

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

Steven Hamrock

**3M** Fuel Cell Components

June 11, 2010



FC034

# Overview

## Timeline

- Project start 4/1/07
- Project end 3/31/11
- 76% complete

## Budget

- Total Project funding \$11.4 million
  - \$8.9 million - DOE
  - \$2.5 million - contractor cost share (22%)
- Funding in FY 2009
- \$2.5 Million
- Funding in FY 2010
- \$2.5 Million

## Barriers

- A. Durability
- C. Performance

## Partners

**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*

**General Motors** *C. Gittleman*

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

*\* denotes subcontractor*

# Project Objectives

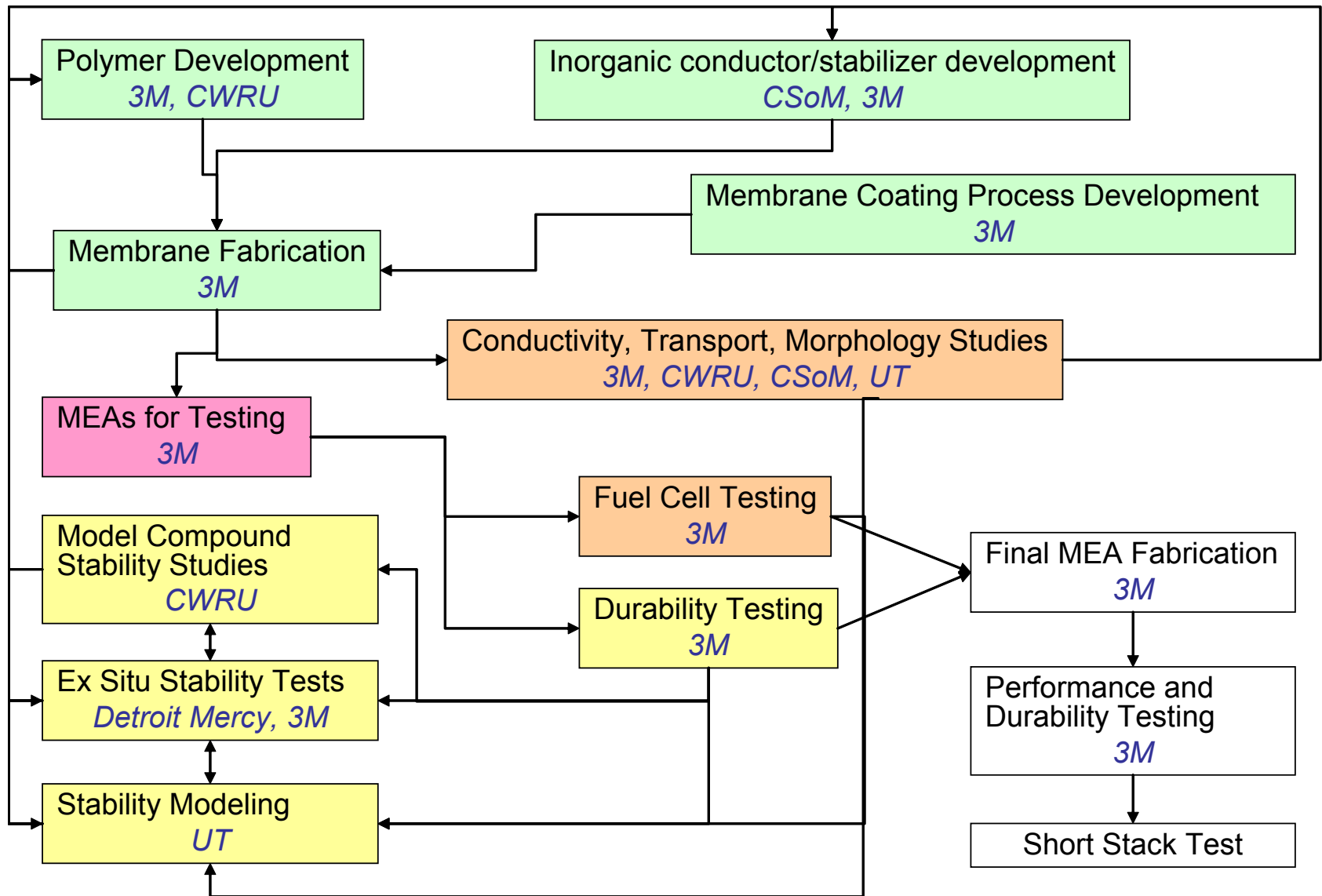
- To develop a new proton exchange membrane with:
  - **higher proton conductivity**
  - **improved durability**
 under hotter and dryer conditions compared, to current membranes.

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

# Project Approach

- 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.
- 2009/2010 Milestones
  - **Q3 2009:** Membrane will have shown improvement over baseline material and measurable progress indicating a pathway to meeting DOE Membrane Technical Targets. The broad material classes showing the higher promise will be identified.
  - **Q3 2010:** 3M will down select for the best performing catalyst/GDL/process based on performance in ex situ testing and single cell testing.

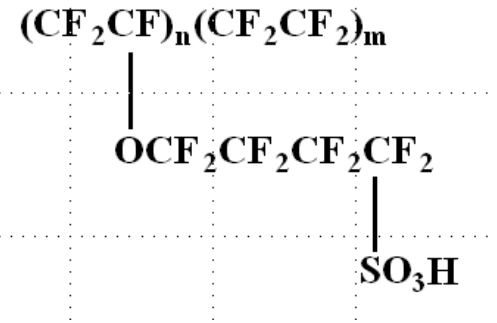
# Collaborations – Flow Of Samples And Information



- **University of Tennessee** - 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 chemical stability.

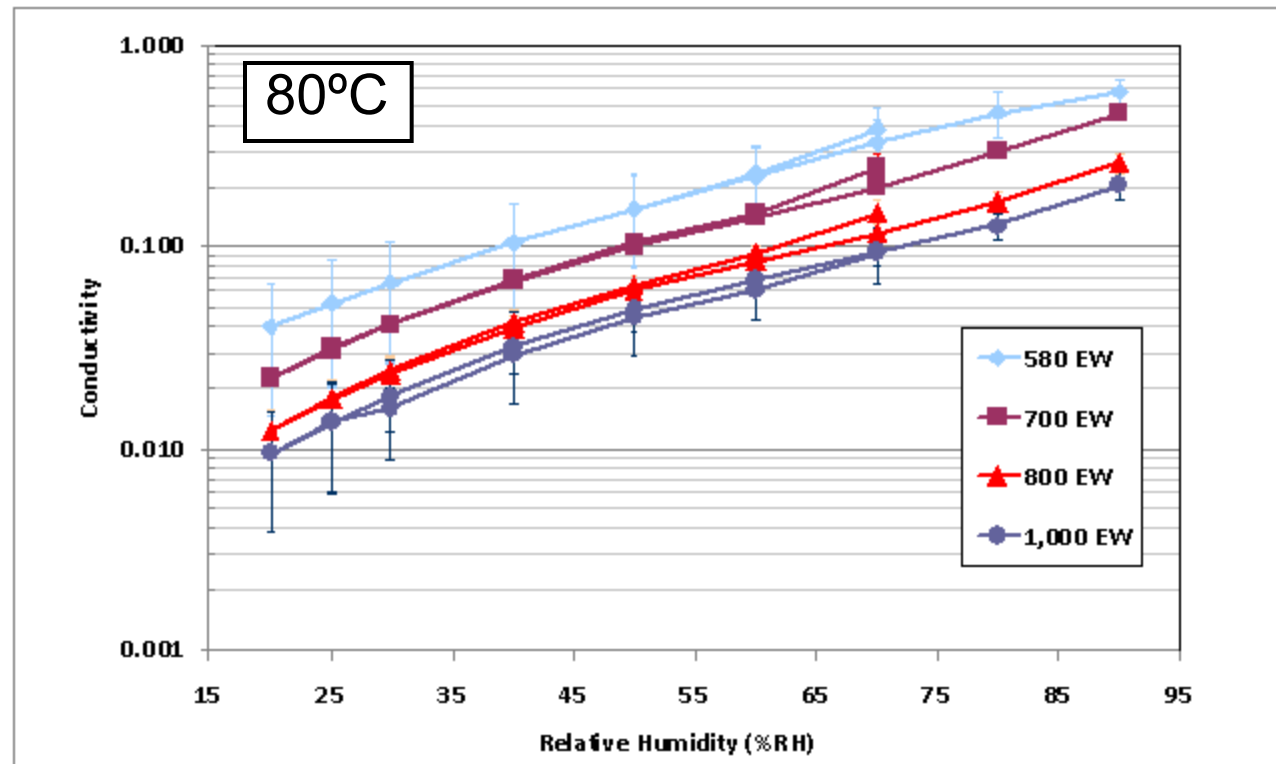
# Conductivity w/ Low EW

Previously Presented Material



- Work is based on 3M Ionomer.
- These ionomers below about 700 EW, meets DOE milestones:
  - RT conductivity > 100 mS/cm at 80%RH, 30°C.
  - 80C conductivity of *ca.* 0.1 S/cm at 50%RH
  - 120°C conductivity of *ca.* 0.1 S/cm at 40% RH.

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



AC 4-point probe measurement.

# Water Mobility Impact on Proton Transport

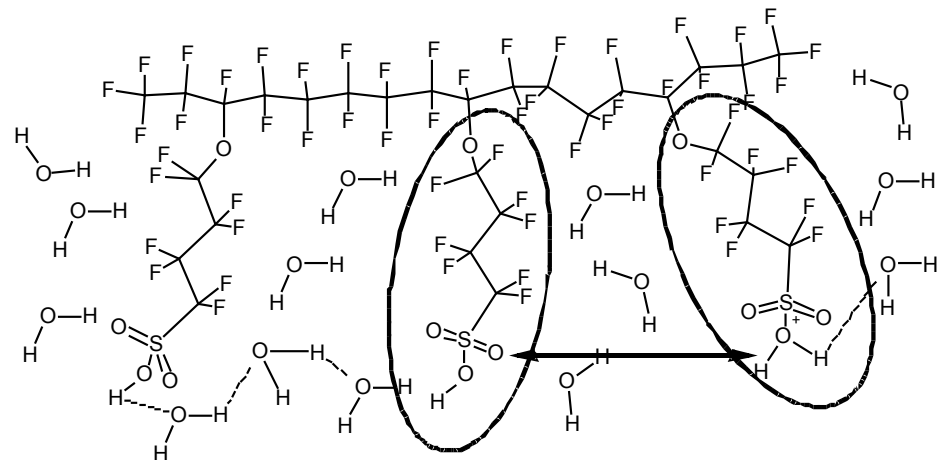
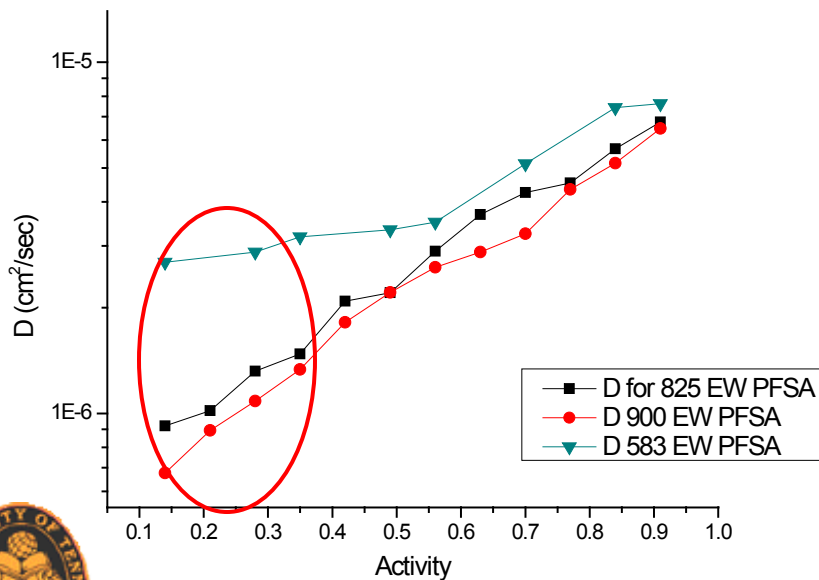
## Probes

- NMR diffusion measurements – Long Range probe of motion
- NMR relaxation data – Molecular scale probe

High Water Mobility suggests that closely packed side-chains positively influence water mobility

Diffusivity of water remarkably high at low RH (micron scale)

Water molecules feel the effects of at least two sulfonates, more weakly interacting with each?



<sup>1</sup>H Diffusion Coefficient

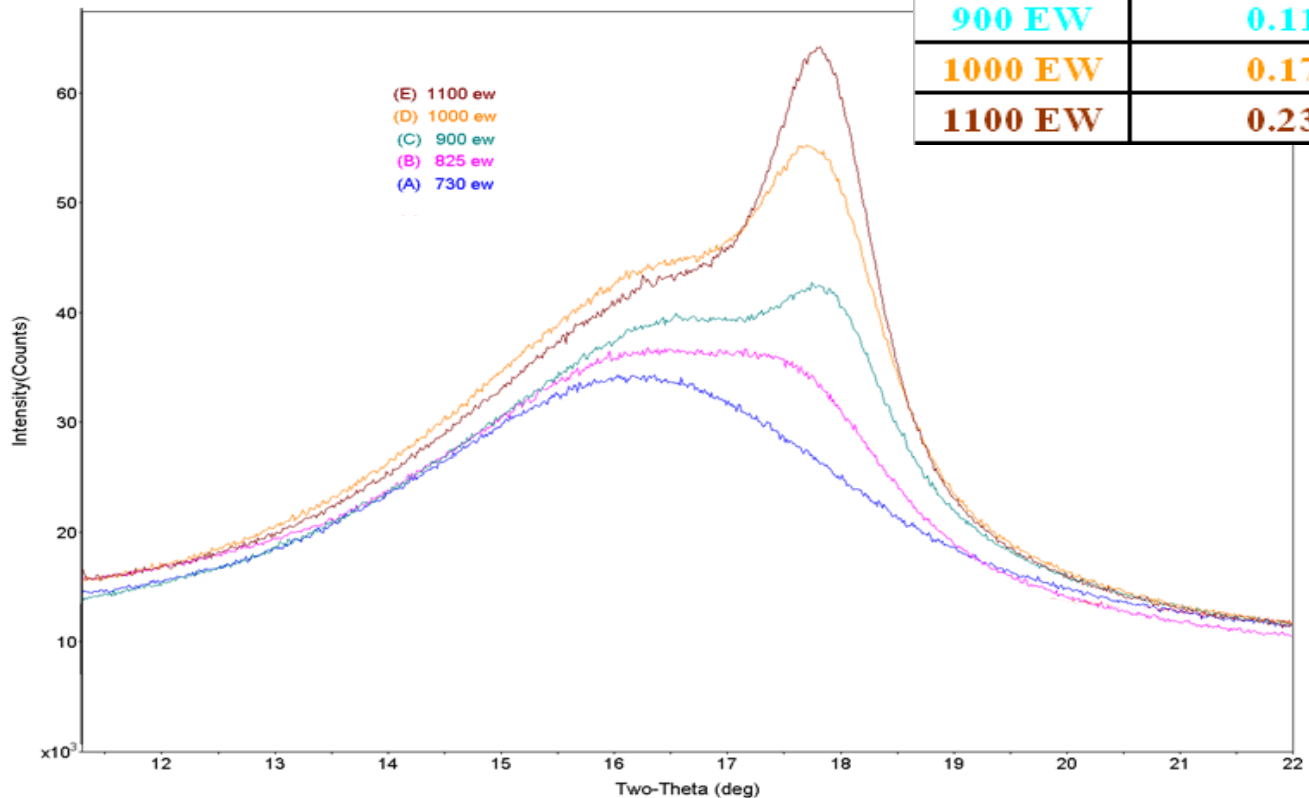




# The Bad News - Loss of Crystallinity

## Wide Angle X-Ray Scattering

Sample	Crystallinity Index
700 EW	>0
825 EW	0.09
900 EW	0.11
1000 EW	0.17
1100 EW	0.23

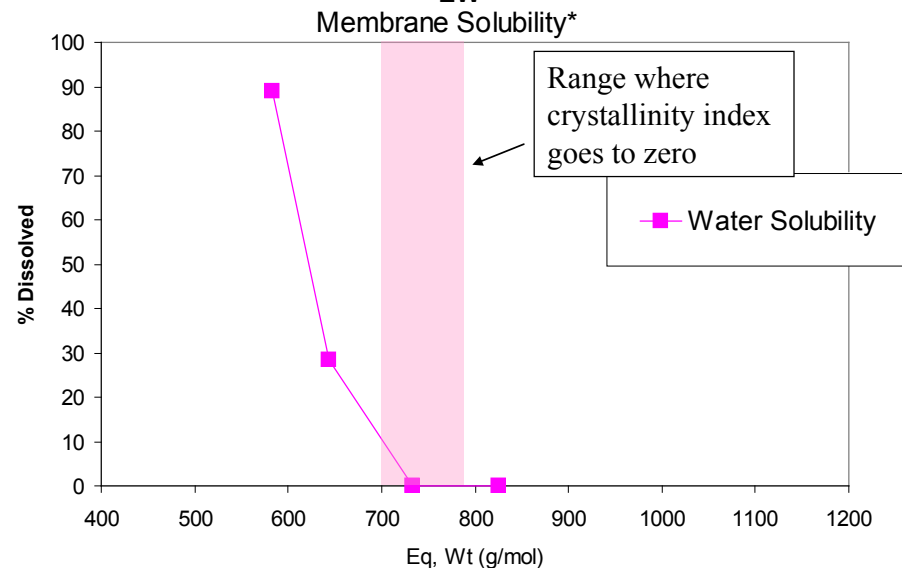
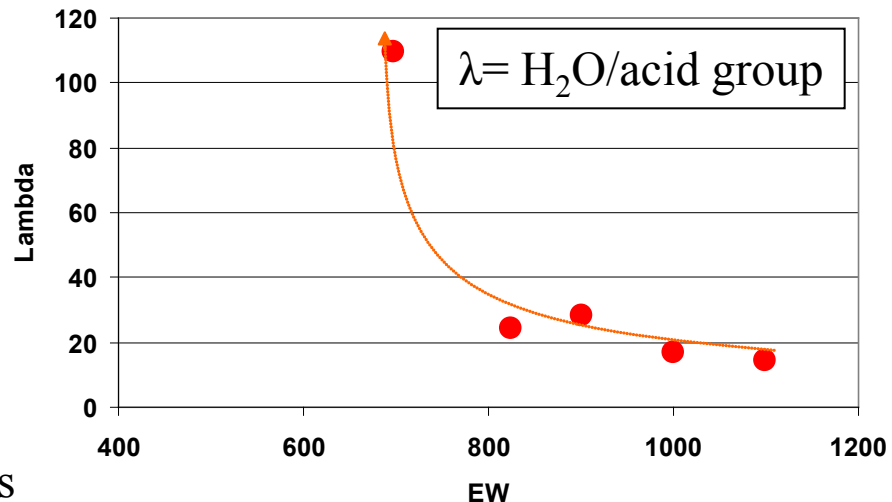


3M CRAL

- Crystallinity from TFE in the polymer backbone is important for good mechanical properties and low water solubility
- WAXS shows little crystallinity below about 800 EW

## More Bad News - Loss of Crystallinity

- At low equivalent weight (EW), membranes swell excessively.
- Solubility starts near where crystallinity is gone. Solubility is determined by boiling, filtering an aliquot of filtrate, and determining fraction of membrane “dissolved”.
- Many mechanical properties parallel this effect – excessive swelling begins before dissolution.
  - Understanding “true” solubility helps defining possible mechanical stabilization methods
  - This experiment only works with well “processed” membranes

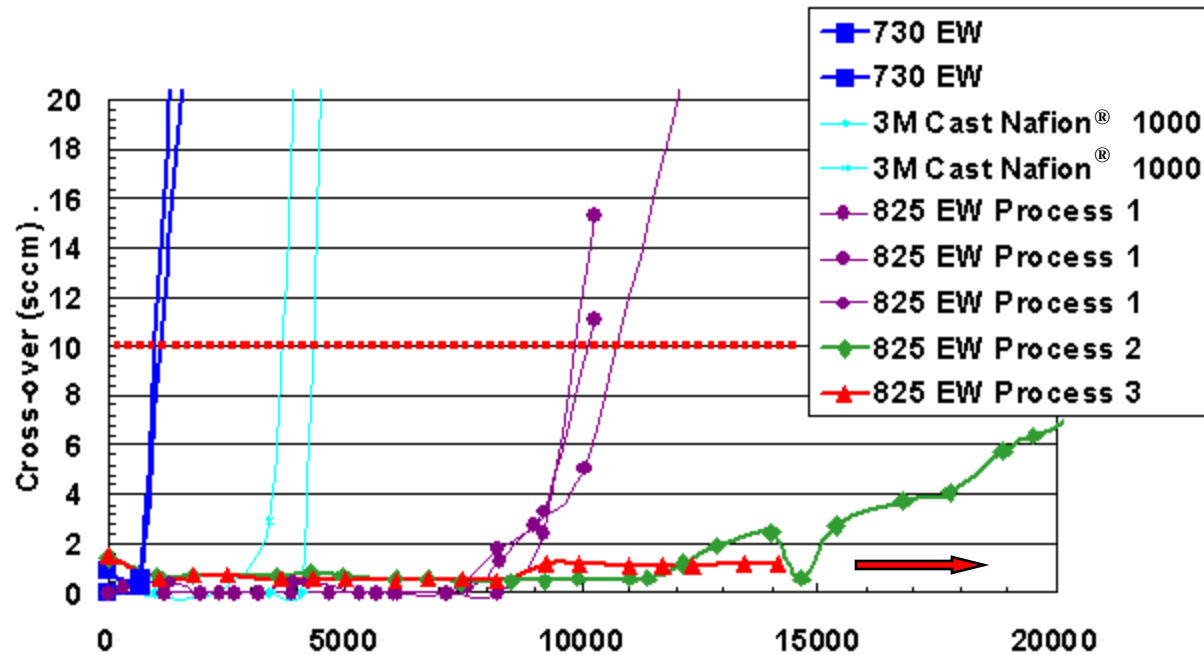


\* Can vary with process conditions

# RH Cycling

Low EW ionomers do poorly in humidity cycle testing.

Performance of 825 EW depends on membrane processing conditions.



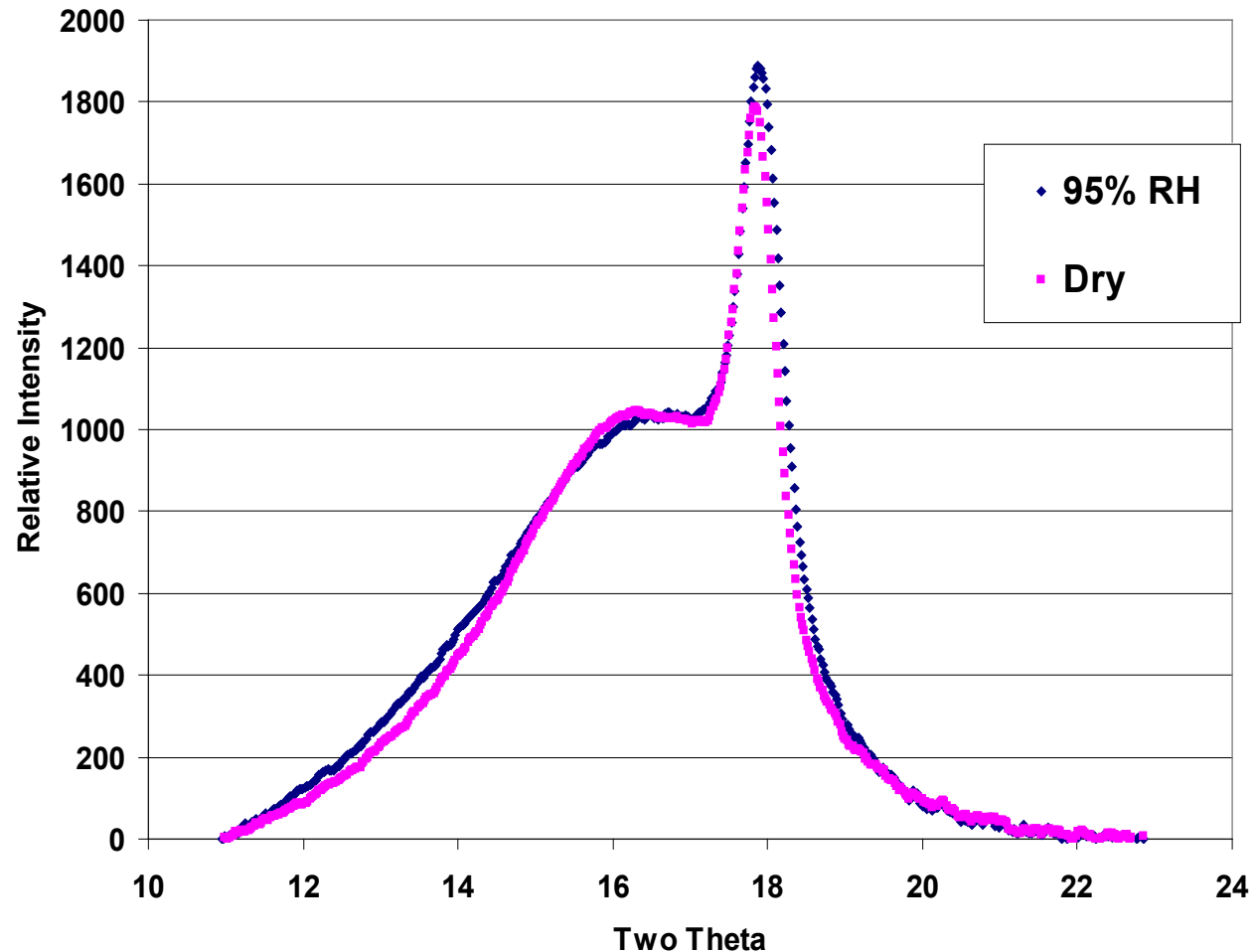
Cell Build: 50 cm<sup>2</sup> cell w/ 2mm lands & 2mm straight channels  
 GDE: Carbon Fiber Paper with MPL & Pt/C electrodes  
 Cycle: 2 min 150% RH air; 2 min 0% RH air flow  
 Conditions: 80°C, 0 kPag, 2 SLPM dry anode & cathode flow, counter-flow  
 Diagnostics: Physical crossover leak (failure = 10 sccm)

**Target:** 20000 RH cycles with no measurable crossover leak or observable mechanical damage

Craig Gittleman - GM

# Not So Bad News - No Loss of Crystallinity Upon Hydration

## Wide Angle X-Ray Scattering



- No decrease in peak intensity due to backbone crystallinity upon hydration for 1100 EW 3M Ionomer.
- Large increase in “ionomer” peak (not shown).
- Lower EW samples and new experimental samples have been evaluated at APS.

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

Some possible solutions:

*blends*

*crosslinking*

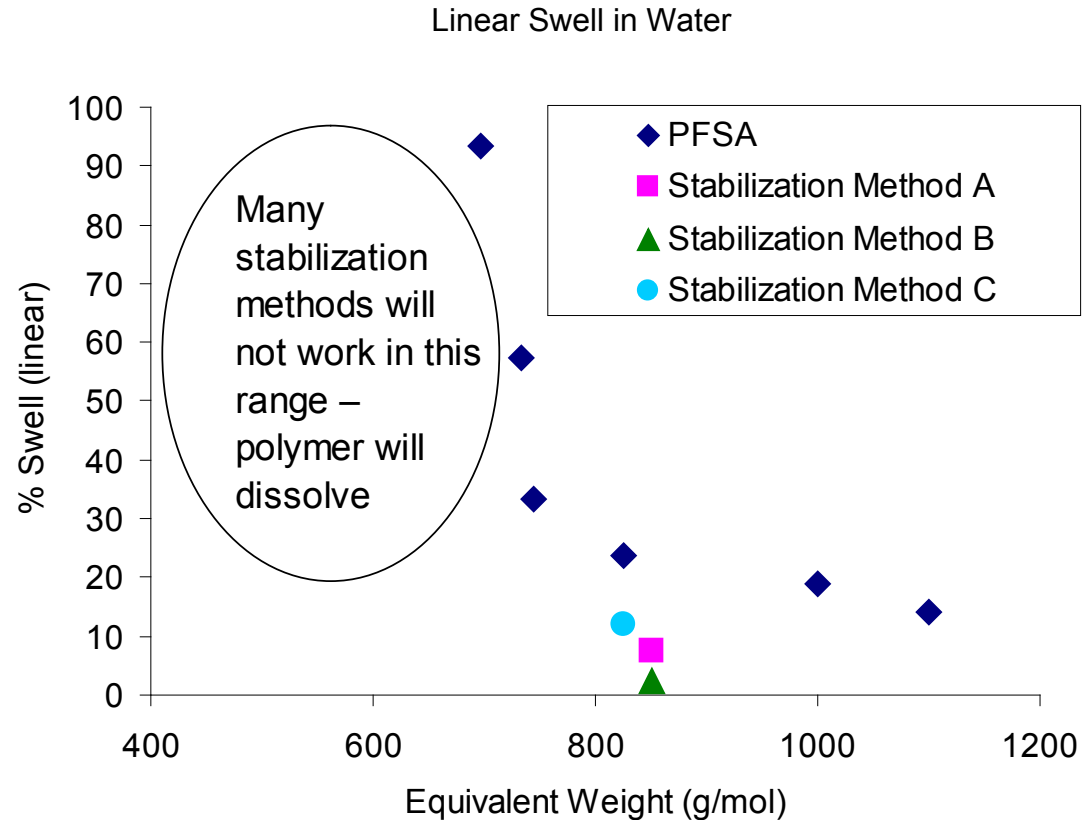
*reinforcement*

*polymer modifications*

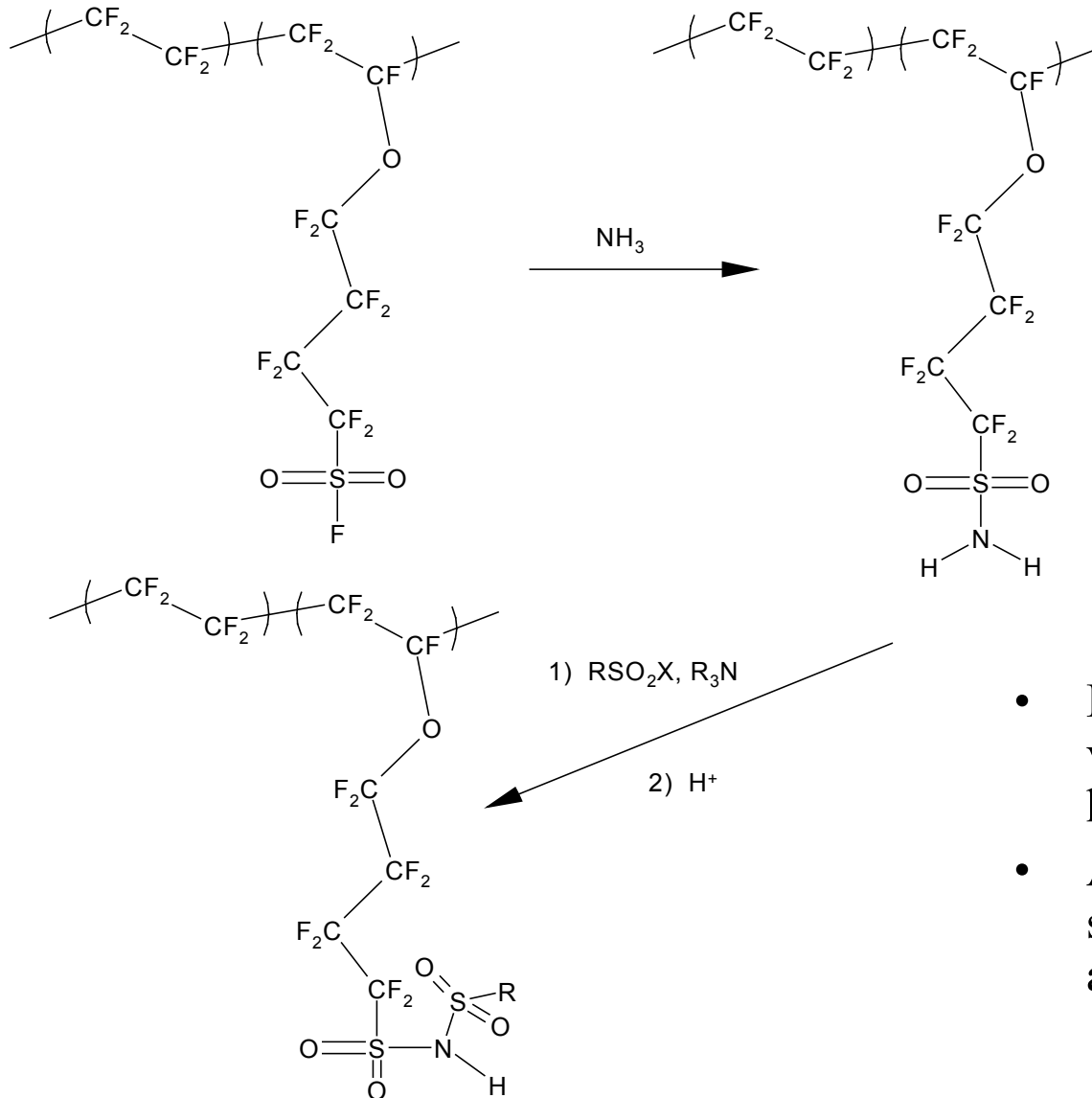
*We are looking at all of these*

# Mechanical Stabilization of the Membrane

- Ways of stabilizing polymers such as blends or reinforcements that don't chemically modify the polymer will not prevent it from dissolving

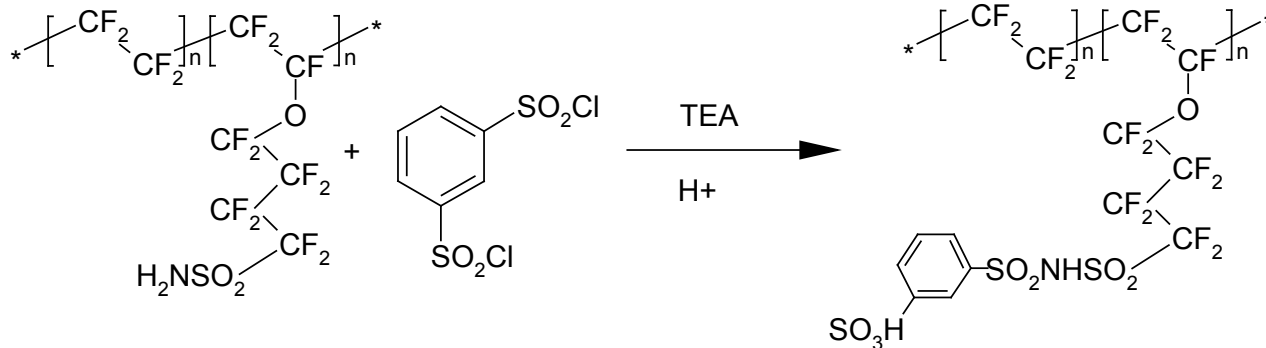
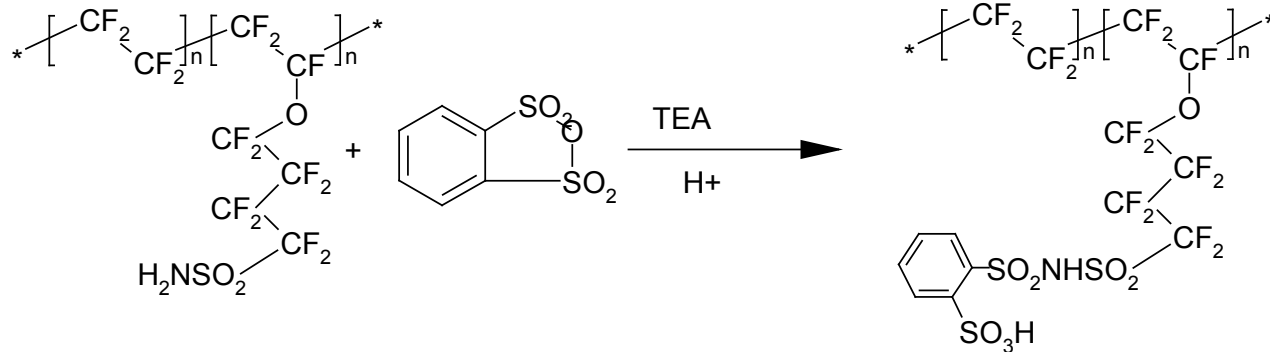


# Polymer Modification – one approach



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

# Addition of More Acids to The Side Chain of The Polymer

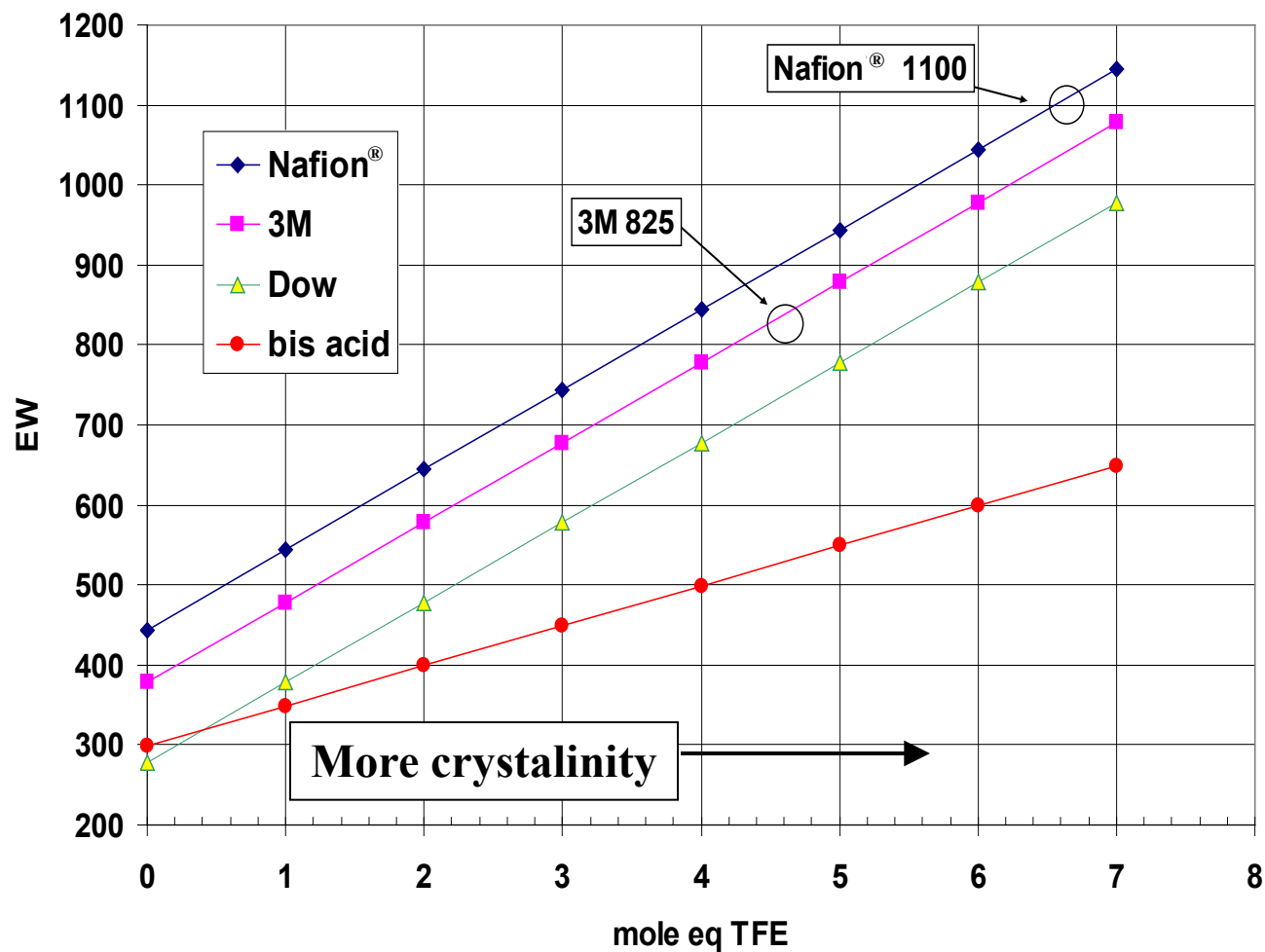


- Ortho and Meta bis acids are prepared in high yield from inexpensive starting materials
- Meta gives some crosslinking



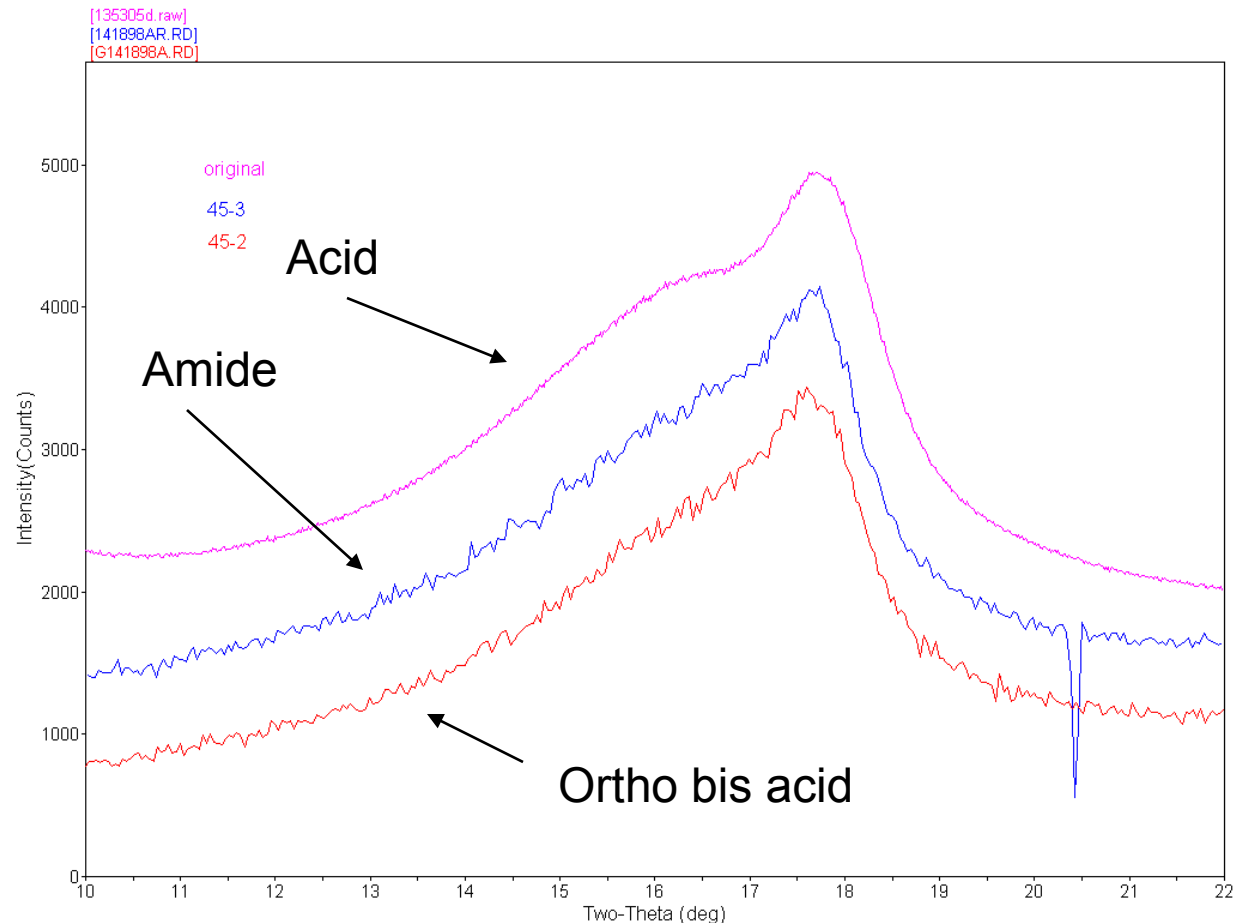
# Multi Acid Side-chains (MASC) Allow Lower EW With More TFE in the Backbone

- 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.



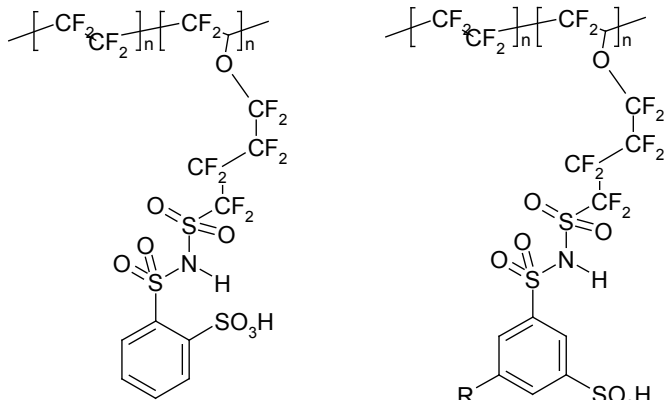
# WAXS of Polymers Made From 1,000 EW Starting Ionomer Precursor

- 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 dry
- WAXS on membranes with different side-chains at different RH's will be run at SSRL the week of July 9.

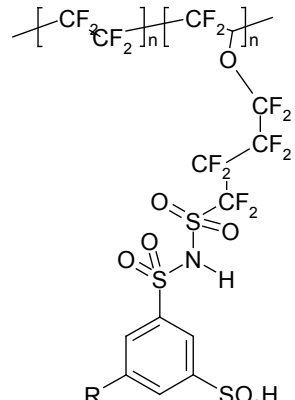


# Multi Acid Side-chain (MASC) Polymers - Conductivity

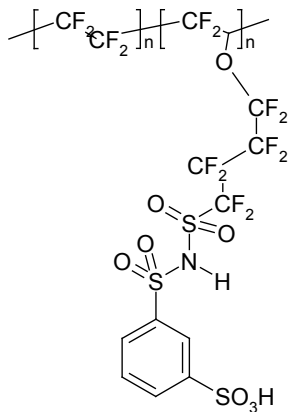
- Multiple acid groups allow raising the conductivity of starting ionomer
- 800 EW starting PFSA precursor with crystalline backbone can be used to make low EW ionomer with higher conductivity.



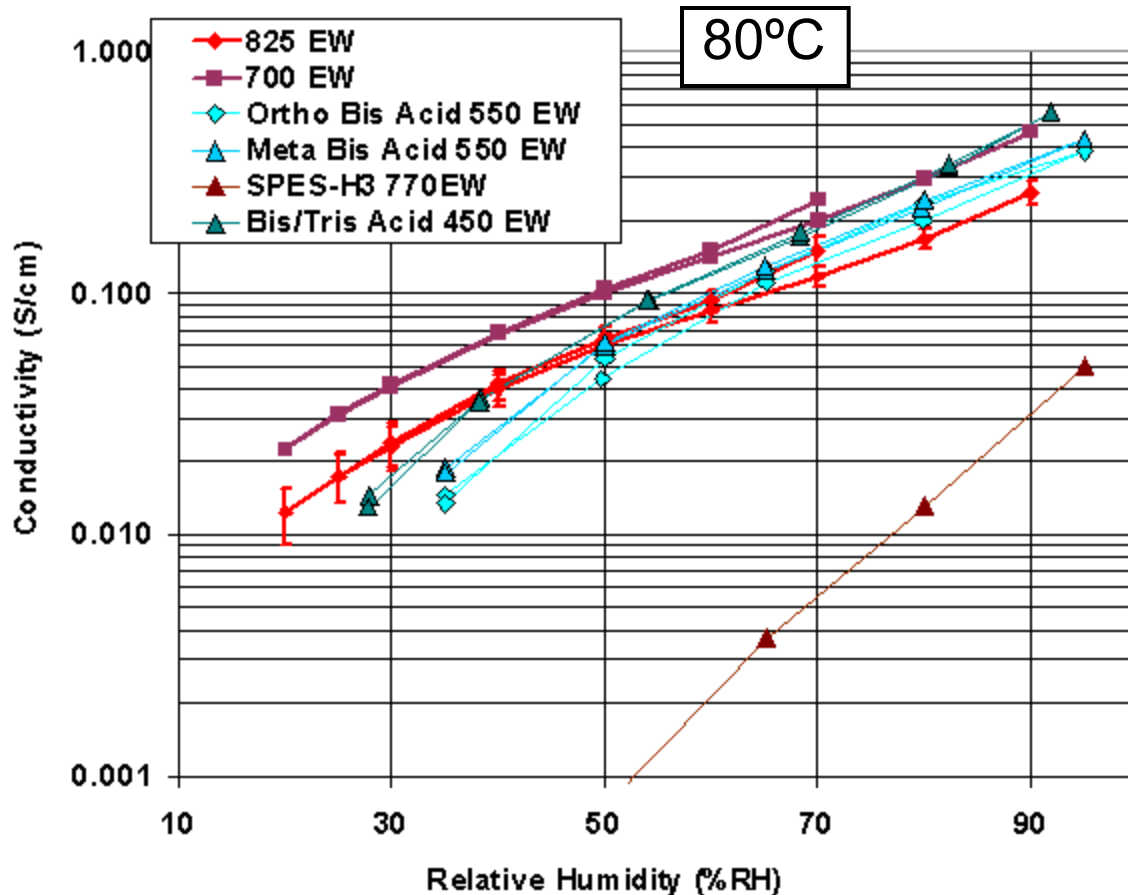
Ortho bis acid



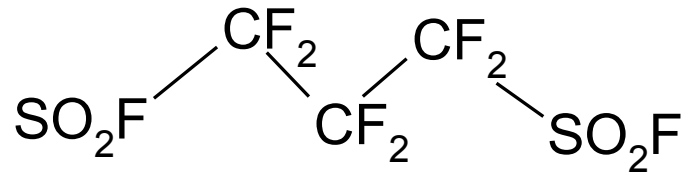
Bis/Tri Acid  
R = 1:1 SO3H/X



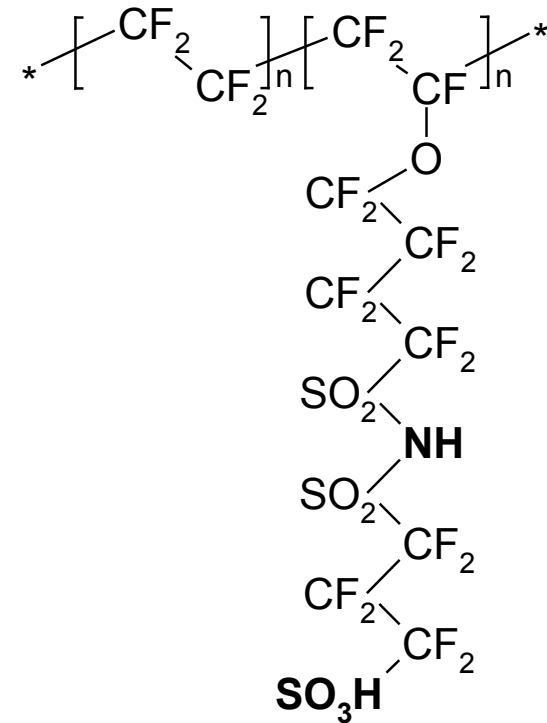
Meta bis acid



# New MASC – Per Fluoro Imide Acid (PFIA)



Polymer-SO<sub>2</sub>NH<sub>2</sub>



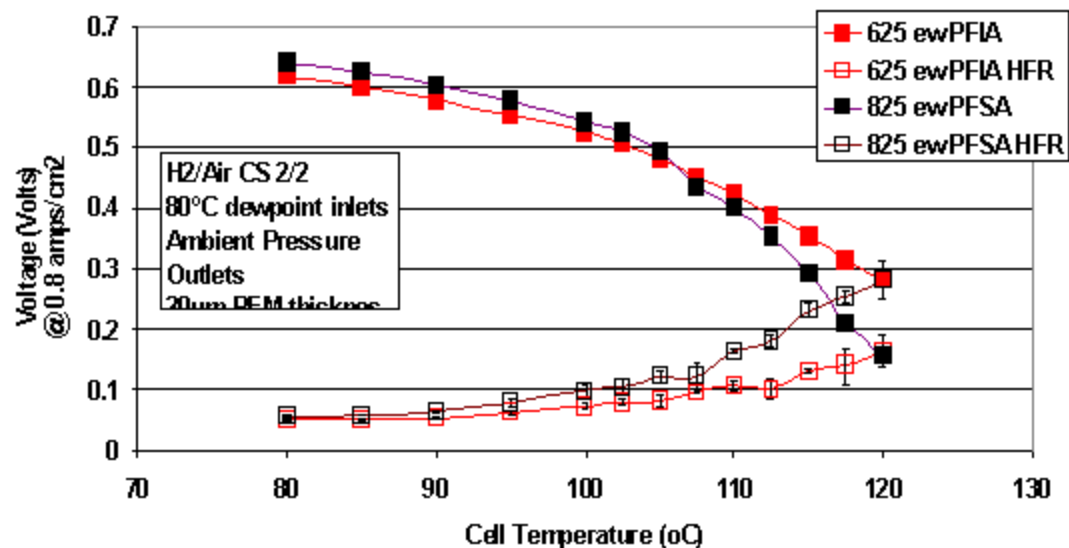
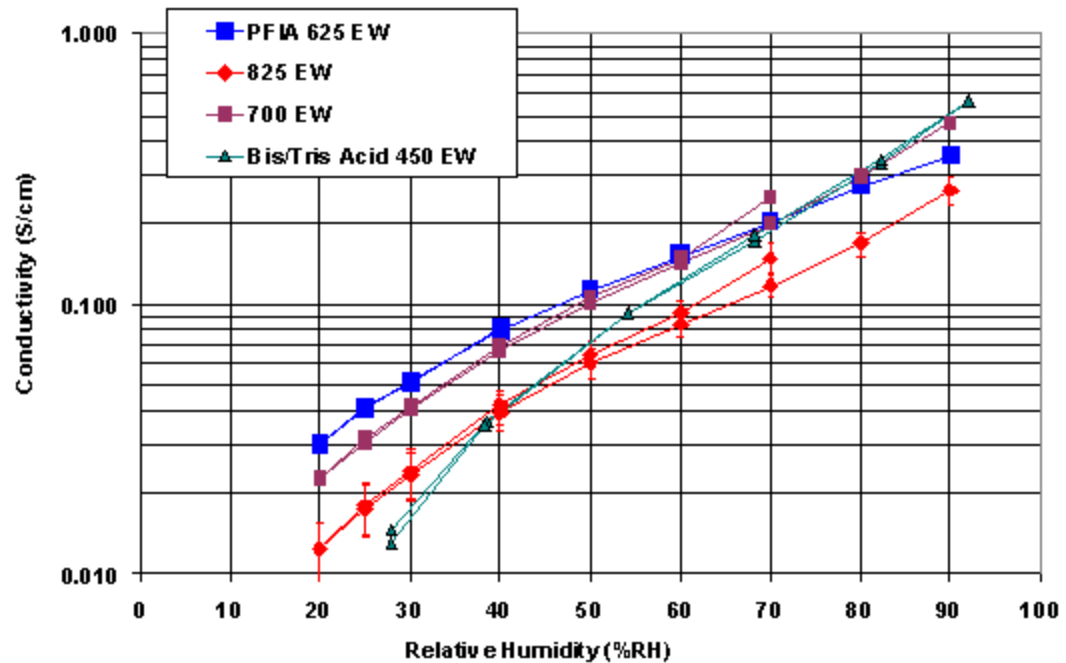
Recent work using a 3M perfluorodisulfonyl fluoride has produced a polymer with a stable multi acid side-chain in high yield without substantial cross-linking. This provides stronger acid groups, giving higher conductivity under drier conditions.

# New MASC – Per Fluoro Imide Acid (PFIA)

Using an 835 EW starting SO<sub>2</sub>F polymer, we have prepared a starting sulfonamide with 85% sulfonamide and 15% sulfonic acid groups.

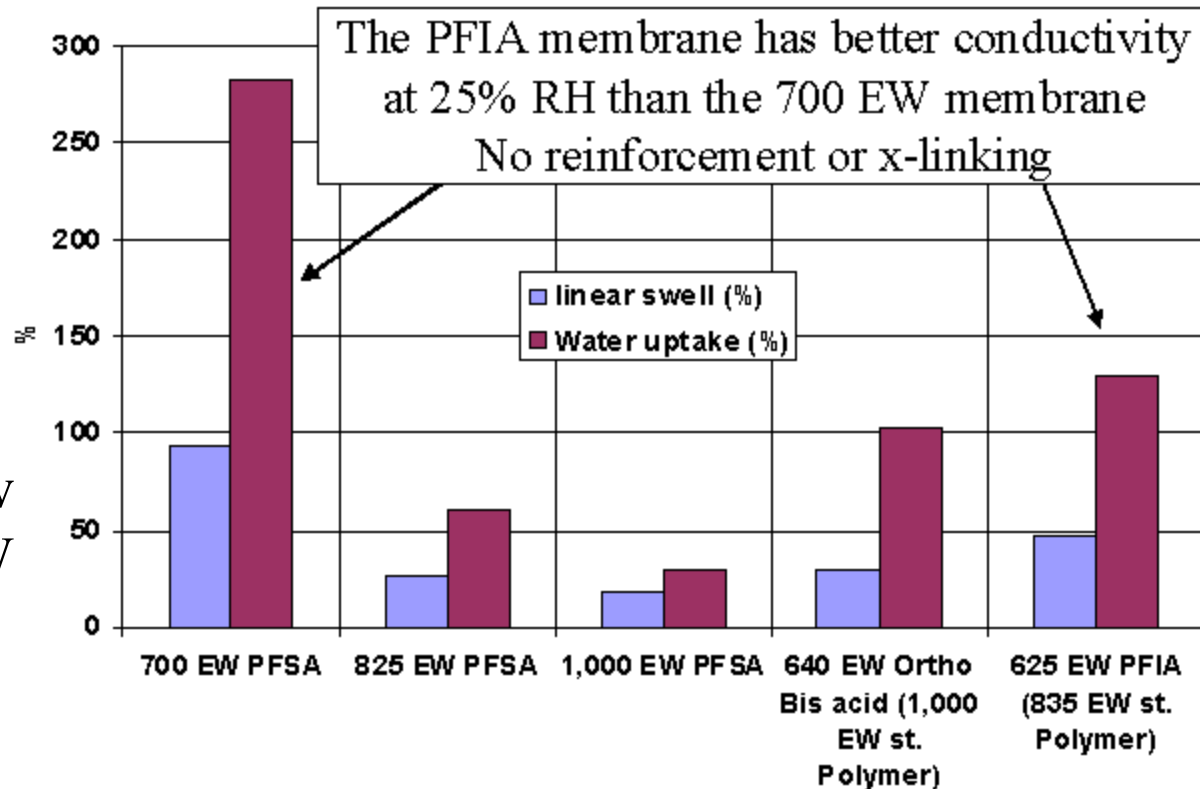
This prepared an ionomer with 625 EW.

This membrane has >100 mS/cm conductivity at 120°C, 40% RH – similar to about 700 EW PFSA



# Multi Acid Side-chains (MASC) - Swelling

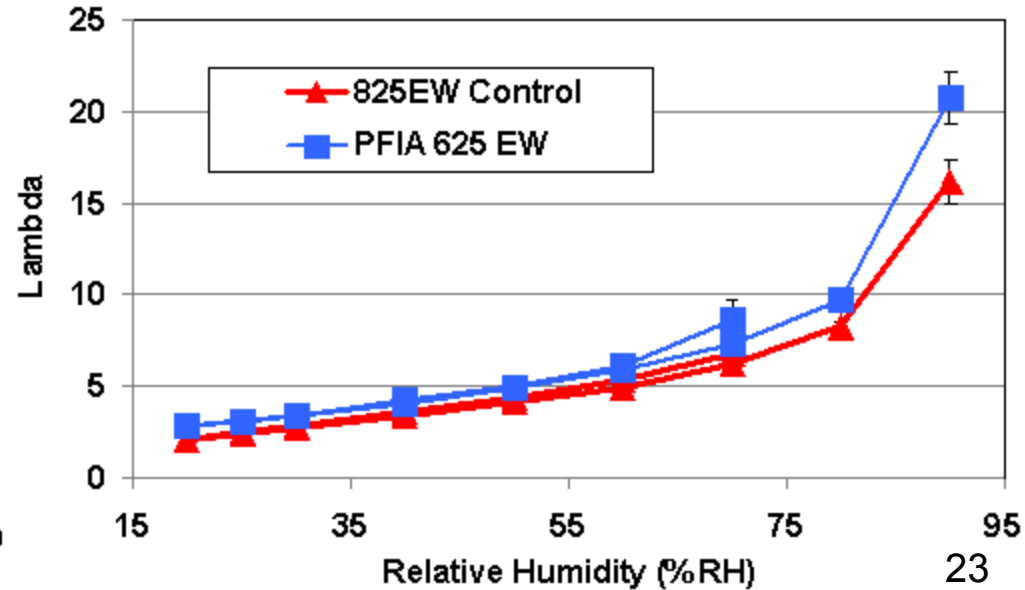
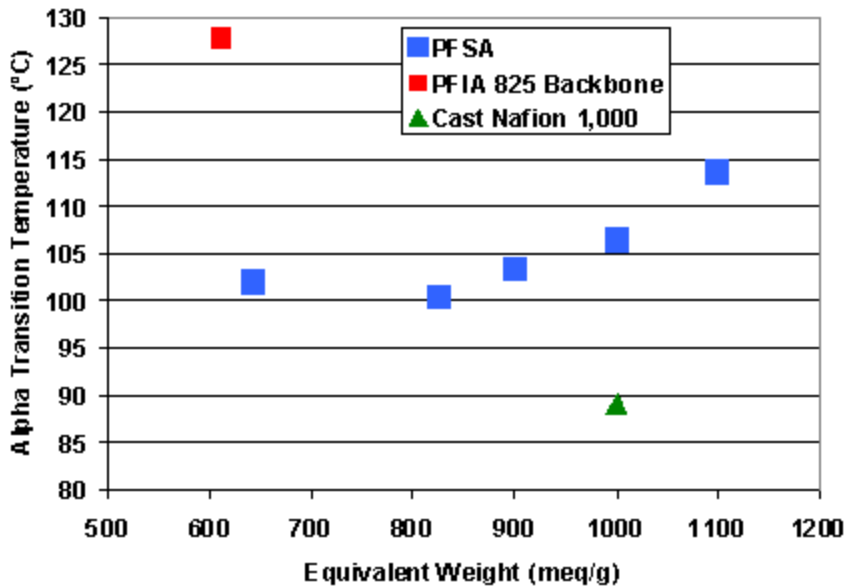
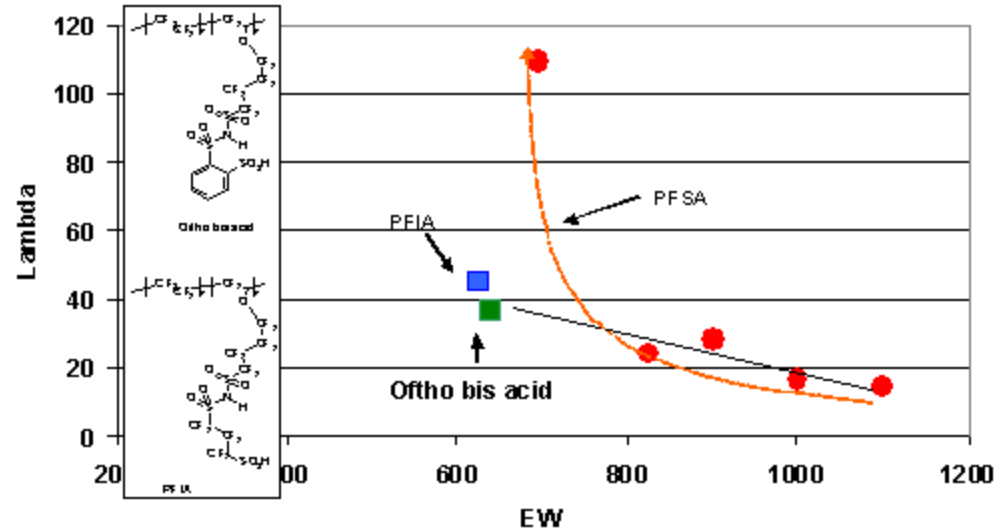
Bis acid show swelling and water uptake (**3 hours boiling**) slightly higher than precursor polymer PFSA, but still very low for such low EW ionomers.



**This test can't be run on a 650 or below 3M PFSA. It dissolves! We are working on making lower EW samples of this type with 800 EW backbone polymer.**

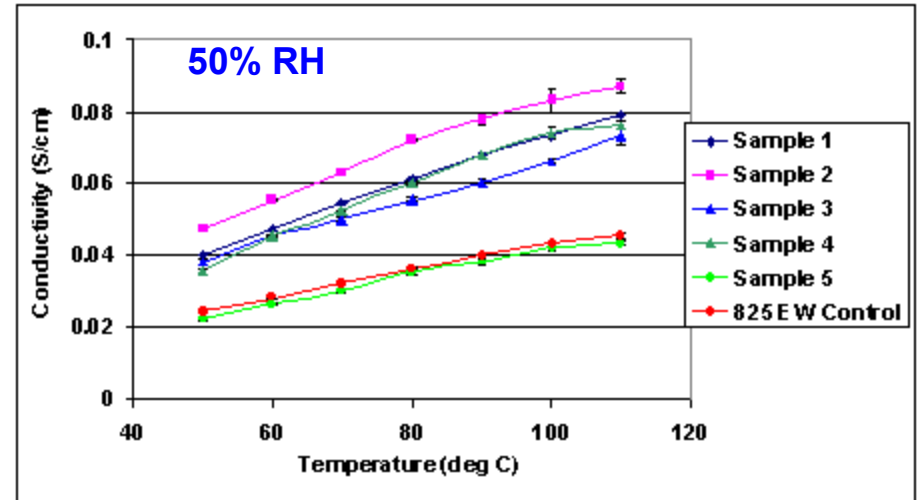
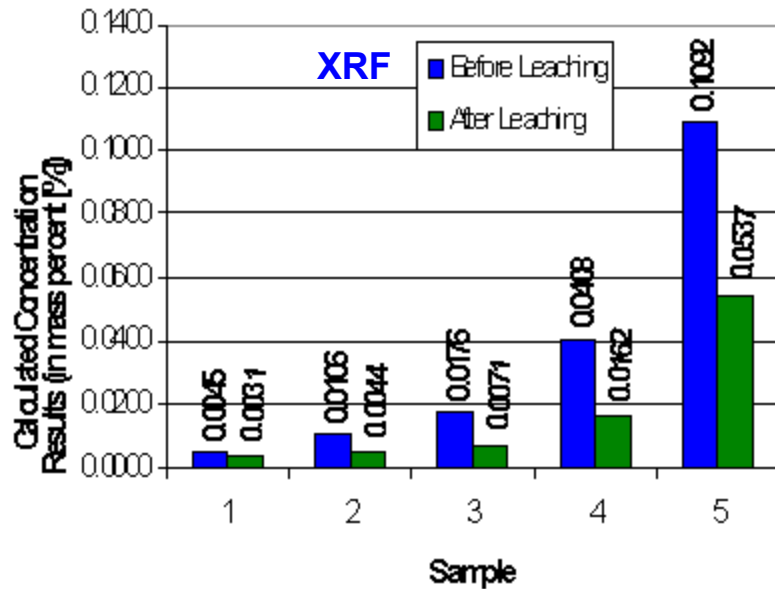
# New Multi Acid Side-chains (MASC's)

- Water absorption as a function of lambda (# H<sub>2</sub>O molecules/acid group) for these new ionomer appears to be equivalent to a standard PFSA at all but the highest %RH conditions.
- In boiling water (3 hours boil) the water absorption is much less than PFSA's of the same EW.
- The PFIA ionomer has a higher  $\alpha$  transition (T<sub>g</sub>) than a PFSA of the same EW.



# Inorganic oxide immobilized HPA based membranes

Leaching Results

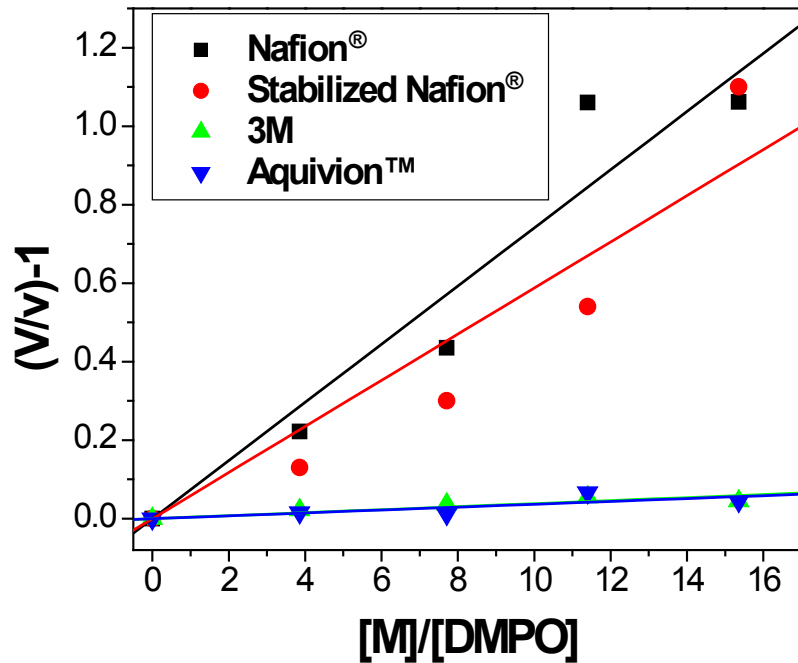


Inorganic oxide/HPA composites provide chemical stabilization and increased conductivity. Currently about 1/2 of the added material remains in the membrane after boiling. The remaining material still contains the HPA and still provides increased conductivity





# Competitive Kinetics



**Figure 1.** Data showing the inhibition of DMPO/OH adduct formation due to the reaction of membranes with hydroxyl radicals. Plots of  $(V/v)-1$  vs concentration ratio  $[M]/[DMPO]$  for Nafion® (■), stabilized Nafion® (●), 3M (▲), and Aquivion™ (▼).

**Table 1. Reaction Rates of Fluorinated Ionomers with Hydroxyl Radicals**

Membrane	$k_M/k_{DMPO}$	$k_M/M^{-1}s^{-1}$
Nafion®	0.0741	$2.7 \times 10^8$
StNafion®	0.0588	$2.1 \times 10^8$
3M	0.0038	$0.14 \times 10^8$
Aquivion™	0.0037	$0.13 \times 10^8$

$k_M$  is the reaction rate constant of membranes with hydroxyl radicals.

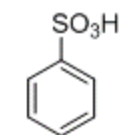
**Results suggest that the 3M and Aquivion™ membranes have higher durability compared to Nafion® and Stabilized Nafion®.**

**Details in Danilczuk, M.; Perkowski, A.J.; Schlick, S. *Macromolecules* web publication 19 February 2010.**

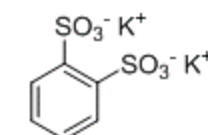
# Aromatic Model Compounds and their Derivatives

## Sulfonic/Phosphonic acids

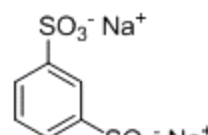
Competitive stability studies show fluorinated groups are more stable. Oxidative attack occurs at aromatic ring in partially fluorinated compounds



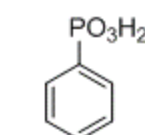
AMC1



AMC7

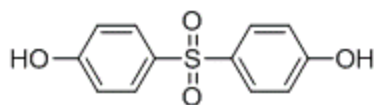


AMC8

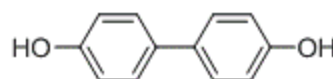


AMC9

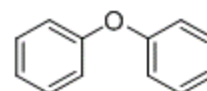
## Sulfones, ether, phenol



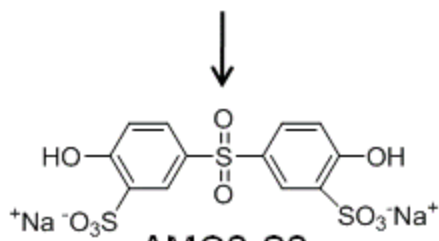
AMC2



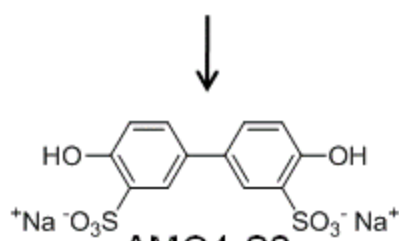
AMC4



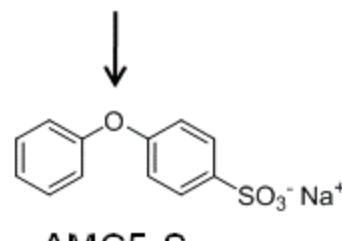
AMC5



AMC2-S2

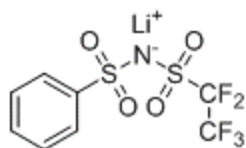


AMC4-S2

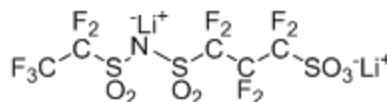


AMC5-S

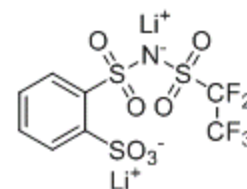
## Sulfonimides



AMC6



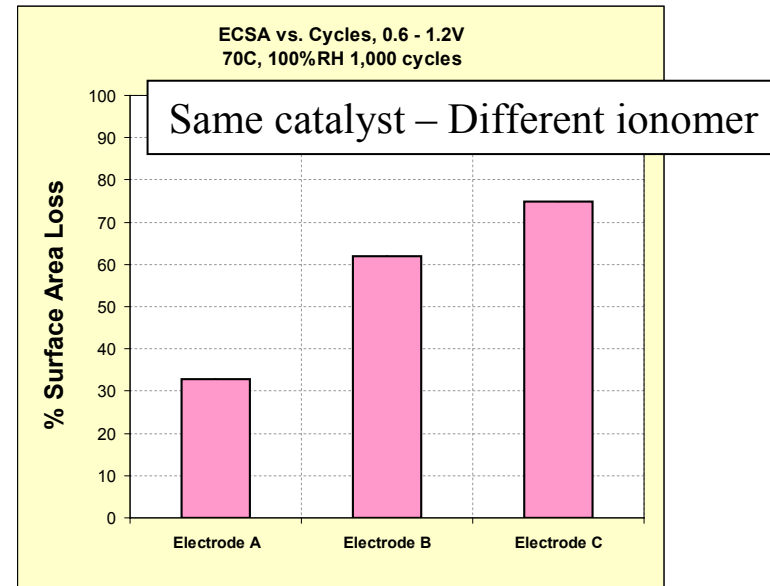
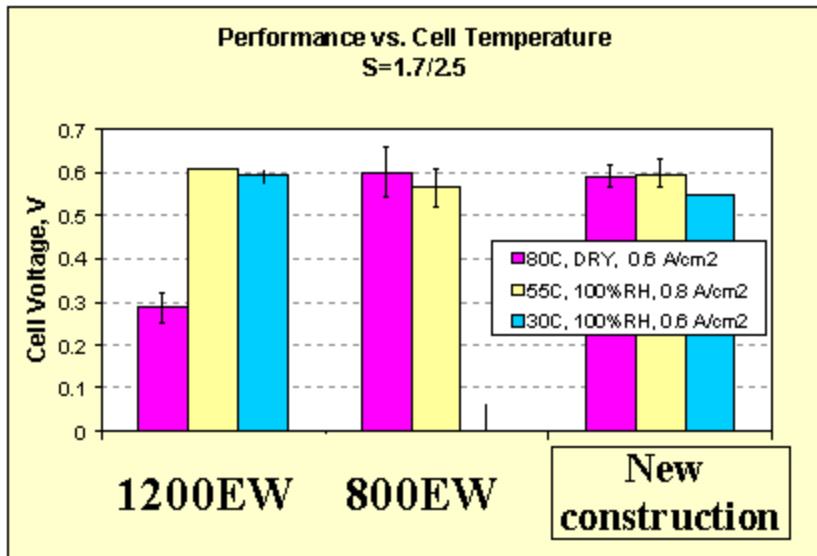
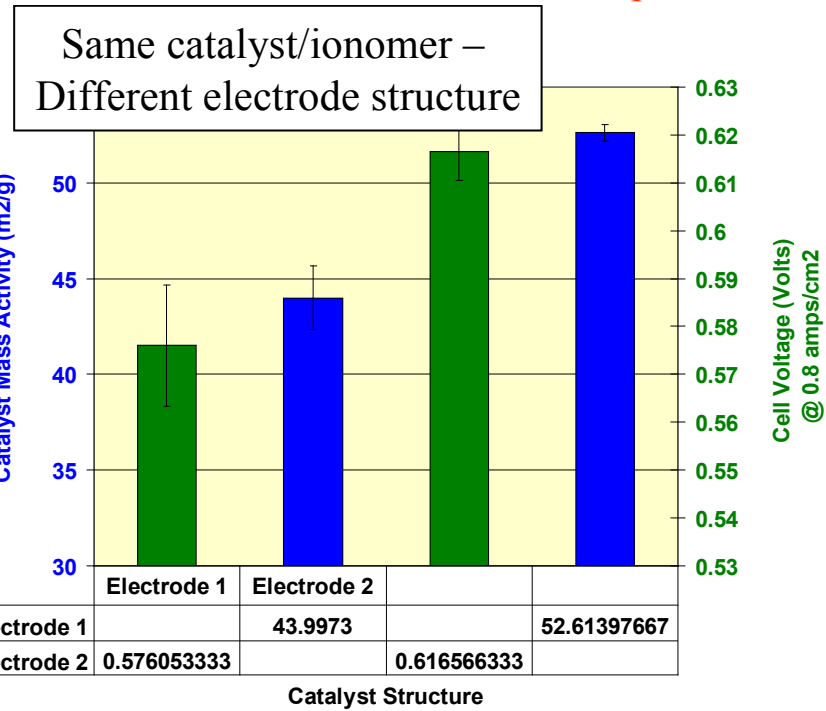
AMC11



AMC12

# New Electrodes

- Developing new electrodes for high temperature dry operation leveraging strength areas-
  - Low EW polymers
  - new processing
  - new polymers
  - **Optimized electrode structures**
- Gains in performance
  - lower EW polymers
  - catalyst structuring
- Gains in durability
  - Increase cycling durability with same catalyst



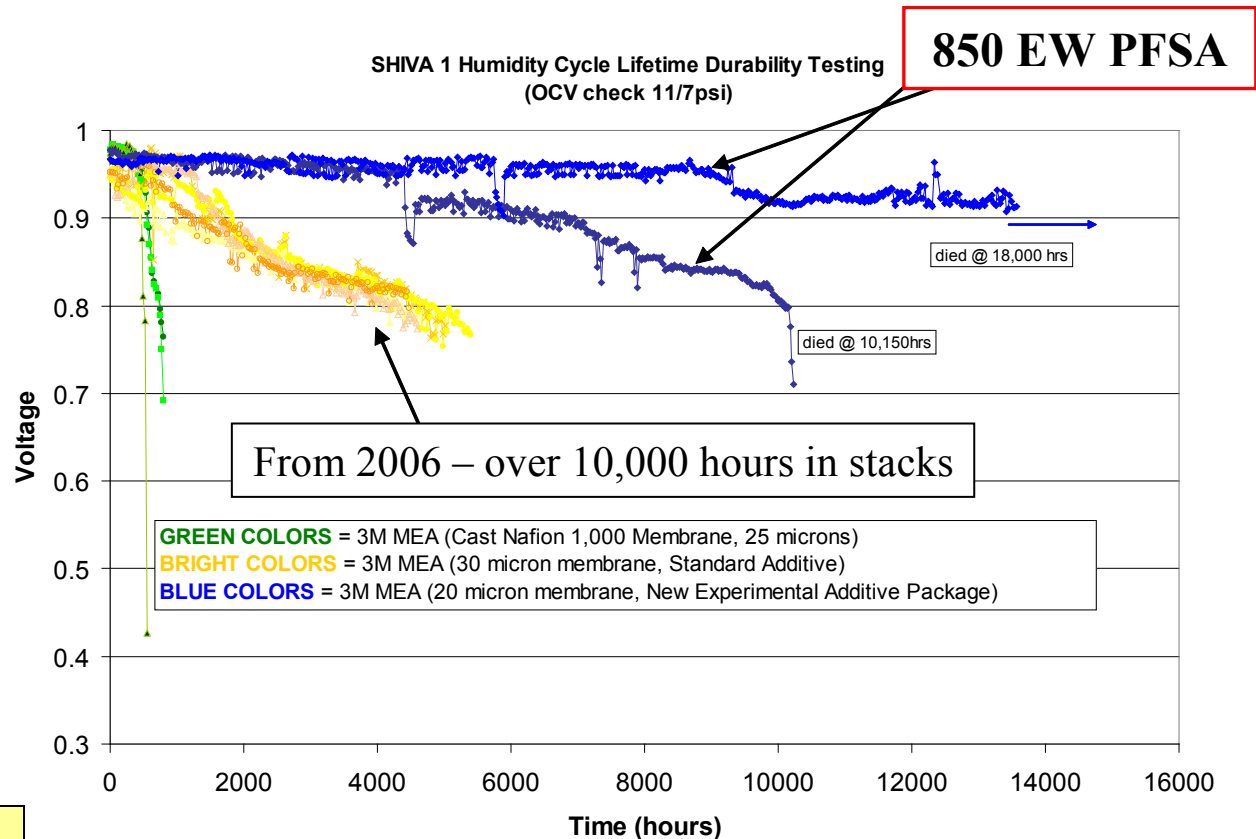
# Fuel Cell Durability Testing

Technical Accomplishments  
and Previously Presented Material

New additive package provides over 10,000 lifetime in automotive accelerated durability protocol. One lasted about 18,000 hours. Durability tests on PFIA membranes have begun.

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

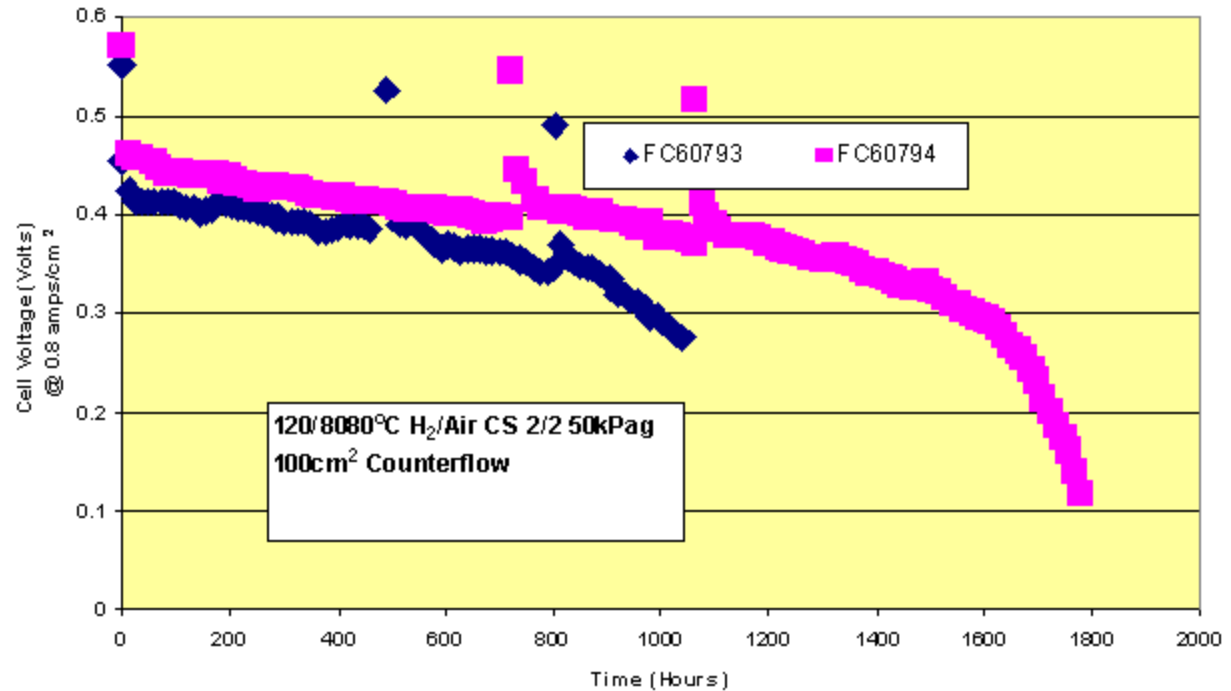
Cell Temperature: 80 °C  
 Inlet Dew points: 64/64 °C  
 Outlet Pressures: 175kPa  
 End of life = < 800 mV OCV w/  
 7 PSIG anode overpressure.



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








# 120°C Steady State Testing – Effect of additives

- Performance at 0.8 A/cm<sup>2</sup>
- Membrane failed at *ca.* 1700 hours.
- New additives provide increased lifetime at 120°C, 24% RH, constant 0.8 A/cm<sup>2</sup> testing.
- This test was run with 825 PFSA.
- Next sample is 625 EW PFIA.



# Summary

- This project involves using experiment and theory to develop an understanding of factors controlling proton transport and the chemical/physical durability of the membranes.
- PFIA membrane meets all performance requirements so far and shows improved durability. Testing of this material with chemical and mechanical / dimensional stabilization is underway.

<b>All membranes are 20 micron</b>		3M 2010 Status	2010 target	2015 target	
Area Specific Resistance at 120° C (H <sub>2</sub> O pp 40-80 kPa)	Ohm cm <sup>2</sup>	.038 (50 kPa) 0.02 (80kPa) <i>625 EW PFIA</i>	0.02	0.02	
Area Specific Resistance at 80° C (H <sub>2</sub> O pp 25-45 kPa)	Ohm cm <sup>2</sup>	0.017 (25 kPa) 0..006 (44 kPa) <i>625 EW PFIA</i>	0.02	0.02	
Area Specific Resistance at 30° C (H <sub>2</sub> O pp 4 kPa)	Ohm cm <sup>2</sup>	0.03 (3.8 kPa) <i>625 EW PFIA</i>	0.03	0.03	
Area Specific Resistance at -20° C	Ohm cm <sup>2</sup>	0.14 <i>700 EW PFSA</i>	0.2	0.2	
O2 cross-over	mA/cm <sup>2</sup>	<0.5	2	2	
H2 cross-over	mA/cm <sup>2</sup>	<2	2	2	
<u>Durability</u> Mechanical (%RH Cycle)	Cycles	10,000+ <i>625 EW PFIA</i>	20,000 Still running	20,000	
Chemical (OCV)	Hours	450 <i>625 EW PFIA</i>	500	500	

# Future Work – What's next

- MASC Polymers testing- PFIA will be used for final membrane/MEA evaluation.
  - Prepare and evaluate shorter (C2) linking group on PFIA.
  - Complete modeling and NMR diffusion work on MASC and PFSA polymers (UT).
  - Complete stability testing on new membranes and model compounds (CASE, UDM)
  - Test new mechanical stabilizing method with PFIA. Evaluate using %RH cycle testing.
  - Select final EW.
- Select HPA additive used with PFIA based on stability and conductivity testing (CSM).
- Complete electrode development and select electrode and GDL for final testing.
  - Select ionomer for electrode (PFSA or MASC, EW).
  - Select catalyst for electrode.
  - Select fabrication process and conditions.
- Make MEA's and perform final testing
  - Performance (Low temp to 120°C, Low to high %RH)
  - Durability (OCV, %RH cycle, Accelerated protocol).