Dimensionally Stable High Performance Membrane

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Project ID # FCP 12

Overview

Timeline

- Start – June 2005
- End – March 2006
- 100% Complete

Barriers

- Freeze/Thaw Durability
- Low RH Operation
- Ionic Conductivity

Budget

- Total Project Funding: $100 K
- Funding Received: $100 K in FY05

Objectives

- Develop MEAs based on dimensionally stable membrane (DSM) with high freeze/thaw durability
- Enhance MEA X-Y (in-plane) dimensional stability
- Develop MEAs with high ionic conductivity and excellent mechanical properties
- Demonstrate concept feasibility for membranes based on patterned support

Approach

Task 1: Polymer Support Development

- Pattern Design
- Method Validation

Task 2: Membrane Fabrication

- Direct Insertion
- Ionomer Dispersion Coating
  - Automated Spraying
  - Blade Coating

Task 3: Membrane Characterization

- Water Uptake
- Mechanical Properties

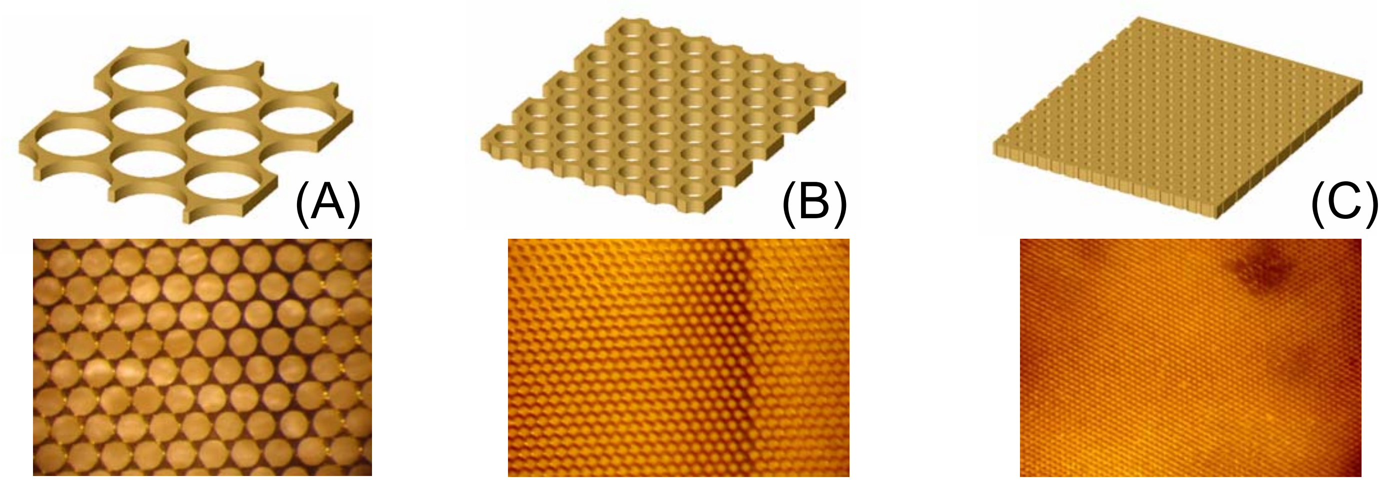
Task 4: Freeze/Thaw and Performance

- Freeze/Thaw Durability
- Performance Evaluation
- MEA Configuration
- Diffusion Media Type

Technical Accomplishments/ Progress/Results

- Supported membranes demonstrate drastically improved freeze/thaw stability compared to Nafion® in *ex-situ* tests.
- Supported membranes show 10X better in-plane swelling stability than Nafion®.
- Supported membranes show more than one order of magnitude less creep rate compared to Nafion®.
- Supported MEA with EW700 ionomer demonstrates superior mechanical properties and 40% performance gain over Nafion®.

Pattern Design

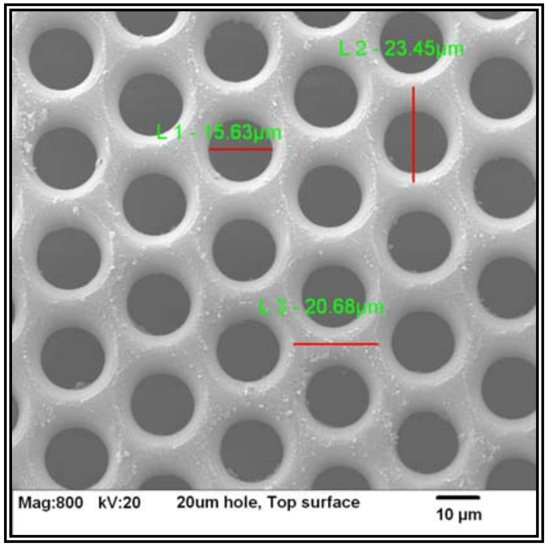


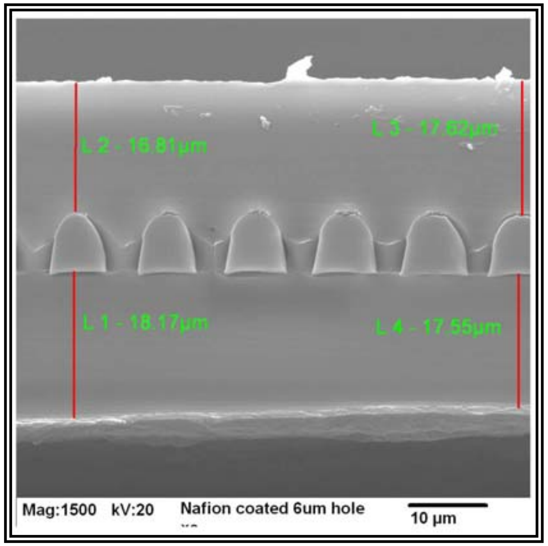
Sample Designation	Hole Diameter (μm)	Wall Thickness (μm)	Percentage Opening (%)
A (H70W7)	70	7	75
B (H25W7)	20	7	50
C (H6W7)	6	7	22

Various support patterns have been successfully fabricated based on Eximer laser technology.

Figures in the top row are schematic illustrations. Figures in the second row are micrographs of the samples.

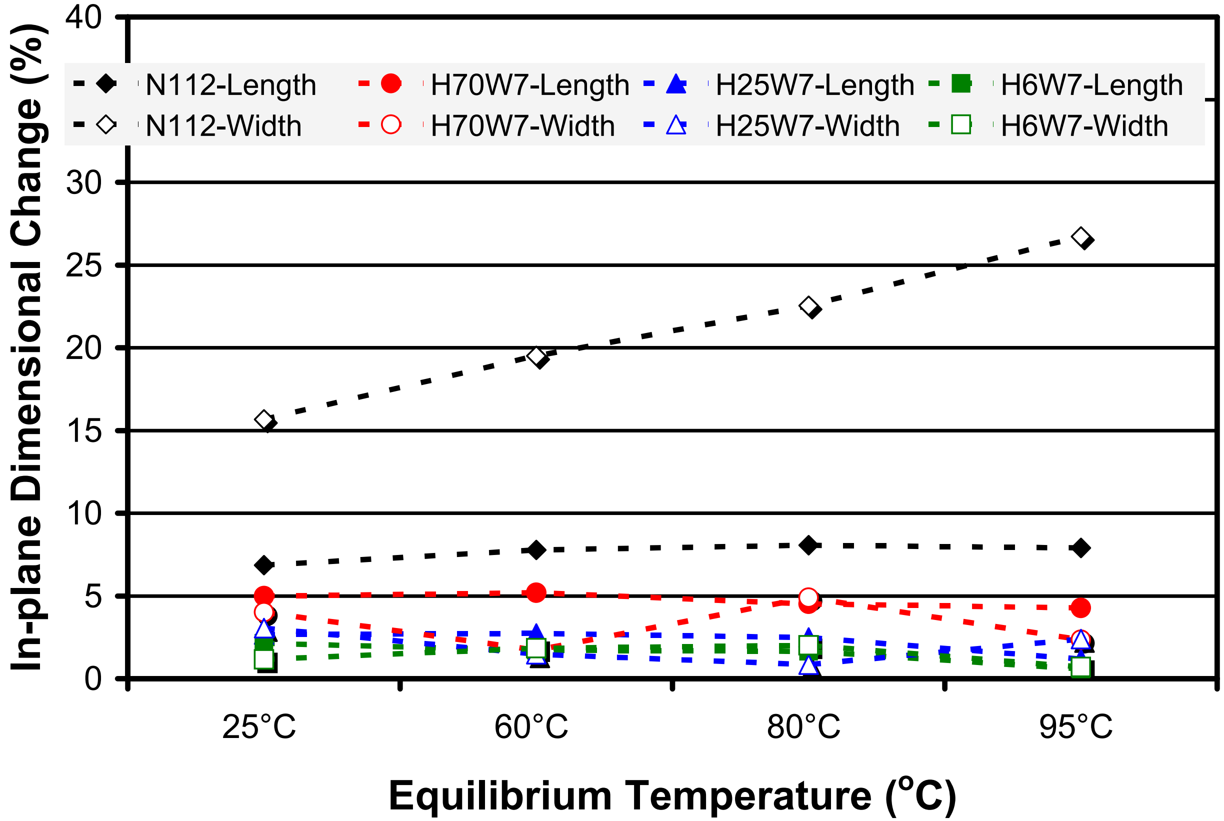
Scanning Electron Microscope Images





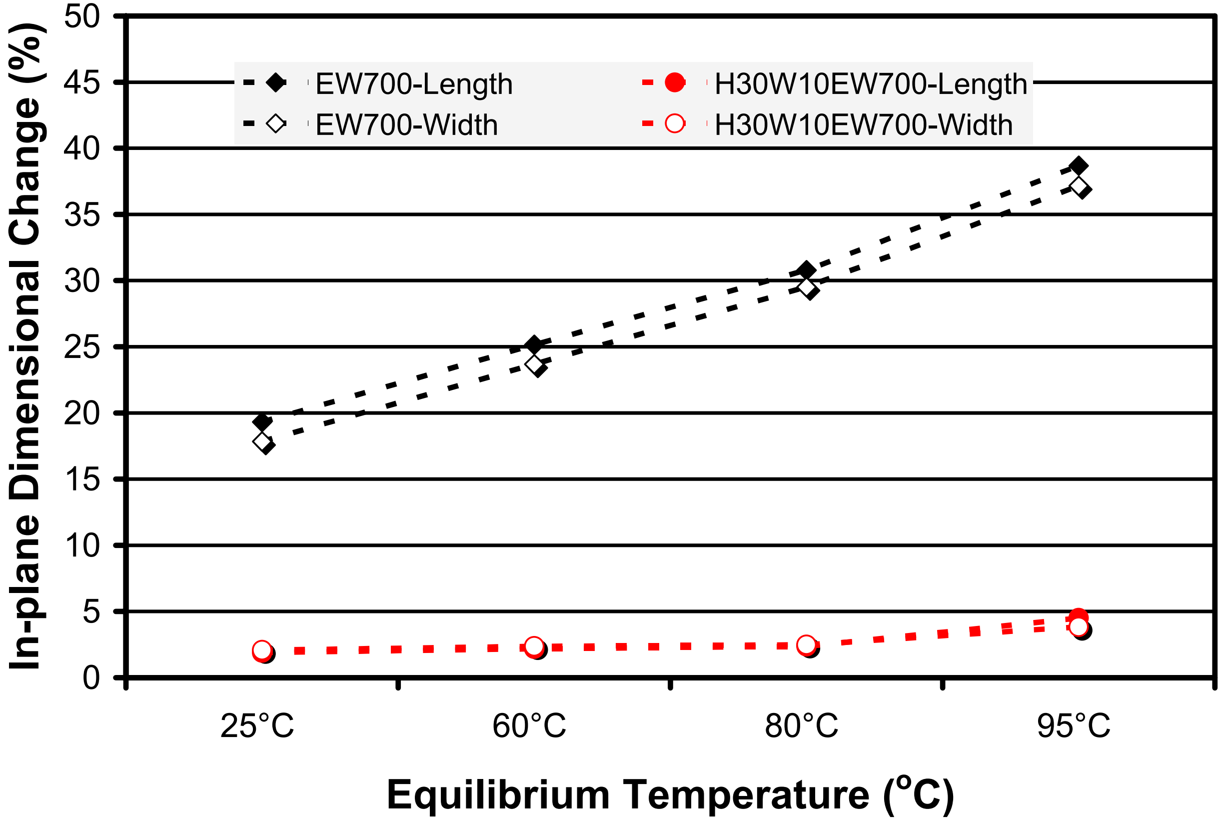
Based on technology developed at GES, DSMs can be readily fabricated with uniformity better than 5%.

Swelling Behavior – EW1100



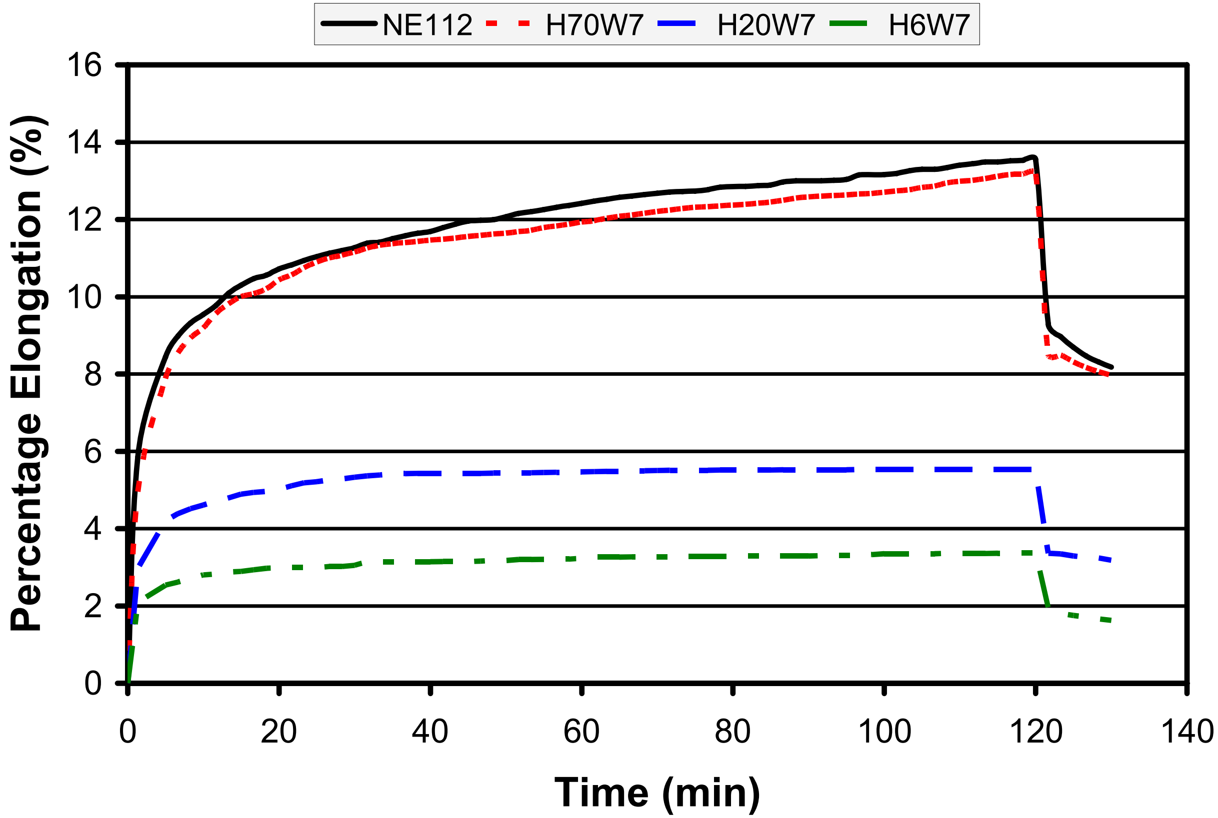
Compared to Nafion, DSMs demonstrate >10X swelling stability at elevated temperatures when submerged in water.

Swelling Behavior – EW700



DSM demonstrates extraordinary dimensional stability compared to non-supported EW700 membranes.

Creep Behavior



0.5 x 15 mm^2 sample, 80°C, 500 mN force, submerged in DI water.

Compared to Nafion, DSMs show more than one order of magnitude improvement on creep rate (percentage elongation / hour).

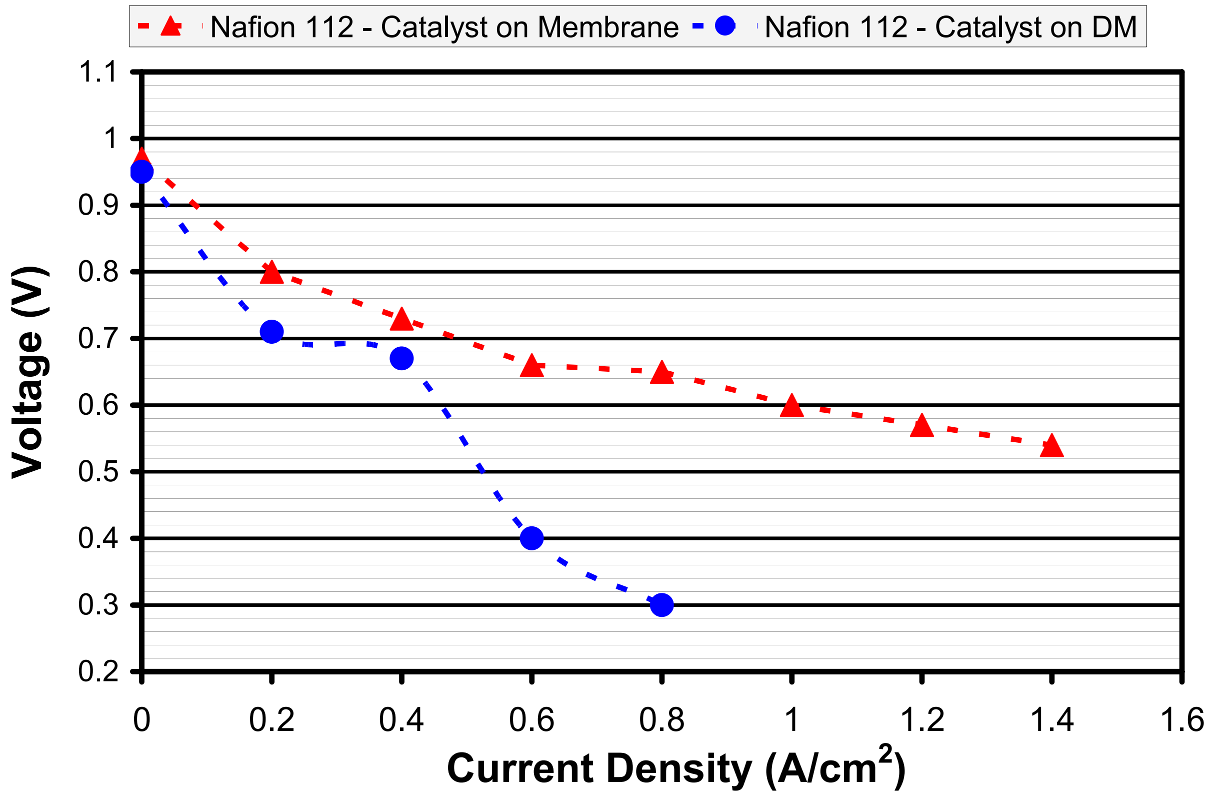
Ex-situ Freeze/Thaw Test

NE112

DSM

After 10 thermal cycles from -40°C to 50°C unconstrained, DSM show no observable degradation while Nafion membrane sustained severe damage.

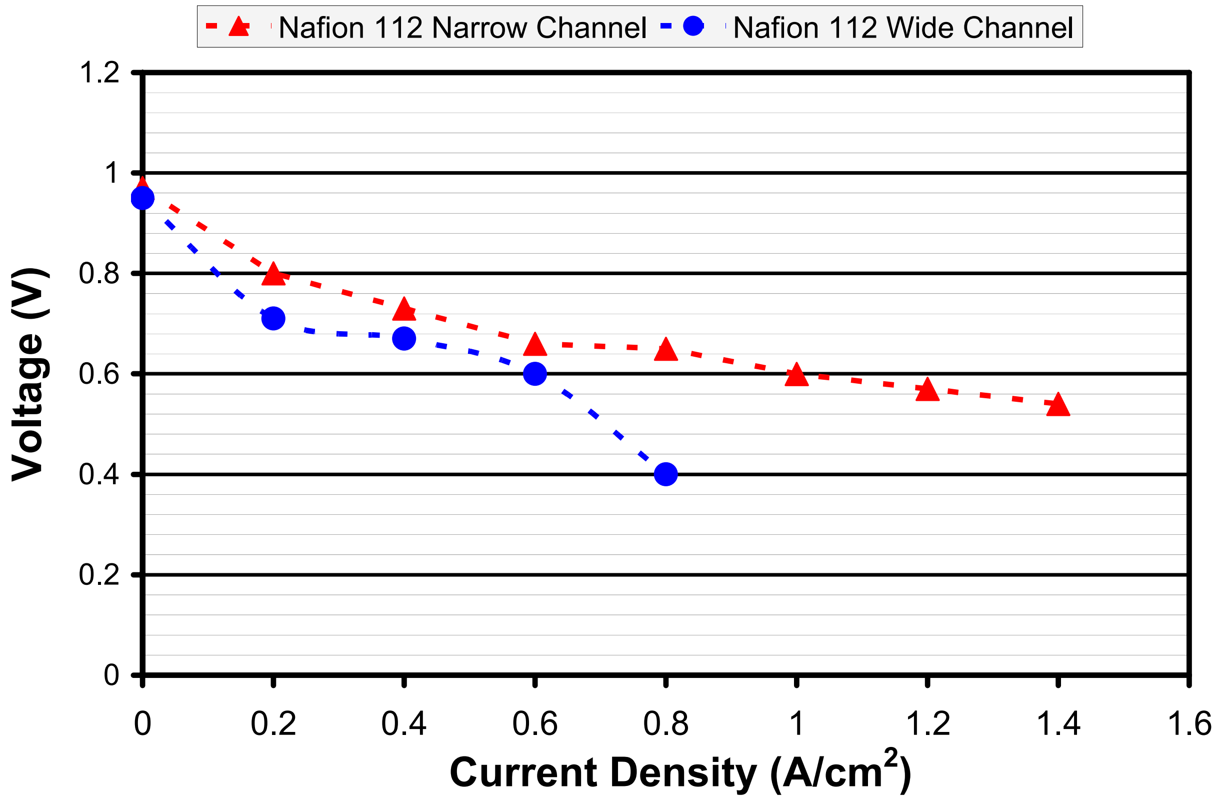
Impact of MEA Configuration



Reactant Gas: H_2 and air, Pressure: 25 Psi balanced, Temperature: 80ºC cell, 64ºC (50% RH) air, 80ºC (100% RH), Gas Stoic: 4*, Mode: Constant current (* Under OCV conditions, the gases supplied at 200 mA/cm^2 equivalent flow.)

MEA with catalyst on diffusion media performed significantly worse than catalyst on membrane.

Impact of Flow Field Geometry



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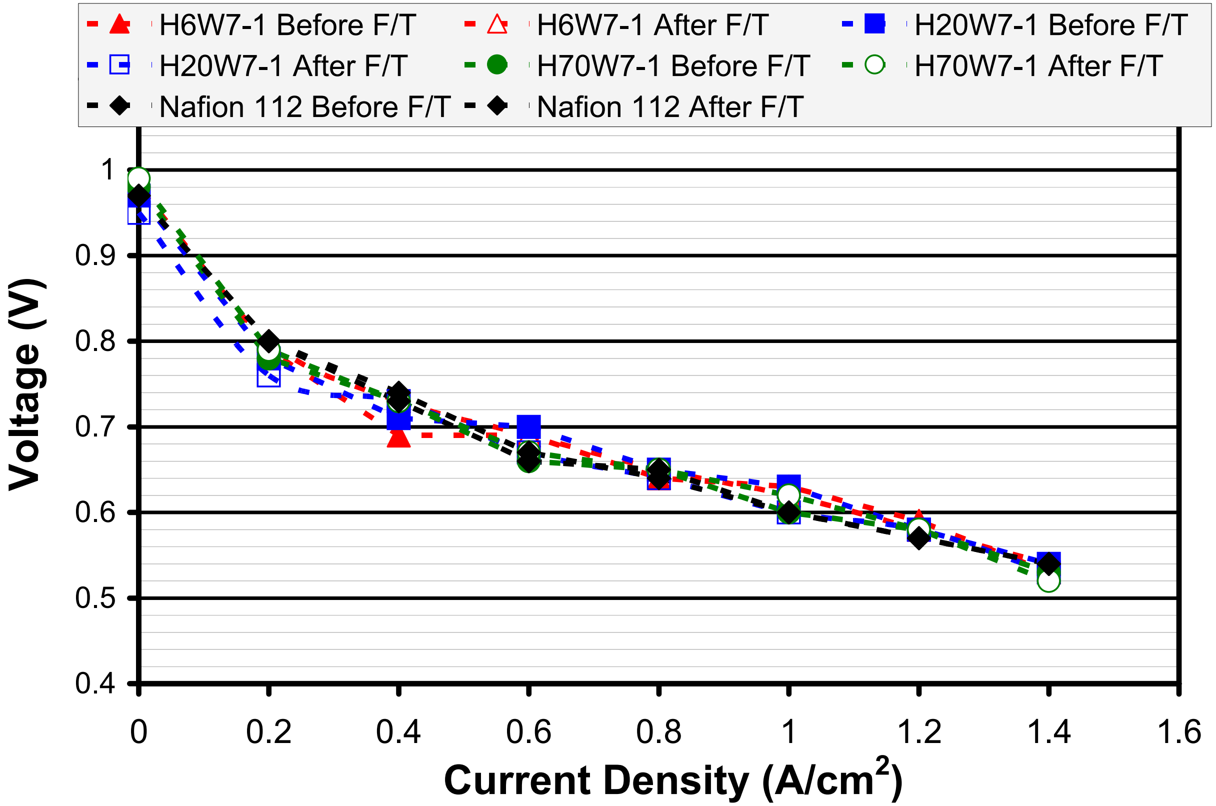
Wide flow channels (2 mm) pose water management problems compared to narrow channels (0.9 mm), given the same gas flow rate.

Freeze/Thaw Impact on Performance



Reactant Gas: H_2 and air, Pressure: 25 Psi balanced, Temperature: 80°C cell, 64°C (50% RH) air, 80°C (100% RH), Gas Stoic: 4*, Mode: Constant current (* Under OCV conditions, the gases supplied at 200 mA/cm^2 equivalent flow.)

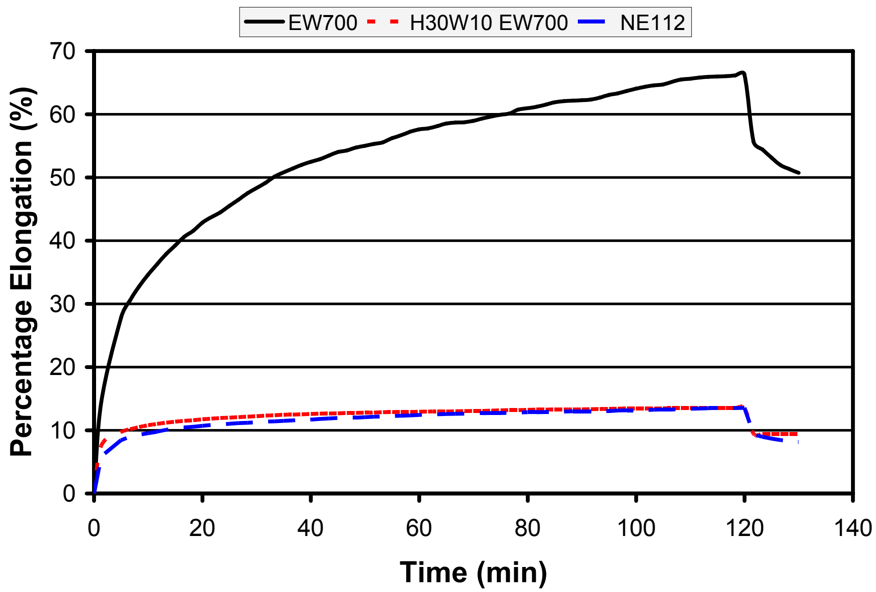
After 40 thermal cycles from -40°C to 50°C, all MEAs demonstrate excellent stability.

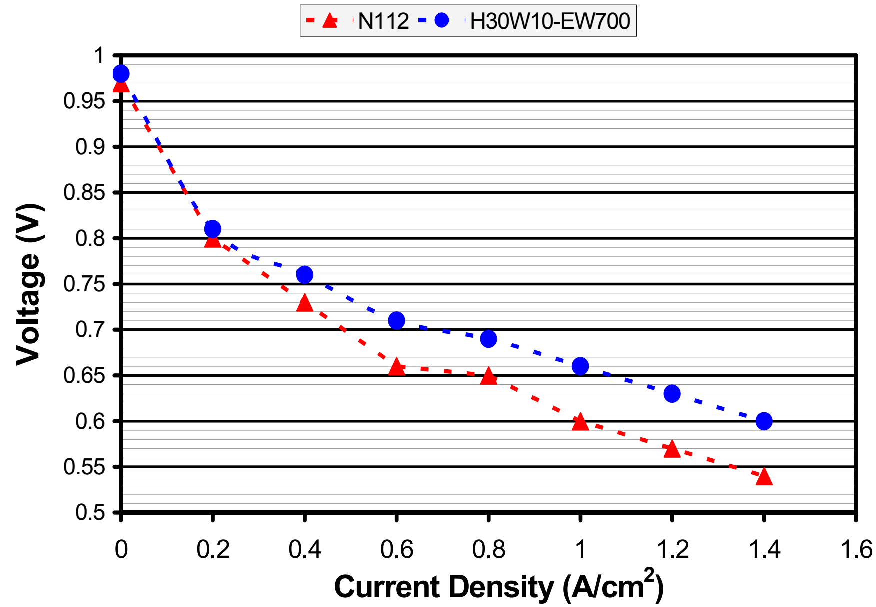
Electrochemical Surface Area (ECSA) Test

Sample Designation	ECSA Before Freeze/Thaw (m^2/g)	ECSA After Freeze/Thaw (m^2/g)
N112	48	46
H70W7	51	48
H25W7	48	47
H6W7	47	49

After 40 thermal cycles from -40°C to 50°C, there is no significant drop of ECSA for all MEAs.

Performance of EW700 Based MEAs





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EW700 based DSMs show comparable mechanical properties to Nafion while providing a 40% performance increase. Unsupported EW700 membrane shows unacceptable poor mechanical properties.

Future Work – Phase II Work Plan

- **Freeze/Thaw Test Protocol Development**
  - Number of Cycles
  - Temperature Range
- **Better Patterning Method**
  - Improve Current Technology
  - Alternative Fabrication Method
  - Alternative Support Material
- **Local Reinforcement**
  - Identification of Problematic Areas
  - Design and Test Locally Reinforced DSMs
- **Identify Best MEA Configuration for Freeze/Thaw Durability**
- **DSM Based Stack Performance Evaluation**

Summary

- DSM with high freeze/thaw durability successfully demonstrated in ex-situ tests.
- Highly uniform DSM successfully developed with projected cost of the patterned support < \$0.02/cm^2.
- DSMs show >10X X-Y (in-plane) dimensional stability compared to Nafion membranes.
- EW700 Based DSM shows a 40% improvement in performance while maintaining comparable/better mechanical properties.

Filed Patents

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 (March 25 2005).

Liu, H. and A.B. LaConti, “Solid Polymer Electrolyte Composite Membrane Comprising Plasma Etched Porous Support,” U.S. Patent Application 20060065522 (March 30, 2005).