Membranes and MEA's for Dry, Hot Operating Conditions

Steven Hamrock

Fuel Cell Components

June 10, 2008

FC13

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start 4/1/07
- Project end 3/31/11
- 25% complete

Barriers

A. Durability

C. Performance

Budget

- Total Project funding $11.4 million
  - $8.9 million - DOE
  - $2.5 million - contractor cost share (22%)
- Funding in FY 2007
- $0.8 Million (6 months)
- Funding in FY 2008
- $1.2 Million (6 Months)

Partners

Case Western Reserve Univ.
Professors T. Zawodzinski and D. Schiraldi
Colorado School of Mines
Professor A. Herring
University of Detroit Mercy
Professor S. Schlick
University of Tennessee
Professor S. Paddison

Project Objectives

- To develop a new proton exchange membrane with:
  - **higher proton conductivity**
  - **improved durability**

  under hotter and dryer conditions compared, to current membranes.

Milestones

- ***Year 1, Quarter 4:*** Complete the development of all pertinent testing methods and install and modify new equipment as appropriate. Screening of new materials developed as part of Task 1 will be underway.
- ***Year 2, Quarter 4:*** Complete the identification of a first set of new, more conductive and durable materials.
- ***Year 3, Quarter 2:*** **Go/no-go decision** based on progress toward meeting DOE 2010 Membrane Technical Targets (**this decision point coincides with the end of Budget Period 1**). 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, based on performance in ex situ and single cell tests, and optimization of the final membrane structure and composition will begin.
- ***Year 4, Quarter 2:*** 3M will down select for the best performing catalyst/GDL/process based on performance in ex situ testing and single cell testing. **Go/no-go decision** for starting Subtask 4.1, Stack Fabrication and Testing.
- ***Year 4, Quarter 3:*** 3M will have assembled a short stack with the best stack components and prepared the stack for independent testing at DOE designated entity.

Project Approach

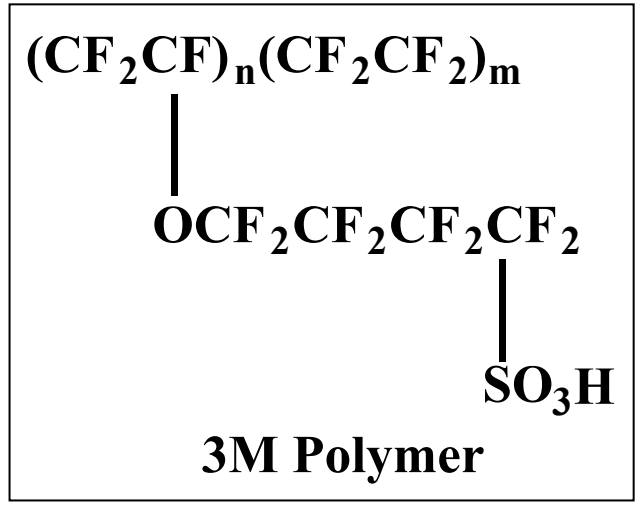
- New polymers, fluoropolymers, non-fluorinated polymers and composite/hybrid systems with increased proton conductivity and improved chemical and mechanical stability
- Developing new membrane additives for both increased conductivity and improved stability/durability under these dry conditions
- Experimental 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.

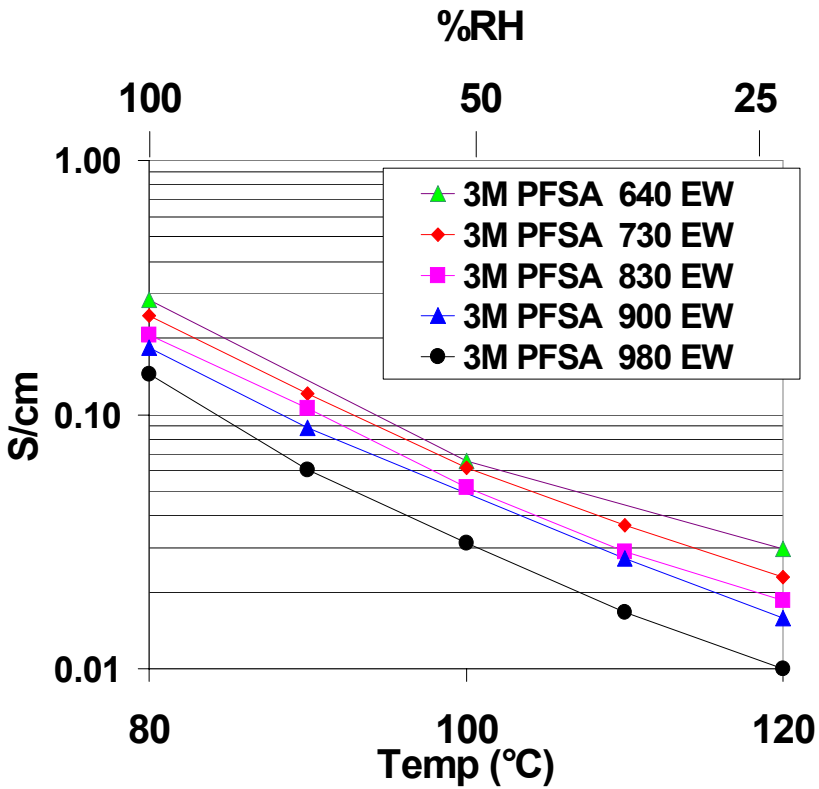
Project Approach

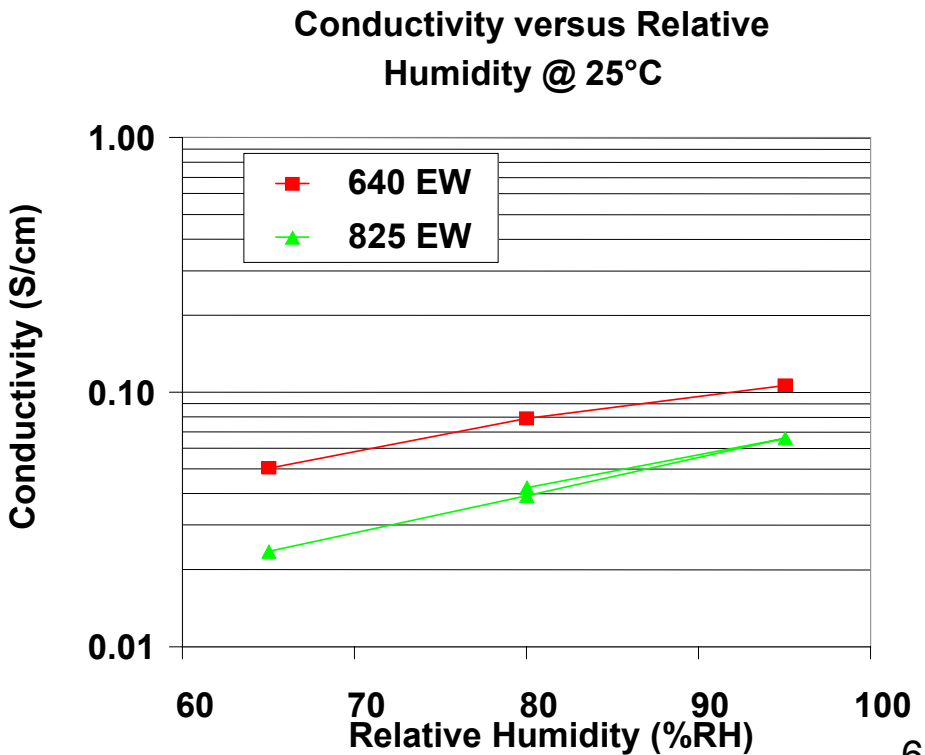
- **Task 1** Membrane Subcomponent Development
  - **Subtask** Materials Development (Polymer development, conductivity enhancing additive development and stabilizing additive development)
  - **Subtask** Studies for Downselection (conductivity, membrane physical properties, failure and degradation mechanisms)
  - **Subtask** Membrane Fabrication Process Development
- **Task 2** MEA Fabrication and Testing (MEA fabrication, performance and durability test method development, initial performance testing, accelerated durability testing)
- **Task 3** Final MEA Design and Integration (membrane fabrication, catalyst interface optimization and integration, final MEA optimization and fabrication)
- **Task 4** Final Fuel Cell Testing (stack fabrication and testing, durability and performance testing)
- **Task 5** Project Management, Deliverables and Reporting (building and testing short stack, reporting)

Conductivity w/ Low EW

- Conductivity vs. temperature for EW ionomers in 640 – 980 EW range.
- The lowest EW ionomer tested so far, 640 EW, shows a conductivity of about 30 mS/cm at 120˚ C, 80˚ C DP, ambient pressure, very dry conditions, and meets DOE milestone for RT conductivity (*ca*. 80 mS/cm at 80%RH, 25C).



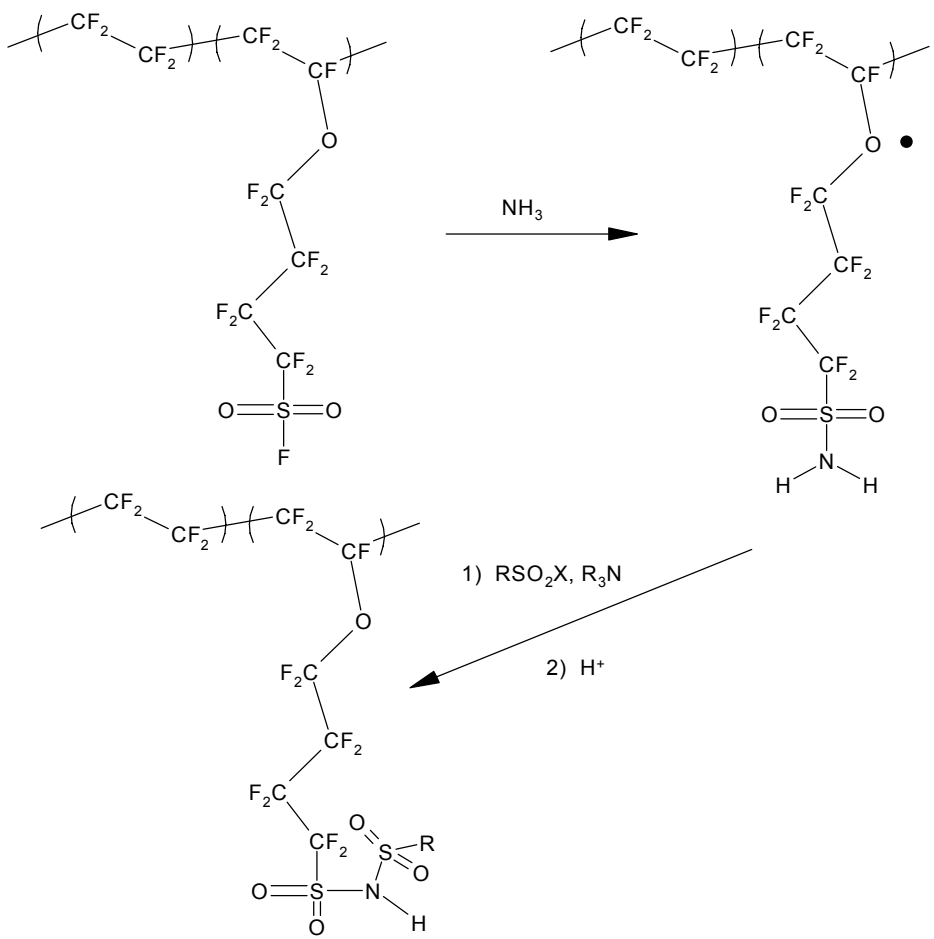




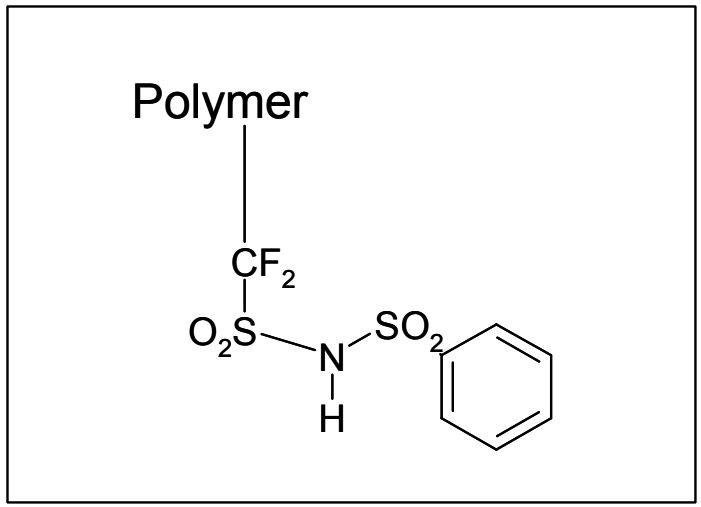
AC 4-point probe measurement.

Polymer Research

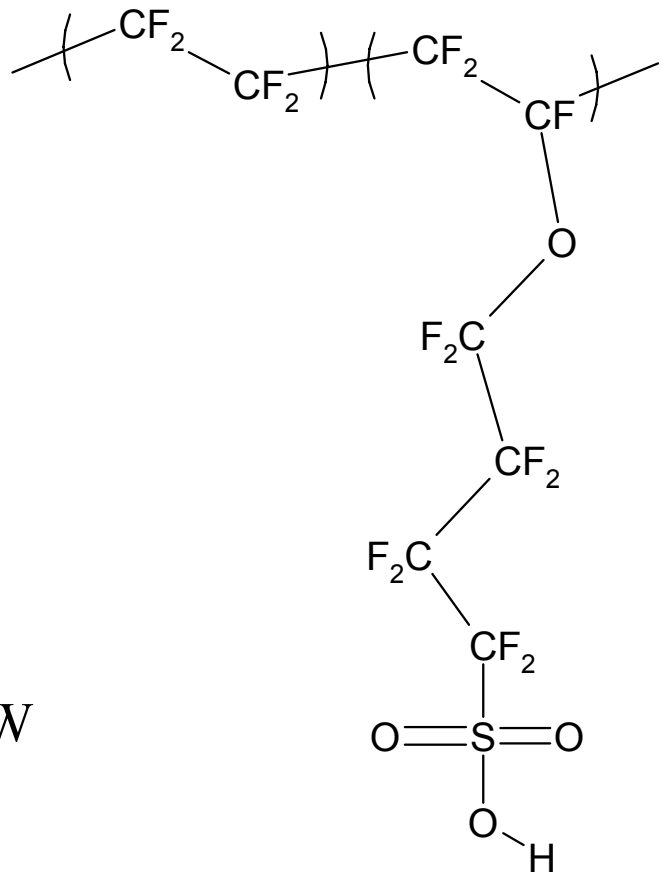
Polymer Modification – one approach



- A few example prepared w/ low MW starting polymer.
- Fluorocarbon/aromatic imides are very chemically stable and highly acetic.
- Aromatic groups will be substituted with additional functionality for stable cross-linking and/or adding additional acid groups including HPA's.



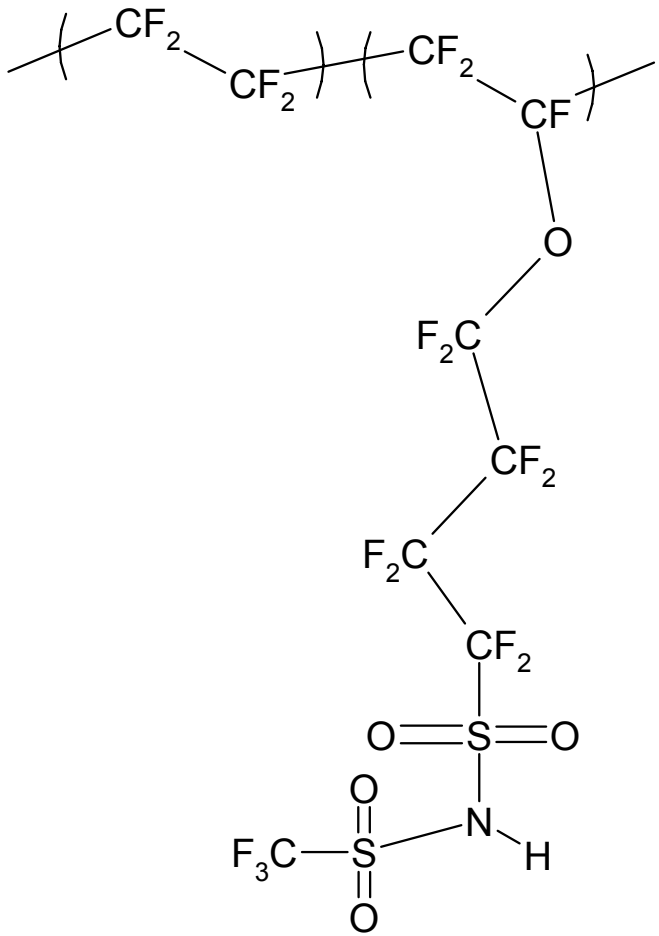
- Changing the nature of the acid group



Sulfonic acid

- Lowest EW limited by monomer MW

- Changing the nature of the acid group



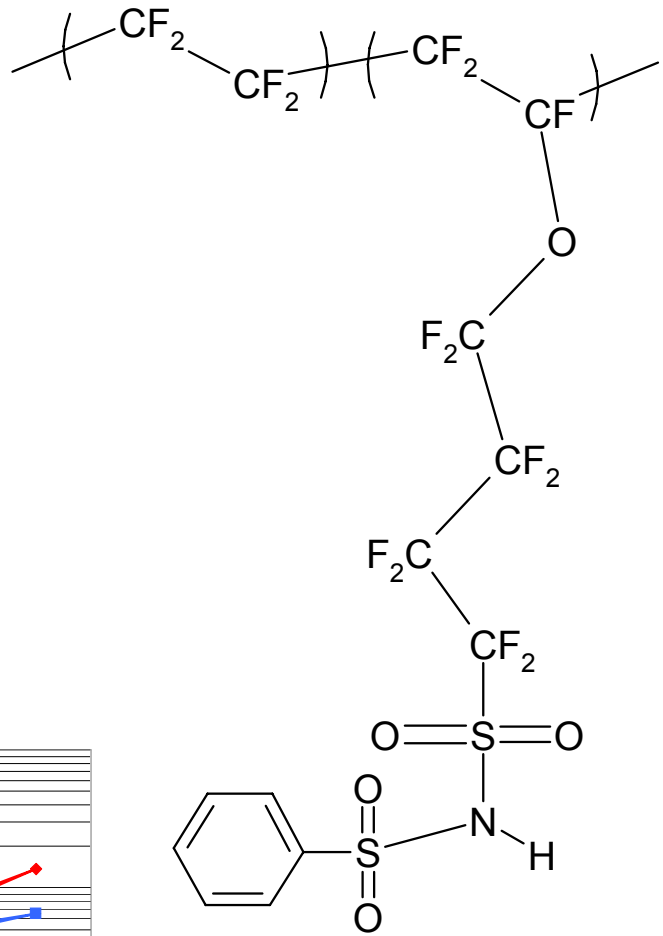
Perfluoro imides

- Similar material prepared by DesMarteau via polymerization of imide monomers with TFE
- Stronger acids than sulfonic acids
- This example has been prepared, not tested yet.

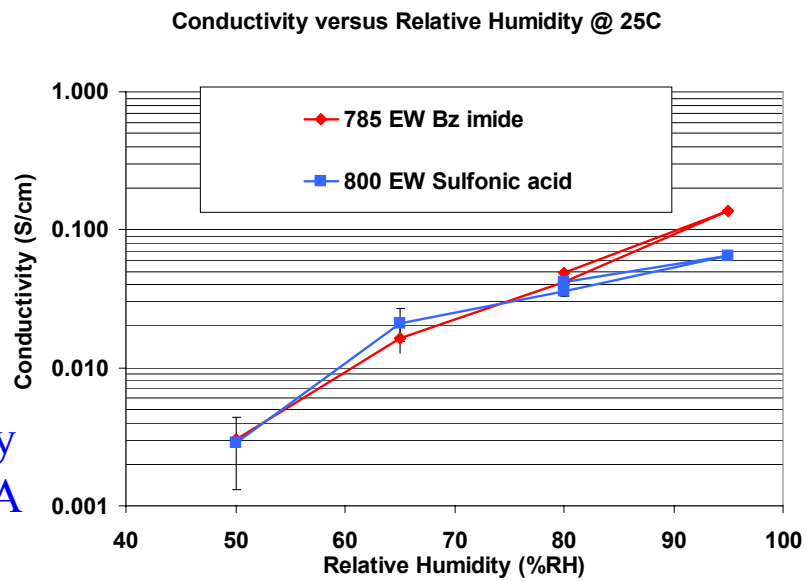
• Changing the nature of the acid group

Aromatic imides

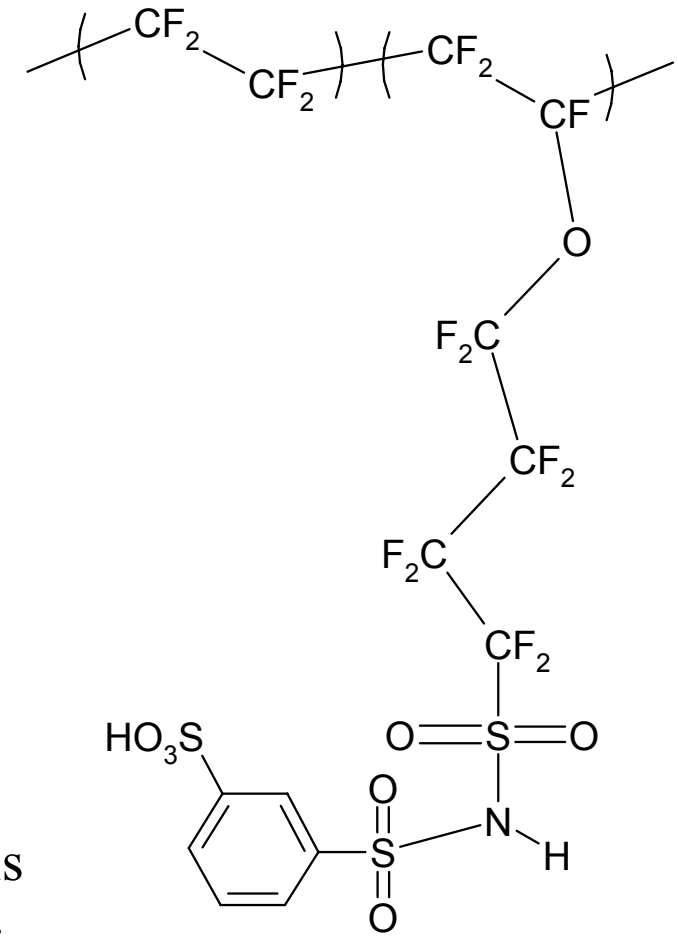
- Useful synthetic handle
- Similar pKa to sulfonic acids
- Excellent thermal, hydrolytic and oxidative stability. Further stability testing underway.



- Starting with a low MW, 640 EW sulfony fluoride, a 785 EW imide ionomer was prepared.
- This material has similar conductivity to an 800 EW PFSA control at 25ºC.



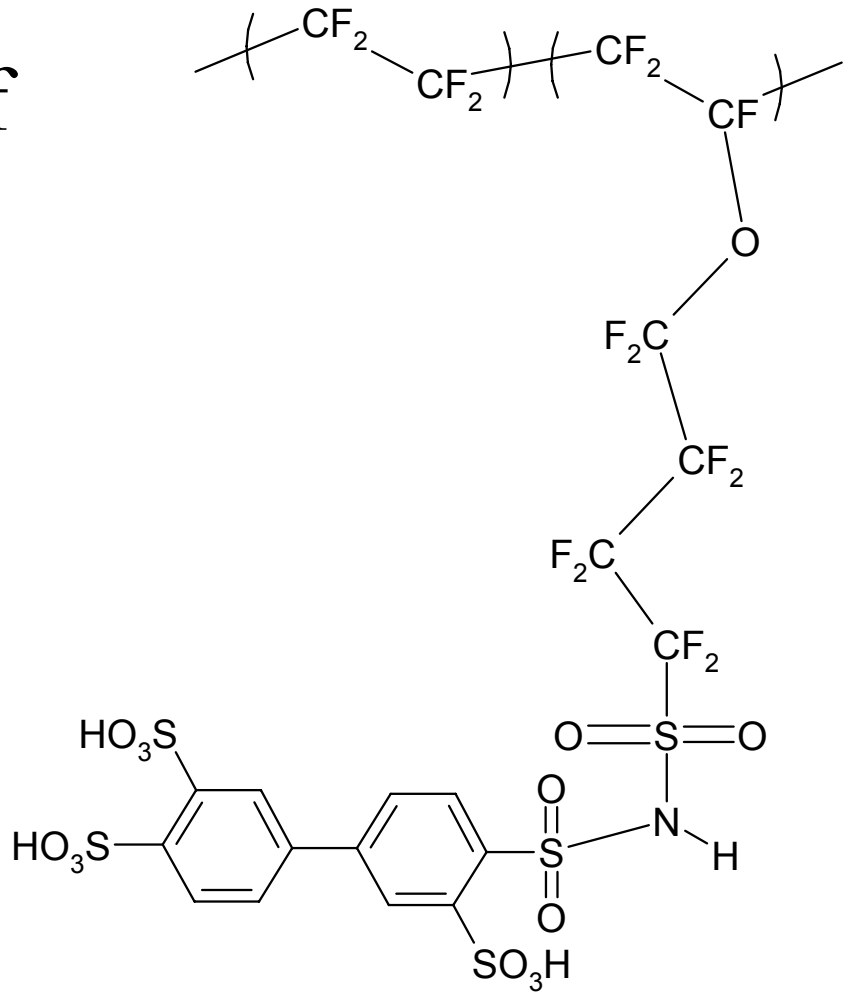
- Changing the nature of the acid group



Aromatic imides

- Multiple acid groups
- This example has been prepared
- starting with a 640 EW polymer, this ionomer should have an EW of 430.

- Changing the nature of the acid group

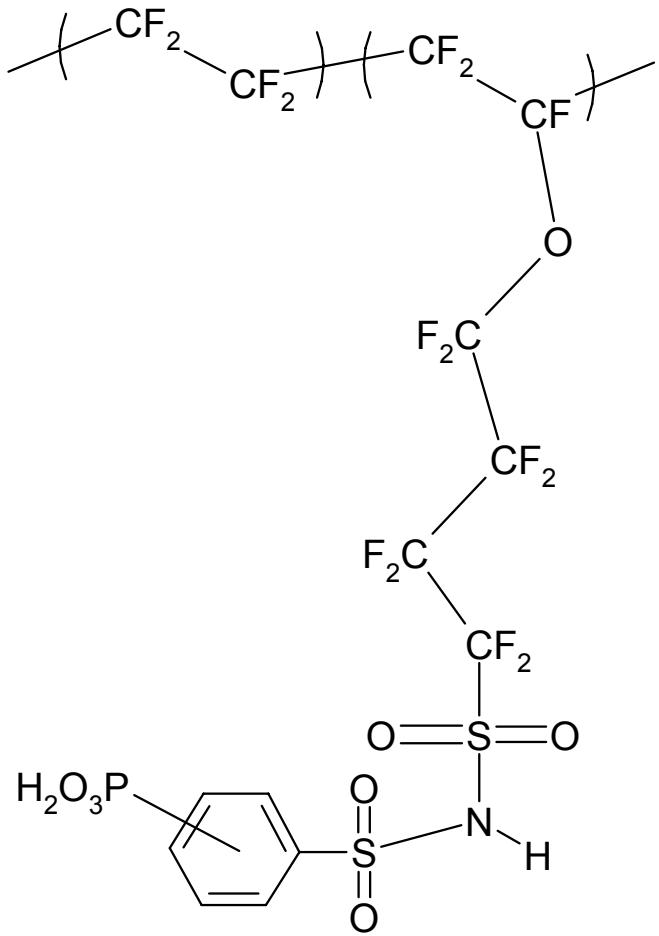


Aromatic imides

- Multiple acid groups
- EW could be < 280 !!
- By increasing and/or changing size and shape of pendant group, we hope to increase free volume of ionic regions, increasing water retention under hotter, drier conditions.

One possible example – has not been prepared

- Changing the nature of the acid group

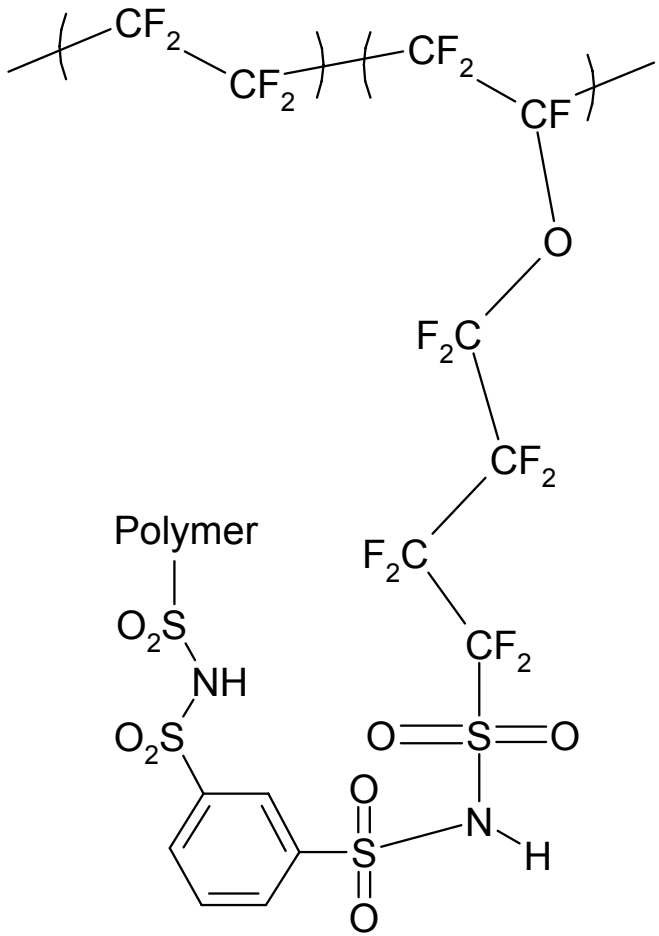


Linking group (HPA's Zircania)

Aromatic imides

- Phosphonic acid groups can allow:
  - Attachment of HPA's,
  - Attachment of zirconia particles or zirconyl phosphate particles for increased conductivity, better mechanical properties, or latent cross-link.

- Changing the nature of the acid group



Cross-linking group

Aromatic imides

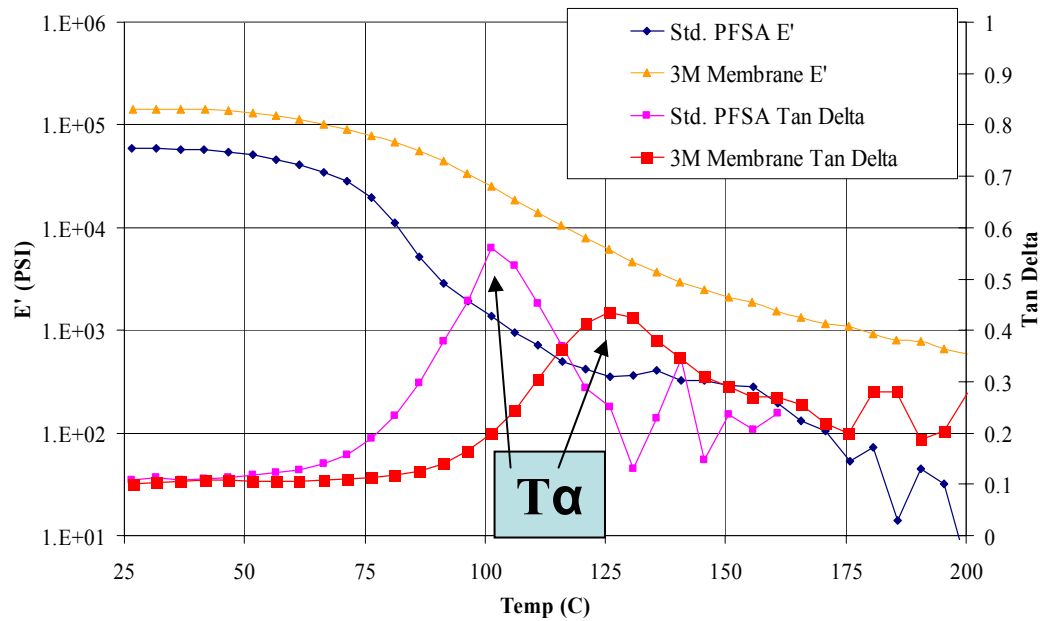
- Crosslinking the ionic region can allow lower EW's to be more stable and prevent disruption of ionic structure at temperatures approaching Tα.

Cross-linking polymers – Objectives

- Minimize swelling at high hydration levels.
- Increase/eliminate **α** transition.
- Conductivity and mechanical properties can be compromised above this transition
- Improve mechanical properties.

- **Compare properties of crosslinking hydrophobic matrix vs ionic domain.**
  - Measure water uptake and conductivity.
  - Measure durability
    - wet/dry cycling
      - H_2O_2
      - Single cell tests

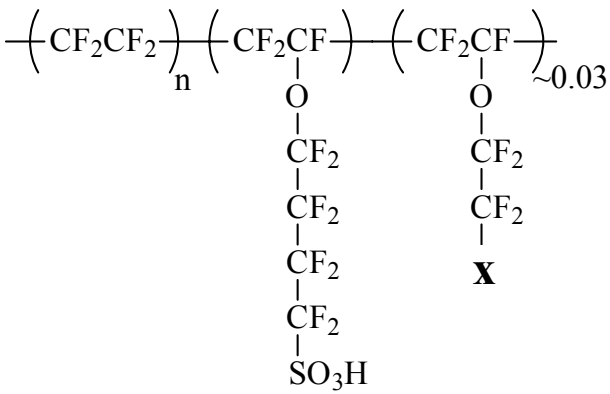
Changing or cross-linking the acid group may also have a big impact on Tα. A higher Tα may improve conductivity at higher temperatures.



Relevant previous work - DMA of Nafion™ and 3M Membrane (Both 1,000 EW) showing Tα

Crosslinked ionomer using cure site monomer

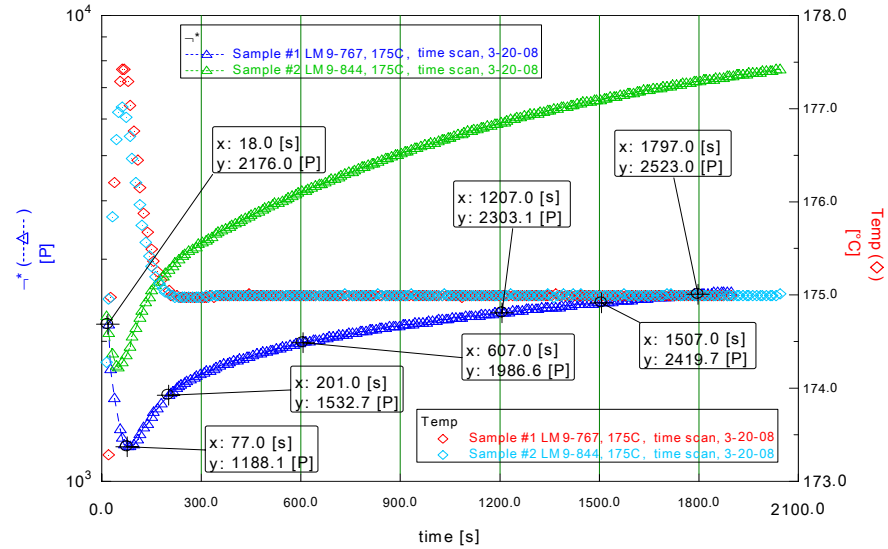
Crosslinking the hydrophobic matrix



Ionomer with Cure Site Monomer

- Standard fluoroelastomer cure systems for initial experiments.
- **This is being used to understand the effects of cross-linking. More stable cross-links will be developed if this approach is successful.**

Cure Rheology



Melt viscosity increase shows polymer is being cross-linked in SO_2F form.

Swelling Experiments based on x-y dimensions SO_3H form			
Sample	**Water**	**Glycol**	**Methanol**
Uncrosslinked Sample	30.6	63.3	soluble
Crosslinked Sample	24.4	52.4	73.7

Swelling measurements show hydrolyzed samples are cross-linked.

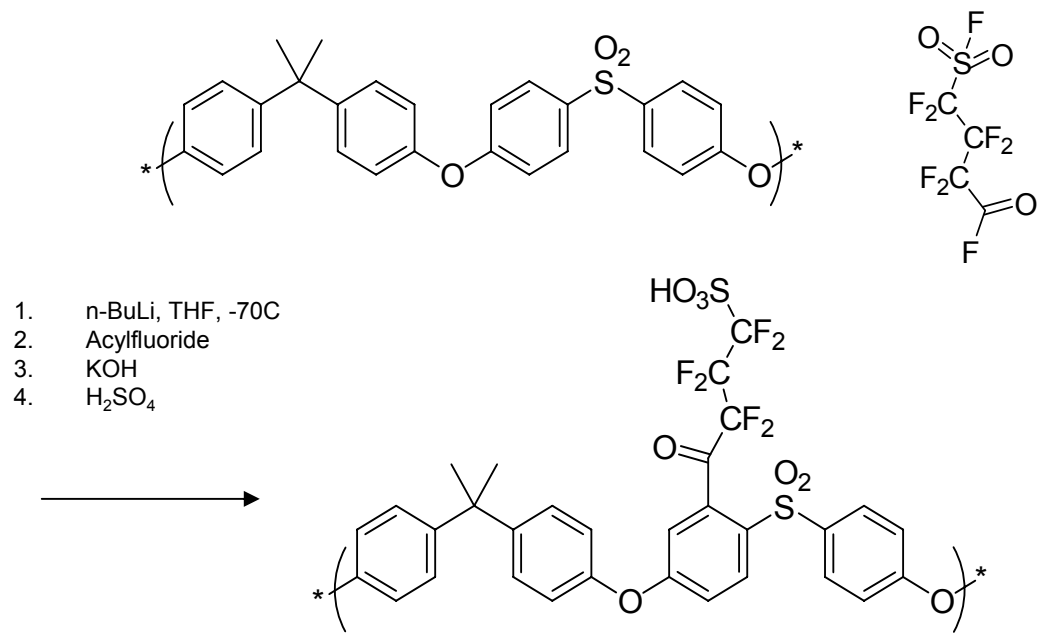
Polymer Research

New polymer structures with hydrocarbon polymers

- Hydrocarbon ionomers with fluorochemical acids attached for improved conductivity.
  - Initial coupling reactions have been run.
  - Can be made into composites with PFSA's?
- Prepare 'hybrid' polymers with perfluorinated and aromatic regions as hydrophobic and hydrophilic portions
  - Initial reactions have been run.
  - Durable linkages are key.

Example: Side-chain addition

- Model reactions carried out on small molecules to test
- Friedel-Crafts acylation unsuccessful
- Lithiation/Electrophilic Addition (at right) successful

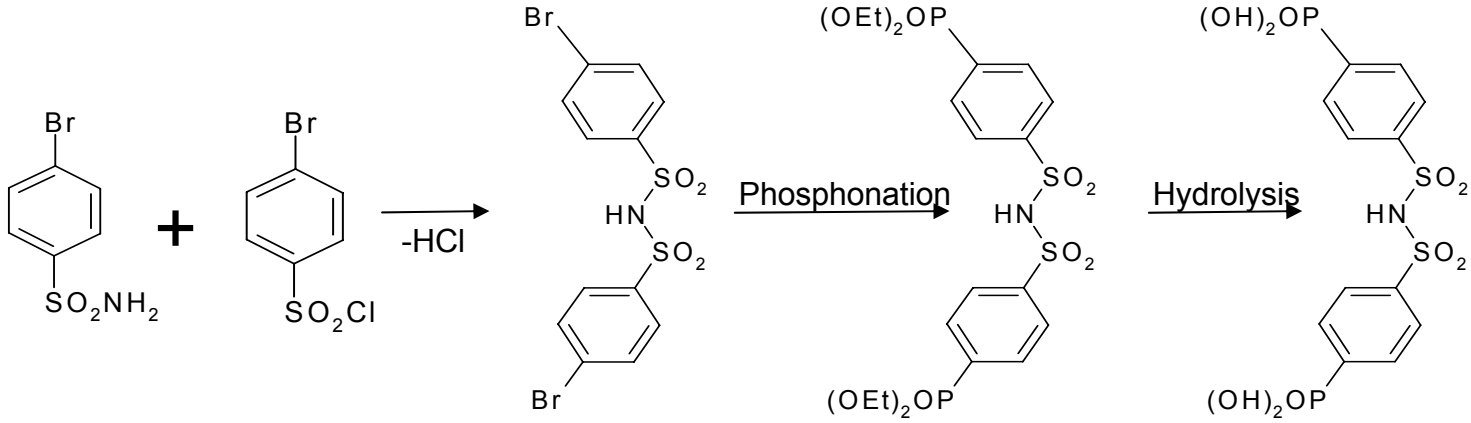


- Cross-linking occurred in all trials and products formed gels and were partially soluble
- In one case IEC=0.66 meq/g was obtained (Target was 0.86) and conductivity was around 80 mS/cm

Studies of Transport in Polymer Electrolytes

- This activity is just getting started; collaborative between Case Western and Colorado School of Mines.
- Use NMR relaxation and diffusion to probe local and long-range motion
- Extend analysis as function of protogenic group, water content, equivalent weight, polymer composition, blockiness etc.
- Look for:
  - tortuosity analysis
  - chain to chain hand-off? interaction?
    - use polarization transfer, 2-D methods
    - sidechain mobility: C-13 relaxation
  - changes in activation energies
    - threshold for increase as f(EW)?
- Eventually implement Electrophoretic NMR
- First samples will be 3M PFSA of varying EW

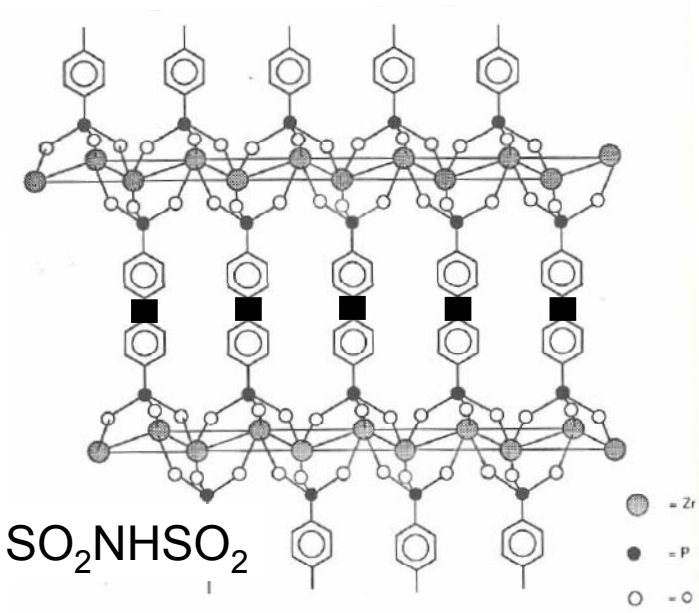
Phosphonic Acids containing Bis sulfonyl imide



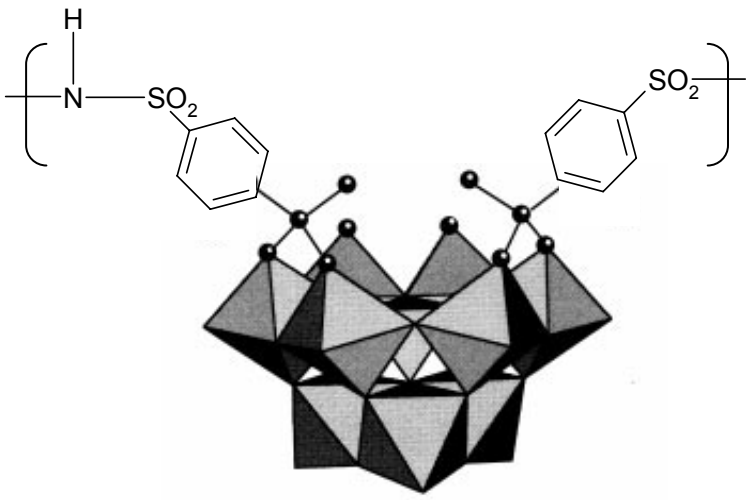
Zirconyl phosphate structure where imides control distance between platelets?

This bis-phosphonate has been prepared.

We will attempt to attach this molecule to HPA's to generate chains or oligamers. These may immobilize the HPA's

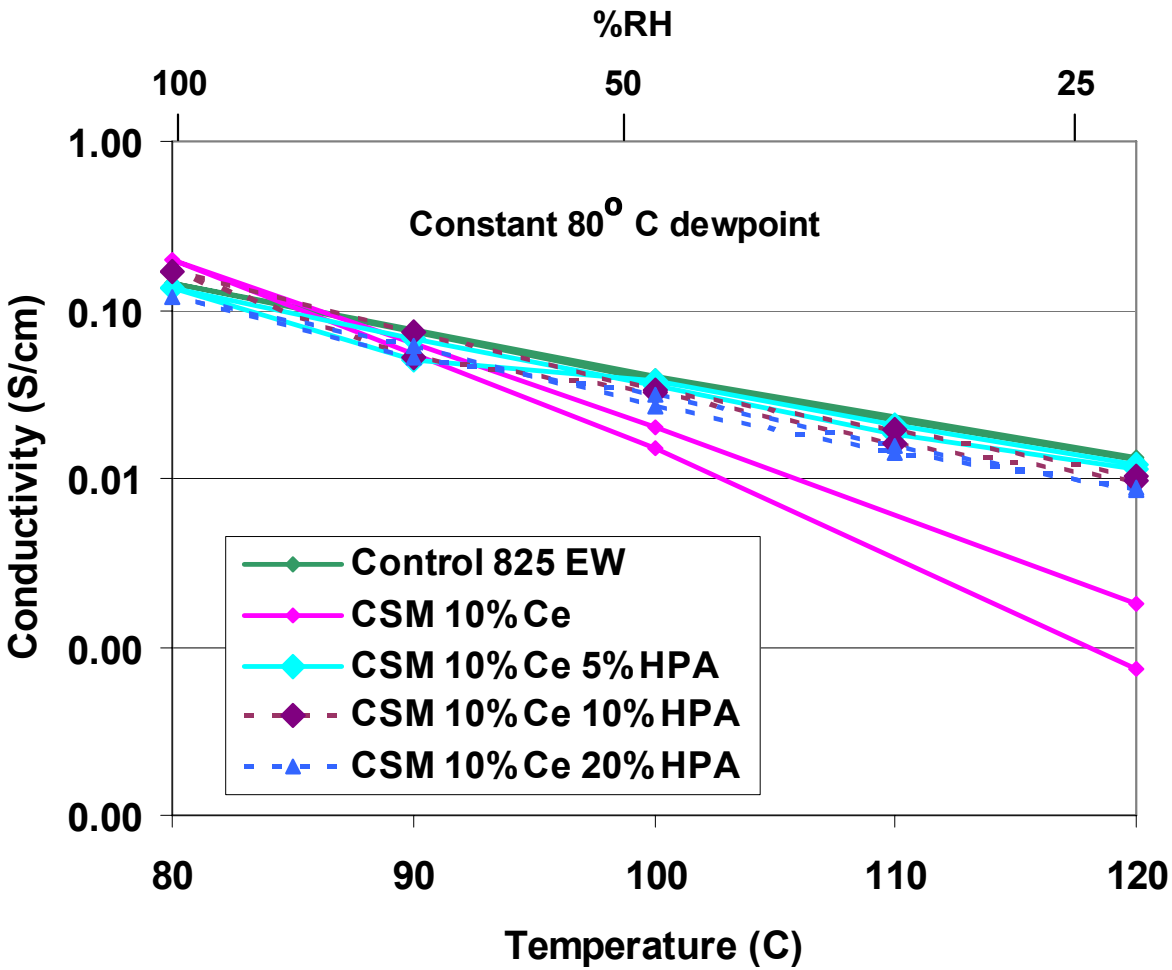


■ = SO_2NHSO_2



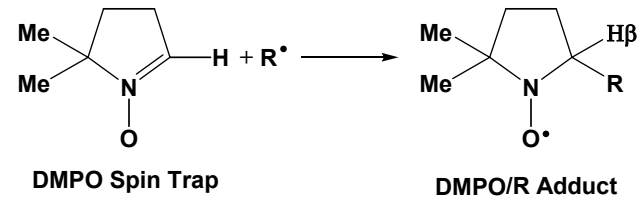
Impact of HPA salts on conductivity

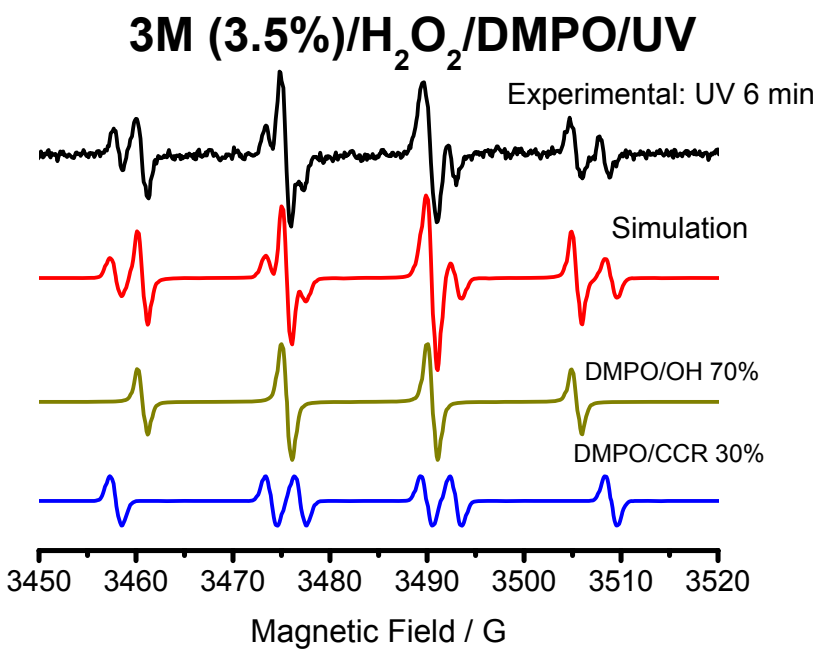
- Addition of Ce and other cations can improve membrane oxidative stability, but lower membrane conductivity and fuel cell performance, particularly under hot, dry conditions.
- Addition of HPA's can mitigate this.
- Studies of the effects of HPA's immobilized via different routes on conductivity are ongoing

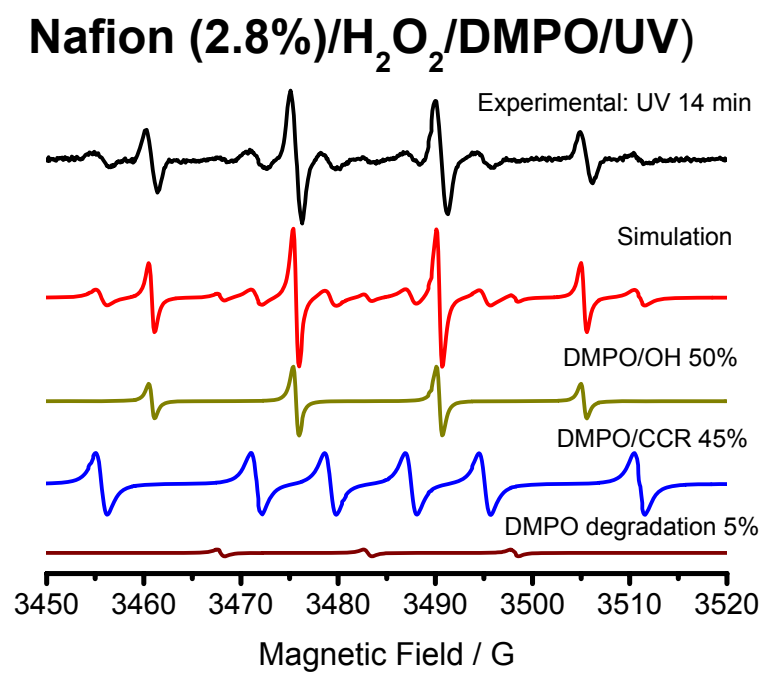


Carbon-centered Adducts in Nafion™ and 3M in Aqueous Solutions

Oxygen Radicals Formed by UV-irradiation, DMPO as the Spin Trap



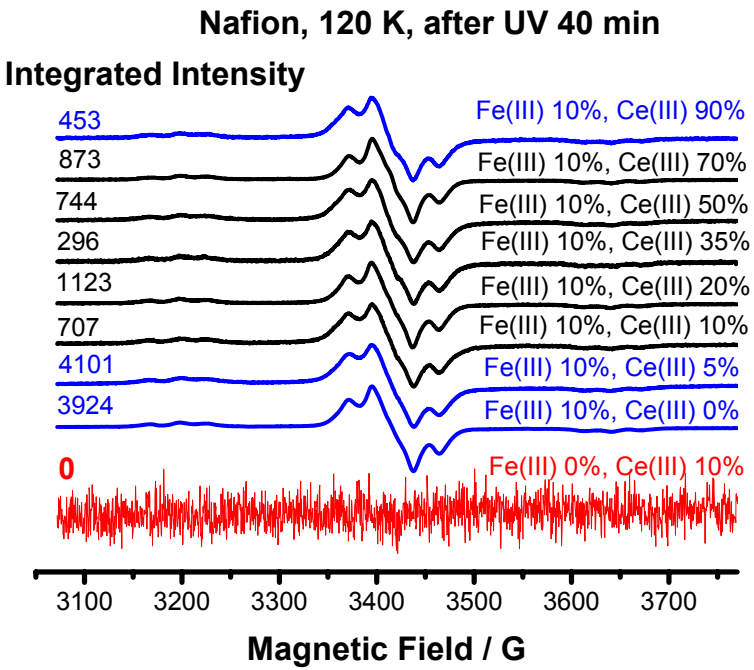


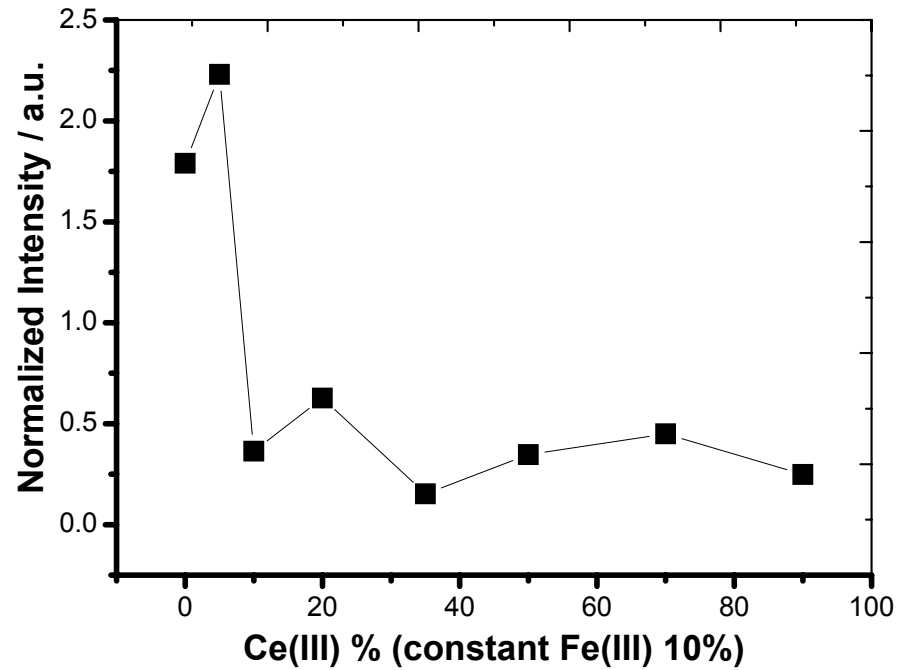


Carbon-centered radical (CCR) and •OH radical adducts were detected. The magnetic parameters for the CCR adducts in Nafion™ and 3M solutions are different, suggesting: (a) formation of different radicals, and (b) attack of •OH radicals on the side chain.

Effect of Ce(III) on the Intensity of the Chain End Radical RCF_2CF_2•

Nafion™ Membranes with <u>Constant Fe(III) Concentration</u>



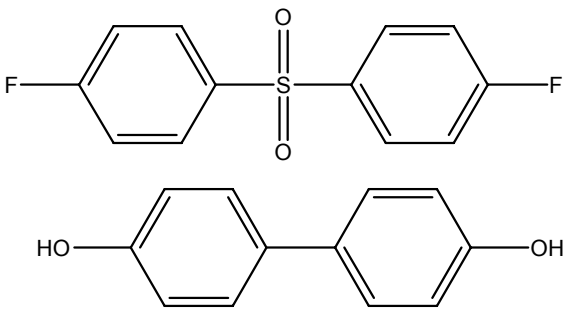


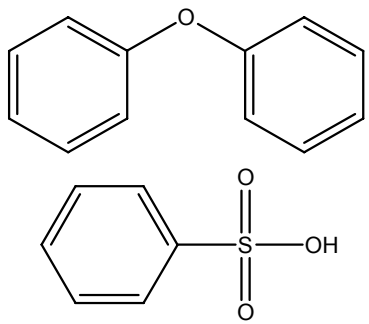
The chain end radical is not generated when the membrane contains only Ce(III), and no Fe(III).

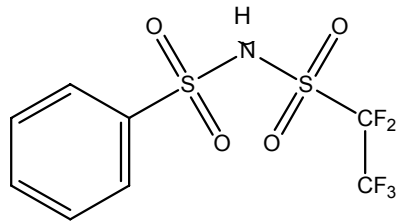
For a constant 10 % neutralization by Fe(III), <u>Ce(III) is an effective stabilizer</u> of membrane fragmentation when the degree of neutralization by Ce(III) is ≥10%.

Model Compounds – Approach and recent progress

- Developed initial approach to testing aromatic sulfonic acid model compounds
  - Initial evaluation of MC's has begun.
  - Many aromatic sulfonic acids and other model compounds readily degrade in Fenton's reagent solution
  - Systematically 'harvesting' small molecule analogs from synthetic activity to explore degradation pathways
  - Considering oxidation, hydrolysis and other degradation modes
- Recently received new LC/MS for rapid turnaround on degradation product analysis
- Extensive analysis of perfluorosulfonic acid degradation products, ^{19}F NMR carried out
- Developing new methods to explore other possible degradation pathways
  - Could sulfonate cleavage be more favorable in presence of Pt?
- **Collaboration beginning between Case Western and Detroit-Mercy**

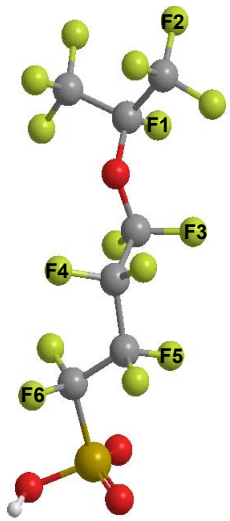




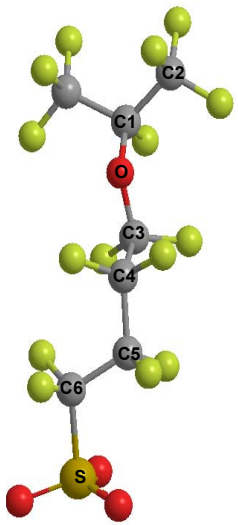


Bond Dissociation Energies of 3M fragment

- Nafion™, 3M ionomer and the short side chain (Dow) ionomer have been investigated.
- All show, qualitatively, that the C-S bond is the weakest. Possible sight of side-chain attack?
- An investigation into the energetics and kinetics of reaction of the fragments with hydroxyl radicals has begun.



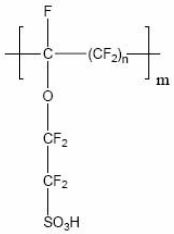
Fluoride bond	Energy of C-F bond dissociation (kcal/mol)
F1	103.60
F2	114.92
F3	108.78
F4	105.14
F5	102.77
F6	105.43



Bond type	Energy of bond dissociation (kcal/mol)
C6-S	61.15
C5-C6	79.96
C4-C5	75.77
C3-C4	80.96
O-C3	81.26
C1-C2	76.83

Meso-scale modeling of Morphology

Dissipative Particle Dynamics (DPD) simulations



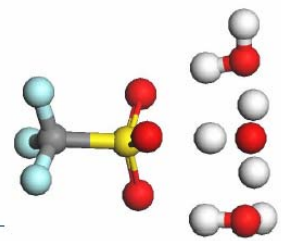
n = {9, 15, 21}; m = 15

A bead (repeat unit) $-CF_2CF_2CF_2CF_2CF_2CF_2-$

B bead (repeat unit)

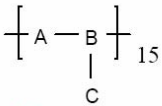
C bead

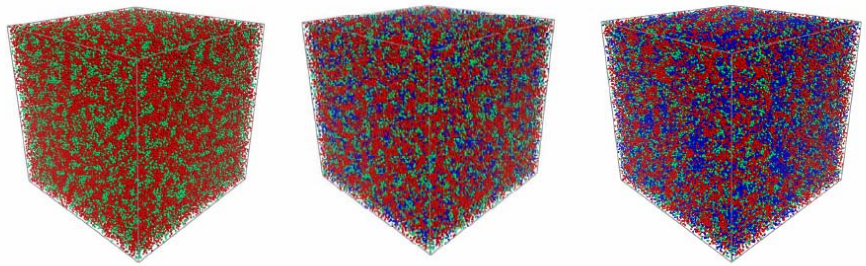
W bead 6 H_2O



Equilibrated morphologies

SSC with n = 9, EW = 678, MW ≈ 10,000 g/mol



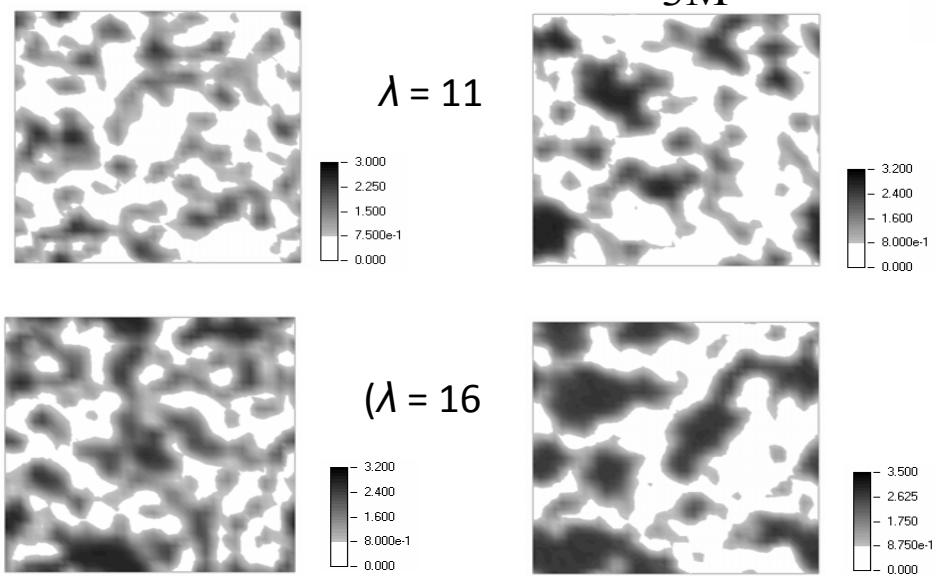


$\lambda = 3$ $\lambda = 7$ $\lambda = 9$

The morphologies of SSC PFSA membrane with different water contents at t = 1000, Δt = 5.6 ps; T = 298 K.

(*A*, *B* beads in red, *C* bead in green and *W* bead in blue)

SSC **EW = 678** 3M



$\lambda = 11$

($\lambda = 16$

- Nafion™, 3M ionomer and the short side chain ionomer have been investigated.
- It appears that the longer side in the 3M membrane results in larger water domains with higher density than the SSC PFSA membrane.
- Need to account for backbone crystalinity.
- Add other protogenic groups (size and acidity?).

Test Method Development

Performance Testing

- Developed Humidity Performance Test - Hold the dew point constant at 80°C and gradually raise cell temperature from 80 to 120°C (Record performance and impedance)

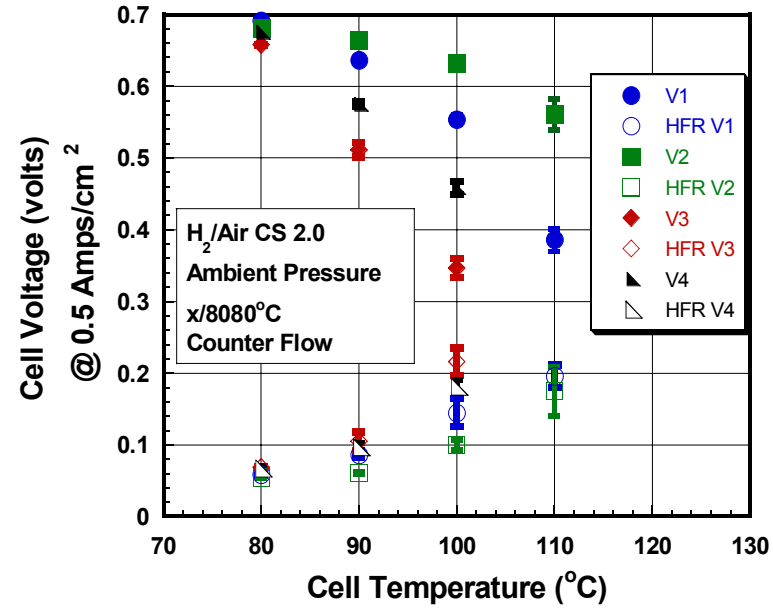
Durability Testing Protocol Development

- 95ºC OCV Hold
  - One station running this protocol and we have begun to run samples.
- SHIVA 1 Automotive Protocol
  - Protocol carried over from previous automotive development.
  - Four Cells commissioned. One sample set started.
- SHIVA 2 Automotive Protocol with 120ºC Excursion
  - Equipment upgrade complete
  - New protocol currently being tested
- Mechanical Membrane Humidity Cycle
  - Equipment upgrade complete
  - New protocol currently being tested

Fuel Cell Testing

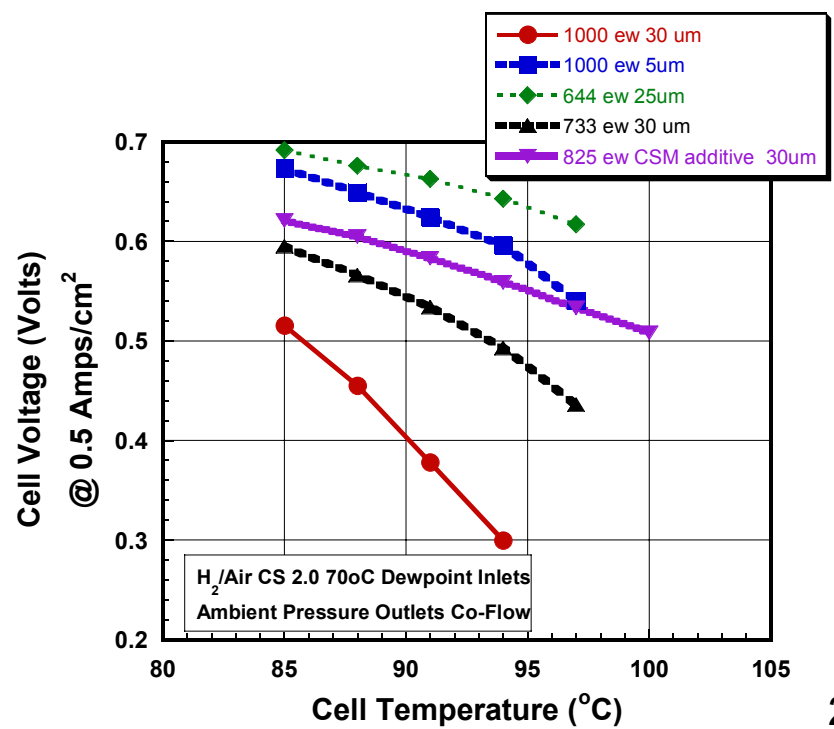
Down selection of screening electrode

- Time was spent evaluating different electrodes for increased performance in the screening of MEAs. We do not want the electrode to limit evaluation of new PEMs.
- Cursor study of such electrode variables as:
  - I/C ratio
  - Ionomer EW
  - GDL type
  - Catalyst type
- **We have down-selected V2 for our screening process.**



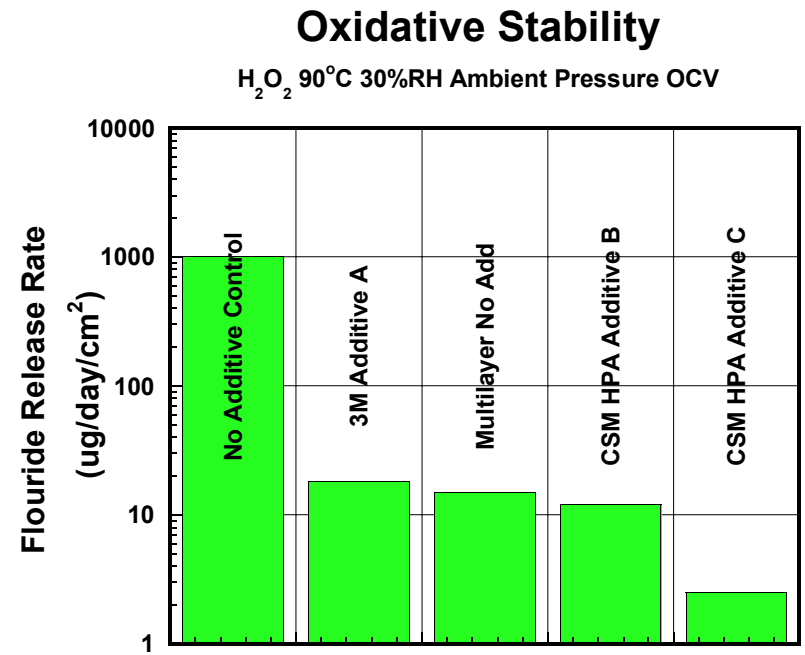
Performance Gains

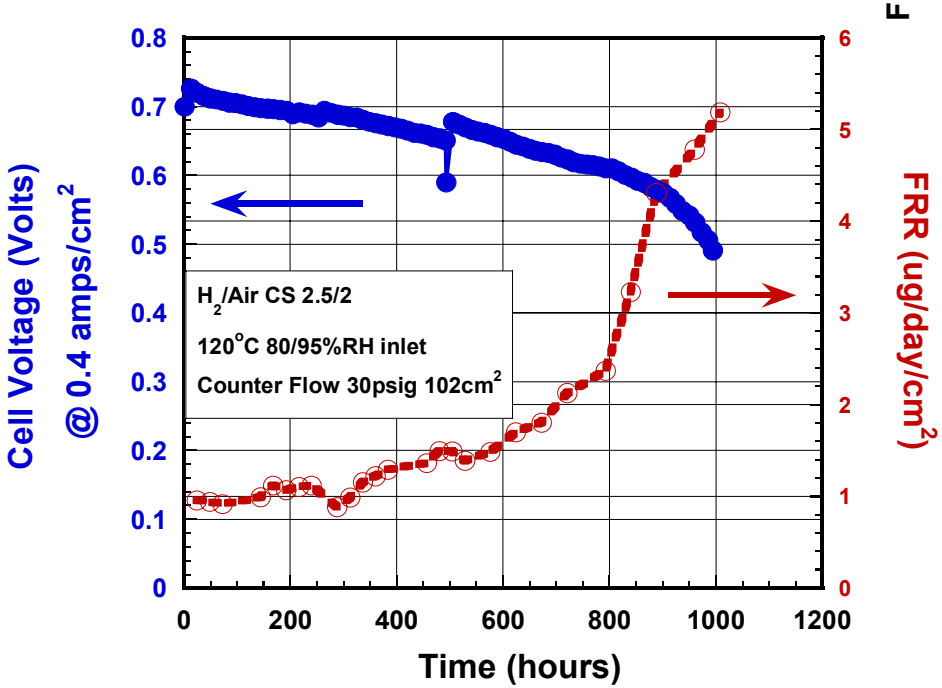
- Over 300 samples have been screened for performance.
- Gains in performance seen with –
  - Thinner PEMS
  - Lower ew
  - New Chemistries
  - New Additives



Oxidative Stability/Durability Gains

- We have screened over 200 samples over our contract so far.
- Variables showing an influence on FRR include:
  - Additives
  - Different PEM constructs.
  - Electrode effects.





- Additive A in 825 EW 3M membrane also provides about 1,000 hours lifetime at **120º C.**
- Relatively high humidity and pressure.
- Future testing will be done at lower pressure, drier conditions.

Future Work

- Continue preparation and evaluate conductivity and durability of low EW and new imide containing polymers.
- Prepare and test membranes crosslinked in both the hydrophilic and hydrophobic regions.
- Produce low EW/MW ionomer segments for 'Hybrid' polymers.
- Demonstrate synthesis of aromatic membrane or monomer unit with perfluorosulfonic acid side chain and 'Hybrid' polymers: Key focus on creating stable 'links'.
- Probe key factors in transport using NMR relaxation and diffusion, SAXS, QCM measurements, conductivity and other spectroscopy measurements. Develop better understanding of effect of low lambda on proton transport.
- Prepare and test zirconyl analogs of new polymers and small molecules.
- Immobilize stabilizing metal ions/HPA through synthesis of novel HPA as stand alone insoluble salts or grafting to ionomer backbone or inorganic nanoparticle.
- Describe degradation pathways for current group of model compounds.
- Quantify the intensity of the •OH radicals in the Fenton reaction based on Ce cations in aqueous solutions.
- Quantify the intensity of the carbon-centered radicals (CCRs) generated in the Fenton reaction in aqueous solutions in the presence of model compounds.
- Assess mechanism of Ce stabilization in dry 3M and Nafion™ membranes.
- Complete hydrated morphology comparison of the three PFSA ionomers: Nafion™, SSC, and 3M ionomer. EW comparison and degree of hydration (λ=3-20)
- Undertake first principles modeling of crystallinity through a comparison of the three PFSA ionomers and aromatic backbone ionomers with perfluorinated sulfonic acid side chains.
- Complete chemical stability comparison of Nafion™, SSC, and 3M ionomer. (1) Bond dissociation energies; (2) Kinetics and thermodynamics of reaction with hydroxyl and peroxyl radicals.
- Begin longer term single cell durability testing.

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 new membranes are being investigated. We expect the final membrane will combine some or all of these. **We will not "down select" just one approach.**

		2008 Status	2010 target	2015 target
Conductivity at 120º C	S/cm	0.03 (25%RH)	0.1	0.1
Conductivity at 80º C	S/cm	0.05 (50%RH) 0.29 (100%RH)	0.1	0.1
Conductivity at 30º C	S/cm	0.08 (80% RH)*	0.07	0.07
Conductivity at -20º C	S/cm	Not tested	0.01	0.01
O2 cross-over	mA/cm^2	Not tested	2	2
H2 cross-over	mA/cm^2	<2	2	2
Durability w/ cycling**	hours	> 5000 (80ºC) <1000 (120ºC)	5000 (80ºC) 2000 (120ºC)	5000 (80ºC) 5000 (120ºC)

*** tested at 25ºC**

**** not same EW membrane as conductivity test**