



# **Dimensionally Stable High Performance Membrane**

**Han Liu, Min Chen, Jason Willey and Pamela Maxwell  
Giner Electrochemical Systems, LLC**

FCP-013



# Overview

## Timeline

- Start – August 2006
- End – August 2008
- 85% Complete

## Barriers

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

## Budget

- Total Project Funding: \$750 K
- Funding Received: \$375 K in FY08

## Objectives

- ❑ Develop Membrane-Electrode Assemblies (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

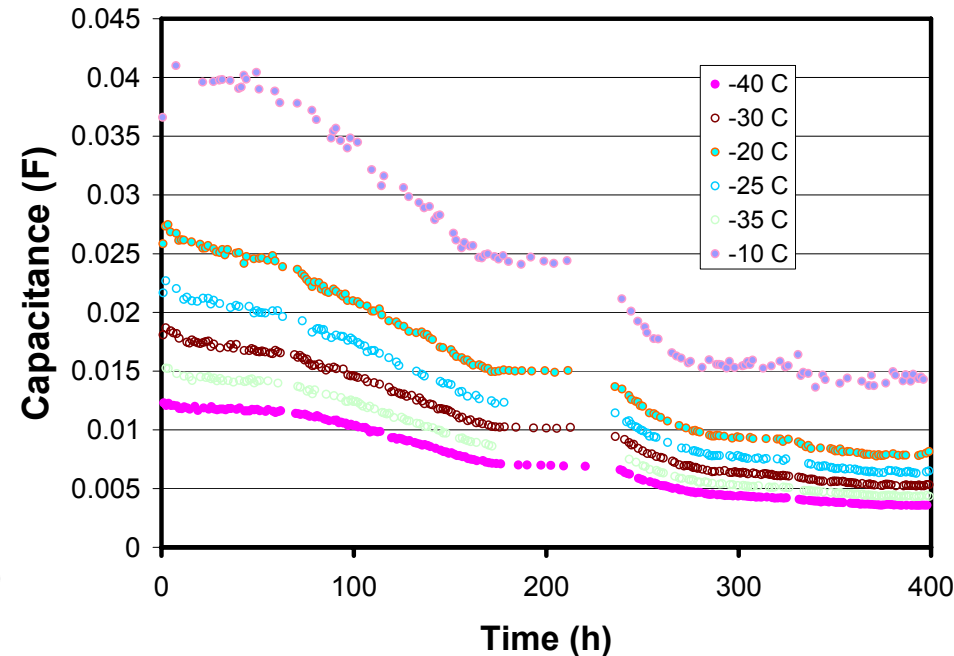
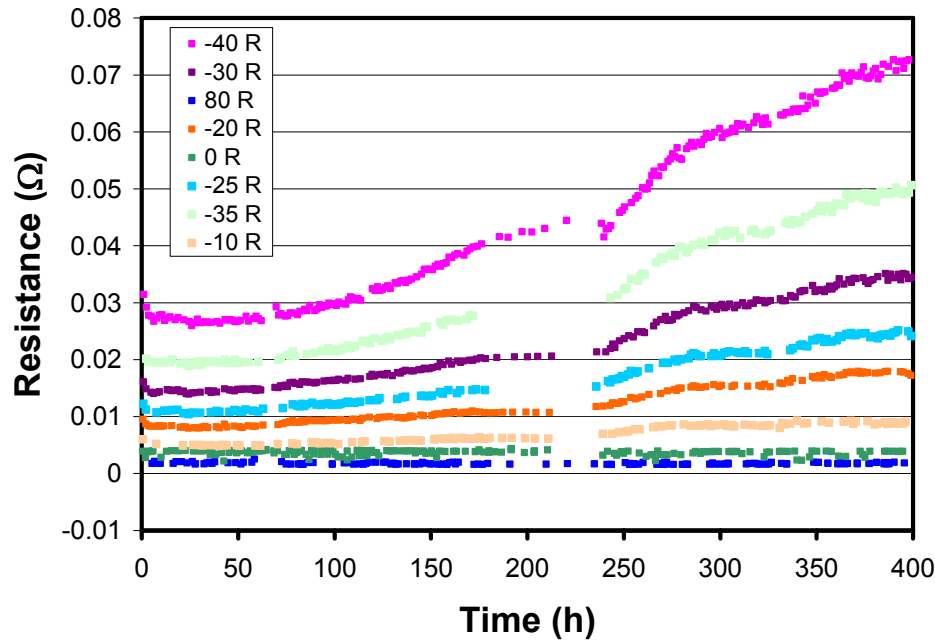
## Task 5: Stack Test



## Technical Accomplishments/ Progress/Results

- ❑ Successfully developed new membrane support fabrication process that can be readily scaled up for continuous low cost mass production of DSM™.
- ❑ The DSM™ show 10X better in-plane swelling stability and more than one order of magnitude less creep rate than Nafion® 112.
- ❑ Localized mitigation for the DSM™ completely eliminates edge failures.

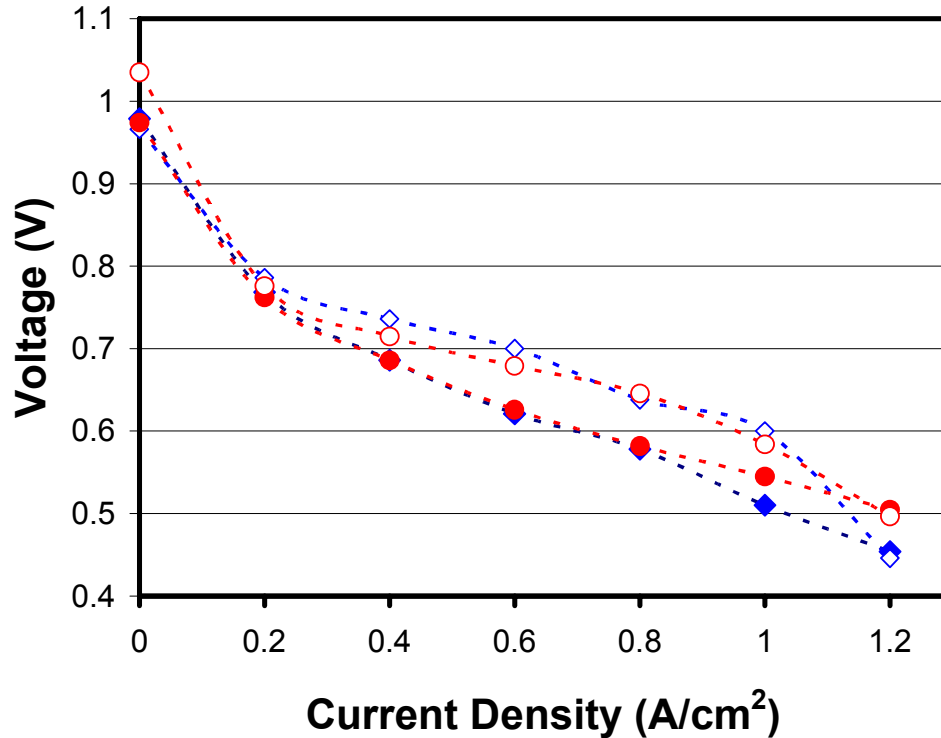
# Freeze/Thaw Cycling (Nafion 112)



**Resistance @ -40°C increases with number of cycling while impedance @ 80°C remains constant. Capacitance decreases with time.**

# Freeze/Thaw Cycling (Nafion 112)

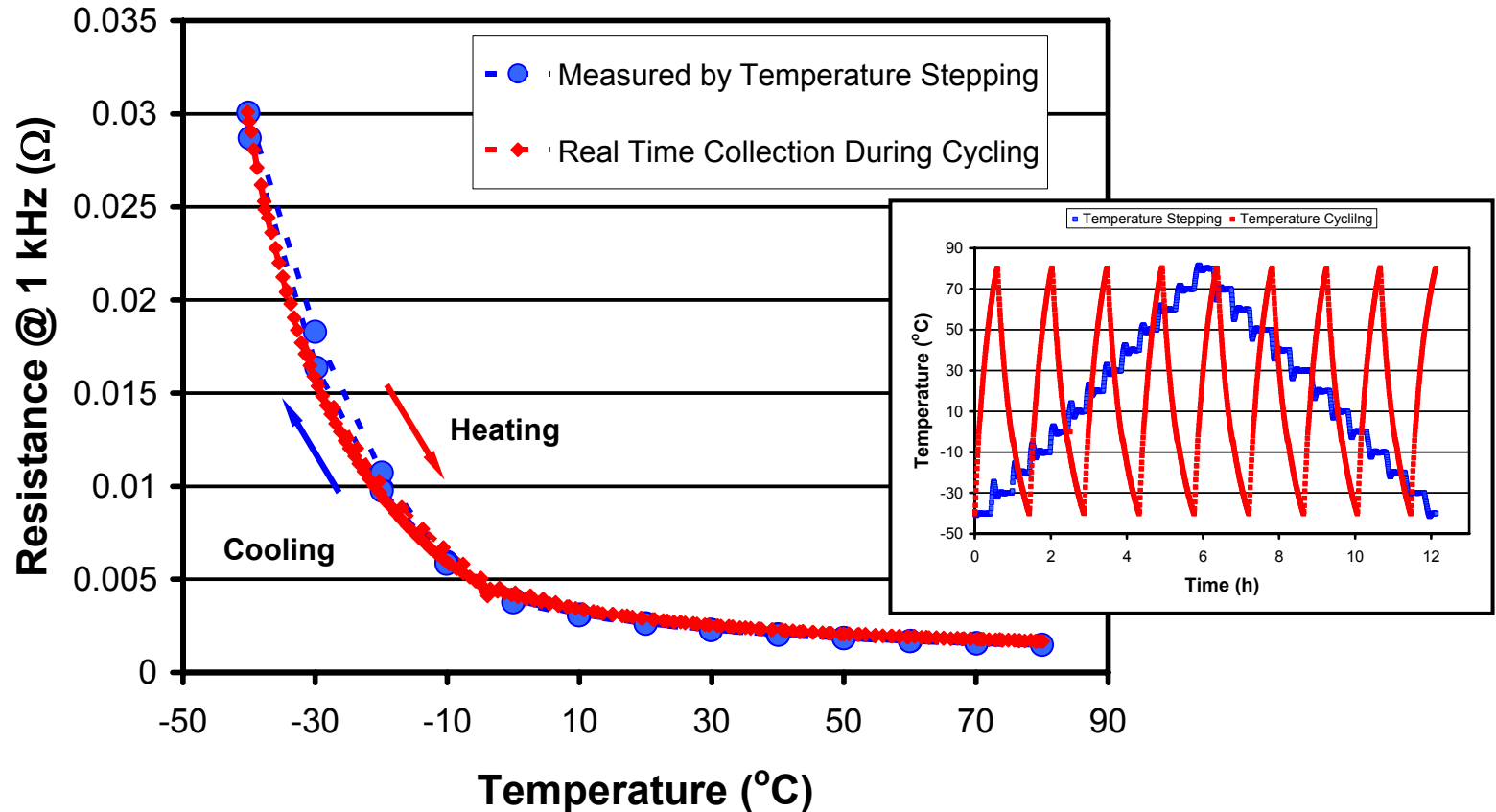
◆ before F-T 7psi  
 ◇ before F-T 25psi  
 ● after F-T 7psi  
 ○ after F-T 25psi



Reactant Gas: H<sub>2</sub> and air, Pressure: balanced, Temperature: 80°C cell, 64°C (50% RH) air, 80°C (100% RH), Gas Stoic: 2\*, Mode: Constant current (\* Under OCV conditions, the gases supplied at 200 mA/cm<sup>2</sup> equivalent flow.)

**The resistance increase at low temperature does not lead to any detectable performance loss after the F/T cyclings.**

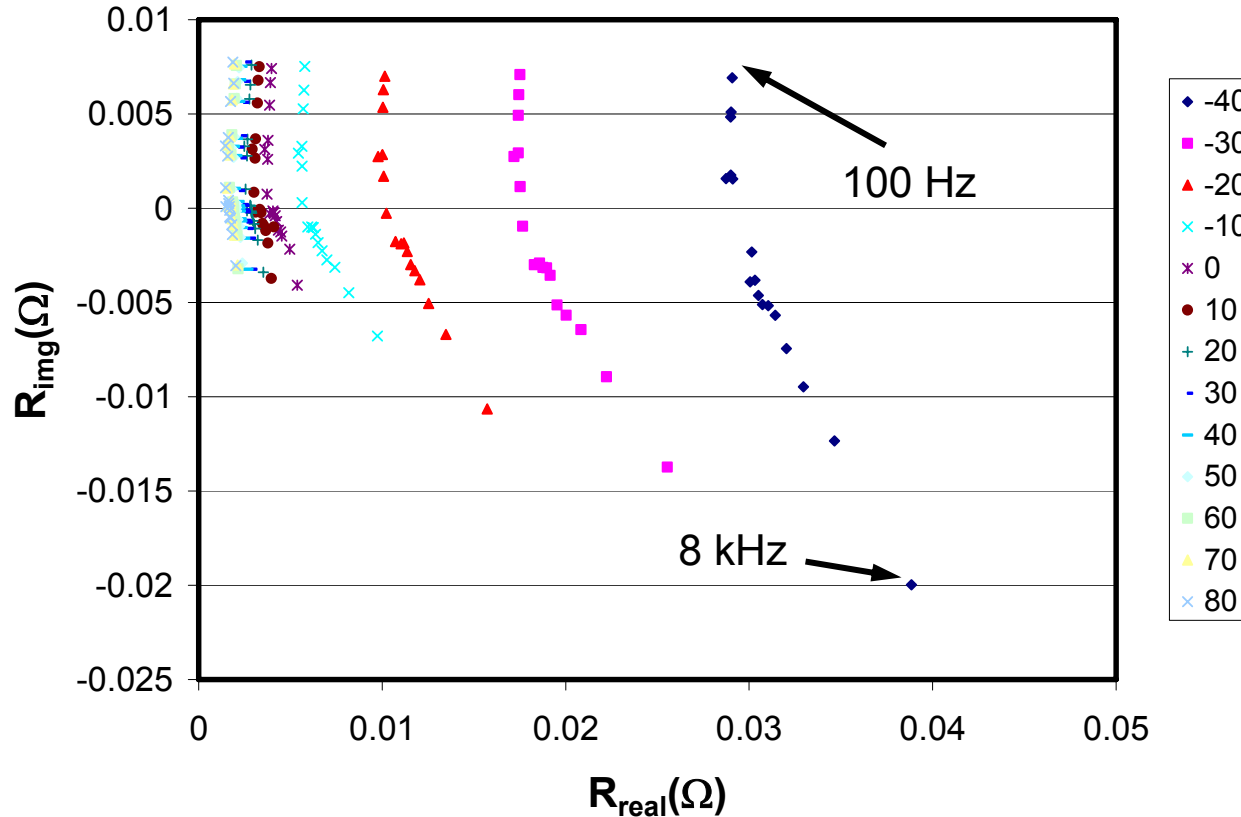
# Freeze/Thaw Cycling (Nafion 112)



**Results from the new temperature stepping protocol indicate that the measured resistance is not an artifact of delayed heat transfer.**



# Freeze/Thaw Cycling (Nafion 112)



More detailed impedance data can be obtained from the new temperature stepping protocol.

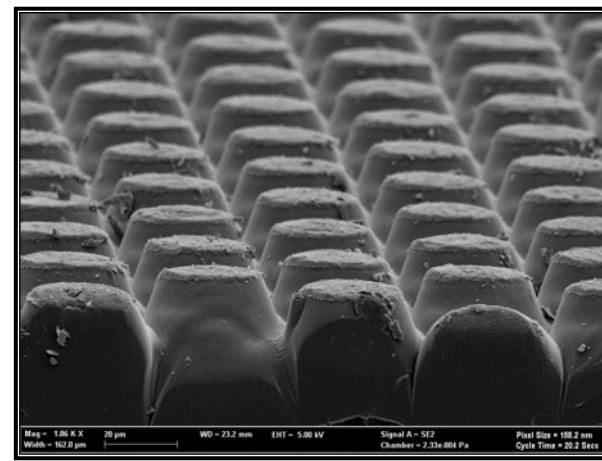
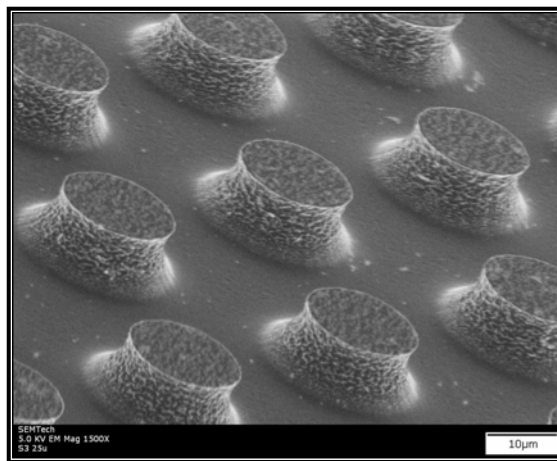
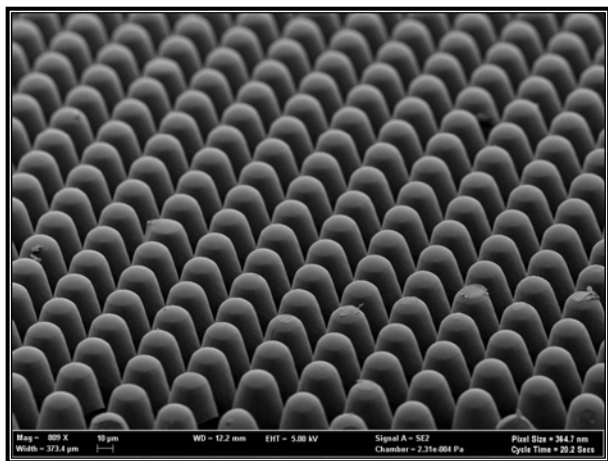


## Freeze/Thaw Cycling (Nafion 112)

Material	% elongation at break	
	Before Cycling	After 385 F/T Cycles (Dry)
Membrane (machine direction)	1290	40
Membrane (cross direction)	320	25
MEA (machine direction)	960	52
MEA (cross direction)	510	37
	Before Cycling	After 200 F/T Cycles (Wet)
Membrane (machine direction)	> 300	> 300
Membrane (cross direction)	> 300	> 300

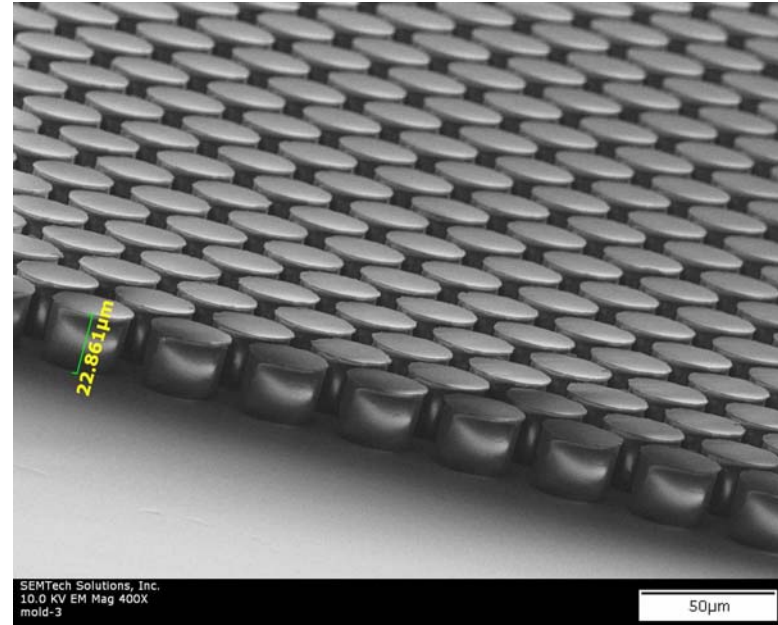
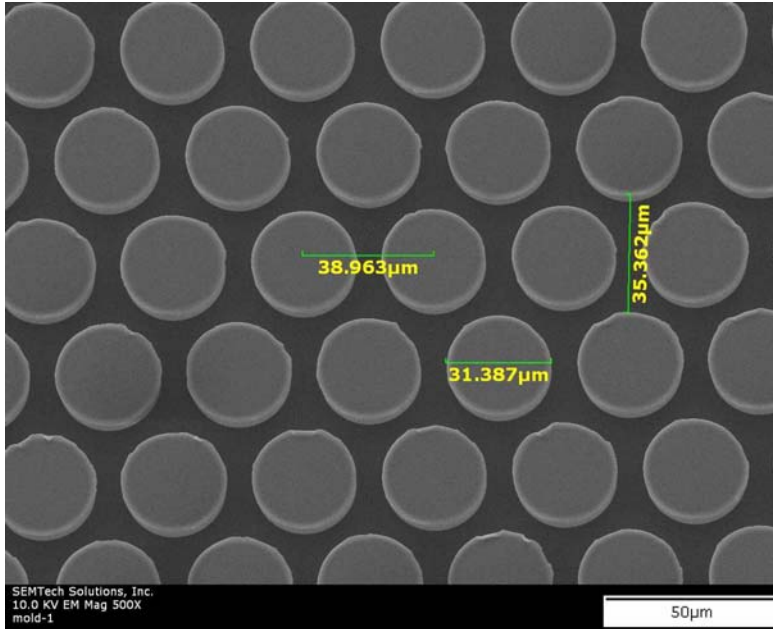
Previous data from GES show N112 becomes brittle after F/T cycling under dry conditions. There is no detectable difference after similar experiments under wet conditions.

# Low Cost Fabrication of DSM™ Support



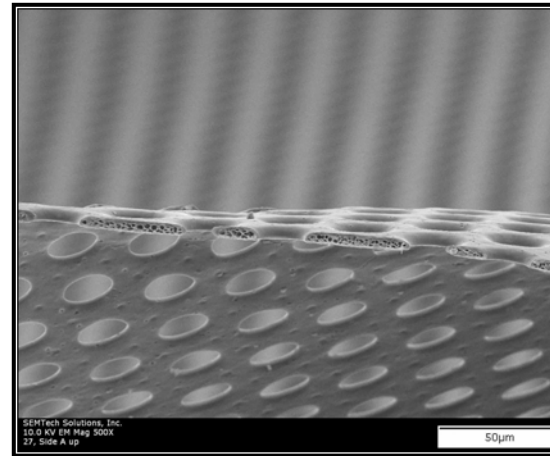
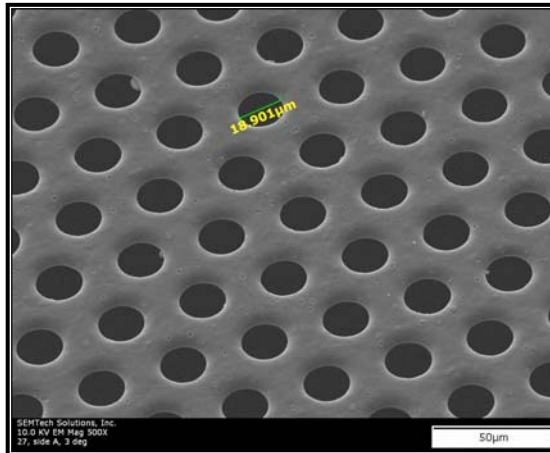
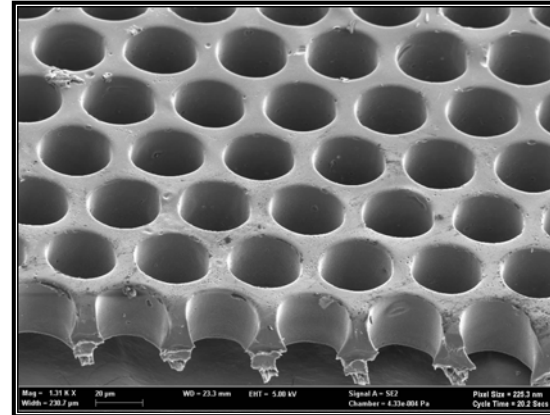
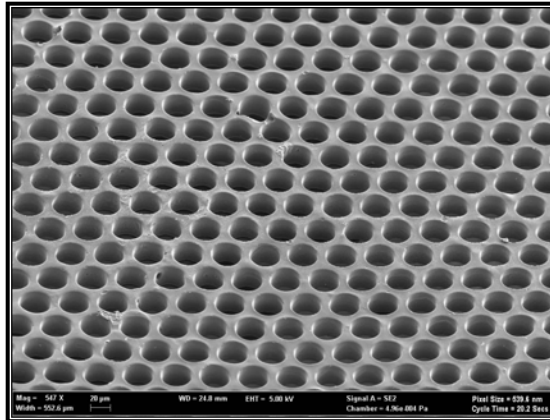
Various technologies have been used to develop micromolds for DSM™ support fabrication.

# Low Cost Fabrication of DSM™ Support



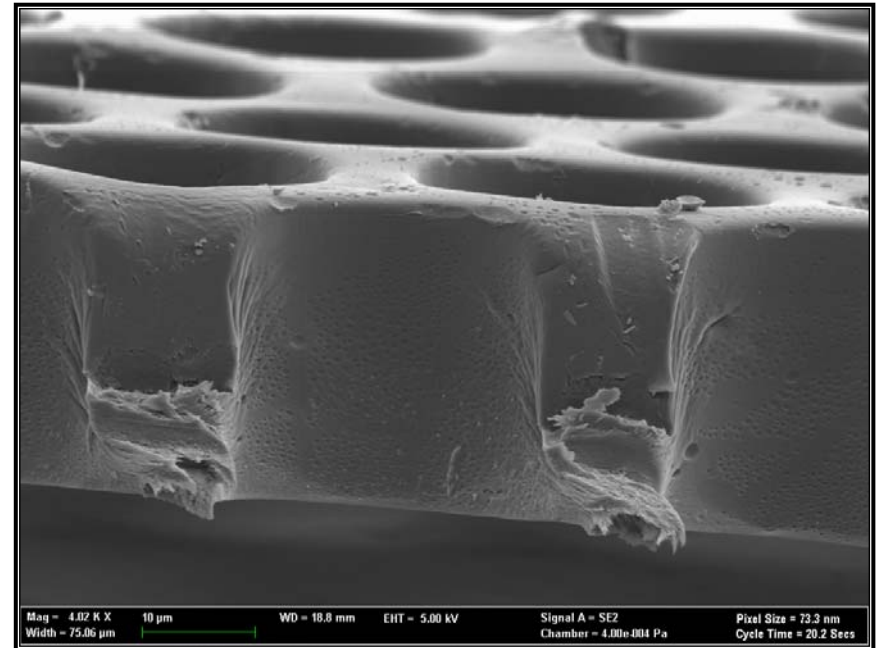
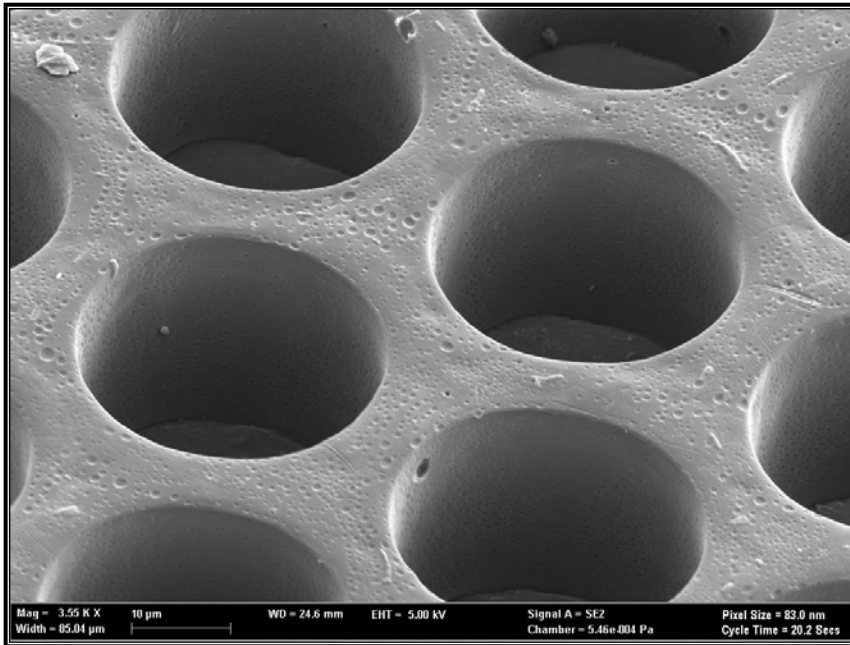
**New micromolds can replicate the dimensions of the laser drilled support structure.**

# Low Cost Fabrication of DSM™ Support



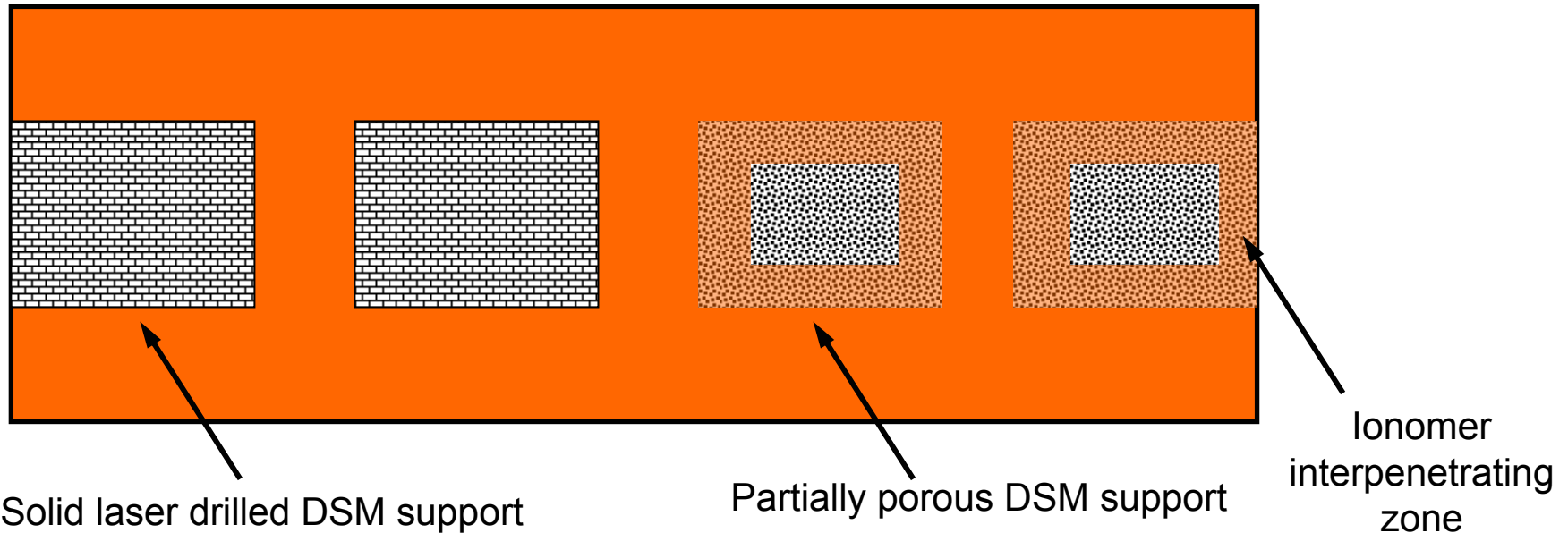
Support structure with difference thicknesses can be readily prepared.

# Low Cost Fabrication of DSM™ Support



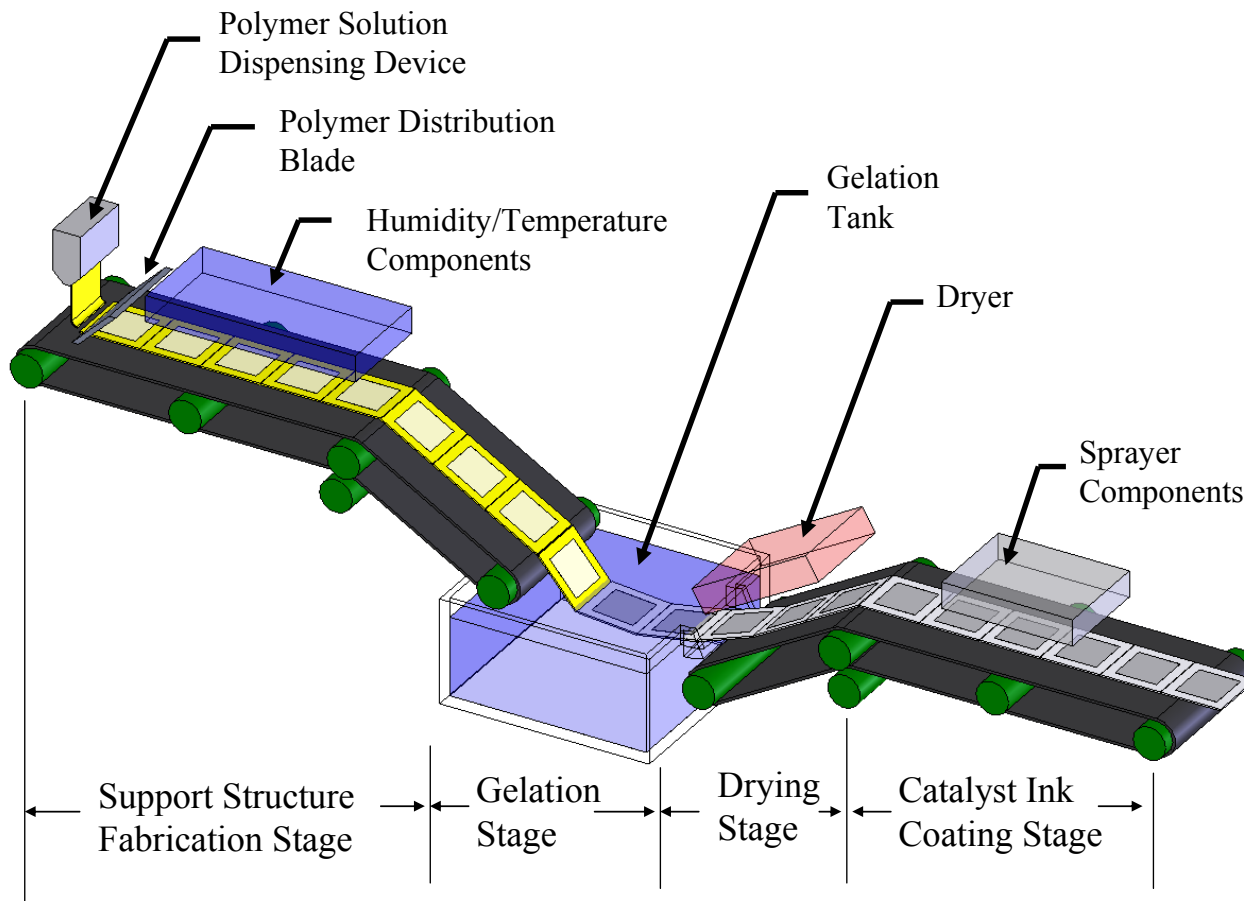
The support structure can be prepared with controlled surface/bulk porosity, which can further enhance ionomer adhesion, although adhesion has never been an observed problem for DSM™ based on laser drilled support.

## Low Cost Fabrication of DSM™ Support



Since the support structure can be prepared with controlled porosity, an ionomer interpenetrating zone can be formed, which enhances conductivity without sacrificing mechanical properties.

# Low Cost Fabrication of DSM™ Support



**Schematic illustration of full DSM™ MEA fabrication line. Direct catalyst inking, instead of decal transfer, can be used due to high mechanical stability of DSM™.**

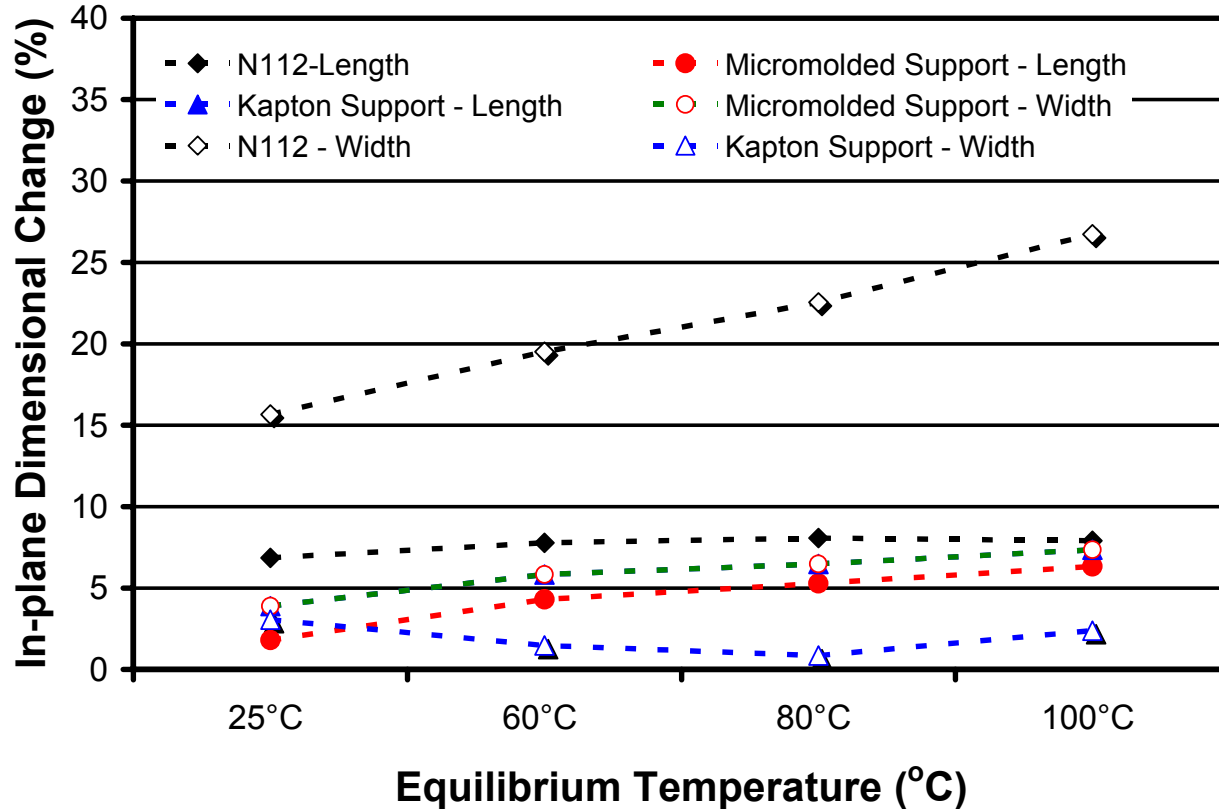


## Low Cost Fabrication of DSM™ Support



**A section of prototype DSM™ fabrication belt for continuous manufacturing of DSM™ support.**

# Low Cost Fabrication of DSM™ Support



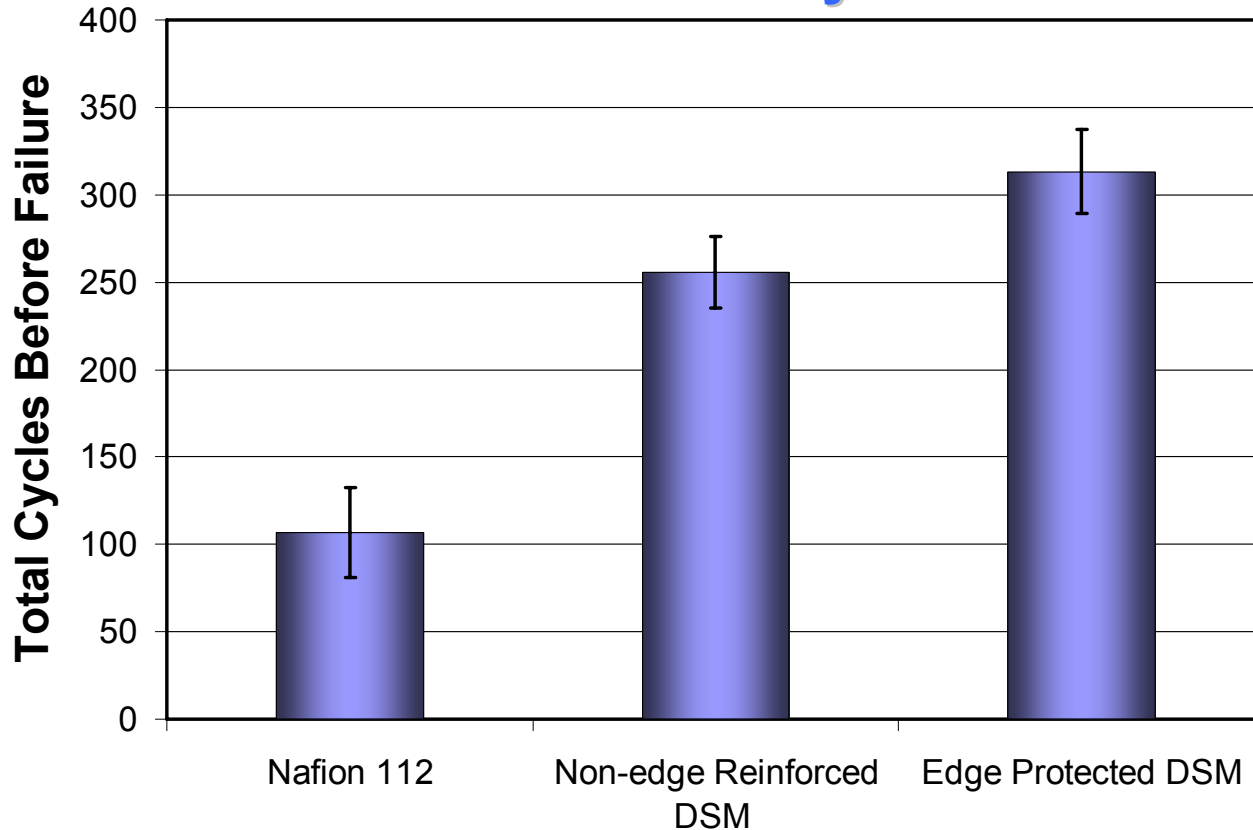
The DSM with micromolded support structure shows similar dimensionally stability compared to laser drilled samples.



## RH Cycling Experimental

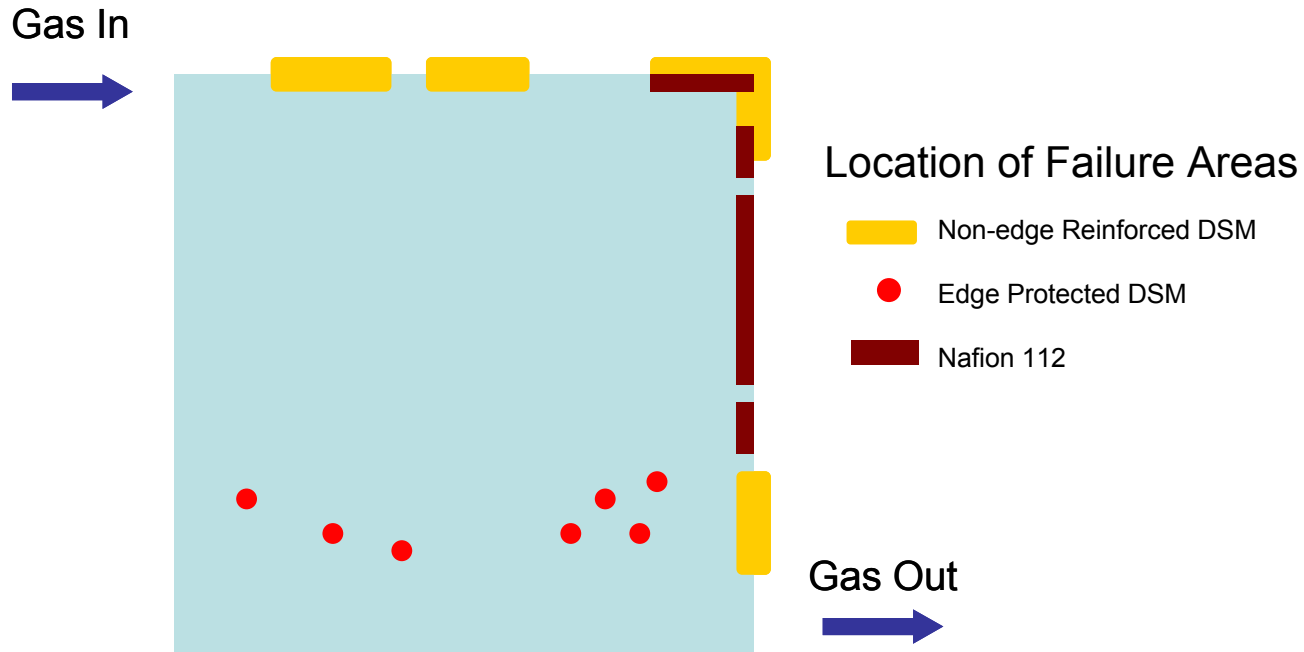
- ❑ Based on accelerated RH cycling protocol developed by GM.
- ❑ All tests were conducted at 95°C, ~ 5 cycles per hour.
- ❑ All cells were tested to failure (0.8A/cm<sup>2</sup>, <0.1V).

## Effect of Localized Reinforcement on RH Cycling Durability



**DSM™ with edge protection enhances the durability to > 3X compared N112 membranes.**

## Effect of Localized Reinforcement



**DSM™ with edge protection completely eliminate edge failures.**



## Future Work

- Demonstrate the feasibility of continuous fabrication.
- Investigate alternative polymer support materials.
- Study the effect of interpenetrating zone and porosity of the support structure.
- Evaluate the effect of MEA structure on freeze/thaw durability.

## Summary

- ❑ New fabrication method offers unique DSM™ support with controlled porosity, pattern configuration and feasibility for continuous MEA manufacturing.
- ❑ DSM™ show 10X better in-plane swelling stability and more than one order of magnitude less creep rate compared to Nafion.
- ❑ Edge protected DSM™ completely eliminates edge failures and enhances the durability to > 3X better than the N112 membranes.