Dimensionally Stable High Performance Membrane

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Project ID: FC24

Overview

Timeline

- Project start date: 08/07/2006
- Project end date: 08/06/2008
- Percent complete: 40%

Budget

- Total DOE Funding: $749,613
- Funding received in FY06: $374,938
- Funding for FY07: $374,675

Barriers

- A. Durability
- C. Performance

Objectives

- Develop MEAs based on dimensionally stable membrane (DSM) with high freeze/thaw durability
- Enhance MEA RH cycling durability
- Develop/improve fabrication technology for support structure
- Develop/evaluate localized reinforcement strategy
- Evaluate the effect of MEA configuration

Approach

Task 1: F/T Protocol Development

- Longer, Wider Range
- In-situ Monitoring

Task 2: Enhanced Patterning

- Micromolding
- Micromachining
- Material Screening

Task 3: Selective Reinforcement

- Identify Weak Area
- Develop Reinforcement Strategy

Task 4: MEA Configuration

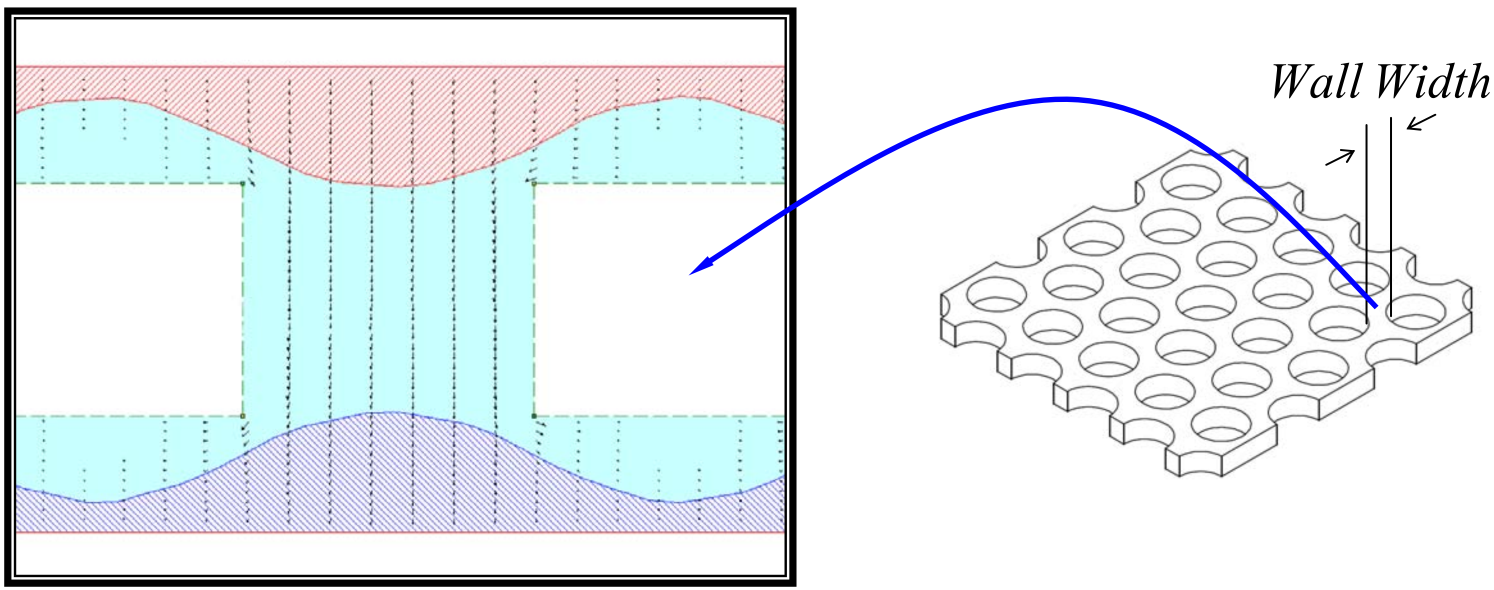
- Channel Width
- Compression
- Catalyst Layer Configuration

Task 5: Stack Test

Technical Accomplishments/ Progress/Results

- Supported membranes show 10X better in-plane swelling stability than Nafion® 112.
- Supported membranes show more than one order of magnitude less creep rate compared to Nafion® 112.
- Supported membranes show 2-3X durability than Nafion® 112 in accelerated RH cycling tests.
- Preliminary results from micromolding are promising.

Design Concerns for Support Structure



Although there is no conductivity penalty from tortuosity, the support structure has to be designed to avoid additional current distribution penalty.

Design Concerns for Support Structure

Ionomer utilization factor (IUF) is defined as:

$$IUF = r_{open} + (1 - r_{open})(I_{wall\text{-}avg}/I_{hole\text{-}avg})$$

For 50% opening support, it can be approximated to:

$$IUF = 0.5 + 0.5*(I_{wall\text{-}low} + 0.25*(I_{hole\text{-}high} - I_{wall\text{-}low}))/(I_{hole\text{-}high} - 0.25*(I_{hole\text{-}high} - I_{wall\text{-}low}))$$

$$IUF_{low} = 0.5 + 0.5*(I_{wall\text{-}low}/ I_{hole\text{-}high})$$

Where r_{open}: percentage of opening. $I_{wall\text{-}avg}$: average current in the wall region. $I_{hole\text{-}avg}$ average current in the hole region. $I_{wall\text{-}low}$: lowest current in the wall region, $I_{hole\text{-}high\text{-}}$: highest current in the hole region.

Equivalent thickness is defined as the thickness of a non-supported membrane that has the same through-plane conductivity compared to a supported membrane

$$T_{eq} = T_{support}/r_{open} + (T_{total} - T_{support})/IUF$$

Where T_{eq} is the equivalent thickness, $T_{support}$ is the thickness of the support structure, T_{total} is the thickness of the supported membrane.

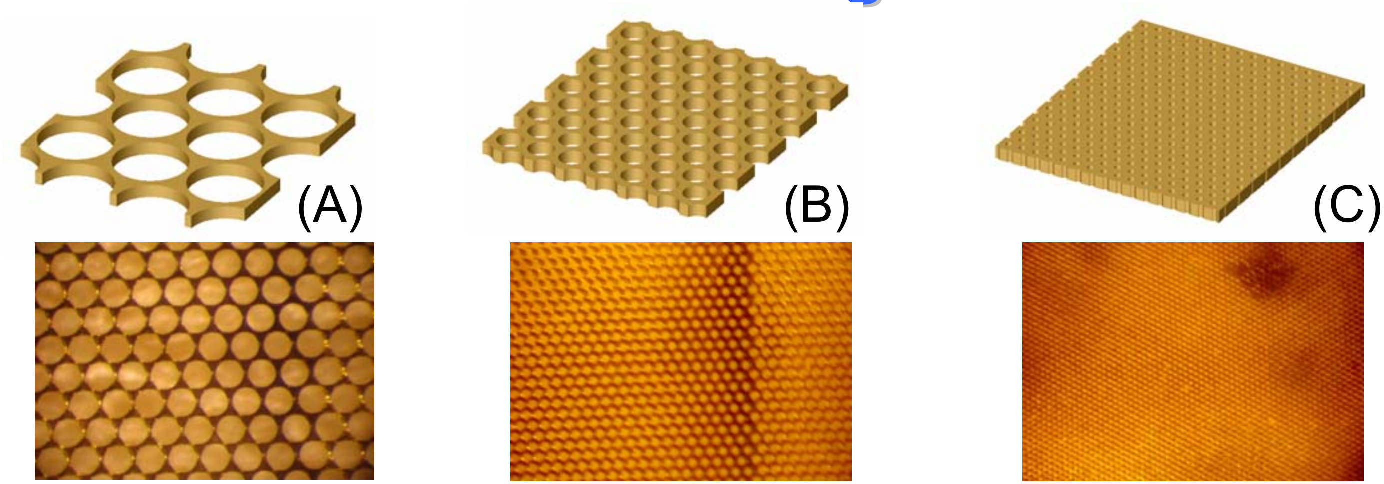
Design Concerns for Support Structure

Wall Width[1]	Percentage of Opening	Support Thickness	Total Membrane Thickness	IUF	Equivalent Thickness
8	50	8	18	0.96 - 0.98	26
8	50	8	25	> 0.99	33
8	50	8	50	> 0.99	58
8	75	8	18	0.96 - 0.98	22
8	75	8	25	> 0.99	28
8	75	8	50	> 0.99	54

1. All units are micron (μm).

With proper selection of support configuration, the ionic conductivity penalty of 8% or lower can be achieved for 50 μm membranes.

Pattern Design

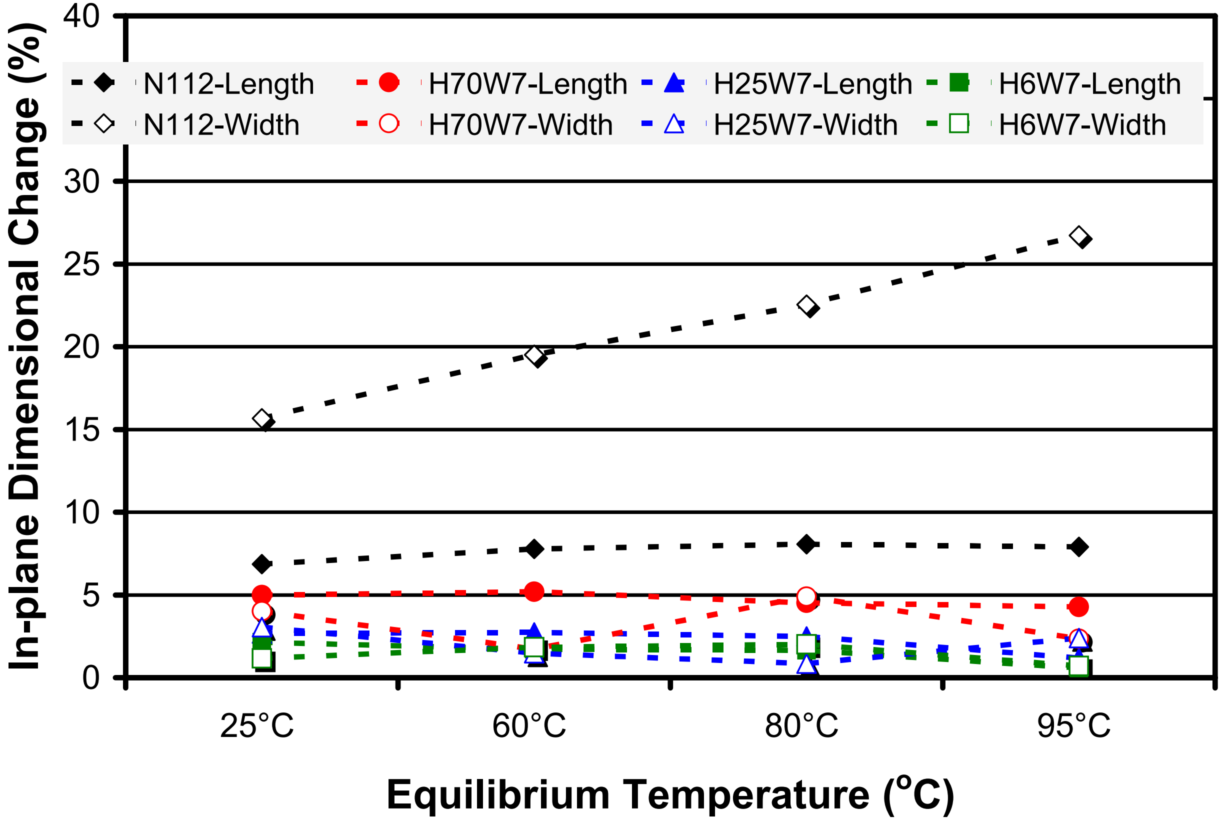


Sample Designation	Hole Diameter (μm)	Wall Thickness (μm)	Percentage Opening (%)
A (H70W7)	70	7	75
B (H25W7)	20	7	50
C (H6W7)	6	7	22

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

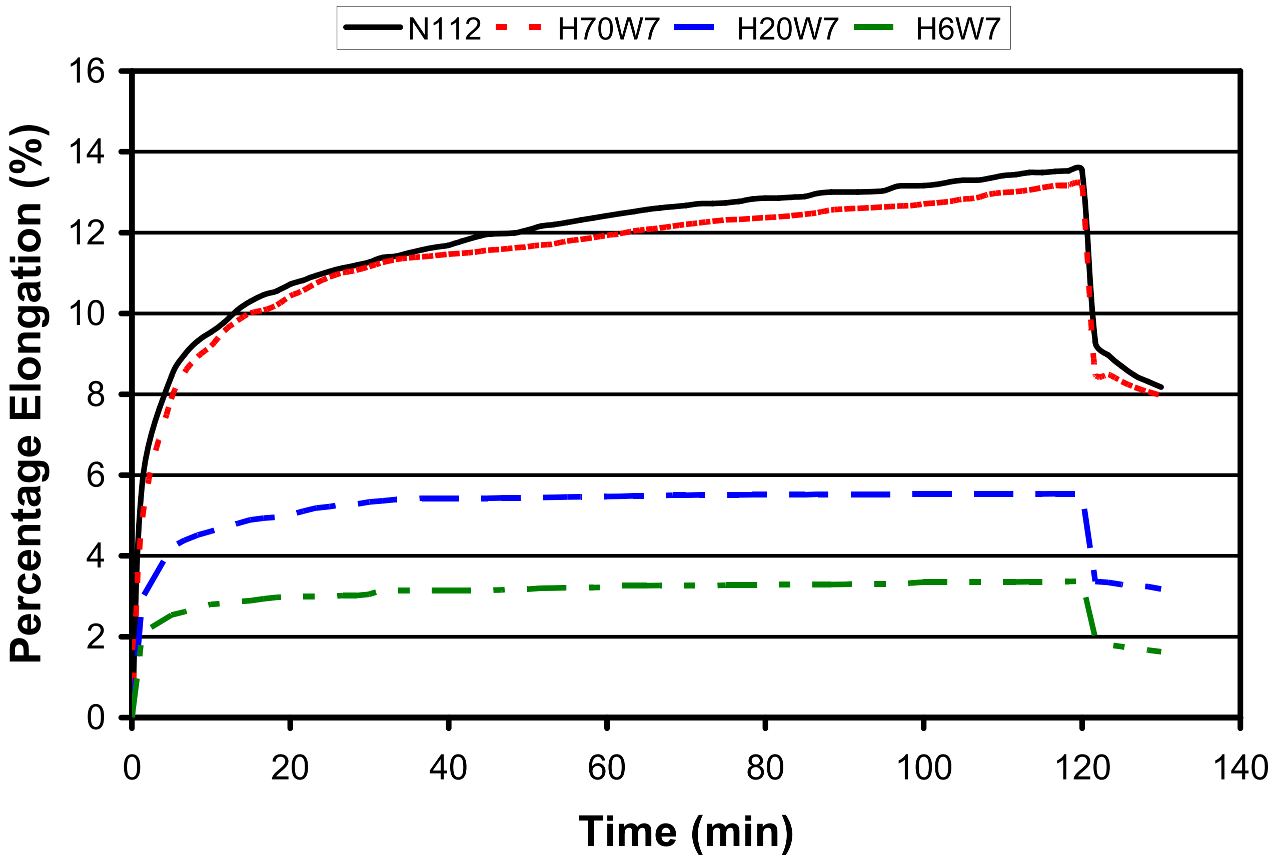
Figures in the top row are schematic illustrations. Figures in the second row are micrographs of the samples.

Swelling Behavior – EW1100



Compared to Nafion (N112), DSMs fabricated with EW1100 ionomer demonstrate >10X swelling stability at elevated temperatures when submerged in water.

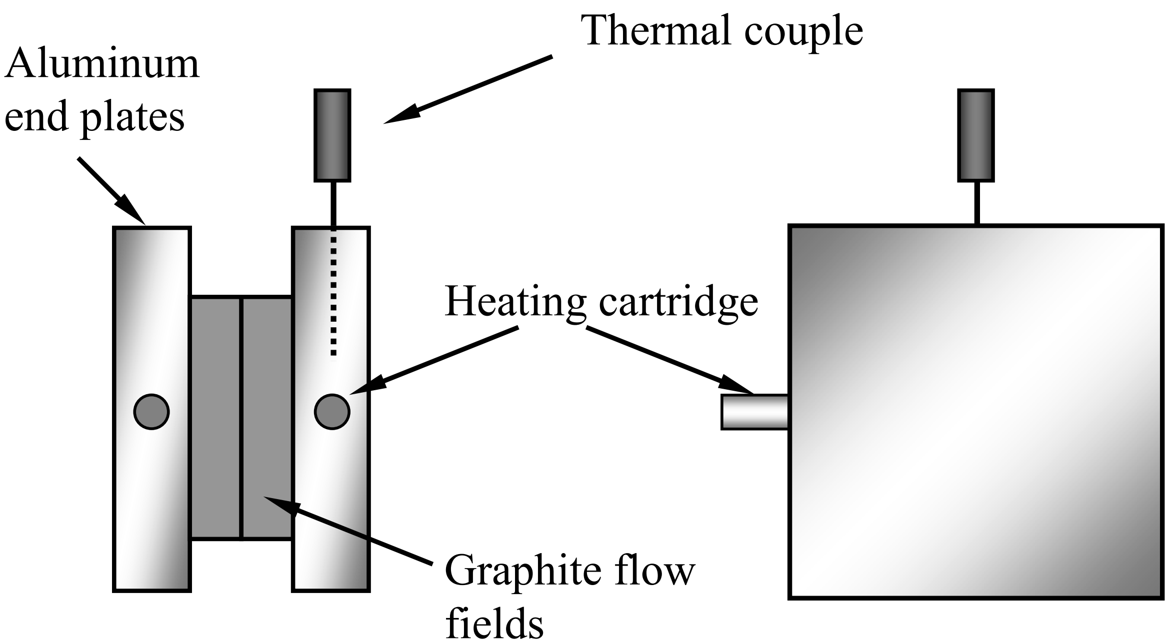
Creep Behavior



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

Compared to Nafion (N112), DSMs fabricated with EW1100 ionomer show more than one order of magnitude improvement on creep rate (percentage elongation / hour).

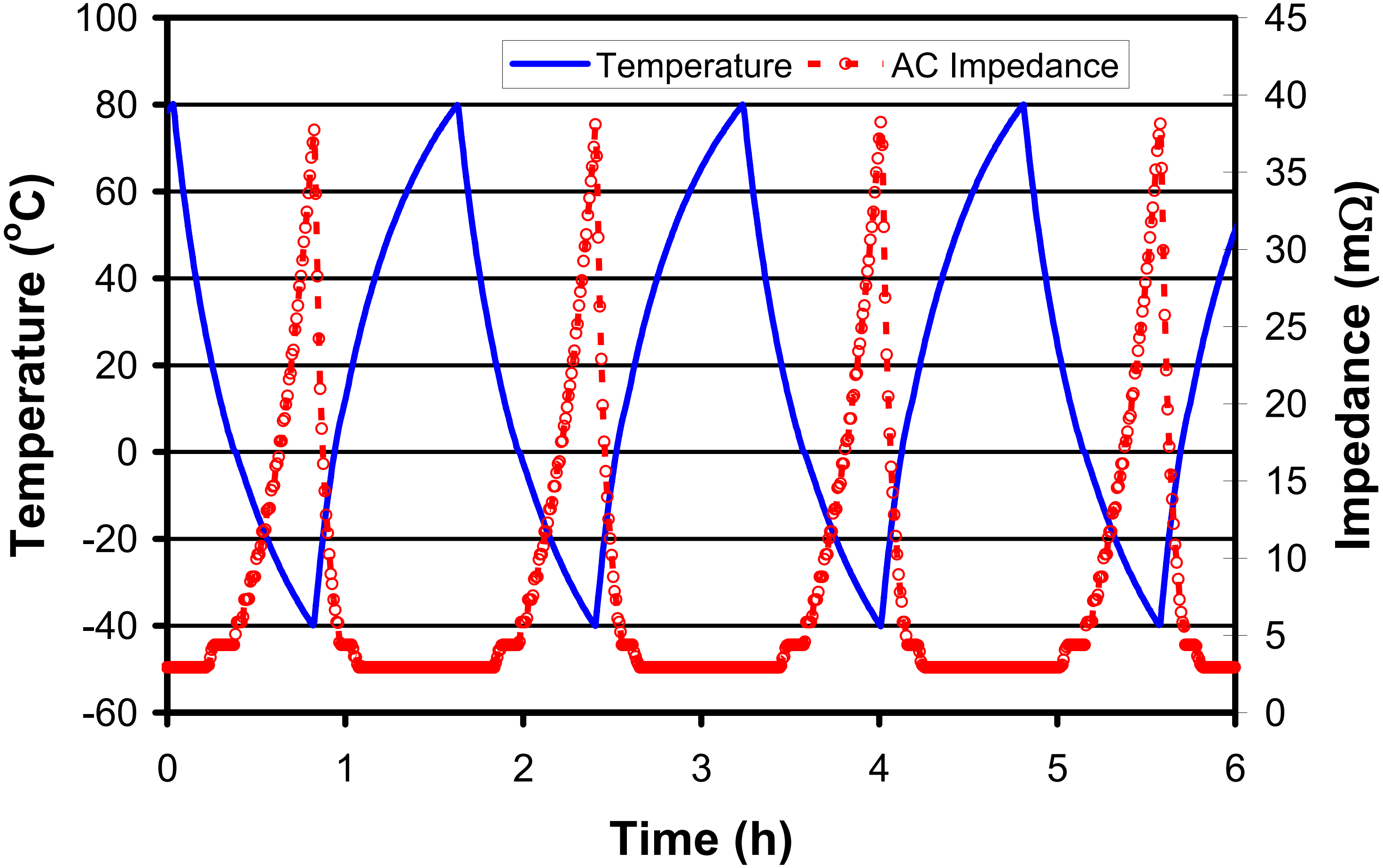
Freeze/Thaw Cycling Experimental



- Cell Area: 50 cm^2
- Cycling Range: -40°C to 80°C
- Cycling Period: 1.5 h

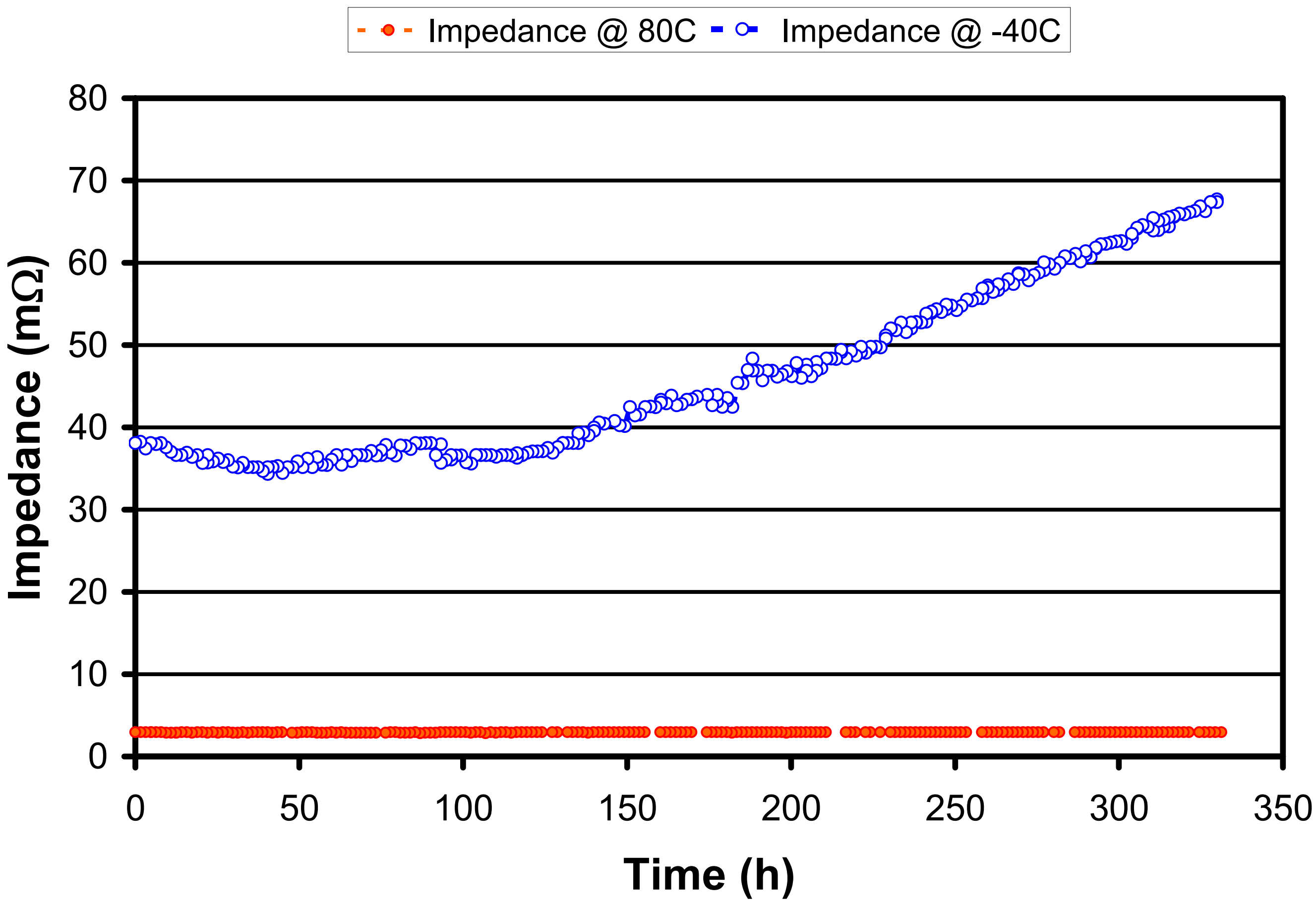
To enhance F/T cycling speed, the fuel cell fixture was heated locally while the environment temperature was kept constant.

Freeze/Thaw Cycling Experimental



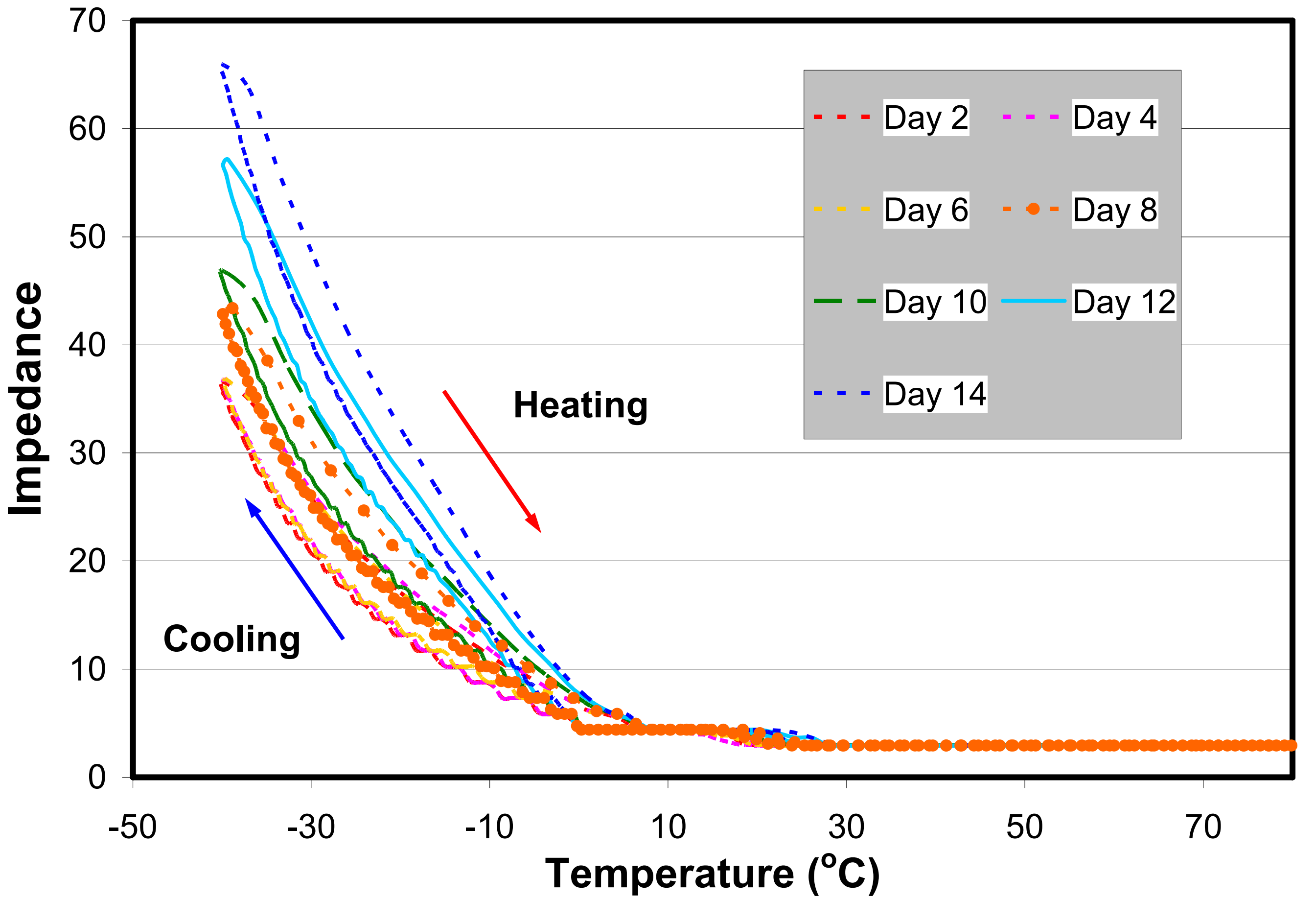
AC impedance (1 kHz) is monitored during thermal cycling.

Freeze/Thaw Cycling



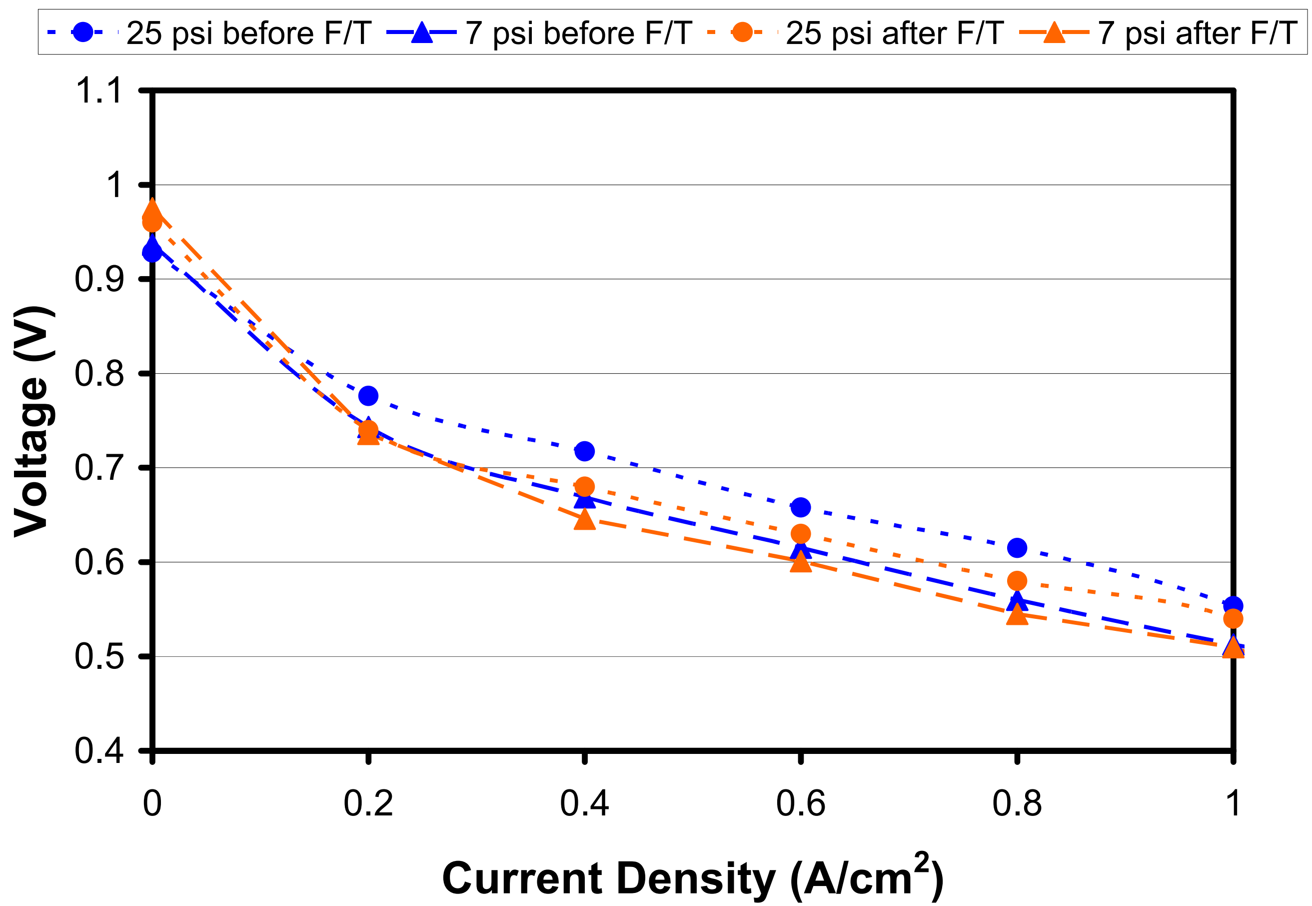
N112 impedance @ -40°C increases with number of cycling while impedance @ 80°C remains constant.

Freeze/Thaw Cycling



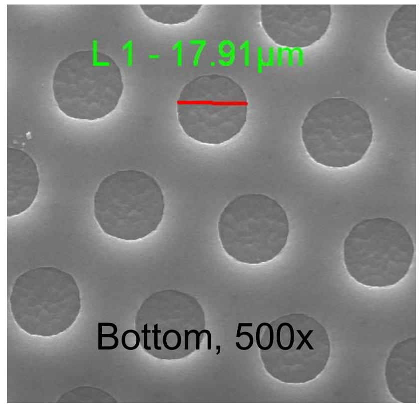
N112 impedance vs. temperature over long term F/T cycling.

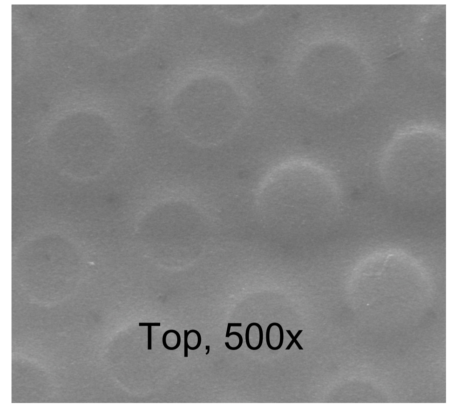
Freeze/Thaw Cycling

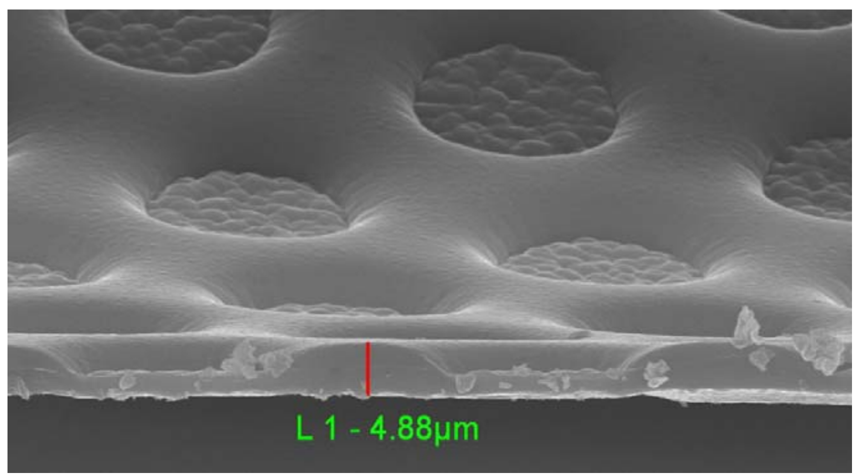


No performance degradation of N112 is observed at 7 Psig, minor performance loss is observed at 25 Psig after 200 thermal cycles.

Support Fabrication

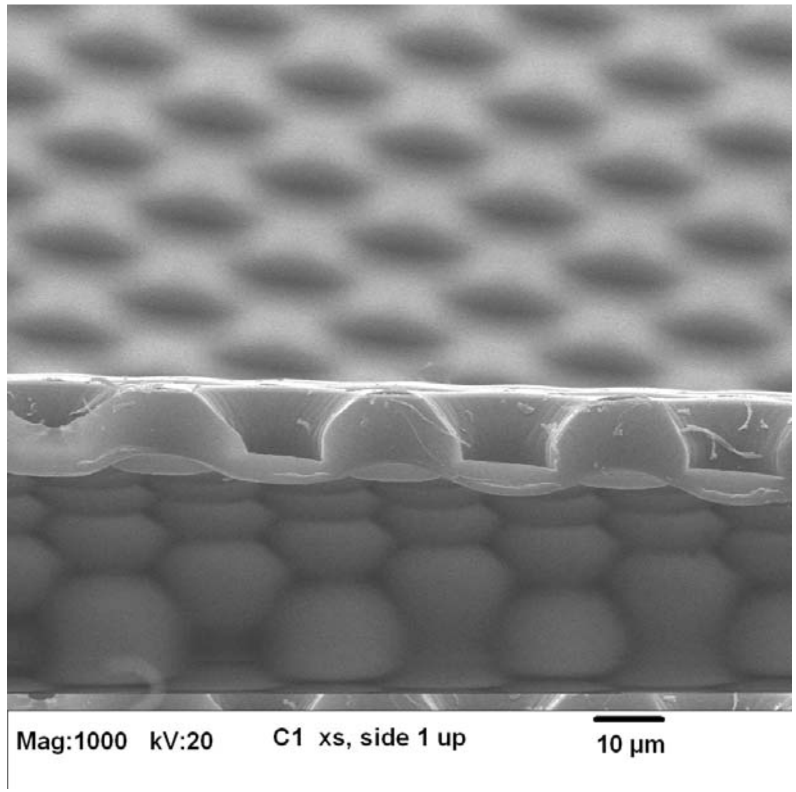






Alternative support fabrication process is being developed for high volume, low cost manufacturing. PVDF was used for this sample.

Support Fabrication

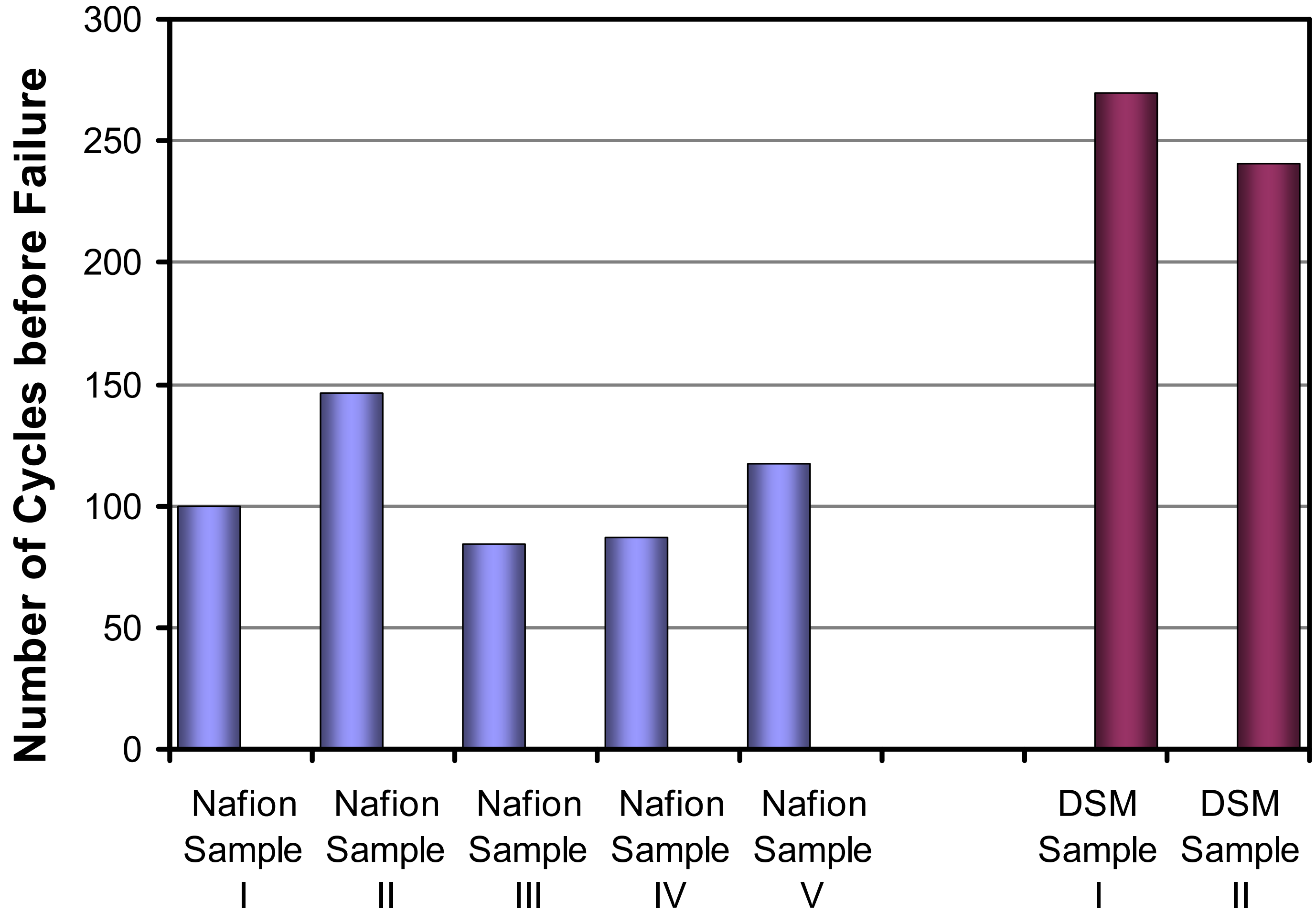


Polysulfone samples also show highly defined features. Post-molding process is being developed to create through-holes.

RH Cycling Experimental

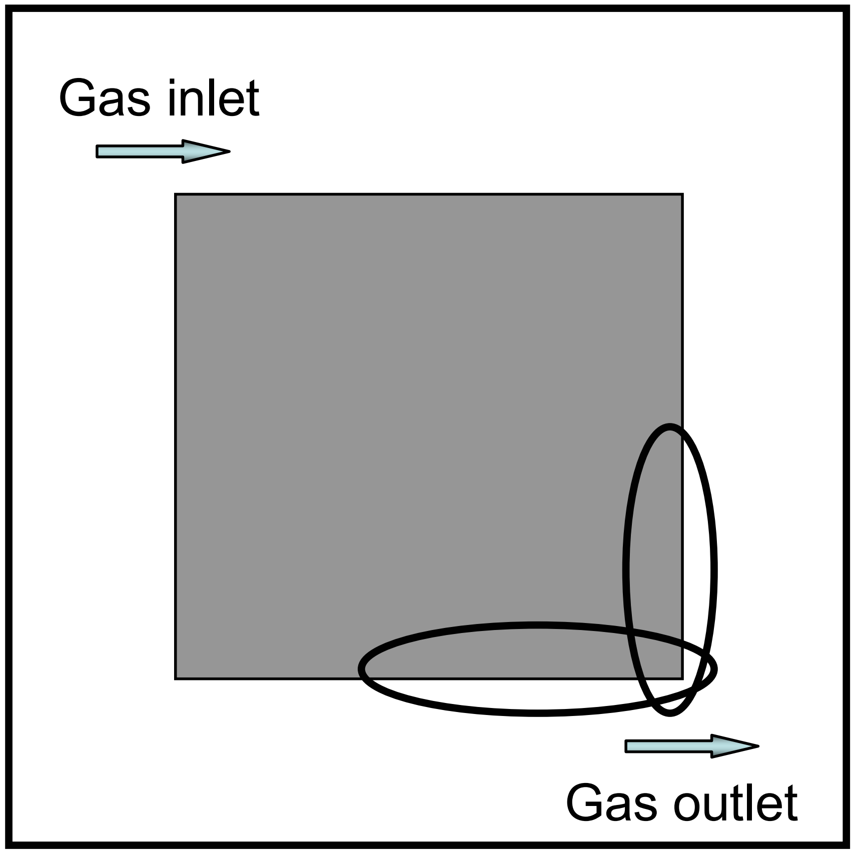
- Based on accelerated RH cycling protocol developed by GM.
- All tests were conducted at 95^{o}C, ~ 5 cycles per hour.
- All cells were tested to failure (0.8A/cm^2, <0.1V).

RH Cycling Results



DSM demonstrated 2-3X durability compared to Nafion 112-based MEAs.

RH Cycling Results



Failure-prone area has been identified to be edge failures closed to the gas outlet, which can be characteristic to the protocol.

Future Work

- **Freeze/Thaw Test Protocol Development**
  - Number of Cycles
  - Temperature Range
  - Reproducibility Study
- **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

- DSMs show >10X X-Y (in-plane) dimensional stability compared to Nafion membranes (N112).
- DSMs show 2-3X durability in RH tests compared to Nafion membranes (N112).
- Freeze/thaw protocol development underway.
- Preliminary results from alternative membrane fabrication are promising.