DOE Hydrogen Program

Dimensionally Stable Membranes

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Project ID #
FC21

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Dimensionally Stable Membranes for High Temperature Applications

Timeline

- Begin 4/3/2006
- Review 4/2/2009
- 33% Complete

Budget

- Total project funding (to 2009)
  - ❑ $899K DOE Funding
  - ❑ $529K Recipient
  - ❑ 37% Cost Share
  - ❑ $150K received FY 2006
  - ❑ $300K for FY 2007

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

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Dimensionally Stable Membranes: 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.

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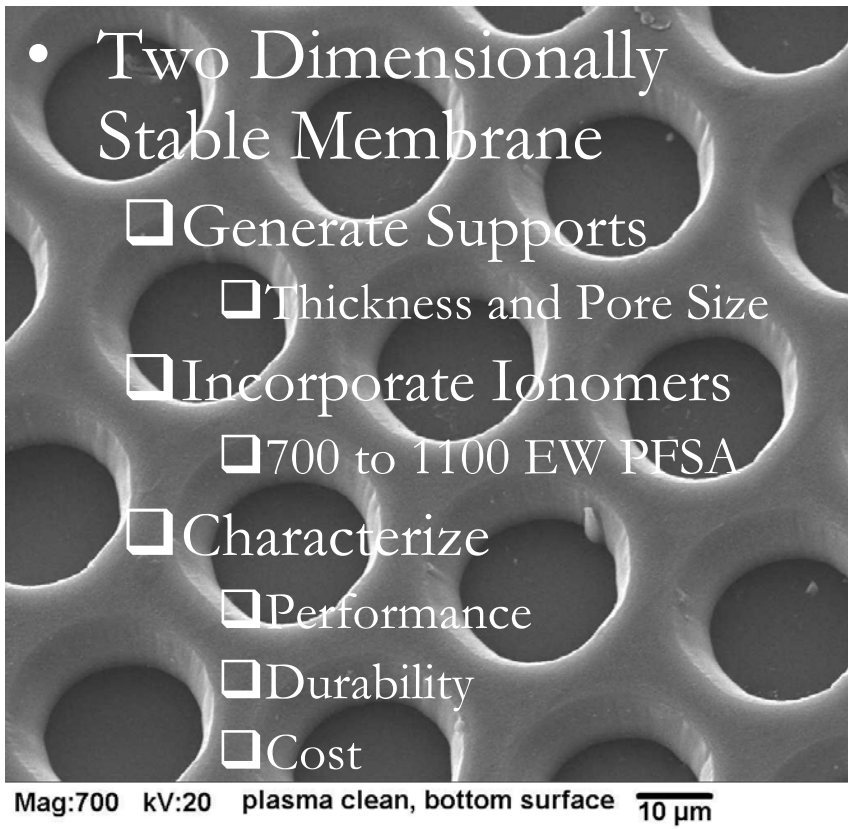
Approach: Lower EW of perfluorosulfonic Acid ionomers to increase low RH conductivity and support the ionomer with two and three-dimensional non-ionic materials

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



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

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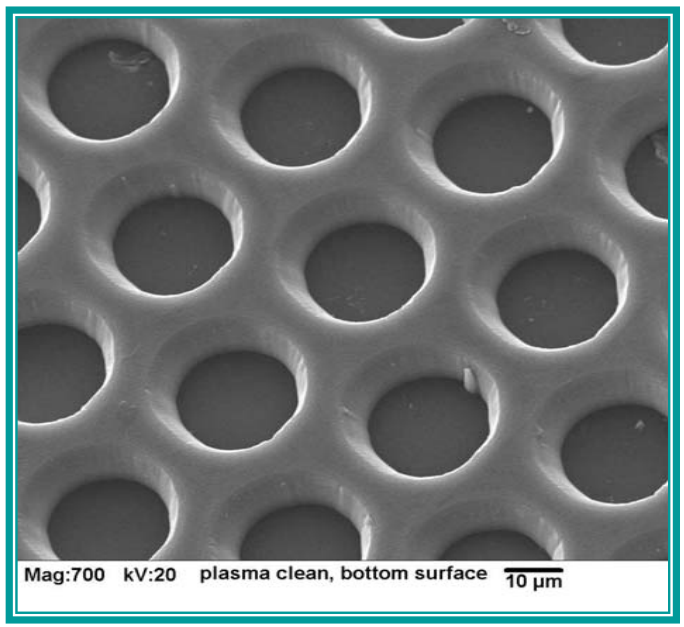
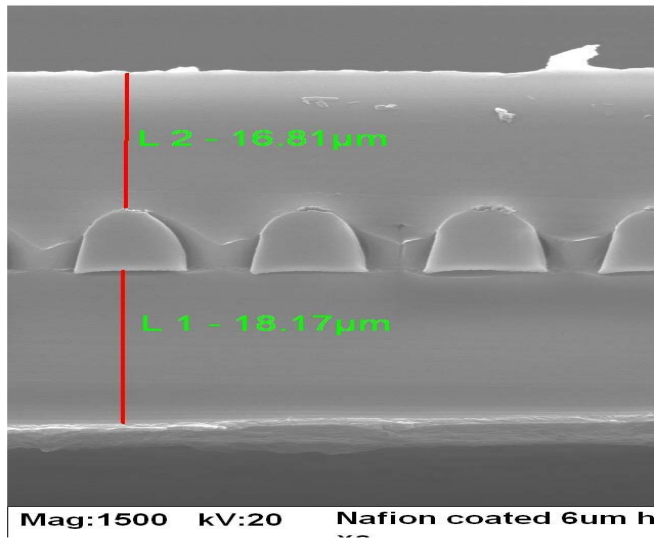
APPROACH:

- 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/in²





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APPROACH: Why DSMs?

- Limitations of Ionomers based on $-SO_3H$ functionality

  - ❑ Water uptake/retention as a function of RH
  - ❑ Conductivity Limitations
    - ❑ Dependence on Water
    - ❑ Functionality

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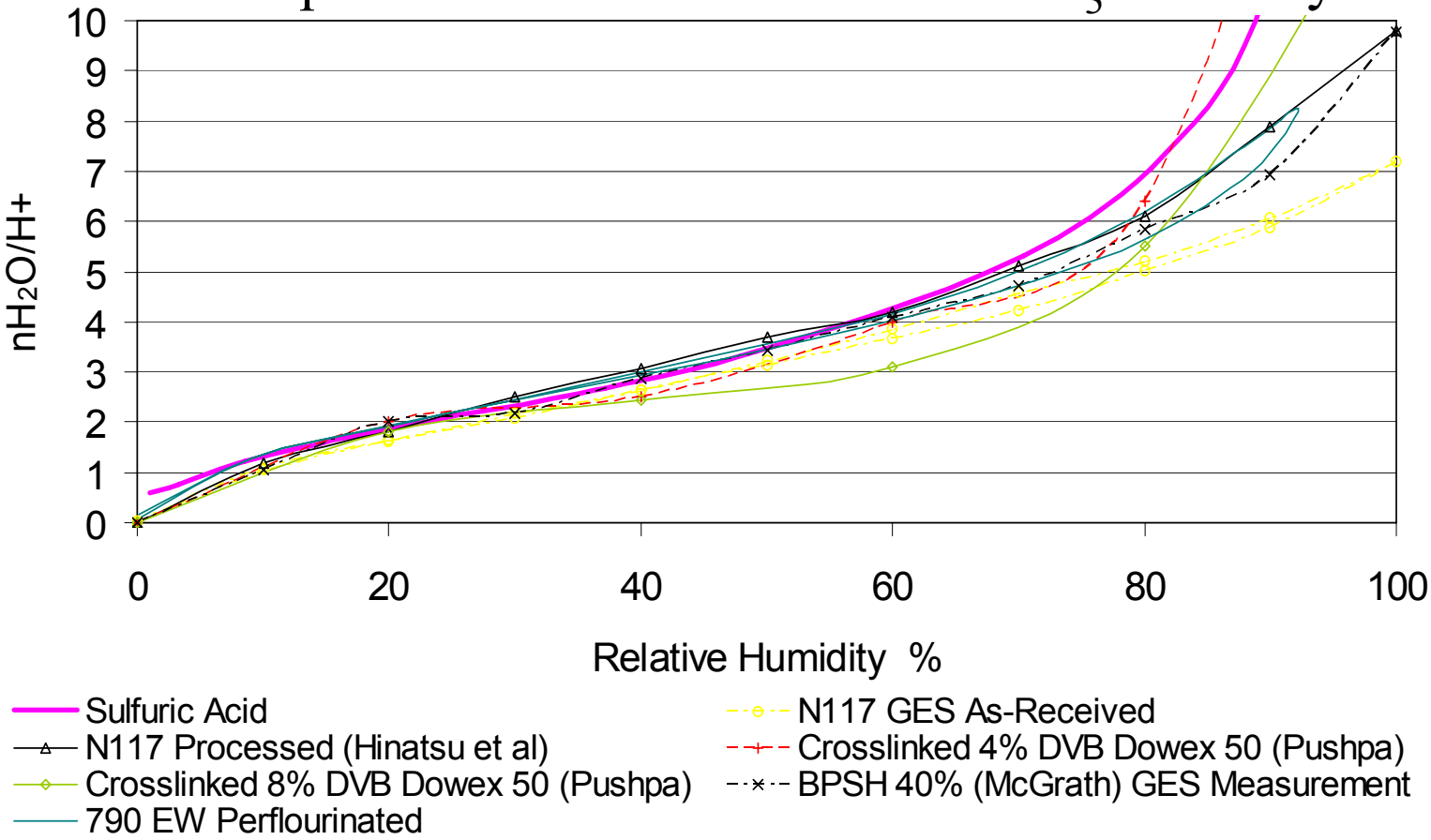
APPROACH: Why DSMs?

Water Uptake of Ionomers based on $-SO_3H$ Moiety



Water Content is the same regardless of pendant group

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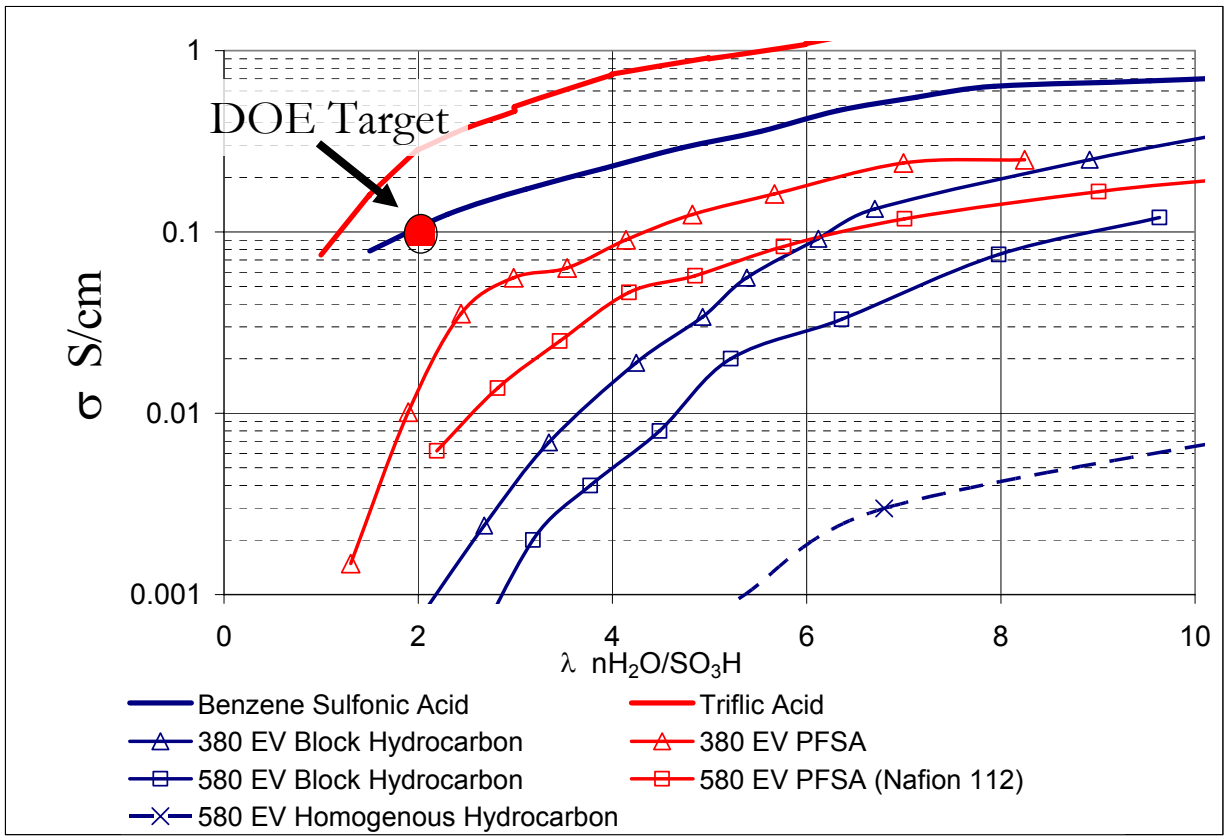
APPROACH: Why DSMs?

Importance Of Ionic Functional Group, Morphology

Conductivity of Various Ionomers and Model Compounds at 80°C



EV = EW/Density

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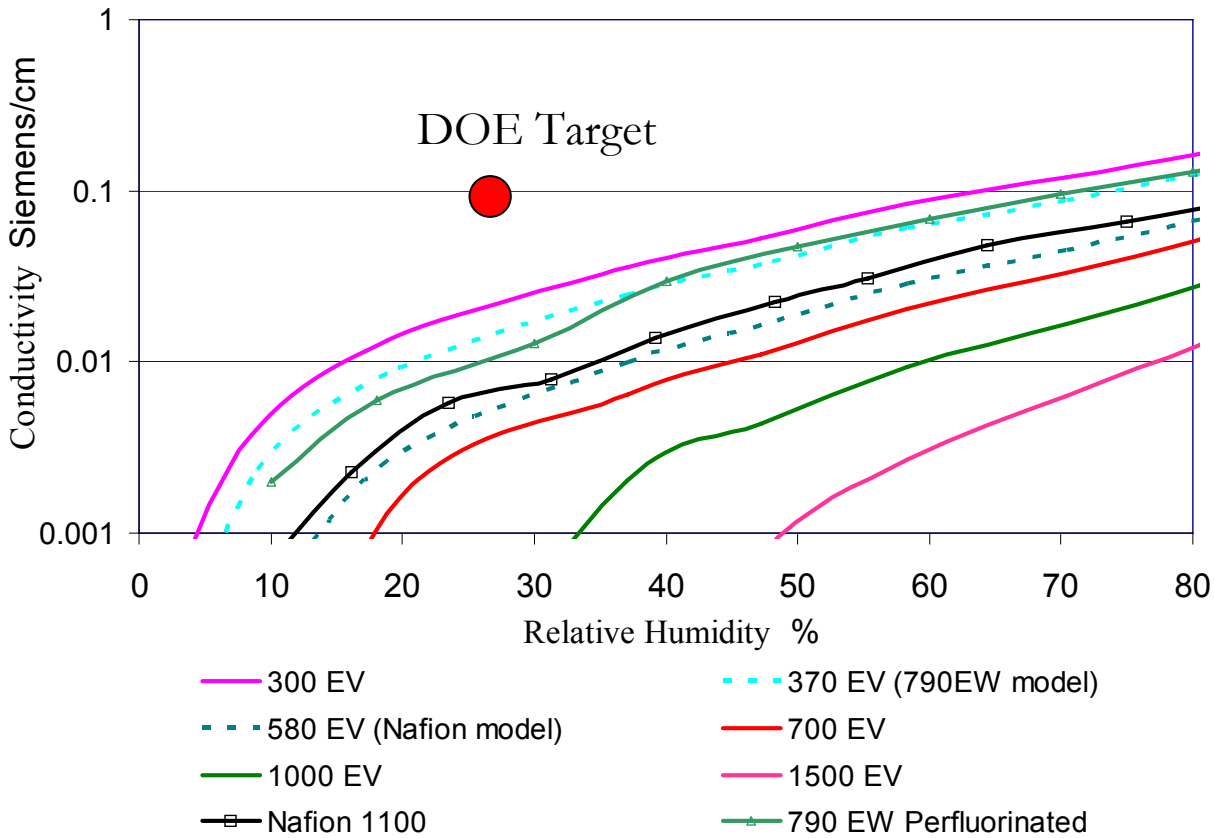
APPROACH: Why DSMs?

Model to Predict Conductivity as a function of RH, Temperature and membrane EW $\sigma = \sigma_{\text{model acid}(T,\lambda)}(c - c_o)^n$



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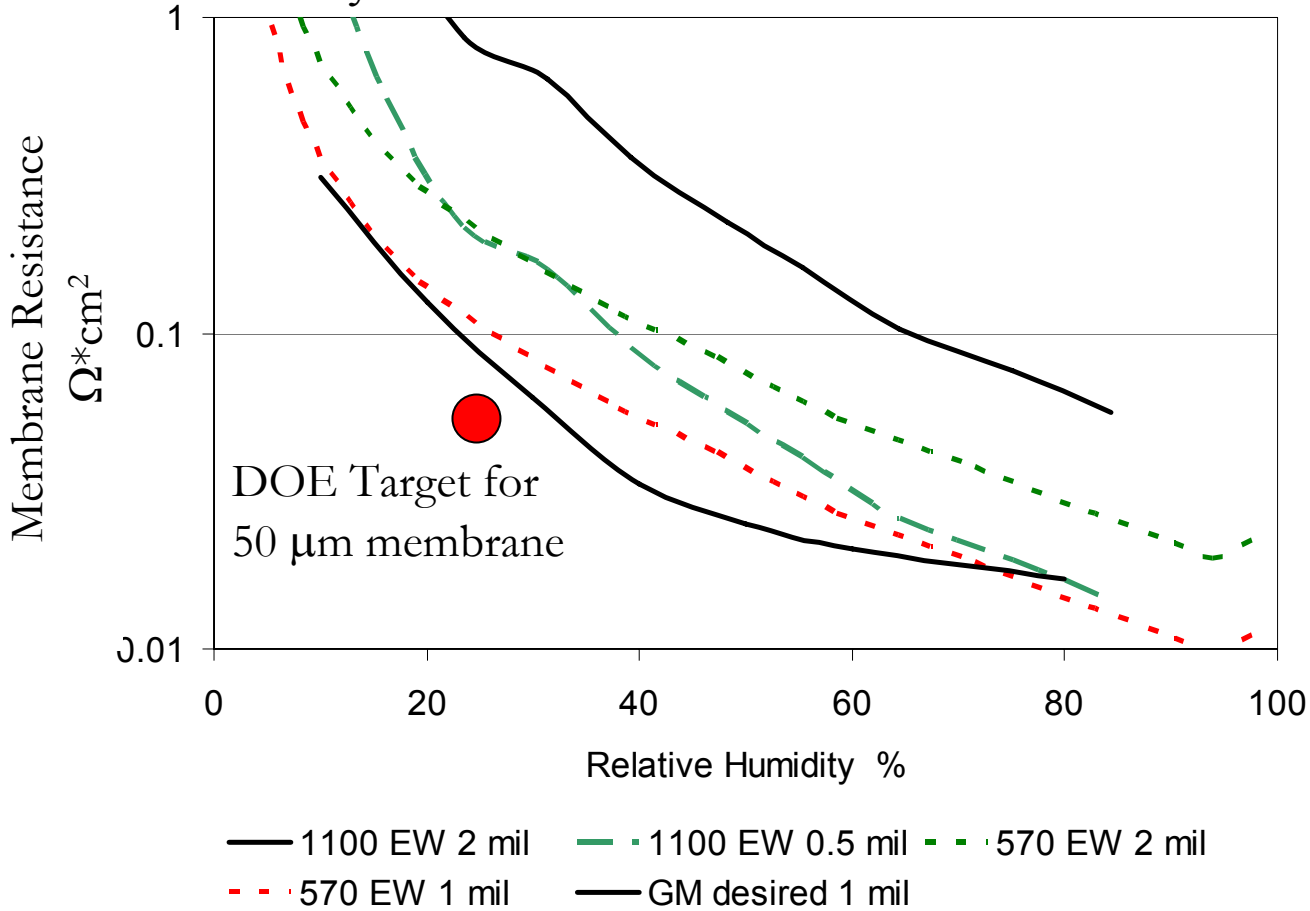
APPROACH: Why DSMs?

Limitations of Ionomers Based on -SO_3H Moiety

Predicted Conductivity at 100°C for Various Perfluorinated Membranes



APPROACH: WHY DSMs?

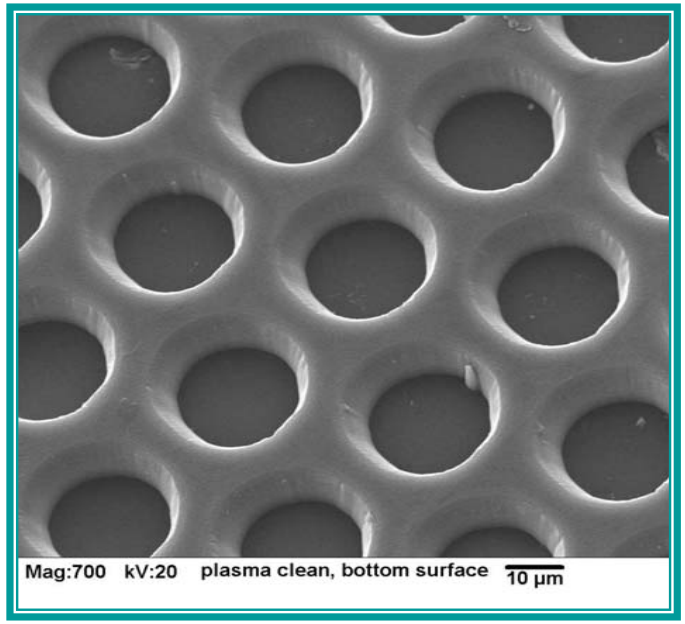
CONCLUSIONS

- -SO_3H Polymers will need
  - Very low EW
  - Perfluorinated End Groups
  - To be very thin
  - THESE THREE REQUIREMENTS LEAD TO POOR MECHANICALS

APPROACH

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

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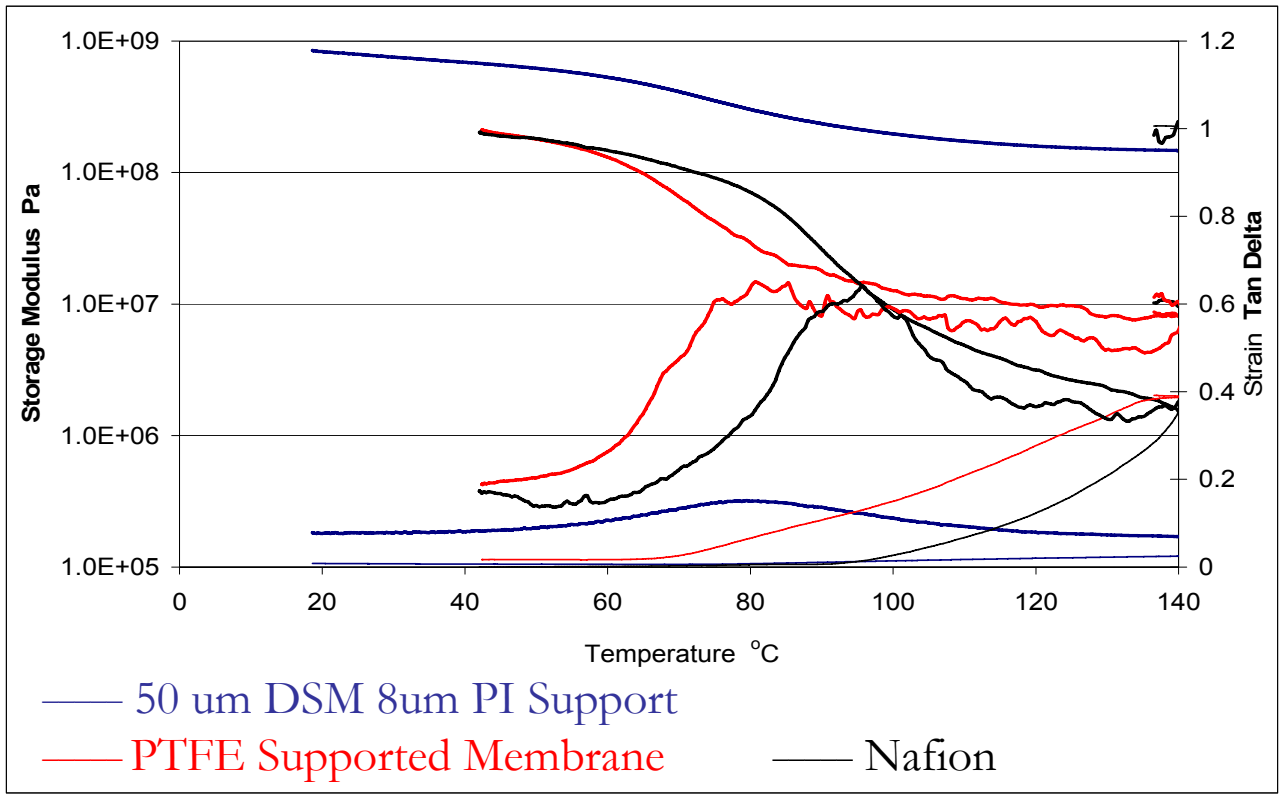
Increased Modulus of Support Material Leads to Proportional Increase in Composite Material



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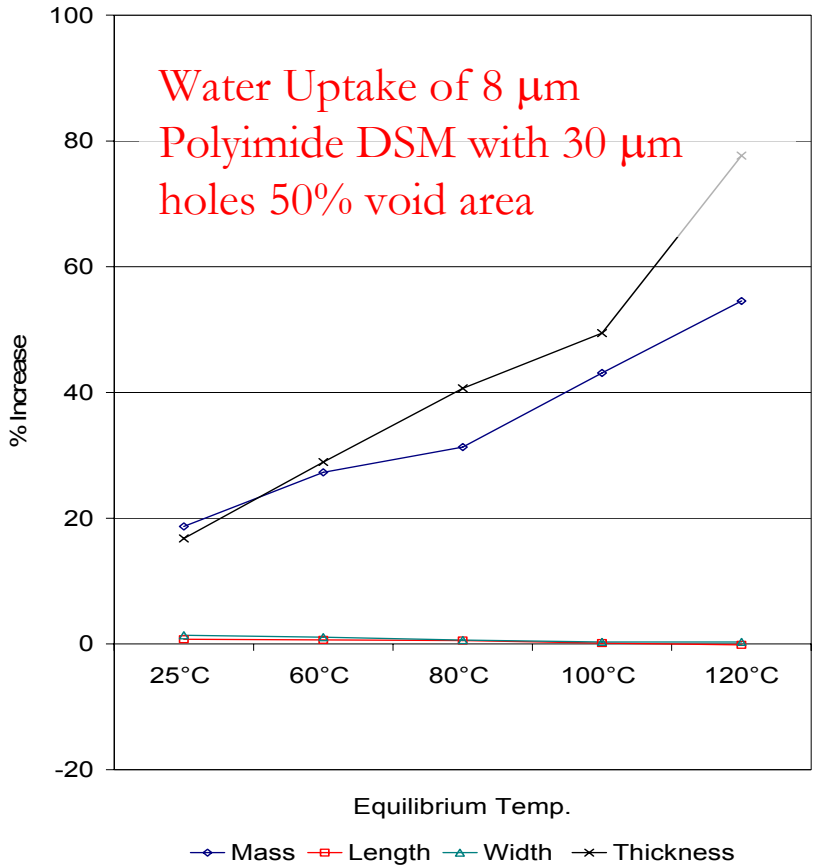
ACCOMPLISHMENTS:

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*

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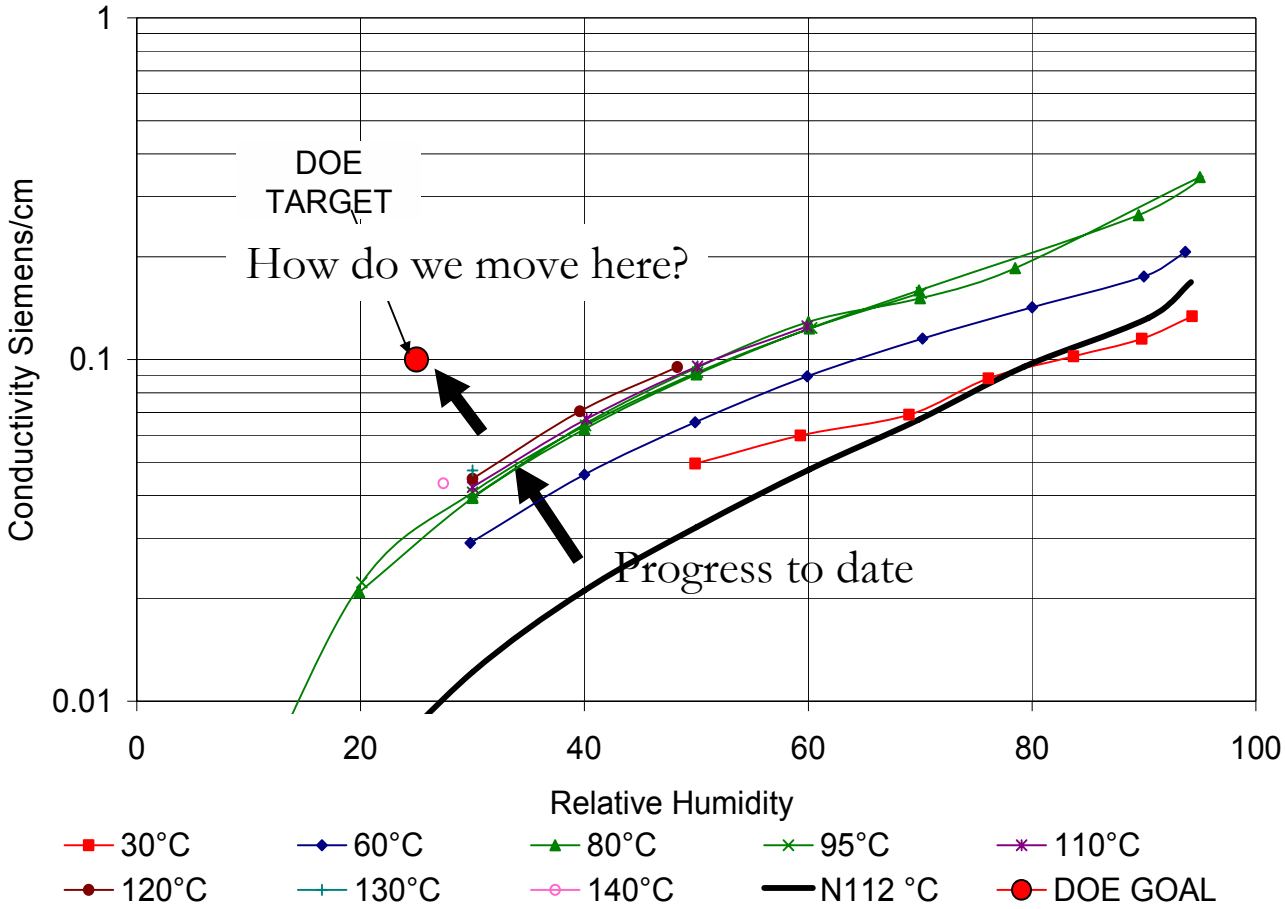
ACCOMPLISHMENTS

In-Plane Conductivity

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



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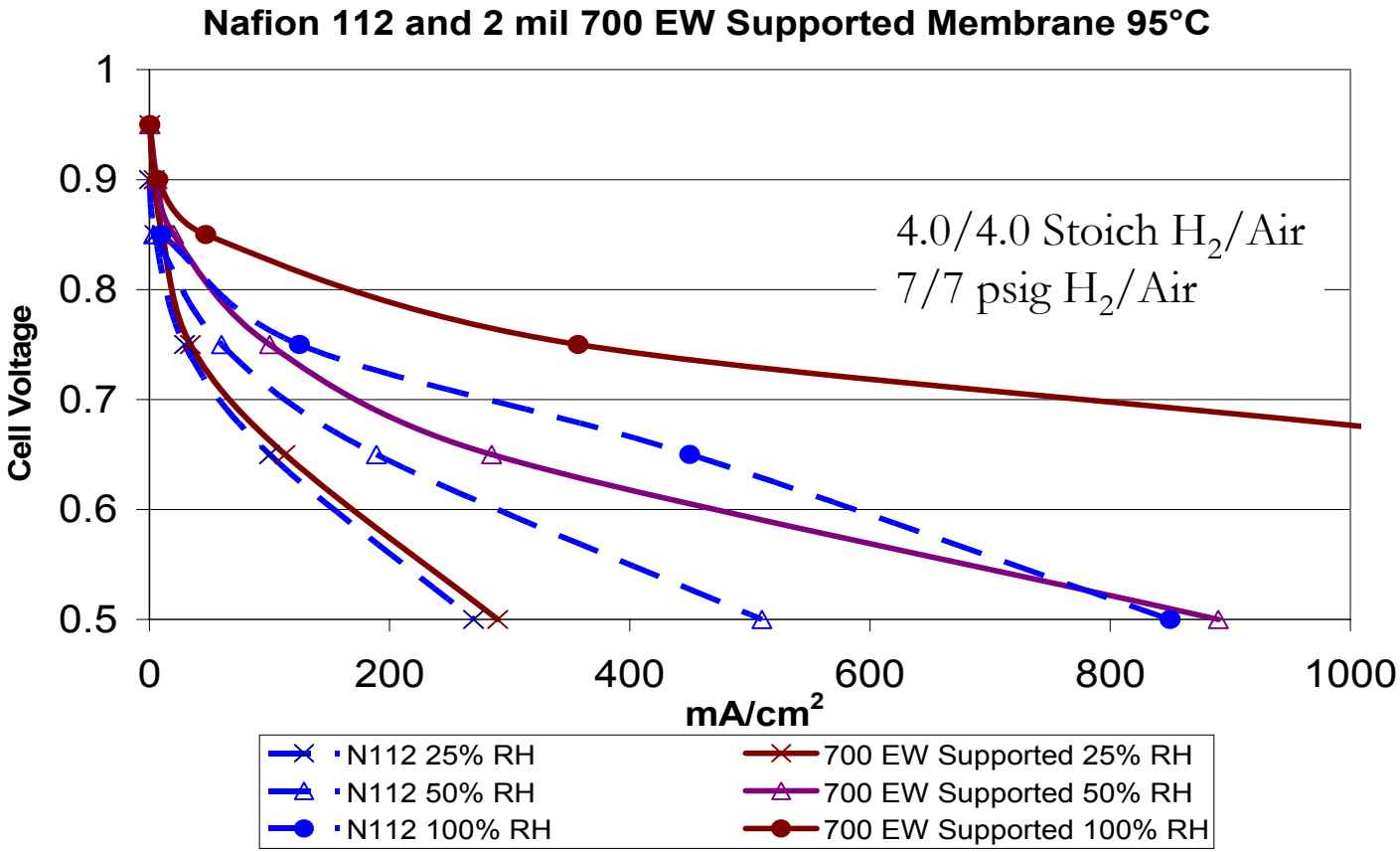
ACCOMPLISHMENTS

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

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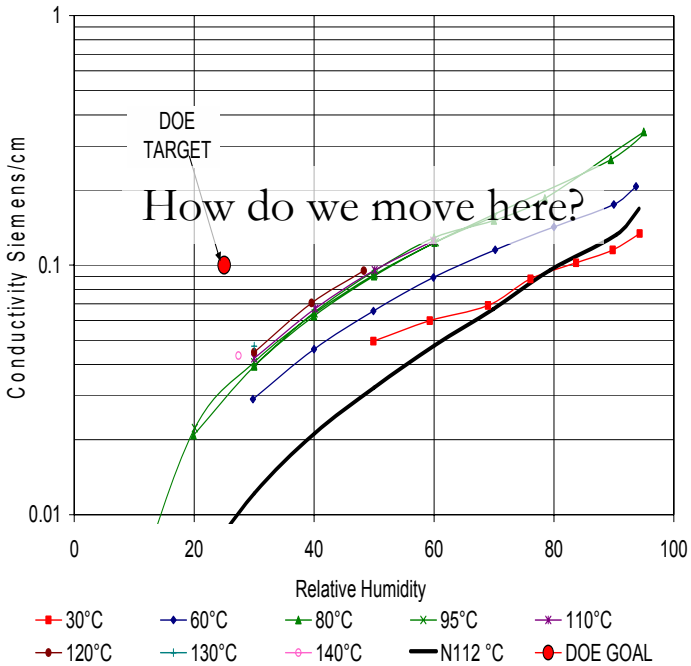
ACCOMPLISHMENTS: Alternative Synthesis



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 800-1300. Difficulty in getting low EW materials

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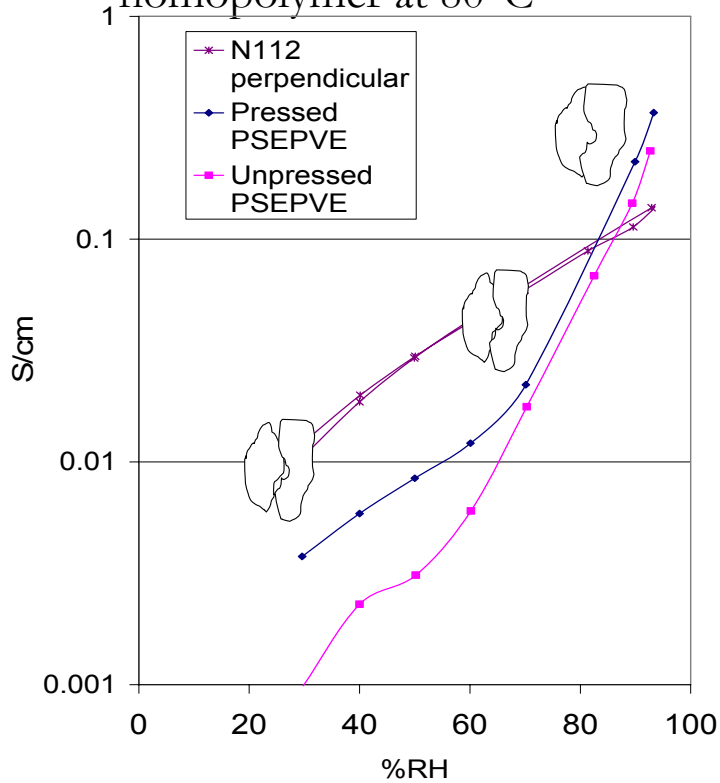
ACCOMPLISHMENTS: Alternative Synthesis

- Need lower EW PFSA's
- Functional Homopolymer has been synthesized
- $(CF_2\text{-}CF)_n$
  $CF_2CF(CF_3)OCF_2CF_2SO_2F$

- Water Soluble
- Terrible Film-Former
- Difficult to hydrolyze to completion

Conductivity of DSM with homopolymer at 80°C



Believe that cracking, at low RH leads to higher resistance

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FUTURE WORK

- Believe that we have achieved Year 2 Milestone using both approaches
  - 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.
    - Laser-drilled ionomers demonstrate 0.1 S/cm at 80% RH and 30°C
    - New PFSA ionomer demonstrates .07 S/cm at 80% RH and 30°C
- Continue to characterize composite materials for fuel cell performance/durability
- Continue to synthesize and characterize new perfluorinated ionomers
- Incorporate new ionomers in three-dimensional supports

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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
  - Will continue fuel cell performance and durability testing
- To reach ultimate DOE Goals we will need even lower EW materials
  - We are working on it