

Dimensionally Stable Membranes

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Project ID
#FC 24

Dimensionally Stable Membranes for High Temperature Applications

Timeline

- Begin 4/3/2006
- Review 4/2/2009
- 50% Complete

Budget

- Total project funding (to 2009)
 - \$899K DOE Funding
 - \$529K Recipient
 - 37% Cost Share
 - \$300K received FY 2007
 - \$300K for FY 2008
 - \$590K DOE funds spent to date

Barriers addressed

- A. Durability
- B. Cost

Technical Targets (DOE 2010 Targets)

- 0.10 S/cm at 1.5 kPa H₂O Air inlet
- <\$40/m²
- > 5000 h lifetime
- Stability in Condensing conditions

Partners

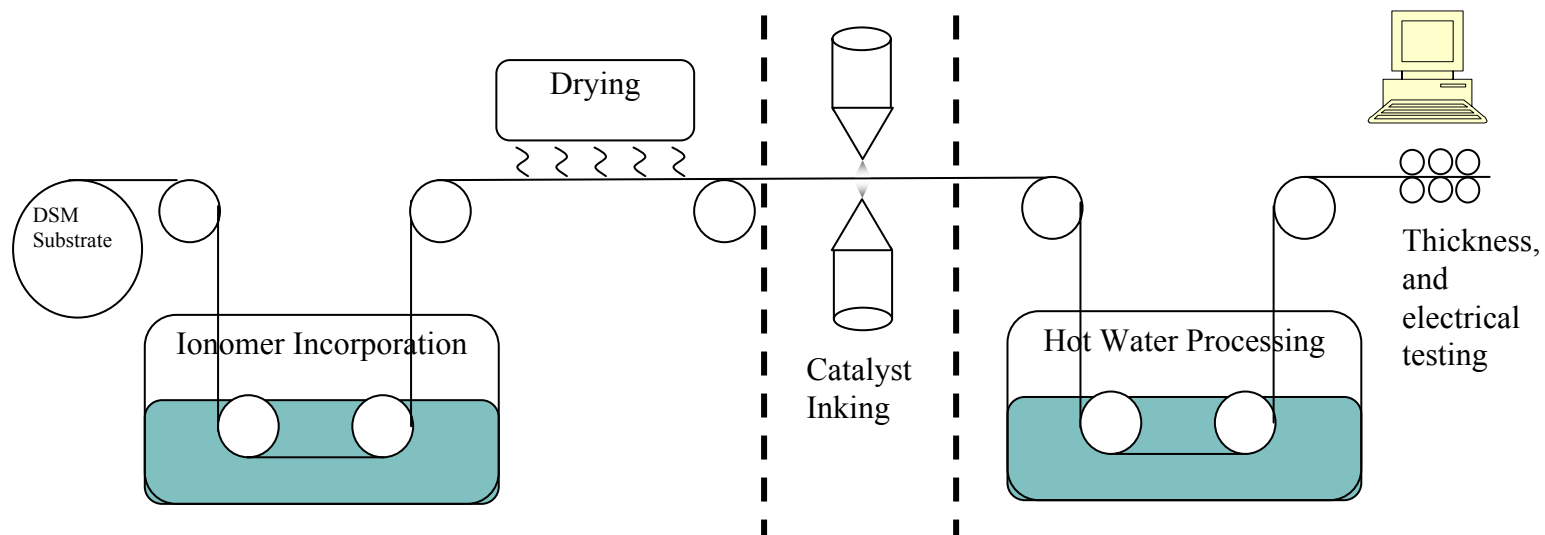
- General Motors
- SUNY-ESF

OVERVIEW

- OBJECTIVES/MILESTONES
- APPROACH and ACCOMPLISHMENTS
 - Rationale
 - Two Dimensionally Stable Membranes™
 - Three Dimensionally Stable Membranes™
- OTHER OPPORTUNITIES
- CHALLENGES

OBJECTIVES: Ultimate Goal

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

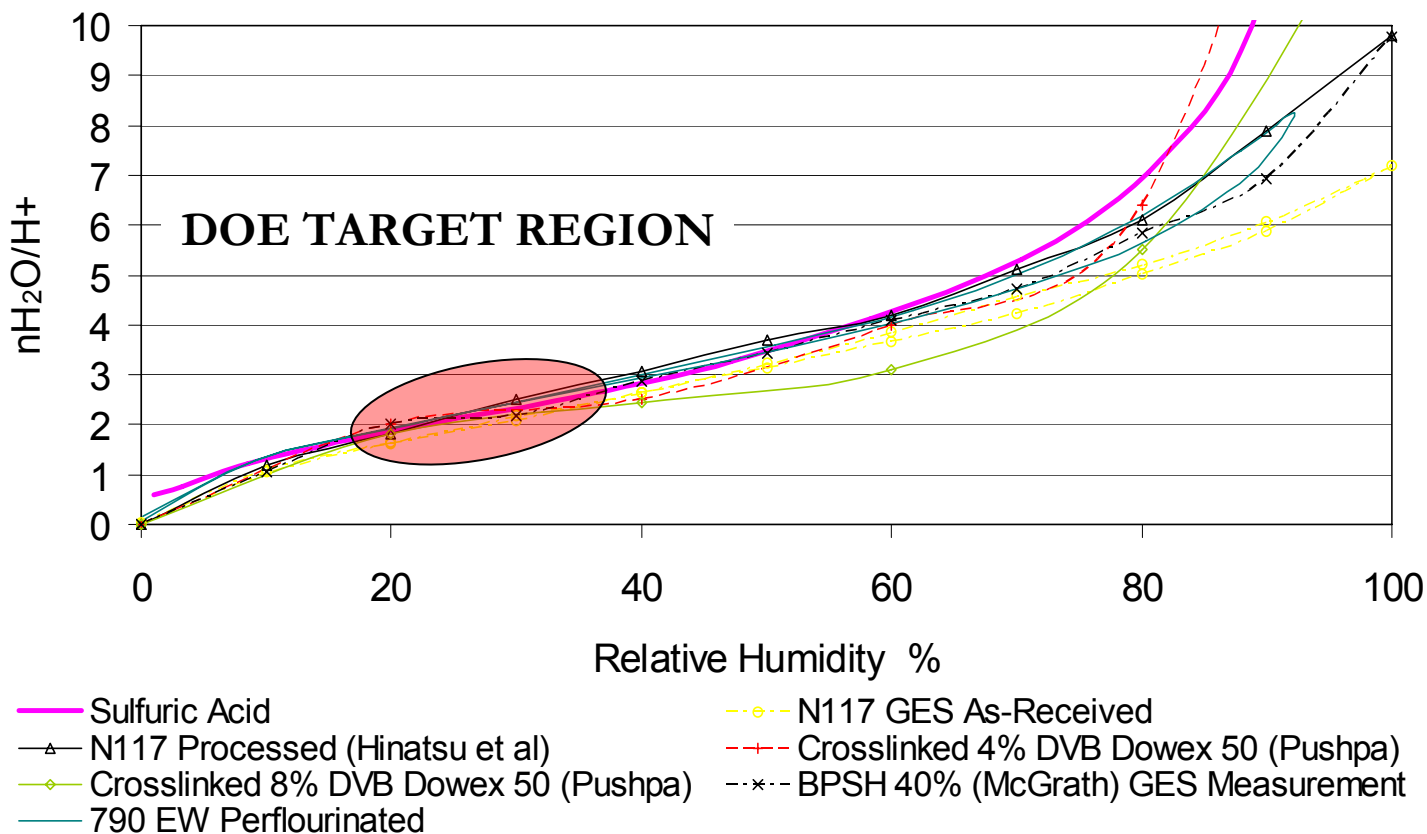


MILESTONES

YEAR	OBJECTIVE
2006	<p>Determine the effect of pore size and substrate thickness on conductivity and water uptake.</p> <p>Demonstrate polymerization conditions suitable for bulk polymerization of the PFSA.</p>
2007	<p>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.</p>
2008	<p>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.</p>

APPROACH: Rationale

Water Uptake of Ionomers based on $-\text{SO}_3\text{H}$ Moiety

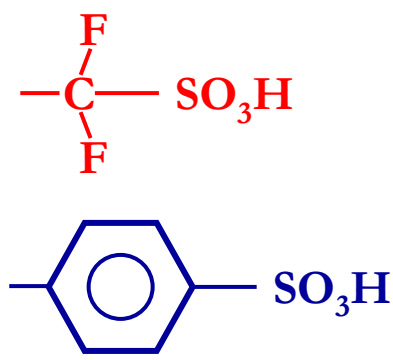
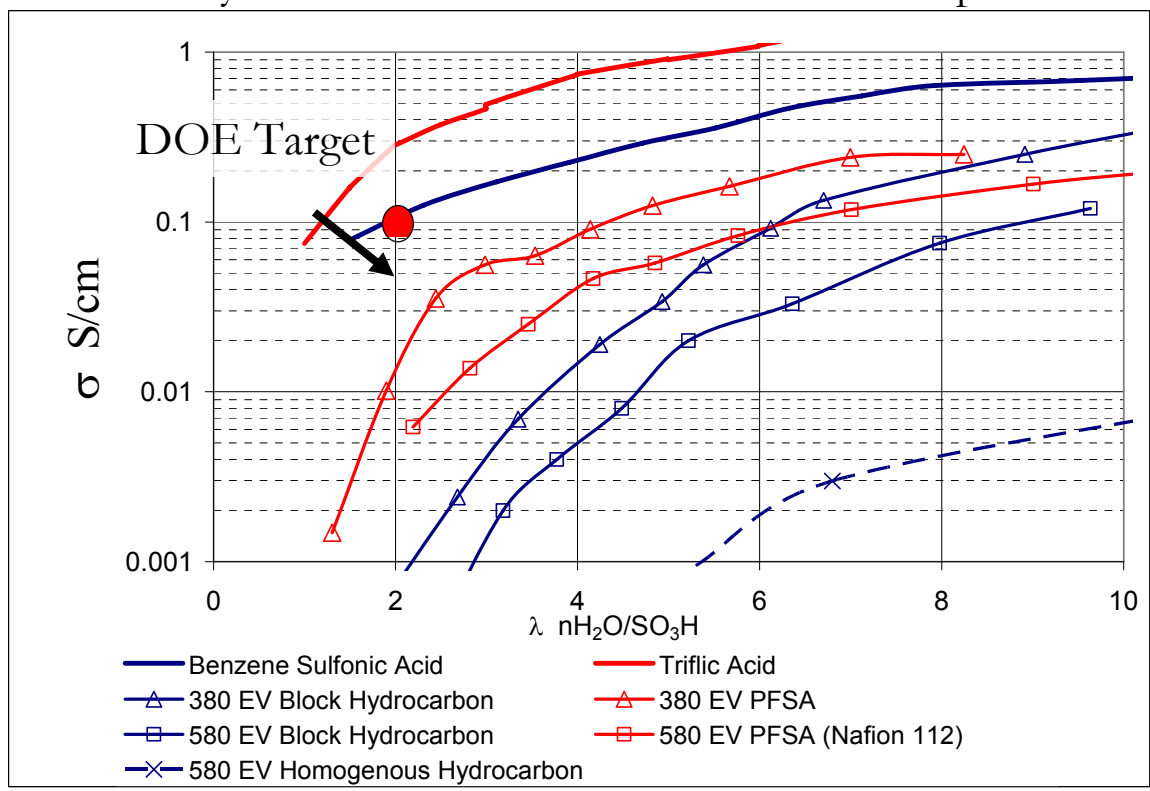


Water Content is the same regardless of pendant group

APPROACH: Rationale

Importance Of Ionic Functional Group, Morphology

Conductivity of Various Ionomers and Model Compounds at 80°C



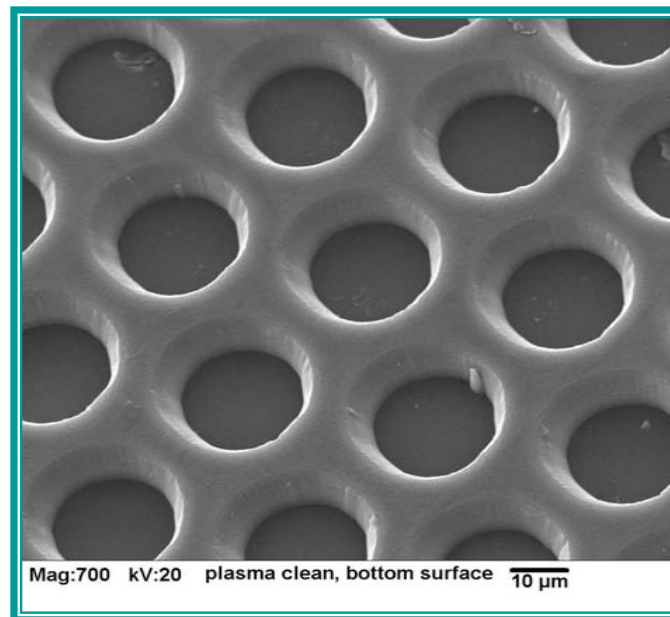
$$\text{EV} = \frac{\text{EW}}{\text{Density}}$$

To meet DOE targets membranes should be perfluorinated and very low EW

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
Polyimide (PI), e.g., Kapton®	2900

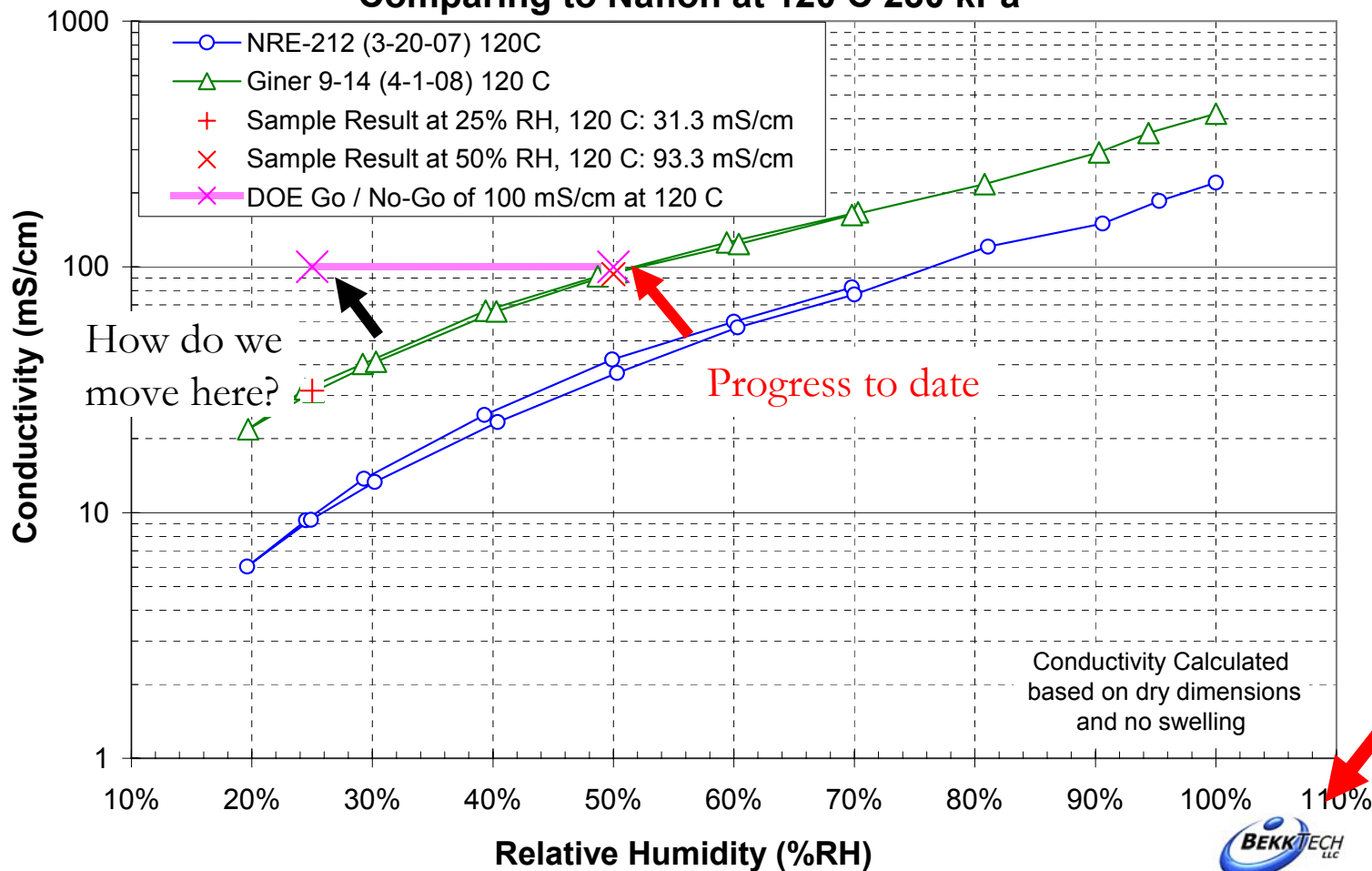


In 2007 Demonstrated no x-y swelling over large matrix of Geometries and compositions, Additionally conductivity was $\sim 2.5x$ Nafion over the entire RH range

ACCOMPLISHMENTS: 2DSM™

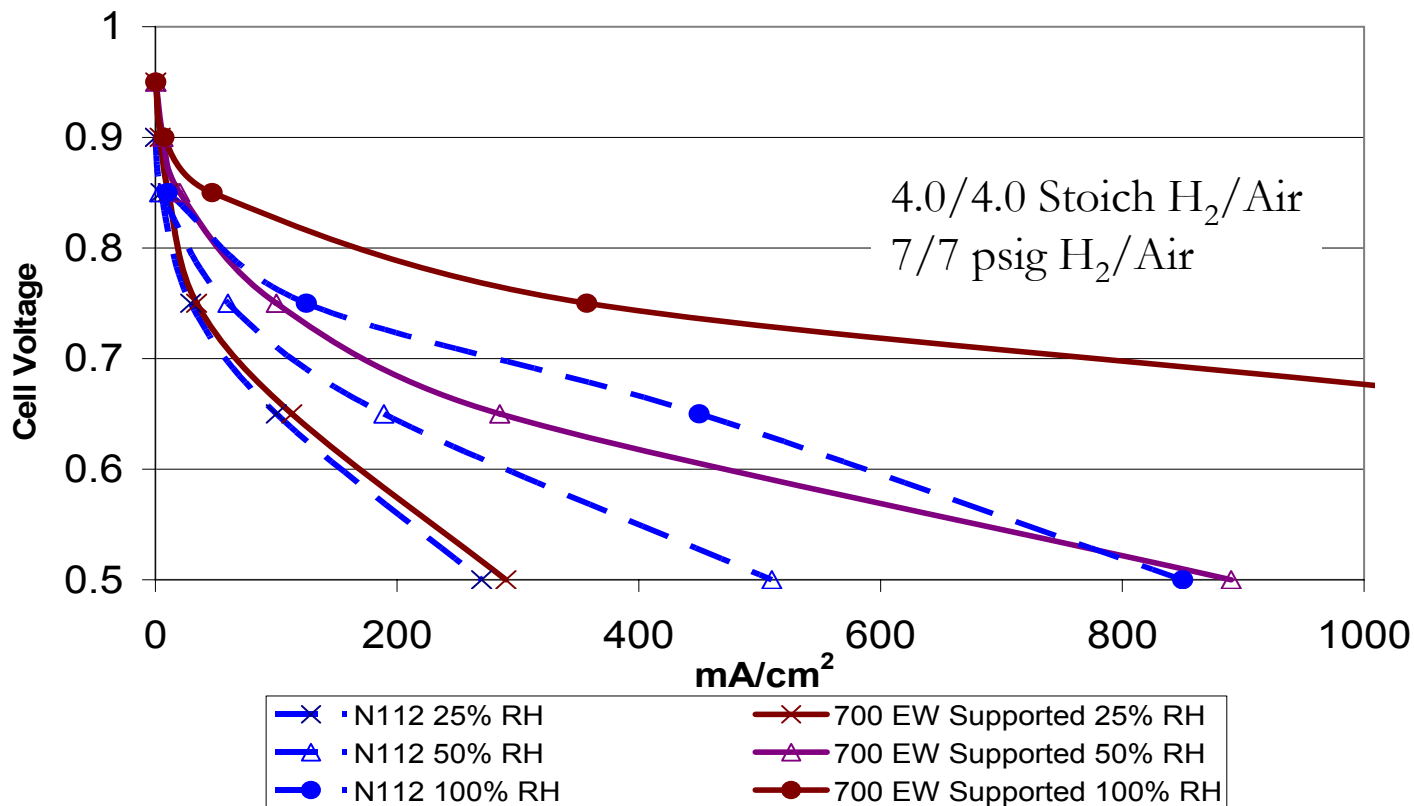
700 EW Membrane with DSM™ Support, Conductivity as a function of RH

Comparing to Nafion at 120 C 230 kPa



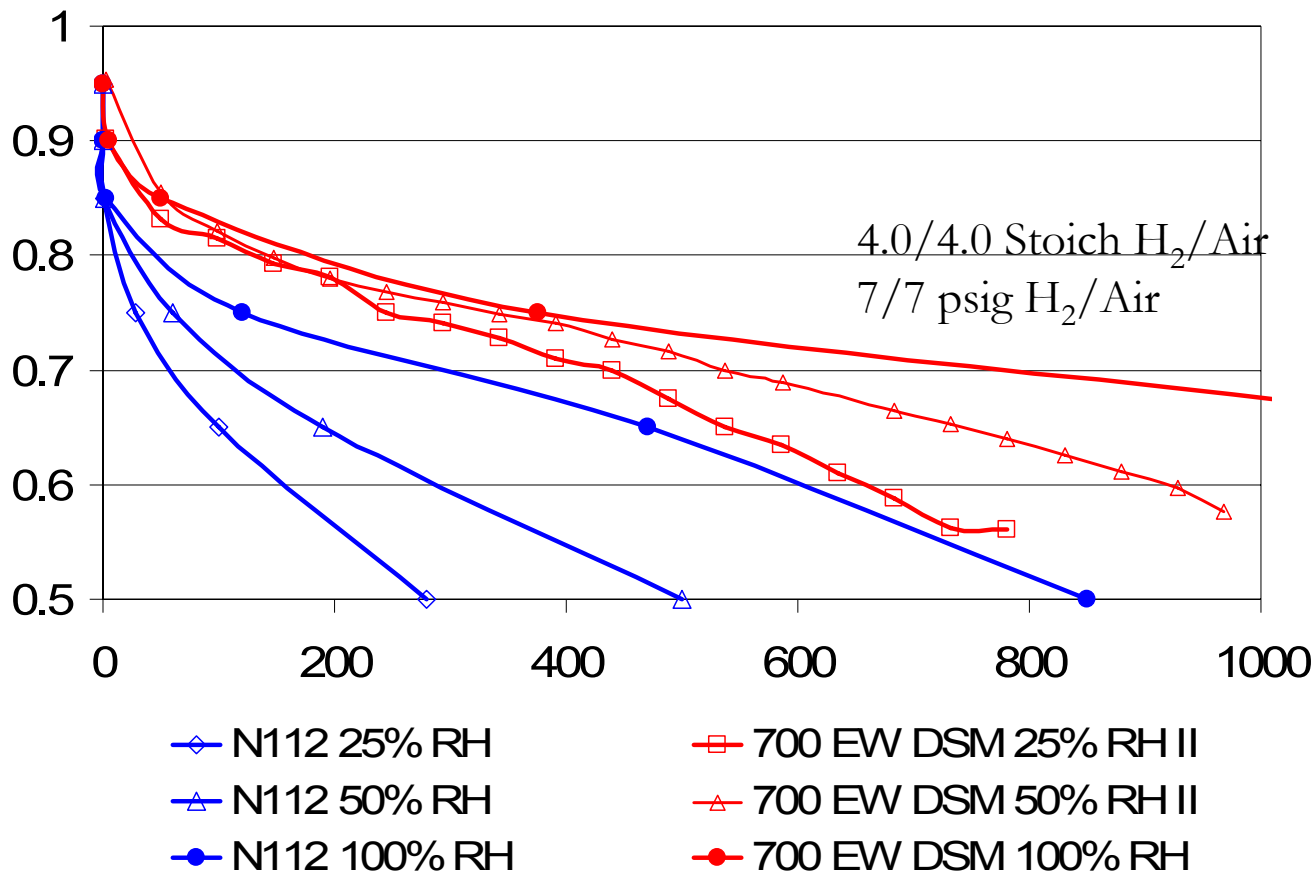
ACCOMPLISHMENTS: 2DSM™ Fuel Cell Performance (2007 presentation)

Nafion 112 and 2 mil 700 EW Supported Membrane 95°C



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

ACCOMPLISHMENTS: 2DSM™ 95°C

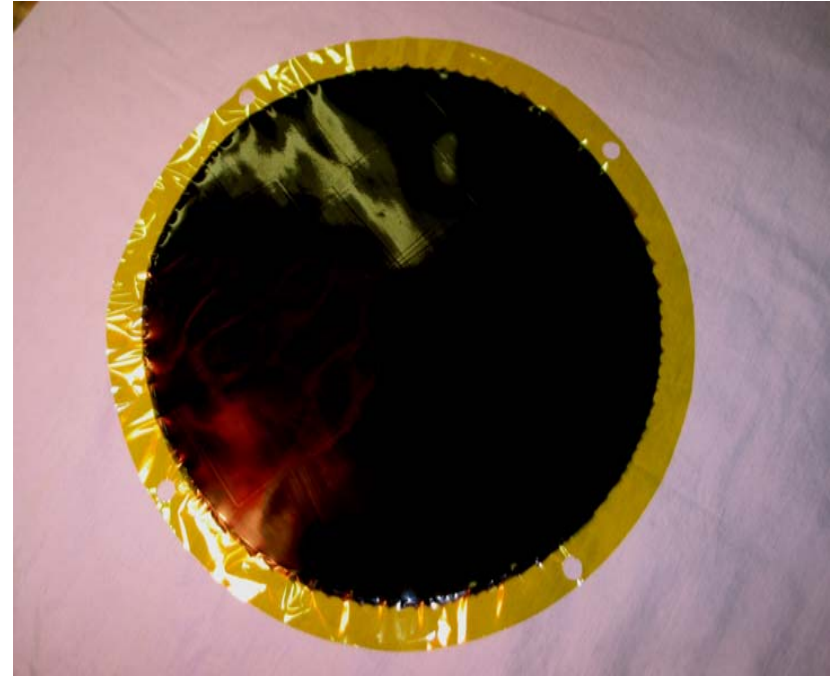


Superior conductivity of DSM membrane is manifest with improved catalyst layer

ACCOMPLISHMENTS: 2DSM™

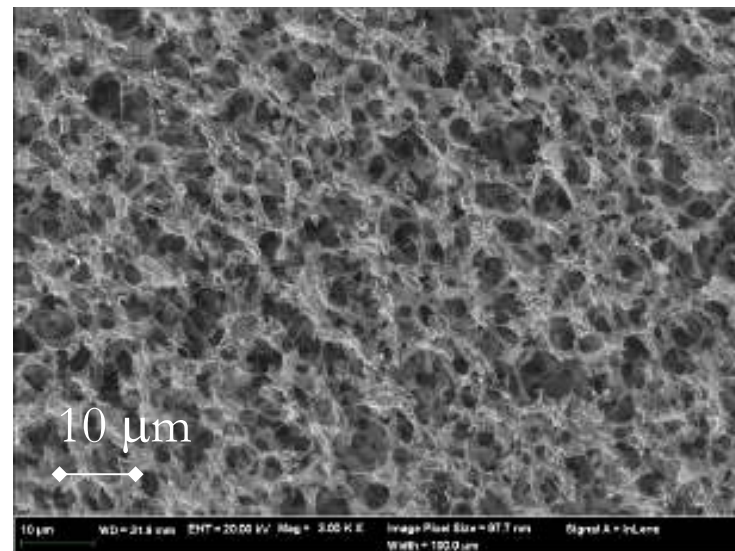
MEA Fabrication

- Generated 200 cm² MEA
- Catalyst Applied Directly To Membrane
- No Decal Transfer



APPROACH: 3DSMTM

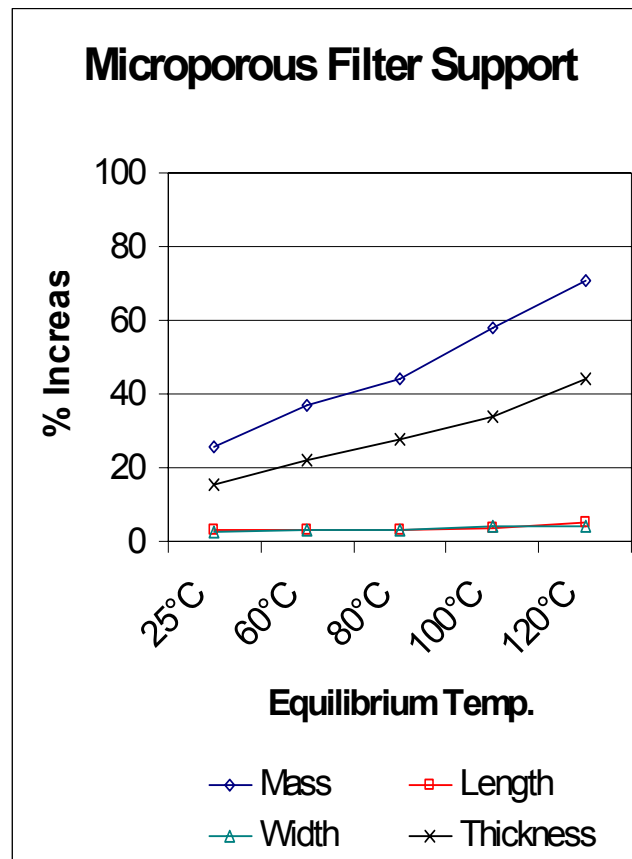
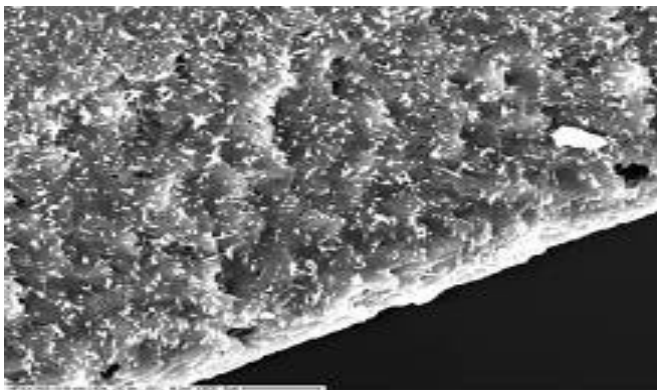
- Cost of Laser Drilling Prohibitively High
- Three-Dimensional Supports Commercially Available
- Using Conventional PFSA Ionomers to Meet Cost Targets
- Synthesizing New Low EW Ionomers to Meet Performance Targets
 - *Work being done by Israel Cabasso's Group at SUNY Syracuse Polymer Research Institute*



ACCOMPLISHMENTS: 3DSM™

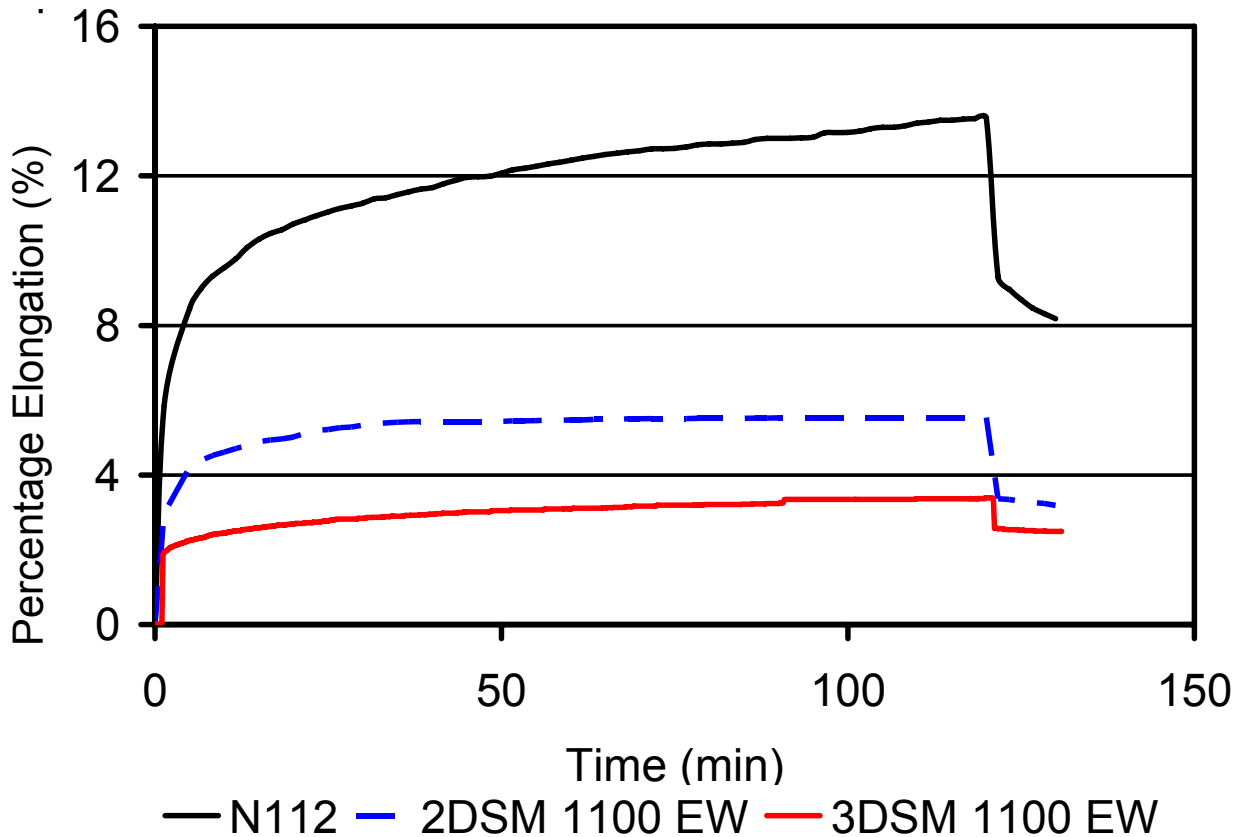
-Commercial PFSA

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



Three-dimensional supports have same ability to limit in-plane swelling as 2DSM

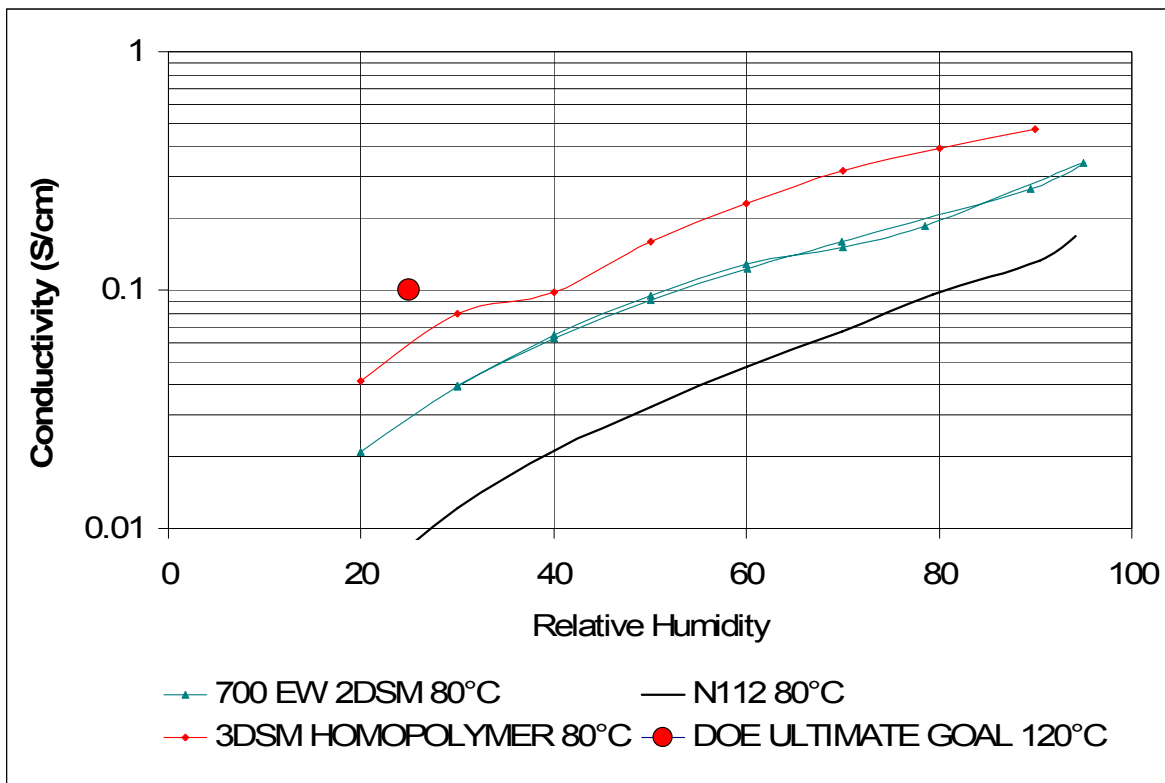
ACCOMPLISHMENTS: 3DSM™ -Creep Behavior Submerged at 80°C



Both 2DSM™ and 3DSM™ Supports greatly limit tension creep rates

ACCOMPLISHMENTS: 3DSM™

Alternative Synthesis: Homopolymer



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



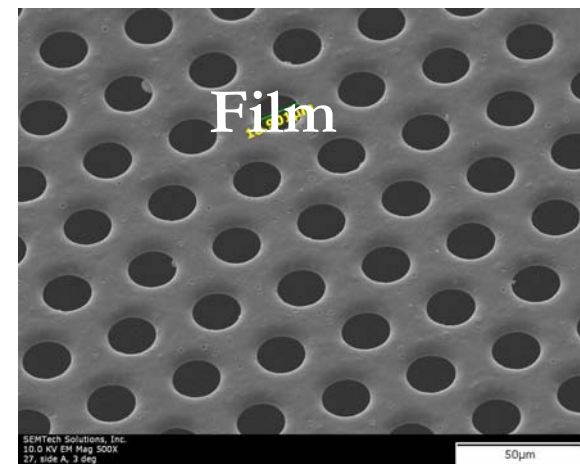
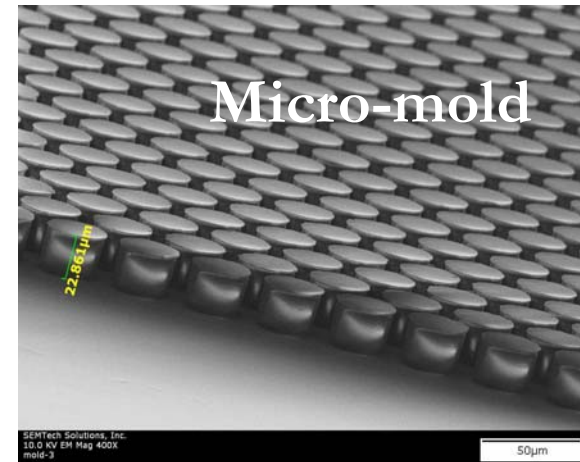
+ ?

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

Getting closer to DOE target!

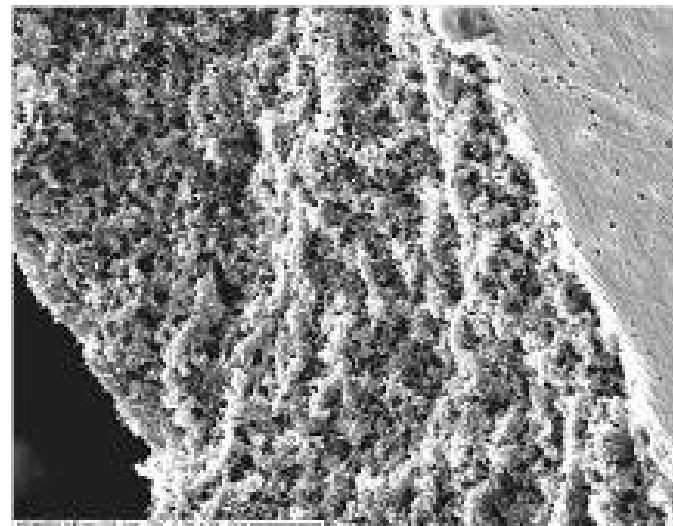
Challenges: 2DSMTM

- Biggest Challenge is Cost
 - Laser Drilling
 - Currently $\sim \$1/\text{cm}^2$
 - Projected $\sim \$0.02/\text{cm}^2$
 - $\$200/\text{m}^2$
 - In Separate DOE Project Developing Low-Cost Casting Technique
 - SEE HAN LIU POSTER FCP-013
 - (DE-FG02-05ER84322)



Challenges: 3DSM™

- Commercial Supports are too Thick
 - ~100 μm
 - Need ~ 10-25 μm
 - Can be made thinner, need the application
 - Trying to make our own
- Excessive Swelling
 - Working on Cross-linking syntheses



In-situ bulk polymerization in three-dimensional support

Future Work: 2DSM™

- Characterize RH cycling stability
 - MEA fabrication and catalyst uniformity are big questions
- Characterize thin membrane for fuel cell performance and durability
 - First Comparisons were with 2 mil film to compare to N112
 - Big advantage of these systems is ability to go very thin, so we will

Future Work: 3DSM™

- Characterize Fuel Cell Performance
 - Developing a thin membrane is a challenge
- Characterize RH Cycling durability
- Working with toll coater to produce large continuous film
 - Needed to any real durability data as hand-made films lack consistency
- Use cross-linking and other strategies to limit swelling of new low EW ionomers

SUMMARY

- Year 2 Milestones Achieved
 - Interim Conductivity targets have been met
 - Demonstrated by Becktech
 - .0852 S/cm at 30°C and 80% RH vs Goal of 0.07
 - .031 S/cm at 25% RH and 120°C is below DOE target
 - 0.10 S/cm achieved at 120°C and 50% RH
 - *NEARING ULTIMATE GO/NO-GO TARGET*
 - *0.08 S/cm Demonstrated at 80°C and 50% RH*
 - 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 incorporate the low EW materials that have been developed at SUNY, Syracuse