V.C.3 Dimensionally Stable High Performance Membrane (SBIR Phase III)

Cortney Mittelsteadt (Primary Contact),
Avni A. Argun, Castro Laicer, Jason Willey
Giner Electrochemical Systems, LLC (GES)
89 Rumford Avenue
Newton, MA 02466
Phone: (781) 529-0529
E-mail: cmittelsteadt@ginerinc.com

DOE Manager
HQ: Donna Ho
Phone: (202) 586-8000
E-mail: Donna.Ho@ee.doe.gov

Contract Number: DE-EE0004533

Project Start Date: October 1, 2010
Project End Date: September 30, 2013

Fiscal Year (FY) 2011 Objectives

- Develop and characterize membrane electrode assemblies (MEAs) based on the Dimensionally Stable Membrane (DSM) membrane support technology.
- Identify a cost-effective route to fabricate 10-12 µm thick microporous DSM support films with 50% area coverage (pore density) and 10-20 µm diameter holes.
- Qualify the DSM supports by mechanical, freeze/thaw, and wet/dry testing.
- Develop a continuous coating process using molds.
- Investigate alternative molding procedures.
- Go/No-Go Decision: Demonstrate, by the fourth quarter, a scalable method to produce the desired DSM substrates.

Technical Barriers

This project addresses the following technical barriers from the 3.4.4 (Fuel Cells) and 3.5.5 (Manufacturing R&D) sections of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance
(A) High-Volume Membrane Electrode Assembly (MEA) Processes

Technical Targets

Progress has been made in achieving objectives within the Fuel Cell 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	2015 Target	GES 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 0.01	 0.093[b] 0.083 Not tested
Operating Temperature	°C	≤120	95
Area Resistance	$Ohm*cm^2$	0.02	0.03[c]
Cost	$\$/m^2$	20	~$100
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 18 μm DSM operating at 95°C with H_2/air at 20 psi. H_2/air stoichiometry 1.1/2.0.

FY 2011 Accomplishments

- Supplied four laser manufacturing companies with polyimide and polysulfone samples to generate a closely packed (50% area density) microporous DSM support via continuous drilling of pores using direct laser ablation method.
- Established an ultraviolet (UV)-shielded cleanroom to fabricate photo-curable polymers as candidates for DSM supports.
- Collaborated with University of Massachusetts Amherst (UMass), Colorado Photopolymer Solutions, and NanoImprint Lithography Technology to optimize the use of photo-curable polymers for rapid microreplication process.
- Designed a protocol to screen various DSM supports which includes procedures to test acid/alcohol resistance, water uptake, substrate adhesion, and mechanical strength for roll-to-roll fabrication.
- Revisited the phase inversion solvent cast method from Phase II and improved the tensile strength and elastic moduli of cast DSM supports by 3-5 fold.

Introduction

Lowering the equivalent weight (EW) of perfluorinated ionomers is one of the few options available to improve polymer electrolyte membrane conductivity, especially in the low relative humidity (RH) regime. GES believes that an approach utilizing perfluorinated ionomers of low EW is an optimal method to achieve the DOE membrane metrics. GES has developed DSMs (Figure 1) to provide a better support for the conductive ionomer. DSMs are composite membranes that include a highly conductive and high acid content ionomer incorporated into a thin and durable polymer support with well-defined pores. Utilizing high strength engineering polymers, DSMs have completely restrained in-plane swelling. Providing a direct through-plane non-tortuous path minimizes the conductivity penalty due to the support structure. Additionally, when filled with low EW perfluorinated sulfonic acid (PFSA) ionomers, they meet nearly all of the DOE's 2015 durability and performance targets, including those for freeze/thaw cycling and wet/dry cycling operation.

As currently manufactured, DSMs are far too expensive for automotive or even stationary applications. This project is directed toward the commercialization of DSMs for highly reliable fuel cell systems operated under harsh environments. The overall objective of this project is to develop a scaled-up fabrication process geared towards roll-to-roll manufacturing of DSMs.

Approach

A major milestone for the project is to identify a cost-effective route to fabricate 10-12 µm thick microporous DSM support films with 50% area coverage (pore density) and 10-20 µm diameter straight pore holes. Currently, four types of DSM support fabrication techniques have been evaluated based on several criteria including DSM performance, scalability, developmental cost, and final DSM cost. Table 2 shows a brief description of each technique along with their strong and weak points.

Results

Continuous Laser Micromachining. This technique involves the use of a dedicated laser to drill holes through a patterned mask, and it allows for direct, one-step generation of porous films without any intermediate processing steps. Throughout the evaluation of this technique, four laser manufacturing companies have received and tested both polyimide and polysulfone films to generate the hole pattern shown in Figure 1. All four companies have failed to meet the stringent requirements for resolution, speed, and projected cost. As an example, a roll-to-roll continuous laser drilling setup reached a lateral accuracy of ±40µm, much worse than the upper limit of ±3.5 µm to ensure separation of pores. At continuous operation and very high volume, the final cost (excluding the capital equipment) is estimated to reduce to $200/m^2, still an order of magnitude higher than the targeted value of $20/m^2. Based on these results and the high initial and operational costs, the use of continuous laser micromachining is largely eliminated.

TABLE 2. Side-to-Side Comparisons of Various DSM Support Fabrication Techniques

Technique	Description	Pros/Cons
Laser Micromachining	Continuously drilling holes using a dedicated laser	Pro: One step fabrication/materials Con: Slow process and high initial costs
UV Microreplication	UV curing of polymers between a mold and a substrate	Pro: Rapid film formation Con: High material risk
Phase Inversion Solvent Casting	Precipitation of polymers on a mold using a non-solvent	Pro: Ease of processing Con: Waste solvent and film shrinkage
Thermal Perforation	Perforation of polymers using an array of microneedles	Pro: One step fabrication/materials Con: Resolution/ Ragged features

Microreplication of Photo-Curable Polymers. This is a soft lithography approach where ultra-fine (sub-micron) patterns can be generated. It requires the production of a master template, followed by several microreplication processes to obtain the resulting DSM support and eventually the DSM itself after application of the ionomer layer(s). Figure 2 shows an exemplary process flow where a low surface energy mold is applied on a precursor-coated backing layer followed by UV curing to freeze the polymer

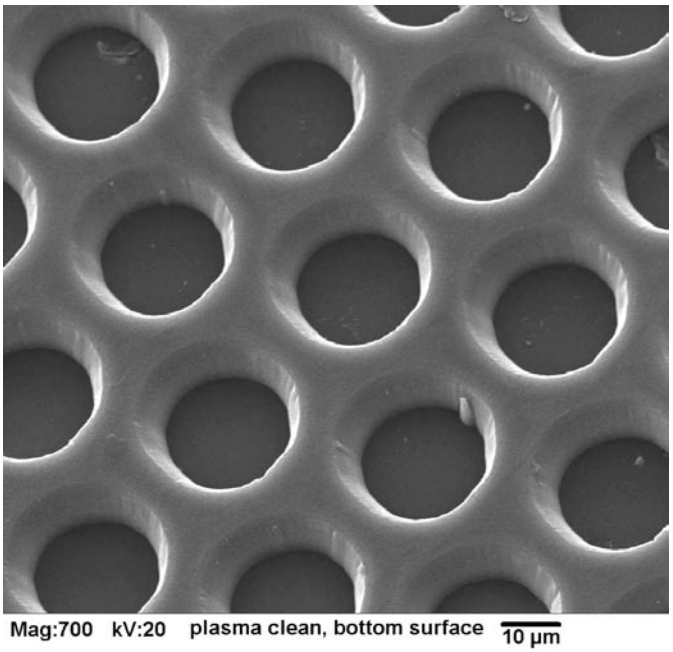

FIGURE 1. Scanning Electron Microscope Photograph of Matrix Support for Low EW PFSA

in place. When the mold is removed, this results in a continuous DSM support with well-defined pores. Due to low material costs and fast processing, this is one of the most promising techniques to meet the target cost of $20/m^2. GES has successfully evaluated a series of photo-curable polymers as DSM support candidates. A UV-shielded cleanroom facility was established to accommodate UV-sensitive material processing. To screen and validate polymers as DSM supports prior to the microfabrication at UMass, commercially available formulations of polyimide, epoxy, thiol-ene, and urethane were cast from their precursors and monomers to desired thickness. Controlled exposure to UV-light yielded films that were tested for water uptake, acid resistance, and dimensional stability at temperatures up to 95°C. Polymers that successfully passed the first stage were then subjected to extensive mechanical testing by immersing the films in hot (80°C) water and determining their static (tensile strength, elongation, modulus) and kinetic (creep under stress) mechanical properties. Photo-curable polymers showed very little water uptake, high dimensional stability, and low creep elongation, all superior to that of the ionomers in water (Nafion®). However, their tensile strength and moduli suffer possibly due to the presence of unreacted monomers.

Phase Inversion Solvent Casting. Phase inversion solvent casting technique, first used during Phase II of this project, aimed to develop a new technology to fabricate DSM supports that are less expensive and easier to scale up compared to the laser micromachining. Poly(dimethyl siloxane) (PDMS) elastomer molds, inverted (pin) pattern of Figure 1, were replicated by GES from a master template fabricated at Harvard University's Center for Nanoscale Systems. In this process, polysulfone was dissolved in a solvent, followed by casting on PDMS to fill the micromold as shown in Figure 3. This assembly was then transferred into a gelation bath filled with non-solvent (e.g. water),

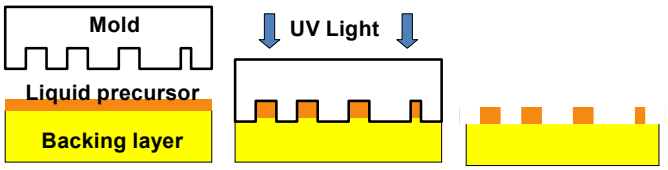

FIGURE 2. Liquid Displacement Method using a Prefabricated Mold followed by UV-Curing to Yield Porous DSM Support

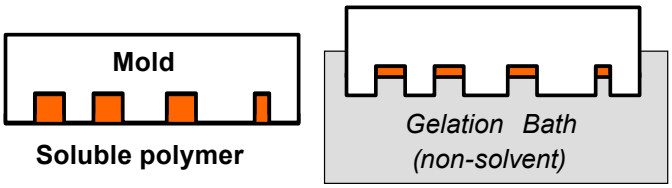

FIGURE 3. Schematic Representation of the Phase Inversion Solvent Casting Process to Precipitate a Polymer in a Non-Solvent

miscible with the initial solvent. This combination yielded the rapid precipitation of the polymer inside the micromold to form a film with well-defined micropores. In Phase II, this approach showed great promise for integration into a fast roll-to-roll process; however, the support prepared by this process is usually not strong enough to withstand further processing and has sponge-like morphology to result in high water uptake. To circumvent this issue, a film has been cast on a PDMS micromold followed by annealing at temperatures above its Tg to show 3-5 fold increase in both eleastic moduli and tensile strength.

Thermal Perforation with Microneedles. If a scalable route can be established for direct perforation of polymers to yield porous support layers, it may prove to be a very attractive technique since the resulting support structure will have identical performance unlike the case for photo-curable and solvent cast films where further material validation is required upon fabrication. To further explore this path, GES has partnered with an acclaimed company in the area of microfabrication to employ embossing (puncturing) of softened thermoplastics using an array of microneedles. Figure 4 shows the preliminary results from a trial run performed for GES where an array of microneedles is used to puncture an 8 µm thick polysulfone (PSU) film. PSU is the ideal material choice for this application due to its low cost, superior mechanical properties and low softening temperature as well as its insignificant dimensional changes in all three axes.

Conclusions and Future Directions

The goal by the end of fourth quarter is to demonstrate a scalable process for cost-effective manufacturing of DSM for fuel cells. In addition to further investigation of feasibility of direct laser machining and mold-based phase inversion cast methods, GES has shown two additional methods that will be capable of performing this goal. The microreplication method requires further validation of mechanical properties of photo-curable polymers, which will be performed in collaboration with UMass. The PSU supports generated by thermal perforation method will be inspected by GES to determine whether the method can produce a material with closely packed micropores to meet the 50% porosity

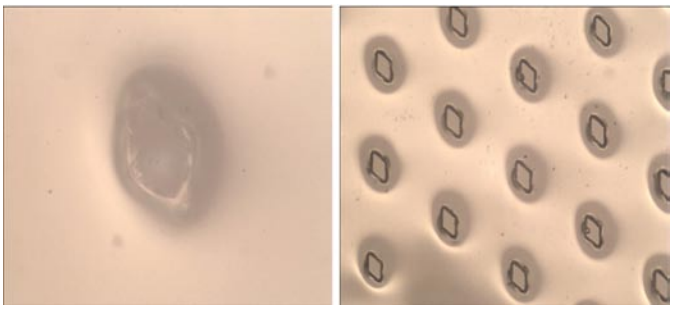

FIGURE 4. Optical Micrographs of a PSU Film Punctured using Microneedles shown at 10X (left) and 40X (right) Magnification

requirement. GES will select the most promising fabrication route and focus on scaling, performance optimization, and cost reduction.

FY 2011 Publications/Presentations

1. Mittelsteadt, C.M. "DE-EE0004533 Giner Electrochemical Systems Q1 Report" Jan. 2011.

2. Mittelsteadt, C.M. "DE-EE0004533 Giner Electrochemical Systems Q2 Report" Apr. 2011.