V.B.2 High-Temperature Membrane with Humidification-Independent Cluster Structure

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Subcontractor:
Giner, Inc., Newton, MA

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Projected End Date: December 31, 2013

Overall Objectives

- Develop membranes that are capable of operation at up to 120°C for automotive applications.
- Demonstrate improved mechanical properties leading to increased durability.
- Quantify performance and life improvements at conditions relevant to automotive fuel cells.

Fiscal Year (FY) 2013 Objectives

- Design composite membrane with polymer support structure to increase durability at automotive cycling conditions at operating temperatures up to 120°C (overall goal: meet DOE 2020 targets).
- Characterize chemical and mechanical stability using accelerated stress tests.
- Fabricate membrane electrode assemblies (MEAs) to assess in-cell durability at 95°C.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the DOE Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1]:

(A) Durability

(B) Cost

(C) Performance

Technical Targets

This project is developing a multi-component composite (mC^2) membrane to meet the following DOE 2020 technical targets for membranes:

- Membrane area specific resistance: 0.02 Ωcm^2
- Membrane durability:
  - Mechanical: 20,000 relative humidity (RH) cycles (from 0% RH to 90°C dewpoint) with <10 sccm crossover
  - Chemical: >500 hours at steady-state open circuit voltage

FY 2013 Accomplishments

- Supported membrane: Fabricated supported membrane using advanced ionomers and Giner Inc.'s 2DSM™ polymer support materials.
- Swelling: Demonstrated negligible in-plane swelling of the supported membrane.
- Conductivity: Increased in-plane conductivity to three times that of conventional Nafion®.

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INTRODUCTION

This project is focused on the development of composite polymer electrolyte membranes (PEMs) that can operate at low RH and over a wide temperature range (-20 to 120°C). Their main application is in transportation fuel cells. In addition, FCE is considering use of these membranes for co-production of hydrogen from high-temperature fuel cells. The higher operating temperature imparts improved tolerance to impurities, such as carbon monoxide, thereby increasing the co-production efficiency and simplifying the system.

The goal is to develop a structure in which ion-conducting clusters remain intact at low RH. A major challenge is that current proton conducting polymers cannot sufficiently hold on to water under these conditions. Since the conduction mechanism relies on movement of hydrated species, the conducting path is compromised, resulting in low performance. Membranes that can operate at lower RH at elevated temperatures up to 120°C will reduce the fuel cell system complexity and cost by reducing or eliminating the need for a humidifier in the system. This project is developing a composite membrane, in which both the ionic conductivity and mechanical properties are enhanced to meet DOE's 2017 and 2020 goals for transportation fuel cells.

APPROACH

The overall concept for mC^2 is shown in Figure 1. The emphasis in the past year has been to incorporate a polymer support for a mechanically stronger membrane with reduced in-plane swelling for improved durability throughout the range of operating conditions expected in automotive applications. The detailed approach to address the DOE target parameters is summarized in Table 1.

RESULTS

This year's efforts were focused on incorporating a durable support polymer material into the mC^2 membrane. Micrograph pictures of the 2DSM™ support polymer and a composite membrane incorporating the support polymer at its center are shown in Figure 2. The selected support polymer has very high mechanical strength, temperature stability well beyond the expected membrane operating temperature and excellent chemical resistance in the ionomer and fuel cell environment. It is optimized to provide the largest possible void volume while ensuring excellent mechanical support.

Two grades of advanced ionomer were used, with different equivalent weights. In all cases, the introduction of the 2DSM™ support prevented in-plane swelling, as shown in Figure 3. The water uptake with increasing temperature and therefore humidity resulted in swelling only in the thickness direction of the membrane. This swelling is much more easily tolerated by the fuel cell hardware and is not expected to cause issues due to mechanical failure, electrode delamination and contact loss, as is often experienced with significant in-plane swelling. The data points shown in Figure 3 are the average data from three samples. The error bars represent the range of dimensional change obtained at each temperature. They show that an adequate level of confidence was achieved with the measurement setup.

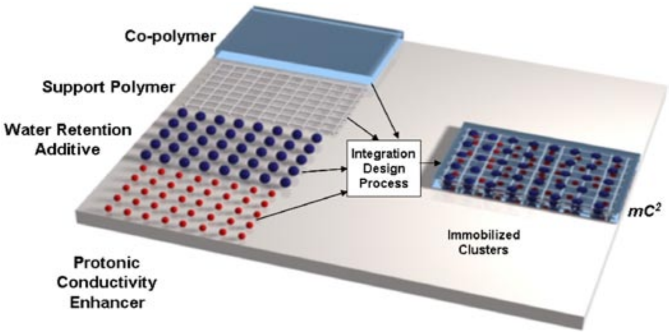
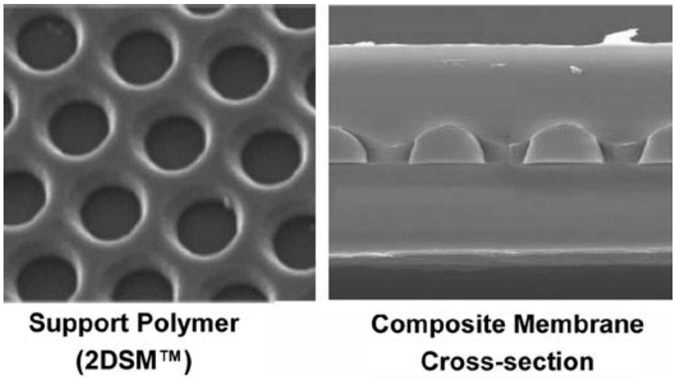


FIGURE 1. Multi-Component Composite Membrane (mC^2) Concept

TABLE 1. Approach for the Composite Membrane

Target Parameter	DOE Target (2017)	Approach
Area specific proton resistance at: 120°C and 40-80 kPa water partial pressure	0.02 Ω cm^2	Multi-component composite structure, lower equivalent weight, polymer support for thinner membrane
80°C and 25-45 kPa water partial pressure	0.02 Ω cm^2	Higher number of functional groups
Hydrogen and oxygen cross-over at 1 atm	2 mA/cm^2	Support polymer for mechanically stronger membrane structure
Minimum electrical resistance	1,000 Ω cm^2	Improved membrane thickness tolerance and additive dispersion
Cost	\$20/m^2	Simplify polymer processing
Durability Mechanical (Cycles with <10 sccm crossover)	>20,000	Mechanically strong support polymer for reduced swelling
Durability Chemical (Hours at steady-state open circuit voltage)	>500	Chemically stabilized ionomer


Support Polymer (2DSM™)

Composite Membrane Cross-section

FIGURE 2. 2DSM™ Support Polymer and Cross-Section of Supported Membrane Incorporating It

Figure 4 shows the in-plane conductivity of one of the first 2DSM™ samples fabricated. The curve exhibits the expected shape, indicating good stability of the membrane throughout the range of relative humidity. The conductivity of the 25-µm thick sample is >60% higher than a Nafion®

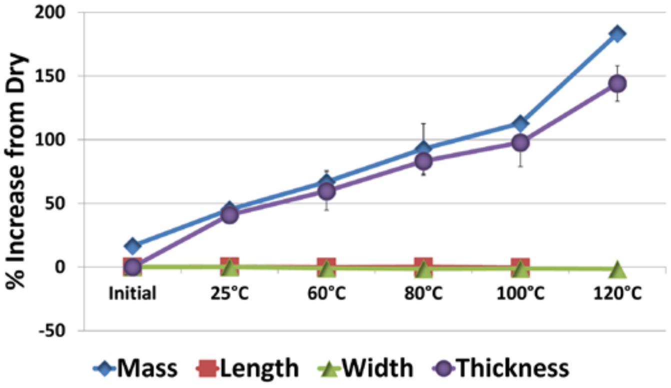


FIGURE 3. Dimensional Stability Measurements Show No Swelling in Length and Width as a Function of Water Uptake

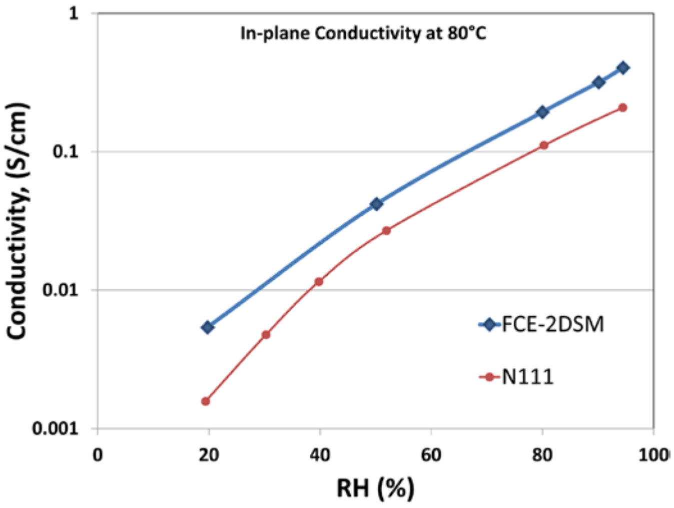


FIGURE 4. Conductivity of the Supported Membrane as a Function of RH is Significantly Improved Compared to a Conventional Nafion® Membrane

membrane of the same thickness. Improvements in the membrane fabrication process and use of the lower equivalent weight ionomer resulted in higher conductivities, up to 3x higher than a 25-µm thick Nafion® membrane, as shown in Table 2.

TABLE 2. Progressively Increased In-Plane Conductivity up to 3x Higher Compared to Nafion®

Sample	Thickness (mm)	In-plane Conductivity (S/cm at 80°C, 50% RH)
N111 (conventional)	25	0.018
DSM-1	25	0.027
DSM-2	20	0.040
DSM-3	25	0.054

CONCLUSIONS AND FUTURE DIRECTION

An mC^2 membrane design with a 2DSM™ support polymer for high-temperature and low-RH operation has been implemented to fabricate membranes with enhanced durability at the DOE target conditions (Table 1). Accomplishments include:

- Successfully incorporated support polymer into advanced ionomer system, resulting in a thin (~25-µm thick) membrane with good handling properties.
- Demonstrated mC^2 with no in-plane dimensional change (swelling) as a function of water content.
- Achieved up to 3x higher conductivity compared to a conventional membrane.

The remainder of the project will focus on fabrication of MEAs and their testing. The tests will include accelerated stress tests to assess membrane durability. Specifically, RH cycling tests to determine the mechanical durability and open circuit voltage tests to assess chemical stability. Testing will also entail fuel cell endurance testing at elevated temperature (95°C) in 25- to 50-cm^2 single cells up to 1,000 hours.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2013 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., May 13–17, 2013.

REFERENCES

1. DOE Office of Energy Efficiency and Renewable Energy (EERE) Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration (MYRD&D) Plan, Section 3.4 "Fuel Cells", http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf.