

Membranes and MEA's for Dry, Hot Operating Conditions

Steven Hamrock

3M Fuel Cell Components

May 19, 2009



FC_13_Hamrock

Overview

Timeline

- Project start 4/1/07
- Project end 3/31/11
- 50% complete

Budget

- Total Project funding \$11.4 million
 - \$8.9 million - DOE
 - \$2.5 million - contractor cost share (22%)
- Funding in FY 2008
- \$2.5 Million
- Funding in FY 2009
- \$2.5 Million

Barriers

- A. Durability
- C. Performance

Partners

Case Western Reserve Univ.* *Professors T. Zawodzinski and D. Schiraldi*

Colorado School of Mines* *Professor A. Herring*

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

Univ. of Tennessee* *Professor S. Paddison*

General Motors *C. Gittleman*

Bekktech Inc. *T. Bekkedahl*

3M *S. Hamrock (Project lead)*

** denotes subcontractor*

Project Objectives-Relevance

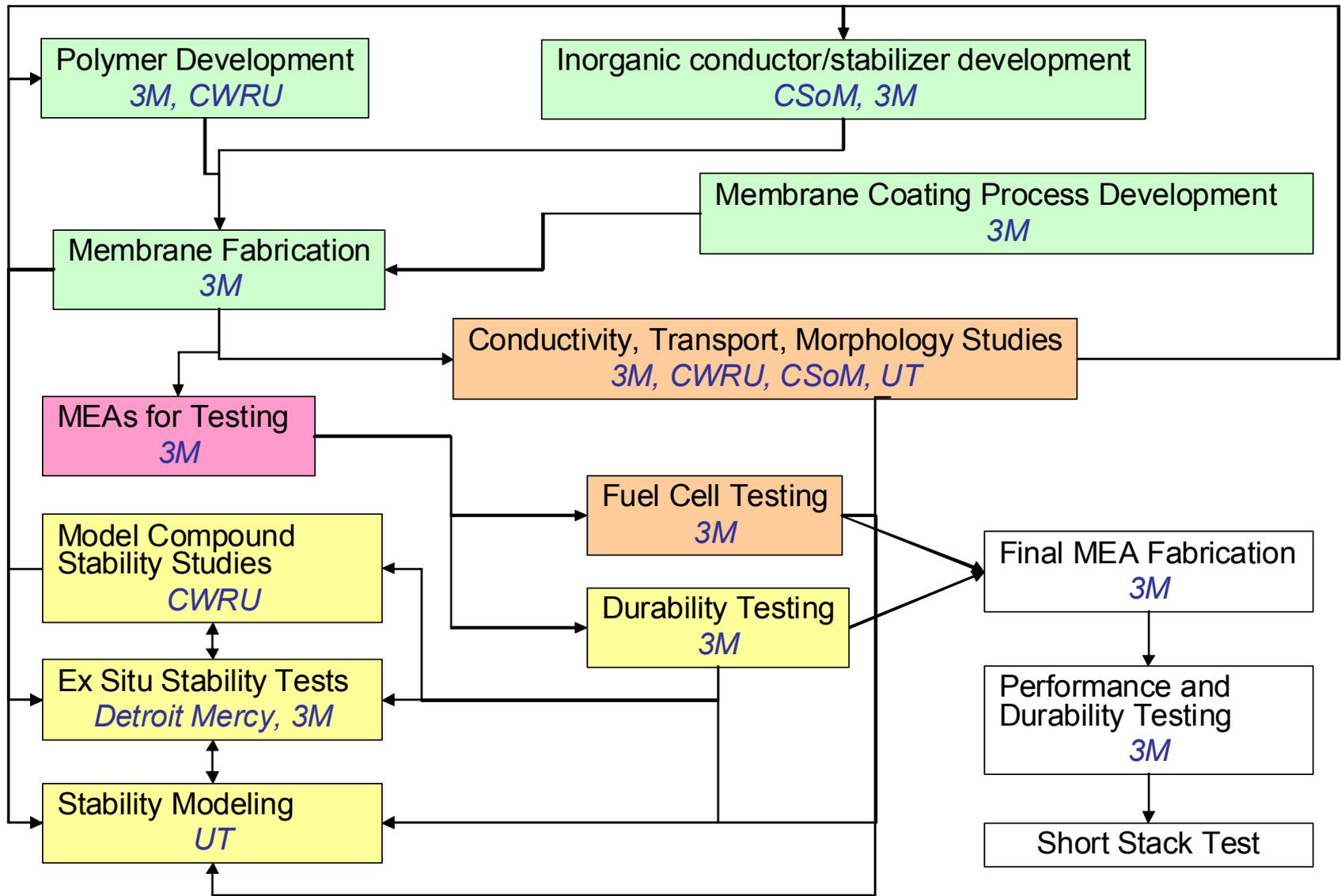
- To develop a new proton exchange membrane with:
 - higher proton conductivity**
 - improved durability**
 under hotter and dryer conditions compared, to current membranes.

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 ²	0.03	0.02	0.02	0.02
80°C and water partial pressures from 25 - 45 kPa	Ohm cm ²	0.03	0.02	0.02	0.02
30°C and water partial pressures up to 4 kPa	Ohm cm ²	0.04	0.03	0.03	0.03
-20°C and water partial pressures up to 0.1 kPa	Ohm cm ²	0.3	0.2	0.2	0.2
Oxygen cross-over ^a	mA/cm ²	5	5	2	2
Hydrogen cross-over ^a	mA/cm ²	5	5	2	2
Cost ^b	\$/m ²	15 ^c	200	20	20
Durability with cycling At operating temp ≤80°C	hours	~2000 ^d	2000	5000 ^e	5000 ^e
At operating temp >80°C	hours	(not avail. ^f)		2000	5000 ^e
Unassisted start from	°C	-20	-30	-40	-40
Thermal cyclability in presence of condensed water		Yes	Yes	Yes	Yes

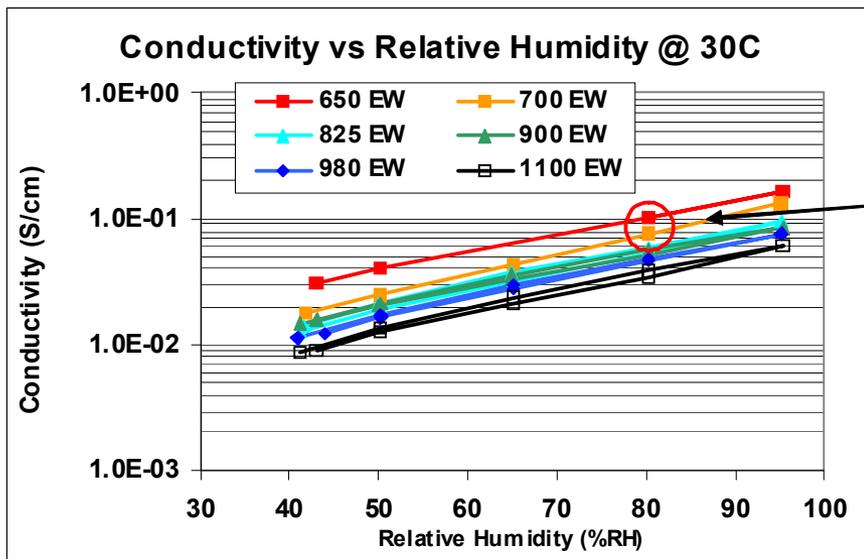
Project Approach

- New polymers, fluoropolymers, non-fluorinated polymers and composite/hybrid systems with increased proton conductivity and improved chemical and mechanical 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, single fuel cells and short stacks using realistic automotive testing conditions and protocols.
- 2008/2009 Milestones
 - **Q1 2008:** 3M will develop new test methods and install and modify new equipment as appropriate. Screening of new materials will be underway.
 - **Q3 2009:** 3M will identify a first set of new, more conductive and durable materials.

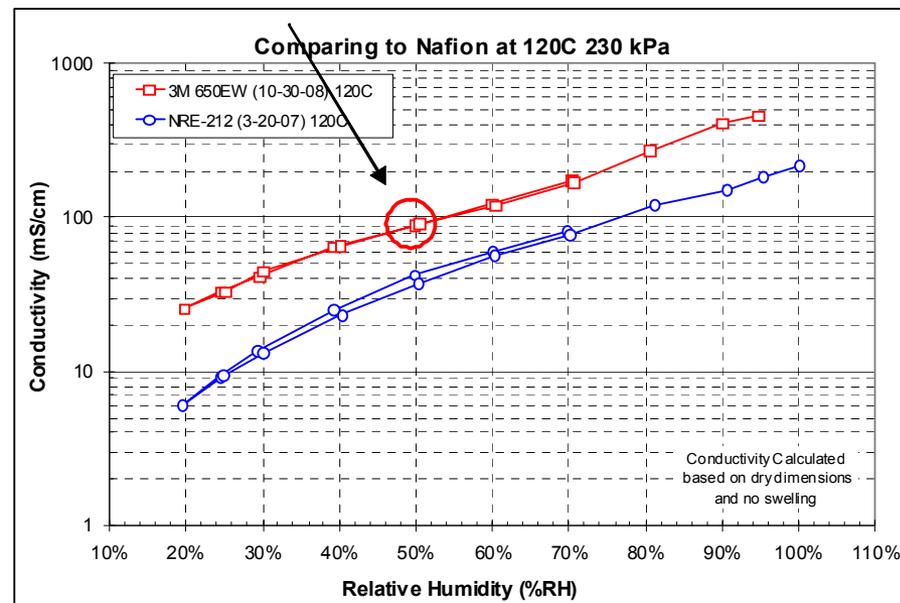
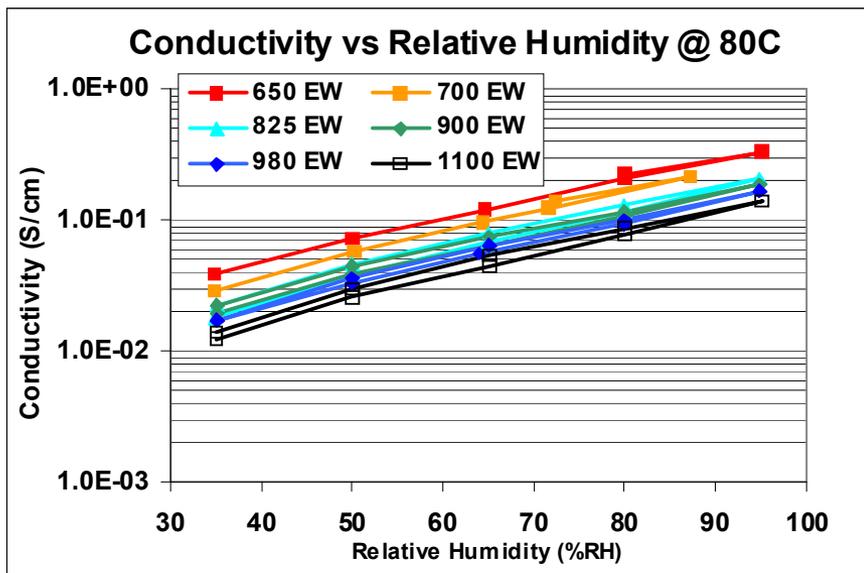
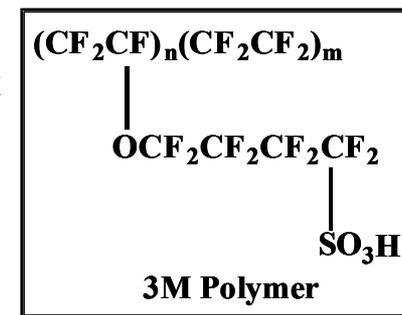
Collaborations – Flow Of Samples And Information



Conductivity w/ Low EW

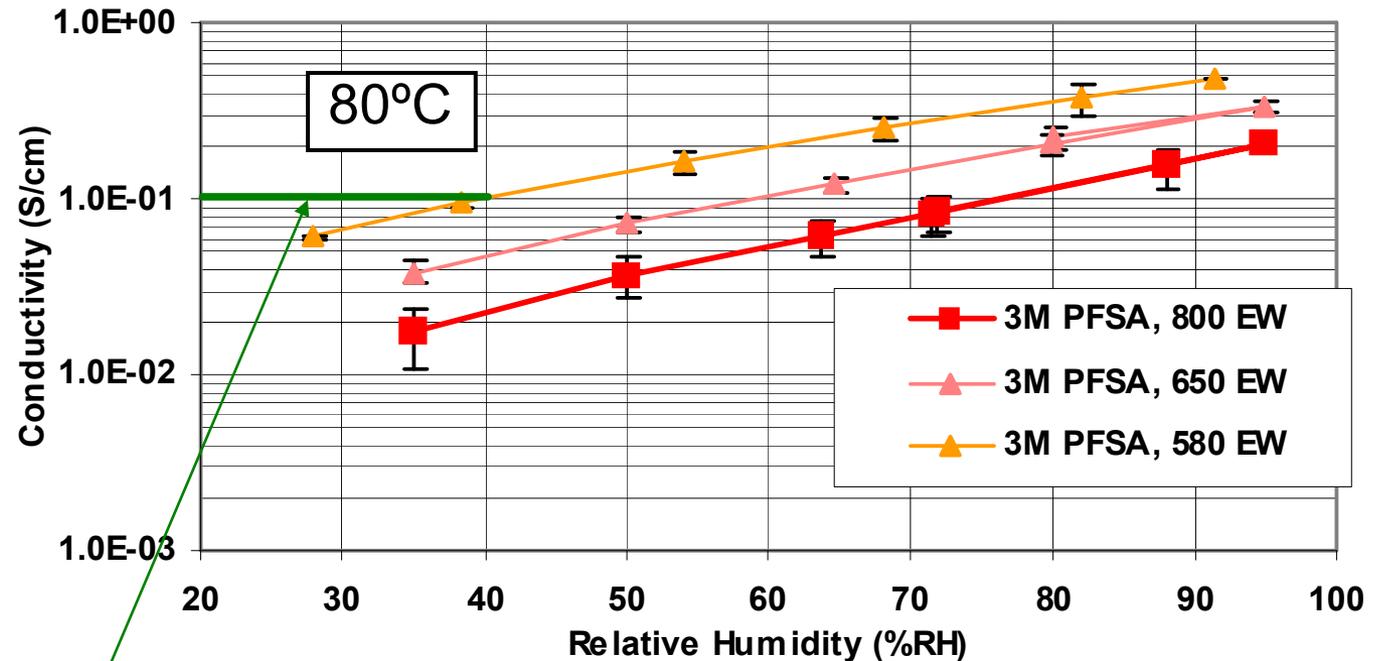


- Conductivity vs. temperature for EW ionomers in 640 – 1100 EW range.
- The 2 lowest EW ionomers shown, 650 and 700 EW, meets DOE milestone for RT conductivity (*ca.* 80 mS/cm at 80%RH, 25C).
- The 650 EW almost meets the 120°C interim milestone (*ca.* 93 mS/cm at 120°C, 50%RH)



Going To Even Lower EW's (<600) Can Provide Conductivity That Meets The DOE 2010/2015 Conductivity Targets At 80°C

- EW's below about 600 will meet conductivity requirements at 80°C, even at 40% RH.
- The conductivities at these very low EW's are slightly higher than expected.

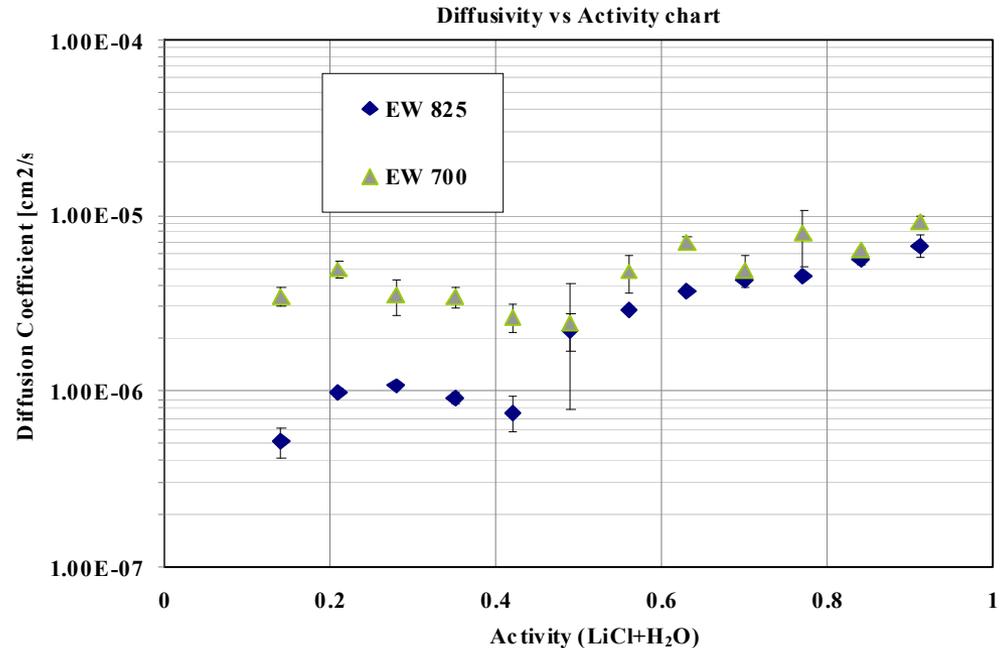
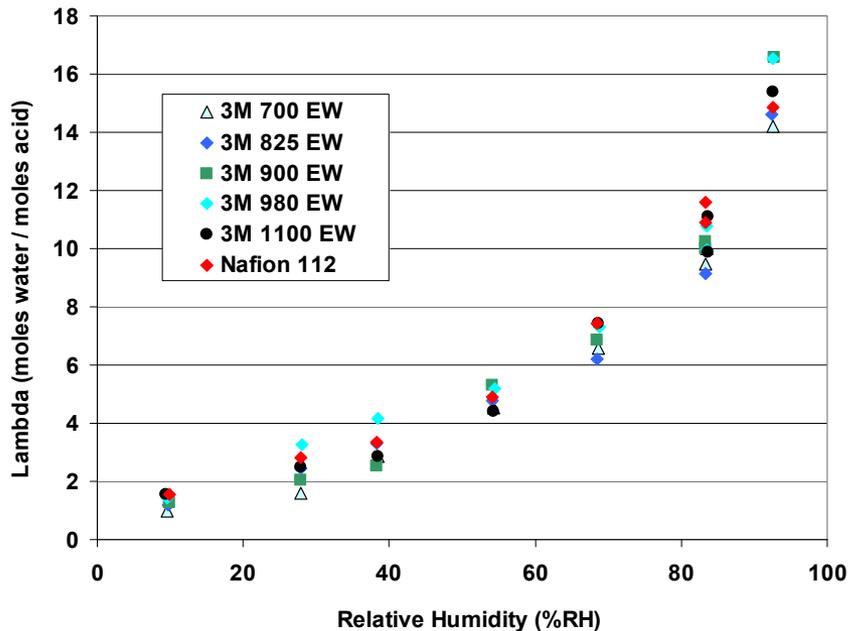


Target %RH

Transport Pathways

- Probed by NMR Diffusion and Relaxation Studies
- Plot shows Diffusion Coefficient vs. Water Content for two samples
- D levels off at low water content; significantly higher for 700 EW than for other PFSA samples to date

Lambda at 80C

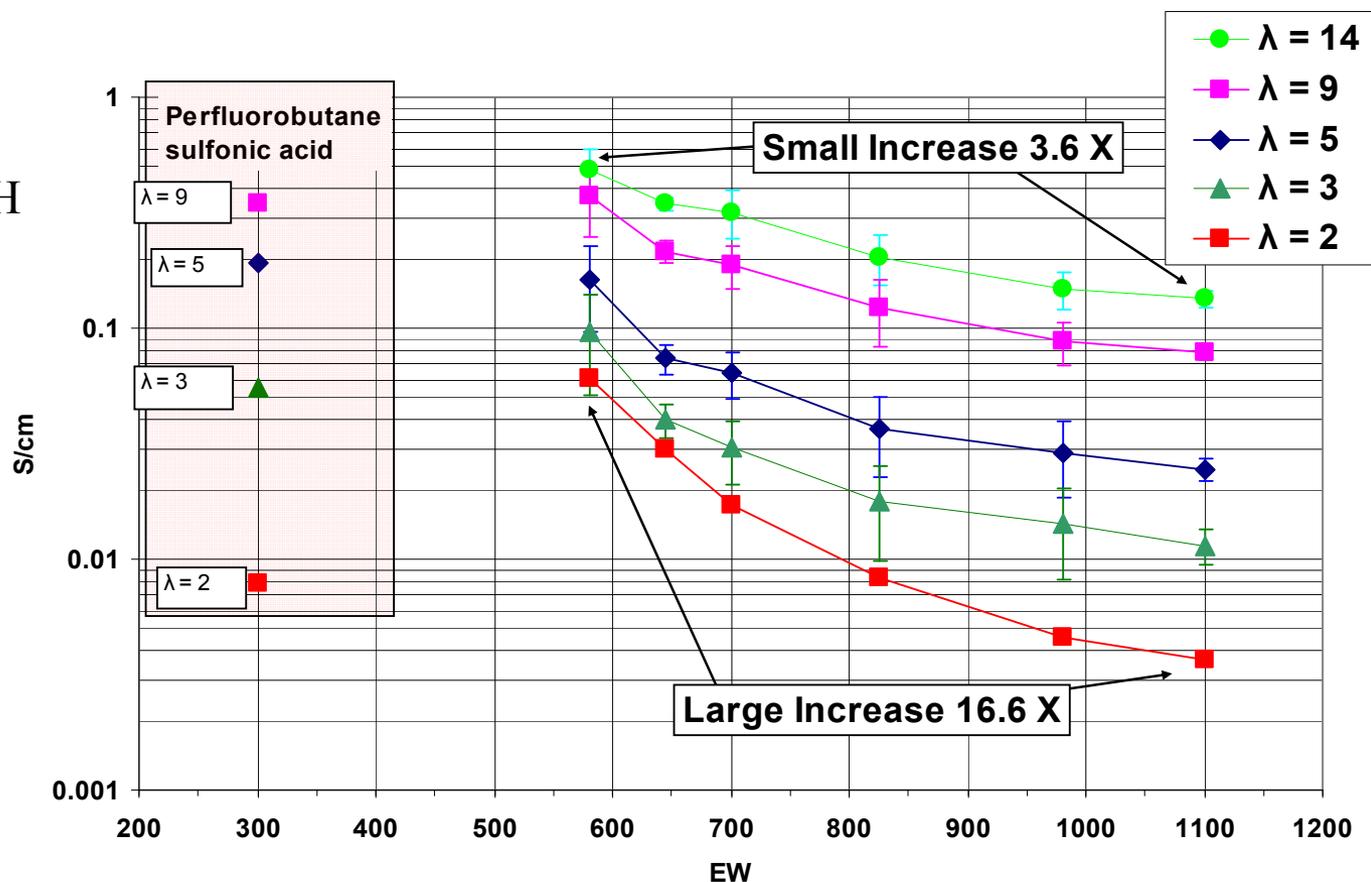


In the range from 700 to 1100 EW, these polymers show similar water absorption at 80°C.

Tortuosity or Intrinsic Interactions?

In- Plane Conductivity At 80°C

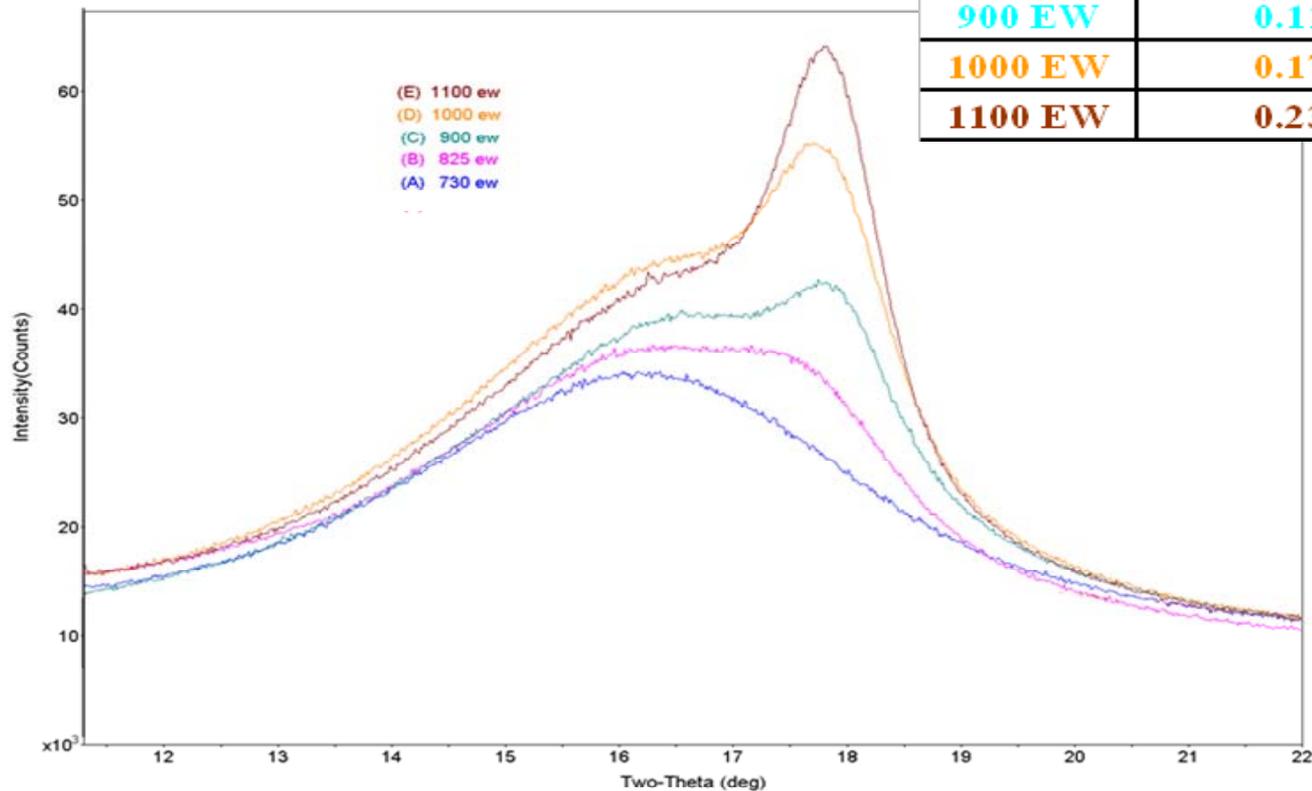
- At lower % RH or λ , the conductivity increases by a much larger factor when the EW is lower compared to the more humidified state.
- This is consistent with the hydrated acid groups being more accessible to one another in the lower EW ionomer, allowing proton transport even with little or no “free”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



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



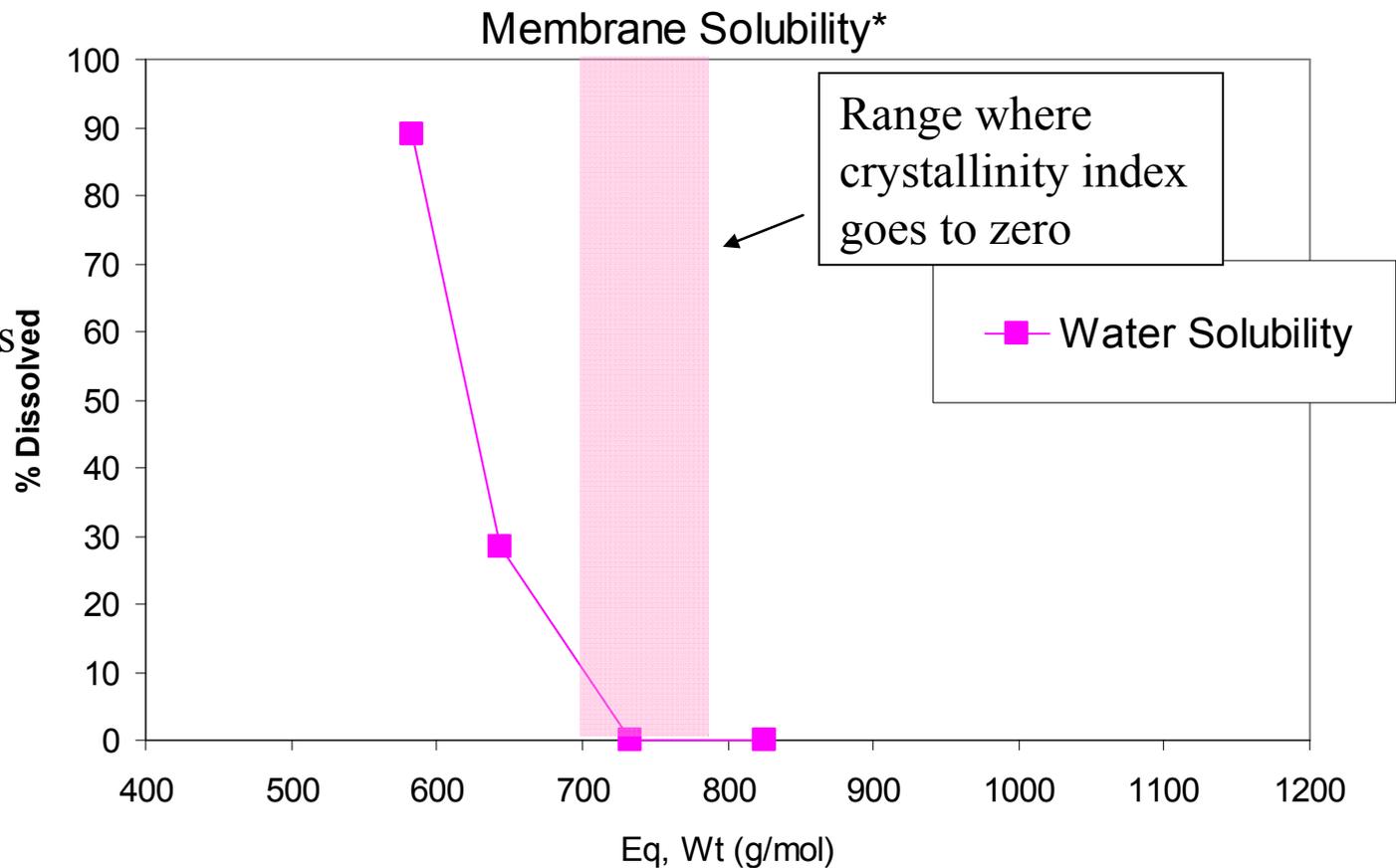
3M CRAL

- 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

- Solubility is determined by boiling, filtering an aliquot of filtrate, and determining fraction of membrane “dissolved”.
- Solubility starts near where crystallinity is gone.
- Many mechanical properties parallel this effect

Understanding “true” solubility helps defining possible mechanical stabilization methods

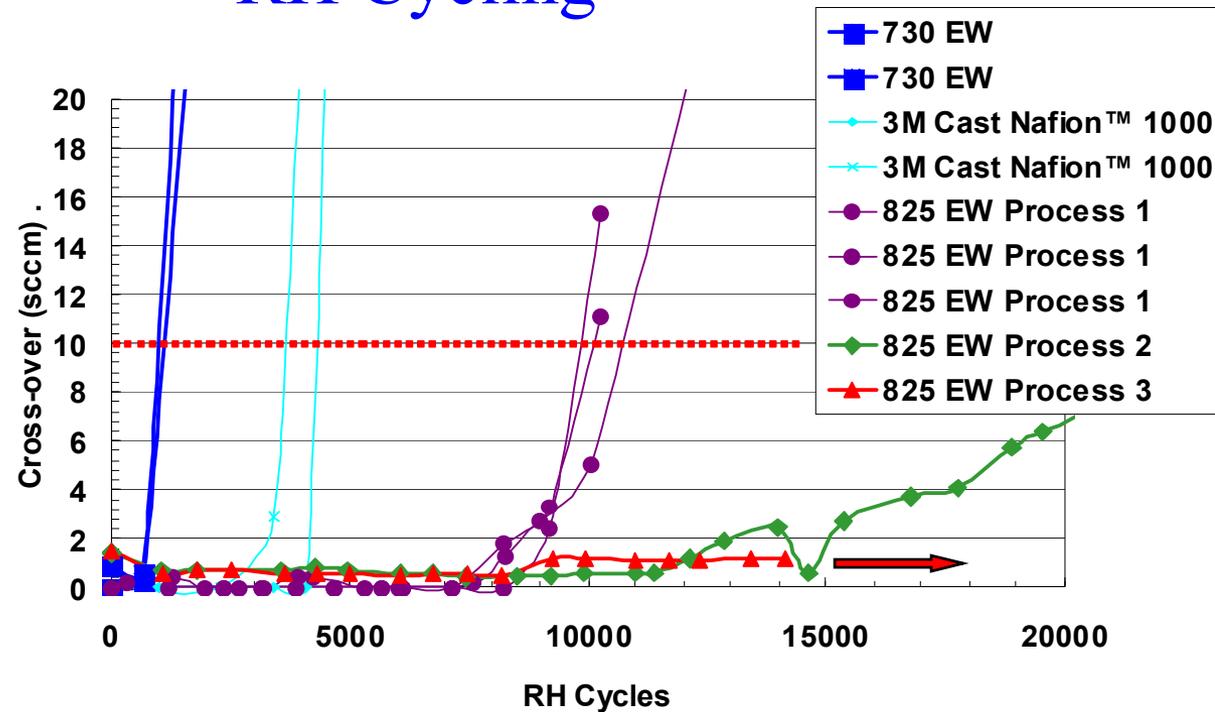


* Can vary w ith process conditions

RH Cycling

Low EW ionomers do poorly in humidity cycle testing.

Performance of 825 EW depends on membrane processing conditions.



Cell Build: 50 cm² 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

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

Some possible solutions:

blends

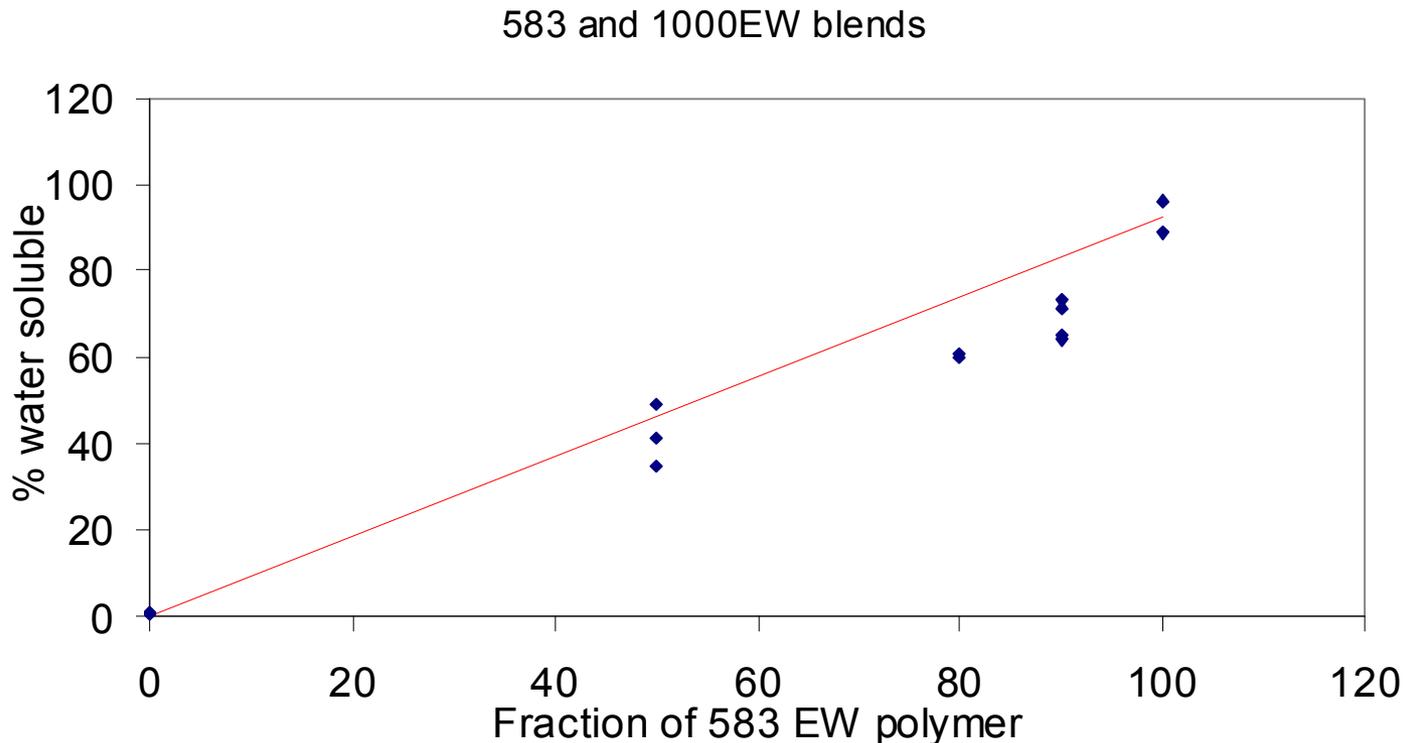
crosslinking

reinforcement

polymer modifications

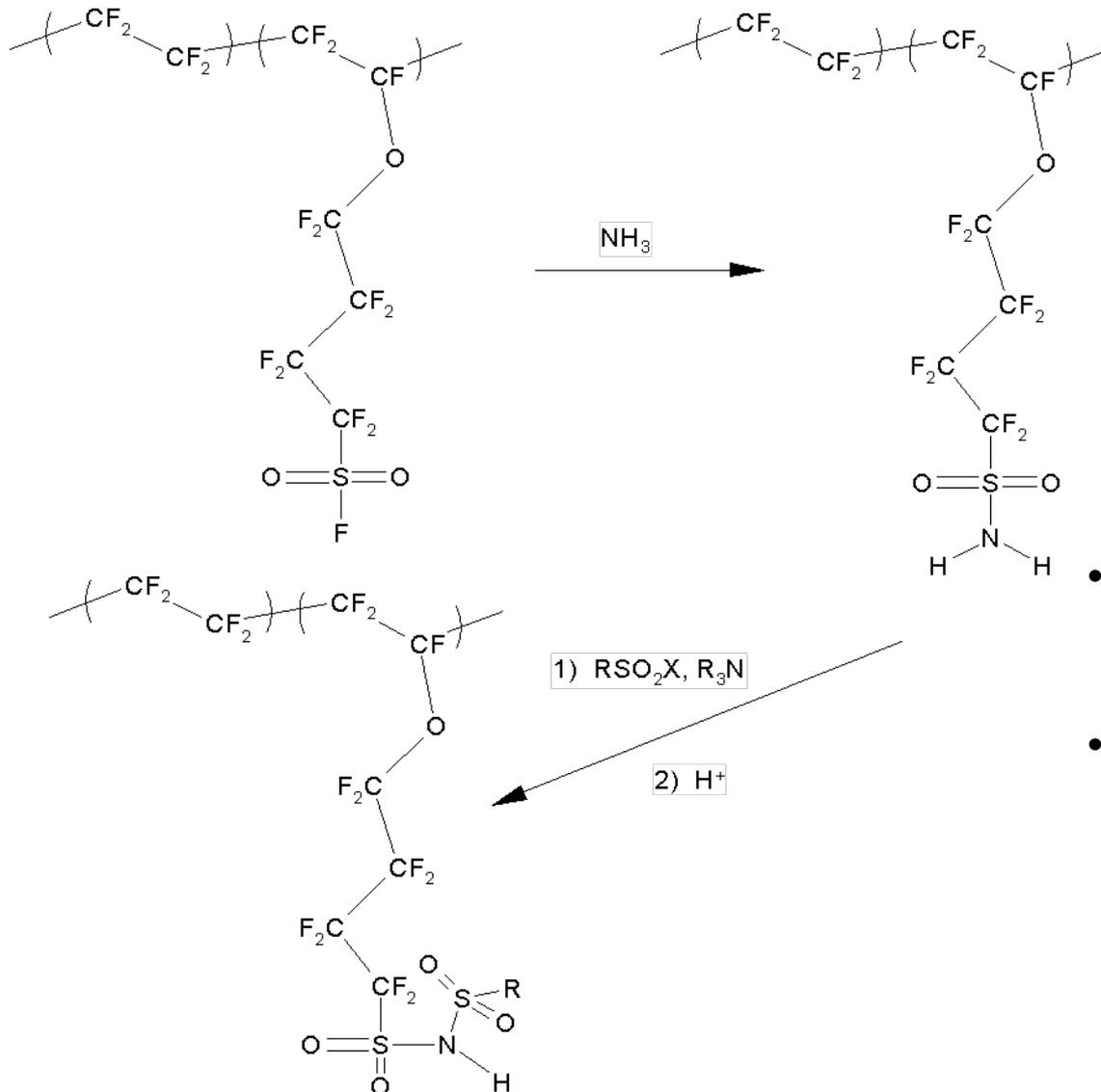
We are looking at all of these

Blends of Water Soluble and Insoluble Ionomers



- In miscible blends of soluble and insoluble ionomers there is little to no evidence of the insoluble ionomer captivating the soluble ionomer.
- We are still evaluating blends with not-so-low EW ionomers and high EW ionomers or non-ionic polymers.

Polymer Modification – one approach

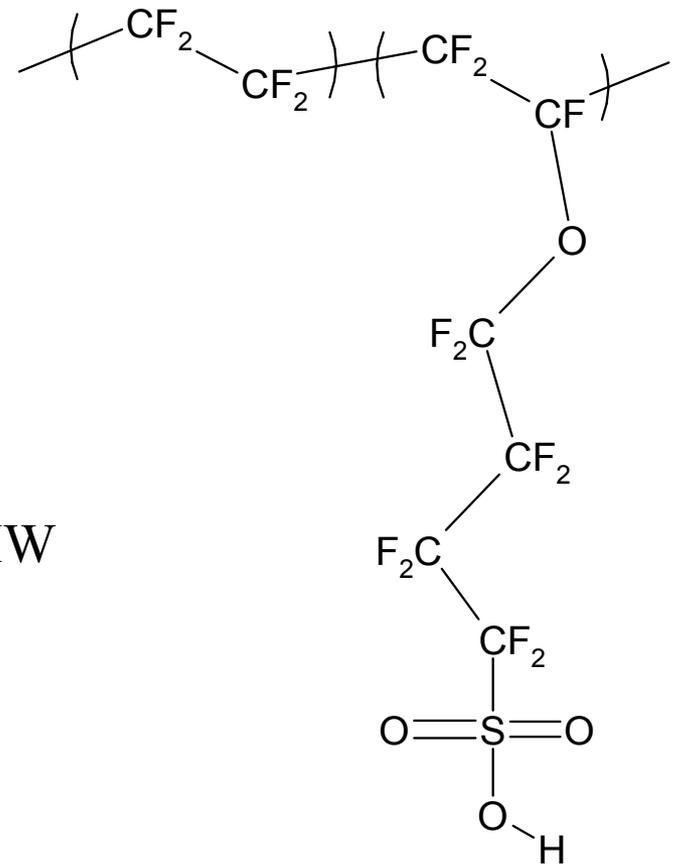


- Bis-sulfonyl imides are very chemically stable and highly acidic.
- Aromatic R groups can be substituted with additional functionality for stable cross-linking and/or adding additional acid groups including HPA's.

- Changing the nature of the acid group

Sulfonic acid

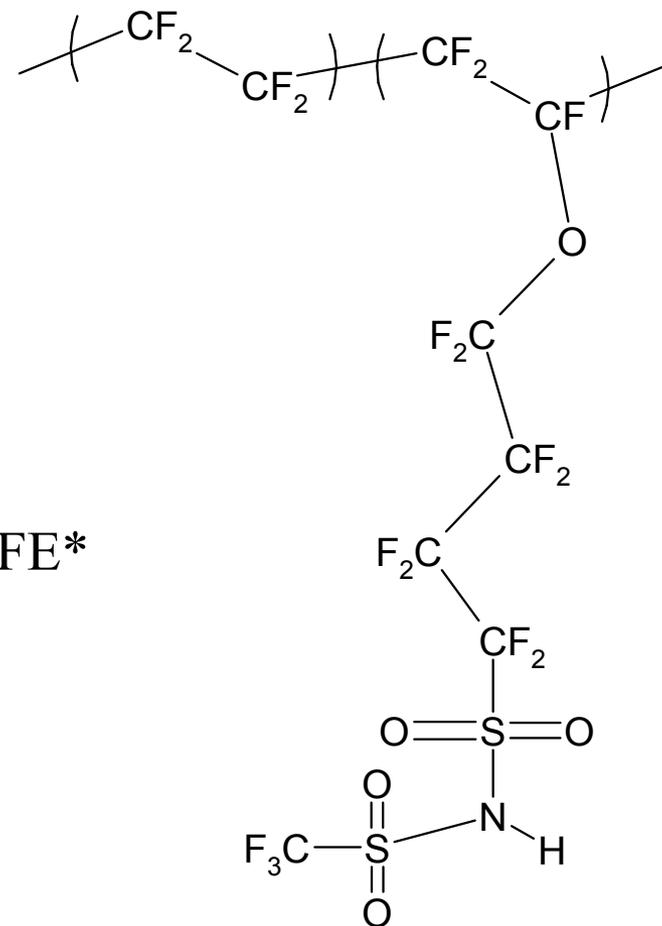
- Lowest EW limited by monomer MW



- Changing the nature of the acid group

Perfluoro imides

- Similar polymers prepared at Clemson via polymerization of imide monomers with TFE*
- Stronger acids than sulfonic acids



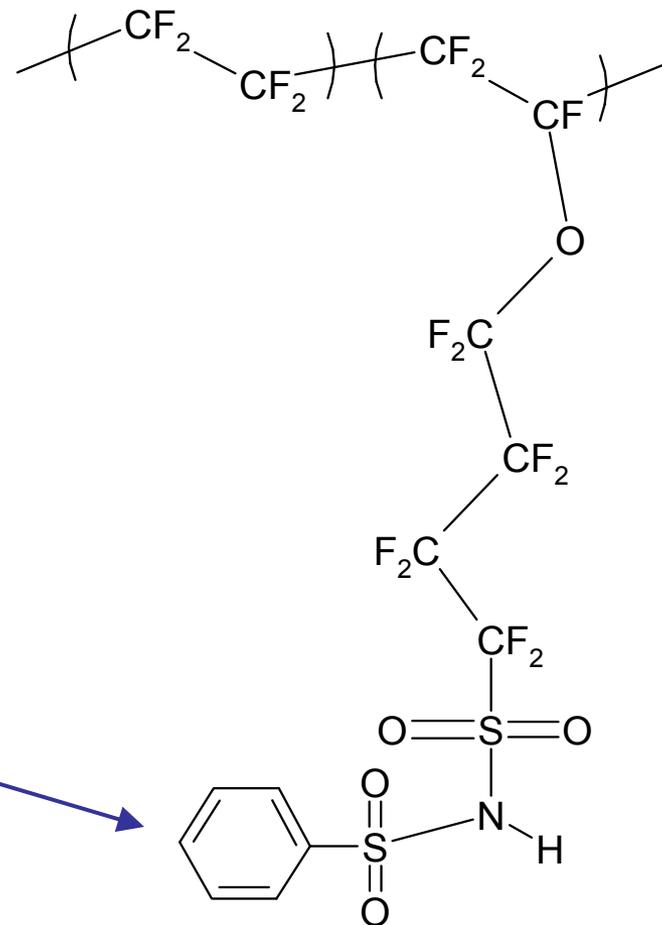
* Creager, S.E *et.al.*, *Electrochem. and Solid State Lett.* **2**(9) 434-436 (1999)

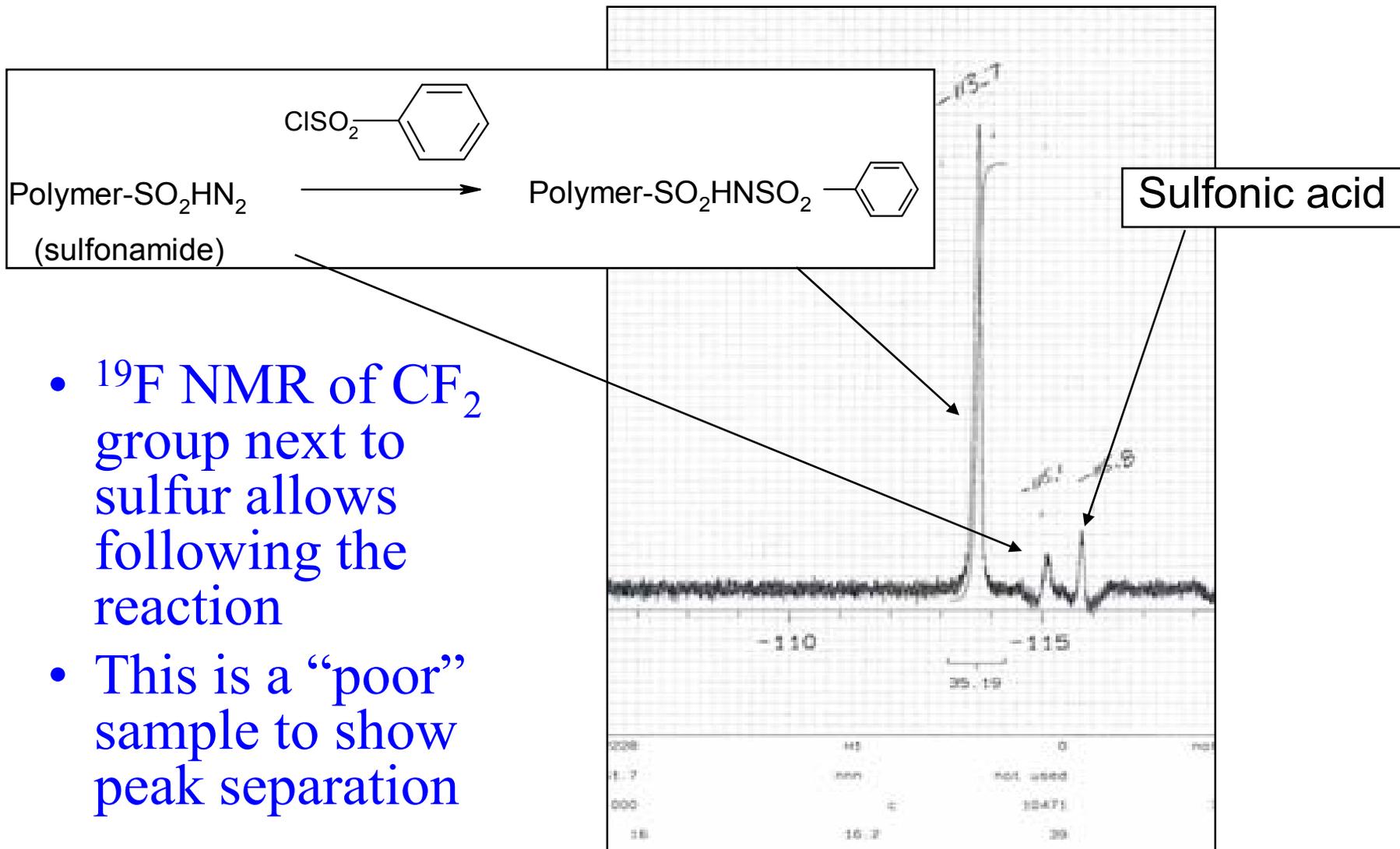
- Changing the nature of the acid group

Aromatic imides

- Useful synthetic handle
- Similar pKa to sulfonic acids
- Very hydrolytically stable in aqueous acid at elevated temperatures

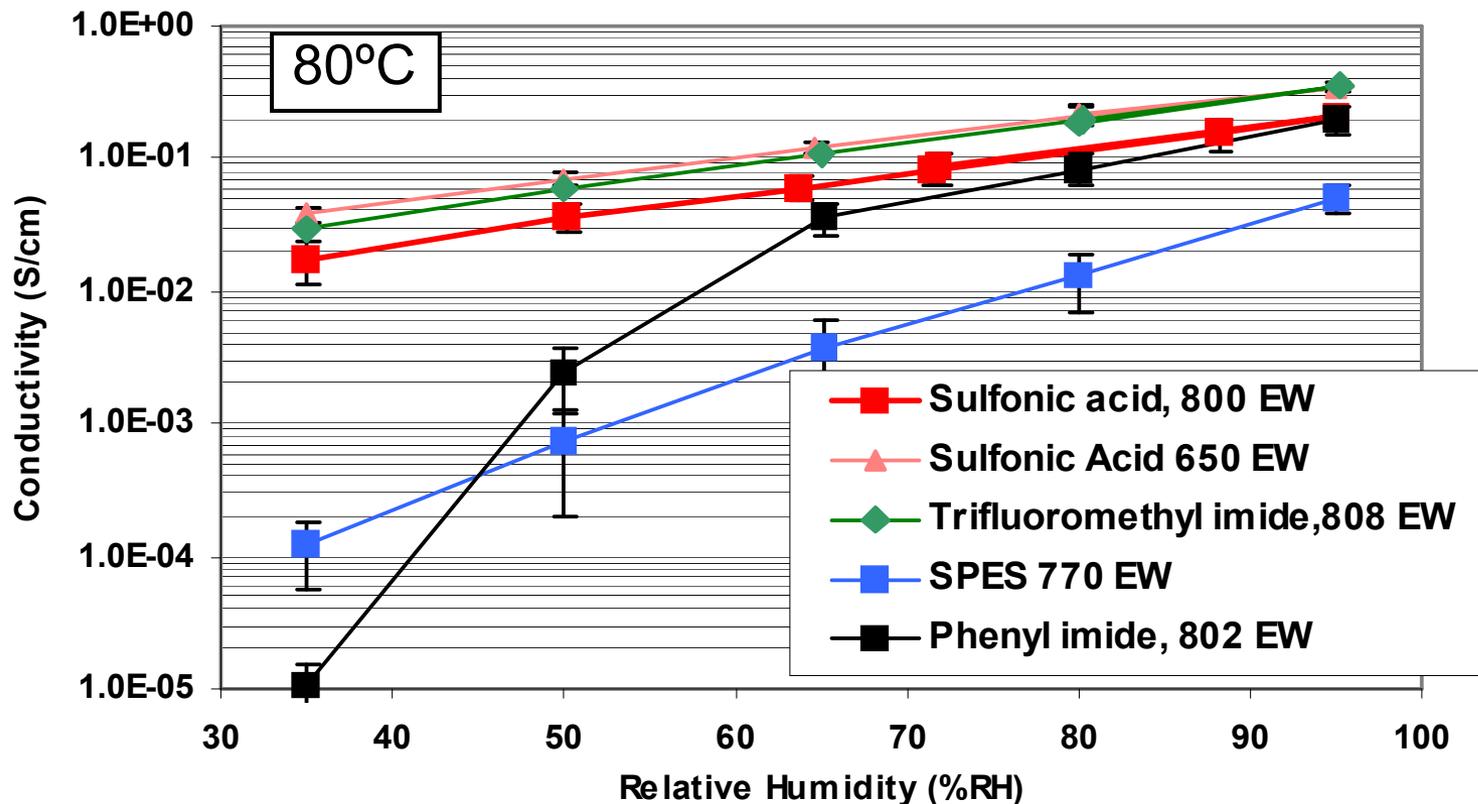
Our interest is using this as a synthetic handle for attachment of additional protogenic groups, cross-links, etc.





New Protogenic Groups

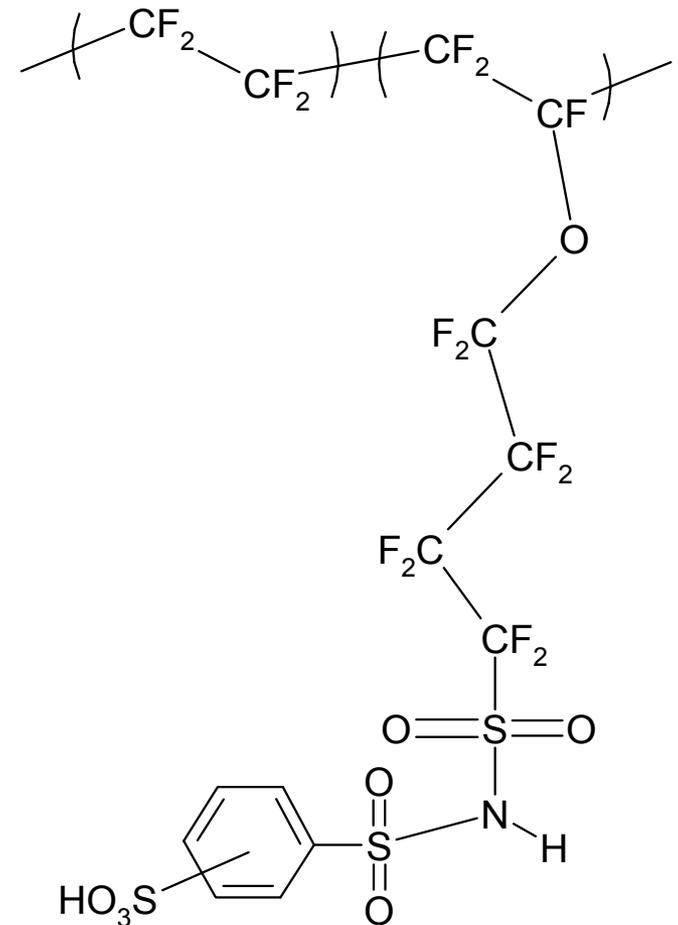
- Conversion of a 650 EW sulfonyl fluoride to the trifluoromethyl imide provided a 808 EW ionomer. The conductivity remained the same (stronger acid but higher EW) as the sulfonic acid
- Conversion of the same sulfonyl fluoride to the an 802 EW phenyl imide resulted in lower conductivity at lower %RH.



- Changing the nature of the acid group

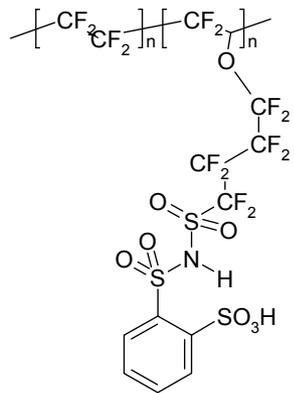
Aromatic imides

- Multiple acid groups
- Two examples have been prepared

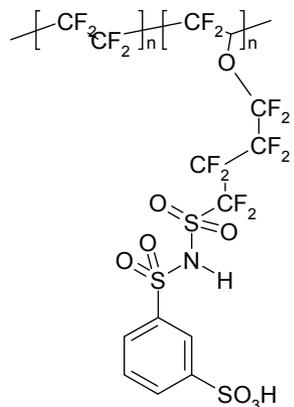


Multiple Acid Groups On A Single Side-chain

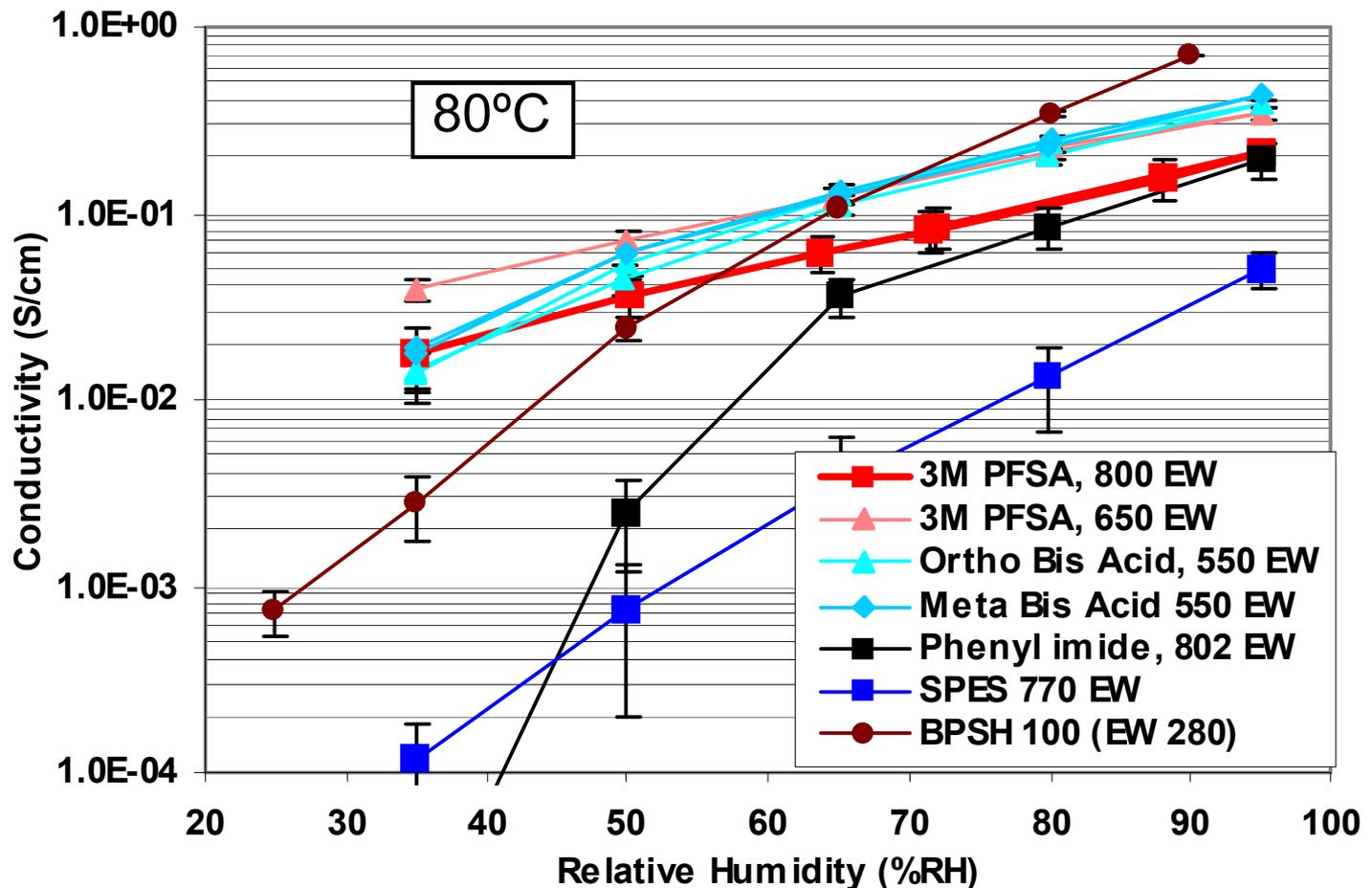
- Multiple acid groups allow raising the conductivity of starting ionomer
- 800 EW starting PFSA precursor with crystalline backbone can be used to make low EW ionomer with higher conductivity.
- These swell much less in liquid water than the PFSA's with the same EW



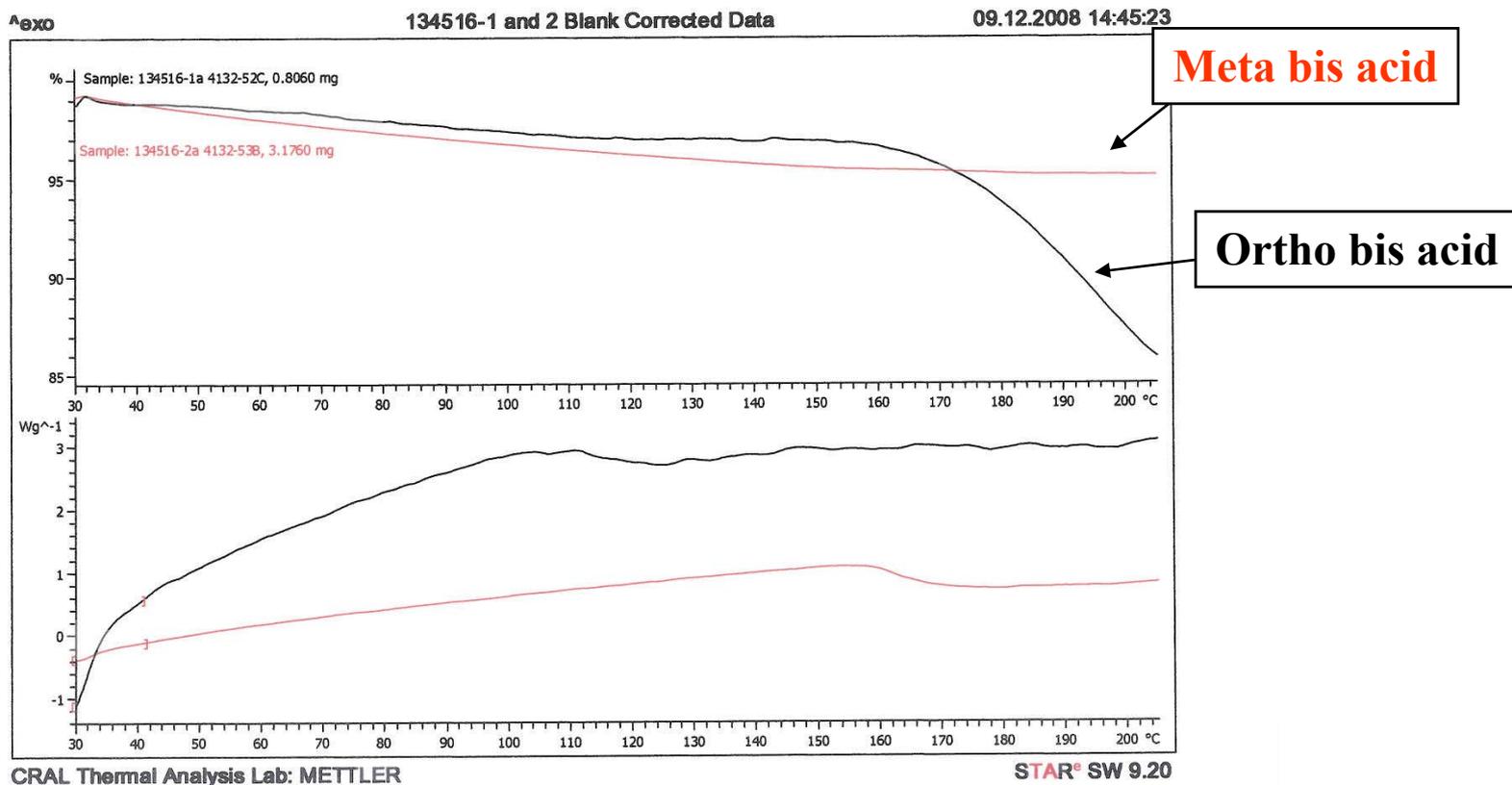
Ortho bis acid



Meta bis acid



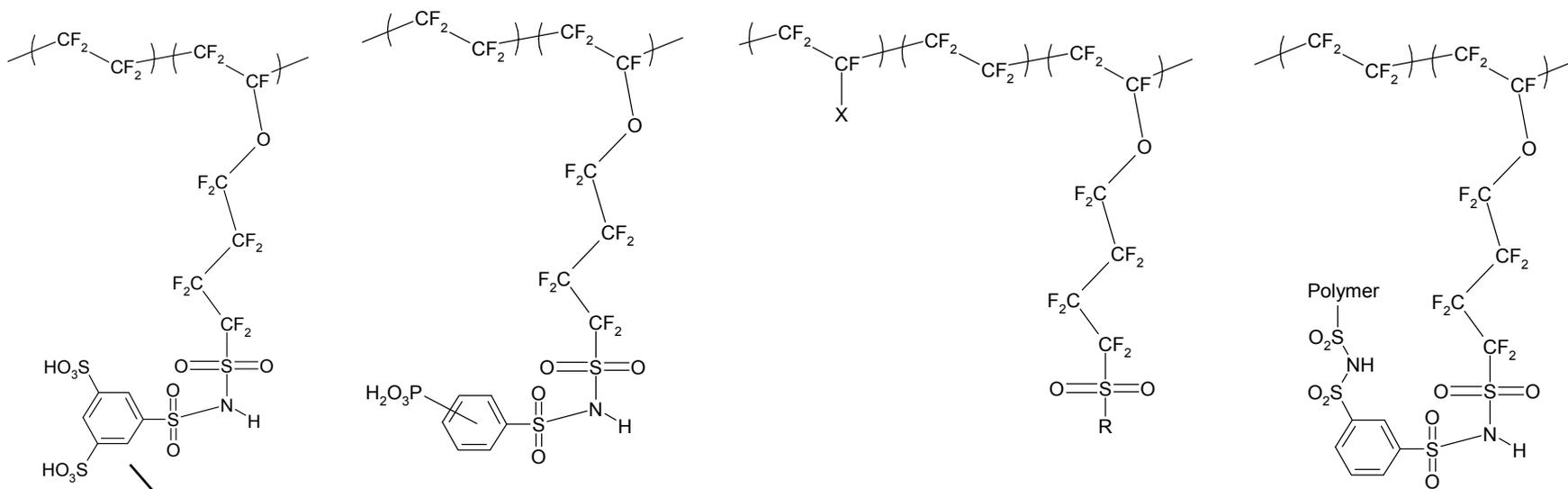
Thermal Gravimetric Analysis



- As is the case with di-sulfonated aromatics, the ortho substitution is less thermally stable than the meta.
- Neutralized samples have much better stability.

Future Work - Other Polymers Are Being Prepared And Evaluated For:

- Adding higher levels of acid groups, sulfonic or inorganic (HPA)
- Impact of imide on morphology
- Cross-linking through multi imide groups, backbone or Zr phosphonate linkages

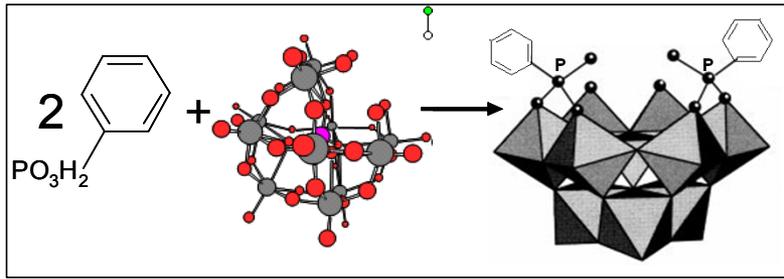


R= OH or imide

Attach sulfonated oligomers and/or polymers

Phenylphosphonate Attached to SiW₁₁ Keggin Imide sidechains

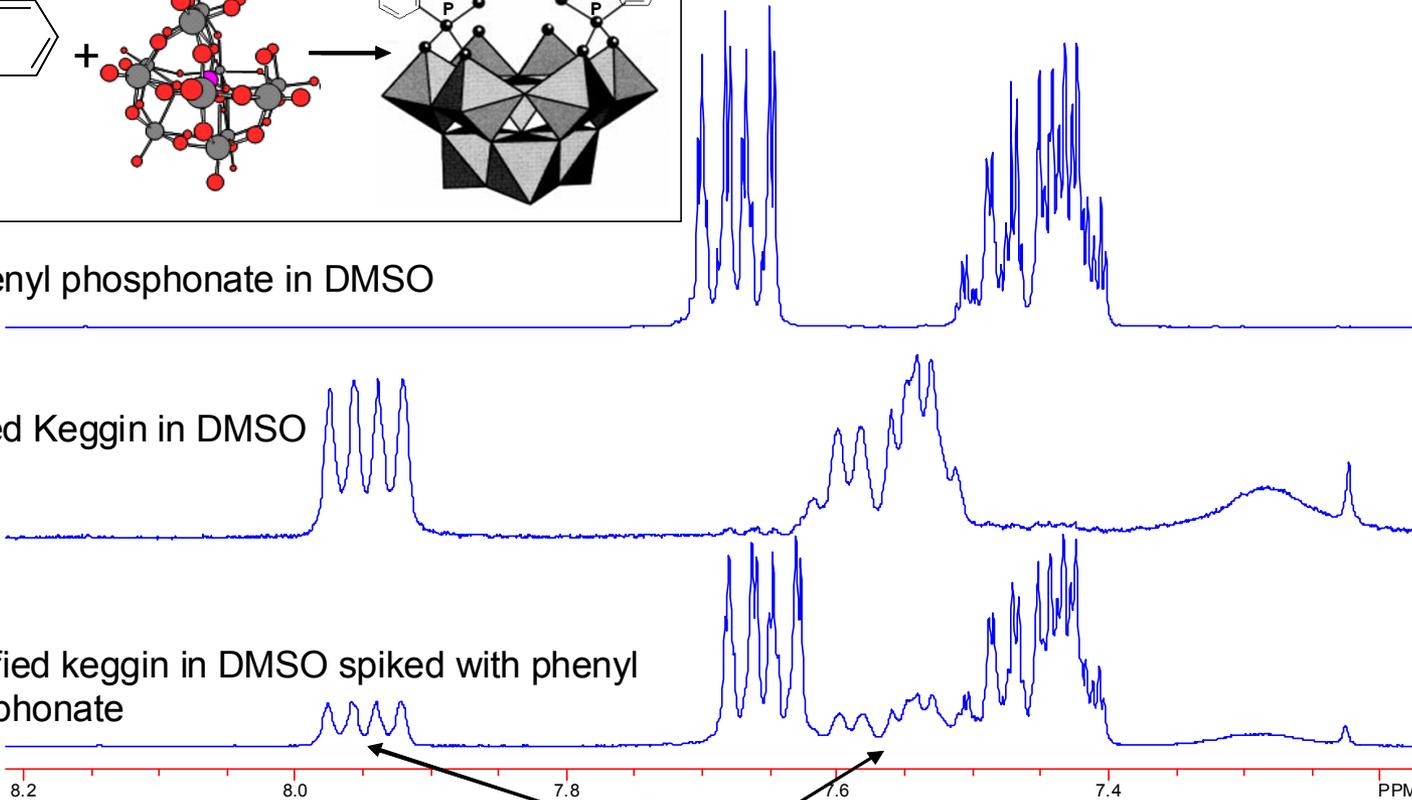
Aromatic phosphonates attach to lacunary HPA's, potentiality allowing immobilization.
Membranes must be stable to liquid water!



Phenyl phosphonate in DMSO

Modified Keggin in DMSO

Modified keggin in DMSO spiked with phenyl phosphonate

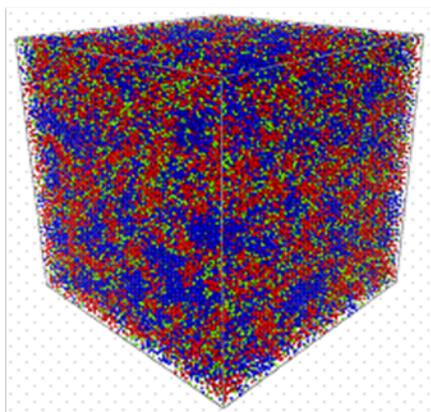


Linewidth differences indicative of slower rotating species (attached to keggin)

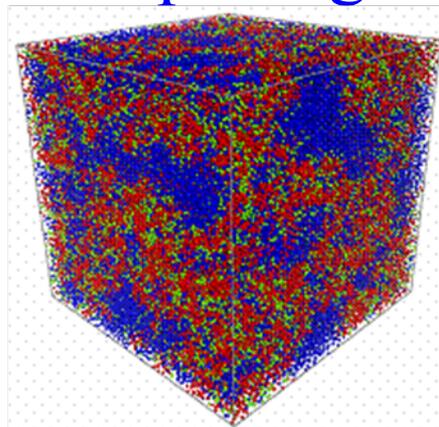
HPA's can increase proton conductivity and oxidative stability (AMR 2008)

Equilibrated morphologies: PFSA Chemistry

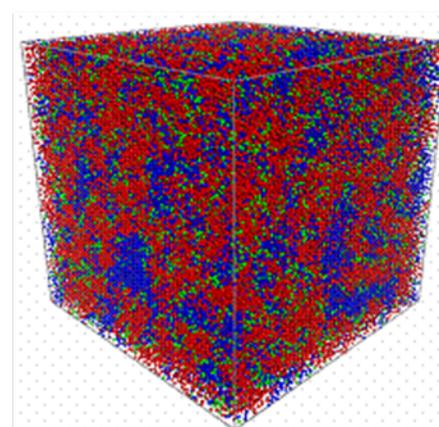
Polymer morphology



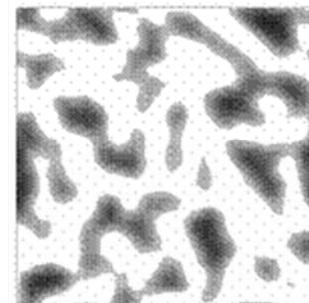
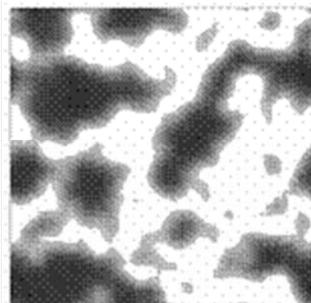
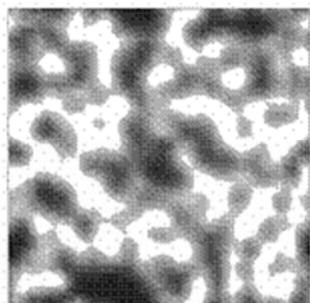
SSC, EW = 678



3M, EW = 678



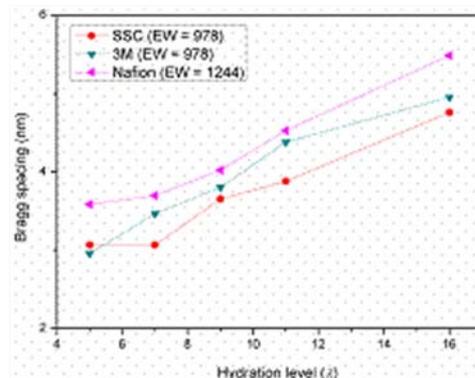
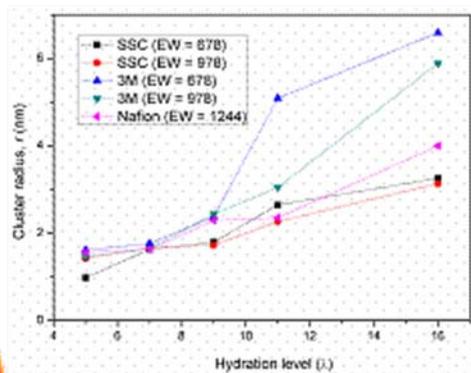
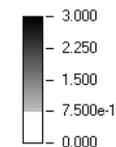
Nafion™, EW = 1278



Simulation Box
(32 nm)³
(PTFE in red,
-CF₂SO₃⁻ green
and water in blue)

$$\lambda = 16$$

(Water density)



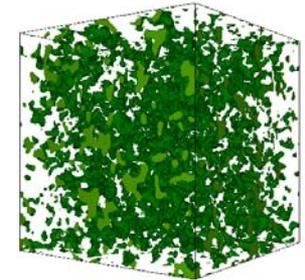
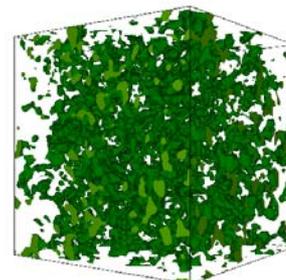
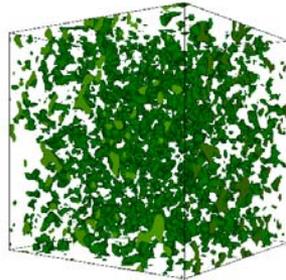
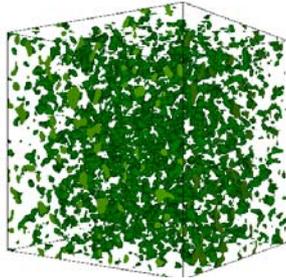
- These mesoscale DPD simulations are able to capture differences in the hydrated morphology as both EW and monomer chemistry is changed.
- At the same EW and water content, the water domains in the 3M ionomer are larger and to some extent less connected than in the SSC ionomer.



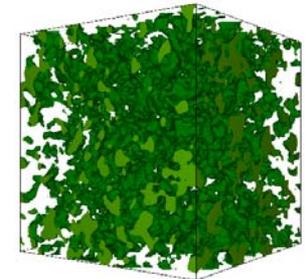
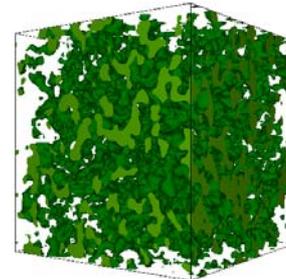
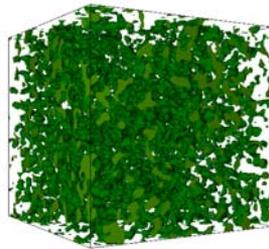
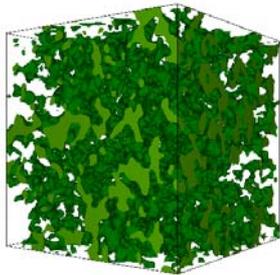
Representative Morphologies from analysis of SAXS data



Dry



Boiled



733 EW

825 EW

900 EW

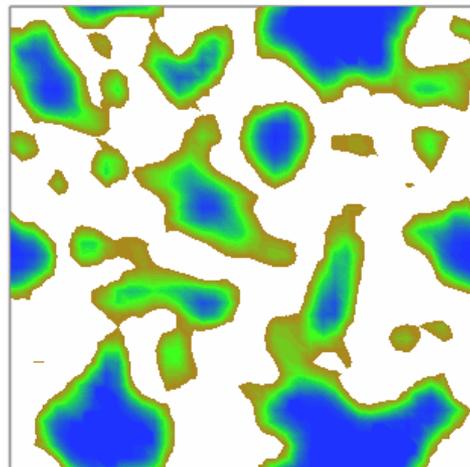
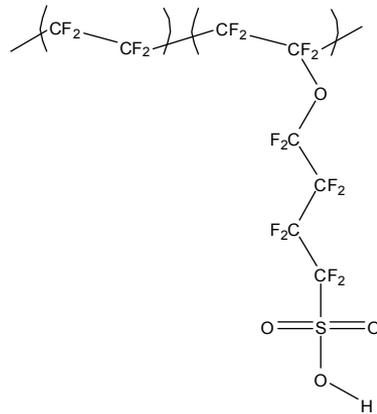
1082 EW

SAXS analysis shows structure which appears similar to mesoscale DPD simulations

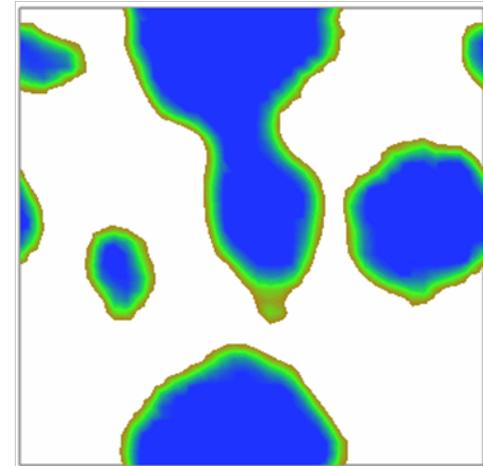
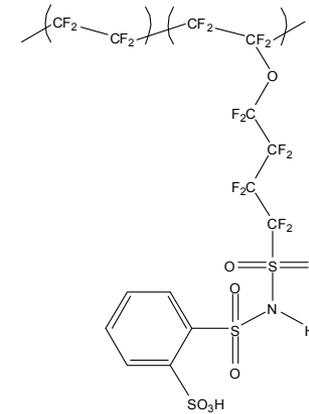


Water contour plots from simulations - Effects of the protogenic group on hydrated morphology

- Initial simulations have been done on the Ortho-bis acid with an EW of 450 and 600.
- Mesoscale DPD modeling suggest that polymer with an imide sidechain bearing 2 acidic protons may have a quite different structure



3M PFSA
EW = 678, $\lambda = 15$



3M PFSulfonylimide
EW = 450, $\lambda = 7.5$



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

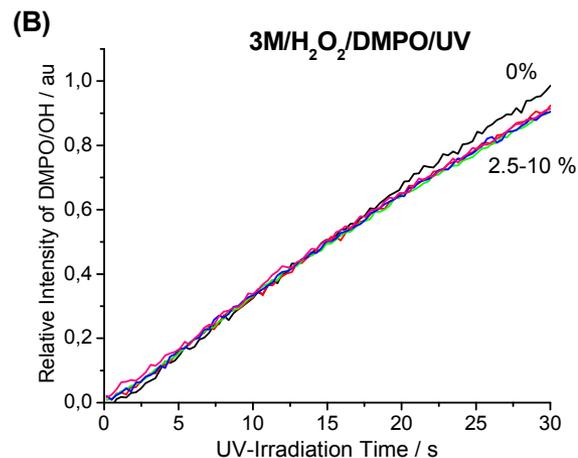
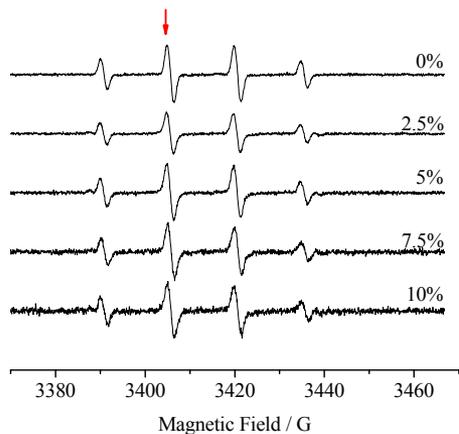
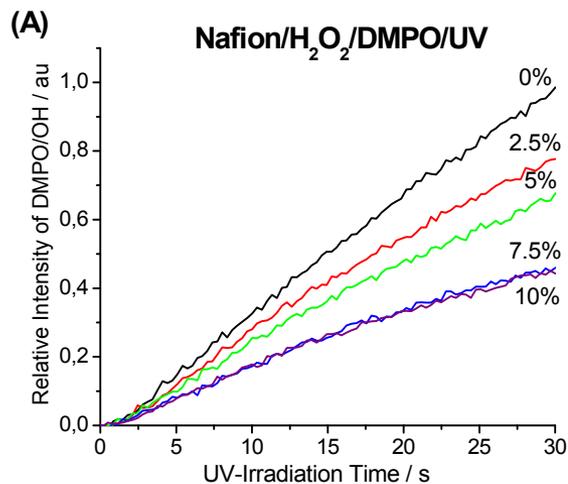
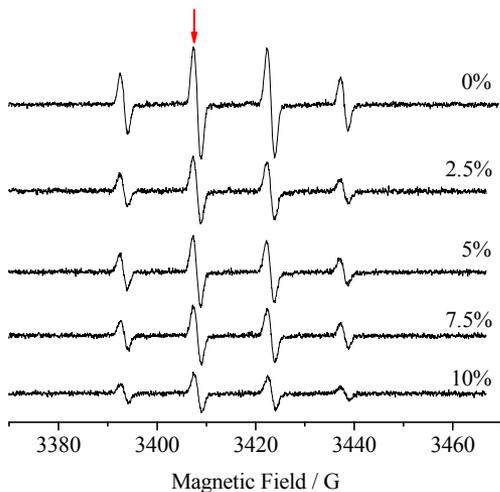


The formalism of
“parallel reactions”
leads to the expression:

$$\frac{V}{v} - 1 = \frac{ka[a]}{k_{\text{DMPO}}[\text{DMPO}]}$$

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

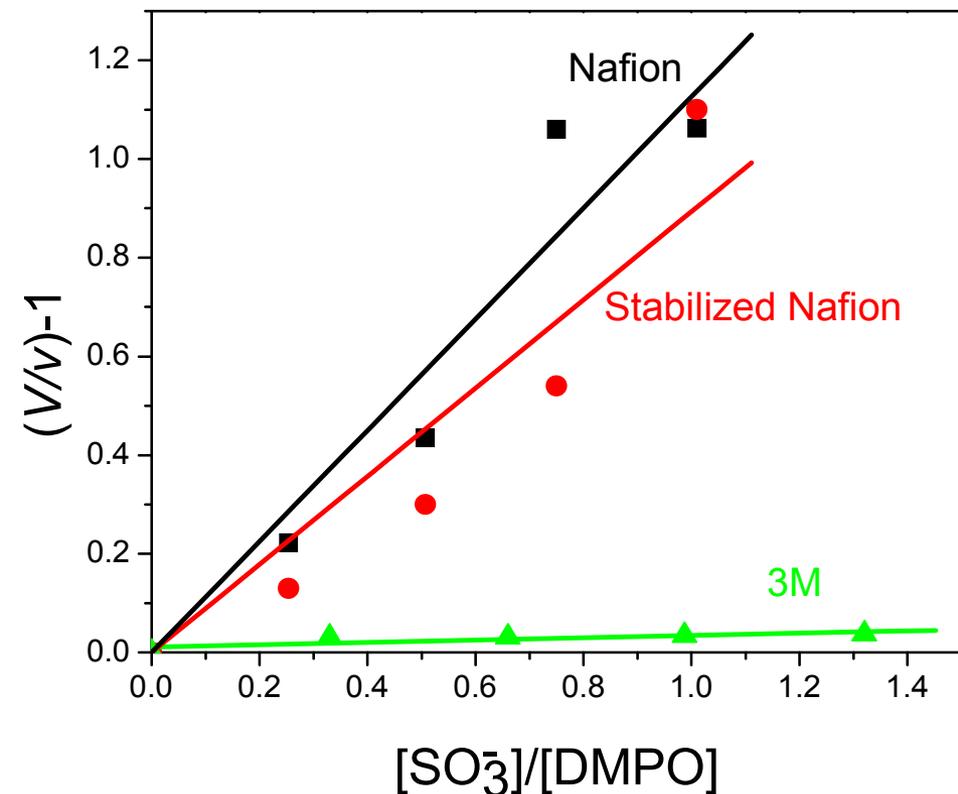
Competition by Perfluorinated Membranes



Inhibition of DMPO/OH formation by the different membrane concentrations (0-10%) in Nafion[®] (A) and 3M membrane (B). [DMPO]= $9 \cdot 10^{-5}$ M, [H₂O₂]= $9 \cdot 10^{-3}$ M.

Downward red arrow on the left shows the ESR signal that was monitored as a function of irradiation time. The black line on the right is for the formation of the DMPO/OH adduct in the absence of membranes.

Reaction Rates of Nafion[®], Stabilized Nafion[®] and 3M



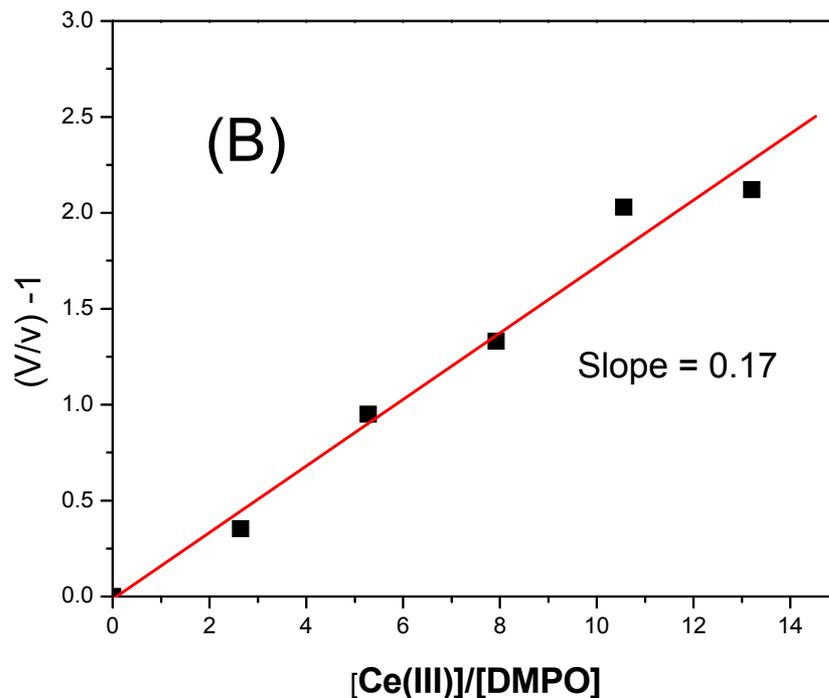
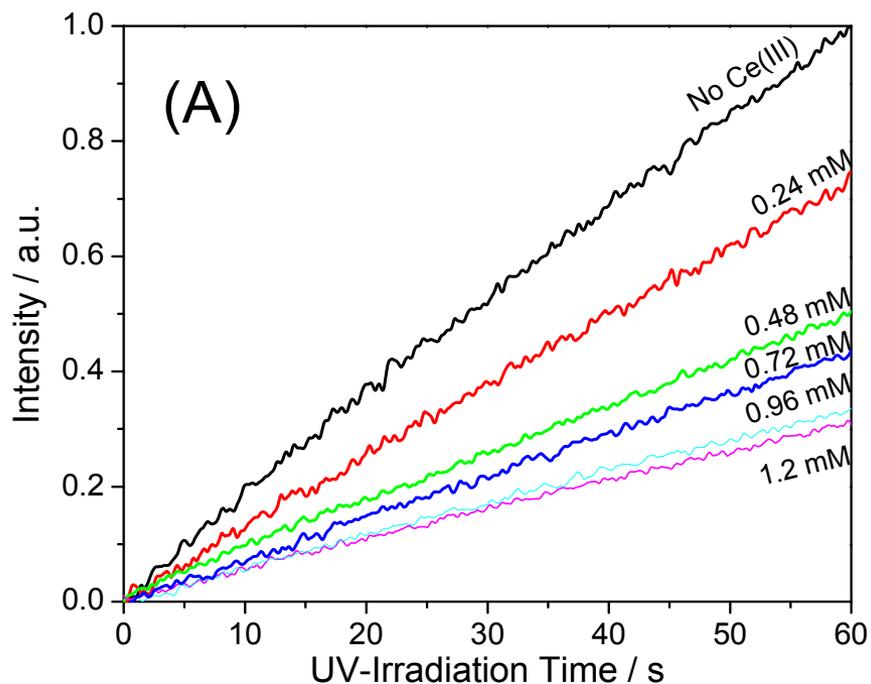
	Slope	$k_a \cdot 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$
Nafion [®]	1.124	4.0
Stab Nafion [®]	0.678	2.4
3M	0.034	0.17

$$k_a(3\text{M}) / k_a(\text{Nafion}^{\text{®}}) \approx 0.04$$

$$k_a(\text{S-Nafion}^{\text{®}}) / k_a(\text{Nafion}^{\text{®}}) \approx 0.6$$

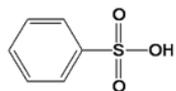
3M membranes appear more stable to attack by hydroxyl radicals compared to Nafion[®] and to stabilized (end group modified) Nafion[®]. We do not see such a large difference in longer term Fentons tests or fuel cell testing.

Ce(III) as Competitor

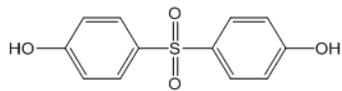


(A) Effect of Ce(III) addition on the formation of the DMPO/OH adduct in solutions (pH=5.3) containing the indicated Ce(III) concentrations. (B) Inhibition of DMPO/OH formation by addition of Ce(III). Slope = $k_{ce}/k_{DMPO} = 0.17$, $k_{DMPO} = 3.6 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ (deduced in competition kinetics with methanol as the competitor for hydroxyl radicals) and $k_{Ce} = 6 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$. This value can be compared with $k_{Ce} = 3 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$ quoted in Coms, F.D.; Liu, Han; Owejan, J.E. *ECS Transactions* **2008**, *16*, 1735-1747.

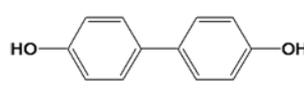
Model Compounds and Degradation Test Conditions



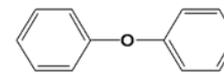
MC1



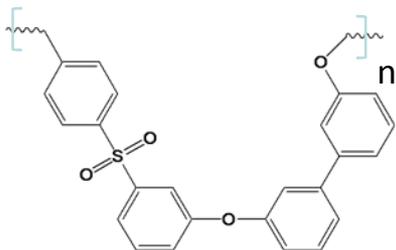
MC2



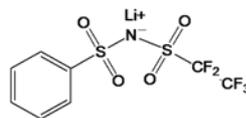
MC4



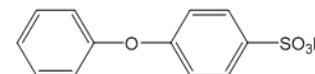
MC5



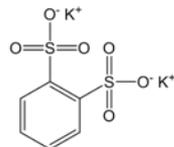
MC3



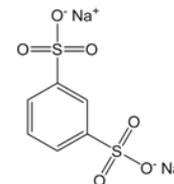
MC6



MC5-S



MC7



MC8

100mM MC + Solvent + 100mM H₂O₂ : exposed to UV light for 1hr

100mM MC + Solvent + 11mM H₂O₂ + 1.25mM Fe(II) : Fenton's degradation test

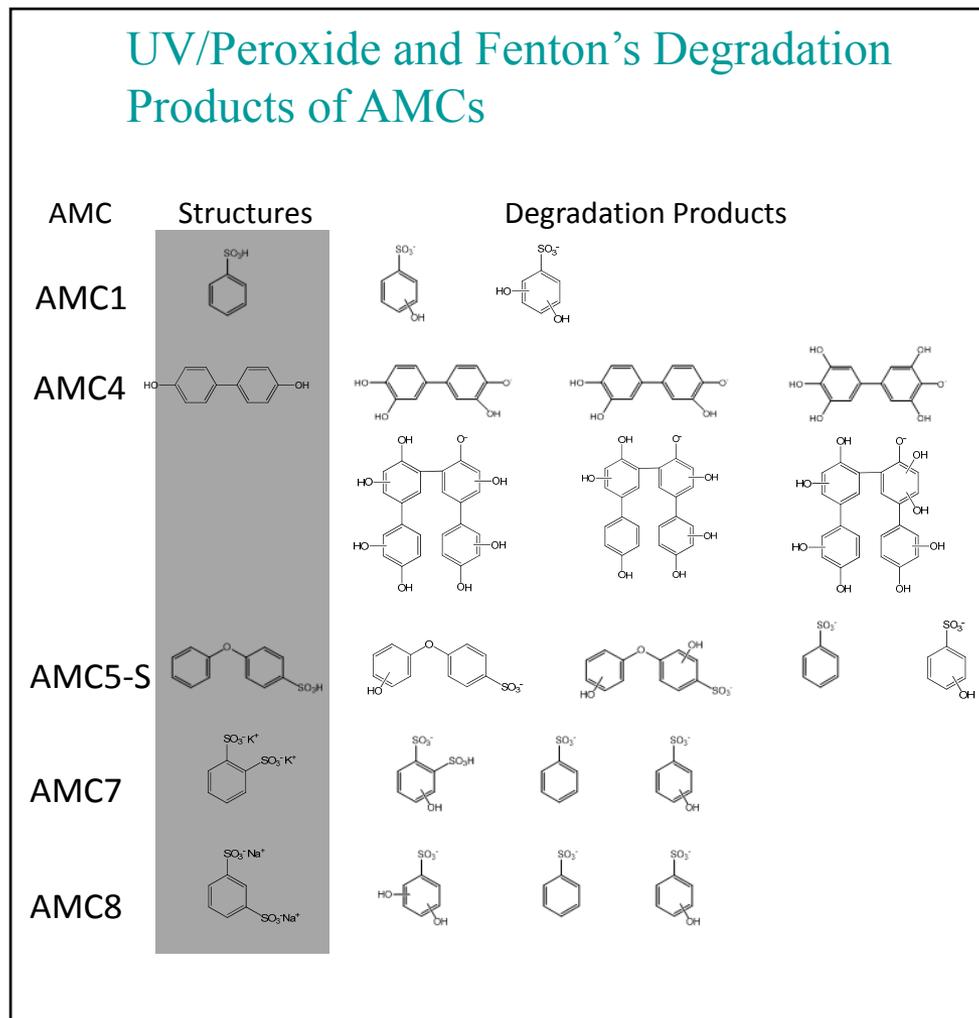
Technique: Liquid chromatography-Mass spectrometry (LC-MS)

Biphenyl Column

Negative-ion electrospray ionization MS

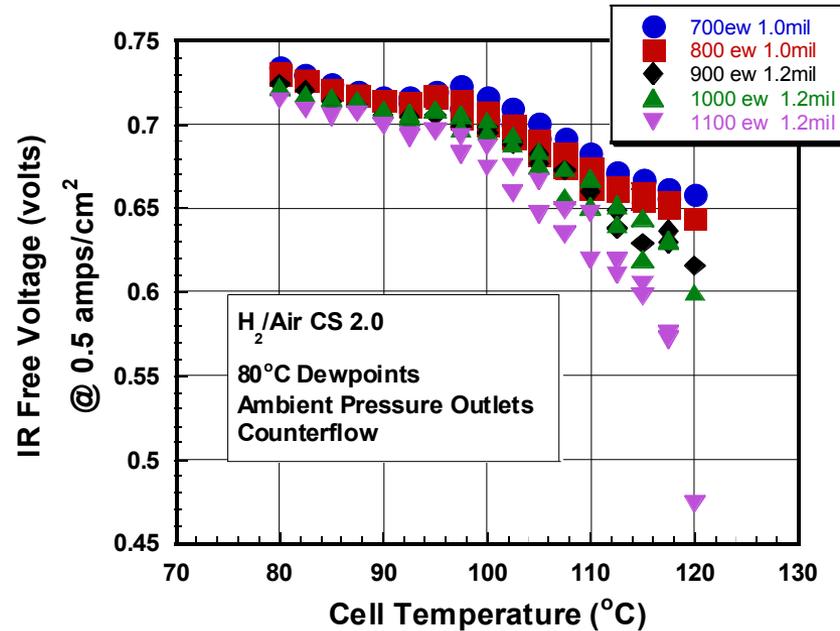
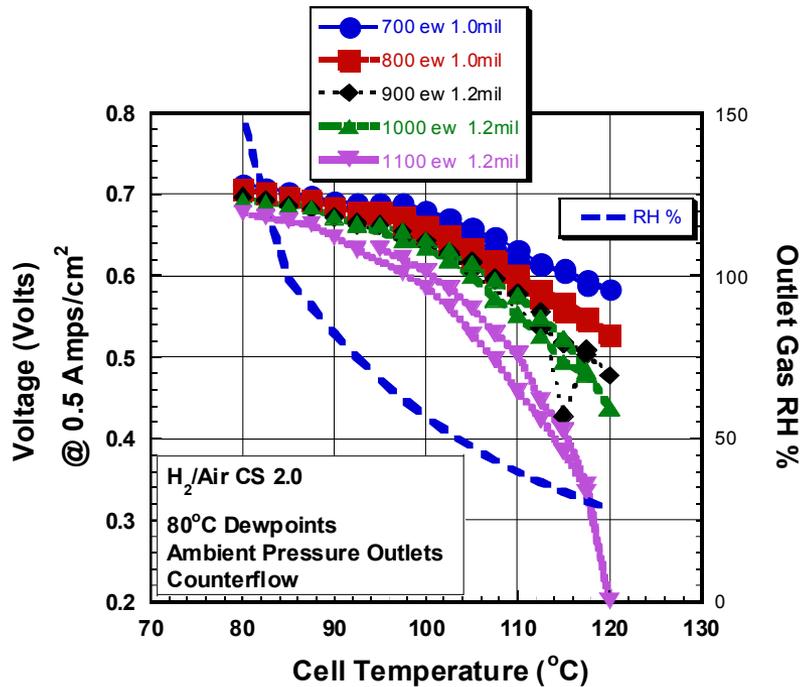
Progress on Aromatic Model Compounds Study

- Aromatic compounds do degrade in the presence of peroxides.
- Major products mono- or di-hydroxylated AMC.
- No aromatic-ring breaking observed.
- AMC containing more than one sulfonic acid groups may show loss of one of the sulfonic acid groups.
- No biphenyl link breaking observed in AMC4 ; extensive hydroxylation and dimerization observed.
- Ether link breaking observed in AMC5.

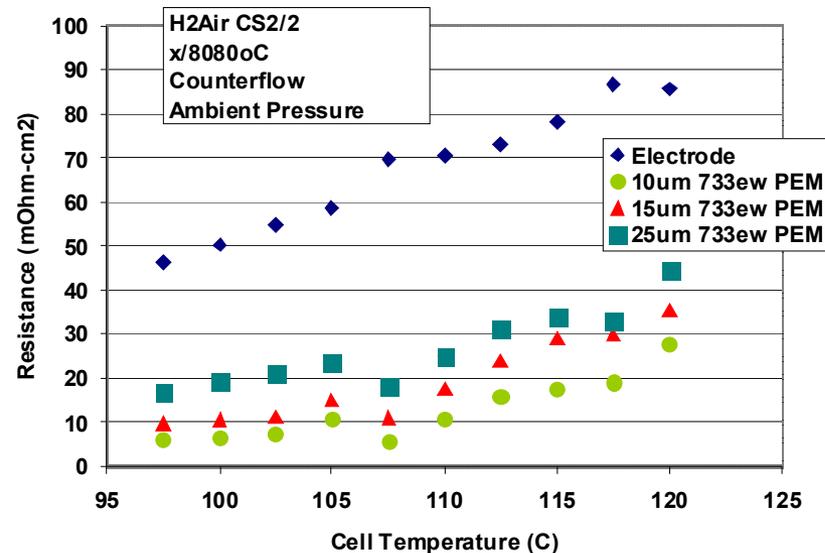


Electrode Resistance and Performance

Fuel cell testing
Performance



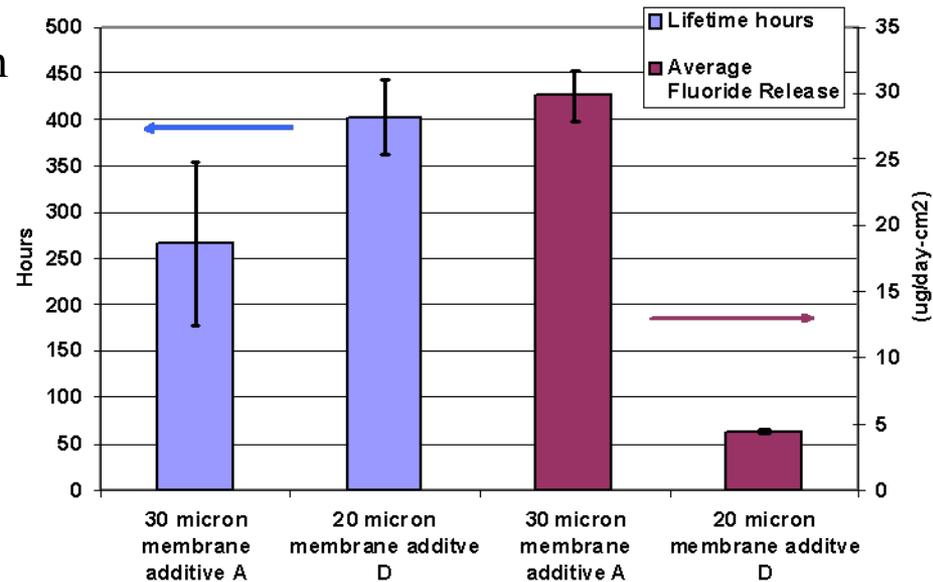
- Lower EW membranes provide better Fuel cell performance under hotter, drier conditions.
- Not all due to Ohmic losses.
- Our screening electrode resistance, as determined by transmission line measurements (TLM), is the dominant resistance. TLM method yields membrane resistances consistent with conductivity values.



Oxidative Stability Gains

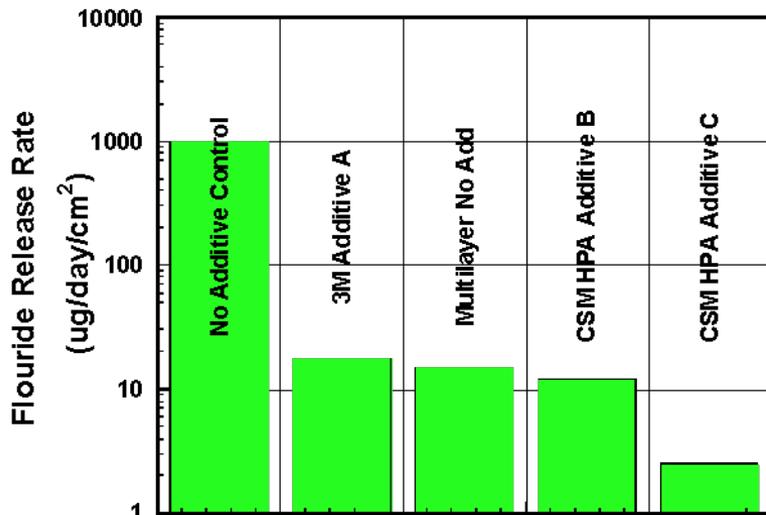
Fuel cell testing
Durability

- Stabilizing additives can have a large effect on MEA lifetimes and fluoride release rates
- We continue to evaluate peroxide mitigation additives. Studies are ongoing to look at the effect of the location of the additive in the MEA.
- In addition, other variables have shown dramatic influences on FRR such as:
 - Different PEM constructs.
 - Electrode effects.



Oxidative Stability

H₂/O₂ 90°C 30%RH Ambient Pressure OCV



OCV, H₂/Air, 95C, 7 PSIG, 50% RH

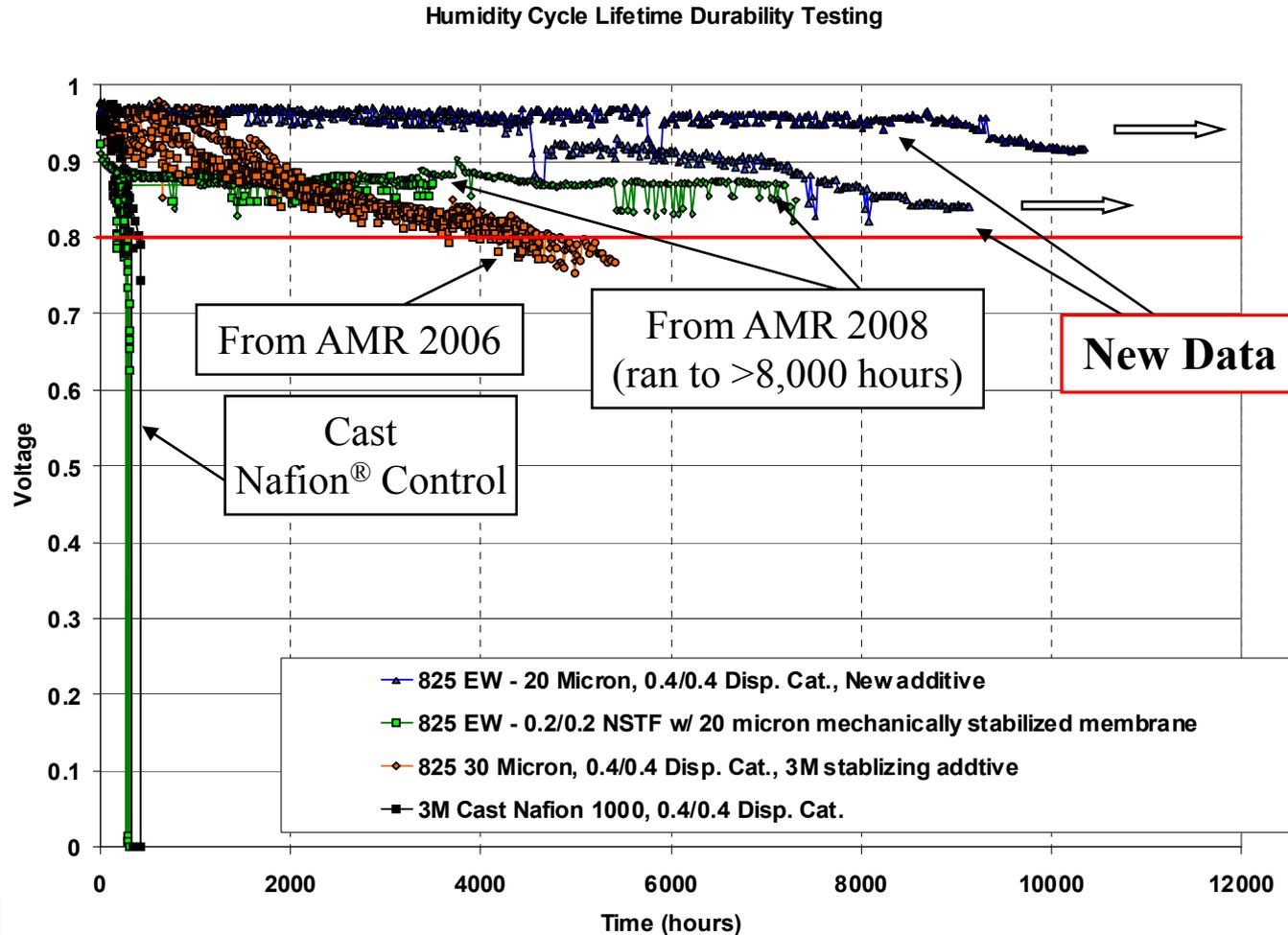
OCV, H₂/O₂, 90C, 0 PSIG, 30% RH

Fuel Cell Durability Testing

Fuel cell testing
Durability

- New additive package provides over 10,000 lifetime in automotive accelerated durability protocol

Test Point	J (A/cm ²)	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



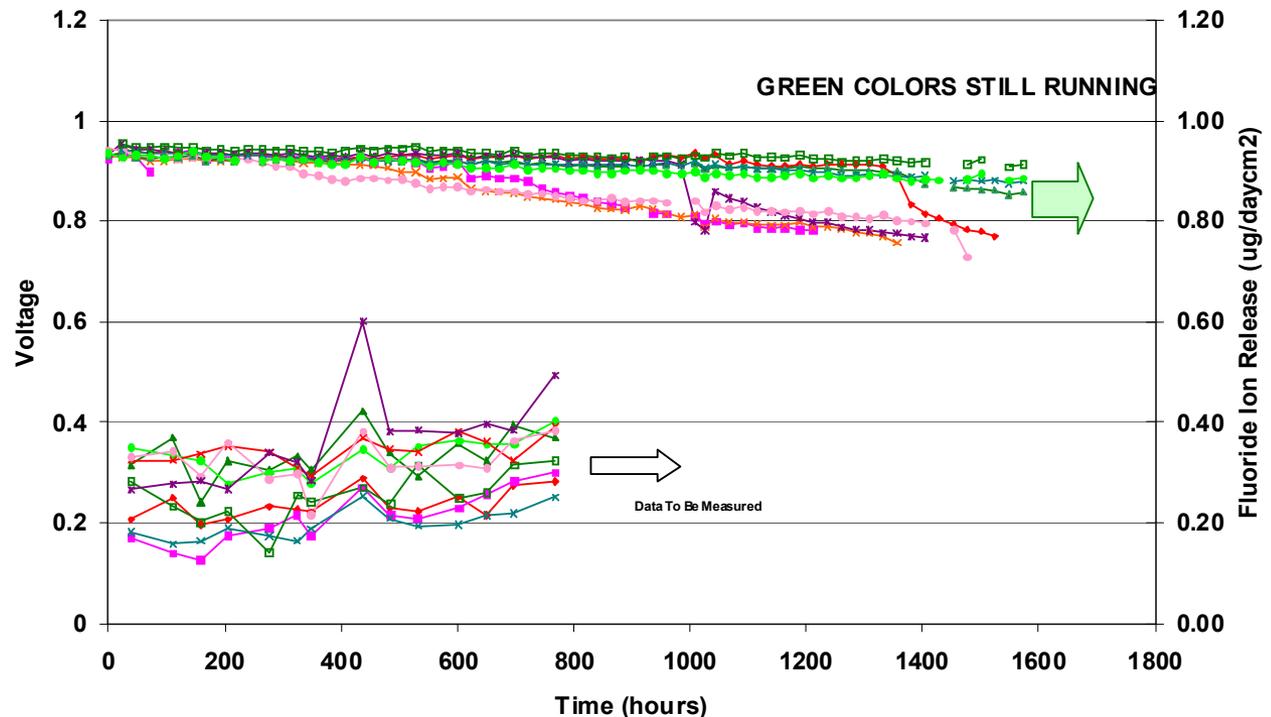
Cell Temperature: 80 °C
Inlet Dew points: 64/64 °C
Outlet Pressures: 175kPa

End of life = < 800 mV OCV
w/ 7 PSIG anode overpressure.

New Durability Protocol

Cycles/Day	Cell Temp	Conditions Description	Time
1	80	Long scan @ 0.6A/cm ² to used collect fluoride data	4.5 hrs
1	80	Short anode overpressure OCV to monitor lifetime	5 min
4	120	Hot Temperature Low RH to degrade MEA (up to 80°C dewpoint)	15 hrs
	30	Low Temperature to Thermal and Humidity Cycle MEA	
2	80	Load Cycle at Various RH to monitor performance	4.5 hrs

Our old protocol was getting too long as material stability improved. New protocol with higher temp conditions (up to 120°C) shows MEA lifetimes of about 1,000 to 2000 h for MEA's which have lifetimes >5,000 h. in old test (3-5 X faster).



Future Work

- Continue preparation and evaluation of the conductivity and durability of low EW PFSA's, new imide containing polymers (Slide 15-24), cross-linked polymers (Slide 24) and membrane additives (Slide 25,36,37).
- Evaluate membranes crosslinked in both the hydrophilic and hydrophobic regions (Slide 24).
- Evaluate additional polymer blends for ionomer stabilization (Slide 14)
- Continue to probe factors in transport using NMR relaxation and diffusion, SAXS, conductivity and other spectroscopic measurements. Continue to develop a better understanding of effect of low lambda on proton transport (Slides 6-9, 20, 22, 26-28).
- Undertake first principles modeling of crystallinity through a comparison of different ionomers (Slides 26,28).
- Develop a better understanding of role of crystallinity on swelling in new polymers using X-ray scattering, mechanical properties testing and modeling (Slides 10-12, 26-28).
- Evaluate impact of new protogenic groups and additives on membrane oxidative and chemical stability using ESR, ex-situ tests and fuel cell tests (Slides 29-34,36-38).
- Investigate the structural basis for the higher stability of 3M membranes compared to Nafion® in ESR experiments. Better understand what this is telling us about membrane stability in a fuel cell (Slides 29-31).
- Evaluate additional stabilizers for perfluorinated membranes (Slides 29-31, 36-37).
- Describe degradation pathways and rates for current group of model compounds and correlate with membrane stability (Slides 33-34).
- Design MEA's for larger scale testing (Slide 35).

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.
- New materials are being synthesized based on this understanding, and evaluation of these materials will further our understanding.
- This “feedback loop” will ultimately allow for materials “designed” to meet performance and durability targets.
- Several approaches or pathways to improving membranes are being investigated. We expect the final membrane will have attributes resulting from some or all of these. **We will not “down select” just one approach.**

		3M 2009 Status	2010 target	2015 target
Conductivity at 120° C	S/cm	0.146 (46%RH) 580 EW PFSA	0.1	0.1
Conductivity at 80° C	S/cm	0.1 (40% RH) 0.13 (50%RH) 0.50 (92%RH) 580 EW PFSA	0.1	0.1
Conductivity at 30° C	S/cm	0.1 (80% RH) 580 EW PFSA	0.07	0.07
Conductivity at -20° C	S/cm	0.014 S/cm 700 EW PFSA	0.01	0.01
O2 cross- over	mA/cm²	<0.5 20 micron	2	2
H2 cross- over	mA/cm²	<2 20 micron	2	2
Durability w/ cycling	hours	10,000 (80°C) 1000 (120°C) 825 EW PFSA	5000 (80°C) 2000 (120°C)	5000 (80°C) 5000 (120°C)