V.B.1 Dimensionally Stable High Performance Membrane

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Overall Objectives

- Achieve mechanically supported, dimensionally stable, and highly conductive fuel cell membranes that meet the DOE performance and cost targets.
- Demonstrate a scalable and cost-effective roll-to-roll method for fabrication of membrane electrode assemblies.
- Commercialize Dimensionally Stable Membranes (DSM™) for use in fuel cells, electrolyzers, and other electrochemical applications that require thin and strong membranes.

Fiscal Year (FY) 2014 Objectives

- Optimize materials and process parameters for the selected DSM™ support fabrication that involves mechanical deformation of dimensionally stable polymers to obtain 5- to 10-µm-thick microporous DSM™ supports with 50% pore density.
- Develop and characterize membrane electrode assemblies using low equivalent weight (EW) ionomers embedded in the DSM™ supports.
- Demonstrate a scalable process and conduct a pilot roll-to-roll run to yield ~1,000 ft of DSM™ roll.

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^2	2	1.5[a]
Hydrogen Crossover	mA/cm^2	2	1.8[a]
Membrane Conductivity Operating Temperature 20°C -20°C	S/cm	 0.10 0.07	 0.093[b] 0.083 0.01 Not tested
Operating Temperature	°C	≤120°C	95°C
Area Resistance	$Ohm*cm^2$	0.02	0.03
Cost	$\$/m^2$	20	<100
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

[a]Crossover measured for 1 atm of pure H_2 and pure O_2 at 95°C and 50% relative humidity.
[b]For 1-µm DSM operating at 95°C with H_2/air at 20 psi. H_2/air stoichiometry of 1.1/2.0.

This project previously pursued multiple micromold-based DSM™ fabrication processes based on the criteria of fuel cell performance and cost reduction. Despite the favorable scalability of all processes for high-volume production, only the DSMs™ fabricated using the mechanical deformation method met the required performance characteristics to achieve the DOE targets:

- Area resistance: <0.02 $\Omega.cm^2$
- Cost: <\$20 m^2
- Lifetime: >5,000 hours
- Durability at 80°C: >20,000 cycles

FY 2014 Accomplishments

- A mechanical deformation method was developed to form DSM™ supports with round and square pores using a variety of dimensionally stable commodity polymers.
- A comprehensive optimization study was conducted to refine the mechanical deformation method to yield ~10-µm thick microporous DSM™ supports with 50% pore density. The process parameters were finalized for successful adaption to roll-to-roll trial.
- By improving the release process of polysulfone (PSU) from nickel micromolds using ultrathin fluoropolymer coatings, film porosity of over 50% has been demonstrated using the mold-assisted mechanical deformation route.
- A detailed route to achieve roll-to-roll production of DSM™ was identified and executed at a pilot size to yield ~ 1,000 ft roll of DSM™. This route involved the fabrication and surface treatment of nickel micromolds, attachment of micromolds onto a tooling belt to form a process drum, roll-coating of perfluorinated sulfonic acid (PFSA) and PSU layers on a 5,000-ft carrier film roll at various thickness values, and mechanical deformation of the PFSA/PSU layers by the process drum to form the final DSM™.

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INTRODUCTION

In proton exchange membrane (PEM) fuel cells, attaining and maintaining high membrane conductivity at various operating conditions is crucial for the fuel cell performance and efficiency. Incorporating ionomers within highly porous, dimensionally stable PEM substrates increases the performance and longevity of PEM devices. 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 fuel cell membrane metrics for conductivity and durability. A scalable, cost-effective method to fabricate these composite membranes is also necessary to achieve the DOE membrane cost target of <$20/m^2. 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, "through" 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 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 (~$100-1,000/m^2) 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^2.

APPROACH

A major goal for this project is the identification and optimization of materials and processes for scalable and cost-effective manufacturing of DSMs™ consisting of low-EW PFSA ionomers. Giner had previously identified the optimum DSM™ support geometry to be a 5- to 10-µm-thick microporous support film with 20-µm pore diameter and 50% pore density. Specifically, the project has investigated in depth a laser ablation method along with three micromolding processes: Phase Inversion, UV Microreplication, and Mechanical Deformation. Giner has evaluated the feasibility of each process for scaled fabrication at low cost. The "Laser Micromachining" process was eliminated first due to issues with extremely slow process speeds, high capital instrumentation demand, and high operation cost. The remaining three micromolding processes rely on fabrication of electroformed nickel "pillar" molds as the initial stage. Figure 1 shows the cross-sectional illustration of the nickel micromold along with a scanning electron micrograph that shows the configuration of 10-µm pillar height pillars to yield 50% area coverage.

The "Phase Inversion" method, first used during Phase II of this project, aimed to develop a DSM™ support that is less expensive and easier to scale up compared to laser micromachining. It involves casting a polymer solution on a micromold followed by rapid precipitation of the polymer in a non-solvent to yield porous films. Despite its ease of application, the presence of residual solvent wastes hinder its widespread application. Additionally, the resulting porous films had poor mechanical properties due to microporosity of inversion-cast films. The "UV Microreplication" method, a soft lithography approach that uses imprint lithography principles, involves the use of a low-viscosity, ultraviolet (UV)-crosslinkable monomer solution placed between a micromold and a backing layer followed by its solidification to form a porous network. This is a highly scalable process that generates materials at low cost and high volume.

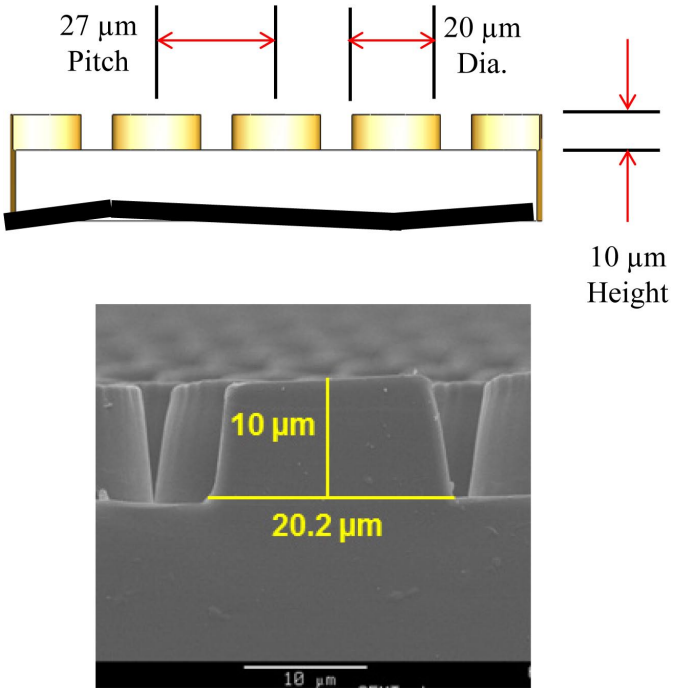

FIGURE 1. A scanning electron micrograph of a micromold pillar—cross-sectional view with dimensions.

However, the crosslinked polymers have failed to pass the durability and mechanical strength criteria during their evaluation as DSM™ support. Upon elimination of the Phase Inversion process due to complications with solvent waste and the UV Microreplication process due to inferior material properties, Giner has continued to investigate the Mechanical Deformation method, which relies on controlled puncturing of high strength engineering polymers with an array of high fidelity micropillars. By eliminating the material risks encountered in phase inversion and UV Microreplication methods , this process has proven to be readily scalable to generate a DSM™ support material at low cost.

RESULTS

During FY 2014, Giner/GES investigated the micromold-assisted mechanical deformation method for scaled and cost-effective fabrication of DSM™. This is a direct perforation route that involves puncturing a high-performance engineering polymer with micromolds to fabricate porous films. It is attractive because the resulting support structure has identical performance to the initial material unlike the case for UV-crosslinked films where further validation is required. This method can also utilize commodity polymers with very fast processing times allowing for roll-to-roll production.

Figure 2 shows the process flow that Giner has developed to apply the mechanical deformation concept to form DSM™ supports. First, a thermoplastic such as PSU is solution

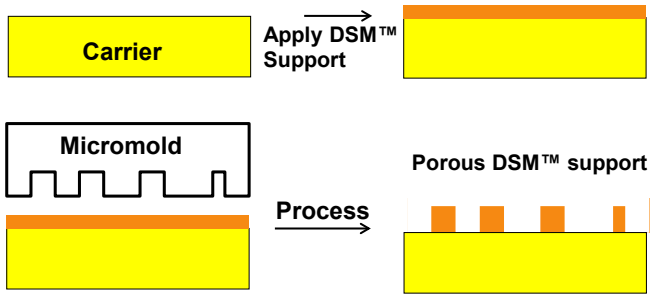

FIGURE 2. Giner's mechanical deformation process to form DSM™ supports (patent pending).

cast on a rigid backing layer. A nickel micromold treated with a low surface energy anti-stick coating is then applied. Upon completion of the process, the micromold is removed, resulting in a continuous DSM™ support with well-defined pores attached to the underlying carrier layer. Using the process scheme shown in Figure 2, Giner performed a series of batch perforation experiments and optimized process parameters to form PSU DSM™ supports with highly regular pores. Using the process flow shown in Figure 2, DSM™ supports were fabricated at two different configurations where the DSM™ support layer was perforated on a carrier film (Figure 3a) or on a PFSA/carrier layer (Figure 3b). Scanning electron micrographs obtained from these two configurations (Figure 3) clearly show the formation of pores without residual layers. Depending on the application, this approach can generate a porous network of PSU either directly on the carrier film or as a PSU/PFSA bilayer configuration. For example, if separation of the DSM™ support material from the underlying carrier layer proves difficult, a PFSA layer can be applied on the carrier polymer prior to the DSM™ support layer. Giner currently uses this bilayer approach to feature a thin (~1.5 µm) PFSA film on the carrier film followed by coating a 3-µm thick PSU film, which brings the total bilayer thickness to slightly below 5 µm. Upon processing the film with micromold pillars, the result is a 10-µm thick porous PSU/PFSA film as shown in Figure 3b. The next step would be to complete the DSM™ fabrication by adding another PFSA layer.

Figure 4 shows the schematic illustration of the continuous, roll-to-roll fabrication process. The carrier layer that is coated with the DSM™ support is fed continuously between a rotating conveyer and the process drum that contains the micromold. The distance between the rotating conveyer and the process drum is adjusted so that a pressure in a preferred range of 100-300 psi can be applied between micropillars and the DSM™ support layer. Once the process is complete, the resulting porous DSM™ support can be transferred to the next processing step to incorporate the ionomer layer. In collaboration with an industrial partner, we are currently implementing a pilot-size roll-to-roll method to

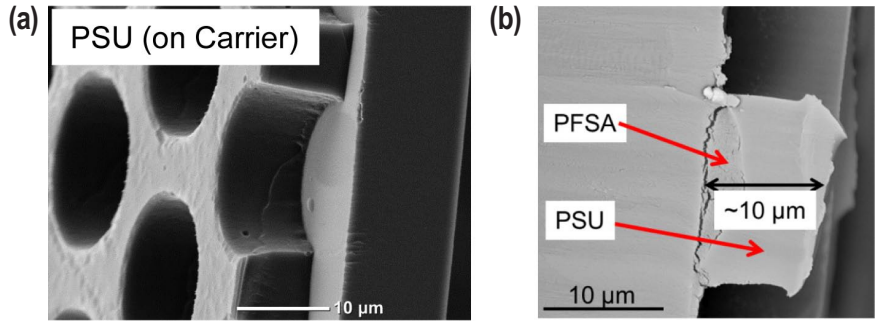

FIGURE 3. Two configurations of the mechanical deformation process. (a) PSU on carrier (b) PSU on PFSA/carrier.

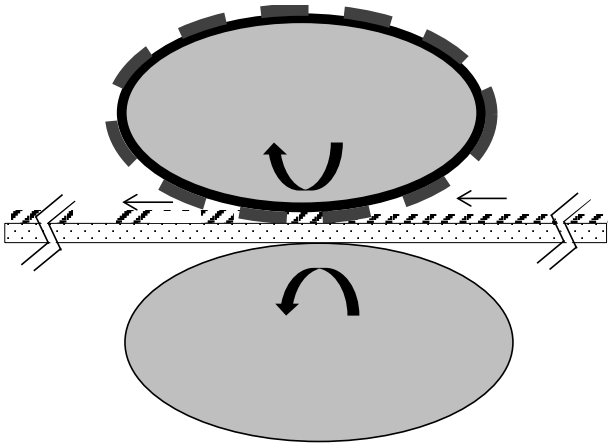

FIGURE 4. Schematic illustration of the roll-to-roll mechanical deformation process.

produce ~1,000 ft of DSM™ roll where each DSM is sized ~45 in^2 (~280 cm^2) between the seams.

CONCLUSIONS

The goal by the end of FY 2014 was to demonstrate the roll-to-roll adaption of the mechanical deformation method for cost-effective manufacturing of DSMs™ for fuel cells. The potential of this method is due to its very low material risk. Giner's process development effort has yielded a clear pathway for large-scale production of DSM™ support materials with targeted dimensional stabilities to allow for incorporation of low-EW ionomers in fuel cells. Upon qualification of these DSM™ supports by Giner in membrane electrode assemblies for fuel cells, the focus will be to extend the material width to 12" using larger micromolds and investigate effective ways to integrate the ionomer layers with DSM™ supports for continuous production of DSMs™.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Mittelsteadt C.K.; Argun, A.A.; Laicer, C.; Willey, J. "*Micromold Methods for Fabricating Perforated Substrates and for Preparing Solid Polymer Electrolyte Composite Membranes*" US Patent Application No. 14/120,353, filed on May 14, 2014.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Mittelsteadt, C.K., A. Argun, C. Laicer, J. Willey, P. Maxwell. "*2014 Annual Merit Review Proceedings– Fuel Cells* " June, 2014.

2. Mittelsteadt, C.K., A. Argun, C. Laicer. "*2014 Fuel Cells Tech Team* " February, 2014.

3. Mittelsteadt, C.K., A. Argun, and C. Laicer "Dimensionally Stable High Performance Membrane," Annual Progress Report, U.S. Department of Energy Phase III Xlerator Program Grant No. DE-EE0004533, December 2013.