

## V.B.1 Dimensionally Stable High Performance Membrane

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### Overall Objectives

- Achieve mechanically supported, low equivalent-weight (EW) thin film ionomers that meet the DOE performance and cost targets for fuel cell membranes
- Demonstration of a cost-effective, roll-to-roll adaptable membrane electrode assembly (MEA) fabrication method
- Commercialization of Dimensionally Stable Membranes (DSM™) for highly reliable fuel cell systems

### Fiscal Year (FY) 2013 Objectives

- Develop a robust, scalable process to fabricate 5- to 12- $\mu\text{m}$  thick microporous DSM™ substrates with 50% pore density
- Optimize DSM™ support materials to yield favorable mechanical properties and negligible dimensional changes in water at 80°C
- Develop and characterize MEAs using the developed DSM™ substrates

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells and Manufacturing R&D sections of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

### Fuel Cells

(A) Durability

(B) Cost

(C) Performance

### Manufacturing R&D

(A) Lack of High-Volume Membrane Electrode Assembly Processes

### Technical Targets

Progress has been made in achieving the DOE targets listed in the Multi-Year Research, Development, and Demonstration Plan. Table 1 lists the DOE's technical targets and where our research and development efforts stand to date.

**TABLE 1.** DOE Technical Targets and GINER/GES Status

Characteristic	Unit	2017 Target	DSM™ Status
Oxygen crossover	mA/cm <sup>2</sup>	2	1.5 <sup>a</sup>
Hydrogen crossover	mA/cm <sup>2</sup>	2	1.8 <sup>a</sup>
Membrane Conductivity	S/cm		
Operating Temperature			
20°C		0.10	0.093 <sup>b</sup>
-20°C	0.07	0.083	
		0.01	Not tested
Operating Temperature	°C	≤120°C	95°C
Area Resistance	Ohm·cm <sup>2</sup>	0.02	0.03
Cost	\$/m <sup>2</sup>	20	~\$50
Lifetime	hours	5,000	Untested
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

<sup>a</sup>Crossover measured for 1 atm of pure H<sub>2</sub> and pure O<sub>2</sub> at 95°C and 50% relative humidity

<sup>b</sup>For 1-mil DSM™ operating at 95°C with H<sub>2</sub>/air at 20 psi. H<sub>2</sub>/air stoichiometry of 1.1/2.0

This project pursued three DSM™ fabrication processes based on the criteria of performance optimization and cost reduction. All three processes (phase inversion, ultraviolet (UV) microreplication, and mechanical deformation) are based on the use of molding technology and are favorably scalable for high-volume production. After evaluation of these processes, the mechanical deformation method was down-selected to prepare fuel cell membranes capable of achieving the following DOE targets:

- Area resistance: <0.02  $\Omega\cdot\text{cm}^2$

- Cost: <20 \$/m<sup>2</sup>
- Lifetime: >5,000 hours
- Durability at 80°C: >20,000 cycles

## FY 2013 Accomplishments

- Comprehensive work on material development for the UV microreplication process yielded a number of polymers that achieved high tensile strength (>10 MPa), high elastic modulus (>100 MPa), and long elongations (>5% at break) while retaining dimensional stability and resistance to acid hydrolysis.
- Preliminary use of the roll-to-roll setup at UMass-Amherst facilities has shown that using a 6" roll, seamless formation of DSM™ supports with dimensions of up to 6" x 19" (~730 cm<sup>2</sup>) can be prepared at web speeds of 8 inch/min.
- By improving the release process of polysulfone from micromolds, a film porosity of over 60% has been demonstrated using a mold-assisted mechanical deformation route. This method is projected to yield <\$20/m<sup>2</sup> DSM™ cost when adapted to a roll-to-roll process.



## INTRODUCTION

In proton exchange membrane fuel cells, attaining and maintaining high membrane conductivity at various operating conditions is crucial for the fuel cell performance and efficiency. Lowering the EW of perfluorinated ionomers is one of the few options available to improve membrane conductivity, especially in the low relative humidity regime. However, excessive changes in membrane dimensions upon application of wet/dry or freeze/thaw cycles yield catastrophic losses in membrane integrity, thus hindering their long-term durability. This is especially of concern when low-EW ionomers are used in thin membrane configurations to minimize resistive losses. Incorporating perfluorinated ionomers of low EW within highly porous, dimensionally stable support materials is an optimal method to achieve the DOE membrane metrics for conductivity and durability. A scalable, cost-effective method to fabricate these composite membranes is also necessary to achieve the DOE target of <\$20/m<sup>2</sup>. Giner/GES has developed DSM™ technology to provide mechanical support for the conductive ionomer. These composite membranes include a highly conductive and high-acid-content ionomer within a thin and durable polymer support with well-defined pores and high (50%) porosity. Utilizing high-strength engineering polymers, the DSM™ approach completely restrains the in-plane swelling of the ionomer. Providing a non-tortuous, through-plane path for ionic transport minimizes the conductivity penalty

due to the support structure. Additionally, when filled with low-EW perfluorinated sulfonic acid (PFSA) ionomers, the DSM™ meets nearly all of the DOE's 2017 durability and performance targets, including those for freeze/thaw cycling and wet/dry cycling operation.

As currently manufactured, DSM™ is far too expensive (~\$100 to 1,000/m<sup>2</sup>) for automotive and stationary applications. A scalable, continuous fabrication method is needed to reduce the cost down to or below the DOE's 2017 cost target of \$20/m<sup>2</sup>.

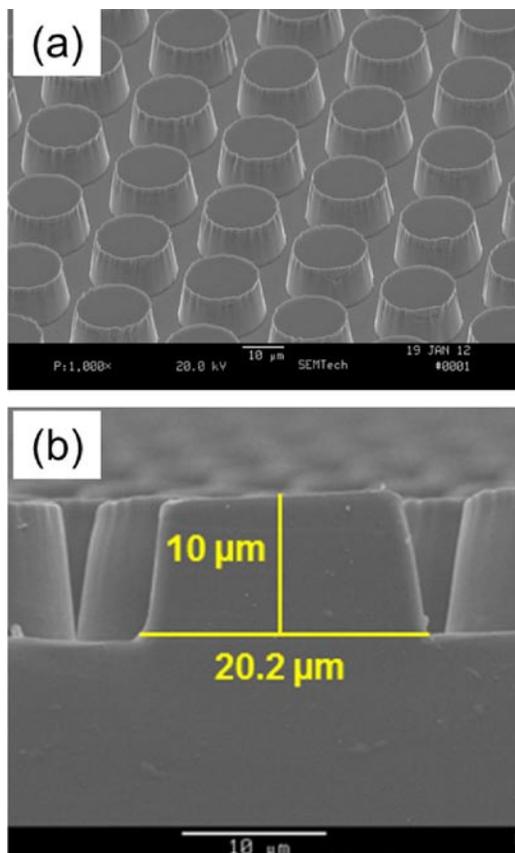
## APPROACH

A major goal for this project is the optimization of materials and processes for cost-effective manufacturing of DSMs™ consisting of a low-EW PFSA ionomer embedded in a 5- to 12-μm-thick microporous support film with 20-μm pore diameter and 50% pore density. The project has investigated three micromolding processes (phase inversion, UV microreplication, and mechanical deformation) and evaluated their feasibility for scaled fabrication at low cost. The *Phase Inversion* process involves casting a polymer solution on a micromold followed by rapid precipitation of the polymer in a non-solvent to yield porous films. First used during Phase II of this project, this method aims to develop a DSM™ support that is less expensive and easier to scale up compared to laser micromachining. The *UV Microreplication* method is a soft lithography approach that uses imprint lithography principles and involves the use of a low-viscosity, UV-crosslinkable monomer solution placed between a low-surface-energy mold (pillars) and a backing layer. This is a highly scalable process that generates materials at low cost and high volume. The *Mechanical Deformation* method relies on puncturing commodity plastics. This process is also readily scalable to generate a proven DSM™ support with proven materials at low cost.

The initial stage of the project involved fabrication of electroformed nickel "pillar" molds by NIL Technology (NILT, Denmark) to be used for generation of the DSM™ supports using all three methods. Figure 1 shows tilted and cross-sectional SEM micrographs of a representative nickel micromold with 10-μm pillar height and 50% area coverage. Upon elimination of the *Phase Inversion* process due to complications with solvent waste and inferior material properties, Giner has continued to investigate both *UV Microreplication* and *Mechanical Deformation* methods.

## RESULTS

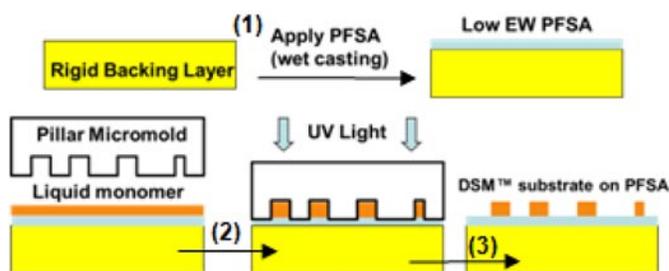
During FY 2013, Giner/GES investigated two micromold-assisted DSM™ fabrication methods: *UV Microreplication* and *Mechanical Deformation*. Based on the results shown in this section, the *Mechanical Deformation* has been selected as the most viable method and is being



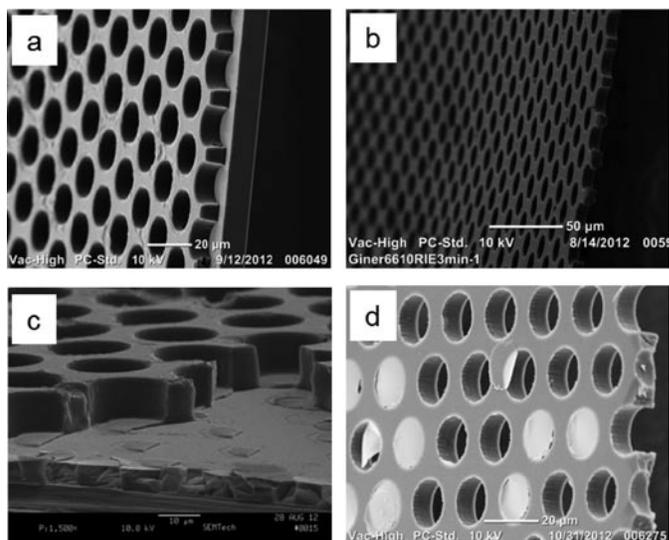
**FIGURE 1.** Scanning Electron Micrographs of Micromold Pillars (a) Tilted View (b) Cross-Sectional View with Dimensions

actively pursued by Giner/GES to achieve the DOE's 2017 targets for cost, performance, and durability.

**UV Microreplication.** This process flow involves the use of a low-viscosity, UV-crosslinkable monomer solution placed between a low-surface-energy mold and a backing layer followed by UV exposure and removal of the crosslinked polymer film to yield a DSM™ support with well-defined cylindrical pores as shown in Figure 2. This process was investigated at UMass-Amherst in collaboration with the Carter Research Group. A state-of-the-art Nanonex NX-200 Universal Imprinter was utilized to investigate microreplication of polymers by imprint lithography. Using low-surface-energy micromolds, 10- $\mu\text{m}$ -thick, 4" wide DSM™ substrates were formed using the process shown in Figure 2. During the imprint process, the precursor monomer fills the mold under an applied pressure and is rapidly crosslinked with UV light to yield porous polymer films. The resulting films showed high tensile strength and were sufficient flexibility for roll-to-roll adaption. Upon optimization of the processing conditions such as wet precursor thickness, applied pressure, and imprint duration, it was possible to obtain porous films with minimal residual layers after releasing from the micromolds. Figure 3, which



**FIGURE 2.** UV Microreplication Process Showing the Fabrication of DSM™ Substrates on a PFSA Ionomer Layer



**FIGURE 3.** Scanning Electron Micrographs of the Porous DSM™ Substrates — Substrate bound (a) and free-standing (b) films free of residual layers. Films with minimal residual layers are shown in (c) and (d)

shows SEM micrographs of processed films, demonstrates the effect of process parameters on the film quality, uniformity, and the extent of residual layers. The wet monomer thickness, surface treatment, and the rigidity of the backing layer were important parameters that affected the quality of the porous films and the thickness of residual layers. Figures 3a, 3b show examples of a porous film produced on a corona-treated, rigid backing layer that is free of residual layers (completely open pores, shown both as a substrate-bound and a free-standing film). However, the use of a plastic (Mylar) backing layer caused residual layers of 0.5-0.8  $\mu\text{m}$  as shown in Figures 3c, 3d. We note that the residual layers are not continuous and appear to stick on the backing layer (Figure 3c), thus leaving the pores partially open for the free-standing film of the DSM™ substrate (Figure 3d). Finally, when spin casting was used to apply the monomer layers, faster spin rates translated into thinner wet monomer thickness to minimize the residual layer thickness (not shown).

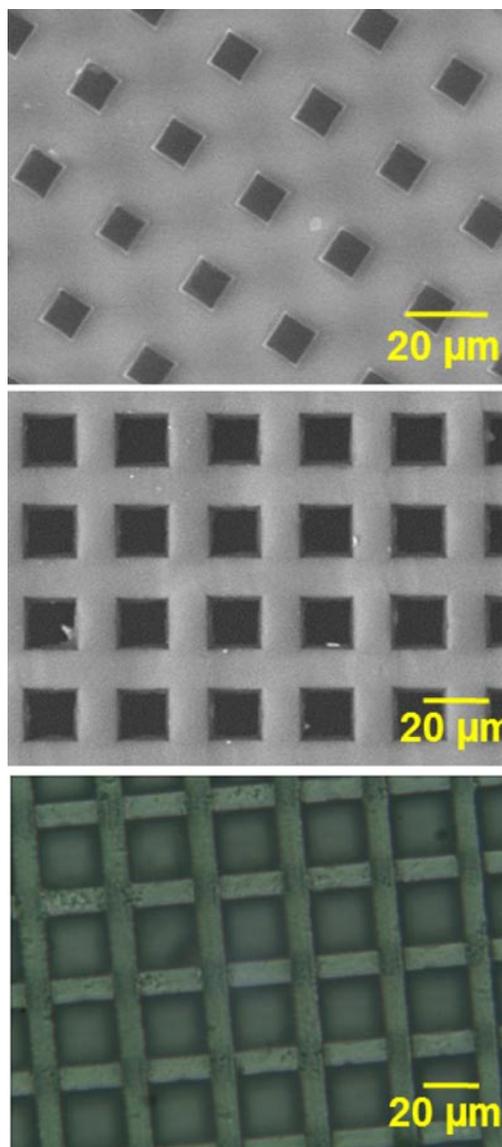
**Mechanical Deformation.** This method is attractive because it uses materials already qualified by laser-drilled DSM™ substrates. This method can utilize commodity thermoplastics with very fast processing times allowing for roll-to-roll production. Preliminary perforation trials conducted with polysulfone have yielded films with 10- to 15- $\mu\text{m}$ -wide pores and ~15-33% porosity as shown in Figure 4 top and center (less than the targeted 50% porosity). This was mainly due to excessive tearing of polysulfone during the mold release step. By improving the release properties of polysulfone from micromolds, a film porosity of over 60% has been demonstrated using a square pattern as shown in Figure 4 bottom.

## CONCLUSIONS

The goal by the end of FY 2013 was to select and optimize a scalable process for cost-effective manufacturing of DSMs™ for fuel cells. Giner's formulation and process development effort for the *UV Microreplication* method has yielded materials with substantial improvements in mechanical properties over the ionomers used in fuel cells. A comprehensive work on material development yielded a number of polymers that achieved high tensile strength (>10 MPa), high elastic modulus (~200 MPa), and good elongation (>10% at break) while retaining dimensional stability and resistance to acid hydrolysis. However, these materials still fail to yield the desired mechanical properties at elevated (~80°C) temperatures. Despite the successes in material and process development, the UV-curable polymers are still not adequate mechanically for use in fuel cells. The *Mechanical Deformation* route was explored to produce prototype polysulfone DSM™ supports with over ~60% porosity. This represents the ideal support geometry with an engineering thermoplastic. The potential of this method is due to its very low material risk and high roll-to-roll adaptability. Upon qualification of these DSM™ supports for fuel cells, the focus of the project will be to scale up this method to fabricate larger (12") micromolds and transfer the batch process to a pilot-size roll-to-roll setup to continuously produce DSMs™.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Mittelsteadt C.K.; Argun, A.A.; Laicer, C.; Willey, J. "Dimensionally Stable Membrane Substrate and Method of Fabrication Thereof" US provisional patent application, 2013.



**FIGURE 4.** Progress in DSM™ Substrates Generated with *Mechanical Deformation* — Top: 11- $\mu\text{m}$  pores, 15% porosity; Center: 16- $\mu\text{m}$  pores, 33% porosity; Bottom: 22- $\mu\text{m}$  pores, 62% porosity

## FY 2013 PUBLICATIONS/PRESENTATIONS

1. Mittelsteadt, C.K., A. Argun, C. Laicer, J. Willey, P. Maxwell. "2013 Fuel Cells Tech Team" March 2013.
2. Mittelsteadt, C.K., A. Argun, C. Laicer, J. Willey, P. Maxwell. "2013 Annual Merit Review Proceedings—Fuel Cells" May 2013.