Dimensionally Stable Membranes™

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Project ID # fc_02_mittelsteadt

Dimensionally Stable Membranes for High Temperature Applications

Timeline

- Begin 4/3/2006
- Review 4/2/2009
- 65% Complete

Budget

- Total project funding (to 2009)
  - $949K DOE Funding
  - $589K Recipient
  - 37% Cost Share
  - $350K received FY 2008
  - $65K Remaining (through Feb '09)
  - $871K 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

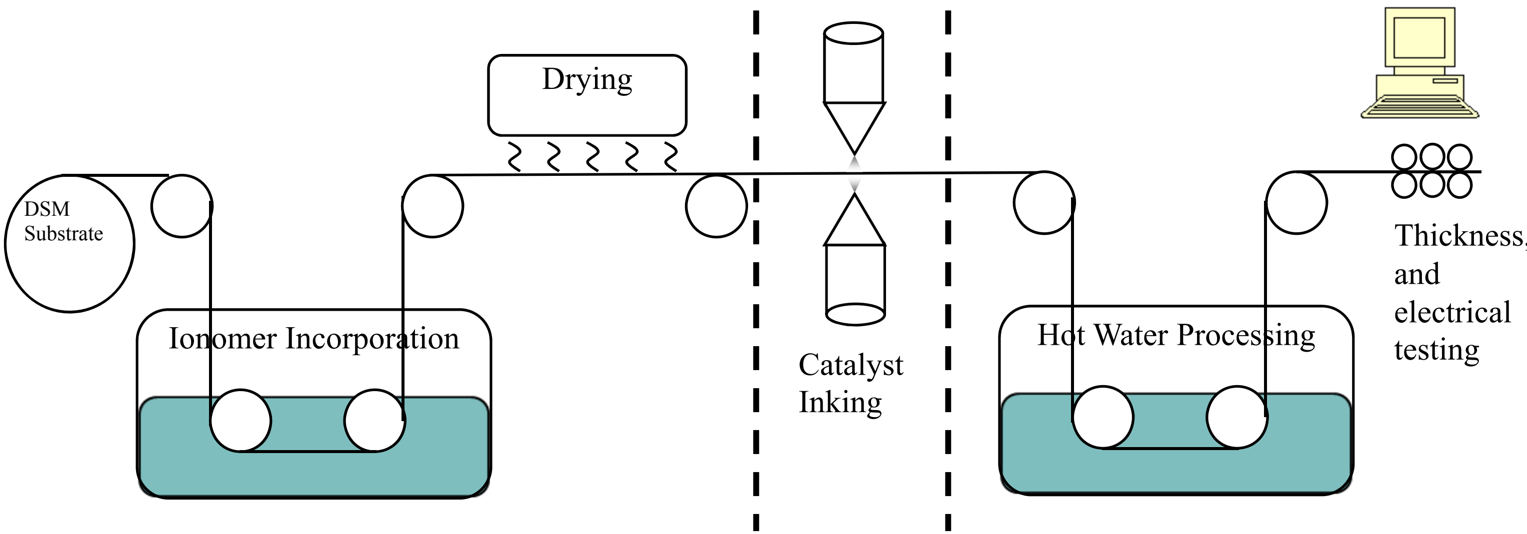
- OBJECTIVES
- APPROACH and ACCOMPLISHMENTS
  - Rationale
  - Two Dimensionally Stable Membranes™
  - Three Dimensionally Stable Membranes™
- CHALLENGES

OBJECTIVES

YEAR	OBJECTIVE
2006	Determine the effect of pore size and substrate thickness on conductivity and water uptake. Demonstrate polymerization conditions suitable for bulk polymerization of the PFSA.
2007	Demonstrate, by the 3rd Quarter, membrane conductivity of 0.07 S/cm at 80% relative humidity at room temperature using non-Nafion materials. Samples will be prepared and delivered to the Topic 2 Awardee.
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.

OBJECTIVES: Ultimate Goal

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



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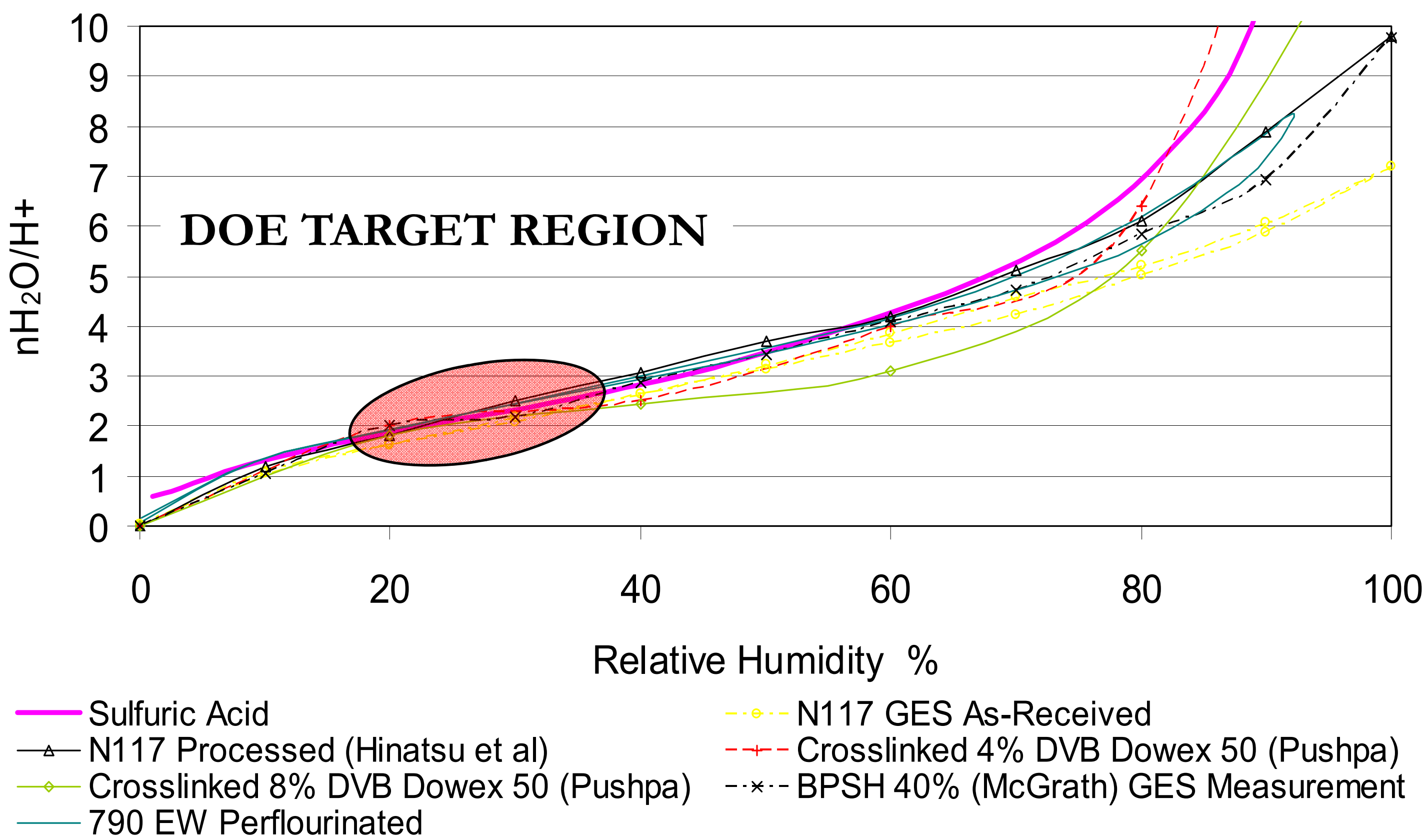
APPROACH: Rationale

- 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

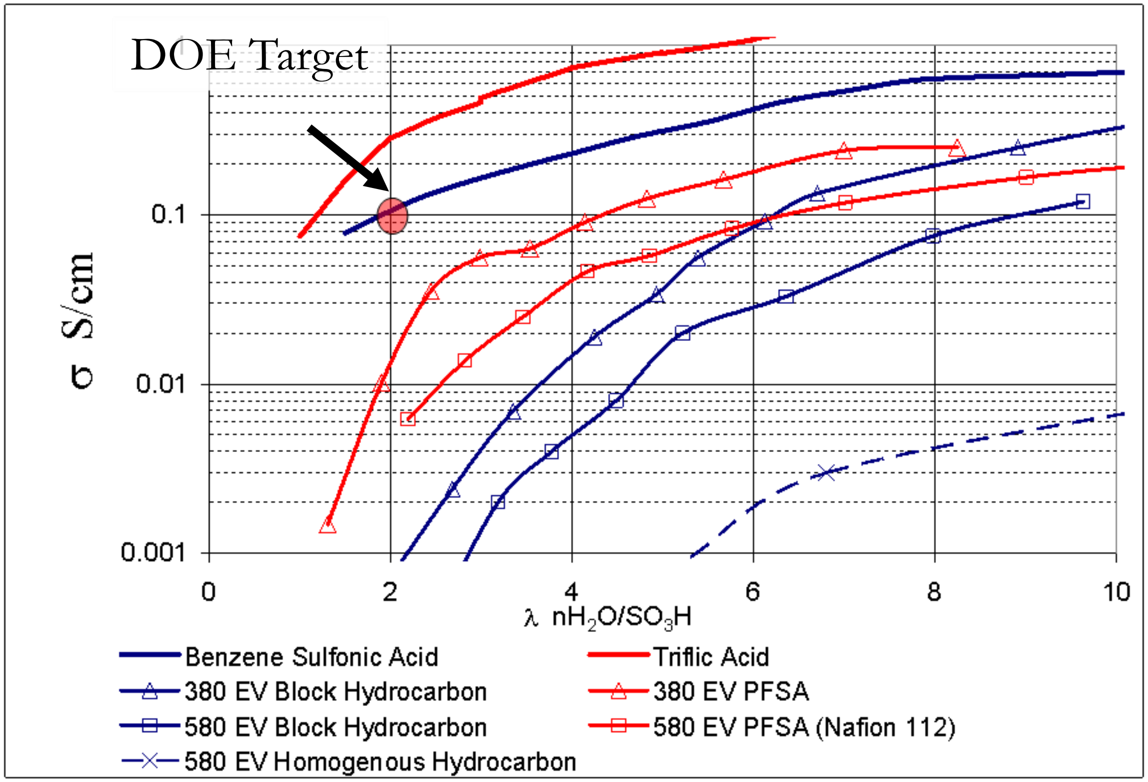


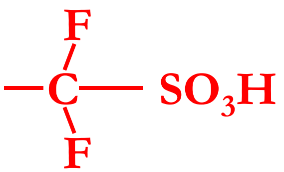
Water Content is the same regardless of pendant group

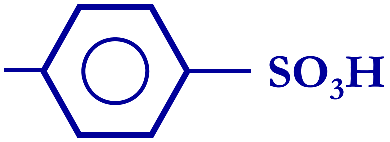
APPROACH: Rationale

Importance Of Ionic Functional Group, Morphology

Conductivity of Various Ionomers and Model Compounds at 80°C





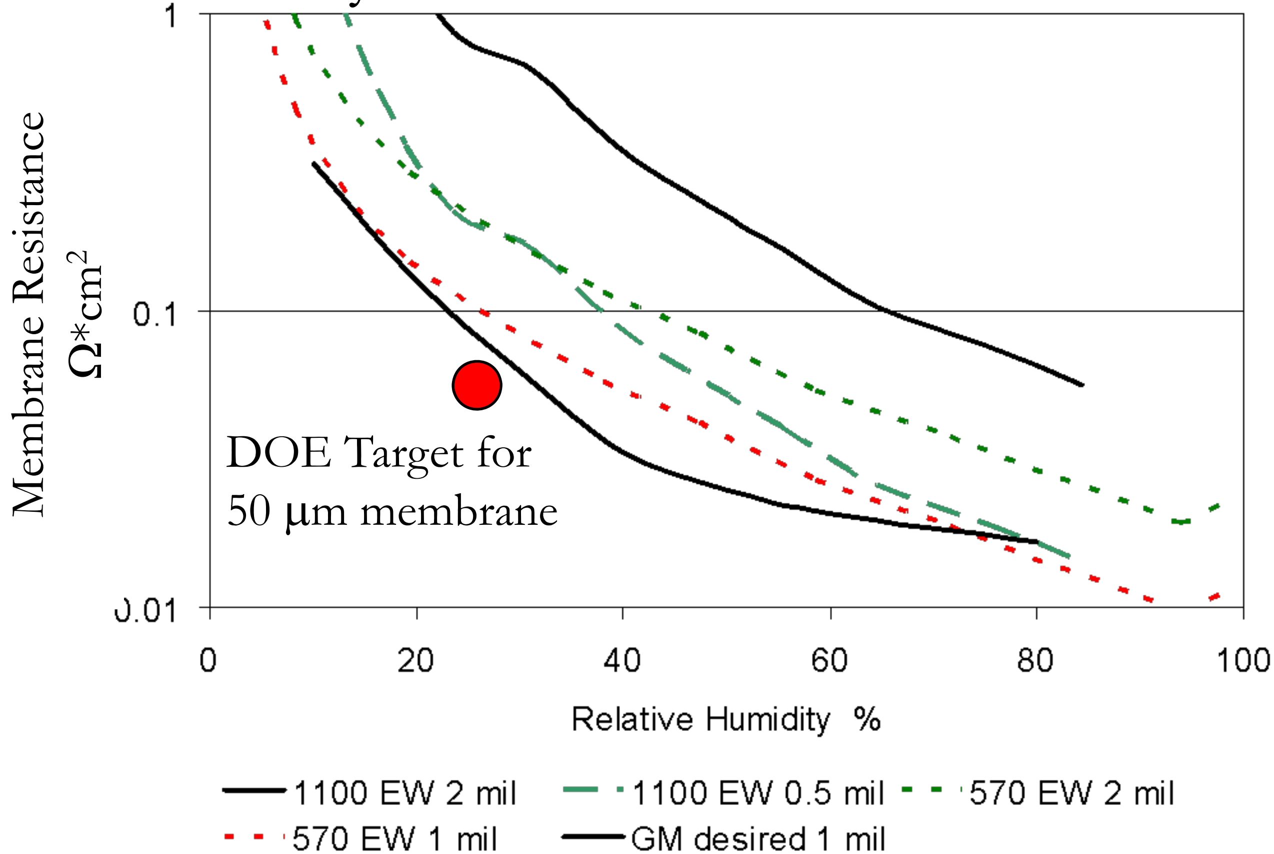


EV = EW/Density

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

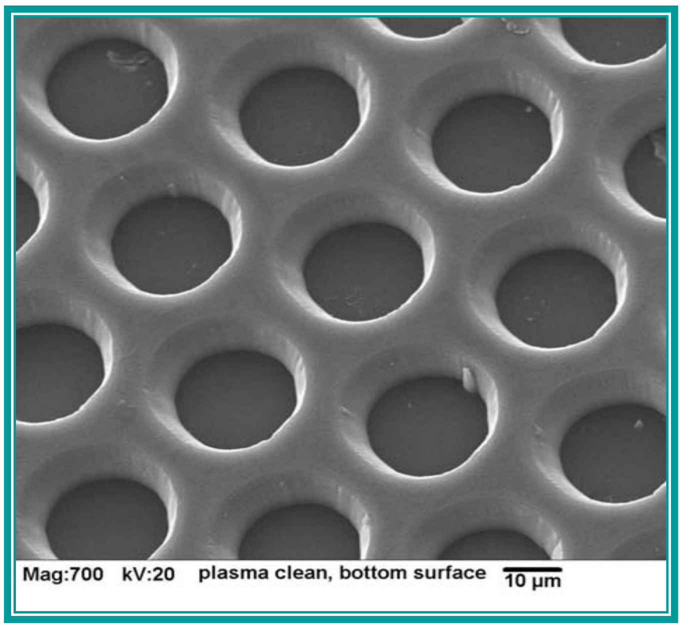
Mag:700 kV:20 plasma clean, bottom surface 10 µm

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

APPROACH: 2DSM™:

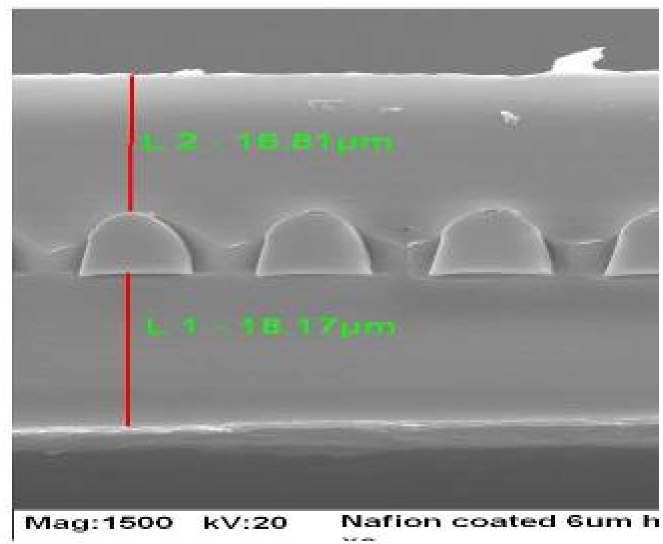
- COMPOSITE POLYMER ELECTROLYTE MEMBRANES

  DSM ™ is high acid content membrane reinforced with high strength polymer support



< 1 Mil Diameter hole

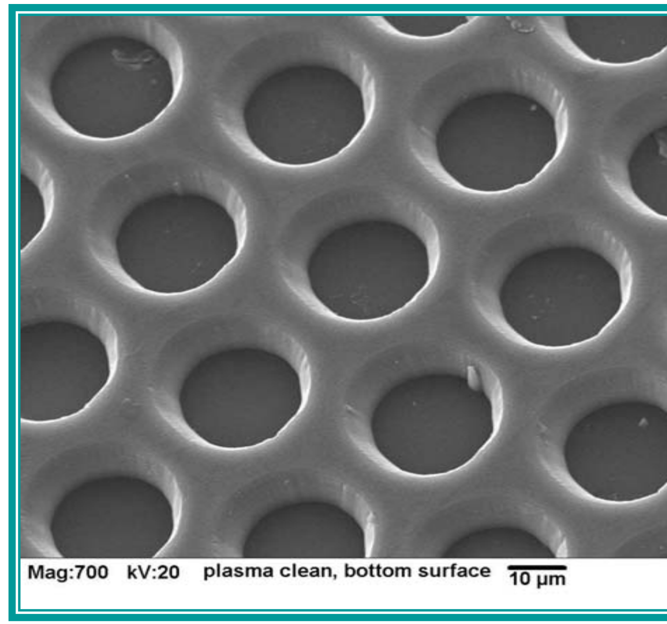
Nearly 1,000,000 holes/in^2



APPROACH: 2DSM™

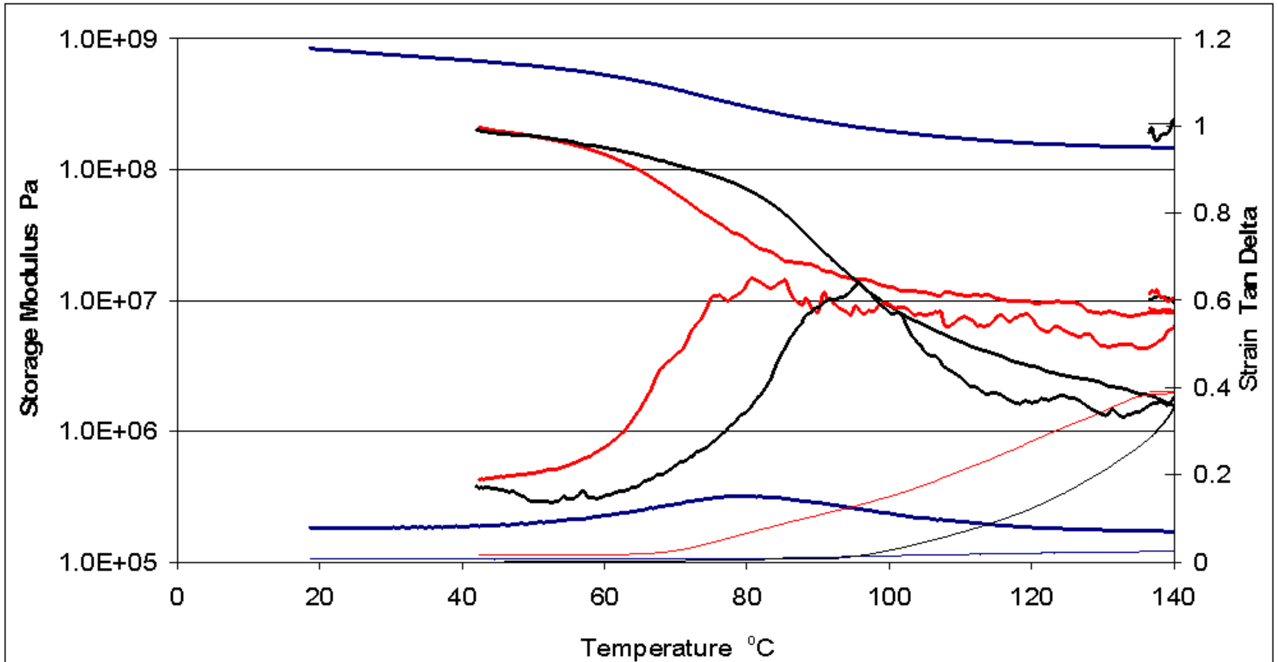
Dimensionally Stable Membrane™ Support Structures Used to Date

Material, condition	**Young's Modulus** (Mpa)
Nafion® 112 Dry 20°C	300
Nafion® 112 Wet 80°C	70
Poly(tetrafluoroethylene) (PTFE)	400
Polysulfone	2600
Poly(etherether-ketone) (PEEK)	2700
Polyimide (PI), e.g., Kapton®	2900



ACCOMPLISHMENTS: 2DSM™

Increased Modulus of Support Material Leads to Proportional Increase in Composite Material



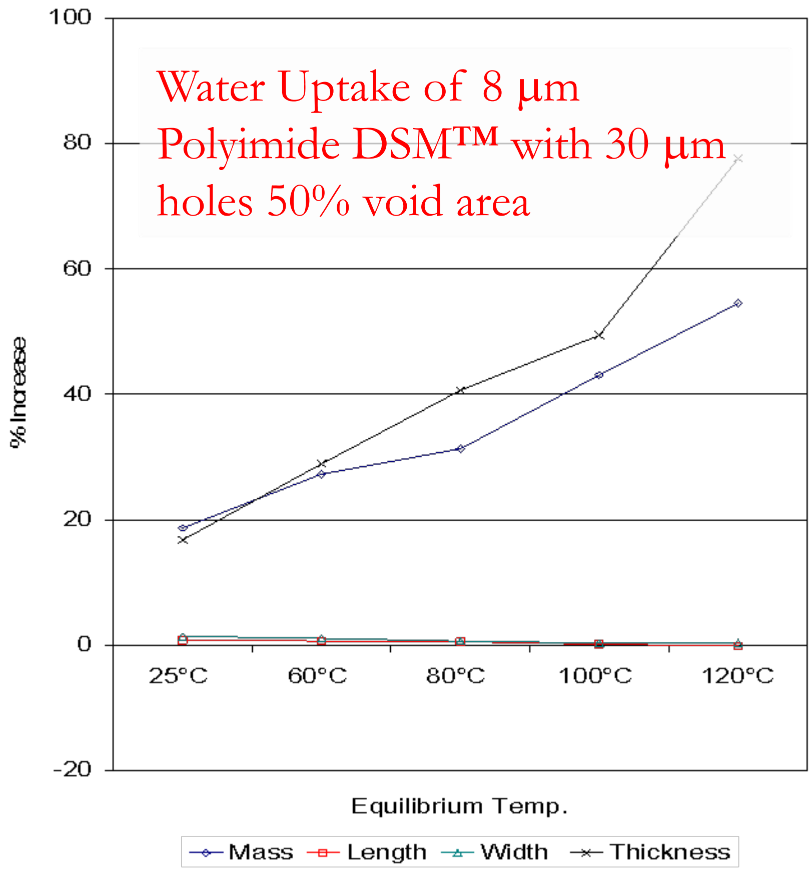
50 um DSM 8um PI Support

PTFE Supported Membrane

Nafion

ACCOMPLISHMENTS: 2DSM™

Effect of Pore Size on Water Uptake

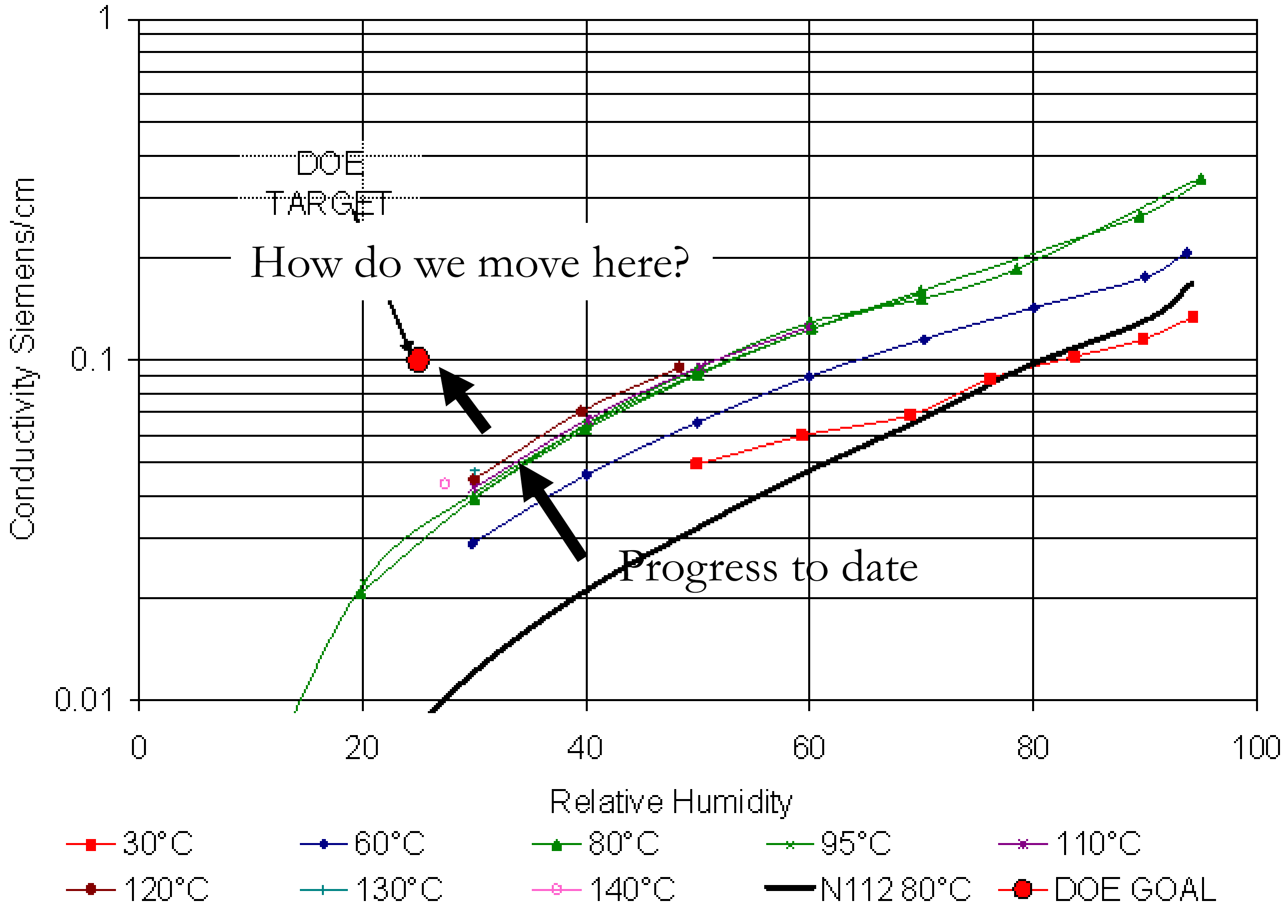


- No macroscopic swelling on the X-Y plane
- *Effect is the same for*
  - *pore sizes of 10-40µm*
  - *Support thickness of 8-25µm*
  - *EW of fill of 700-1100 EW*
- Membrane retains integrity even after tested at 120°C in water.
- *SIGNIFICANTLY Improves, handling and storage of membranes*
- *We were not able to generate 75% void area materials*

ACCOMPLISHMENTS: 2DSM™

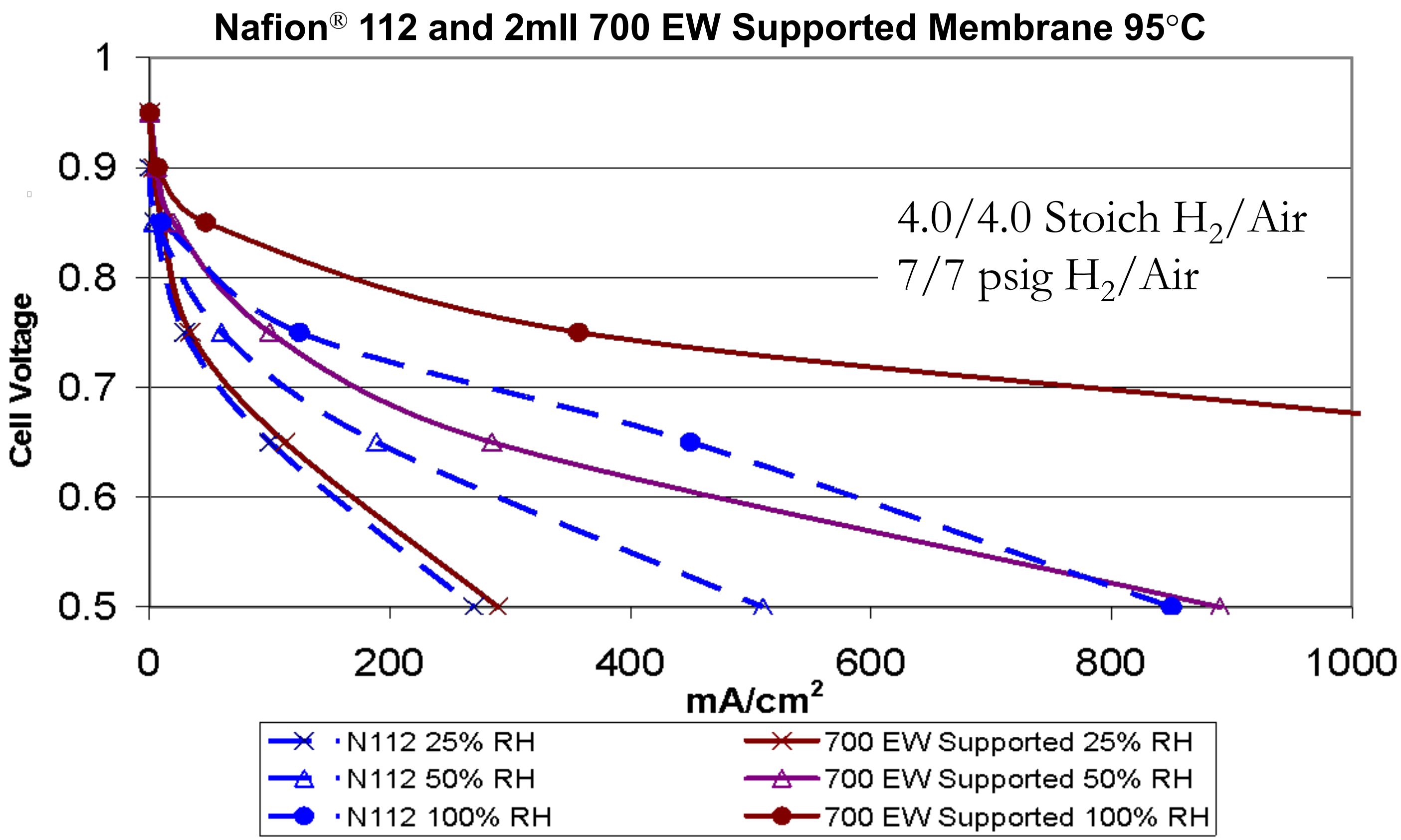
In-Plane Conductivity

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



ACCOMPLISHMENTS: 2DSM™

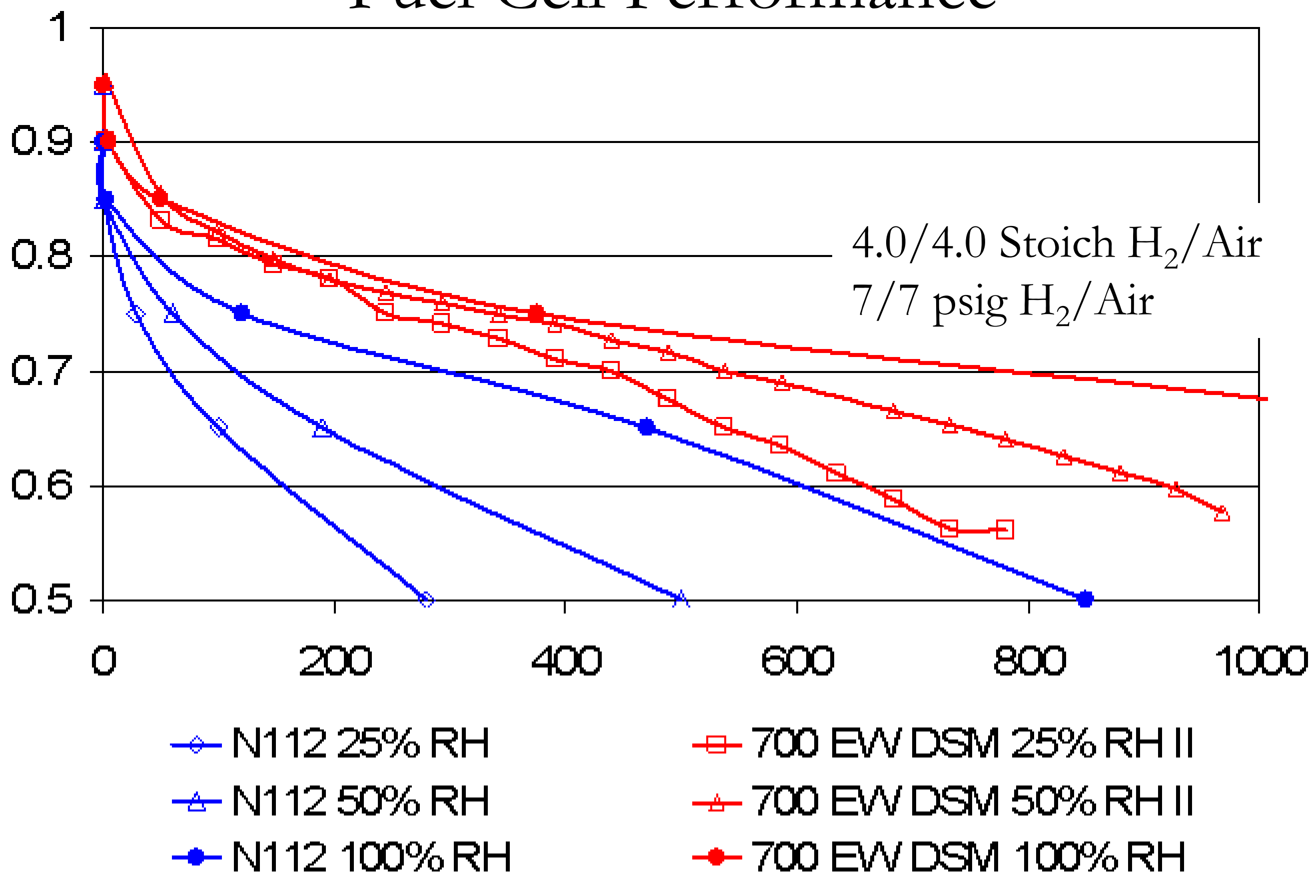
Fuel Cell Performance



25% RH data much worse than predicted based on DSM™ conductivity and high-frequency resistance: Work to do on the catalyst layer

ACCOMPLISHMENTS: 2DSM™

Fuel Cell Performance

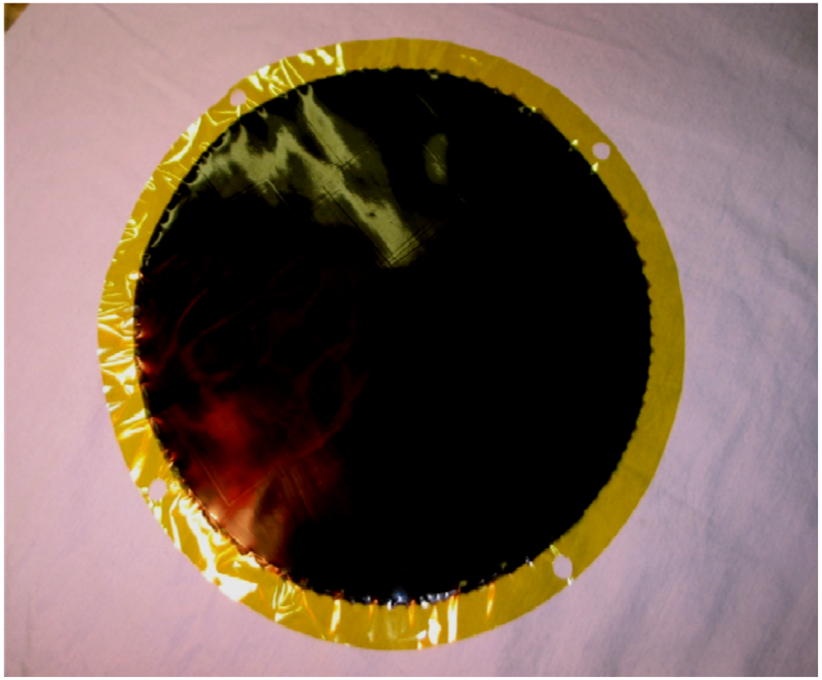


25% RH data much worse than predicted based on DSM™ conductivity and high-frequency resistance: Work to do on the catalyst layer

ACCOMPLISHMENTS: 2DSM™

MEA Fabrication

- Generated 200 cm^2 MEA
- Catalyst Applied Directly To Membrane
- No Decal Transfer



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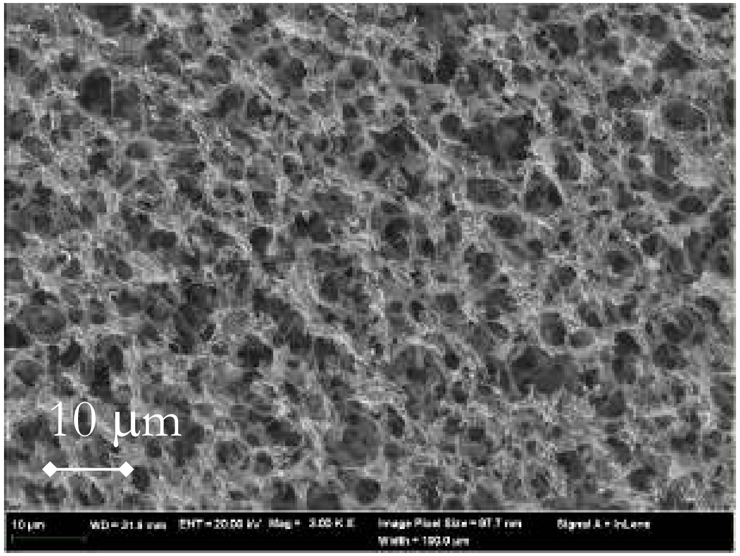
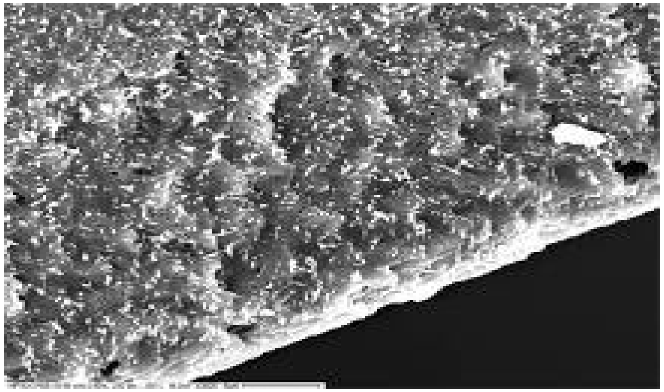
APPROACH: 3DSM™

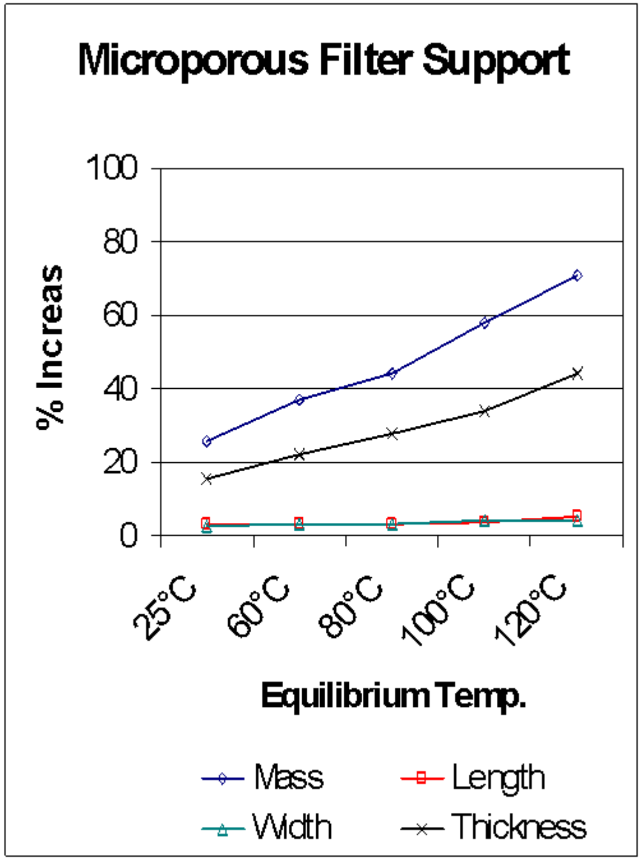
- Cost of Laser Drilling Prohibitively High
- Three-Dimensional Supports Commercially Available
- Using Conventional PFSA Ionomers to Meet Cost Targets
- Synthesizing New Low EW Ionomers to Meet Performance Targets
  - *Work being done by Israel Cabasso's Group at SUNY Syracuse Polymer Research Institute*



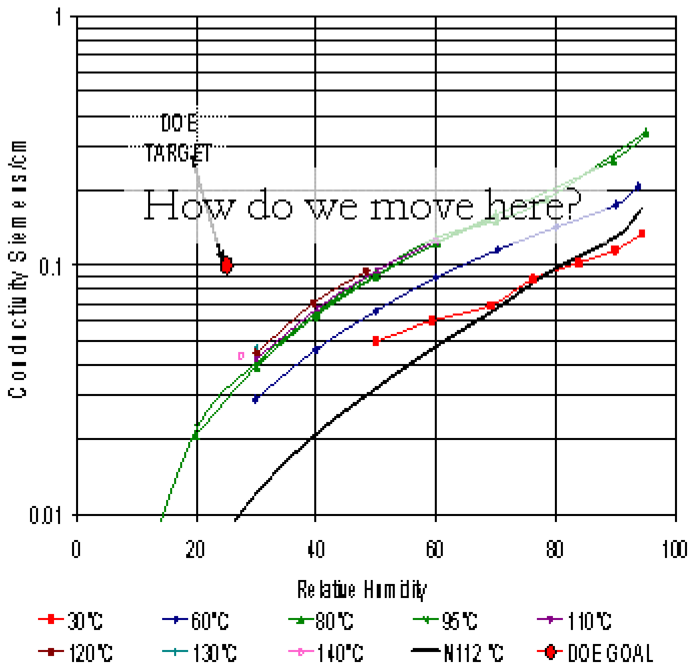
ACCOMPLISHMENTS: 3DSM™ -Commercial PFSA

- Filled Supports With Commercial PFSA Material
- Swelling is Comparable to 2DSM™
- Completely Filling Support was a Major Challenge
- ~33% Conductivity Penalty





APPROACH: 3DSM™ Alternative Synthesis



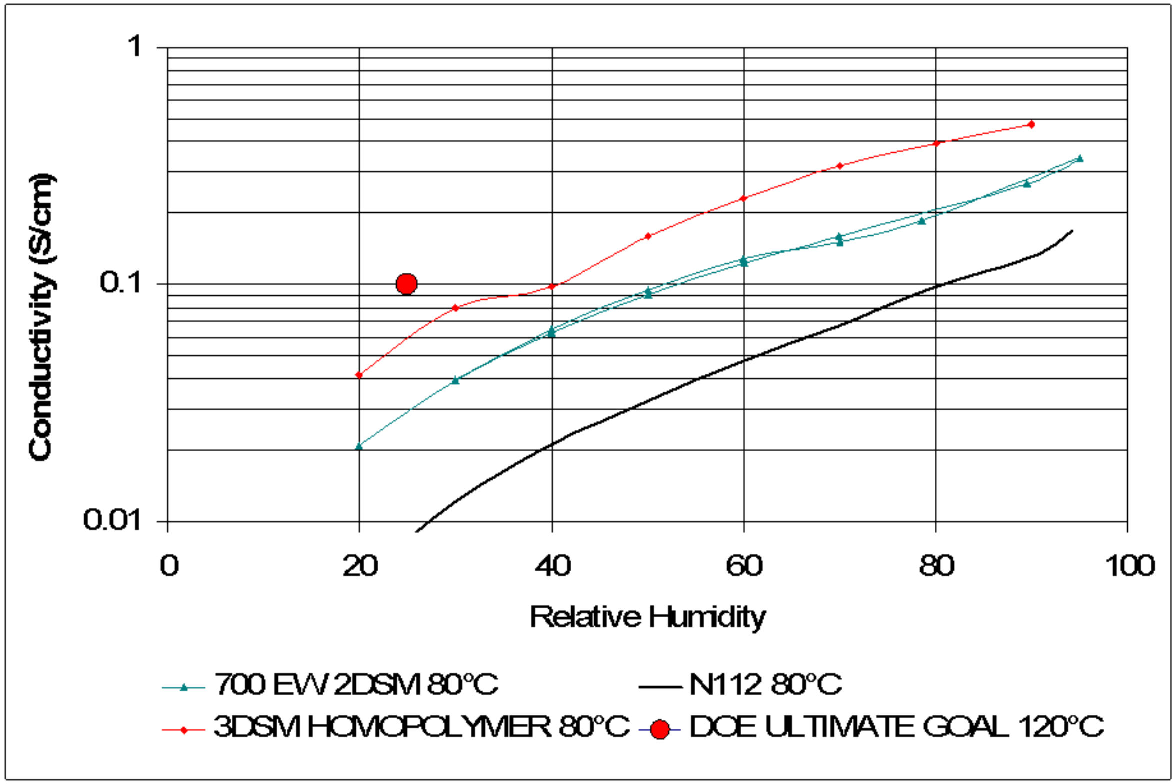
Synthesis of new PFSA Monomers
Working with SUNY-ESF to make new copolymers

CF2=CF
OCF2CF(CF3)OCF2CF2SO2F

\+ ?

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

ACCOMPLISHMENTS: 3DSM™ Alternative Synthesis: Homopolymer



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

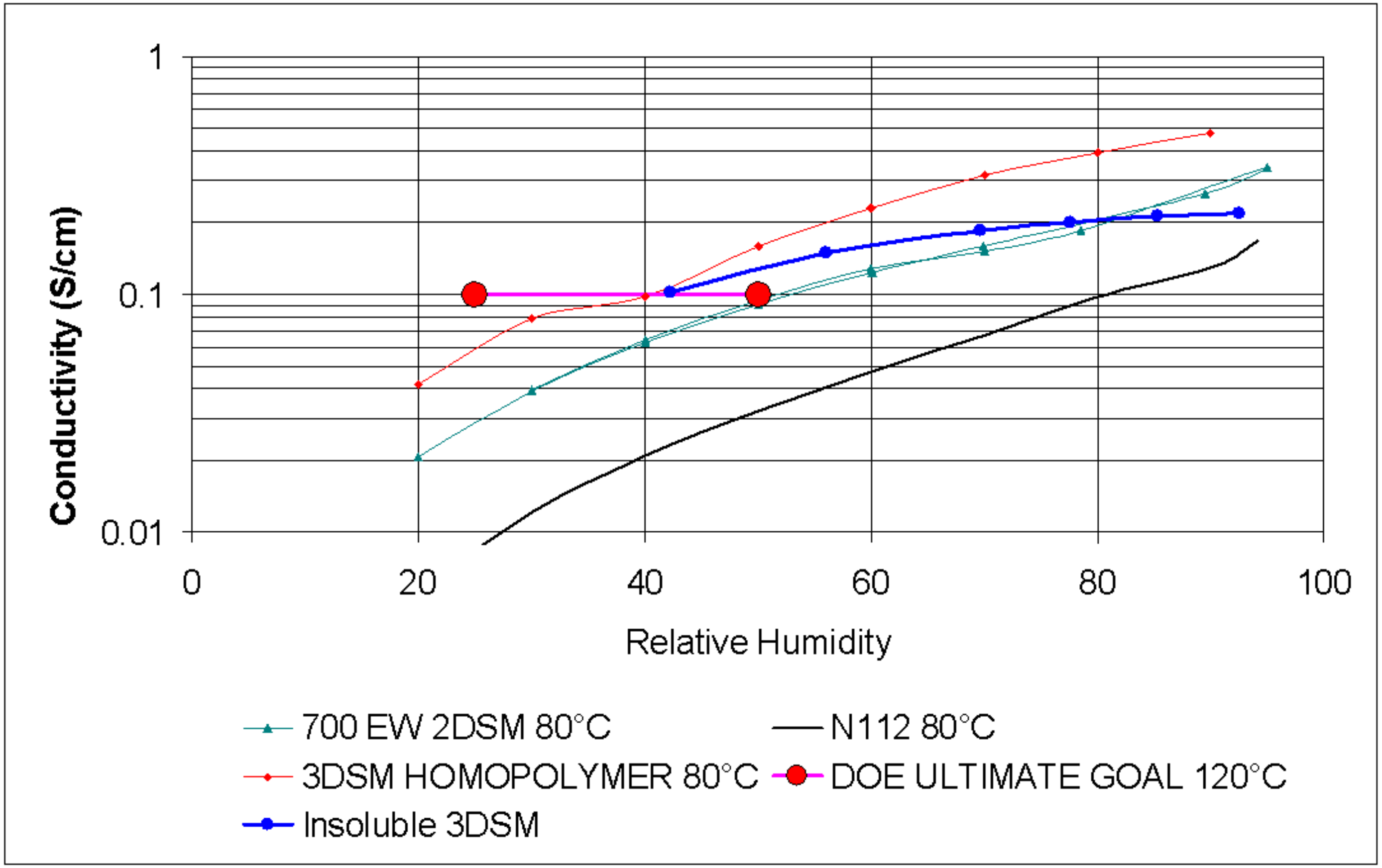
CF_2CF
$OCF_2CF(CF_3)OCF_2CF_2SO_2F$

\+ ?

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

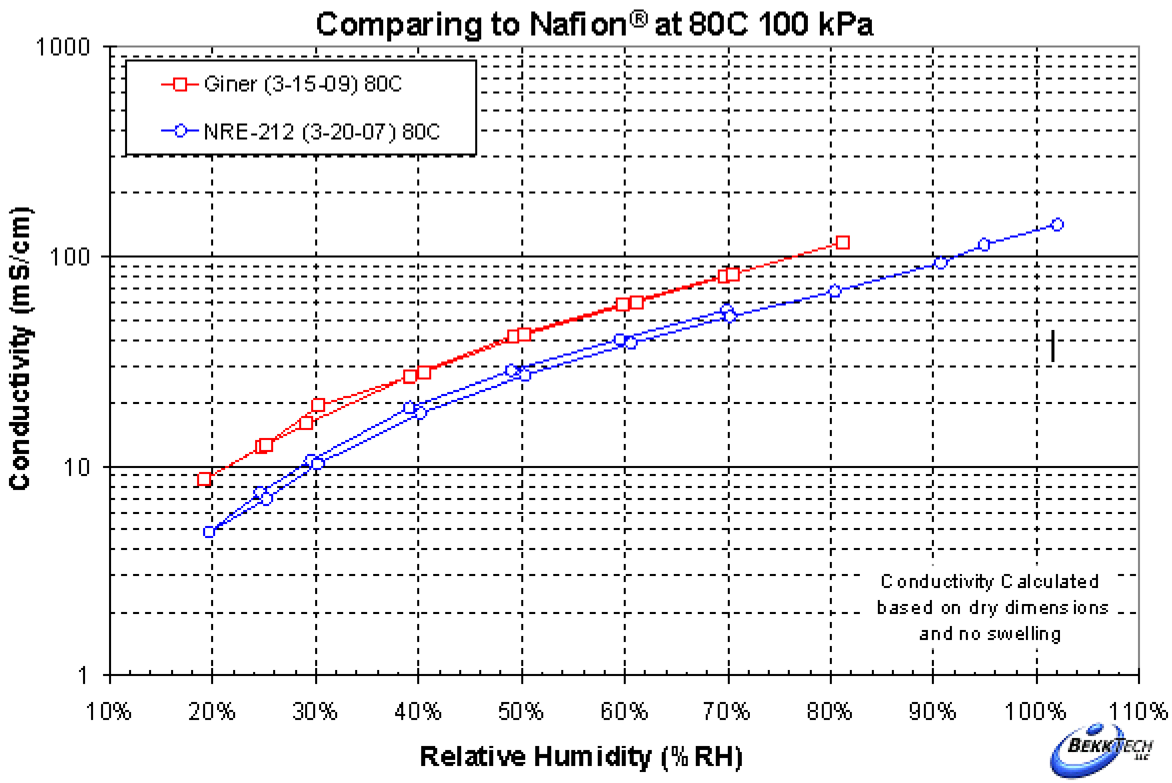
Getting closer to DOE target! This polymer is water soluble

Accomplishments 3DSM™: New Insoluble low EW PFSA



Insoluble High Performing 3DSM™ Generated

Accomplishments 3DSM™: New Insoluble low EW PFSA

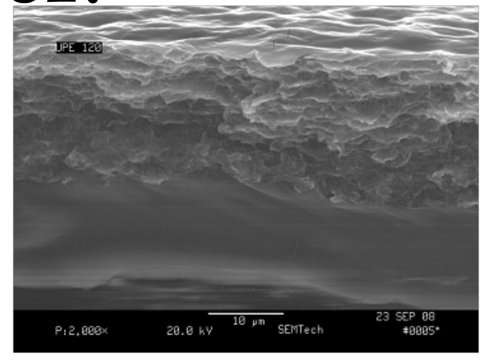


Bekktech testing considerably under our own

Material is inconsistent

Our data matched well for past samples

Accomplishments: 3DSM™: How to make thinner?



- Commercially available supports are ~ 2 mils in thickness after filled and sintered.
- Commercial supports have "skin" from casting process, which is a resistive barrier
- Working with Millipore on thinner, skinless supports

Material/ Pore Size	**Ionomer EW**	**Thickness mils**	**Thru-Plane σ N1100 = 1**
A/1.2μm	1100	2.6	0.6
B/1.2μm	1100	3.9	0.9
C/0.45μm	1100	1.0	0.5
D/0.6μm	1100	0.9	0.1
E/0.6μm	1100	0.45	0.7

Accomplishments: 2DSM™ and 3DSM™ RH Cycling

- Three Membranes Tested (all 2 mils)
  - 3DSM™ with 1100 EW
  - 2DSM™ with 700 EW
  - 2DSM™ with 700 EW
  - Extruded Nafion® 112
- All 4 passed 10,000 Cycles
  - 80°C
    - 2 min 95°C dew point
    - 2 min bone-dry
    - 1SLPM

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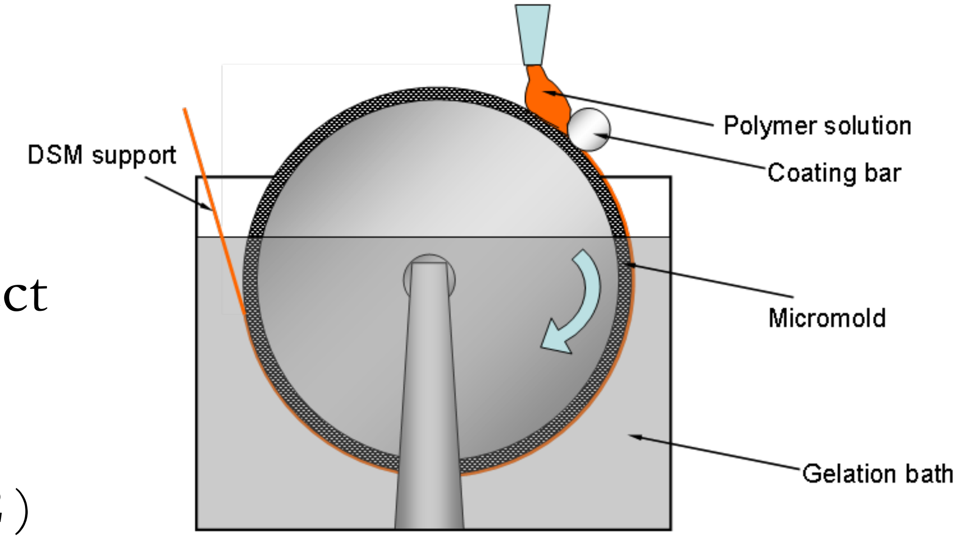
- OTHER OPPORTUNITIES
- CHALLENGES

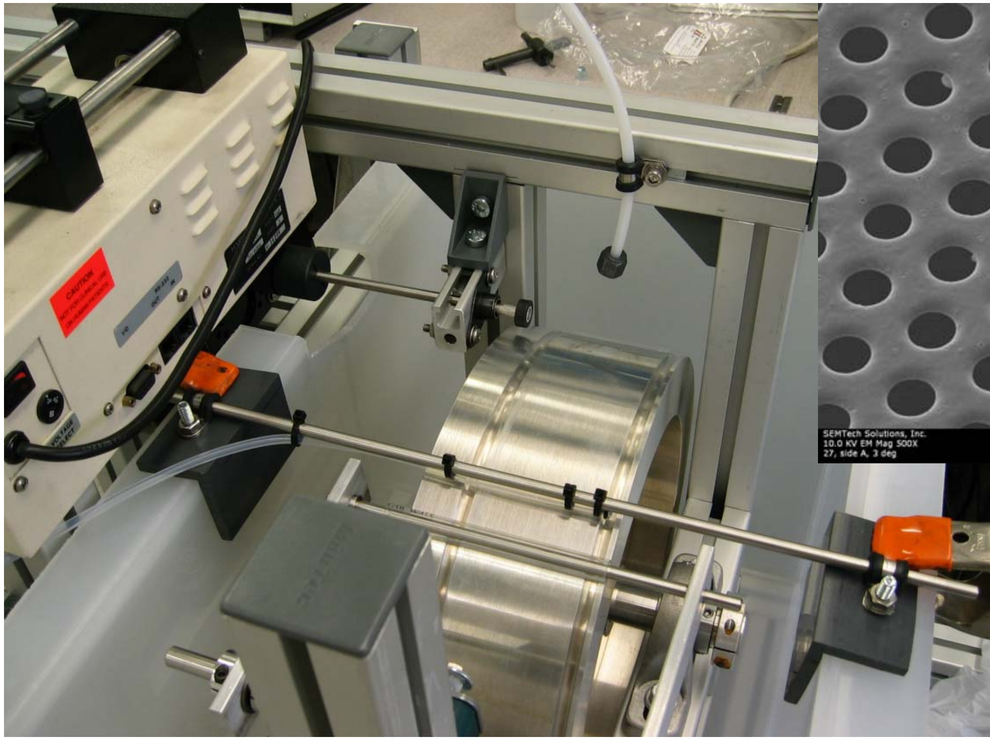
Challenges: 2DSM™

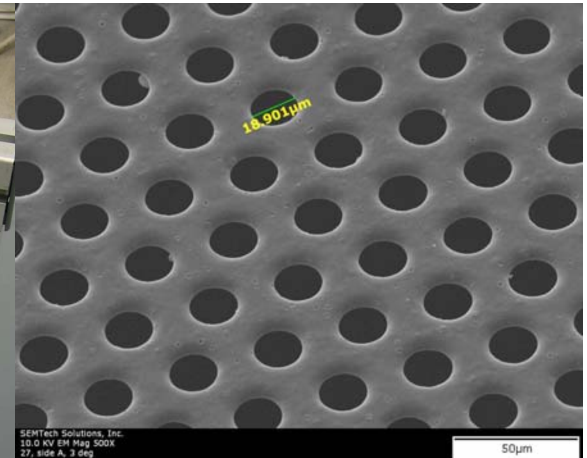
- Biggest Challenge is Cost
  - Laser Drilling
    - Currently ~ $\$1/cm^2$
    - Projected ~$\$0.02/cm^2$
      - $\$200/m^2$
  - In Separate DOE Project Developing Low-Cost Casting Technique
    - (**DE-FG02-05ER84322**)



- *Currently testing continuous roll process*

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

Challenges: 3DSM™

- Incorporate lower EW ionomers into support
- Minimize resistance penalty due to "skin"
- Demonstrate improved fuel cell performance

Proposed Future Work: Thinner, Faster, Stronger

- Need to down-select for last two years
  - 2DSM™
  - 3DSM™
- Develop along that pathway and demonstrate
  - Cost feasibility
  - Fuel Cell Performance
  - RH Cycling Durability

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
- Realistic Pathways for Meeting Cost Targets Seen for both Paths
- 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