007, membrane conductivity of 0.07 S/cm, at 80% relative humidity (RH), at room temperature, and using non-Nafion<sup>®</sup> materials. Samples will be prepared and delivered to the Topic 2 Awardee.
- Go/No-Go Decision: Demonstrate, by the 3<sup>rd</sup> Quarter, membrane conductivity >0.1 S/cm, at 25% RH at 120°C, using non-Nafion<sup>®</sup> 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. 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 <sup>a</sup>
Oxygen Cross-Over	mA/cm <sup>2</sup>	2	1.5 <sup>b</sup>
Hydrogen Cross-Over	mA/cm <sup>2</sup>	2	1.8 <sup>b</sup>
Membrane Conductivity	S/cm		
Operating Temperature		0.10	.06 <sup>a</sup>
20°C		0.07	0.07
-20°C		0.01	Not tested
Operating Temperature	°C	≤120°C	95°C
Area Resistance	Ohm*cm <sup>2</sup>	0.03	0.046 <sup>a</sup>
Cost	\$/m <sup>2</sup>	20	~100
Thermal Cyclability in Presence of Condensed Water		Yes	Yes

<sup>a</sup>95°C with H<sub>2</sub>/Air at 20 psia balanced pressure. H<sub>2</sub>/Air Stoich 1.1/2.0

<sup>b</sup>Cross-over measured for 1 atm of pure H<sub>2</sub> and pure O<sub>2</sub> at 95°C and 50% RH.

### Accomplishments

- Successfully demonstrated that dimensionally stable membranes (DSMs) based on laser drilling pores restrain x-y swelling with a wide range of pore size and thickness.
- Polyimide and polysulfone both shown to be effective supports for the laser-drilled supports.
- 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 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.

- Short-term (DOE 2007 High Temperature Membrane) conductivity targets have been met.



## Introduction

PFSA materials have demonstrated the promising high temperature/low relative humidity 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.

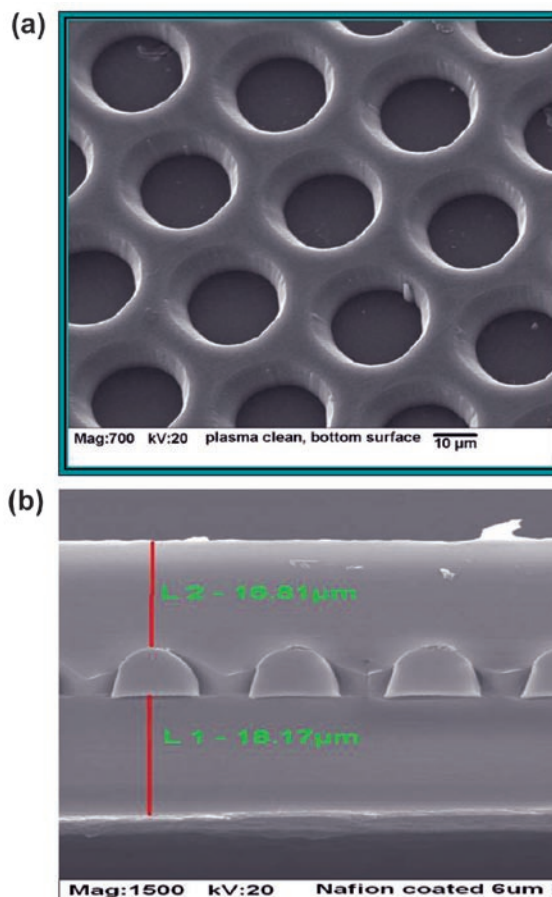
## Approach

GES's approach is to use very high acid content PFSA materials and support them with high-strength non-acidic materials. This involves 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 dimensionally stable membrane, 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 two to three times the conductivity of Nafion<sup>®</sup> 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. Additionally, it is difficult to see how the laser-drilled materials can reach the DOE targets for cost, as their



**FIGURE 1.** Scanning Electron Microscopy Images of Laser-Drilled DSM Support (Top) and Support Filled with PFSA (Bottom)

projected cost when produced in mass are  $> \$200/\text{m}^2$ , due to the large operating expense of the lasers. Laser costs are coming down however, and GES in another DOE sponsored project is looking at cheaper alternatives to fabricating these support materials including micro-molding.

To further increase conductivity PFSA 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. This polymer is a poor film former and is water soluble, but is an interesting material in that it can demonstrate the limit of these materials. Conductivity of the material was characterized. Though the conductivity was much higher than Nafion<sup>®</sup> 112 at high RH as seen in Figure 3, it was much lower at low RH. This may be due to cracking of the material at lower RH, which is visible with the naked eye. We believe that by sintering this material, and possibly carrying out a light cross-linking, we can form a more robust film.

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. The

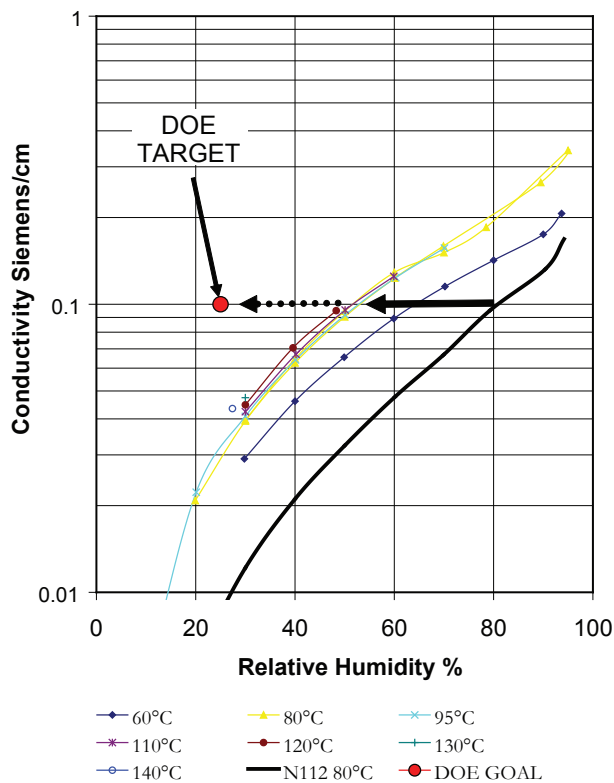


FIGURE 2. Conductivity of DSM Membrane Consisting of 700 EW PFSA in a Polyimide Support

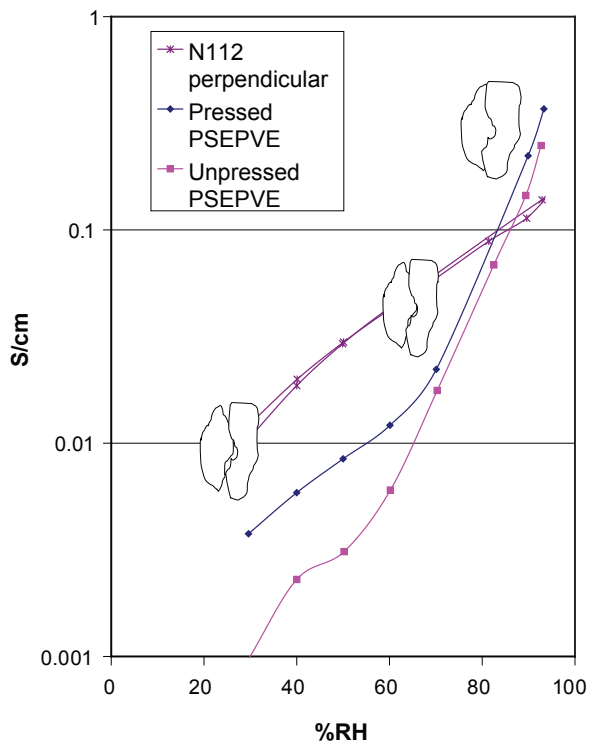


FIGURE 3. Conductivity of DSM with PFSA homopolymer (~500 EW) at 80°C. We believe that membrane cracking under dry conditions leads to poor conductivity at low RH.

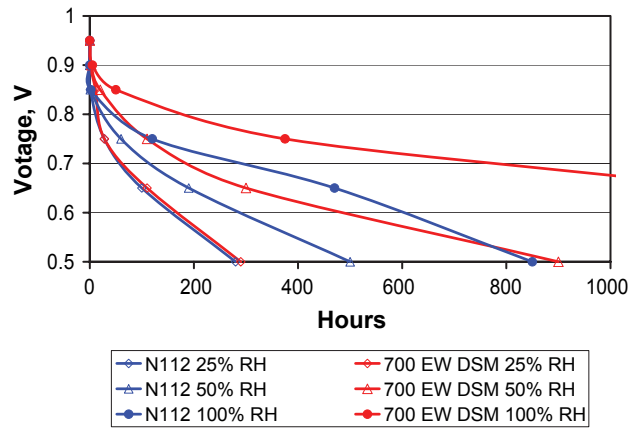


FIGURE 4. Comparison of fuel cell performance of a 2-mil Nafion® 1,100 EW material with that of a 2-mil DSM membrane. Cell is operated at 95°C, 7 psig balanced pressure and 4.0/4.0 stoichiometry H<sub>2</sub>/air.

DSM membrane performs much better than Nafion® 112 at 95°C when fully humidified as seen in Figure 4. However, the performance is 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 believe that the ionomer in the catalyst layer became the limiting factor as the standard 1,100 EW ionomer was utilized in the catalyst layer.

### 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 two to three 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. Further characterization and development of this polymer, we believe, will move us closer to the DOE targets and give insight into the limits of PFSA materials.

### FY 2007 Publications/Presentations

1. Mittelstadt, C.M. "DE-FG36-06GO16035 Giner Electrochemical Systems Q3 06 Report" October 2006.
2. Mittelstadt, C.M. "DE-FG36-06GO16035 Giner Electrochemical Systems Q4 06 Report" January 2007.
3. Mittelstadt, C.M. "DE-FG36-06GO16035 Giner Electrochemical Systems Q1 07 Report" April 2007.
4. Mittelstadt, C.M., Braff, W. Liu, H., Wie, X., Elacqua, E., Cabasso, I. "Dimensionally Stable Membranes", Presentation at Washington, D.C. semi-annual review, May 2007.