

Dimensionally Stable Membranes™

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SUNY-ESF

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 H₂O Air inlet
- <\$40/m²
- > 5000 hour lifetime
- Stability in condensing conditions

Partners

- General Motors
- SUNY-ESF

OVERVIEW

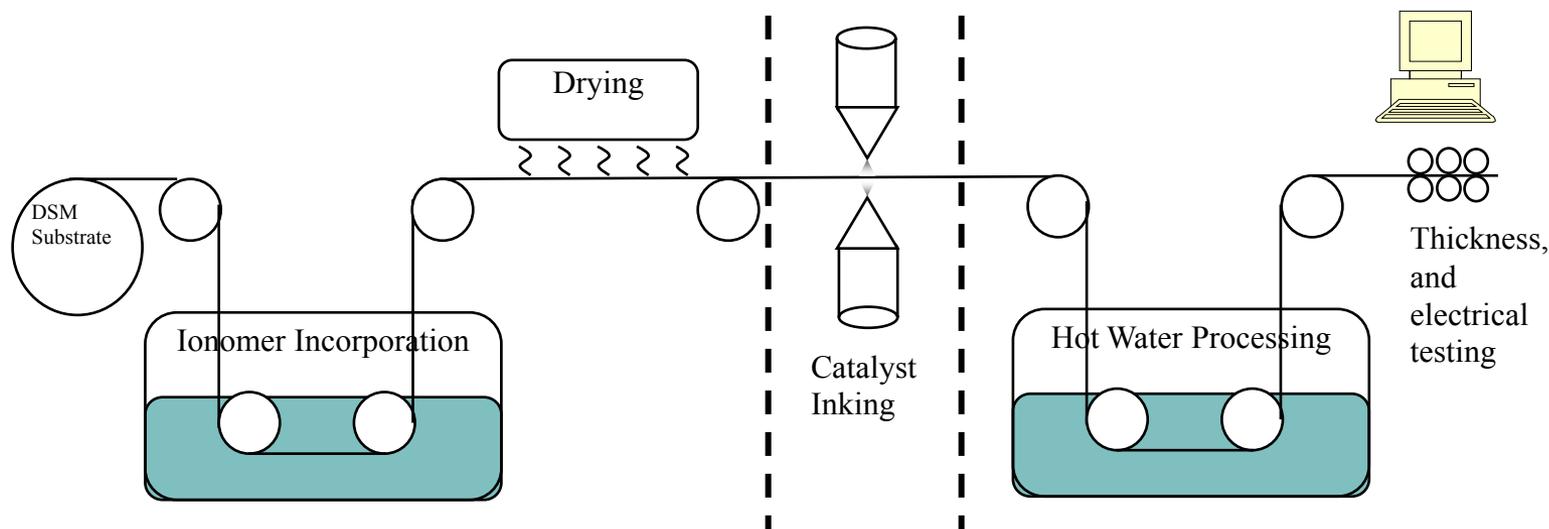
- OBJECTIVES
- APPROACH and ACCOMPLISHMENTS
 - Rationale
 - Two Dimensionally Stable Membranes™
 - Three Dimensionally Stable Membranes™
- CHALLENGES

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



OVERVIEW

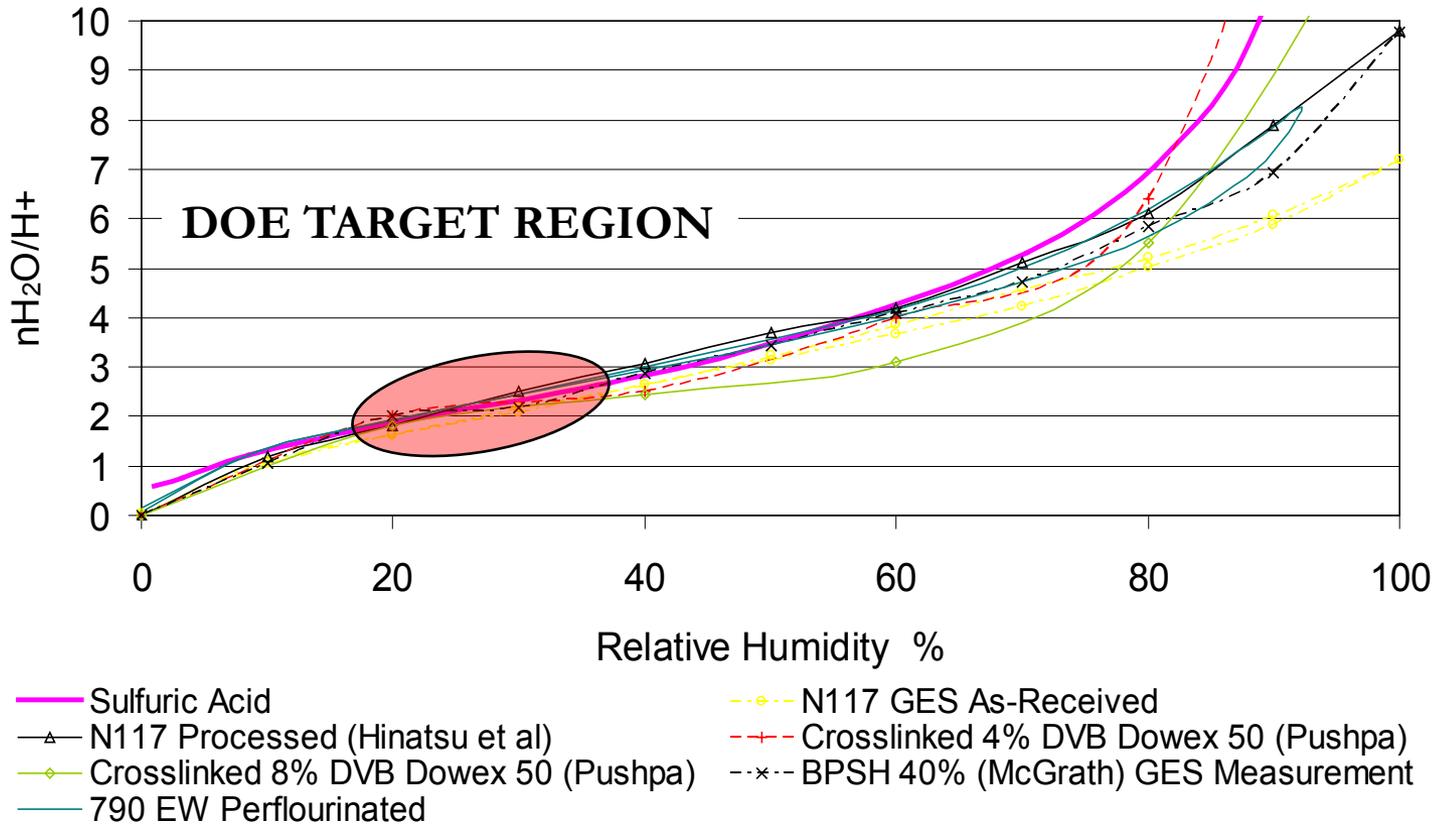
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APPROACH: Rationale

- Limitations of Ionomers based on $-\text{SO}_3\text{H}$ functionality
 - Water uptake/retention as a function of RH
 - Conductivity Limitations
 - Dependence on Water
 - Functionality

APPROACH: Rationale

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

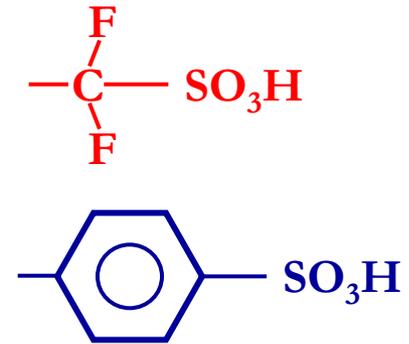
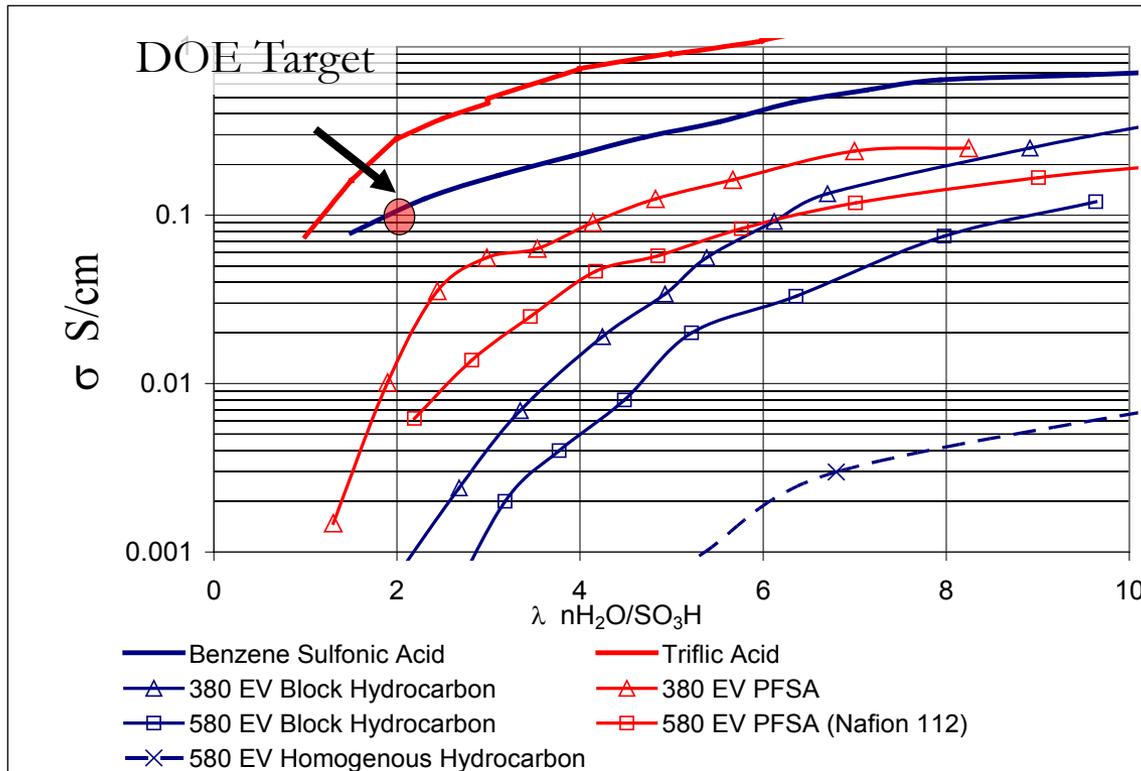


Water Content is the same regardless of pendant group

APPROACH: Rationale

Importance of Ionic Functional Group, Morphology

Conductivity of Various Ionomers and Model Compounds at 80°C

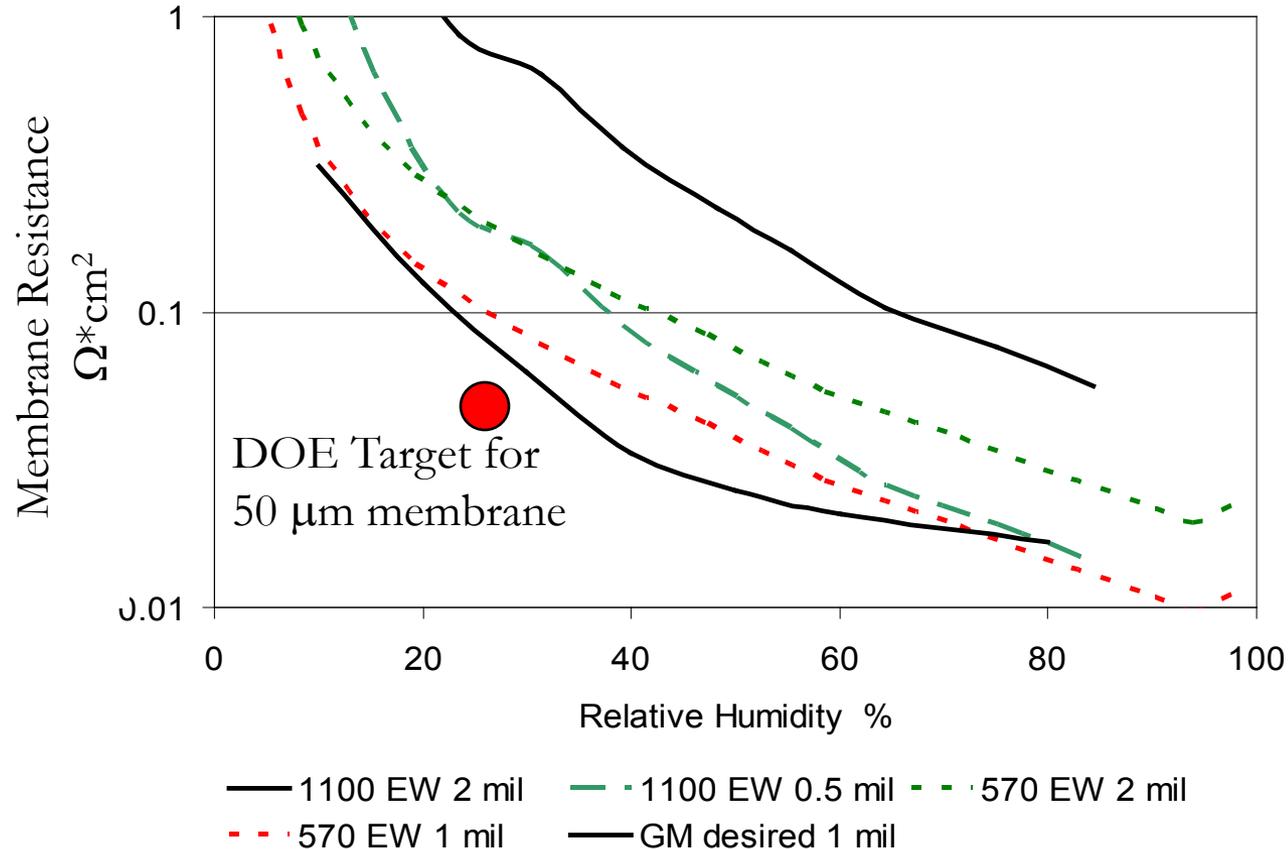


$$\text{EV} = \frac{\text{EW}}{\text{Density}}$$

APPROACH: Rationale

Limitations of Ionomers Based on $-\text{SO}_3\text{H}$ Moiety

Predicted Conductivity at 100°C for Various Perfluorinated Membranes



APPROACH: Rationale

CONCLUSIONS

SO₃H 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 μ m

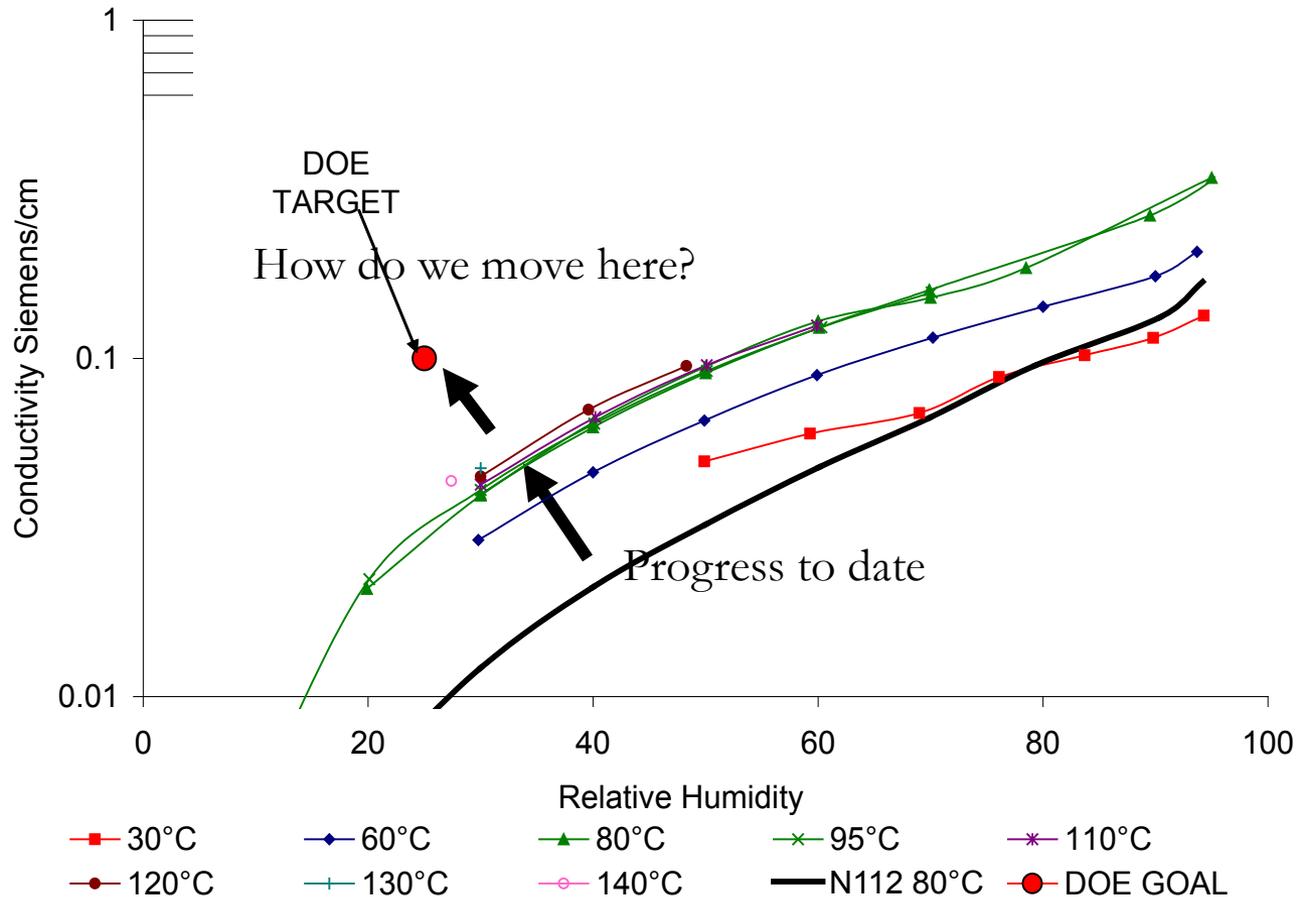
- **Three Dimensionally Stable Membrane**

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

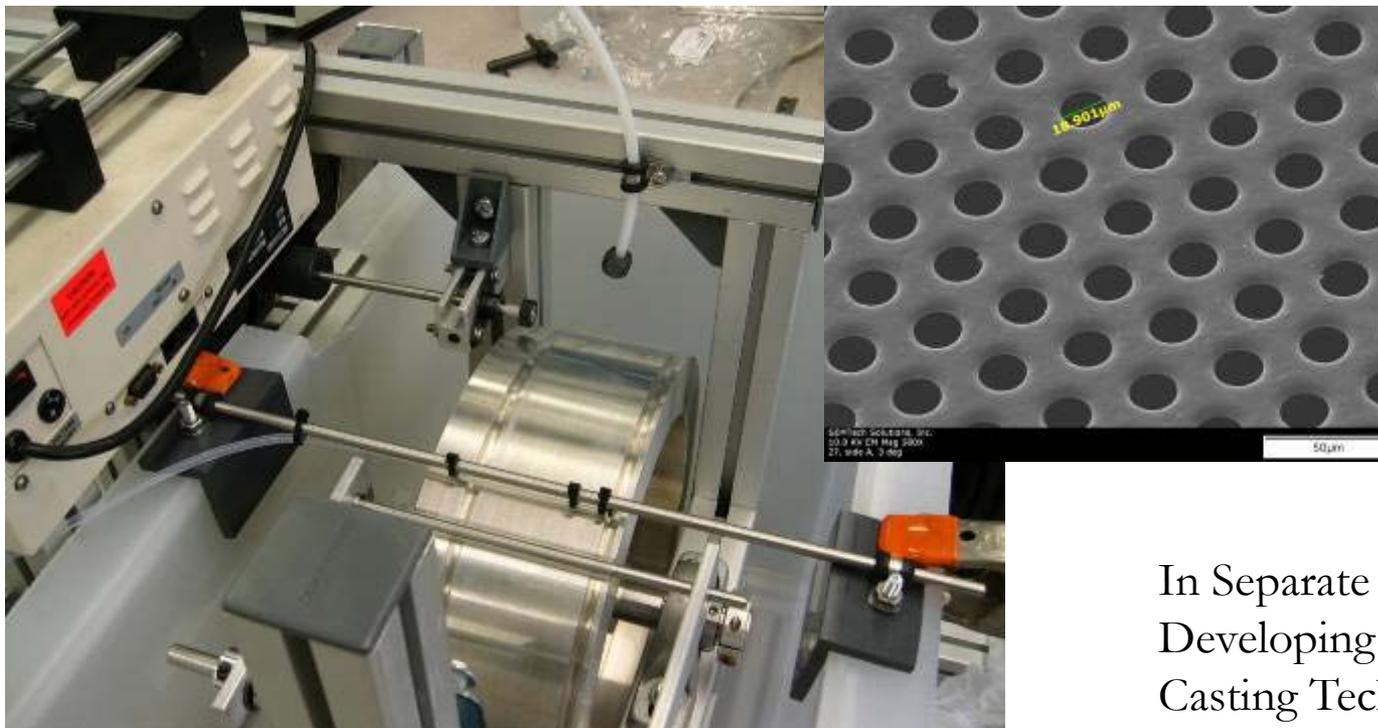
ACCOMPLISHMENTS: 2DSM™

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

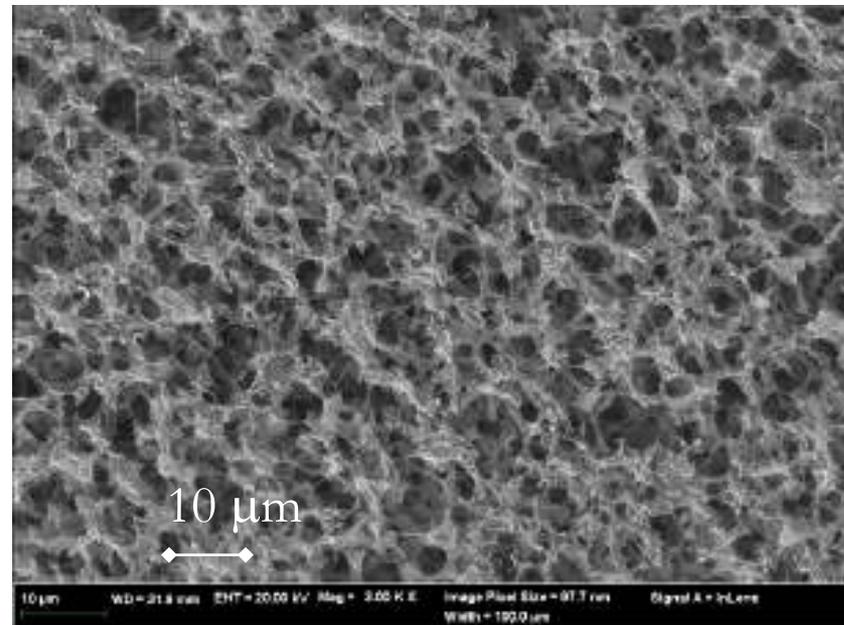
In Separate DOE Project
Developing Low-Cost
Casting Technique
(**DE-FG02-
05ER84322**)
PI: Han Liu

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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*

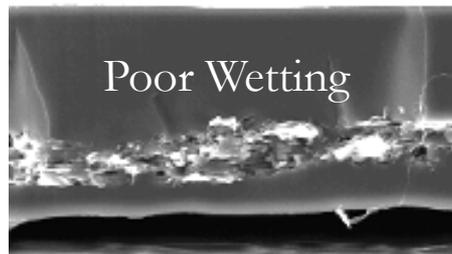
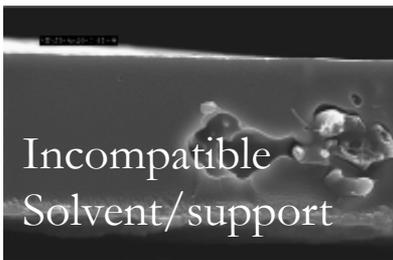
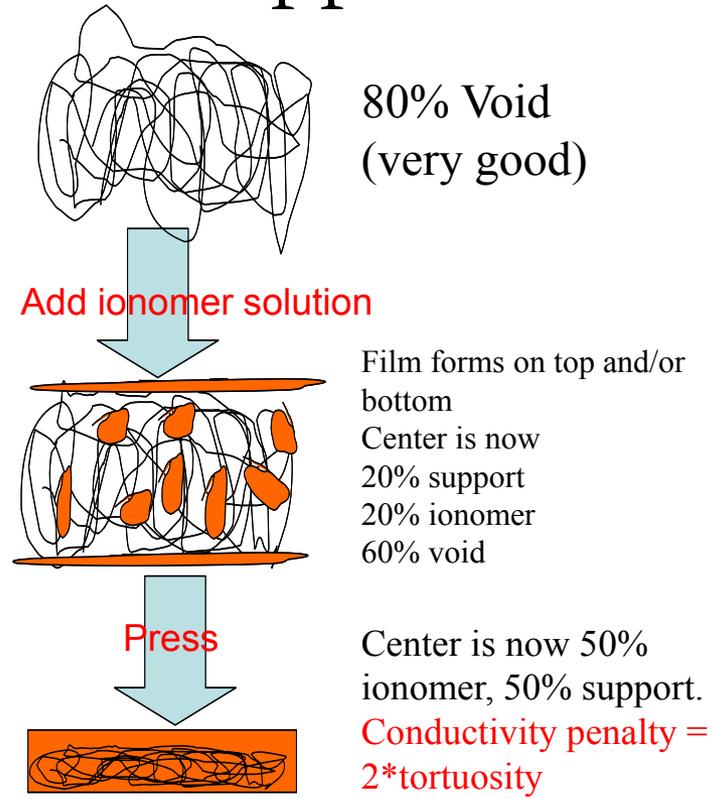


APPROACH: FOCUS OF PAST YEAR

- 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

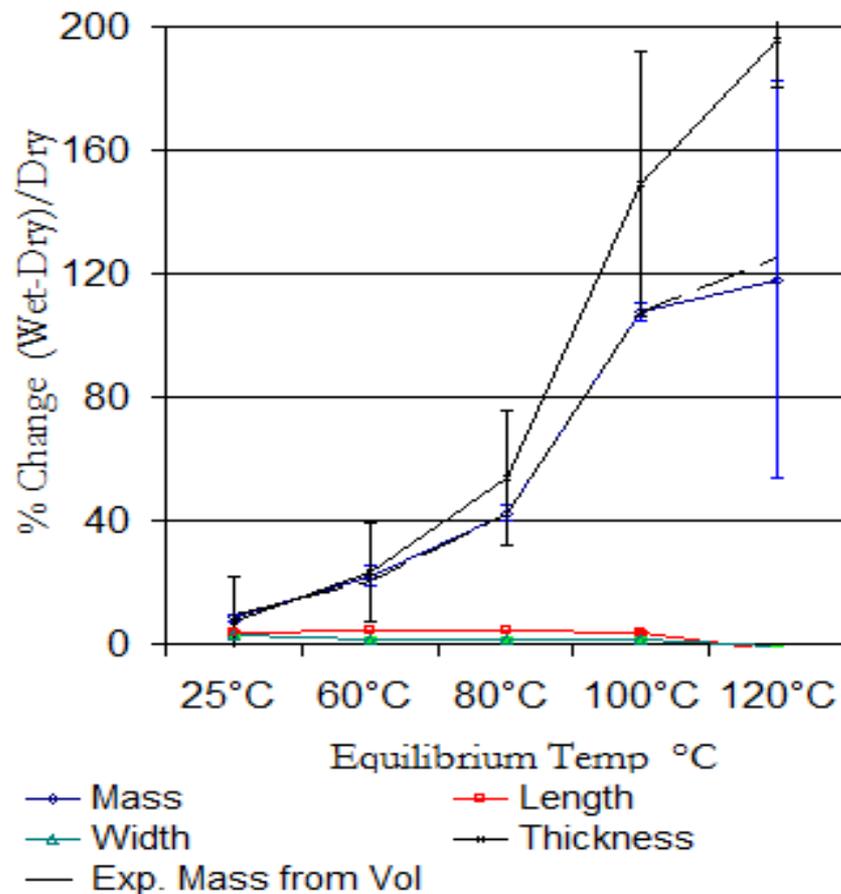
- Advantages:
 - Many commercially available
 - Ionomer is easily added by solution
 - Roll to Roll processible
- Disadvantages:
 - Making thin supports for some materials
 - Support/Solution compatibility
 - **Getting high ionomer content**
 - High wt% dispersion
 - High void volume



ACCOMPLISHMENTS: 3DSM™

Previous Results with 1 mil membrane

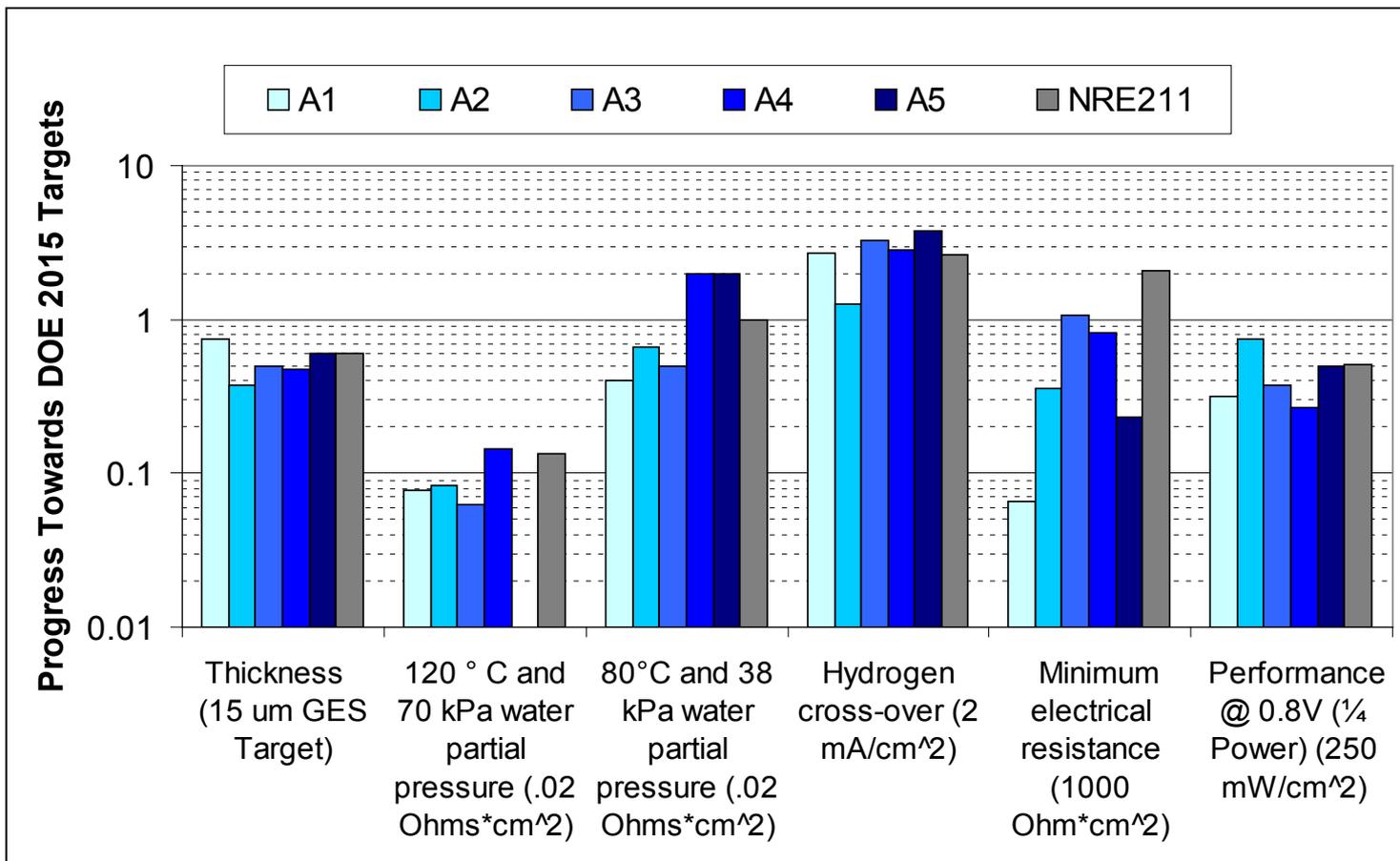
- Custom Membrane from Millipore
- Swelling is Comparable to thick membrane
- Completely Filling Support was a Major Challenge
- Consistency through the plane was a challenge
- ~25% Conductivity Penalty
- 10,000 RH Cycles demonstrated
- *Could not incorporate low EW materials into the matrix*
- *Difficult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





ACCOMPLISHMENTS: 3DSM with ~ 850 EW

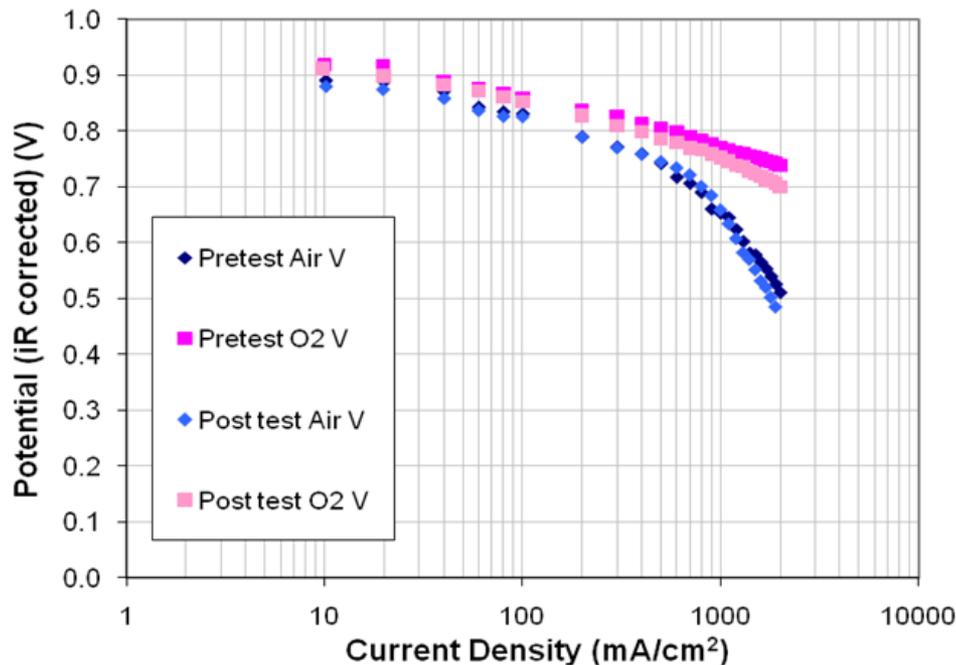
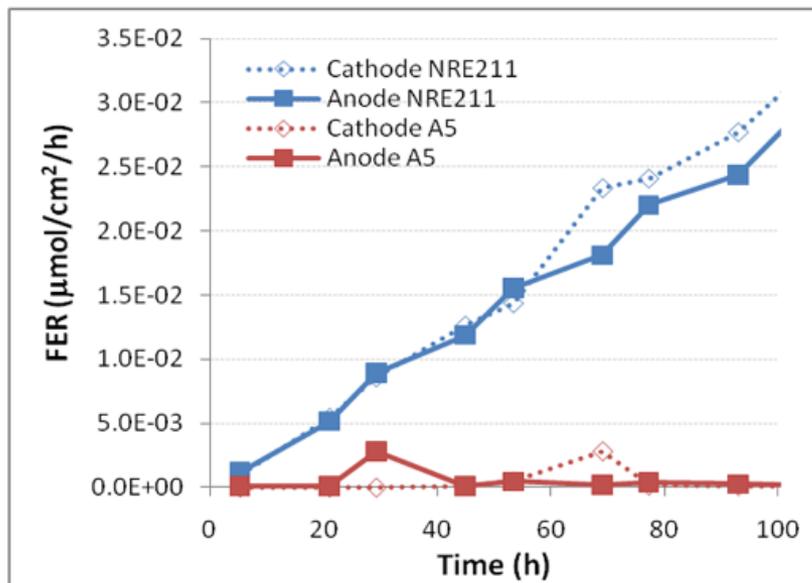
Florida Solar Energy Center (FSEC) Test Results



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

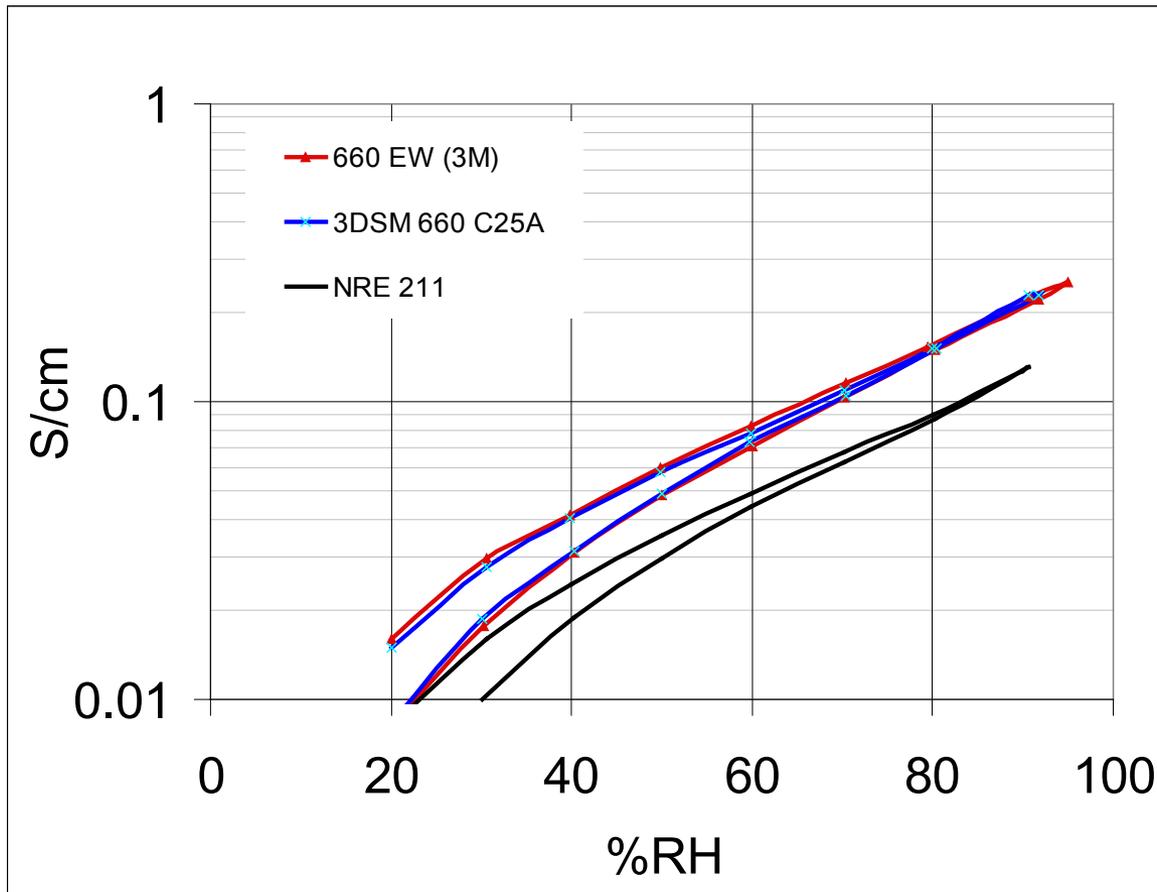
ACCOMPLISHMENTS: Chemical Stability Enhancement

Florida Solar Energy Center Testing



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

ACCOMPLISHMENTS: 3DSM with 3M 660 EW Ionomer

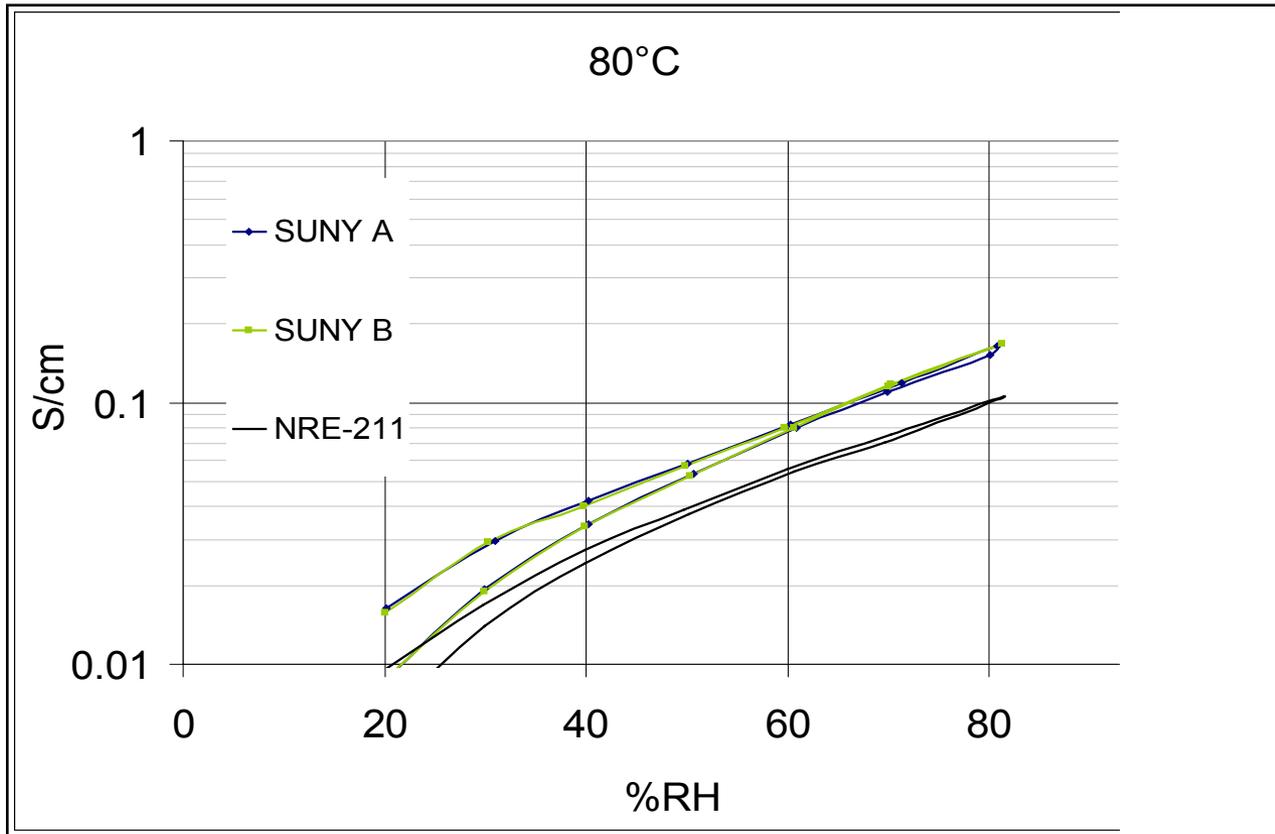


3M gave us another low EW material to test

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/m² for support and processing.
 - Toll-coaters contacted and adding PFSA to membrane is ¢/m²
 - 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

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