# 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

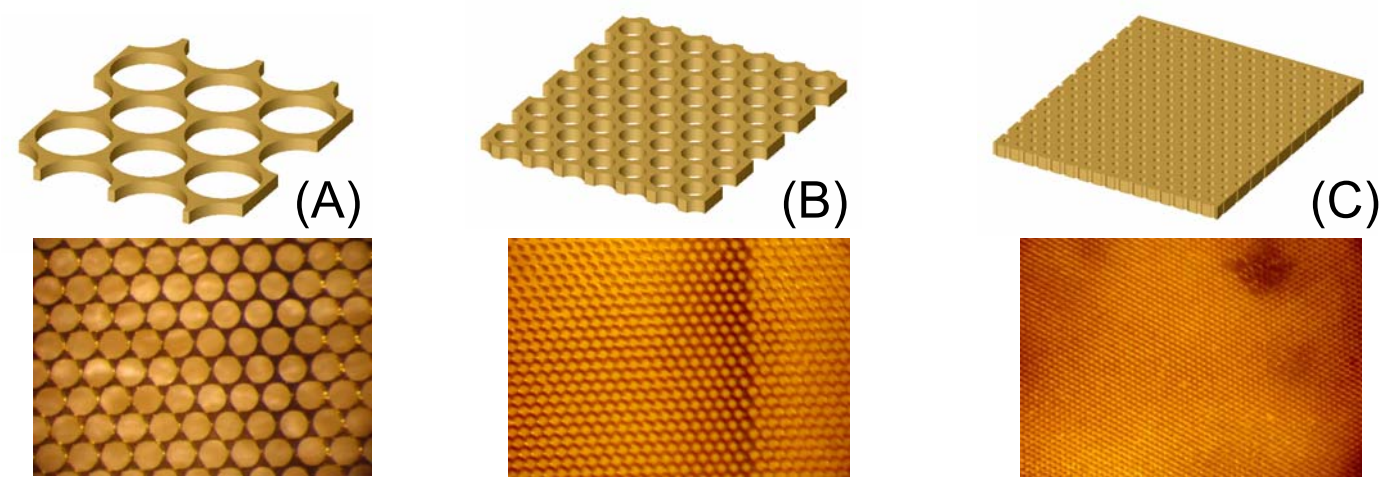
**Task 4: Freeze/Thaw and Performance**

- 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

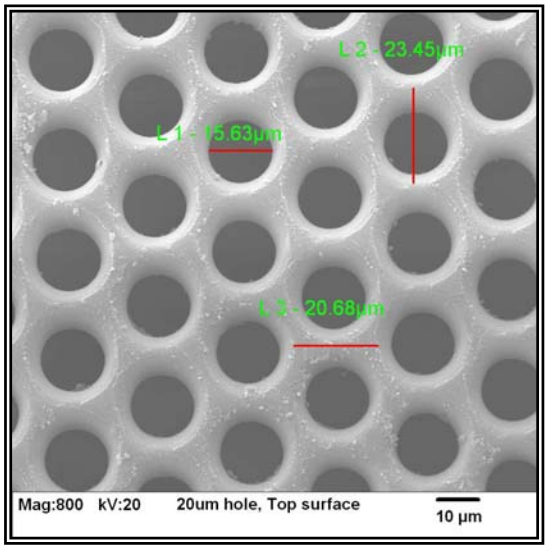


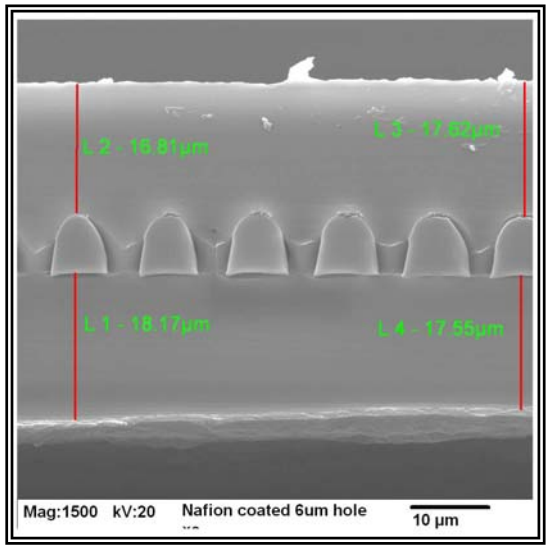

| Sample Designation | Hole Diameter (μm) | Wall Thickness (μm) | Percentage Opening (%) |
|---|---|---|---|
| A (H70W7) | 70 | 7 | 75 |
| B (H25W7) | 20 | 7 | 50 |
| C (H6W7) | 6 | 7 | 22 |

**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.**

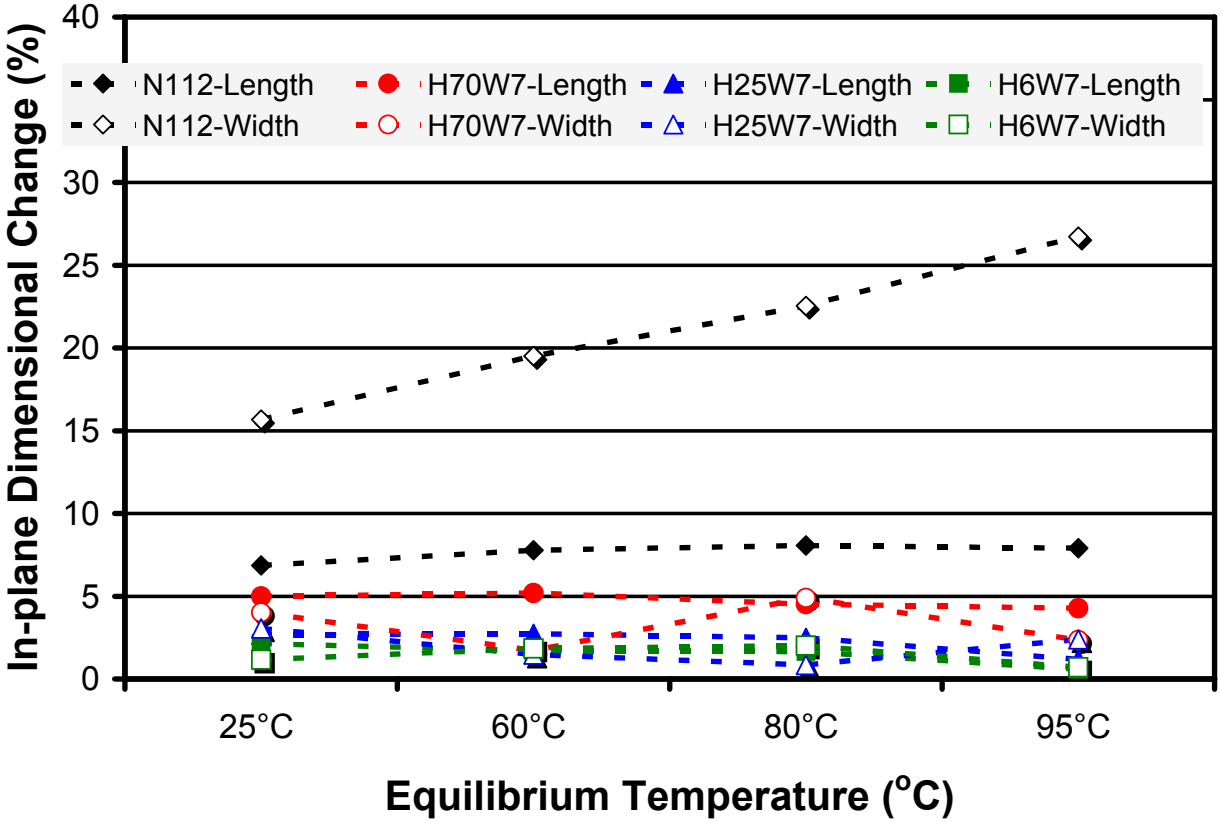
# Scanning Electron Microscope Images



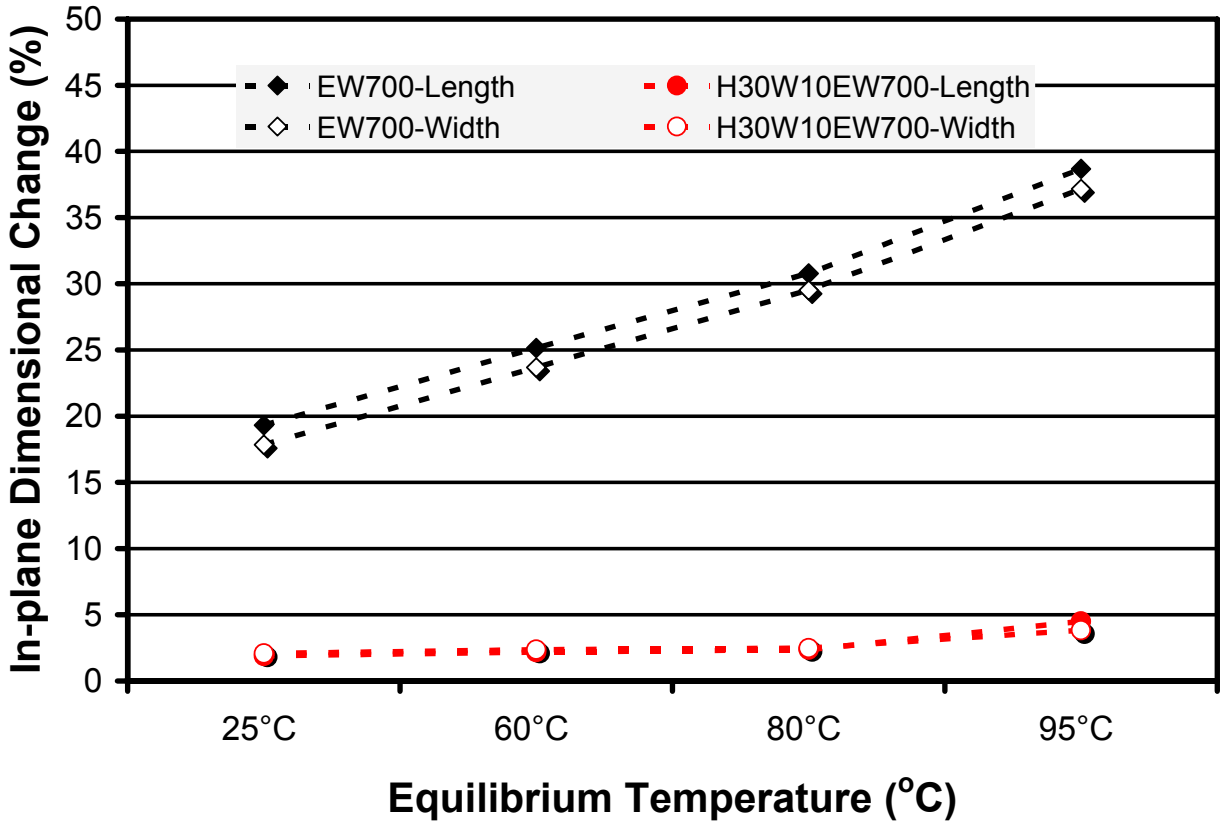

**Based on technology developed at GES, DSMs can be readily fabricated with uniformity better than 5%.**

# Swelling Behavior – EW1100



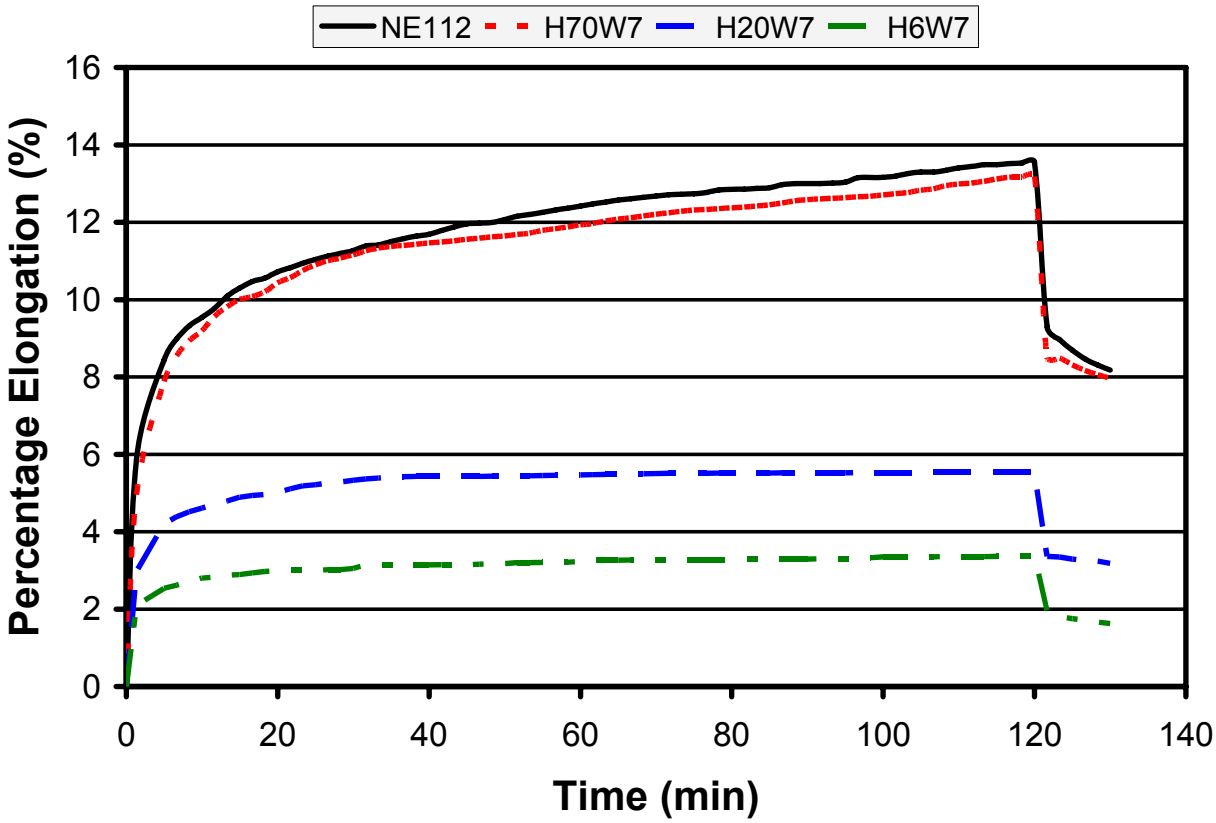

**Compared to Nafion, DSMs demonstrate >10X swelling stability at elevated temperatures when submerged in water.**

# 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).**

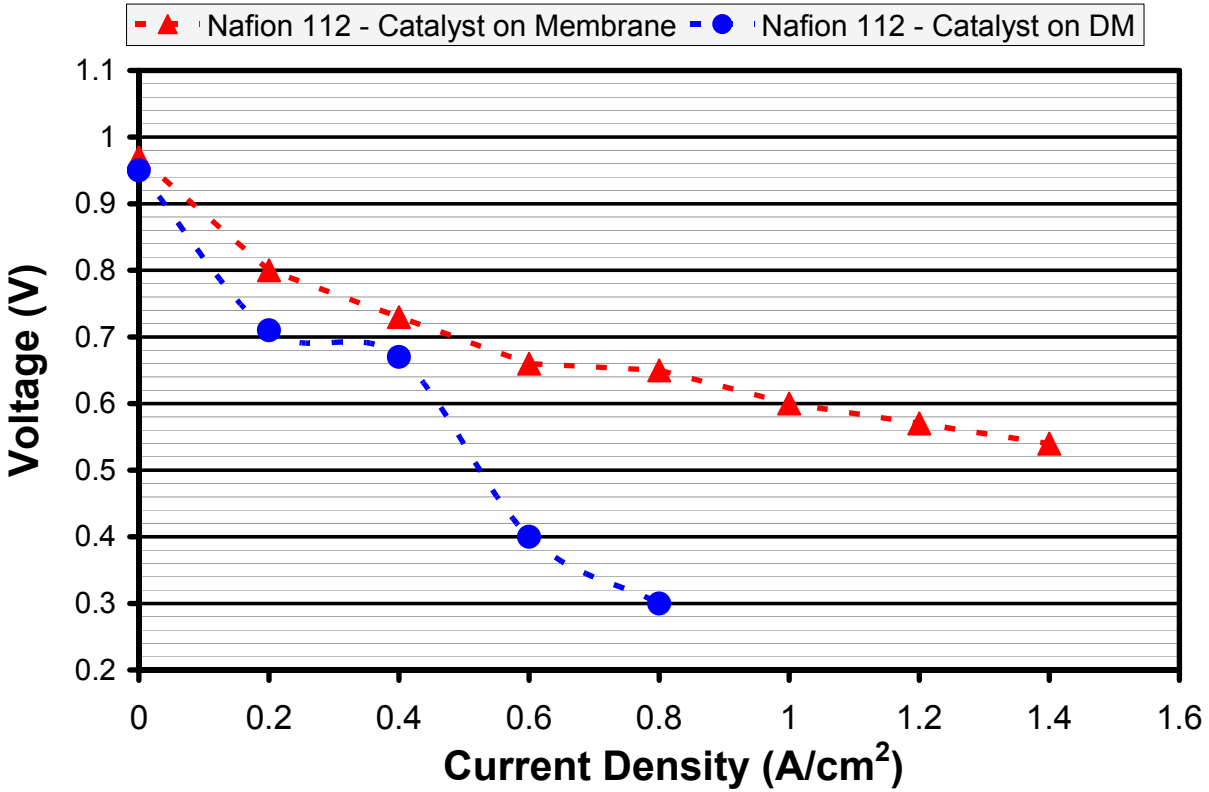
# Ex-situ Freeze/Thaw Test

NE112

DSM

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

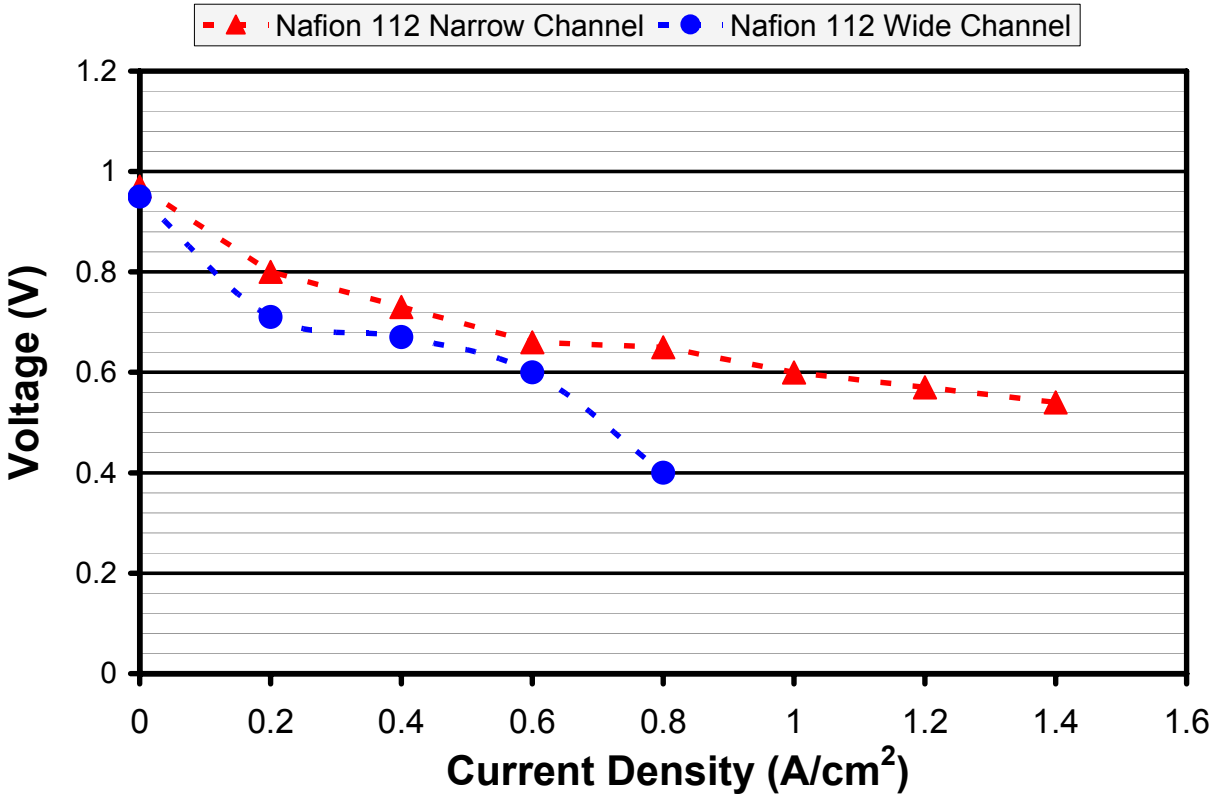
# Impact of MEA Configuration




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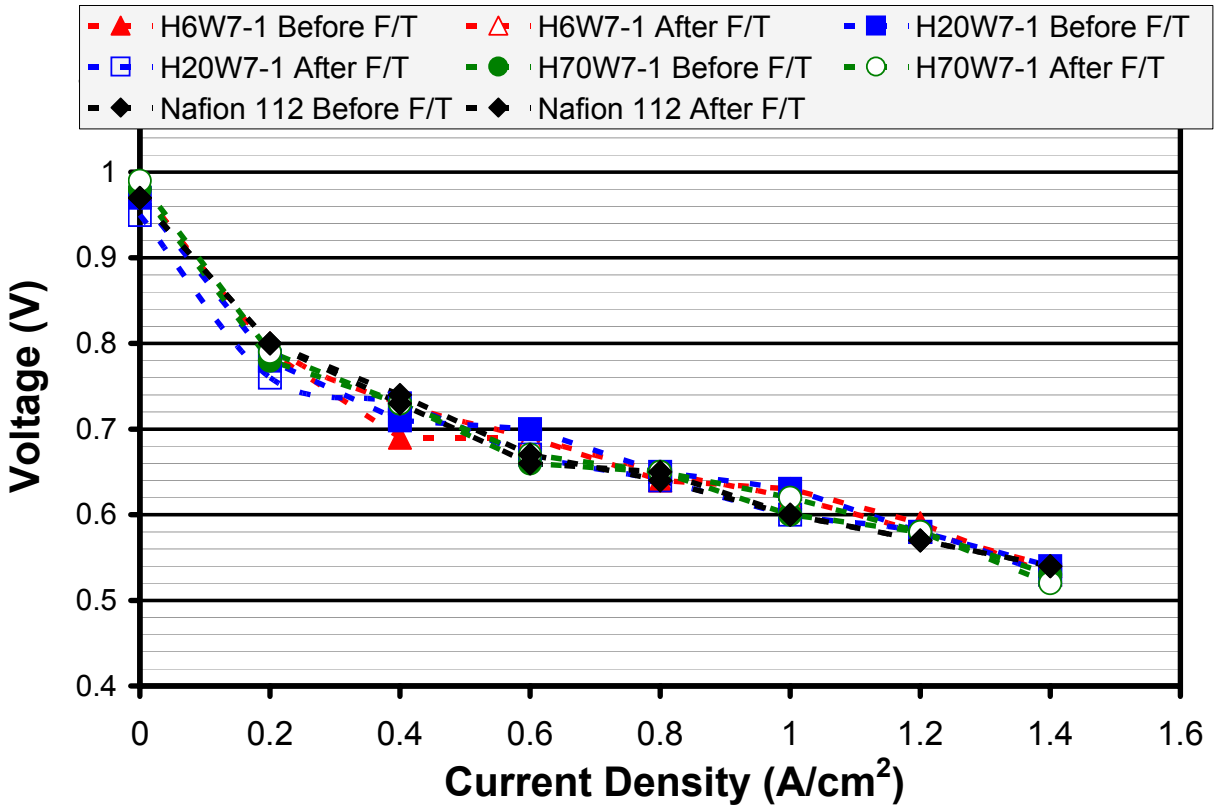
**Wide flow channels (2 mm) pose water management problems compared to narrow channels (0.9 mm), given the same gas flow rate.**

# Freeze/Thaw Impact on Performance

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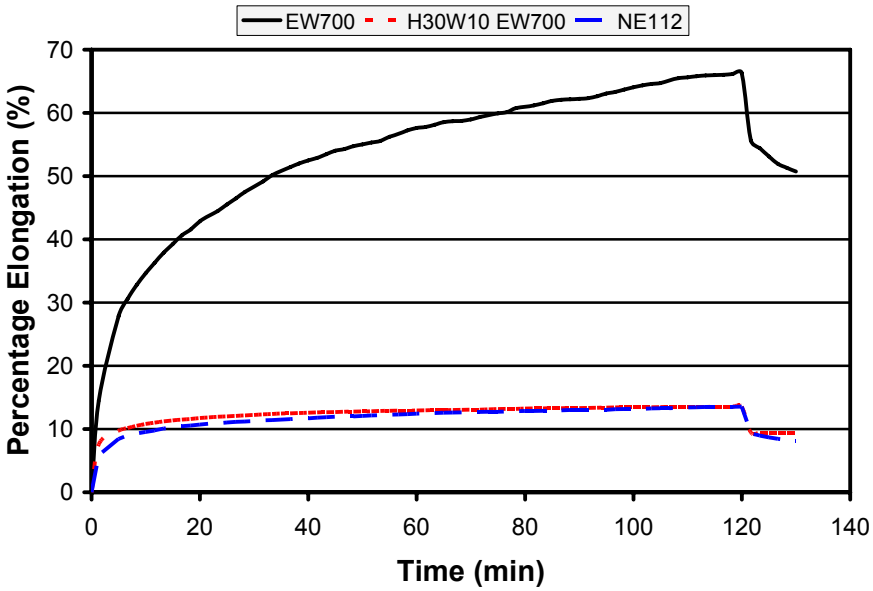
**After 40 thermal cycles from -40°C to 50°C, all MEAs demonstrate excellent stability.**

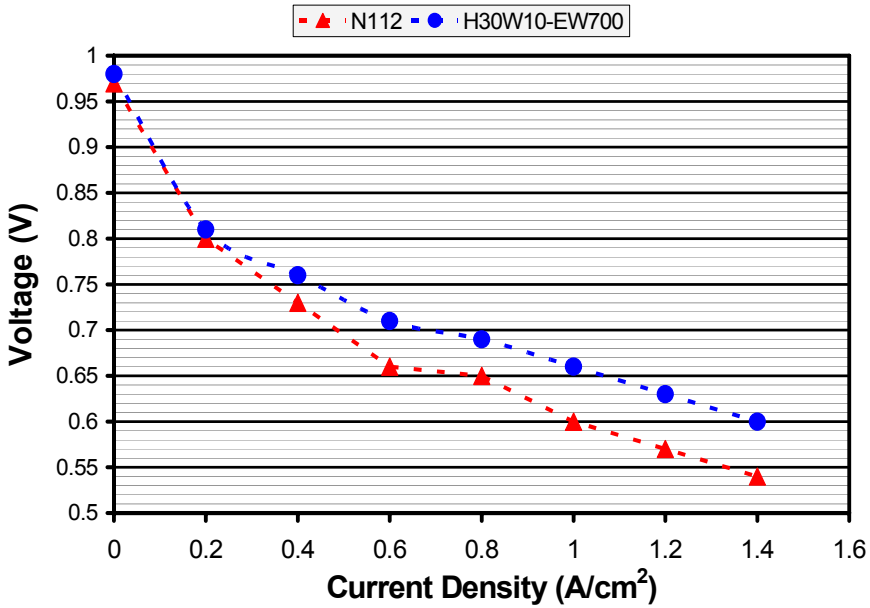
# Electrochemical Surface Area (ECSA) Test

| 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).