# Dimensionally Stable Membranes™

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FC036

# Dimensionally Stable Membranes for High Temperature Applications

## Timeline

- Begin 4/3/2006
- Extension 10/1/2011
- 90% Complete

## Budget

- Total project funding
- $1.5 M DOE Funding (w/go)
  - $529K Recipient
  - 35% Cost Share
  - $241K received FY 2010
  - $108K Remaining (ext. to Nov. '11)
  - $1100K DOE funds spent to date

## Barriers Addressed

A. Durability
B. Cost

Technical Targets (DOE 2010 Targets)

- 0.10 S/cm at 1.5 kPa $H_2O$ Air inlet
- <$40/m$^2$
- > 5000 hour lifetime
- Stability in condensing conditions

## Partners

- General Motors
- SUNY-ESF

# OVERVIEW

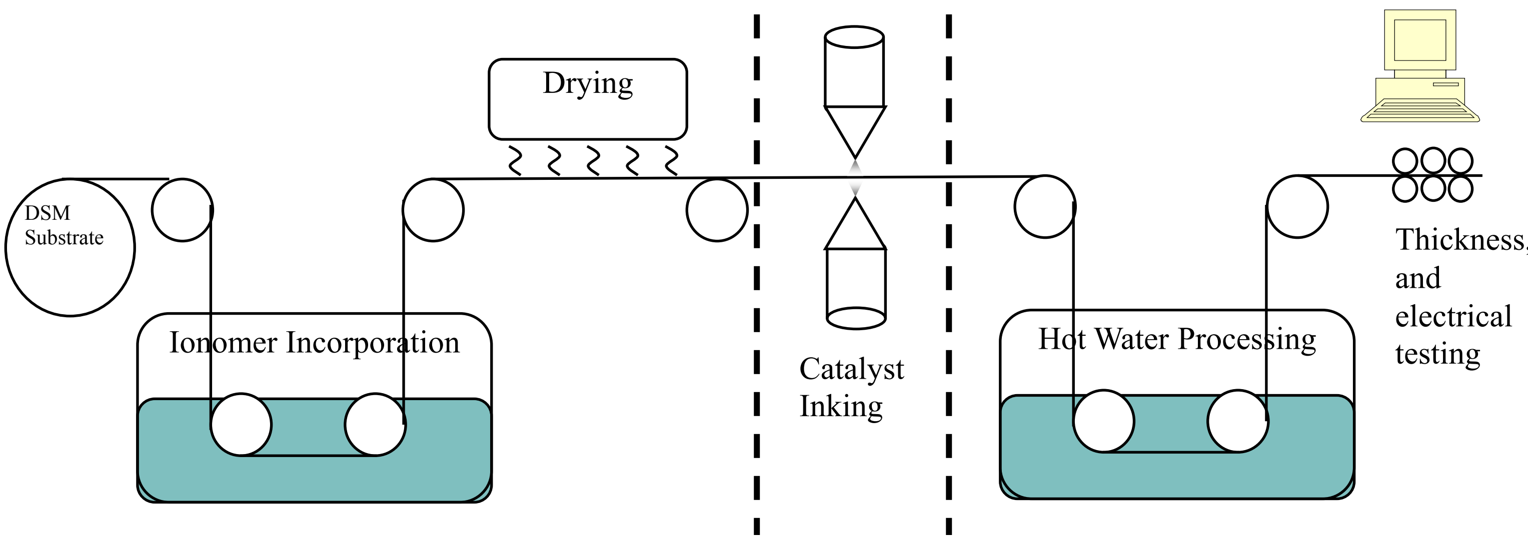
- OBJECTIVES
- APPROACH and ACCOMPLISHMENTS
  - Rationale
  - Two Dimensionally Stable Membranes™
  - Three Dimensionally Stable Membranes™
- CHALLENGES

# OBJECTIVES

| YEAR | OBJECTIVE |
| --- | --- |
| 2006 | Determine the effect of pore size and substrate thickness. Demonstrate polymerization of the PFSA. |
| 2007 | 0.07 S/cm at 80% RH at room temperature. |
| 2008 | **Go/No-Go Decision:** Demonstrate, by the 3rd Quarter, membrane conductivity > 0.1 S/cm at 25% relative humidity at 120°C using non-Nafion® materials. Samples will be prepared and delivered to the Topic 2 Awardee. |
| 2009 | Demonstrate ability to generate these materials in quantities suitable for automotive stack. Prepare samples for Topic 2 Awardee |
| 2010 | Build short stack with optimized materials and demonstrate durability |
| 2011 | Demonstrate how these materials can be produced to meet DOE cost targets |

# OBJECTIVES: Ultimate Goal

*Meet performance targets with film that can be generated in roll at DOE cost targets*



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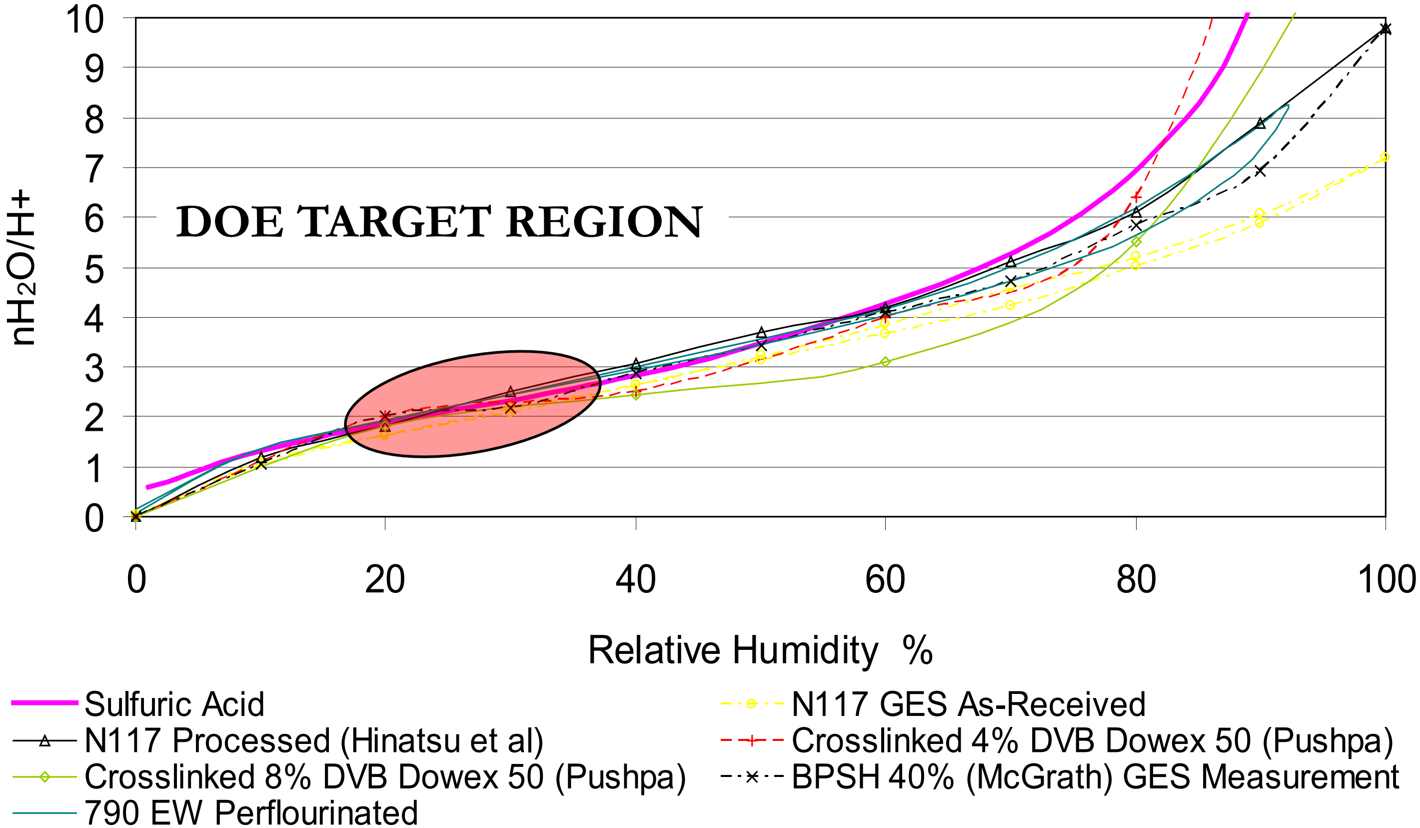
# APPROACH: Rationale

- Limitations of Ionomers based on $–SO_3H$ functionality
  - Water uptake/retention as a function of RH
  - Conductivity Limitations
    - Dependence on Water
    - Functionality

# APPROACH: Rationale

## Water Uptake of Ionomers based on $–SO_3H$ Moiety

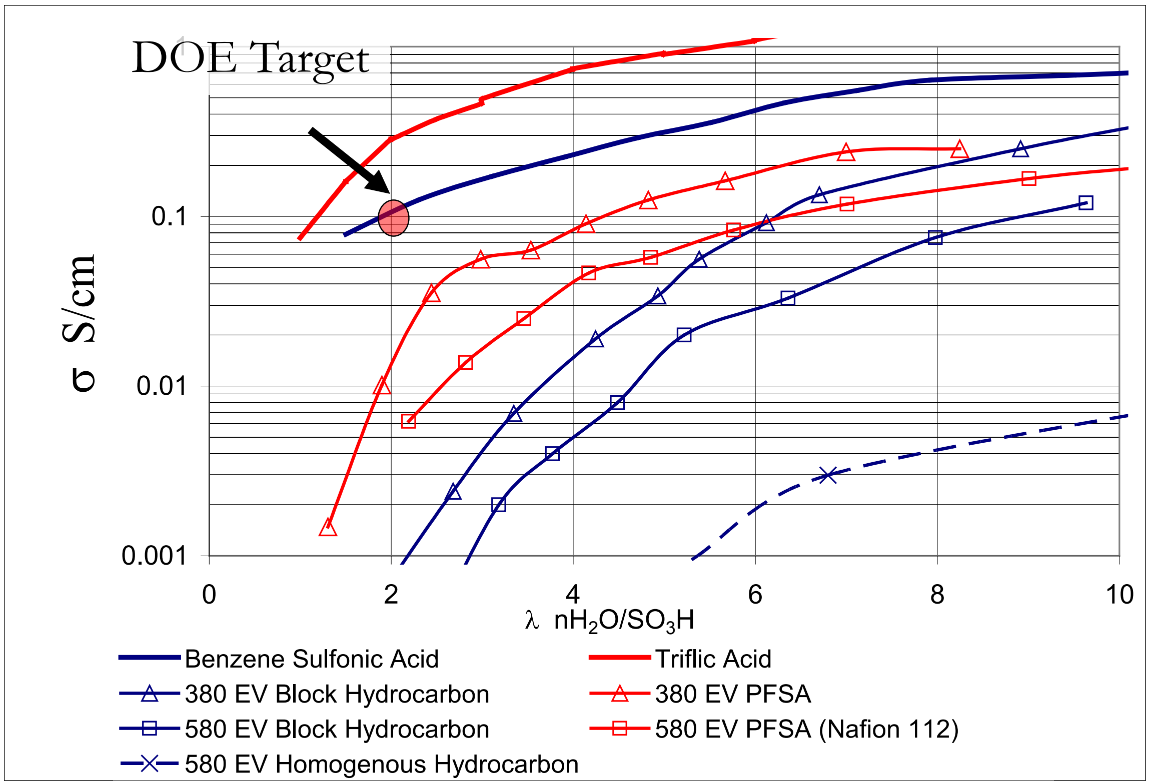


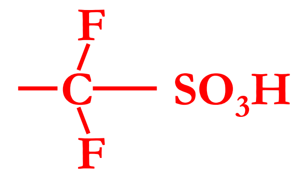

*Water Content is the same regardless of pendant group*

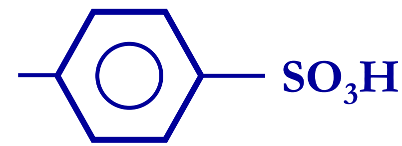
# APPROACH: Rationale

## Importance of Ionic Functional Group, Morphology

Conductivity of Various Ionomers and Model Compounds at 80°C




EV = EW/Density



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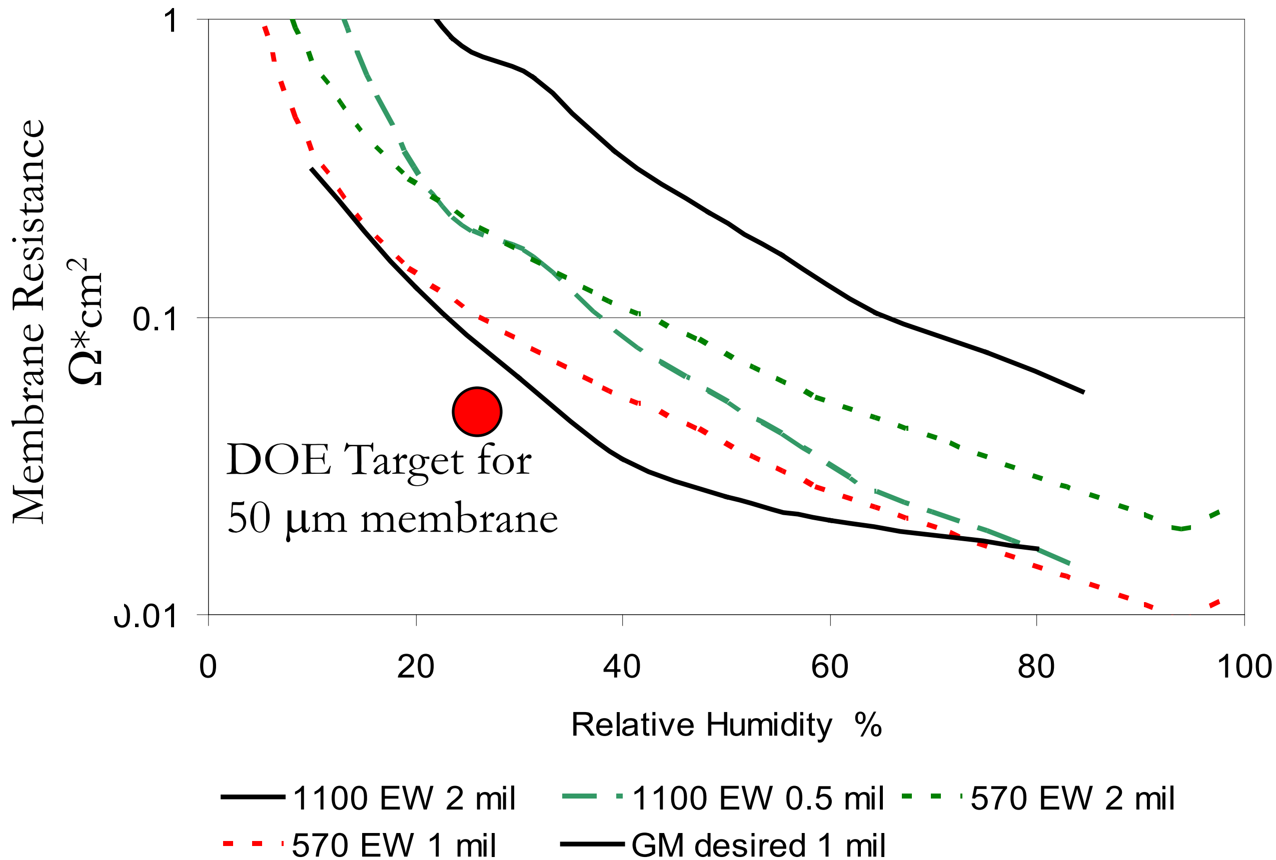
# APPROACH: Rationale

## Limitations of Ionomers Based on $-SO_3H$ Moiety

Predicted Conductivity at 100$^{o}$C for Various Perfluorinated Membranes



# APPROACH: Rationale

## CONCLUSIONS

$SO_3H$ Polymers will need

- Very low EW
- Perfluorinated End Groups
- To be very thin

THESE THREE REQUIREMENTS LEAD TO POOR MECHANICALS

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GES

DOE Hydrogen Program

# APPROACH: Lower EW of perfluorosulfonic acid ionomers to increase low RH conductivity and support the ionomer with two and three-dimensional non-ionic materials

- **Two Dimensionally Stable Membrane**
  - **Generate Supports**
    - **Thickness and Pore Size**
  - **Incorporate Ionomers**
    - **700 to 1100 EW PFSA**
  - **Characterize**
    - **Performance**
    - **Durability**
    - **Cost/Manufacturability**

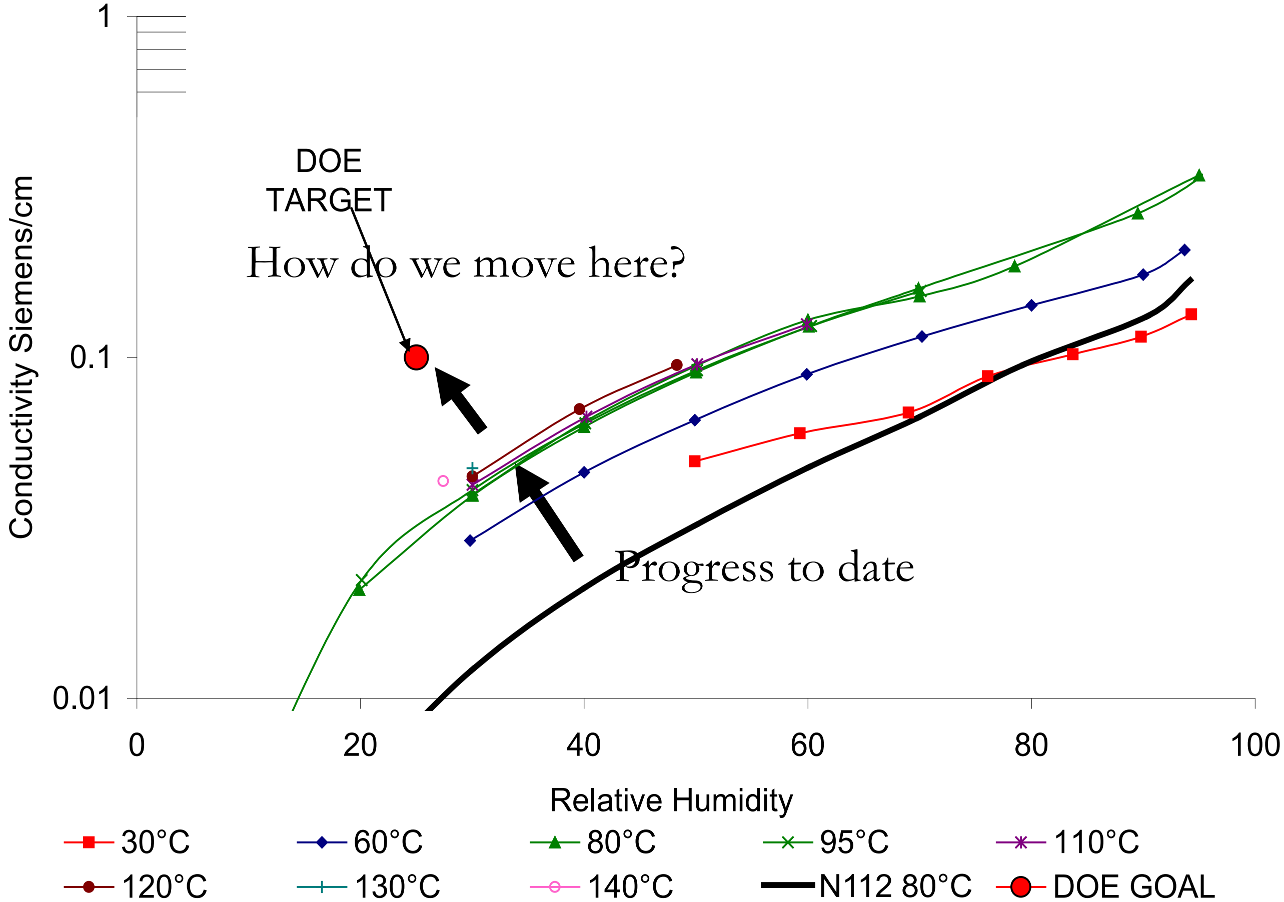
Mag:700 kV:20 plasma clean, bottom surface 10 µm

- **Three Dimensionally Stable Membrane**
  - **Develop Bulk Polymerization Methods**
  - **Polymerize in Selected Supports**
  - **Characterize**
    - **Performance**
    - **Durability**
    - **Cost/Manufacturability**

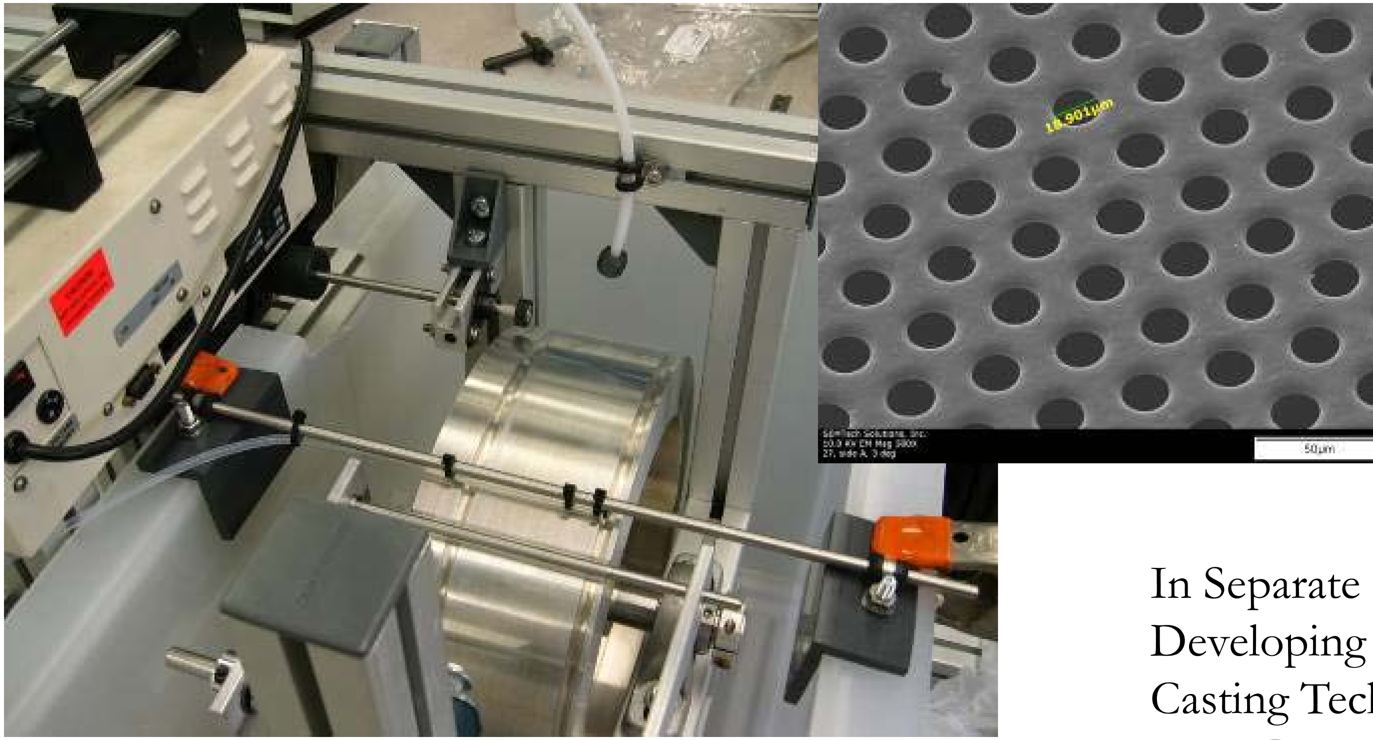
# ACCOMPLISHMENTS: 2DSM™

## In-Plane Conductivity

700 EW Membrane with DSM™ Support, Conductivity as a function of RH



# CHALLENGES: 2DSM™




**Automatic solution dispensing**
**Automatic speed control**
**Manual support collection**
**Solution recycling can be implemented**

In Separate DOE Project Developing Low-Cost Casting Technique
(**DE-FG02-05ER84322** )
PI: Han Liu

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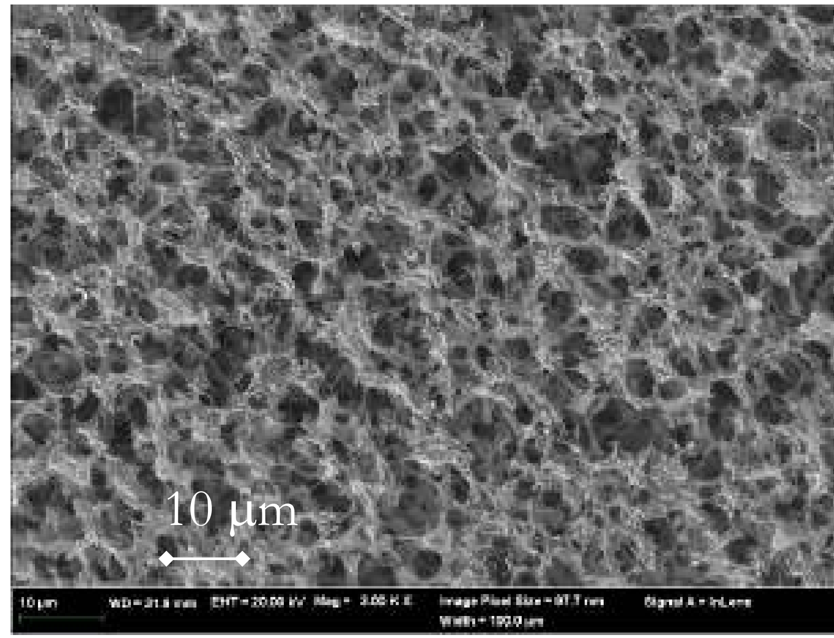
# APPROACH: 3DSM™

- Cost of Laser Drilling Prohibitively High
- Three-Dimensional Supports Commercially Available
- Using Conventional PFSA Ionomers to Meet Cost Targets
- Synthesizing New Low EW Ionomers to Meet Performance Targets
  - *Work being done by Israel Cabasso's Group at SUNY Syracuse Polymer Research Institute*

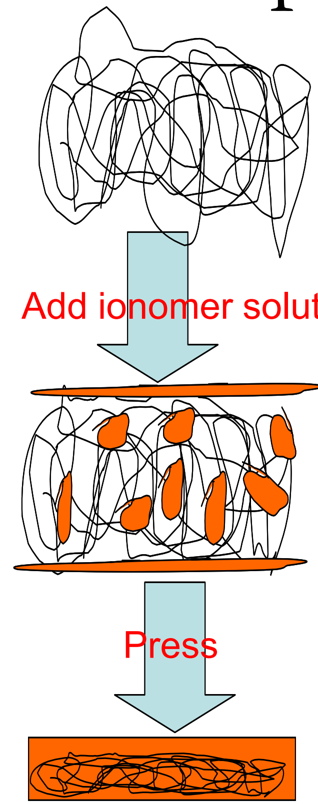


# APPROACH: FOCUS OF PAST YEAR

- THINNER!
- Lower EW ionomers into Thin supports
- Two Support Materials have been used
  - Type "ThinB" is easier to make thin, more difficult to make compatible with lower EW materials
  - Type "ThinC" more difficult to make thin, easier to incorporate low EW materials
- Demonstrate Chemical Stability
- New Ionomers for lower EW (SUNY-ESF)

# Three Dimensional Supports

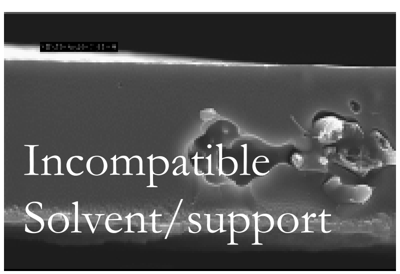
- Advantages:
  - Many commercially available
  - Ionomer is easily added by solution
  - Roll to Roll processible
- Disadvantages:
  - Making thin supports for some materials
  - Support/Solution compatibility
  - Getting high ionomer content
    - High wt% dispersion
    - High void volume




80% Void (very good)

Film forms on top and/or bottom
Center is now
20% support
20% ionomer
60% void

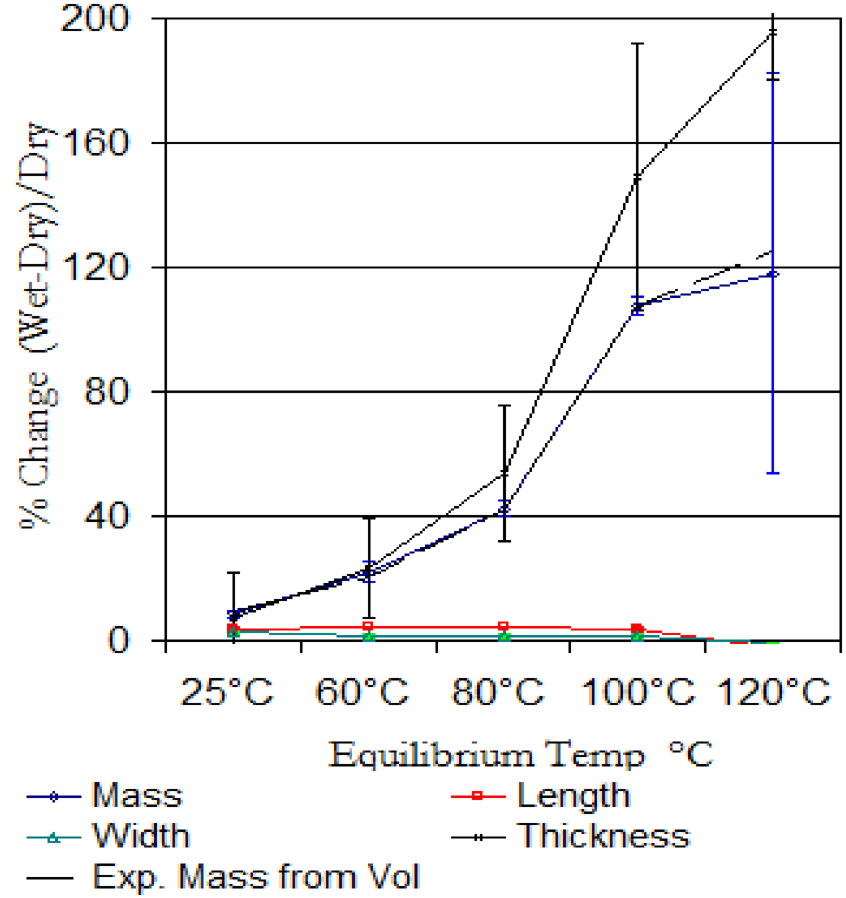
Center is now 50% ionomer, 50% support.
Conductivity penalty = 2*tortuosity





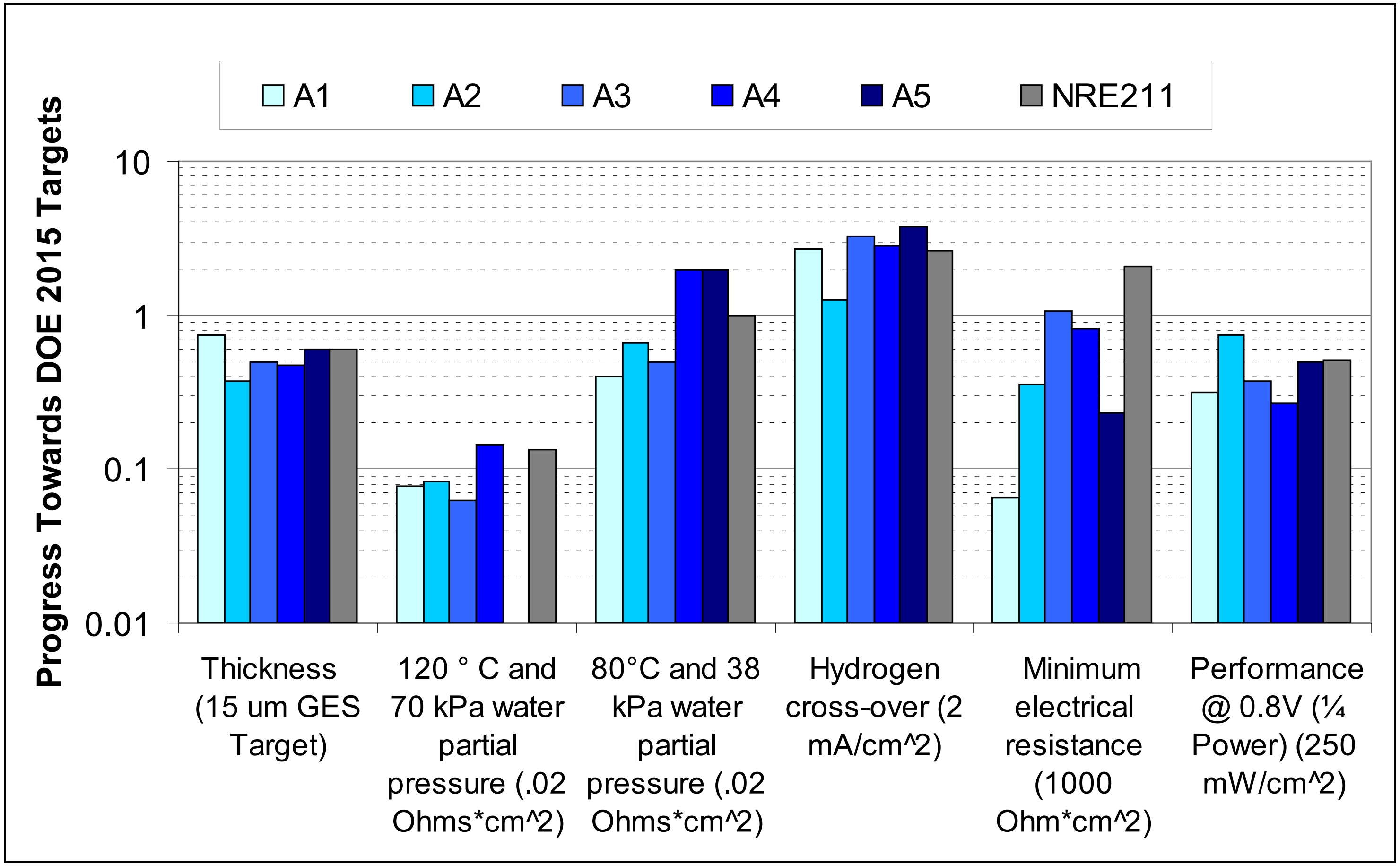
# ACCOMPLISHMENTS: 3DSM™
# Previous Results with 1 mil membrane

- Custom Membrane from Millipore
- Swelling is Comparable to thick membrane
- Completely Filling Support was a Major Challenge
- Consistency through the plane was a challenge
- ~25% Conductivity Penalty
- 10,000 RH Cylcles demonstrated
- *Could not incorporate low EW materials into the matrix*
- *Difficult making membranes below 25um*



# ACCOMPLISHMENTS: 3DSM with ~ 850 EW

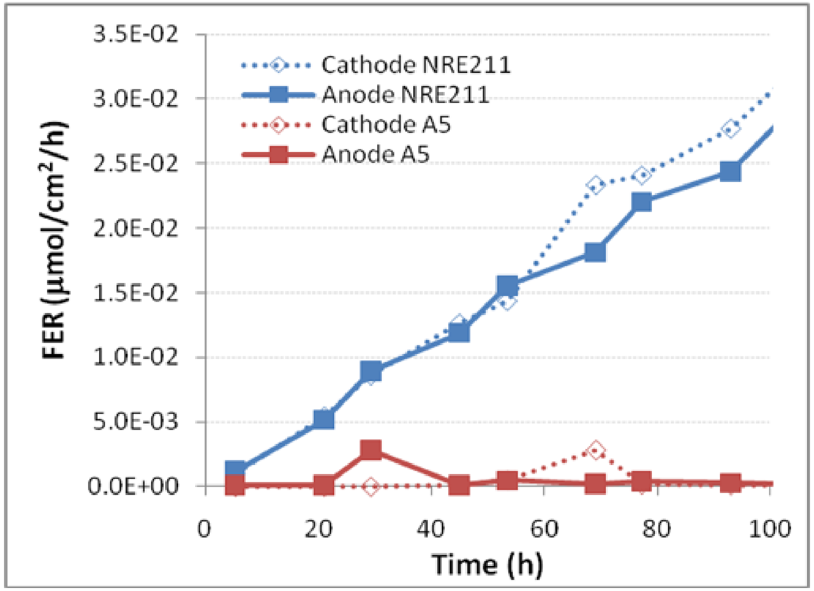
## Florida Solar Energy Center (FSEC) Test Results

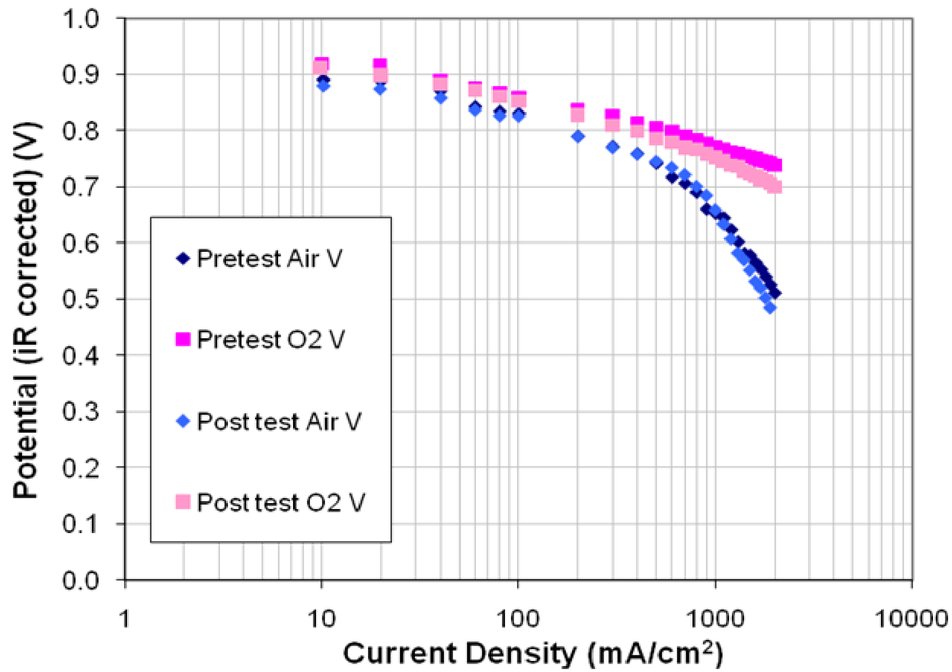



*If we had 18 um membrane with our lowest EW ionomer resistance would be ~ 1/3*

# ACCOMPLISHMENTS: Chemical Stability Enhancement

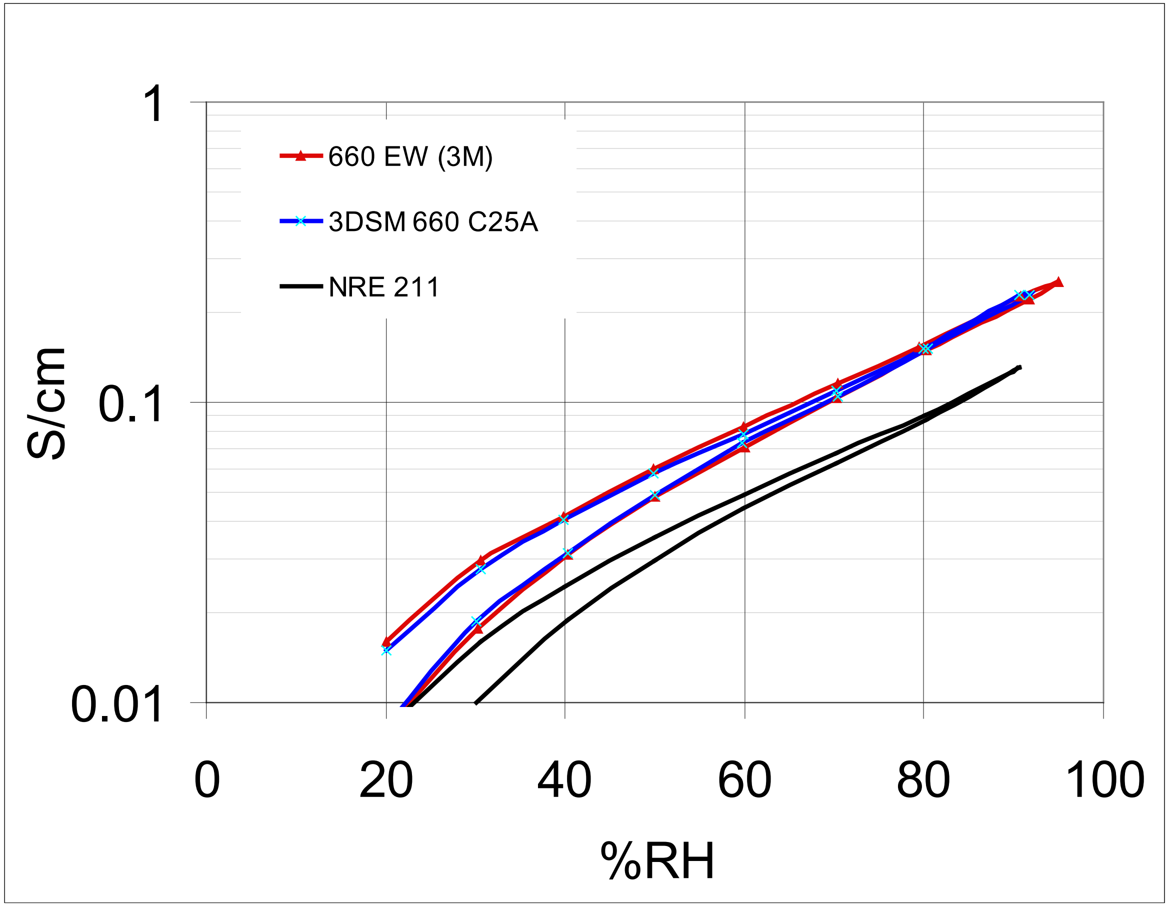
## Florida Solar Energy Center Testing




Fluoride release during OCV testing demonstrates much enhanced chemical stability.
Testing before and after durability testng showed little performance change

# ACCOMPLISHMENTS: 3DSM with 3M 660 EW Ionomer

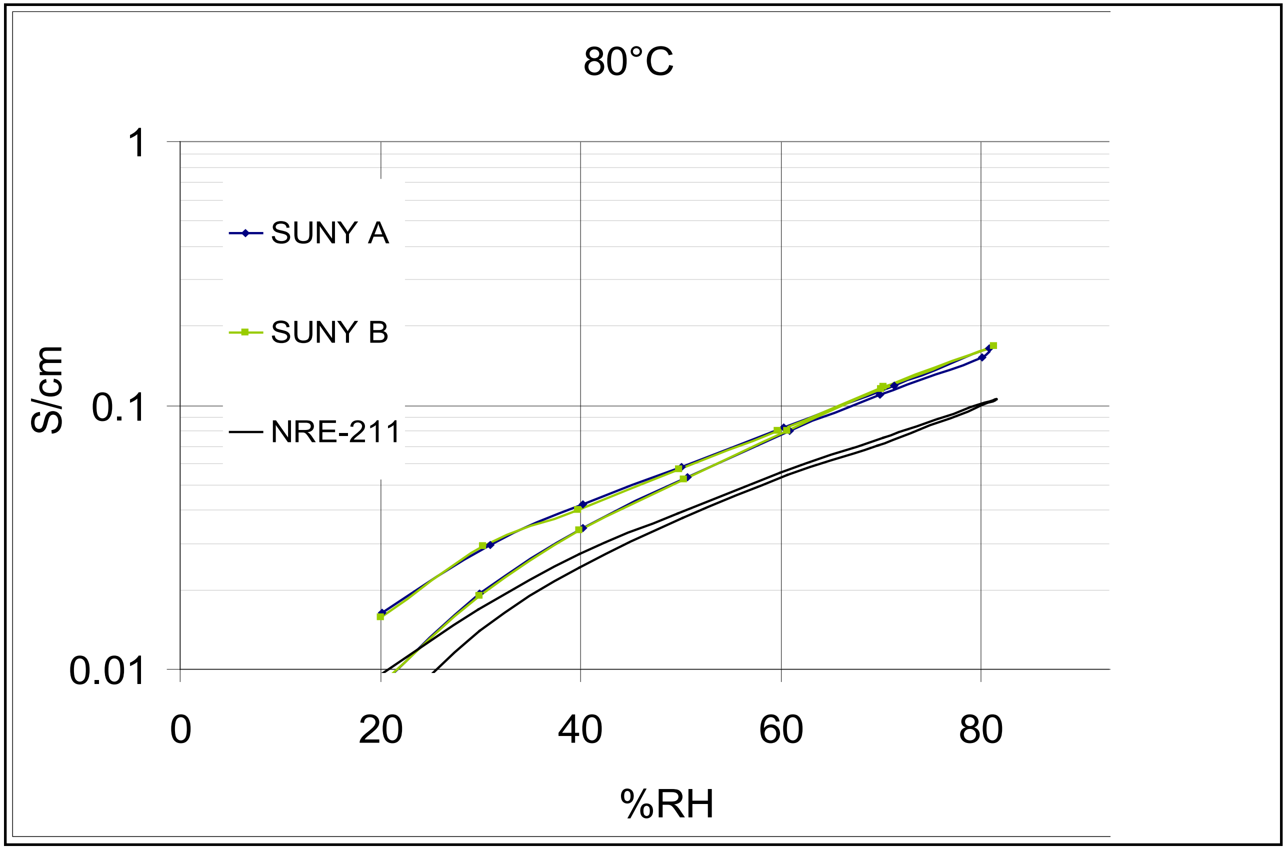



3M gave us another low EW material to test

Improved from Nafion

Still needs to be better

# ACCOMPLISHMENTS: 3DSM with SUNY Ionomer




SUNY continues to make alternative PFSA's but reaching DOE goals with "workable" materials is daunting

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# CHALLENGES

- **Lower EW in Thinner Supports**
  - 12-15 um target
  - Get as close to DOE target as possible at low RH
- Demonstrate Cycling to 20,000 Cycles
- This project extended through October to achieve these goals

# SUMMARY

- Year 1 Milestones Achieved
  - DSMs with a wide range of pore size and thickness restrain x-y swelling
  - Polyimide and polysulfone both shown to be effective supports
  - Effective methods of generating new PFSA polymers have been generated
- Year 2 Milestones Achieved
  - Conductivity targets have been met
    - Discrepancy between Bekktech and GES results
  - Fuel Cell Performance Improvements Shown
    - Electrode Improvements
- Durability demonstrated through RH cycling
- Realistic Pathways for Meeting Cost Targets Seen for both Paths.
  - Millipore estimates \$10/m$^2$ for support and processing.
  - Toll-coaters contacted and adding PFSA to membrane is ¢/m$^2$
  - Key question is cost of PFSA
- To reach ultimate DOE Goals we need to incorporate the low EW materials into a thinner support.
- *Membranes developed will have commercial applications in GES electrolyzers*

# OBJECTIVES: Ultimate Goal

*Meet performance targets with film that can be generated in roll at DOE cost targets*