V.M.20 Dimensionally Stable High Performance Membrane

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Objectives

- Develop membrane electrode assemblies (MEAs) based on dimensionally stable membrane (DSM^{TM}) with high relative humidity (RH) cycling and freeze/thaw durability.
- Identify weak areas of the MEA and develop/evaluate local reinforcement strategy.
- Develop/improve patterning technology for support structure.
- Evaluate the effect of freeze/thaw cycling and impact of 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 project is the development of a DSM™ that has excellent dimensional stability during freeze/thaw 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 against conventional perfluorinated sulfonic acid membranes.

Accomplishments

- DSM™s demonstrate 2-3X longer lifetime than Nafion®112-based MEAs in accelerated RH cycling tests.
- DSM™s show 10X better in-plane swelling stability than Nafion®112.
- DSM™s 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 normal 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

Higher 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 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 the fuel cells, can be used without sacrificing mechanical durability. Thus, higher performance, especially at lower RH levels, can be achieved.

Results

To study the effect of RH cycling on MEA integrity, AC impedance is monitored throughout the RH cycling test. As can be seen from Figure 1, the impedance at 80°C for a Nafion 112 MEA does not show any detectable change over ~190 thermal cycles and 330 h. During normal cell operations, the AC impedance has been widely employed as a characterizing tool to monitor membrane dehydration. Based on ex-situ experiments, Nafion®112 membranes show 2X impedance when the RH is reduced from 95% to 80% [1]. Since there is no change in impedance, the membrane has not been dehydrated during the freeze/thaw cycling. Additionally, since all fuel cell tests are conducted in the 80°C range, there will be no impedance penalty on fuel cell performance after extensive freeze/thaw cycling.

In contrast to the impedance at 80°C, the impedance measured for a Nafion®112 MEA at -40°C exhibits an almost 100% increase over the test period (Figure 1). The underlying mechanism for this observation has not been well understood. During the long test period, frost condenses heavily inside the environment chamber, which can lead to slower thermal transfer from the heat exchanger. The cooling period is 9% longer at the end of cycling compared to the initial value. Such a minor change cannot account for the significant increase of impedance. Alternatively, it is also possible that the ice lens formation starts between the diffusion medium and the catalyst layer after ~120 cycles. Such icing behavior will push the diffusion medium away from the membrane under sub-freezing temperatures and a significant increase of cell impedance would be observed. Once the ice is thawed above 0°C, the diffusion medium springs back and restores contact with the MEA, which causes no significant loss of impedance under normal operating conditions of fuel cells.

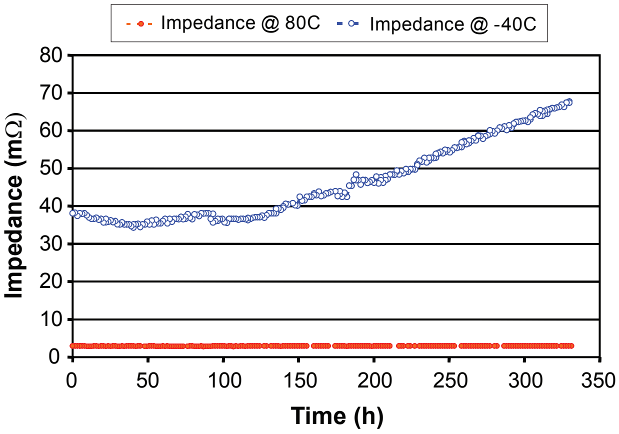

FIGURE 1. Change of AC Impedance of Single-Cell Nafion® 112 MEA over Long-Term Thermal Cycling

The results from fuel cell performance tests support the discussion above; there is no appreciable performance degradation at 7 psi, which indicates that there has been no loss of active catalyst surface area or any severe deterioration of interfaces. On the contrary, a mild performance loss is observed at 25 psi. Such behavior is not well understood. The 25 psi after-freeze (F)/thaw (T) polarization curve is not significantly different from the before-F/T curve at higher current density, which eliminates the possibility of flooding. Overall, the performance loss is fairly small. More repeat experiments are planned.

The main goal for support fabrication is to develop a new patterning technology that can be less expensive and easier to scale-up compared to current technology. The major approach is to develop a method based on a micromolding concept. As shown in Figure 2, a polymer film with a precisely defined pattern can be obtained from the micromolding process.

In order to identify the weak areas of the MEAs and employ localized reinforcement to enhance the durability of the membrane, the effectiveness of the RH cycling protocol must be verified. Similar to F/T cycling experiments, the AC impedance was measured at 1 kHz with an HP 4328A milliohmmeter. It must be stressed that the noise seen in the current density is due to ambient radio frequency (RF)/electromagnetic interference (EMI) noise; the actual current is controlled by the load bank with a far better precision.

An accelerated RH cycling protocol developed by General Motors was adopted to evaluate the MEA local weak area. All tests were conducted at 95°C with ~5 cycles per hour. All cells were tested to failure (0.8 A/cm^2, <0.1 V). As can be seen from Figure 3, the protocol successfully introduced RH cycling on the membrane as exemplified by the periodical change of the cell impedance. The RH cycling induces 6X impedance variation from wet state to dry state. Based on the ex-situ resistance value of Nafion®112 [1], such impedance

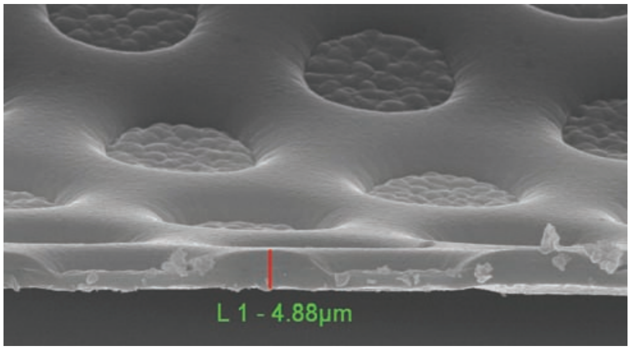

FIGURE 2. Scanning Electron Micrographs of Micromolded Support Structures

change represents an RH range from 40% to saturated conditions, which agrees with the experimental target.

Since there is certain sample-to-sample variation for the RH tests, the RH cycling test for Nafion®112 was repeated five times while two DSM™ samples were tested with the same test protocol. As clearly demonstrated in Figure 4, the DSM™ samples exhibit significantly better durability (2 to 3X) compared to Nafion®112 MEAs. The DSM™-based MEAs can potentially have even better lifetimes, since chemical degradation under this test protocol is quite severe and can also lead to cell failure. If the chemical degradation rate can be reduced, then mechanical advantages of the supported membranes can be further exploited.

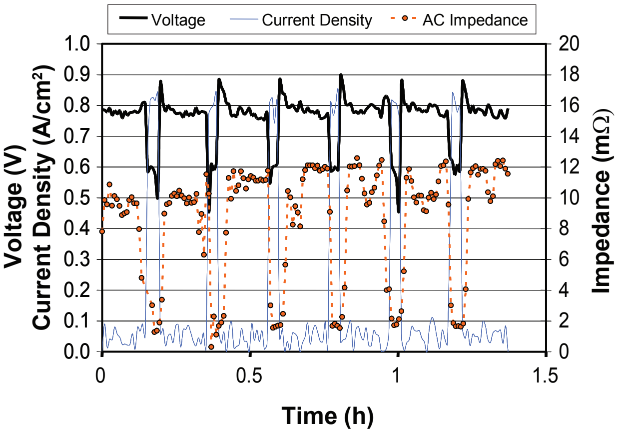

FIGURE 3. Cell Voltage, Current Density and Impedance Profile of Nafion® 112 during RH Cycling Test

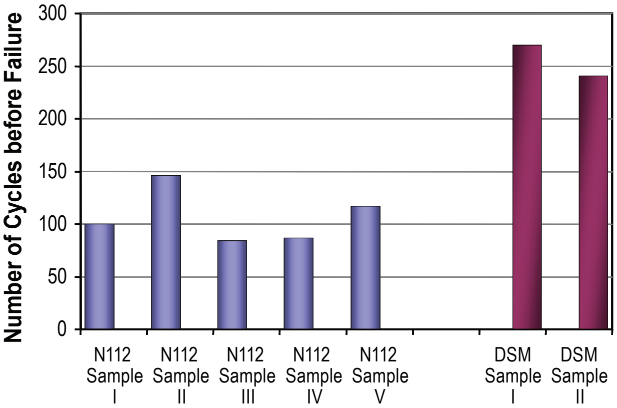

FIGURE 4. DSM Samples Show Significantly Longer Lifetimes Compared to Nafion® 112 Samples for RH Cycling Tests

Conclusions and Future Directions

DSM™ demonstrates superior mechanical strength and significantly better mechanical stability compared to unsupported membranes. Consequently, an improvement of 2-3X in lifetime has been demonstrated in accelerated fuel cell tests. 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 DSM™s based on existing technology.
- Study the freeze/thaw cycling behavior of the corresponding DSM™-MEAs with more comprehensive AC impedance characterization (different frequencies with phase angle information).
- Design and test locally reinforced DSM™s.
- Identify best MEA configuration for freeze/thaw durability.
- Assemble a short stack, ~200 W, to test the performance of DSM™-based MEAs.

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.

FY 2007 Publications/Presentations

1. Liu, H., 2006 DOE Hydrogen Program Review, Arlington, VA, 2007.

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).