

V.D.2 Dimensionally Stable High Performance Membrane

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State University of New York
Environmental Science Forestry (SUNY-ESF)
Syracuse, NY

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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 (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 2008, 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 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 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 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		
95°C		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		5,000 hours	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 of 1.1/2.0

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

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

Accomplishments

- Successfully demonstrated that dimensionally stable membranes (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 (Bekktech) using a two-dimensional laser-drilled (2DSM) support material, resulting in passing the go/no-go 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-ESF 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 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%.
- 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 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. Fuel cell testing has been carried out on a 2 mil DSM 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 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.

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

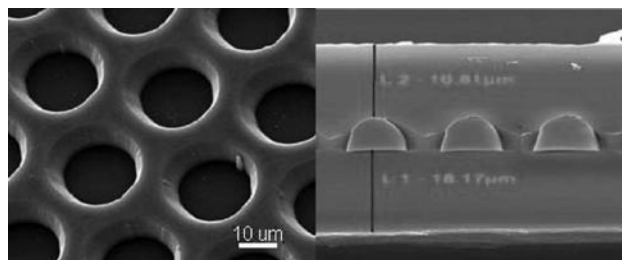


FIGURE 1. Scanning electron microscope images of laser-drilled DSM support (left) and support filled with PFSA (right).

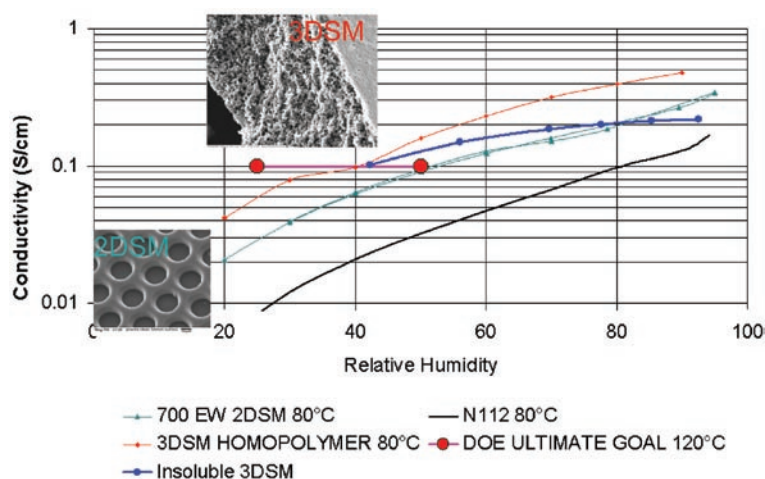


FIGURE 2. Conductivity of 2DSM membrane consisting of 700 EW PFSA in a polyimide support as well as two 3DSMs: one with the SUNY-ESF homopolymer at 80°C and a second with highly cross-linked PSEPVE. Insets of the 2DSM and 3DSM membranes are shown.

the dimensional stability and improved mechanical properties of the 2DSM. We successfully incorporated 1100 EW PFSA ionomers into commercially available PES and unsaturated polyester (UPE) and tested the membranes under electrolysis conditions, as seen in Figure 3. Electrolysis conditions were used as the membranes were too thick for fuel cell testing. 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. As seen in the figure, a 4 mil PES membrane behaves similarly to a 5 mil unsupported membrane, showing that the conductivity penalty due the support is slightly greater than 25%. The thinnest PES porous support commercially available is 4 mils thick. We are currently working with Millipore on thinner supports so that we can conduct fuel cell testing on the 3DSMs. They have supplied us with 1 and 2 mil thick UPE and have successfully incorporated low EW PFSA ionomers into the 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 mils with only a 20% conductivity penalty compared to neat 1100 EW PFSA. Unfortunately, we have not been as successful in incorporating the lower weight PFSA materials into this support, which will be an area of concentration in the upcoming year.

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 year 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

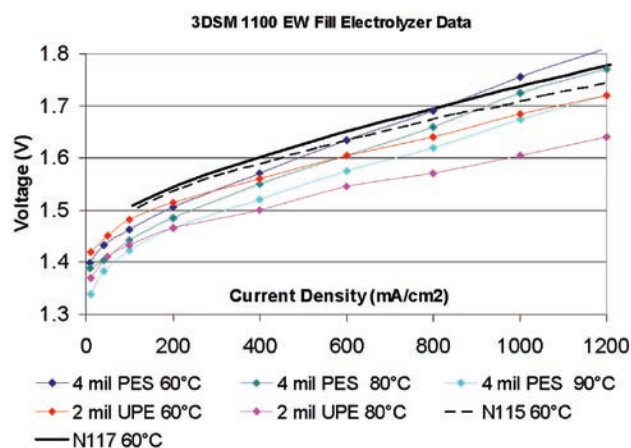


FIGURE 3. Electrolyzer performance of a 4 mil thick PES 3DSM and a 2 mil thick UPE 3DSM membrane with 1100 EW.

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	1100 EW	1	1	0.05
0.45 μm UPE	1100 EW	2	2.1	0.023
0.7 μm UPE	1100 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

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 Giner Electrochemical Systems. 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 10,000 cycles. We are currently focusing on preparing thin 3DSMs with low EW ionomer for fuel cell testing. Millipore is assisting in this effort.

Special Recognitions & Awards/Patents Issued

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

FY 2009 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 2008.
3. Liu, H., M. Chen, J. Willey, C. Mittelsteadt, A. LaConti, "High Performance, Dimensionally Stable Membrane" 2008 Fuel Cell Seminar & Exposition, Phoenix, Arizona, Oct. 27-30, 2008.
4. Liu, H. "Performance and Durability of Dimensionally Stable Membrane" Fuel Cells Durability & Performance 4th Annual International Conference, Las Vegas, NV, Dec. 11-12, 2008.