V.G.18 Dimensionally Stable High Performance Membrane

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Objectives

- Demonstrate low-cost, scalable, continuous manufacturing process of the dimensionally stable membrane (DSM™) support structure.
- Develop membrane electrode assembly (MEA) based on DSM™ with high relative humidity (RH) cycling and freeze/thaw (F/T) durability.
- Identify weak areas of the MEA and develop/ evaluate local reinforcement strategy.
- Evaluate the effect of F/T cycling and impact on MEA configuration.

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

Technical Targets

The goal of this DOE Small Business Innovation Research project is the development of a DSM™ that has excellent dimensional stability during F/T and RH cycles and superior mechanical properties under wide temperature range and RH conditions. The membrane should also demonstrate better durability than Nafion® under accelerated operating conditions. Additionally, better performance and mechanical properties are targeted toward conventional perfluorinated sulfonic acid membranes.

Accomplishments

- Successfully developed a low-cost manufacturing process for DSM™ with good scalability.
- Localized reinforcement, with edge protection, demonstrates further improvement on MEA lifetime. Edge-protected DSMs™ demonstrated more than 3X longer lifetime than Nafion® 112-based MEAs in accelerated RH cycling tests.
- DSMs™ based on the new manufacturing process show 10X better in-plane swelling stability than Nafion® 112.
- DSMs™ show more than one order of magnitude less creep rate compared to Nafion® 112.
- Micromolding-based fabrication technology produces samples with well-defined patterns.

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Introduction

By developing a novel membrane support structure, a polymer electrolyte membrane with extremely high mechanical strength and XY stability can be prepared. In addition to its high strength compared to conventional uniform microporous support material, the support structure can be designed to specifically reinforce certain weak areas, which can significantly enhance the lifetime of the MEAs without sacrificing performance.

Approach

Improved mechanical properties of the DSM™ are achieved by employing a high-strength support structure fabricated from high-performance engineering plastics. The pattern design of the support structure is completely customizable so that the weak areas, such as edges, can be specifically reinforced to further enhance the durability.

By employing the high-strength support structure, lower-equivalent-weight ionomers, which are too mechanically weak to be implemented in fuel cells, can be used without sacrificing mechanical durability. Thus, higher performance, especially at lower RH levels, can be achieved.
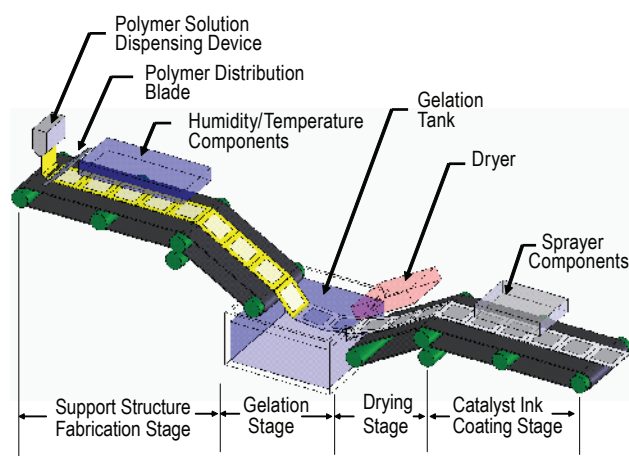
Results

Previous studies at GES showed that the percent elongation at failure of the Nafion® membrane reduces drastically after F/T cycling under dry conditions (Table 1). These F/T cycling tests under dry conditions were conducted for >380 cycles from -40°C to 80°C. For the F/T test in this project, the membrane sustained ~300 cycles. With similar tensile strength tests, the N112 membrane does not show any significant decrease in percent elongation at failure after the F/T tests. The percent elongation at failure of the membrane after F/T test maintains at >300%, which is significantly higher than the results obtained from the dry F/T tests. More cycling will be conducted to match the number of cycles in the dry F/T test. It is unlikely that the membrane will become brittle, since the presence of water at elevated temperature should facilitate chain movement that can relieve any structural change during the freezing process.

To reduce the manufacturing cost of a DSM™ support, a micromolding process was developed. The concept of micromolding is to cast a thin layer of polymer solution to a mold with microscopic surface features, such as cylinders. The mold, with the polymer solution, is then transferred into a gelation bath. This process is usually referred to as phase-inversion, which has been widely used in membrane manufacturing for water filtration and purification applications. Once the polymer solution is in contact with the gelation liquid, usually water, the polymer starts to precipitate and solidify. When the polymer solidifies completely, it forms a patterned support structure that can be readily lifted off and processed further to form a supported membrane.

The whole membrane manufacturing process, starting from a polymer solution and resulting in finished MEAs, is schematically illustrated in Figure 1. The system is designed for roll-to-roll continuous fabrication. As shown in Figure 1, humidity/temperature components can be employed in the Support Structure Fabrication Stage. This set of devices is to ensure that the support structure has an open hole structure without

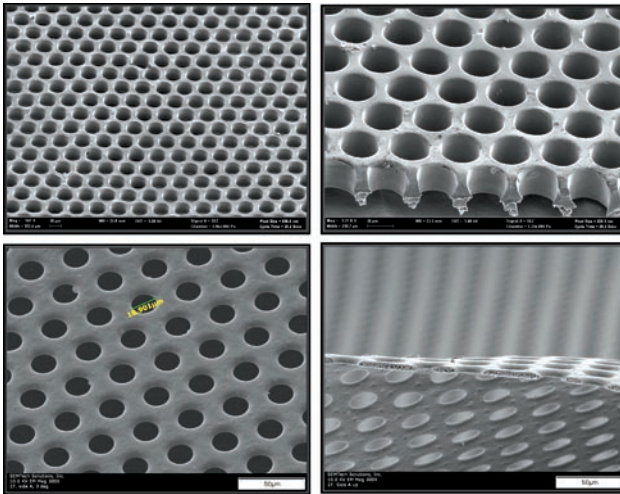**FIGURE 1.** Schematic Illustration of MEA Fabrication Based on DSM™ Technology

surface skins. After the gelation stage discussed above, the supported structure is passed through a drying stage before ionomer solution is coated onto the support structure. The catalyst ink can also be directly coated onto the DSM™ due to the exceptional dimensional stability of the DSM™. Based on this system design, mass production of MEAs can be achieved in a cost-effective fashion.

Before fabricating the support structure, a micro-mold with well defined microscopic features must be prepared. Four fabrication technologies have been employed:

(1) Direct laser micromachining on Kapton® thick film.
(2) Direct laser micromachining on epoxy coated metal shim.
(3) Deep reactive ion etch silicon hard mold.
(4) Flexible mold based on soft-lithography technology.

Mold samples have been successfully prepared based on the technologies above. Based on several criteria, such as ease to fabricate, overall cost, implementation flexibility, feature size and definition, soft-lithography is identified as the best fabrication approach. This technology is currently being developed in the Center for Nanoscale Systems at Harvard University, where GES is a club member.

Preliminary samples show excellent feature definition based on a semi-automatic batch type coating machine (Figure 2). As shown in Figure 2, support structures with a thickness of 5 – 30 microns have been successfully developed. Several preparation parameters can be adjusted to optimize the product properties, such as coating speed, solution concentration, mold pattern and depth. Additionally, the formulation of the polymer solution can be changed with pore former/modifier to create a support structure with high surface

TABLE 1. Percent Elongation at Break of Nafion® 112 Membranes Before/After Dry/Wet F/T Thermal Cycling

Material	% elongation at break	
	Before Cycling	**After 385 F/T Cycles (Dry)**
Membrane (machine direction)	1290	40
Membrane (cross direction)	320	25
MEA (machine direction)	960	52
MEA (cross direction)	510	37
	Before Cycling	**After 200 F/T Cycles (Wet)**
Membrane (machine direction)	> 300	> 300
Membrane (cross direction)	> 300	> 300

FIGURE 2. Scanning Electron Micrographs of Micromolded Support Structures

porosity. The surface pores on the support structure will facilitate mechanical binding between support structure and the ionomer, which eliminates concerns of potential delamination issues. Additionally, the ionomer can partially penetrate the support structure, creating an ionomer interpenetrating zone. This zone will be ionic conductive and lowers the conductivity penalty from the support structure.

Currently, polysulfone (PSU) is employed as the material for the support structure. Several other candidates have also been investigated. The main requirements for support materials are: high mechanical strength, excellent hydrolysis resistivity in strong acidic conditions and can be solution cast to form uniform films. Three major candidates are identified as shown in Table 2. All three polymers have significantly higher strength compared to the currently used polysulfone material (Table 2).

**TABLE 2.** Mechanical Strength of Different Candidate Materials for Support Structure Fabrication

Polymer	Tensile Strength (psi)
Primospire	30,000
Celazole PBI	23,000
Torlon PAI	22,000
PSU	10,200

To test the compatibility of the polymers with the micromolding process, a suitable solvent system must be found for these polymers. Primospire from Solvay Advanced Polymers was the first candidate to be characterized. Primospire is a type of polyphenylene produced by Solvay Advanced Polymers. The manufacturer claims that Primospire can serve as a polymeric replacement for steel applications, which is

exemplified by the very high tensile strength. Unlike polyimide (Kapton®), which also has a very high strength, the Primospire can be dissolved by certain solvents. The solvent recommended by the manufacturer is a 1:1 toluene: N-methyl-2-pyrrolidinone (NMP) mixed solvent. However, this solvent system is not compatible with current micromolding processes since toluene is not soluble in water. During the coagulation process, the toluene can be trapped inside the polymer phase and can potentially lead to defects. This problem can be remedied by changing the coagulation solution from pure water to a solvent mixture so that toluene can be extracted from the membrane. Alternatively, a more suitable solvent can be used to avoid the problem with toluene. Thus, a wide spectrum of organic solvents are used to test the solubility of the Primospire: NMP, dimethylacetamide, tetrahydrofuran anhydrous, propylene carbonate, n,n-dimethylformamide, methyl ethyl ketone, diethyl-carbonate, dimethyl-carbonate, acetone, toluene, chloroform, 1:1 toluene/NMP,1:2 acetone/NMP. Among these solvents, five solvent systems show promising results. The dissolution tests were conducted at 80°C since none of these solvents can dissolve the polymer at room temperature. It is identified that NMP is the best solvent for Primospire for the micromolding process.

As expected, the X-Y swelling stability of the PSU-supported membrane is comparable to the Kapton®-supported membrane (Figure 3). Compared to an unsupported Nafion® 112 membrane, the PSU supported membrane shows a strong benefit in terms of X-Y swelling stability.

As discussed in a previous report, RH cycling induces significant stress on MEAs. MEAs based on Nafion® 112 membranes can fail within ~100 cycles. Low voltage threshold was used to determine the end of life for the MEAs. Once the voltage drops below 0.1 V, the experiment stops and the MEA is tested for leakage. During this report period, it was found that
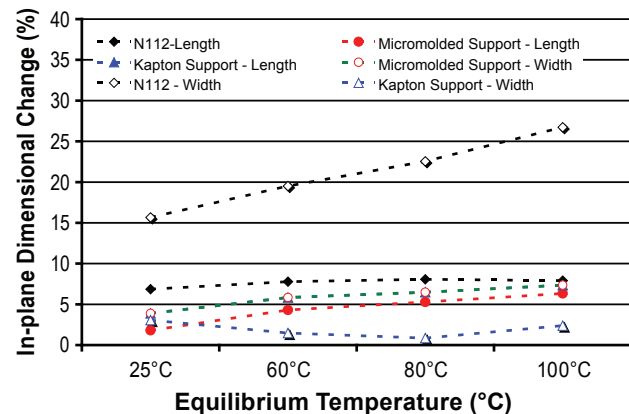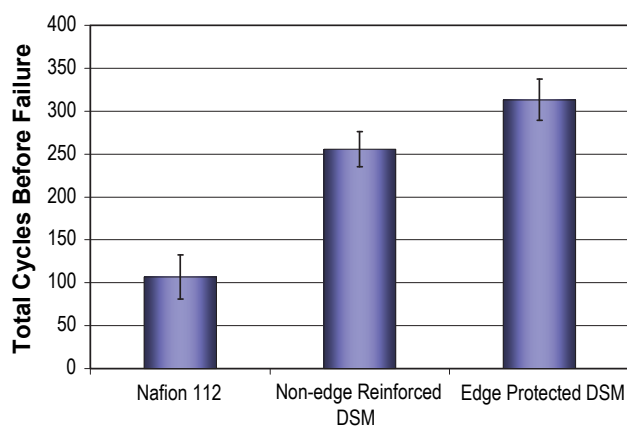

FIGURE 3. Water Swelling Stability of DSM™-Based on Micromolded Support Structure

certain samples do not show any voltage decay during the experiment. As an example, one experiment was stopped at 22 hours and the MEA was tested for leakage. Severe edge failure was observed for this sample while no significant voltage drop was observed. Thus, certain edge failures do not immediately lead to voltage drop, presumably due to the location of the failure and balanced gas pressure. This phenomenon can lead to artificially better lifetimes for the MEAs. Thus, voltage is not a reliable parameter to judge the starting point of membrane failure.

In order to reliably determine membrane failure, the RH cycling test is paused approximately every 24 hours. Gas crossover rate is then measured to verify membrane integrity. This method generates more reliable results than the voltage drop measurements.

To eliminate/reduce edge failures, catalyst edge overlap MEA configuration was employed. In catalyst edge overlap strategy, the laser micromachined area is smaller than the catalyst edge. Thus, the electrochemical reaction is completely stopped. This is the preferred mitigation approach for large MEAs since it can potentially eliminate the edge problem while the surface area loss due to catalyst overlap is minimal. Alternatively, sub-gasketing can also be used to reinforce the edge area. However, thin sub-gaskets are extremely difficult to handle, adding a significant manufacturability problem to the already complicated fuel cell stack structure.

By adding protection to the edges, the lifetime of the MEAs was further extended (Figure 4). The edge-protected DSM^{TM} MEAs show more than 3X lifetime compared to Nafion®-based MEAs. Additionally, the catalyst overlapped DSM^{TM} completely eliminates the edge failure problem. Pinhole formation, instead of edge failures, leads to failure in the active area. Thus, the failure mode will be more gradual compared to a catastrophic edge failure.

Conclusions and Future Directions

DSM^{TM} demonstrates superior mechanical strength and significantly better mechanical stability compared to unsupported membranes. Consequently, an improvement of 3X in lifetime has been demonstrated in accelerated fuel cell tests. A low-cost, scalable manufacturing process is being developed to demonstrate a continuous fabrication of the support structure. To further improve the performance and decrease the fabrication cost, the following areas will be studied:

- Further develop alternative fabrication methods. Evaluate the new support structure and compare to the DSMs^{TM} based on existing technology.
- Design and test locally reinforced DSMs^{TM}.
- Evaluate new polymer materials for DSM^{TM}.
- Demonstrate continuous DSM^{TM} support fabrication.

Special Recognitions & Awards/Patents Issued

1. Liu, H., A.B. LaConti, C. Mittelsteadt, T.J. McCallum, "Solid Polymer Electrolyte Composite Membrane Comprising Laser Micromachined Porous Support," U.S. Patent Application 20060065521.

2. Liu, H. and A.B. LaConti, "Solid Polymer Electrolyte Composite Membrane Comprising Plasma Etched Porous Support," U.S. Patent Application 20060065522.

References

1. M.F. Mathias, R. Makharia, H.A. Gasteiger, J.J. Conley, T.J. Fuller, C.J. Gittleman, S.S. Kocha, D.P. Miller, C.K. Mittelsteadt, T. Xie, S.G. Yan and P.T. Yu, The Electrochemical Society Interface, Fall (2005).

FIGURE 4. DSM Samples Show Significantly Longer Lifetimes Compared to Nafion® 112 Samples for RH Cycling Tests