



DOE Hydrogen Program

# Membranes and MEA's for Dry, Hot Operating Conditions

Steven Hamrock

**3M** Fuel Cell Components

May 11, 2011



FC034

# Overview

## Timeline

- Project start 4/1/07
- Project end 3/31/11
- 99% complete

## Budget

- Total Project funding \$11.4 million
  - \$8.9 million - DOE
  - \$2.5 million - contractor cost share (22%)
- Funding in FY 2010
- \$2.6 Million
- Funding in FY 2011
- \$0.7 Million

## Barriers

- A. Durability
- C. Performance

## Partners

**3M Company** *S. Hamrock (Project lead)*

**Case Western Reserve Univ.** *Professor D. Schiraldi*

**Colorado School of Mines** *Professor A. Herring*

**Univ. of Detroit Mercy** *Professor S. Schlick*

**Univ. of Tennessee** *Professors S. Paddison and T. Zawodzinski*

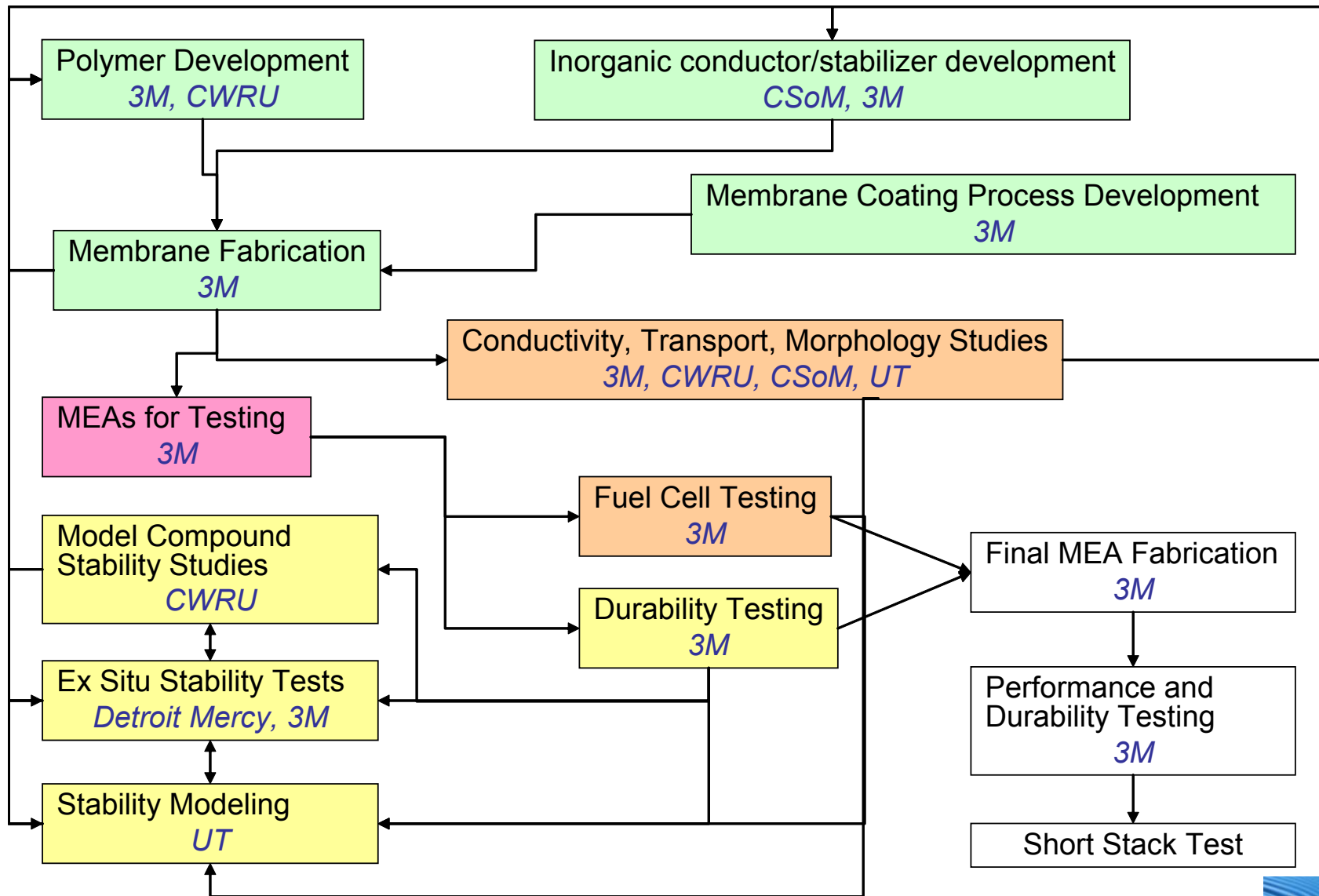
# Project Objectives

- To develop a new proton exchange membrane with:
  - higher proton conductivity**
  - improved durability**
 under hotter and dryer conditions compared, to current membranes.

Characteristic	Units	2006 status	2005 target	2010 target	2015 target
Maximum operating temperature	°C	80	120	120	120
Area specific resistance at:					
Maximum operating temp and water partial pressures from 40 – 80 kPa	Ohm cm <sup>2</sup>	0.03	0.02	0.02	0.02
80°C and water partial pressures from 25 - 45 kPa	Ohm cm <sup>2</sup>	0.03	0.02	0.02	0.02
30°C and water partial pressures up to 4 kPa	Ohm cm <sup>2</sup>	0.04	0.03	0.03	0.03
-20°C and water partial pressures up to 0.1 kPa	Ohm cm <sup>2</sup>	0.3	0.2	0.2	0.2
Oxygen cross-over <sup>a</sup>	mA/cm <sup>2</sup>	5	5	2	2
Hydrogen cross-over <sup>a</sup>	mA/cm <sup>2</sup>	5	5	2	2
Cost <sup>b</sup>	\$/m <sup>2</sup>	15 <sup>c</sup>	200	20	20
Durability with cycling					
At operating temp ≤80°C	hours	~2000 <sup>d</sup>	2000	5000 <sup>e</sup>	5000 <sup>e</sup>
At operating temp >80°C	hours	(not avail. <sup>f</sup> )		2000	5000 <sup>e</sup>
Unassisted start from	°C	-20	-30	-40	-40
Thermal cyclability in presence of condensed water		Yes	Yes	Yes	Yes

- New polymers, fluoropolymers, non-perfluorinated polymers and composite/hybrid systems with increased proton conductivity and improved stability
- Developing new membrane additives for both increased conductivity and improved stability/durability under these dry conditions
- Experimental and theoretical studies of factors controlling proton transport both within the membrane and mechanisms of polymer degradation and membrane durability in an MEA
- New membrane fabrication methods for better mechanical properties and lower gas crossover.
- Focus on materials which can be made using processes which are scalable to commercial volumes using cost effective methods
- Testing performance and durability. Tests will be performed in conductivity cells and single fuel cells using realistic testing conditions and protocols.
- 2010/2011 Milestones
  - **Q3 2010:** Year 4, Quarter 2: 3M will down select for the best performing electrode for final membrane tests. The selection will be based on performance under hot and dry to cool and wet conditions, stability towards Pt dissolution, carbon corrosion and fluoride release. The GDL and MEA fabrication process will also be selected.
  - **Q4 2010:** Year 4, Quarter 3: 3M will begin final testing of MEA comprising the down selected components (membrane, electrode, GDL) for performance and accelerated durability.

# Collaborations – Flow Of Samples And Information



- Use experimental and computational methods to understand the relationship between polymer structure and ion transport.
  - A hierarchical modeling approach that combines both atomistic and mesoscopic simulations is being developed and applied to study the hydrated morphology of fluoroionomers with different protogenic groups and equivalent weights (EWs) .
- NMR spectroscopy and other physical measurements are being used to study proton and water transport and water uptake in new ionomers and PFSA's.

## University of Detroit, Mercy

- Use spectroscopic methods (ESR, IR) to study degradation pathways in new ionomers and PFSA's.
  - Development of the competitive kinetics approach for ranking membrane stability to attack by hydroxyl radicals.
  - Study early events in the fragmentation of model compounds and determine the attack site.
- ATR-FTIR of perfluorinated membranes and model compounds.

## Case Western Reserve University

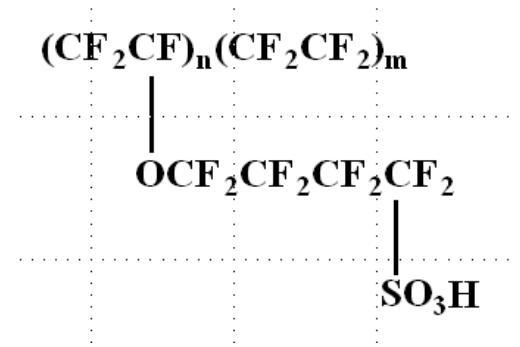
- Perform chemical degradation studies of functional groups used in new ionomers to better understand relative stability.
  - Ex situ stability studies of functional groups being used in new ionomers.
  - Use this understanding to develop (with 3M) new, stable protogenic groups and crosslinking chemistry.

## Colorado School of Mines

- Develop stable inorganic, HPA-based additives that contribute to conductivity and/or chemical stability.
  - Prepare composite membranes using new additives and evaluate (with 3M) conductivity and stability.
- Study morphology of new membranes using SAXS, other techniques.

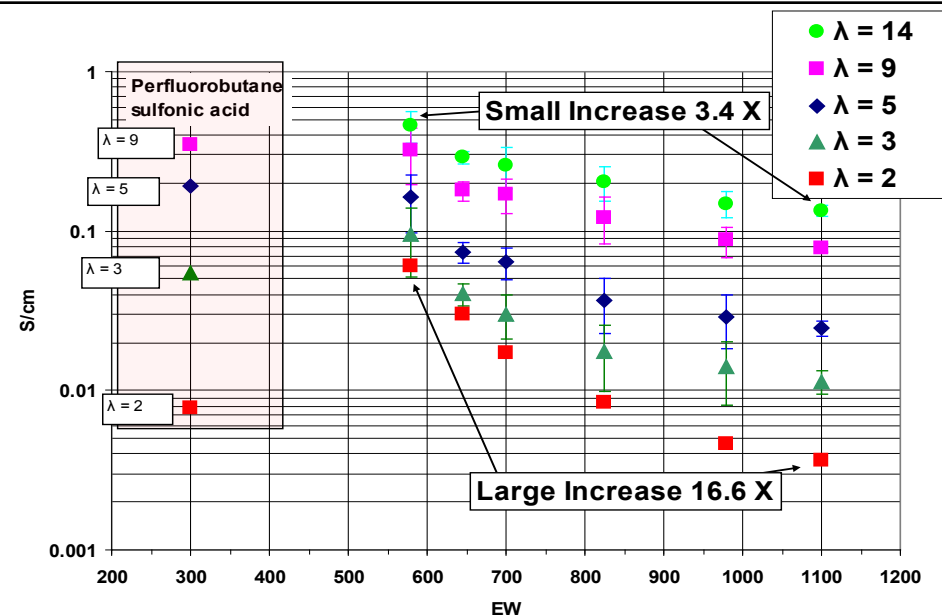
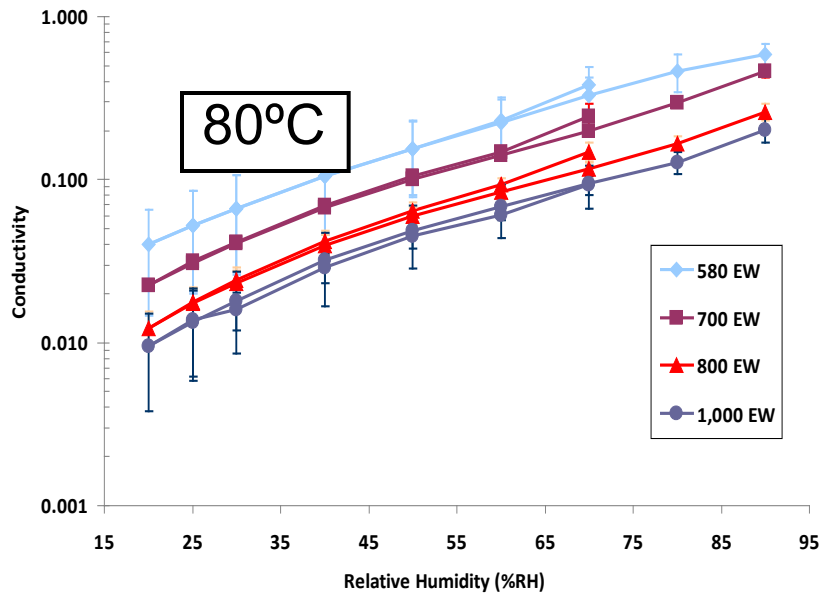
# In- Plane Conductivity At 80°C

- At lower % RH or  $\lambda$ , the conductivity increases by a much larger factor when the EW is lower compared to the more humidified state.
- This increase is consistent with the hydrated acid groups being more accessible to one another in the lower EW ionomer, allowing proton transport even with little or no “free” water.



EW's below about 600 will meet conductivity requirements at 40% RH, even at 80°C.

Lower EW ionomers have higher conductivity than  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$  (300 MW/EW) at a given lambda value, showing the importance of the phase separated morphology.



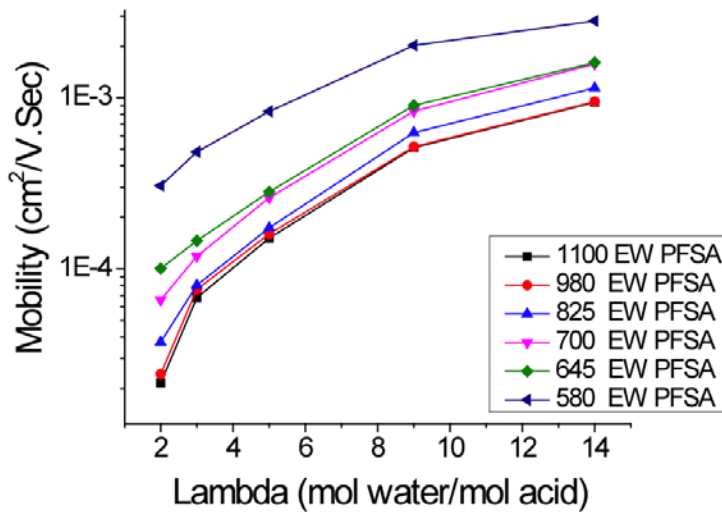
# Correcting the conductivity for Concentration Effects

Technical Accomplishments  
and Previously Presented Material

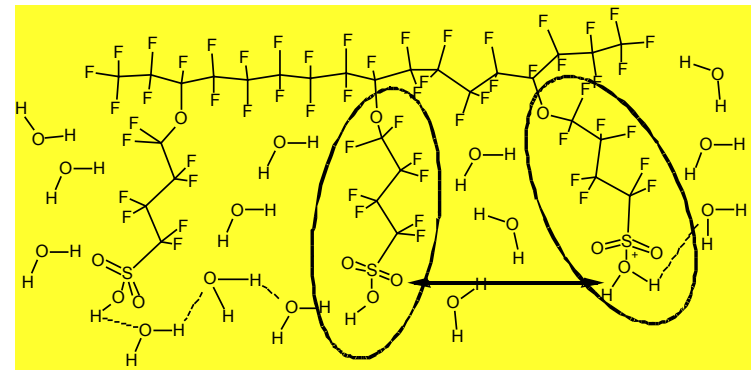
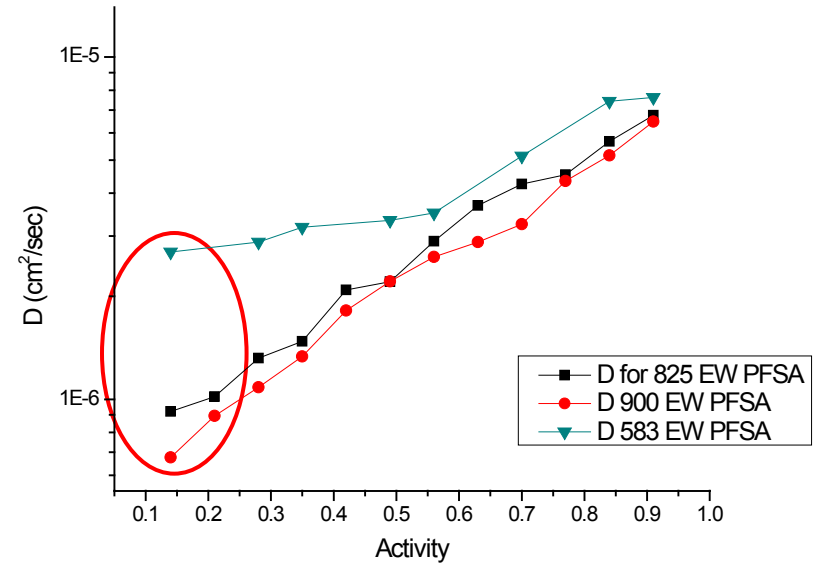
$$\sigma \propto C_{H^+} \mu_{H^+}$$

Correction for Concentration by \* (EW + 18λ/ρ) gives proton mobility

**Dramatic increase in Proton Mobility for 580 EW at all water contents**



NMR Diffusion: micron scale mobility

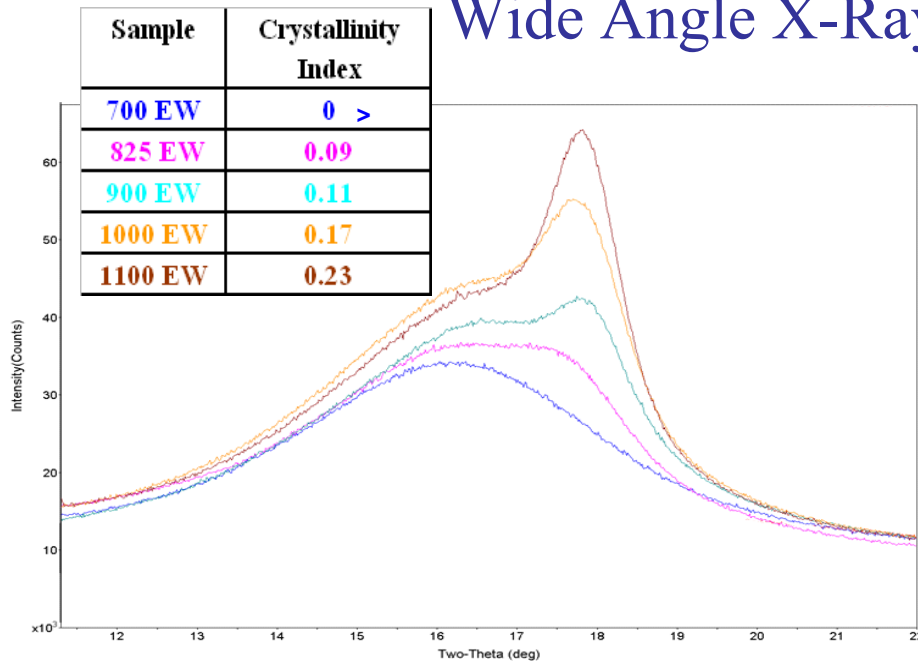


Low EW--close packing of sites allows water bridging, looser binding

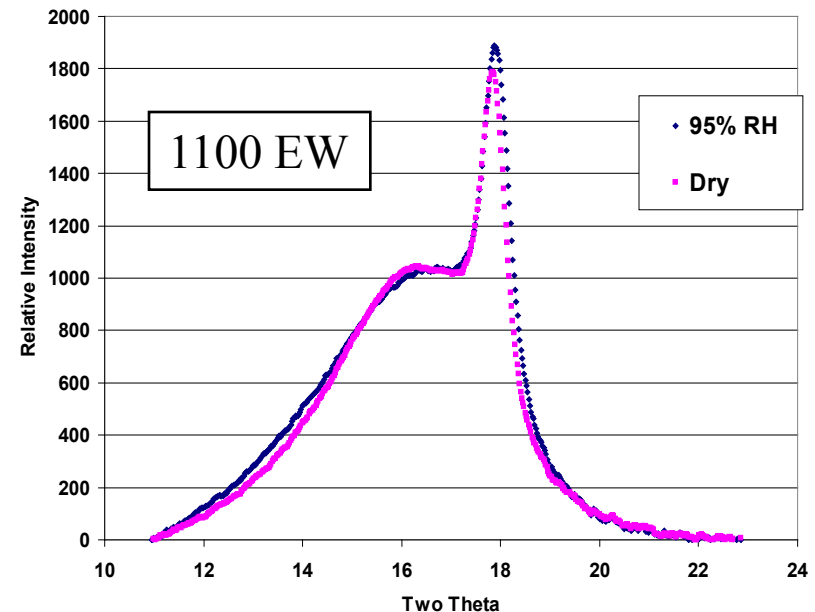


# The Bad News - Loss of Crystallinity

## Wide Angle X-Ray Scattering



- Crystallinity from TFE in the polymer backbone is important for good mechanical properties and low water solubility.
- WAXS shows little crystallinity below about 700 EW.



3M CRAL

- No decrease in peak intensity due to backbone crystallinity upon hydration for 800 -1100 EW 3M Ionomer.
- Large increase in “ionomer” peak (not shown).

- **3M PFSA's with EW *ca.* 700 swell excessively in boiling water.**
- **PFSA's with EW's below 700 can begin to dissolve.**

So, we can make low EW that can give great conductivity, but mechanical properties and durability can be compromised.

Approaches investigated in this program were:

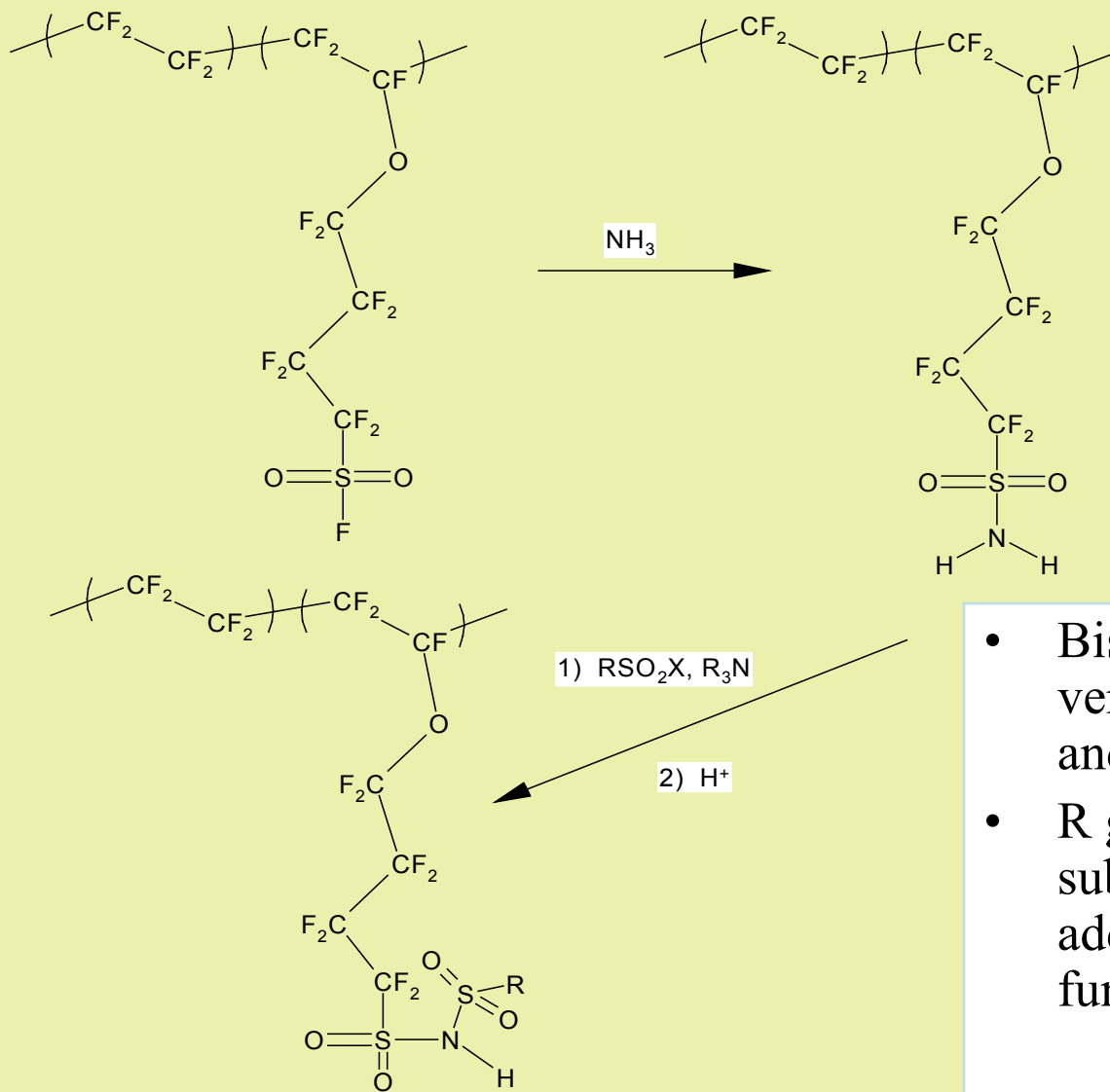
*blends*

*crosslinking*

*reinforcement*

*polymer modifications*

# Polymer Modification – one approach



... give great properties and is used.

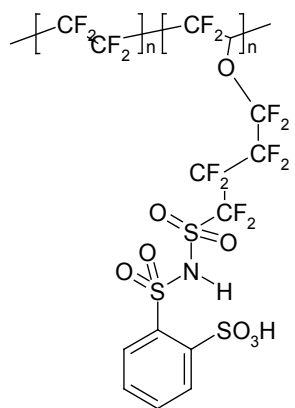
... program were:

- Bis-sulfonyl imides are very chemically stable and highly acidic.
- R groups can be substituted with additional acid functionality.

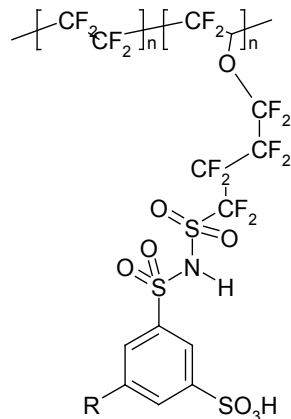
# Adding More Acid to the Polymer

## Multi Acid Side Chain ( MASC) Ionomers

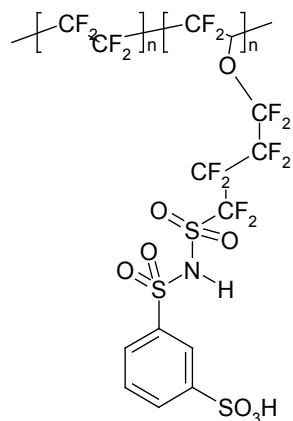
Technical Accomplishments  
and Previously Presented Material



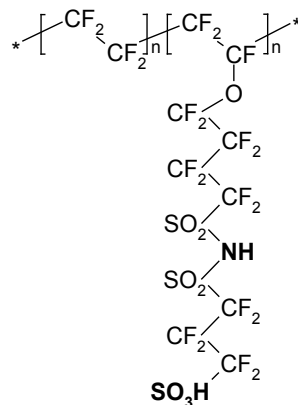
Ortho bis acid



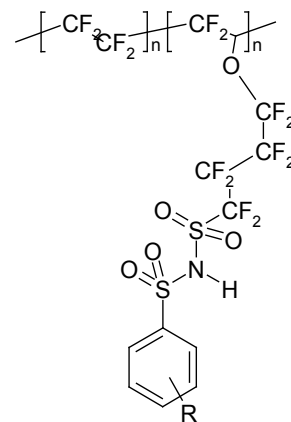
Bis/Tri Acid  
R = 1:1 SO3H/X



Meta bis acid



PFIA



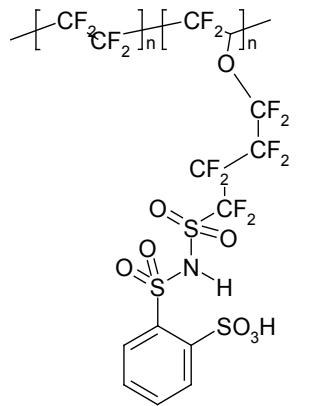
A variety of other  
Polymers have been  
prepared and evaluated

- New ionomers with Multi Acid Side Chains (MASC Ionomers) have been developed.
- Side-chains are functionalized in high yields ( $\geq 95\%$ )
- This allows for backbone crystallinity and low EW.

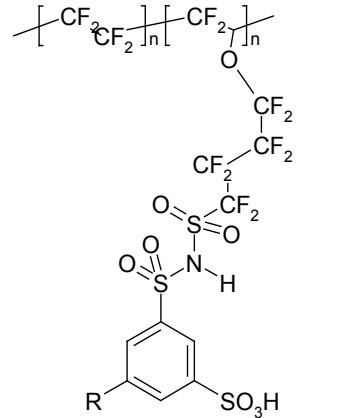
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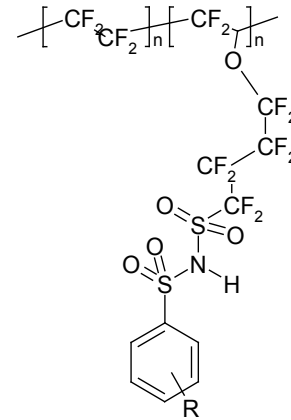
Technical Accomplishments  
and Previously Presented Material



Ortho bis acid

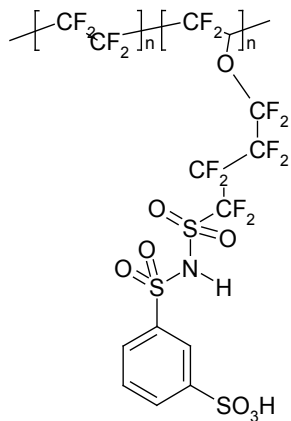


Bis/Tri Acid  
R = 1:1 SO3H/X

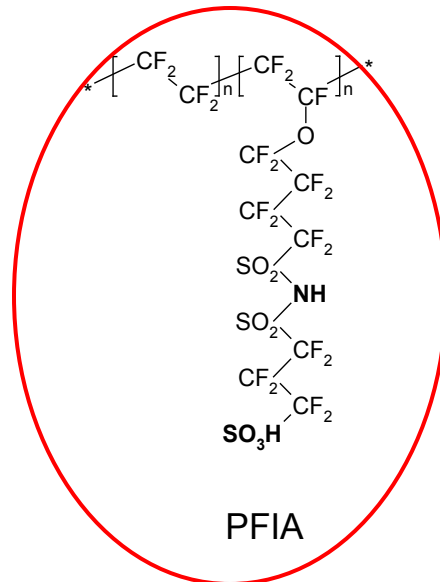


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Meta bis acid



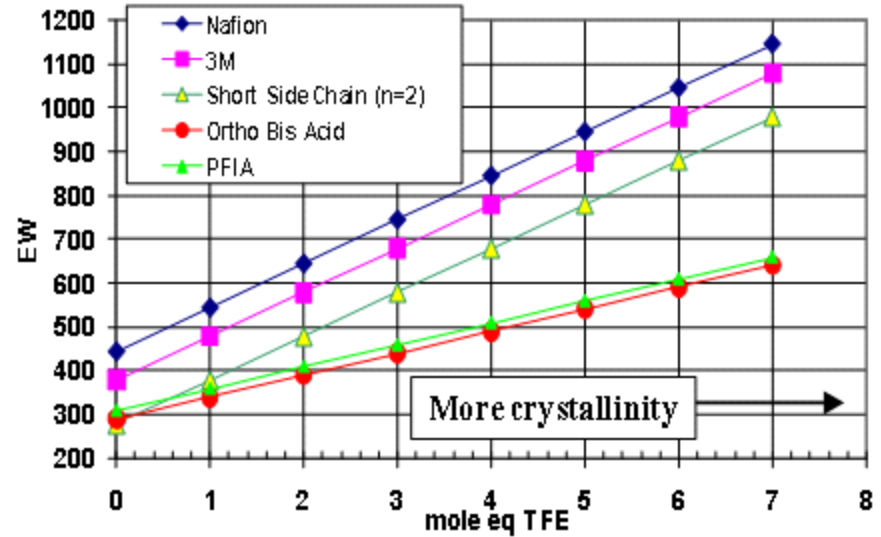
PFIA

**Down selected for final evaluation**

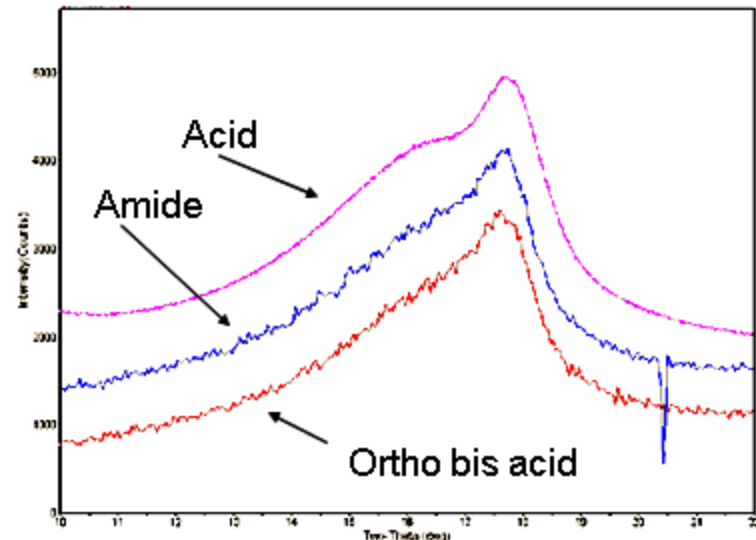
# Multi Acid Side-chains (MASC) Allow Lower EW With More TFE in the Backbone

Technical Accomplishments  
and Previously Presented Material

The slope of each line gives the EW of the ionomer/ the ratio of TFE units to protons in the polymer, and the intercept is the MW of the acid functional monomer/ the number of protons. This shows the utility of having multiple acid groups on each side-chain in providing polymers having high crystallinity and low EW.



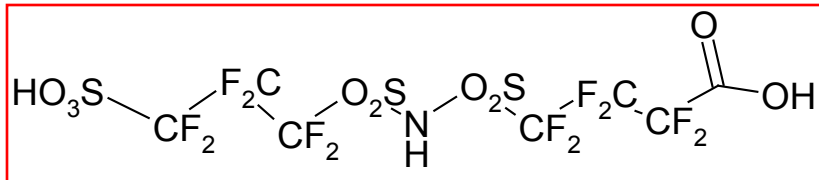
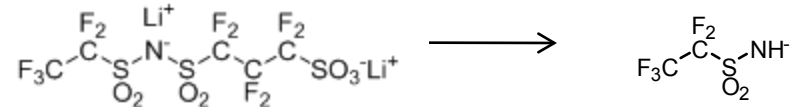
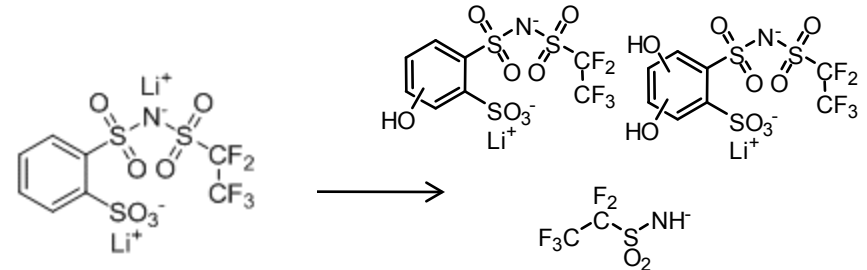
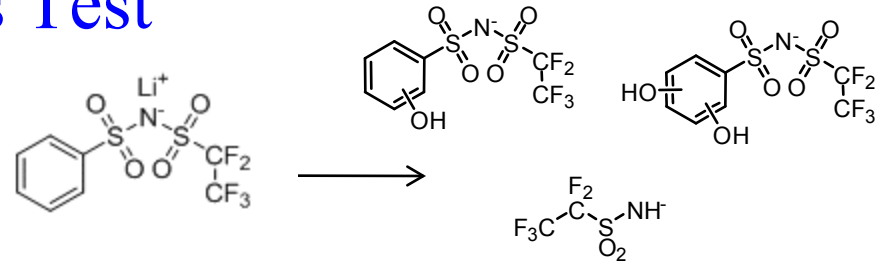
- Ortho bis imide made from 1,000 EW SO<sub>2</sub>F polymer have an EW of about 640.
- Backbone crystallinity is not effected by larger side-chain.
- Same results are seen for different EW, higher %RH



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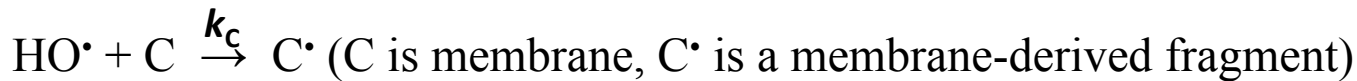
# Stability of protogenic groups towards oxidation – Fenton's Test

- Aromatic hydrocarbon acid groups oxidize primarily via hydroxylation of the rings
- For aromatic molecules, mono- and di-hydroxylation of the rings was observed, as well as the  $\text{CF}_3\text{CF}_2\text{SO}_2\text{NH}_2$  fragment for all three.



**Analysis of the degradation products of PFIA show a fragment corresponding to the entire side-chain along with smaller fragments – consistent with a backbone degradation mechanism. Additional degradation studies and analysis are ongoing.**

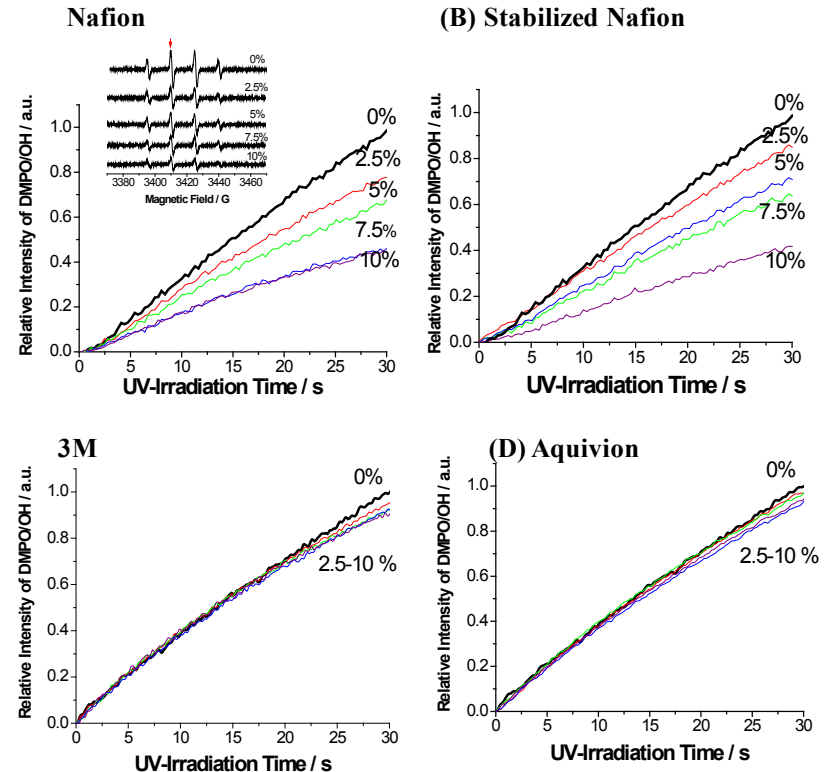
# Competition Reactions for HO• in the Presence of DMPO as the Spin Trap



$$\frac{V}{v} - 1 = \frac{k_c [C]}{k_{\text{DMPO}} [\text{DMPO}]}$$

$V$  and  $v$  are reaction rates for the formation of the DMPO/OH adduct in the absence and in the presence of the competitor C (the membrane). Plot of  $\frac{V}{v} - 1$  vs  $\frac{k_c}{k_{\text{DMPO}}}$  gives the ratio  $\frac{[C]}{[\text{DMPO}]}$  and a measure of the ability of the ionomer to be attacked by hydroxyl radicals.

The intensity of the DMPO/OH adduct as a function of irradiation time for the indicated membrane concentrations is shown. The thicker black line in each case shows the formation of hydroxyl radicals in the absence of membranes.



- The adduct of the carbon-centered radical, DMPO/CCR, was not detected in the water dispersion of PFIA at various concentrations (2.5-10 % wt).
- The DMPO/OH adduct in the PFIA dispersion had very low stability. For this reason it was not possible to perform the competition kinetics experiments needed for ranking the membrane stability.

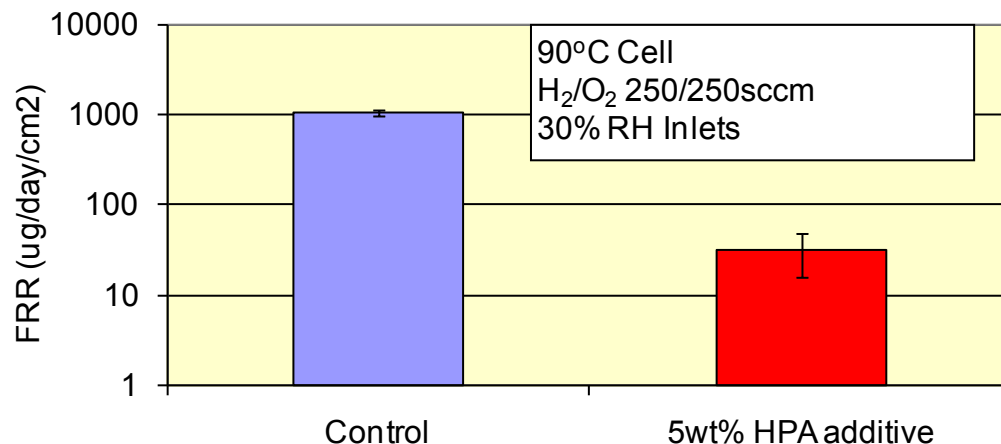


# Chemically stabilizing additives

Technical Accomplishments  
and Previously Presented Material

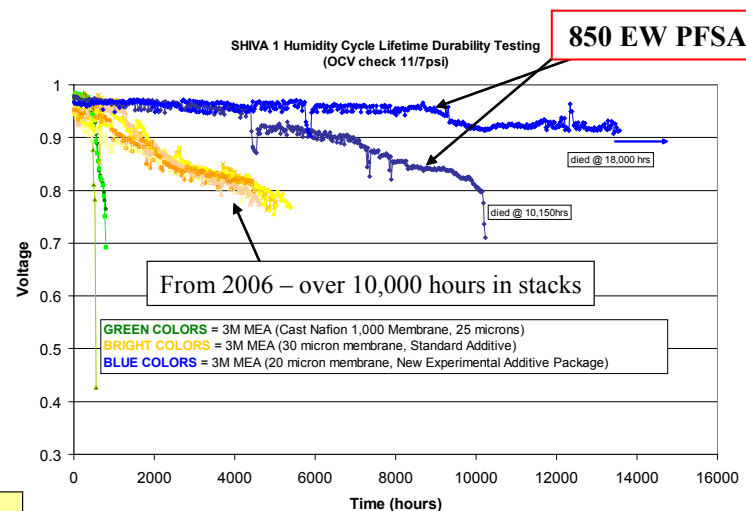
- Both HPA and non-HPA additives have been developed. HPAs have the advantage that they do not consume IEC and we have shown that they can sometimes *increase* membrane conductivity but the disadvantage that they are *soluble in H<sub>2</sub>O*.
- Some progress has been made in stabilizing the HPA based system to H<sub>2</sub>O, but we were not successful in making it stable enough.

*The non HPA additive system was down-selected for use in our “final membrane”*



Test Point	J (A/cm <sup>2</sup> )	Duration (min)	Stoich.
1	0.20	5	5
2	0.02	20	15
3	0.80	15	1.7
4	0.80	10	3
5	0.02	20	15
6	0.80	15	1.7
7	0.20	20	5
8	1.00	20	1.7

Cell Temperature: 80 °C  
Inlet Dew points: 64/64 °C  
Outlet Pressures: 175kPa  
End of life = < 800 mV OCV w/  
7 PSIG anode overpressure.

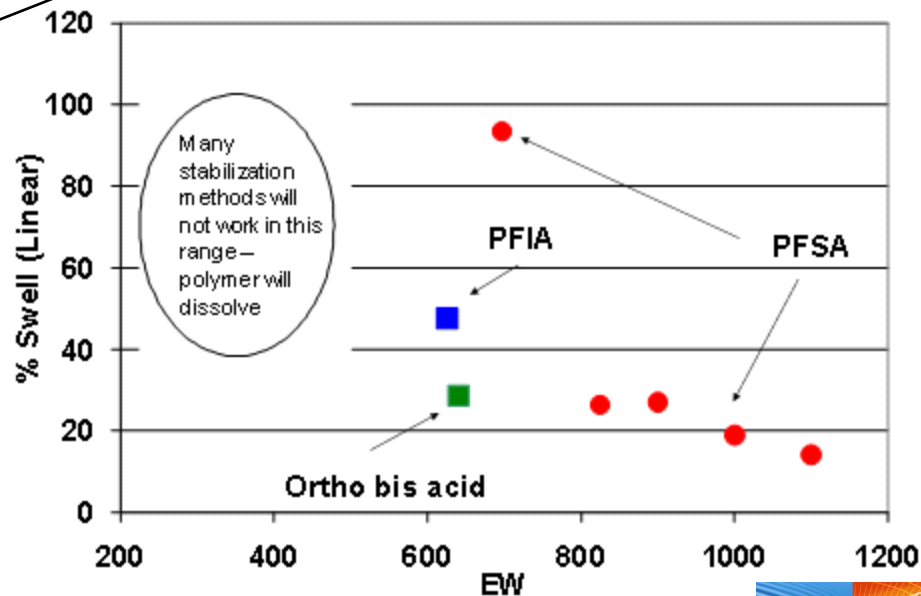
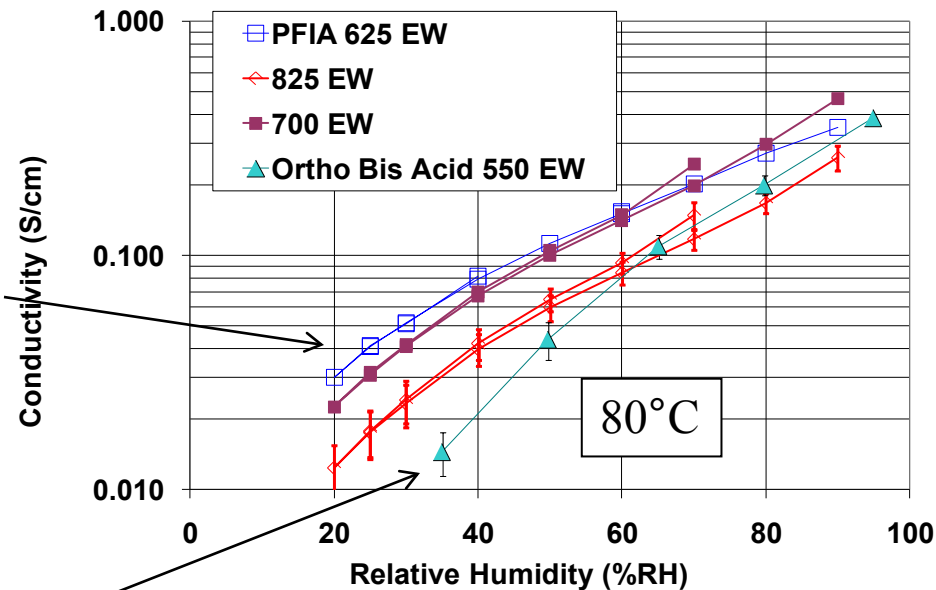
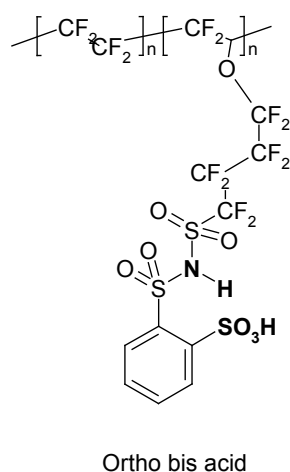
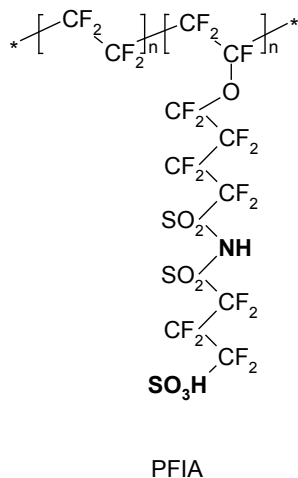


Outlet % RH cycles from ca. 59% to >100%

# Multi Acid Side-chain (MASC) Polymers

Technical Accomplishments  
and Previously Presented Material

- Multiple acid groups allow raising the conductivity of starting ionomer
- 800 EW starting PFSA precursor with crystalline backbone can be used to make low EW ionomer with higher conductivity.
- In boiling water (3 hours boil) the in-plane swelling of two MASC ionomers is much less than PFSA's of the same EW but still higher than the PFSA prepared from the same precursor.



*625 EW PFIA was down-selected for use in our “final membrane”*

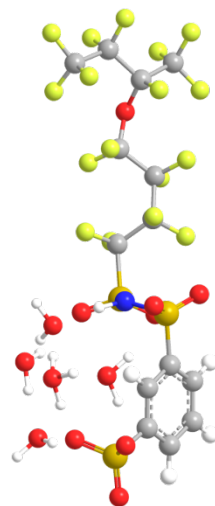
# 3M Imide-Based Oligomeric Fragments

- Proton dissociation in the *ortho* bis acid occurs first through hydrogen bonding of the 2 protogenic groups.
- The electron withdrawing  $-CF_2-$  groups in the PFIA system promote proton dissociation after only 3  $H_2O$
- Proximity of protogenic groups in the *ortho* bis acid system hinders 2<sup>nd</sup> proton dissociation due to localized excess positive charge in the surrounding water molecules.
- Larger protogenic group separation in the *meta* bis acid and the PFIA systems allow for a more widely spread charge distribution which aids in 2<sup>nd</sup> proton dissociation.

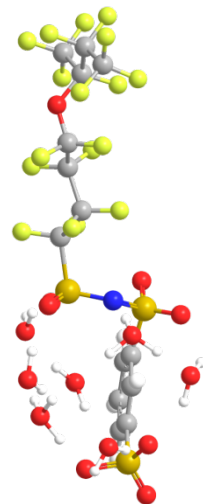
This is consistent with conductivity measurements on the PFIA and Ortho Bis Acid.

Meta Bis Acid shows lower conductivity at low %RH too??

*Meta* Bis Acid

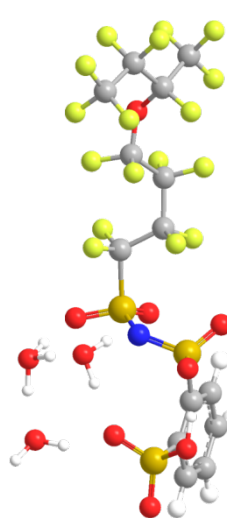


+ 5  $H_2O$

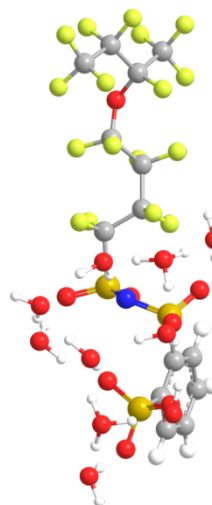


+ 7  $H_2O$

*Ortho* Bis Acid

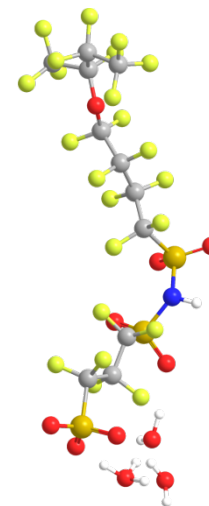


+ 3  $H_2O$

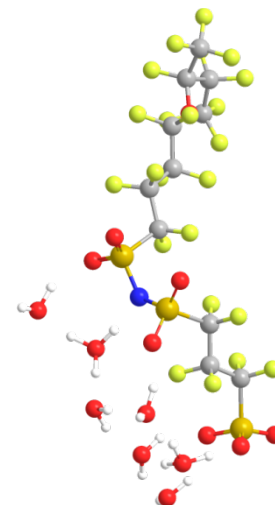


+ 10  $H_2O$

PFIA



+ 3  $H_2O$

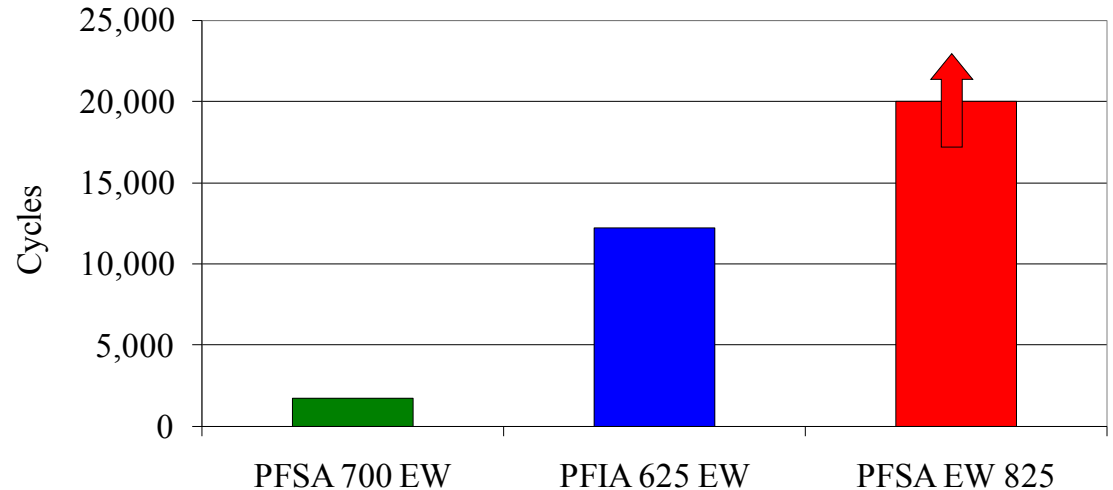
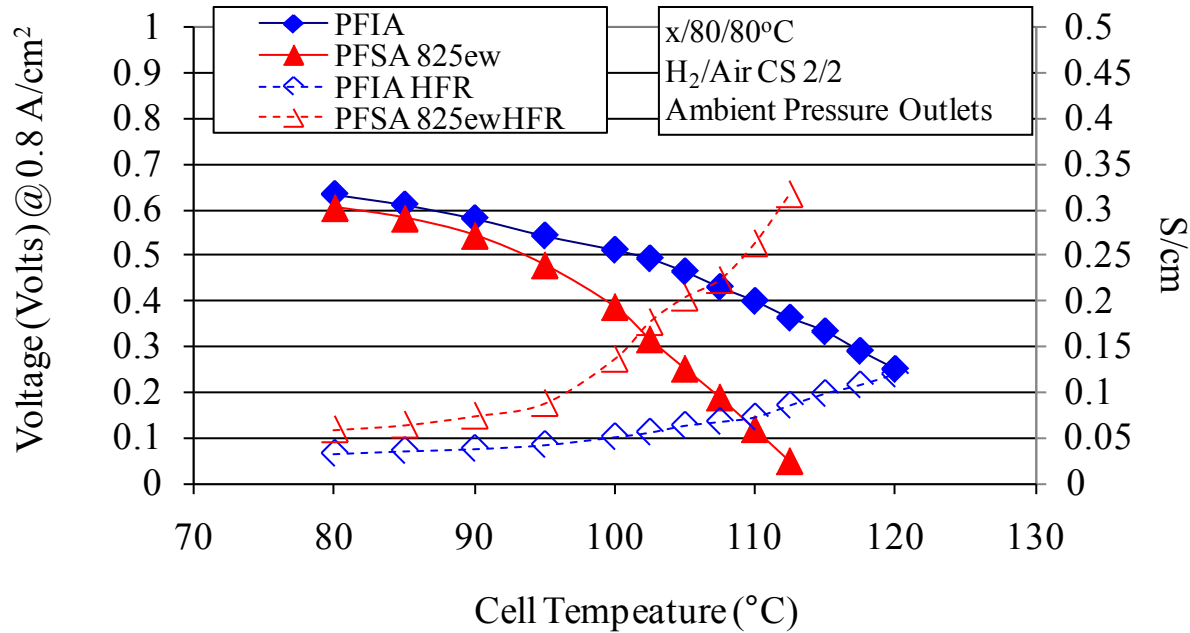


+ 7  $H_2O$

# New Multi Acid Side-chains (MASC's)

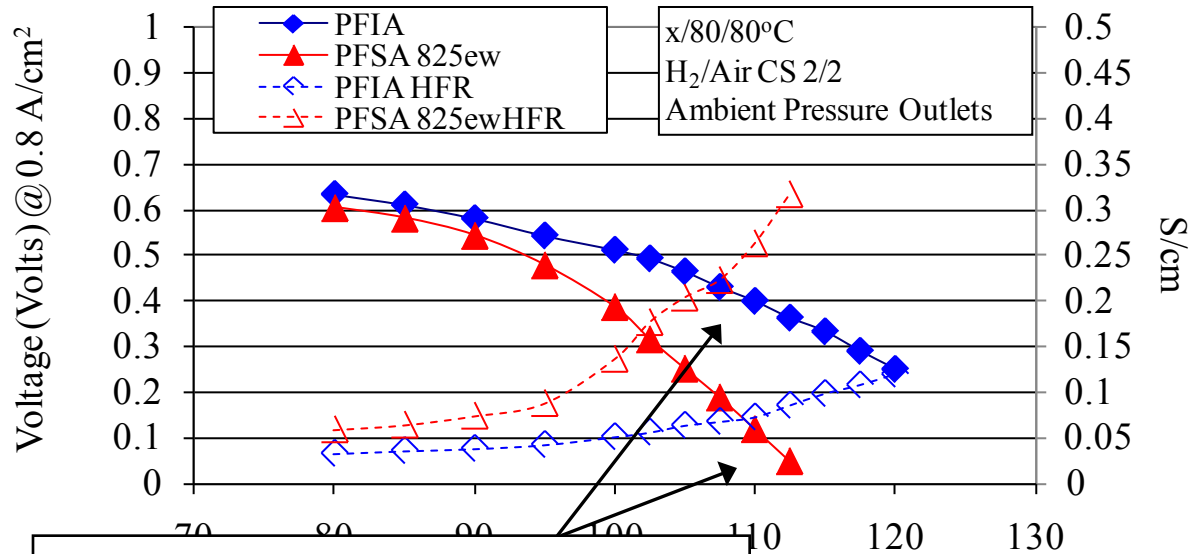
Technical Accomplishments

- We have begun fuel cell testing on the new 625 EW PFIA membrane for performance and durability.
- The new ionomer provides lower resistance and improved performance under hot, dry operating conditions.
- Lifetime in the humidity cycle test is lower than the 825 EW PFSA, but much higher than the 700 EW PFSA.
- Lifetime in OCV test is equivalent to 825 EW PFSA.

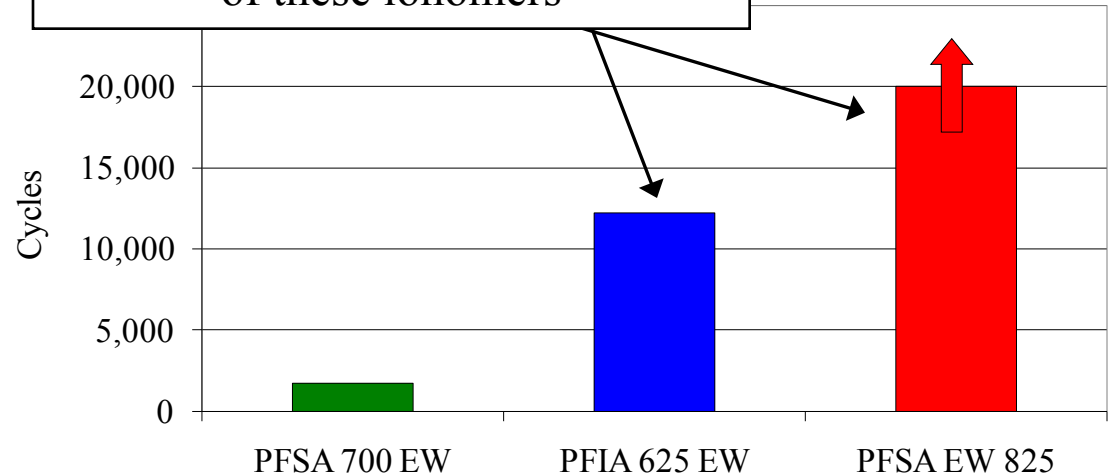


# New Multi Acid Side-chains (MASC's)

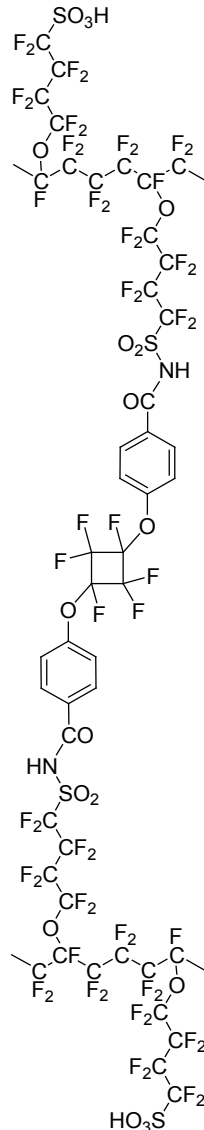
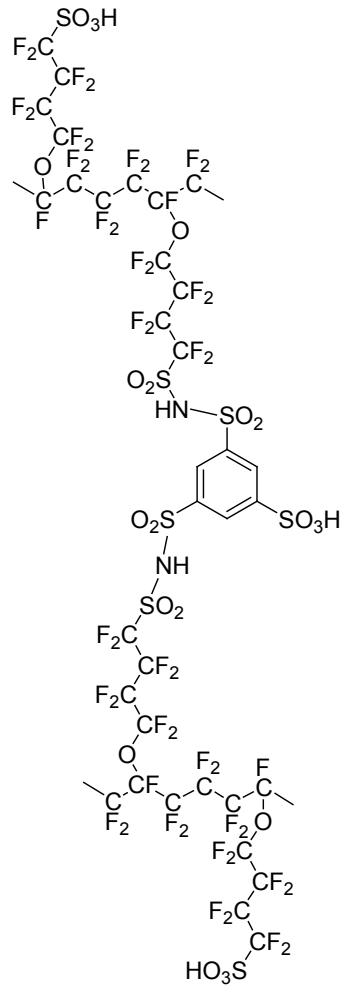
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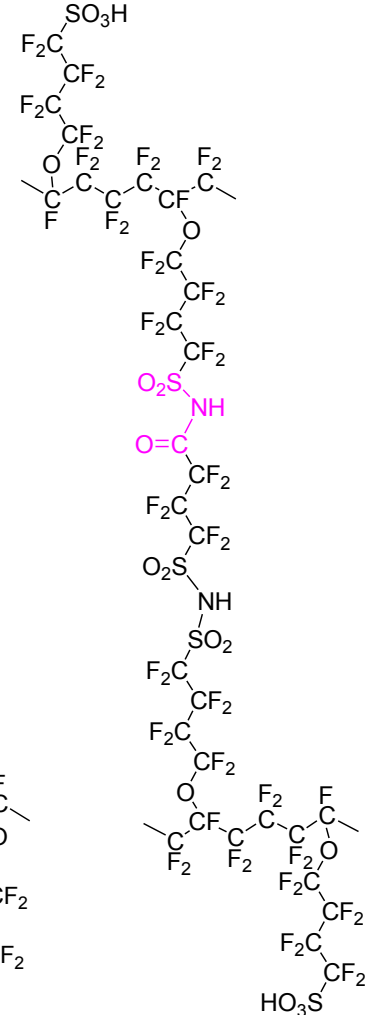
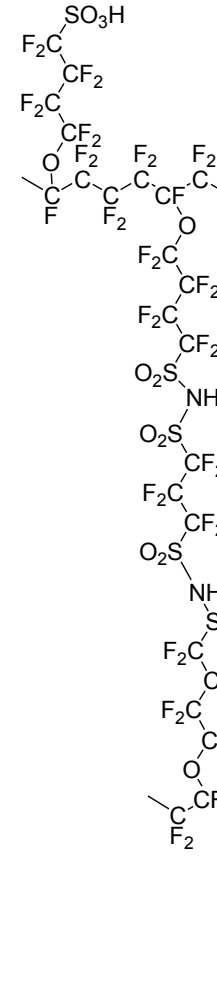
The same 825 EW ionomer precursor was used to make both of these ionomers



# Several cross-linked membranes were prepared

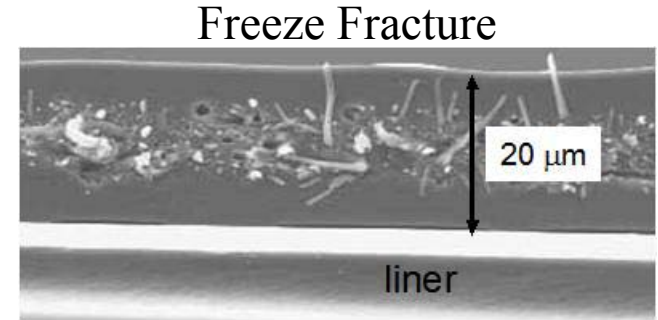
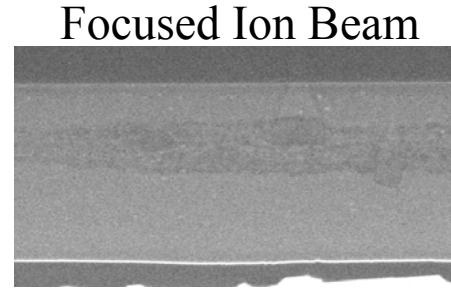
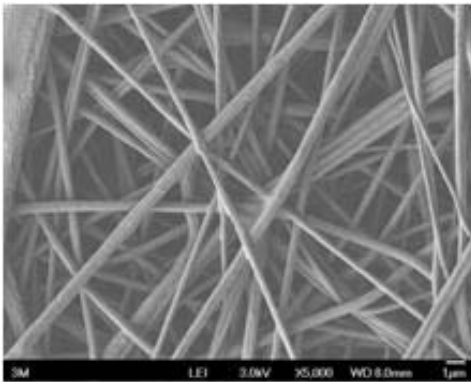


- All soluble membranes became insoluble in water and organic solvents after cross-linking.
- All cross-links were stable under acidic condition except the one in red which showed poor hydrolytic stability.
- More work needs to be done to develop methods of controlling cross-link density.



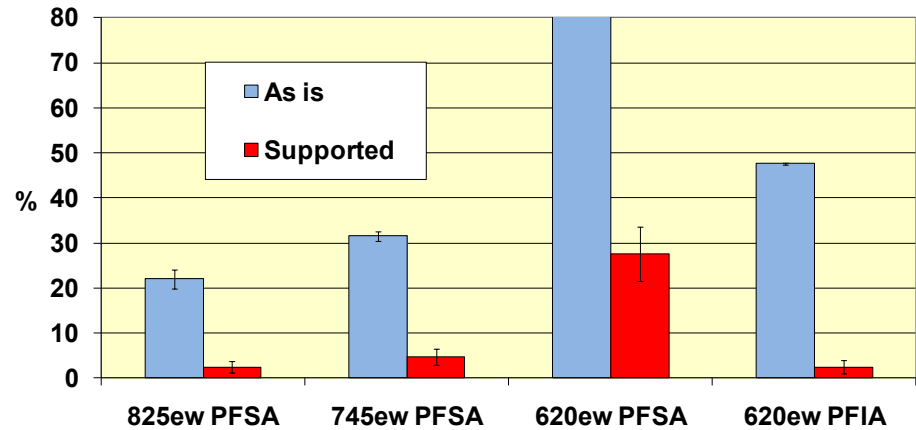
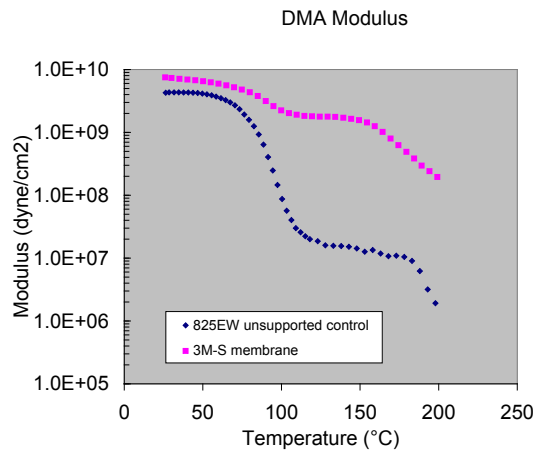
*Membranes down-selected for final testing in this program were not cross-linked*

# Supported Membrane



SEM Image of Nanofiber Support

SEM Cross Sections of Supported Membrane



Linear Swell in Liquid Water

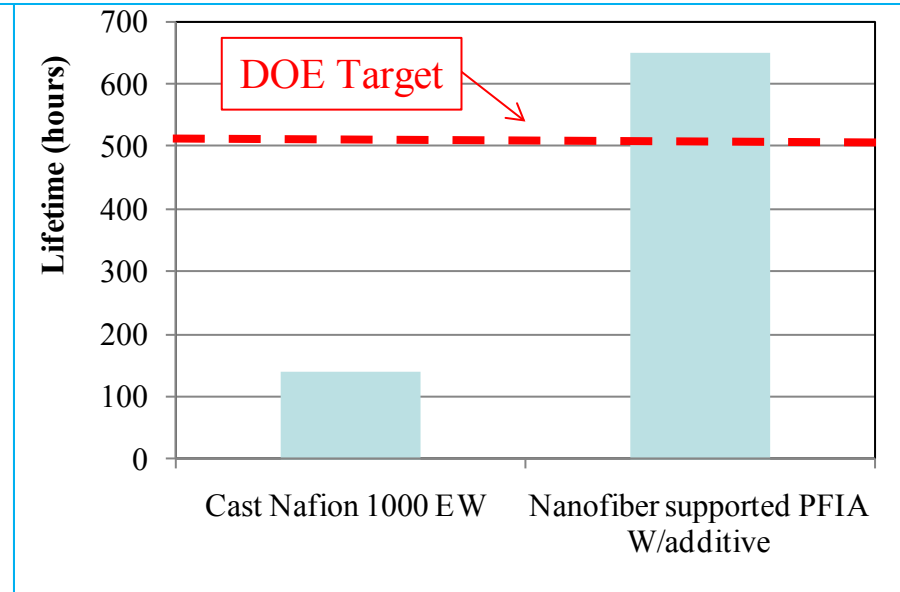
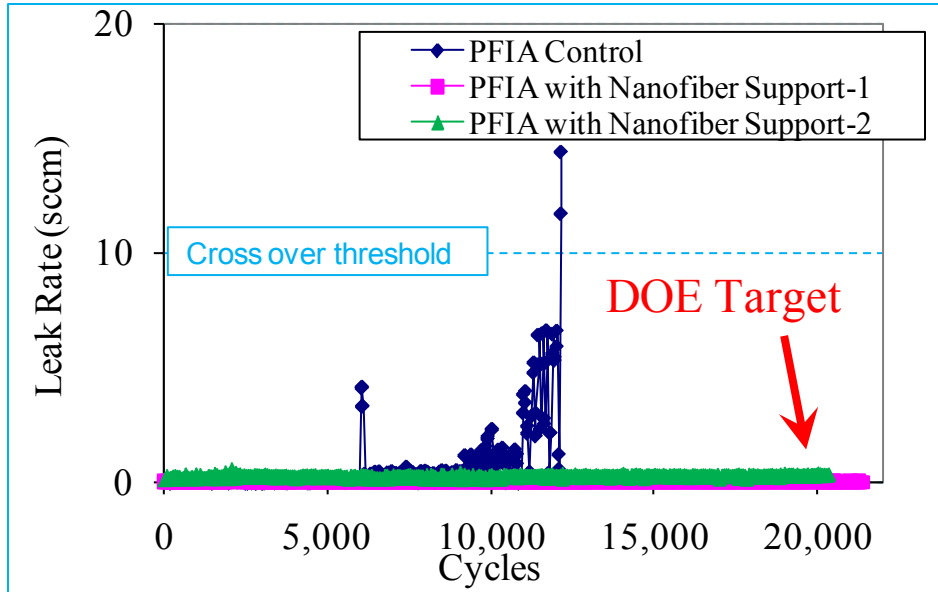
Modulus of Supported Membrane

*Nanofiber supports were down-selected for use in our “final membrane”*

- Chemically inert fibers
- Composite membrane feasibility demonstrated
- Increase modulus over operating conditions
- Dramatically reduced swell in boiling water

# Durability Testing

FreedomCAR & Fuel Partnership Fuel Cell Tech Team Cell Component Accelerated Stress Test Protocols for PEM Fuel Cell Membranes



Membrane Mechanical Cycle Test (%RH Cycle Test)  
Target 20,000 cycles

MEA Chemical Stability Test (OCV Test)  
Target 500 hrs









- Support technology and process developed with 3M PFSA and PFIA ionomers
- RH cycle durability target met with both supported PFSA (825 EW) and supported PFIA (625 EW) so far.

*PFIA combined with support and chemically stabilizing additives is being tested in our “final membrane”.*



# Summary













- Nanofibers impact on ASR corresponds to volume fraction.
- **PFIA membrane meets almost all performance requirements so far and shows improved durability. Testing of this material with chemical and mechanical / dimensional stabilization is underway.**

All membranes are 15 micron supported or 20 micron unsupported 625 EW PFIA		3M 2011 Status	2015 target
ASR at 120° C (H <sub>2</sub> O pp 40-80 kPa)	Ohm cm <sup>2</sup>	.023 (40 kPa) 0.012 (80kPa)	<0.02 
Cond. at 120° C	S/cm	0.087 (25% RH) 0.167 (40% RH)	
ASR at 80° C (H <sub>2</sub> O pp 25-45 kPa)	Ohm cm <sup>2</sup>	0.013 (25 kPa) 0.006 (44 kPa)	<0.02 
Cond. at 80° C	S/cm	0.154 (50% RH) 0.3 (95% RH)	
ASR at 30° C (H <sub>2</sub> O pp 4 kPa)	Ohm cm <sup>2</sup>	0.02 (3.8 kPa)	<0.03 
Cond. at 30° C	S/cm	0.09 (90% RH)	
ASR at -20° C	Ohm cm <sup>2</sup>	0.10	<0.2 
Cond. at -20° C	S/cm	0.02	
O <sub>2</sub> cross-over	mA/cm <sup>2</sup>	≤1.0	<2 
H <sub>2</sub> cross-over	mA/cm <sup>2</sup>	≤1.8	<2 
<u>Durability</u> Mechanical (%RH Cycle)	Cycles	>20,000	>20,000 
Chemical (OCV)	Hours	>650+	>500 

Additional lifetime tests are still running @ 3,000+ hours

# Summary

- Nanofibers impact on ASR corresponds to volume fraction.
- PFIA membrane meets almost all performance requirements so far and shows improved durability. Testing of this material with chemical and mechanical / dimensional stabilization is underway.**

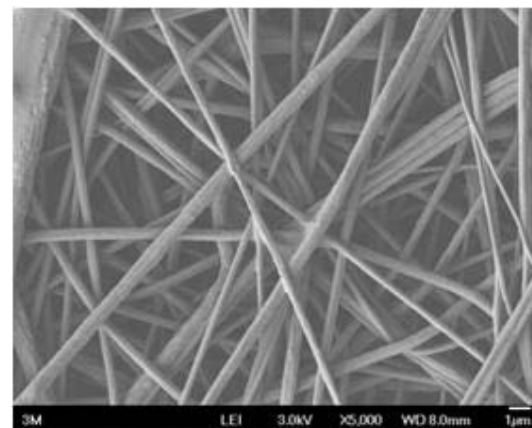
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**Remaining gap**

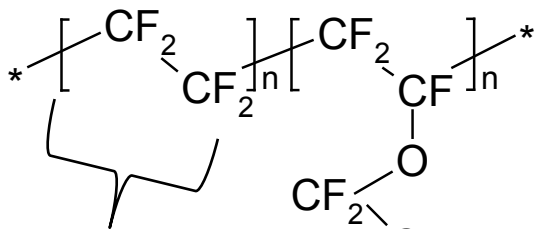
Additional lifetime tests are still running @ 3,000+ hours

# Future Work – What's next

- MASC Polymers testing-
  - Complete testing of 625 EW PFIA membrane
- Key next steps (after this project)-
  - Lower EW PFIA (C<sub>2</sub> chain extender)
  - New additives
  - Build on nanofiber work

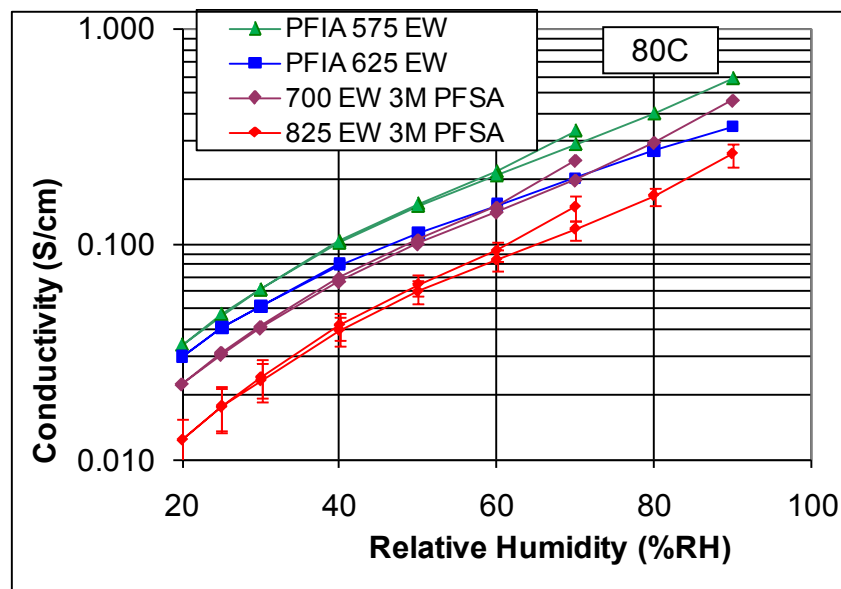
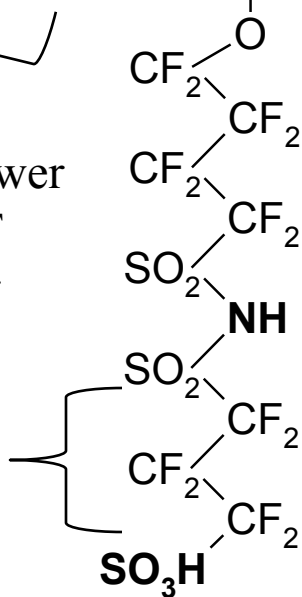


- New fiber chemistry
- Optimize structure



Start with lower EW SO<sub>2</sub>F precursor

Use shorter bis SO<sub>2</sub>F

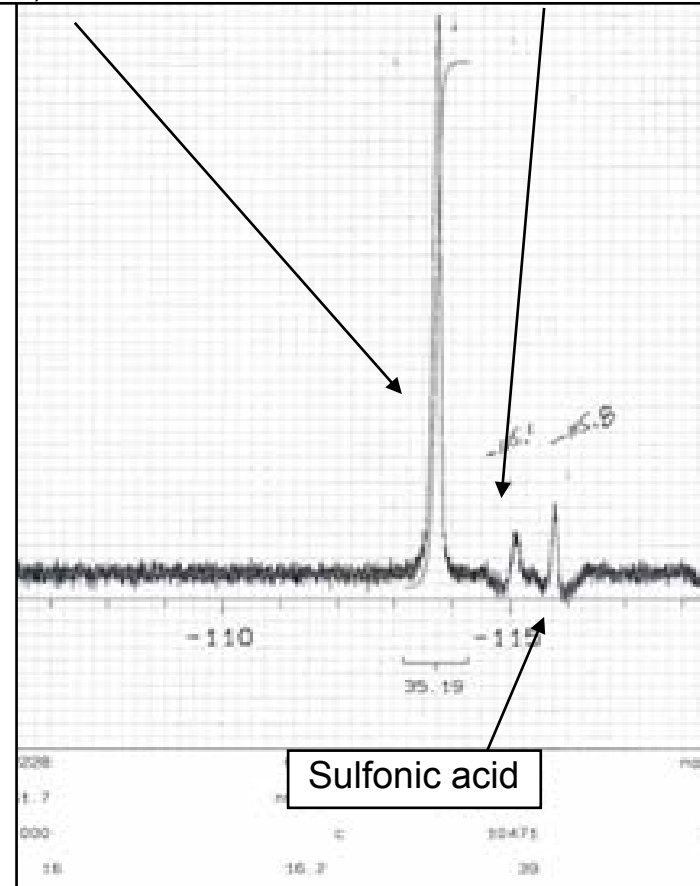
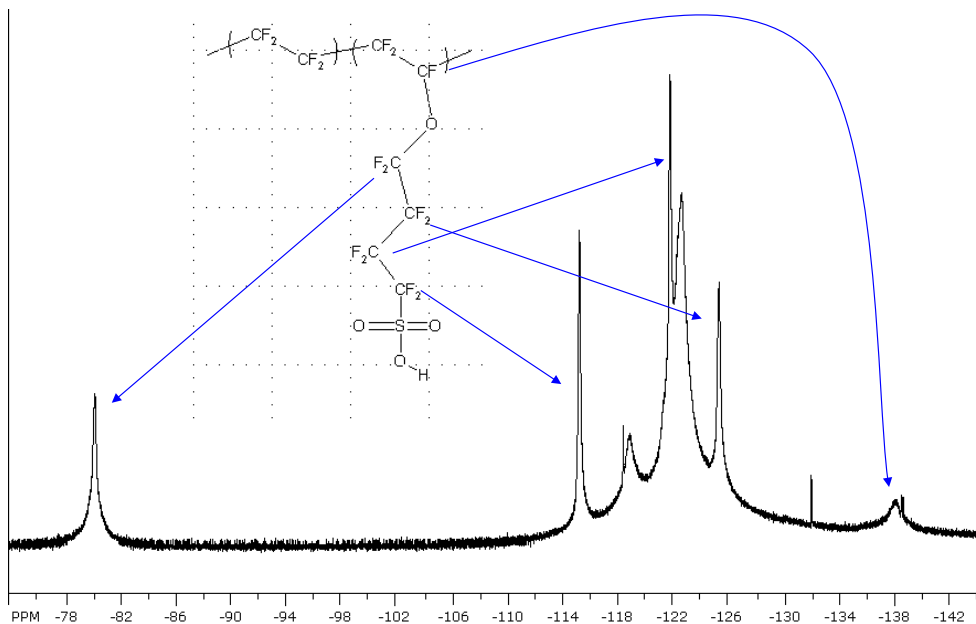
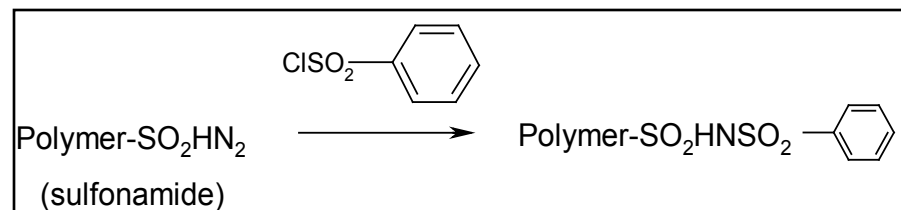


# **Technical Back-up Slides**

# New Multi Acid Side-chains (MASC's)

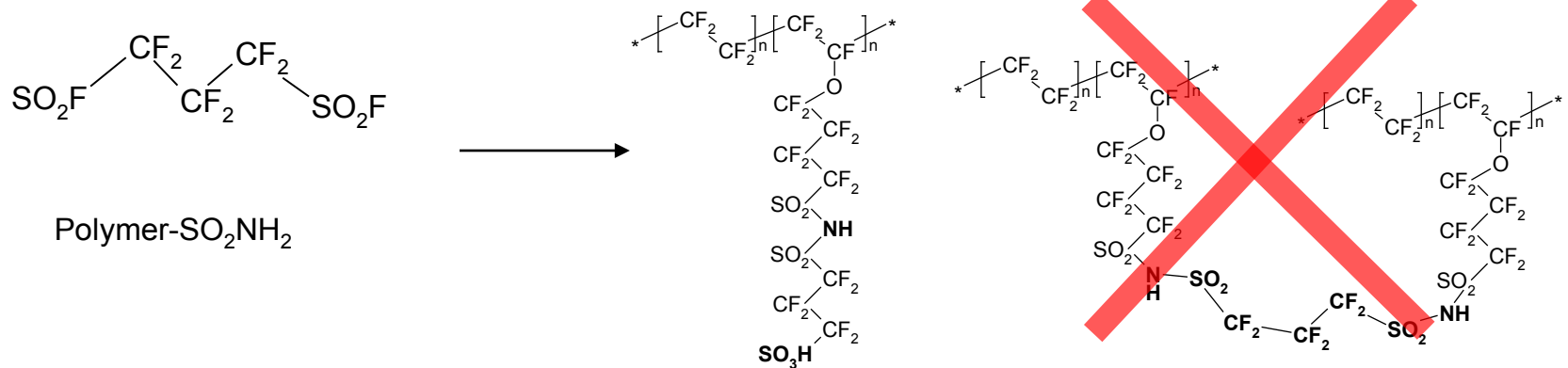
Technical Accomplishments  
and Previously Presented Material

$^{19}\text{F}$  NMR of  $\text{CF}_2$  group next to sulfur allows easily following the reaction



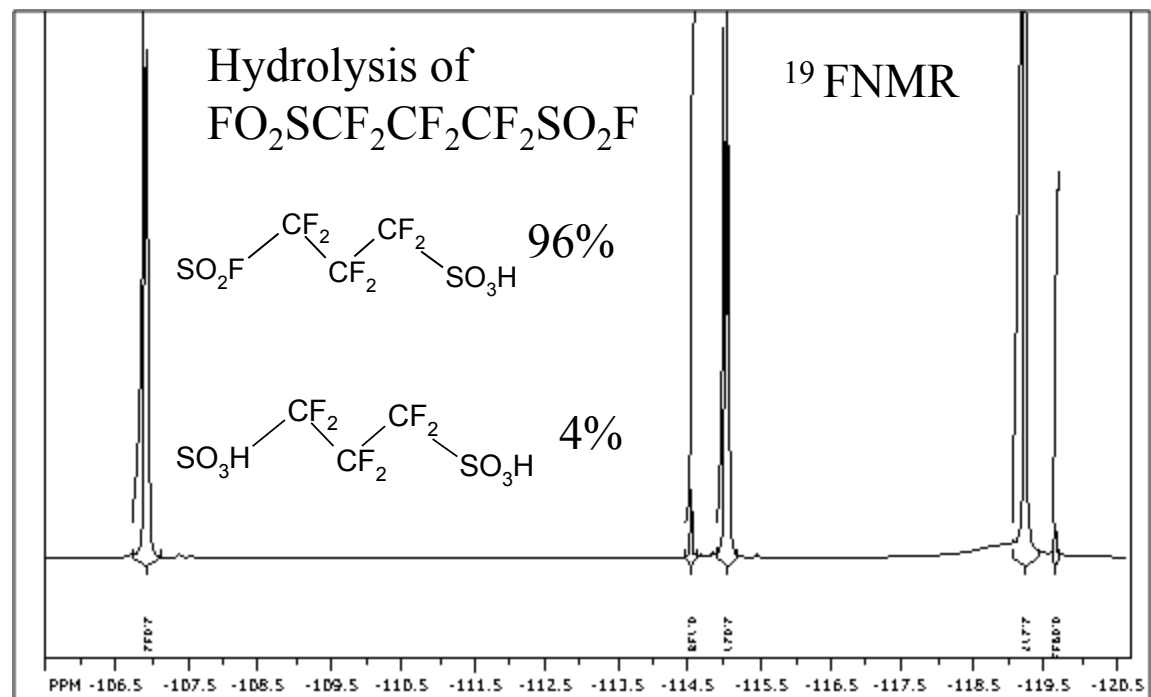
This allows us to monitor the progress of our reactions and prepare MASC polymers in high yield

# New MASC – Per Fluoro Imide Acid (PFIA)



No evidence of cross-linking

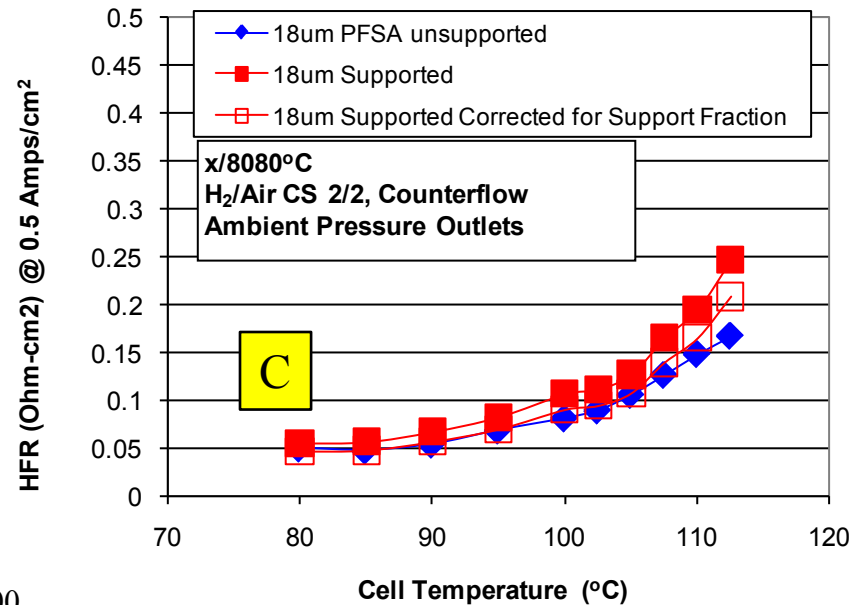
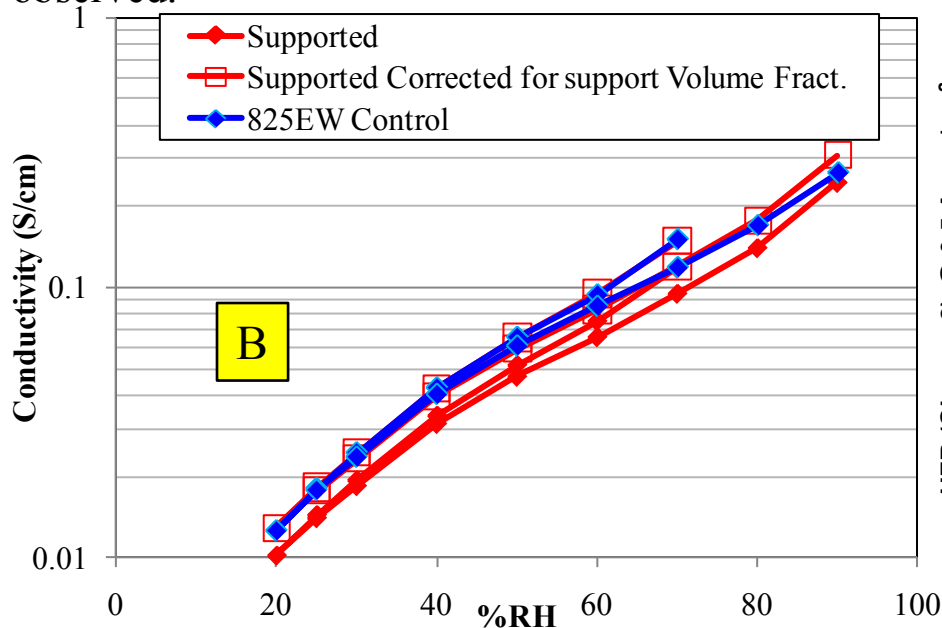
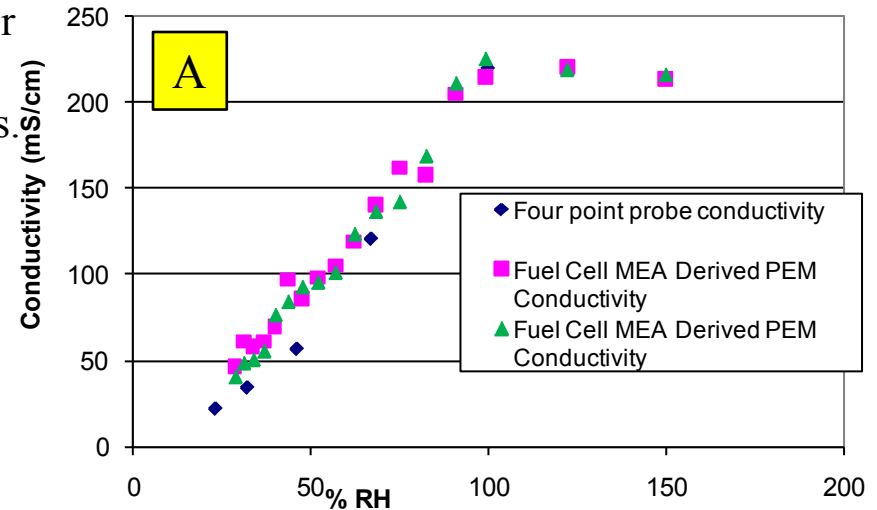
One SO<sub>2</sub>F groups is selectively hydrolyzed by base, indicating a significant difference in reactivity. This is consistent with no observed cross-linking in the PFIA synthesis



# Converting in plane conductivity to ASR

Figure A shows the in plane conductivity of the ionomer (825 EW PFSA in this case) correlates well with calculated conductivity from in cell HFR measurements. (electrode resistance was determined using the “transmission line” method and subtracted \*).

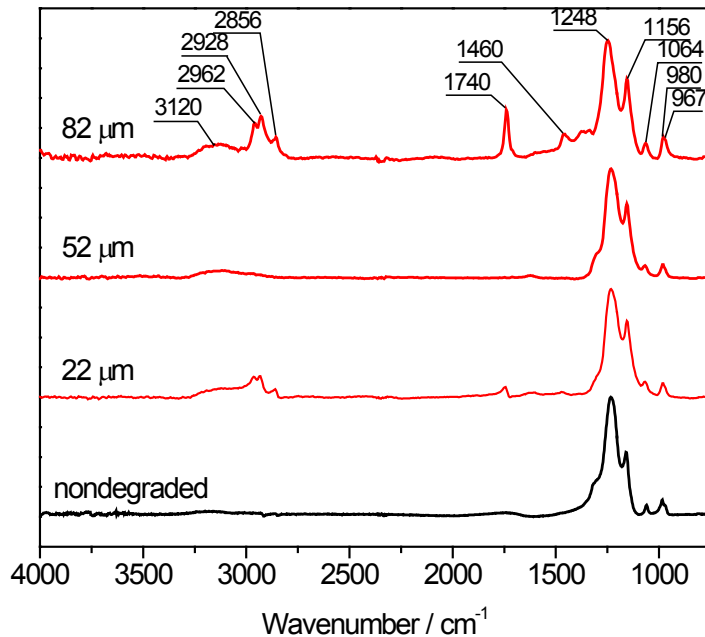
Both in-plane conductivity (Fig B) and HFR (Fig C) show that the effects of the support correspond closely to the value calculated by accounting for the volume fraction of the support. Little or no tortuosity effect is observed.



\* Hamrock SJ (2009) U.S. Department of Energy Hydrogen Program 2010 Annual Merit Review Proceedings - Slide 35



# Comparison of FTIR Spectra of Degraded and Nondegraded Nafion<sup>®</sup>



## Bands assignment:

- 3120 cm<sup>-1</sup> C-H
- 2928 cm<sup>-1</sup>  $\nu_{as}$ (C-H)
- 2962 cm<sup>-1</sup>  $\nu_{as}$ (C-H)
- 2856 cm<sup>-1</sup>  $\nu_s$ (C-H)
- 1740 cm<sup>-1</sup>  $\nu_s$ (C=O)
- 1460 cm<sup>-1</sup> sulfonic anhydrate<sup>1</sup>
- 1248 cm<sup>-1</sup>  $\nu_s$ (CF<sub>2</sub>)
- 1156 cm<sup>-1</sup>  $\nu_{as}$ (CF<sub>2</sub>)
- 1064 cm<sup>-1</sup>  $\nu_s$ (SO<sub>3</sub><sup>-</sup>)
- 980 cm<sup>-1</sup>  $\nu_s$ (C-F) in CF<sub>3</sub>
- 967 cm<sup>-1</sup>  $\nu$ (C-S)<sup>2</sup>

*FTIR spectra of Nafion<sup>®</sup> membranes: degraded for 180h at various depths from the cathode side (in red), and nondegraded (in black).*

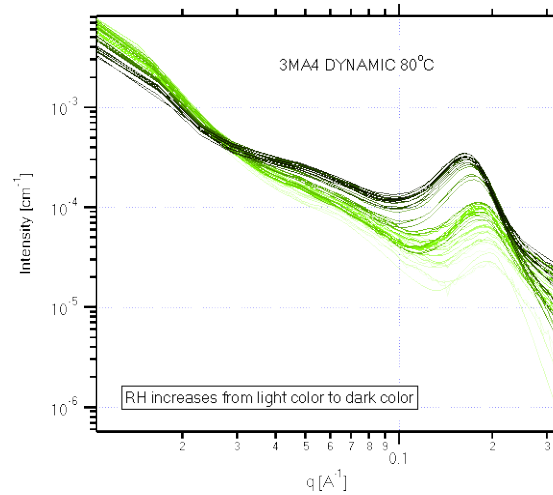
- The C=O band at  $\approx 1700$  cm<sup>-1</sup> is very strong close to the anode in the sample degraded during 180 h, and much weaker close to the cathode.
- The C-H bonds at  $\approx 3000$  cm<sup>-1</sup> are visible and are also stronger close to the anode. These bands may arise from the attack of hydrogen atoms on the tertiary carbon in the membrane.
- **2D spectral-spatial FTIR provides visualization of the extent of degradation as a function of depth.**



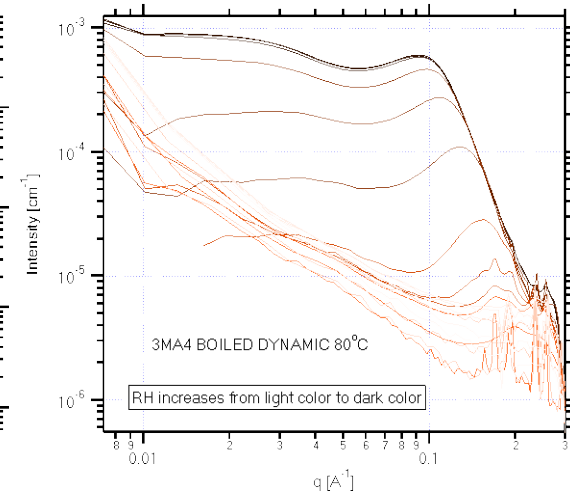
# SAXS Studies

- In-situ studies of polymer morphology by SAXS.
- 4 port temperature and humidity controlled oven used at APS allows 100 mS resolution of dynamics
- Data top right shows wet up of an as cast and boiled 825 EW 3M ionomer.
- Note that the as cast film shows an isobestic point indicating a phase change in morphology on hydration and the boiled film shows much larger Q shifts indicating higher swelling.
- Some modeling was initiated using SAXS morphology that shows a remarkable similarity to the morphologies from the DPD models used by Paddison.

Niccolo V. Aieta, Ronald J. Stanis, James L. Horan, Michael A. Yandrasits, David J. Cookson, Bridget Ingham, Michael F. Toney, Steven J. Hamrock and Andrew M. Herring "Clipped Random Wave Morphologies and the Analysis of the SAXS of an Ionomer Formed by Copolymerization of Tetrafluoroethylene and CF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>H" *Macromolecules*, 2009, 42 (15), pp 5774–5780

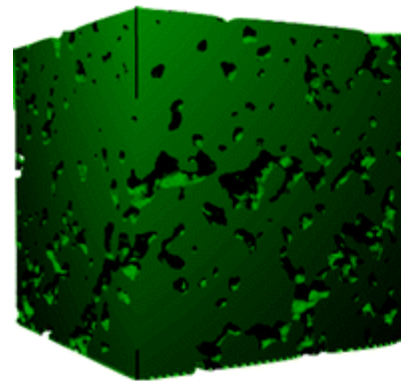


As cast 1<sup>st</sup> wet up

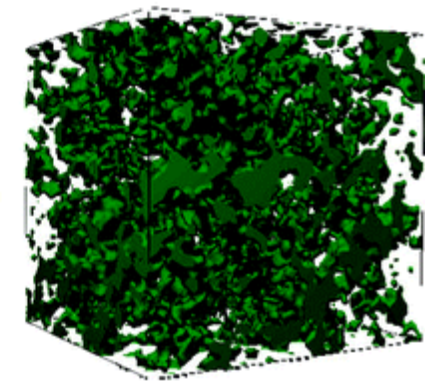
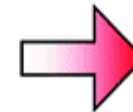


Boiled, swelling

1000 Å per side

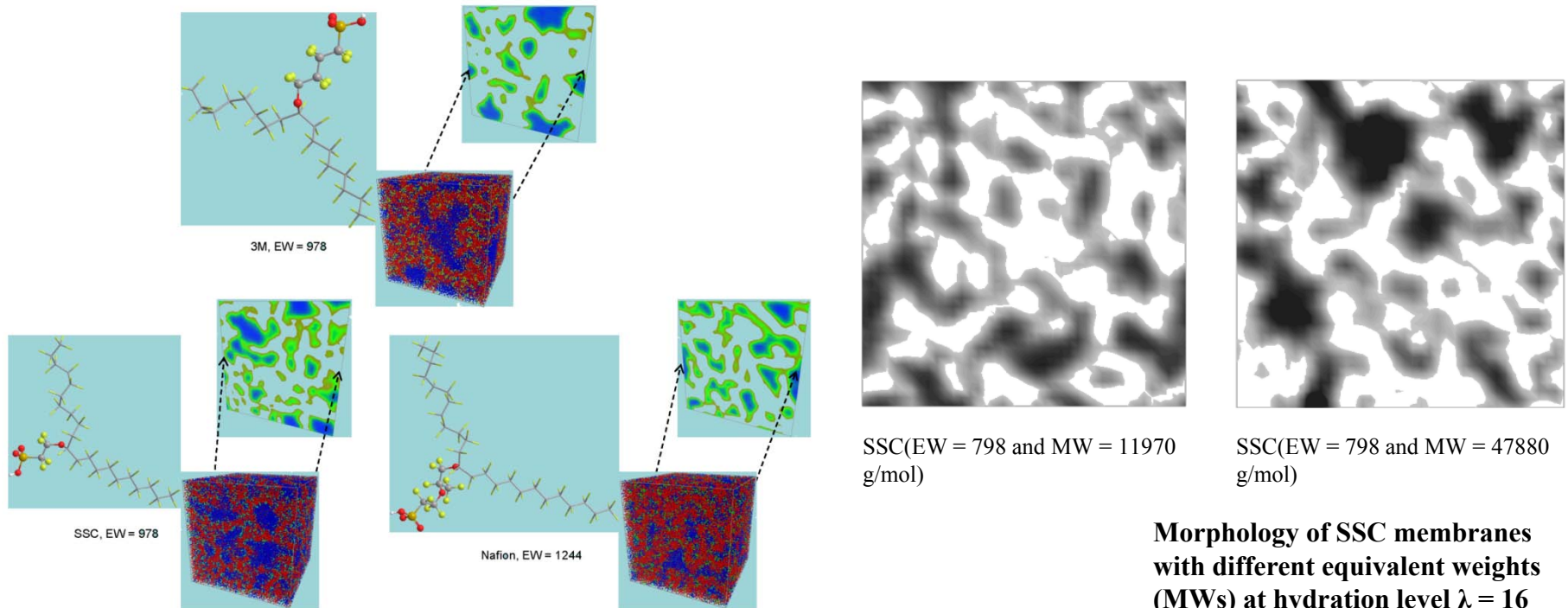


Polymer As Solid  
(real-space)



Water As Solid

# Hydrated morphology of 3M, short-side-chain (SSC), and Nafion<sup>®</sup> membranes: Dissipative Particle Dynamics (DPD) simulations



## Morphology of 3M, SSC and Nafion<sup>®</sup> membranes with similar molecular weights (MWs) at hydration level $\lambda = 16$ H<sub>2</sub>O/SO<sub>3</sub>H.

- As the hydration level is increased, the isolated water clusters present at the lower water contents increase in size eventually forming continuous regions resembling channels or pores.
- 3M PFSA ionomer exhibits much larger clusters of water when compared to SSC ionomer due to the small structural difference in the ionomers, while Nafion<sup>®</sup> shows narrowed water channels (or certainly elongated domains).

## Morphology of SSC membranes with different equivalent weights (MWs) at hydration level $\lambda = 16$ H<sub>2</sub>O/SO<sub>3</sub>H.

- The increase in size of the ion-clustered regions follows with the increase of MW. The larger MWs favor greater aggregation of the fluorocarbon backbone, which in turn drive s the formation of larger water-rich domains.