Dimensionally Stable Membranes™

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SUNY-ESF

FC036

Dimensionally Stable Membranes for High Temperature Applications

Timeline

- Begin 4/3/2006
- Review 4/1/2011
- 80% Complete

Budget

- Total project funding (to 2009)
  - $1.5 M DOE Funding (w/go)
  - $589K Recipient
  - 35% Cost Share
  - $300K received FY 2009
  - $241K to be received in FY 2010
  - $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 h lifetime
- Stability in Condensing conditions

Partners

- General Motors
- SUNY-ESF

OVERVIEW

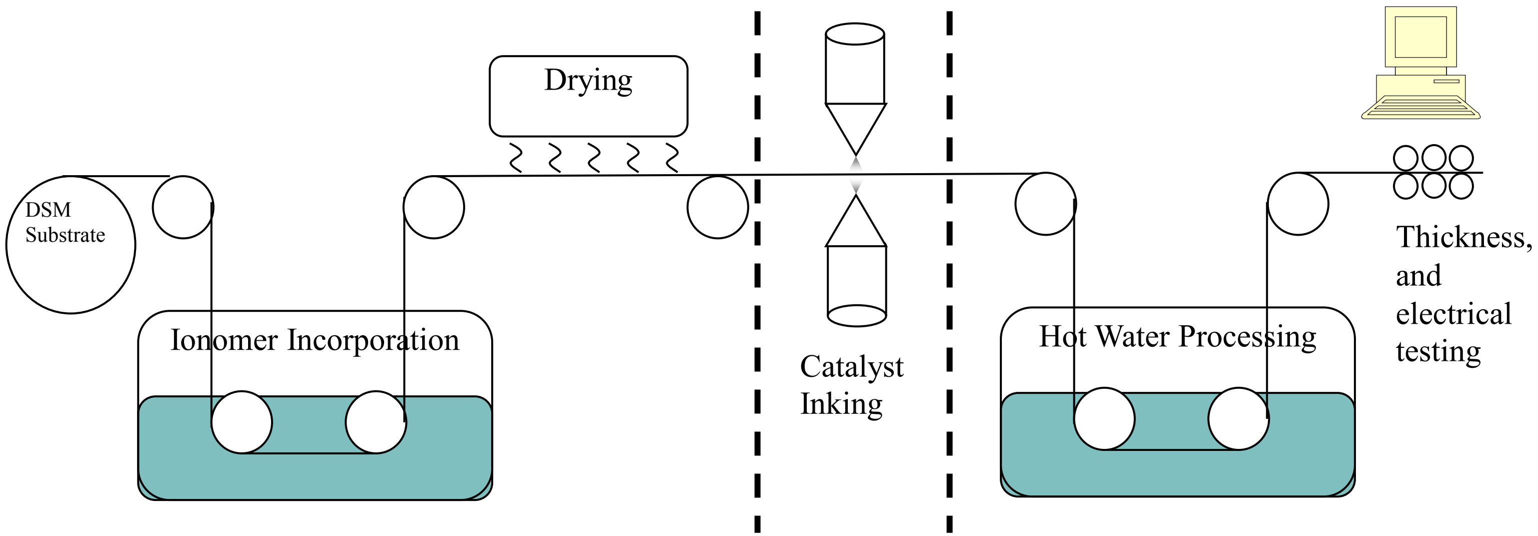
- OBJECTIVES
- APPROACH and ACCOMPLISHMENTS
  - Rationale
  - Two Dimensionally Stable Membranes™
  - Three Dimensionally Stable Membranes™
- CHALLENGES

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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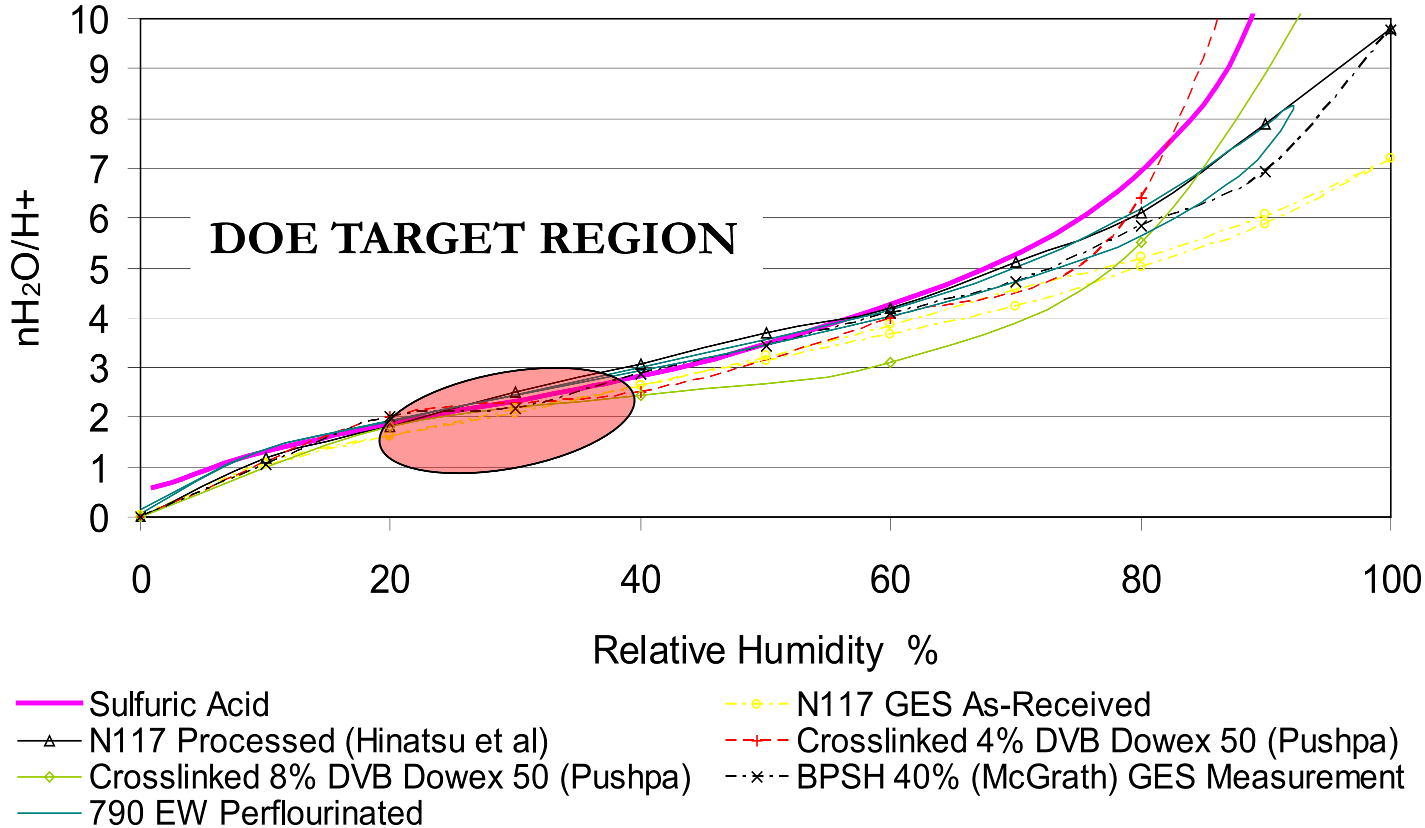
APPROACH: Rationale

- 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

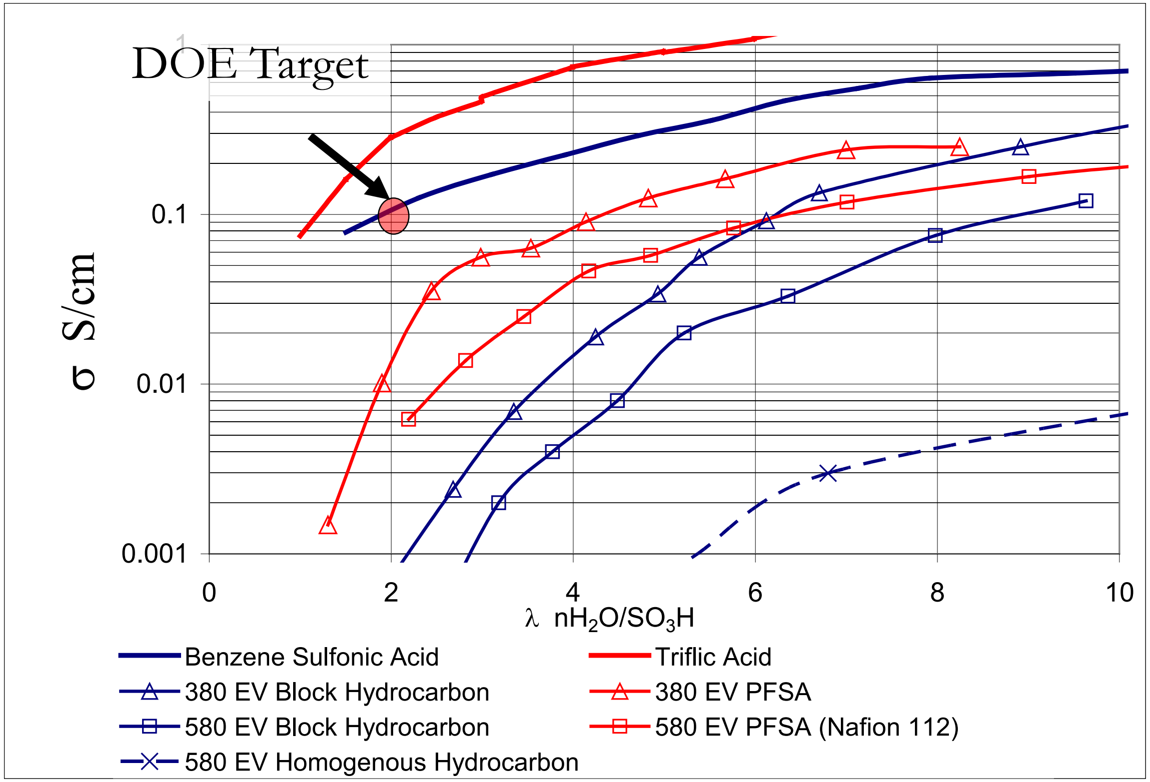


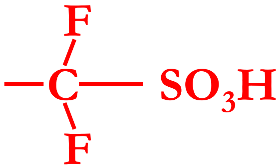
Water Content is the same regardless of pendant group

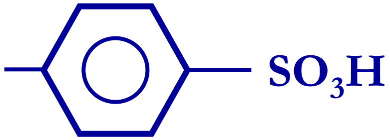
APPROACH: Rationale

Importance of Ionic Functional Group, Morphology

Conductivity of Various Ionomers and Model Compounds at 80°C





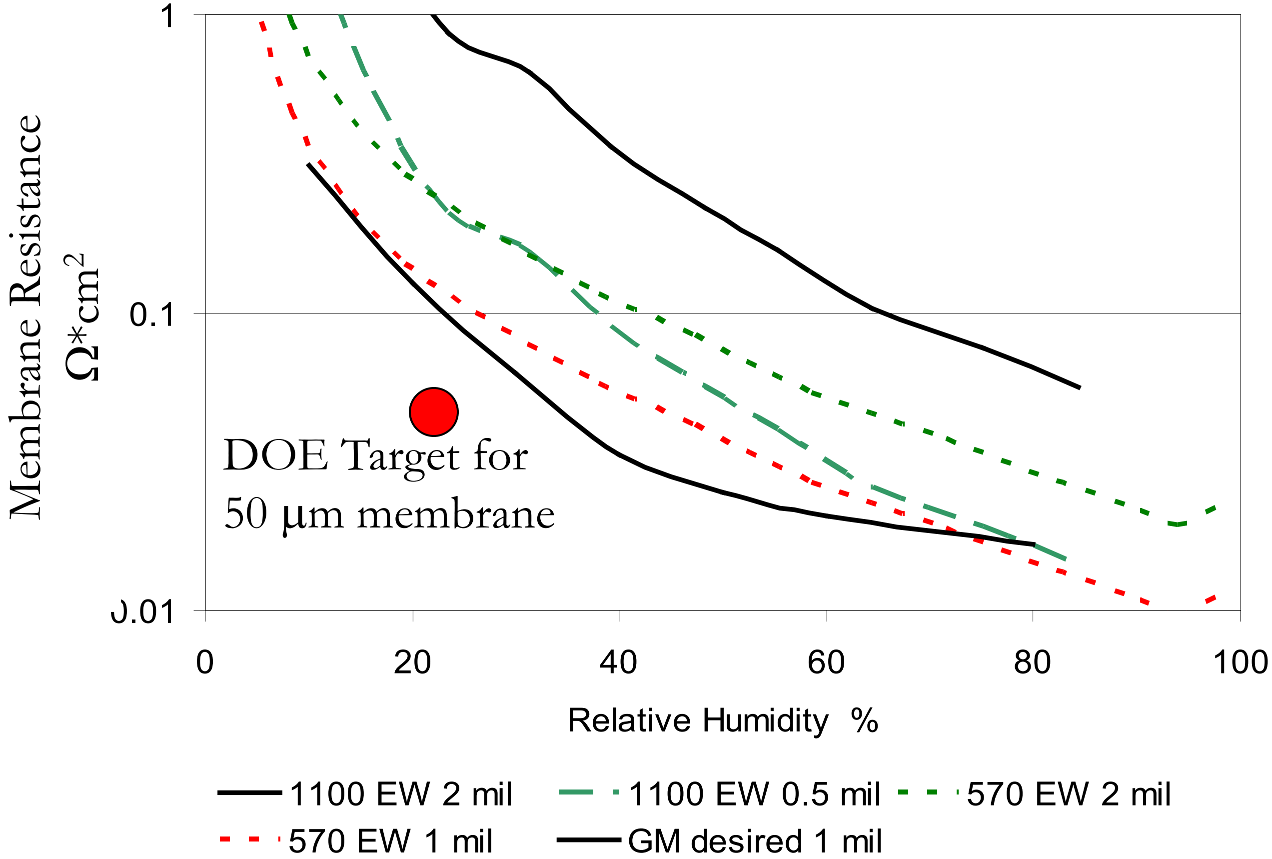


EV = EW/Density

APPROACH: Rationale

Limitations of Ionomers Based on $-SO_3H$ Moiety

Predicted Conductivity at 100°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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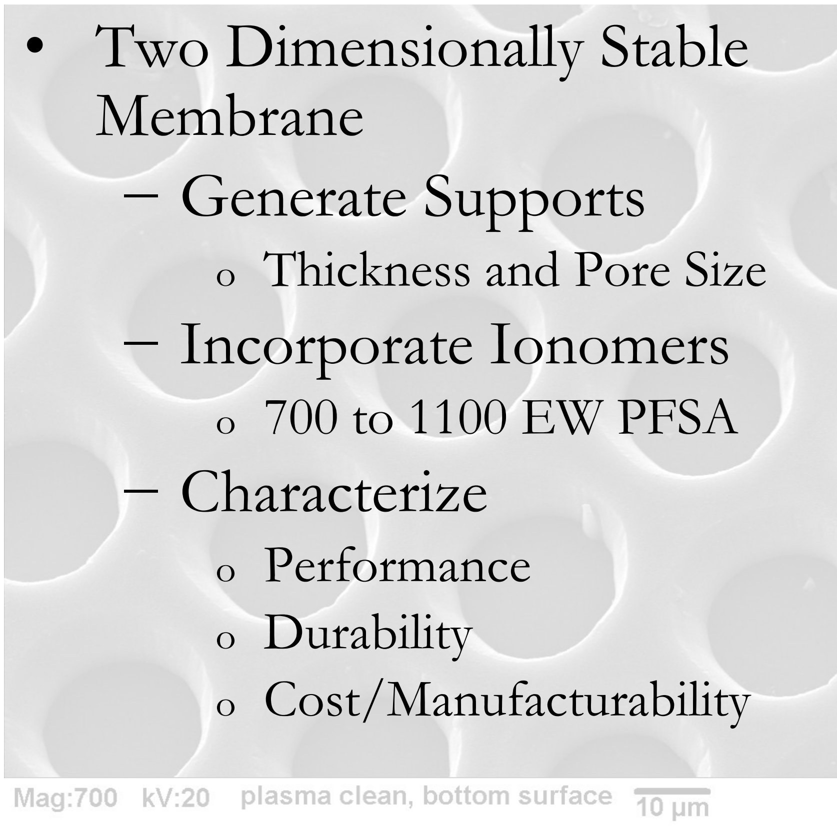
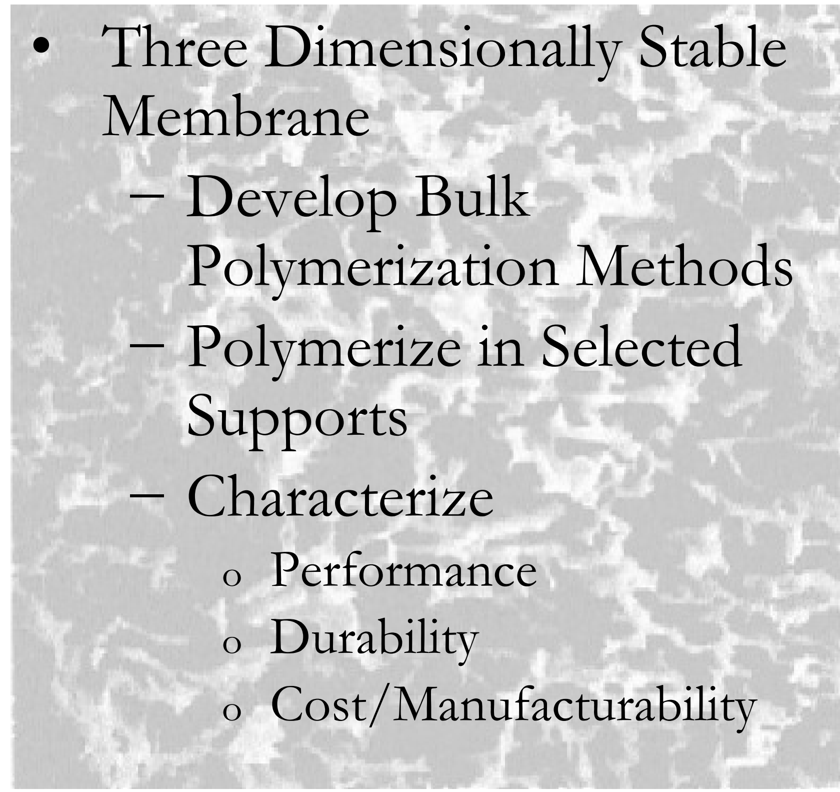
APPROACH: Lower EW of perfluorosulfonic acid ionomers to increase low RH conductivity and support the ionomer with two and three-dimensional non-ionic materials



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

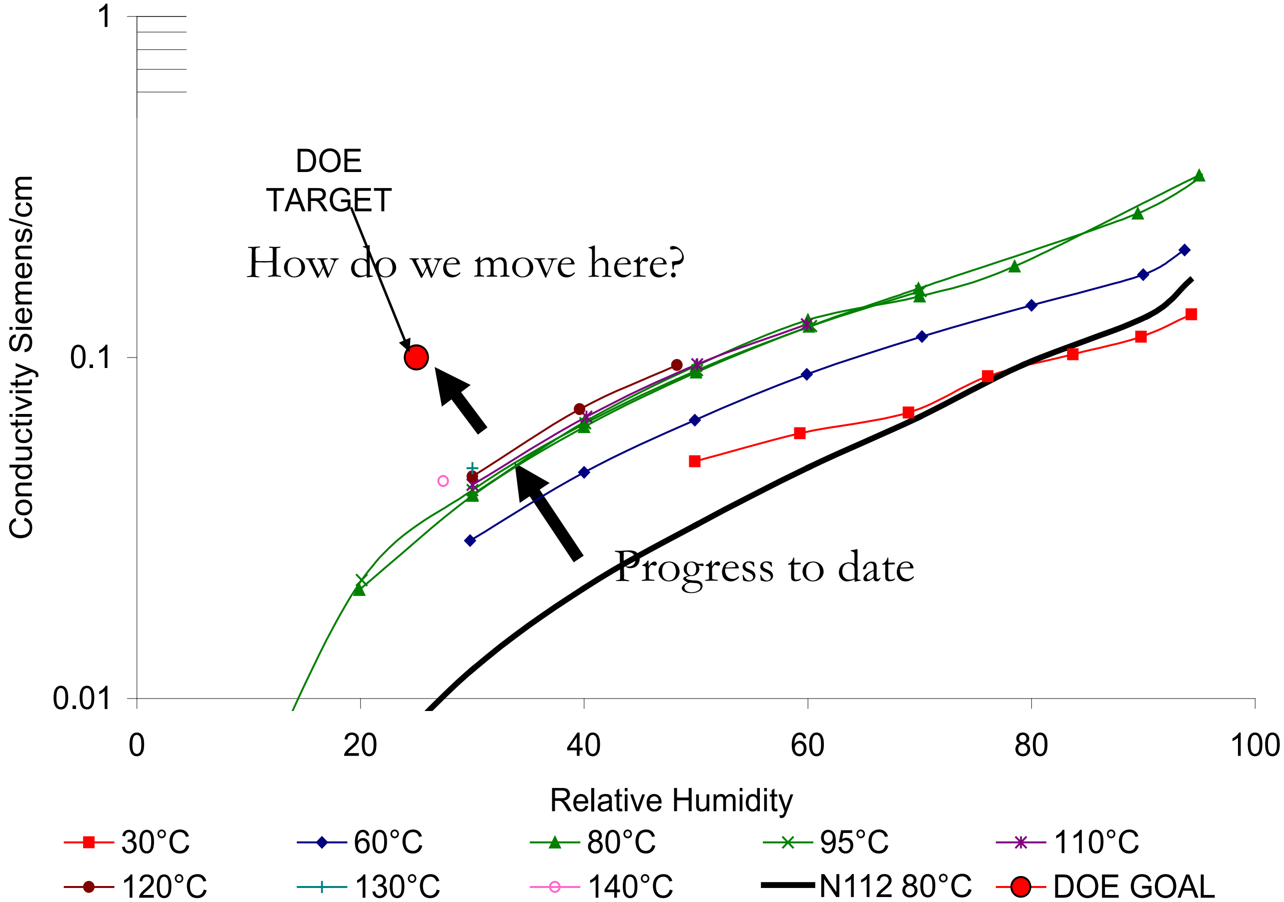


- Three Dimensionally Stable Membrane
  - Develop Bulk Polymerization Methods
  - Polymerize in Selected Supports
  - Characterize
    - Performance
    - Durability
    - Cost/Manufacturability

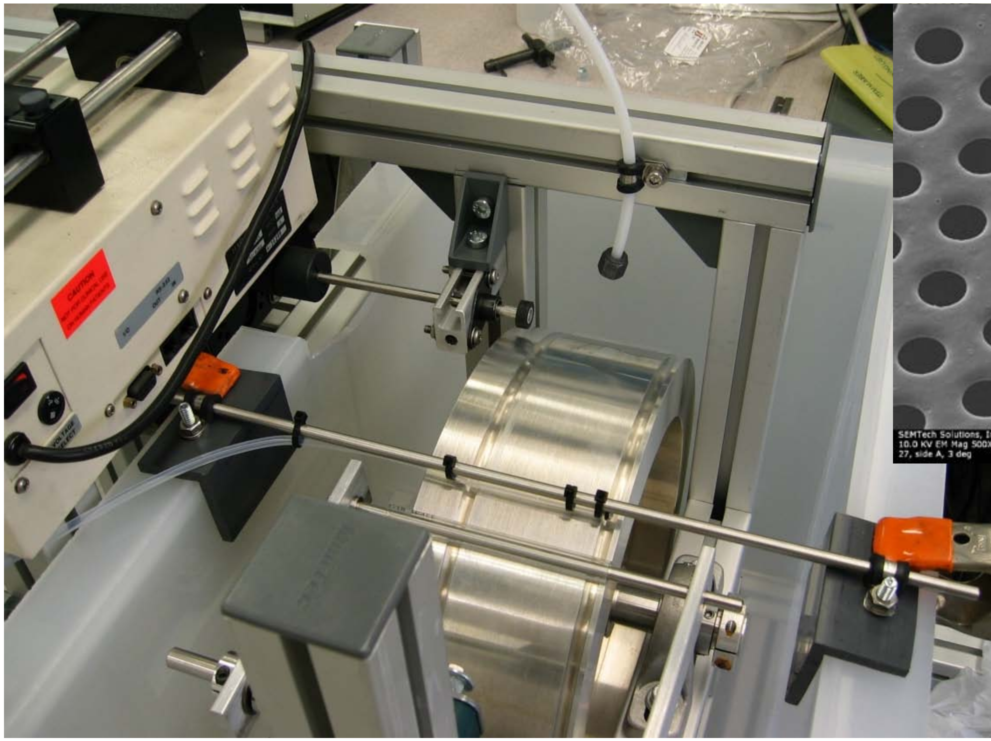
ACCOMPLISHMENTS: 2DSM™

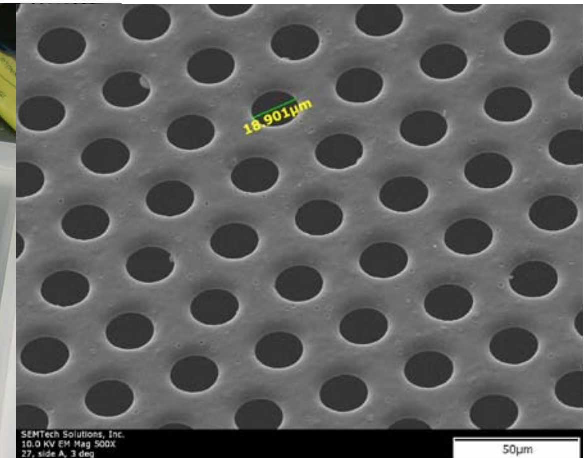
In-Plane Conductivity

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



Challenges: 2DSM™





In Separate DOE Project Developing Low-Cost Casting Technique

(**DE-FG02-05ER84322**)

PI: Han Liu

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

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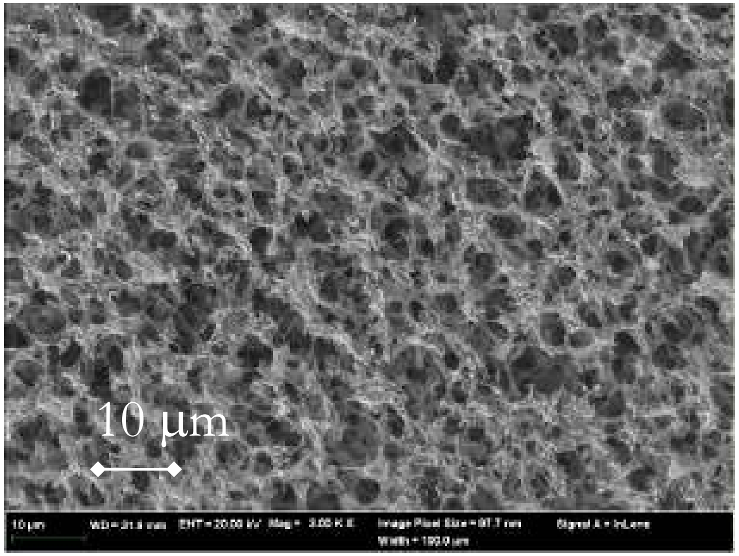
APPROACH: 3DSM™

- 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*

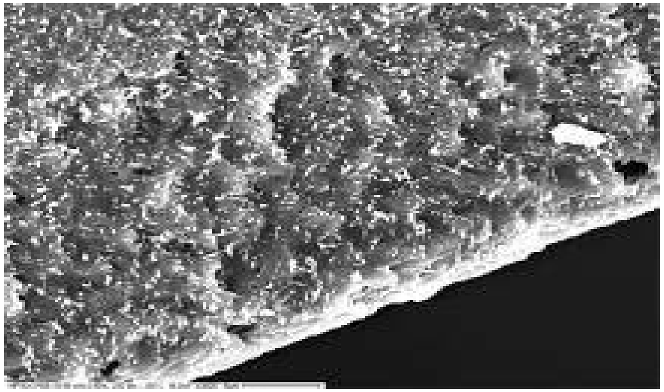


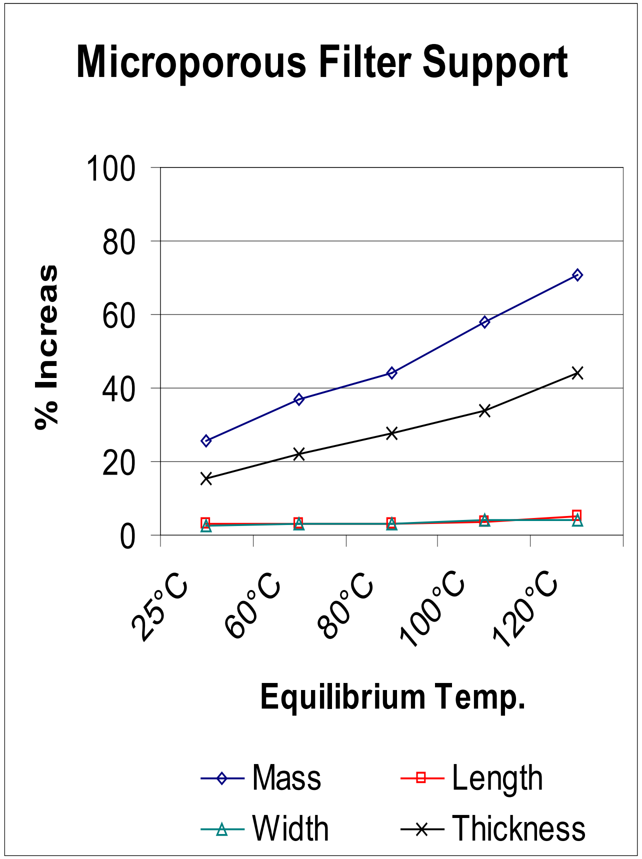
APPROACH: FOCUS OF PAST YEAR

- THINNER!
- Demonstrate Mechanical Durability Through RH Cycling
- Larger, More Consistent Membranes.
- Leave MEA/Fuel Cell Performance to Florida Solar Energy Center

ACCOMPLISHMENTS: 3DSM™
-Previous results with 3-mil membrane

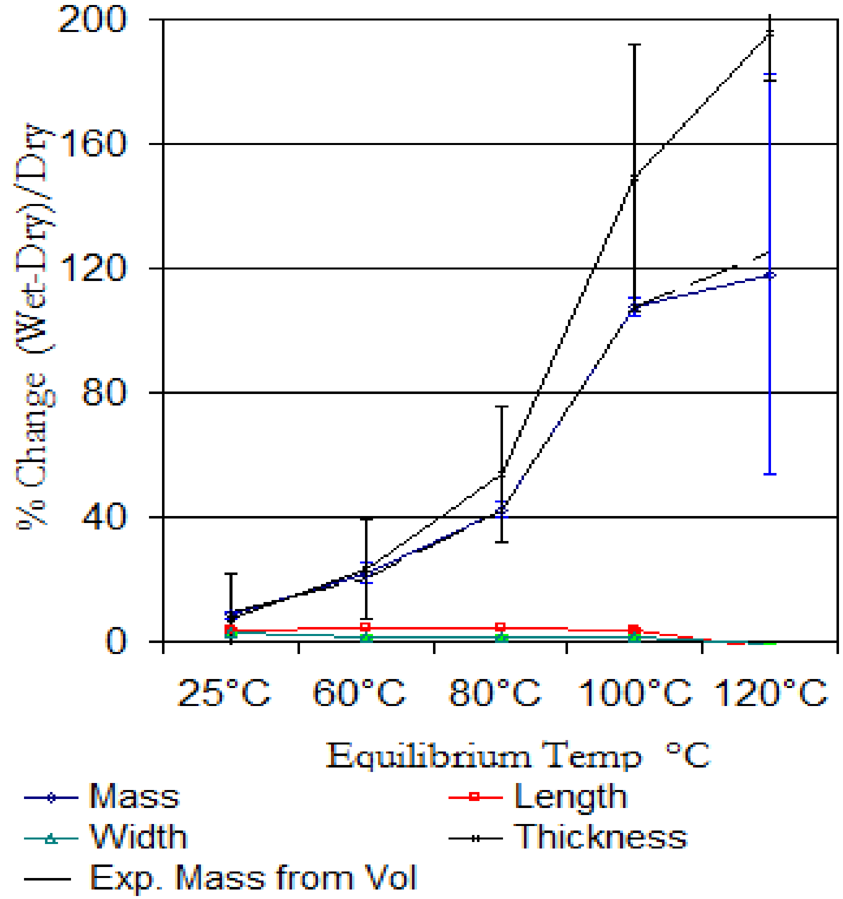
- Filled supports with commercial PFSA material
- Swelling is comparable to 2DSM
- Completely filling support was a major challenge
- ~33% conductivity penalty



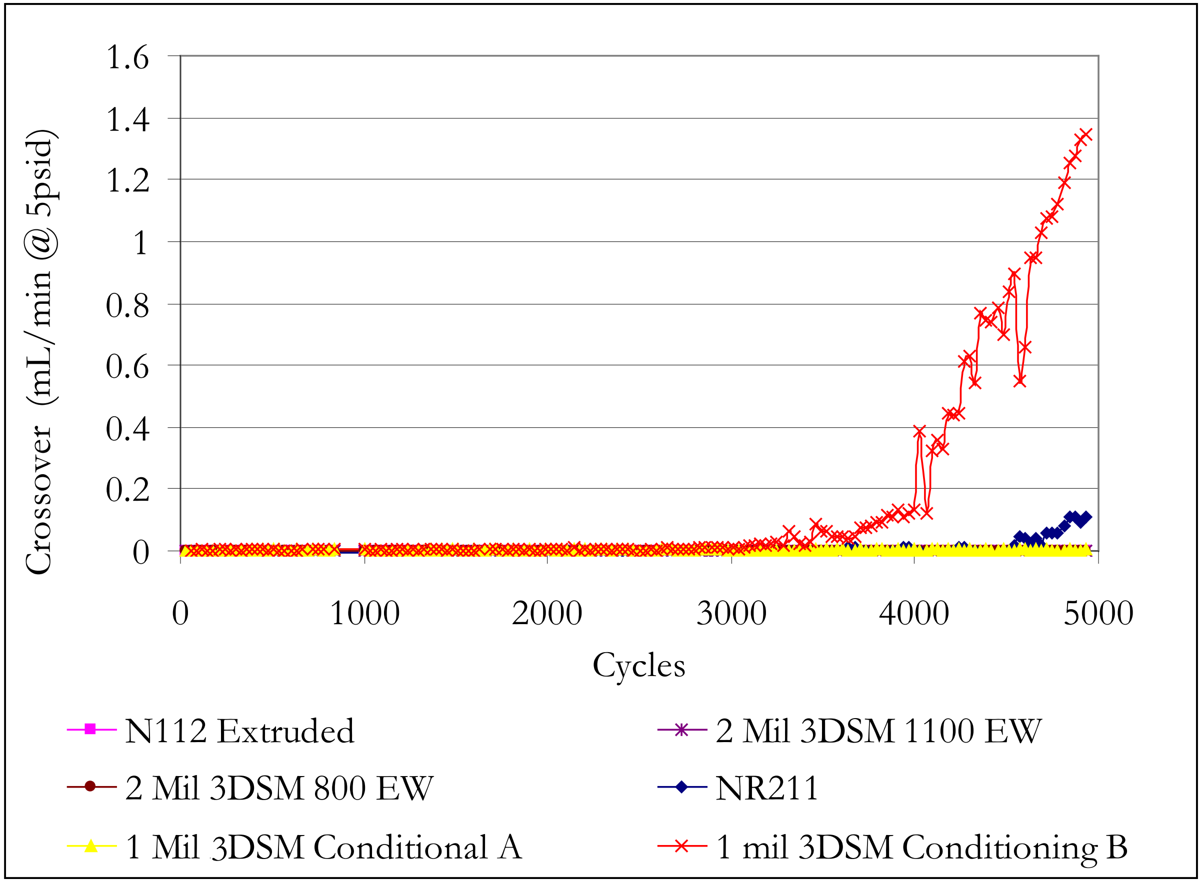


ACCOMPLISHMENTS: 3DSM™
Current Results with 1-mil membrane

- 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



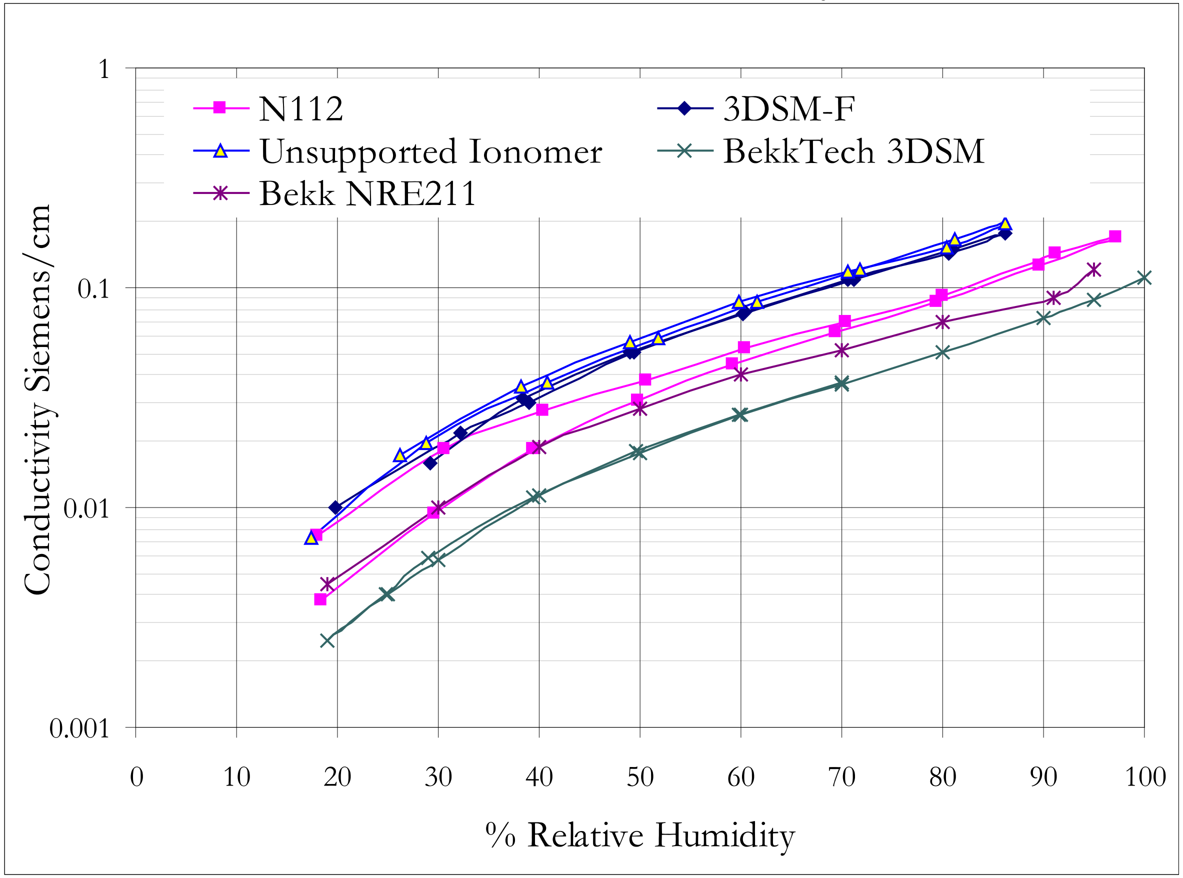
ACCOMPLISHMENTS: 3DSM™ RH Cycling Results



RH Cycling durability dependent on processing. 5000 Cycles demonstrated with 1-mil membrane.

ACCOMPLISHMENTS: 3DSM™

Conductivity at 80°C

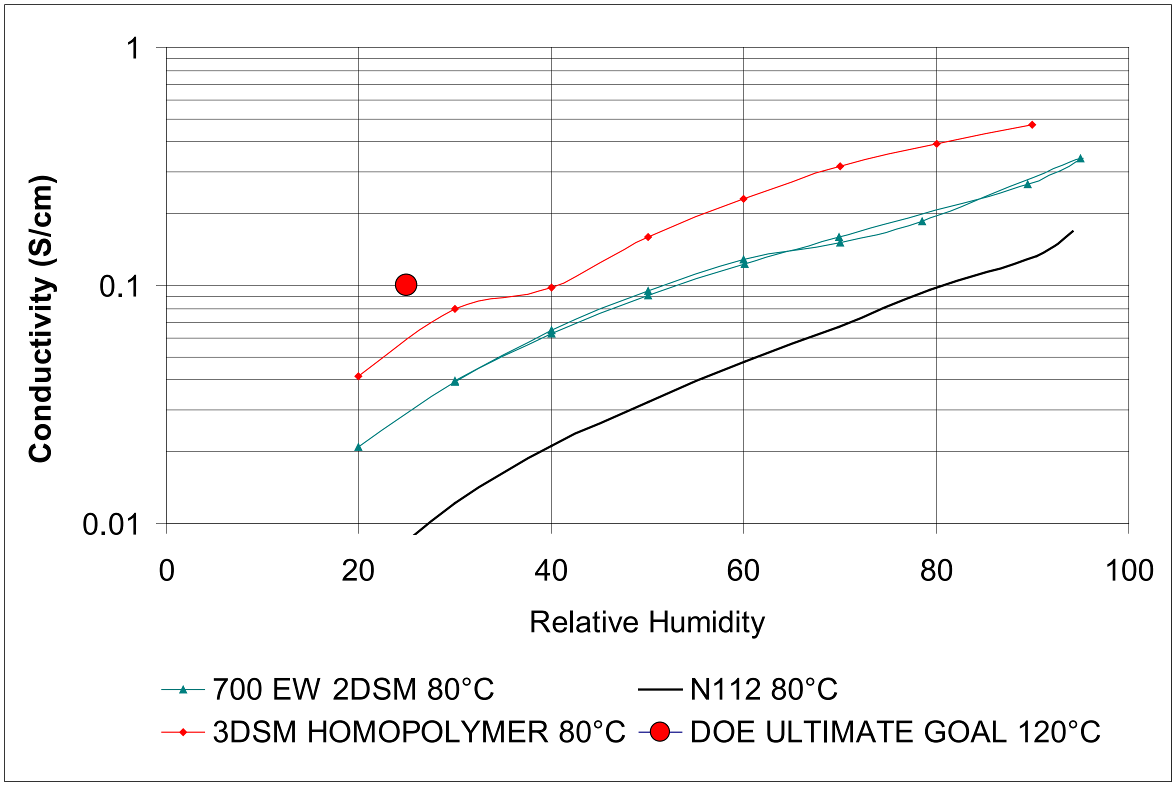


Discrepancy between Bekktech and GES data may have been pretreatment, washing of solvent

Have not yet matched best 2DSM data, but have not yet found a way to incorporate lowest EW PFSA in supports

ACCOMPLISHMENTS: 3DSM™

Alternative Synthesis: Homopolymer



Synthesis of new PFSA Monomers
Working with SUNY-ESF to make new copolymers and homopolymer

CF_2CF
$\quad | $
$\quad OCF_2CF(CF_3)OCF_2CF_2SO_2F$

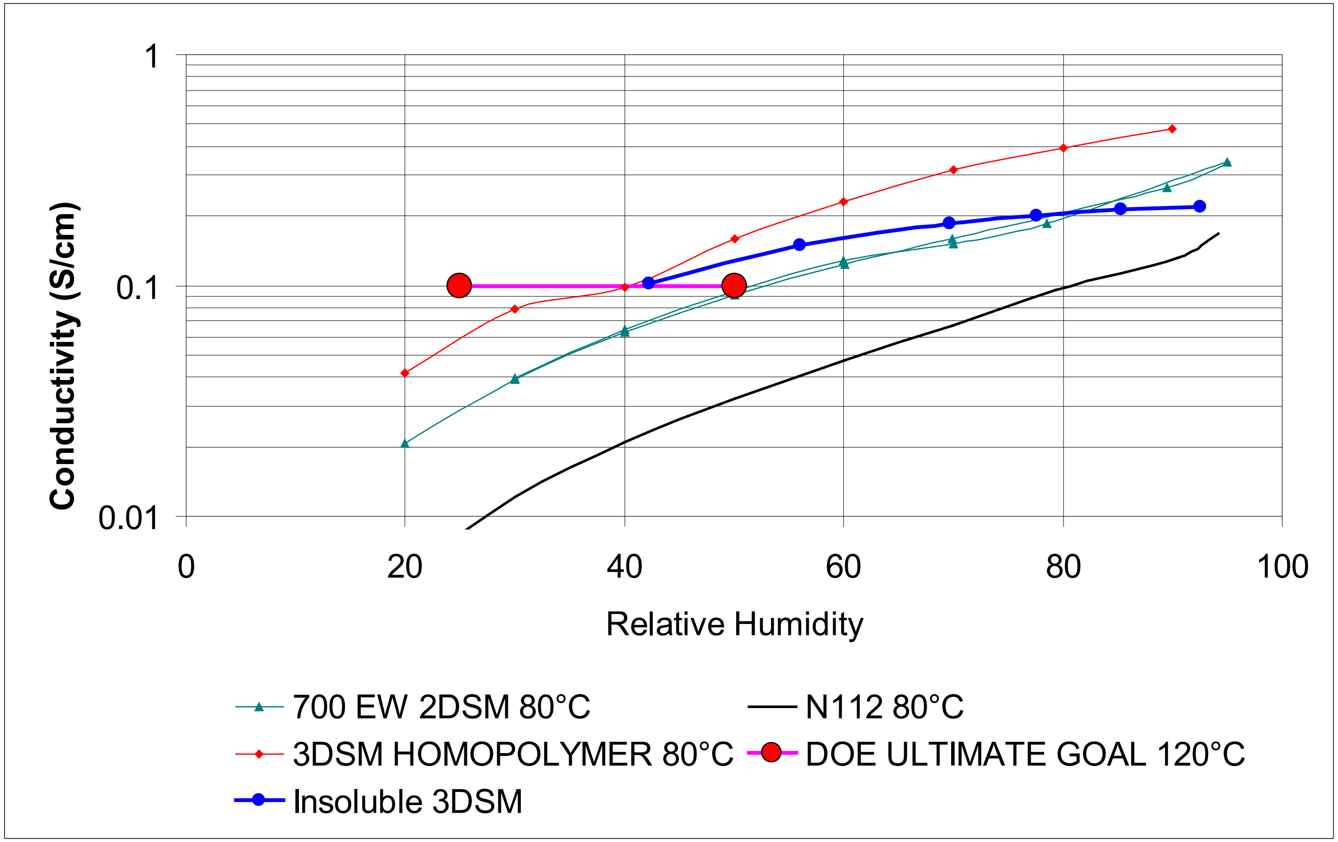
\+ ?

Three non-PTFE copolymers successfully synthesized. EW from 500-1300.

Getting closer to DOE target! This polymer is water soluble is DOE target reachable?

ACCOMPLISHMENTS: 3DSM™

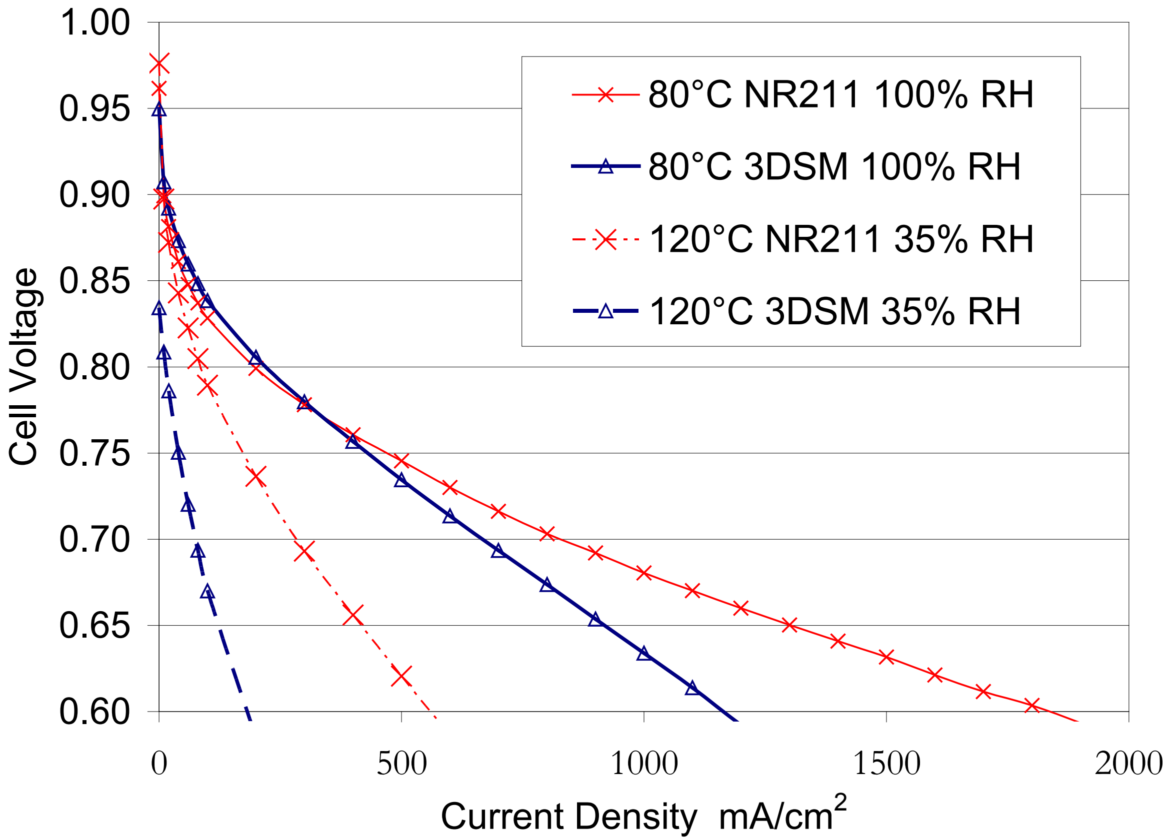
New Insoluble low EW PFSA



Last year successfully generated an insoluble highly conductive polymer, but have had difficult making large, supported films and MEAs

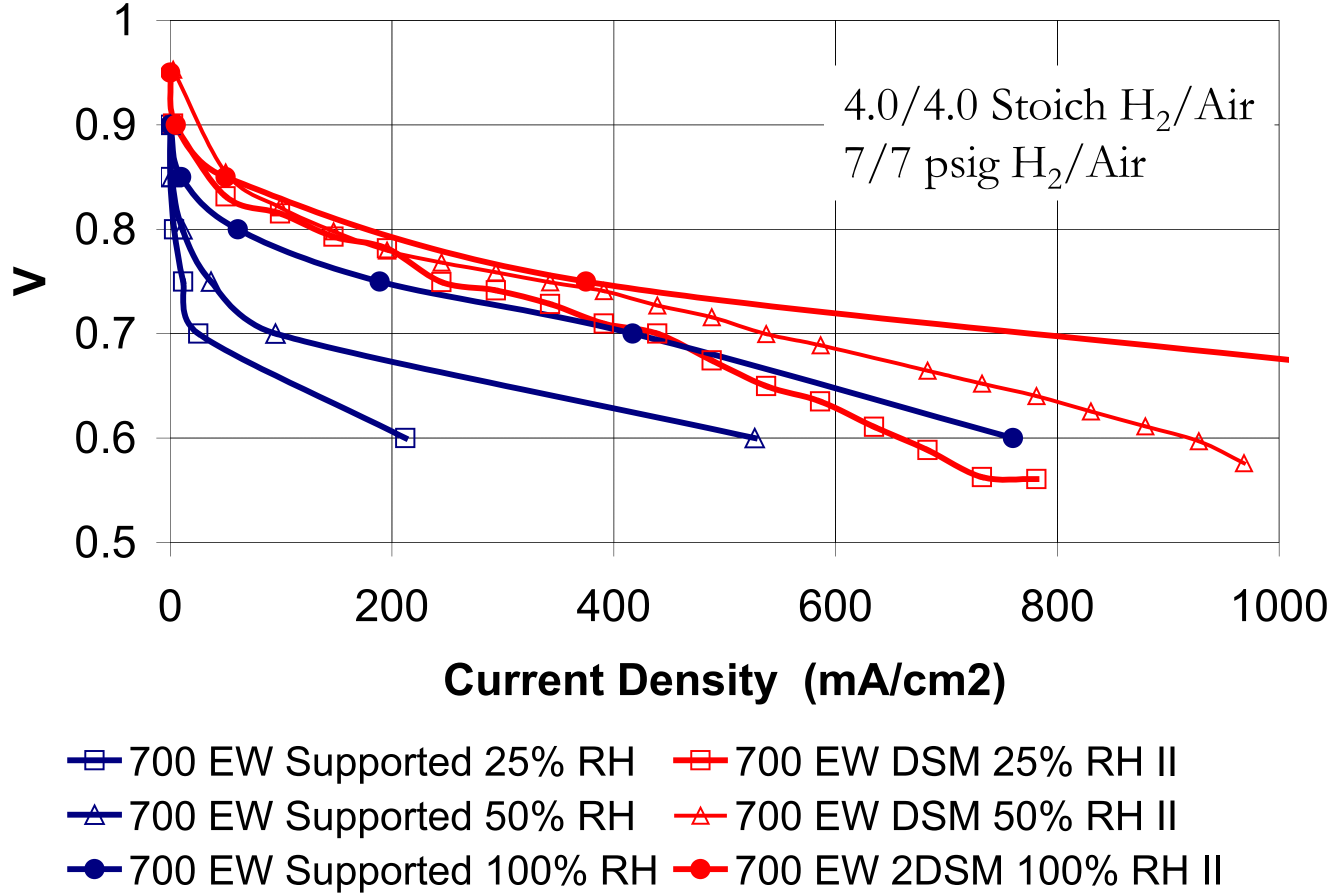
ACCOMPLISHMENTS: 3DSM™

Florida Solar Energy Center Testing



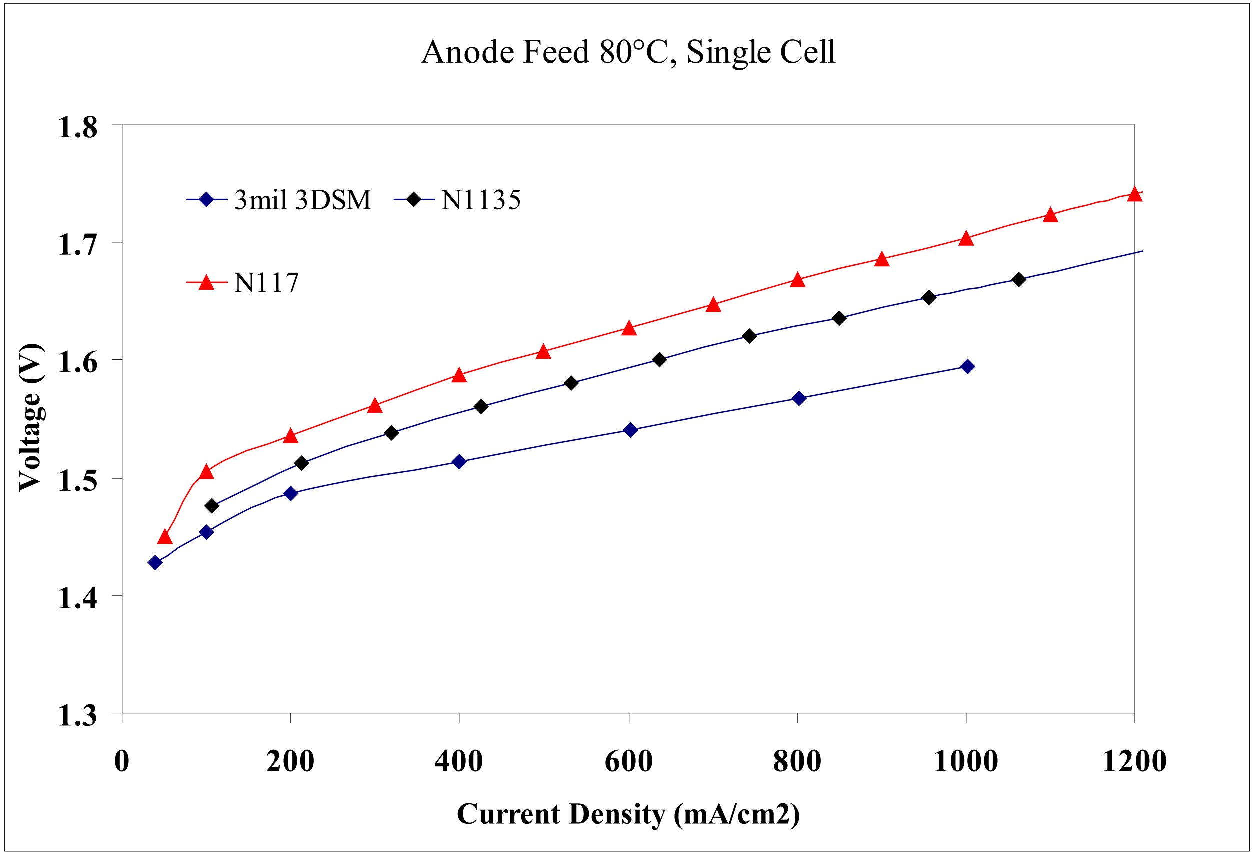
Poor performance is seen for the 3DSM™ MEA, however 1100 EW ionomer used in the catalyst layer.

ACCOMPLISHMENTS: 2DSM™ Fuel Cell Performance 95°C



Reformulating the catalyst layer with same ionomer led to large improvement in performance

ACCOMPLISHMENTS: 3DSM™ Electrolyzer Testing



3DSM shows significant improvement to 1100 EW of comparable thickness

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Challenges: 3DSM

- Incorporate lower EW ionomers into support
- Demonstrate improved fuel cell performance

- *This will be the focus for the last year of the program*
  - *Catalyst layer improvement*
  - *RH cycling of thinner membranes*
  - *Short Stack Testing*

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 will need to continue improving the low EW materials that have been developed at SUNY

OBJECTIVES: Ultimate Goal

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