



**3M**  
Fuel Cell  
Components

**HTMWG**  
**10/14/2010**

# Some durability considerations for proton exchange membranes

**Steven Hamrock**

3M Fuel Cell Components Program

[sjhamrock@mmm.com](mailto:sjhamrock@mmm.com)



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## The membrane in a PEMFC must act as a physical barrier to mixing of the reactant gasses.

- An operating fuel cell creates an aggressive environment for the electrolyte membrane. This includes:
  - Mechanical stresses related to changes in the level of membrane hydration.
  - Thermal variations, sometimes including temperatures exceeding the  $T_{\alpha}$  (or  $T_g$ ) of the ionomer.
  - A chemically aggressive environment including hot water, strong acid, oxidants such as  $H_2O_2$  and reduction by  $H_2$ .
- The membrane must also survive the fabrication process without loss of chemical stability.
- Thermodynamically, no polymer membrane is stable. They all want to be  $CO_2$ ,  $H_2SO_4$ ,  $H_2O$ ,  $HF$ , etc.

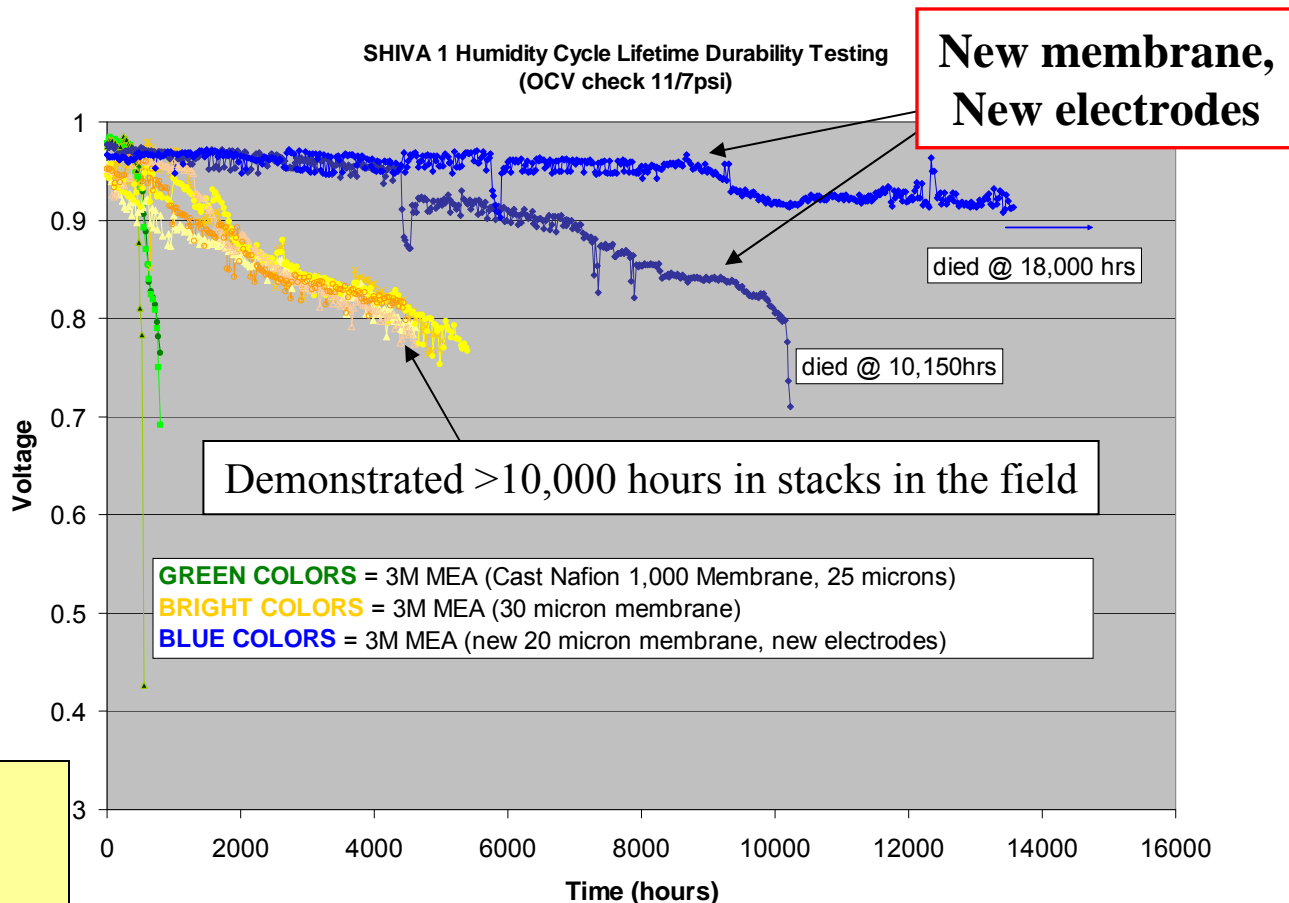
**Membranes and MEA's already last a fairly long time under the right conditions.**

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## Fuel Cell Durability Testing

| 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%**



# Water and temperature management are key issues in operating PEM fuel cell systems.

Current membranes need water to maintain high conductivity, requiring the incoming gas streams to be humidified. The drawbacks to this are:

- Additional expense of humidifiers and parasitic power losses from their operation.
- Dilution of hydrogen and air with water vapor.
- Mass transport “flooding” at high current densities (liquid water begins to collect in catalyst layer and current collector and limit access of gasses to catalyst).
- Increased system complexity.

Also, in order to maintain adequate membrane humidification, temperatures must be below about 90°C. High %RH at higher temps required a lot of water. Operation at higher temperature ( $\geq 120^\circ$ ) would allow:

- Improved heat rejection and simpler cooling systems. (smaller radiators).
- Improved catalyst resistance to poisons like CO in reformed fuels.
- Combined heat and power generation, improving system efficiency. (i.e. hot water and electricity production in stationary residential systems).

**There is a big push for membranes that depend less on water for conductivity, allowing hotter and drier fuel cell operating conditions.**

**US DOE and industry targets are 100 mS/cm conductivity and 5,000 hours durability at 120°C below 40% RH.**



## Operational Issues/challenges for PEMFC's. hotter and drier operation is desired.

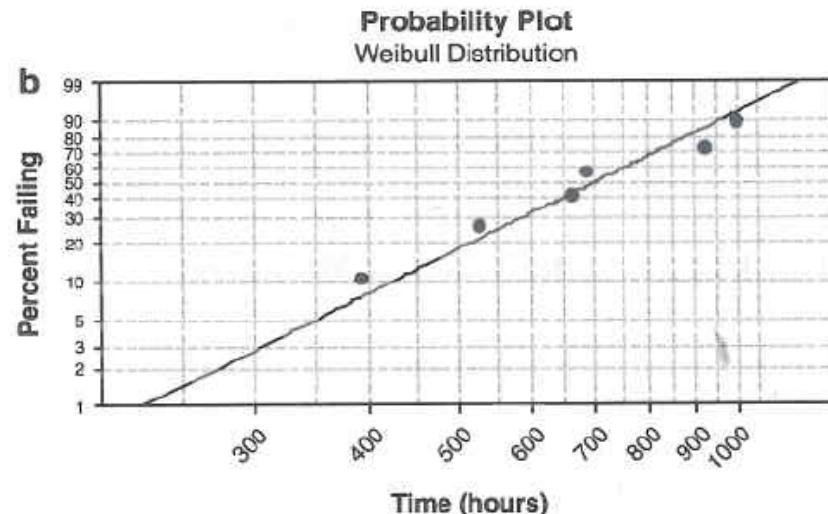
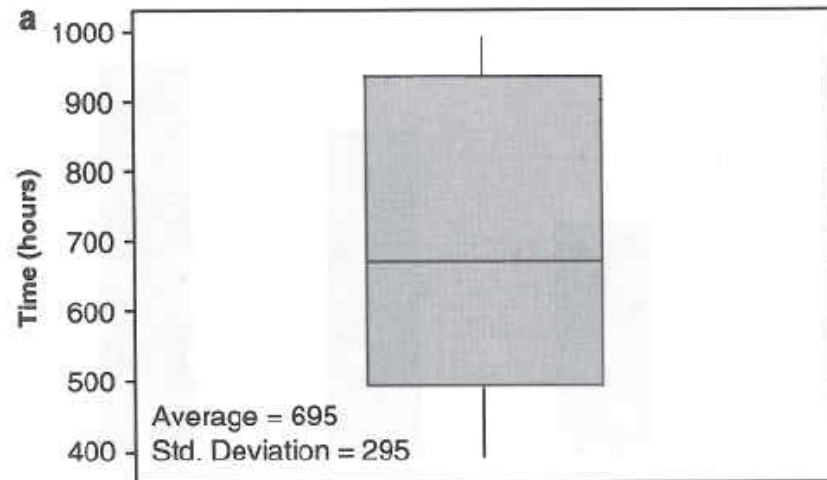
- In addition to lower conductivity, higher temperatures, lower humidity levels and repeated changes in humidity levels decrease membrane durability. Reasons for this include:
  - Many membrane materials have poorer mechanical properties at higher temperatures. Tear, puncture and creep resistance can be compromised.
  - Repeated swelling and shrinking can mechanically stress the membrane.
  - Chemical oxidation of the membrane is increased at lower humidity levels, presumably due to increased peroxide generation at the electrodes, increase peroxide decomposition rates with higher proton activity, and/or less water to dilute or flush out peroxide in the membrane.

# Single cell lifetime doesn't tell whole story

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- In cell durability tests are important but statistics are important.
- For a variety of reasons, single cell lifetimes may not tell you how long a stack might last.
- MEA construction has a big impact on the time to membrane failure, so a consistent component set is important



Hicks and Pierpont in "Polymer Electrolyte Fuel cell Durability" p. 385, Springer, 2009.

**Fig. 8** Analysis of lifetime data using (a) average and standard deviation and (b) statistical probability distribution



## Failure is always related to mechanical properties of the membrane.

- Will be covered in detail by another speaker.
- Can be difficult to separate chemical and mechanical components or durability. Chemical changes in the ionomer can result in changes in the viscoelastic properties of the membrane.
- Membrane structure, composition and mechanical properties can dictate process in conditions (i.e. drying and annealing temperatures in cast membranes). Membranes must be stable under these conditions.



## Thermal stability of the ionomer

- While use temperatures for PEM fuel cells may not be high enough to cause ionomer degradation, thermal treatments are often needed for solution cast membranes to achieve good mechanical properties.
  - Thermal history can also impact conductivity
- $T_g$  or  $T_\alpha$  can often be quite high for ionomers, requiring high temperature processes for film formation.
- Both aromatic and fluorinated sulfonic acid ionomers will desulfonate upon heating.
- Aromatic polymers may be cross-linked via sulfone formation



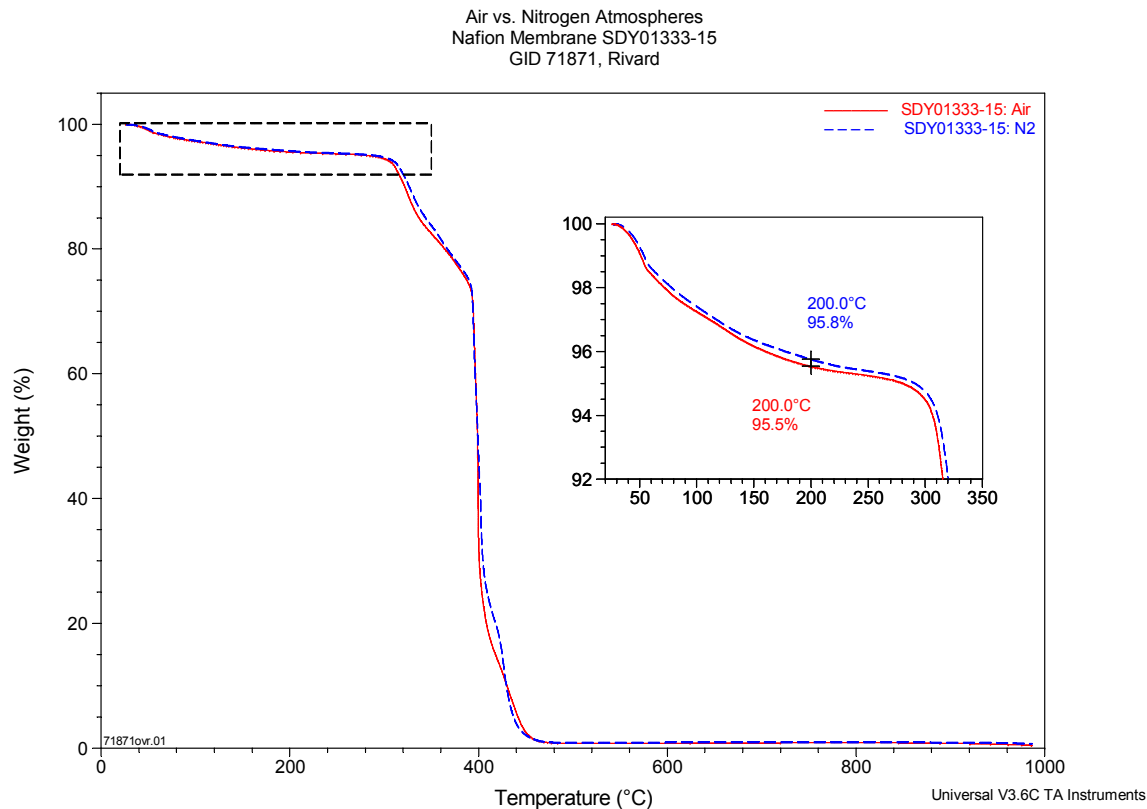


## TGA of Nafion™ 1000 cast film

PFSAs generally have pretty good thermal stability. Up to about 200°C water is lost. (5.5%  $\rightarrow \lambda \approx 3$ ).

At about 300°C sulfonic acid groups are lost. (16%  $\rightarrow$  SO<sub>3</sub>H accounts for 1/2).

Just because this happens at 300°C in TGA does not mean the polymer can be heated this high. We have seen evidence of decomposition at prolonged exposures >200°C

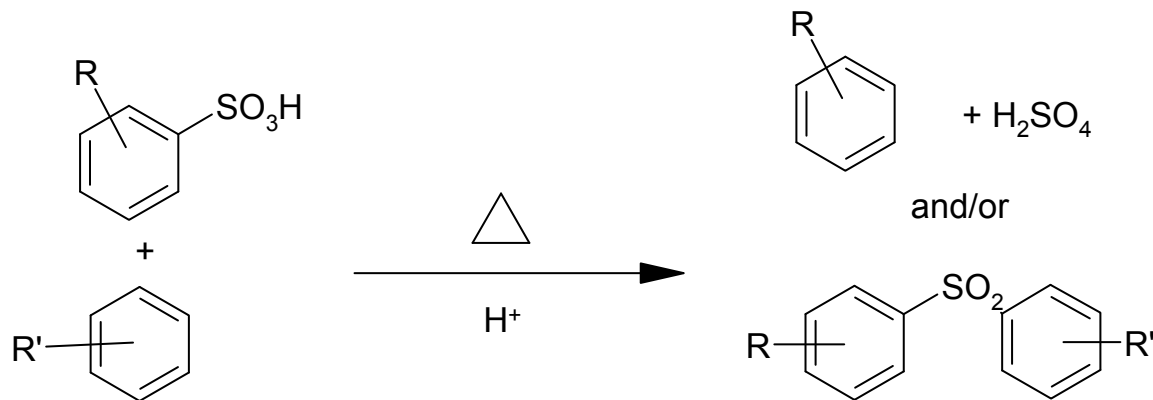


The samples were analyzed using the TA Instruments 2950 Hi-Res Modulated® Thermogravimetric Analyzer (MTGA) in standard TGA mode. An initial heating rate of 50°C/min was applied, with a resolution setting of 4.0. Under these conditions, the instrument heats until weight loss is detected, the temperature stabilizes until weight loss diminishes, and then heating recommences.



## Aromatic sulfonic acids can de-sulfonate, form sulfones

- In the presence of acid at high temperatures sulfonic acids will lose  $\text{SO}_3\text{H}$  and/or form sulfones with other arenes
- Desulfonation typically occurs between 125 and 250°C and is very sensitive to pH and the electron density of the ring.
  - Electron donating groups (R) tend to lower de-sulfonation temperatures, electron withdrawing groups tend to increase desulfonation temps.

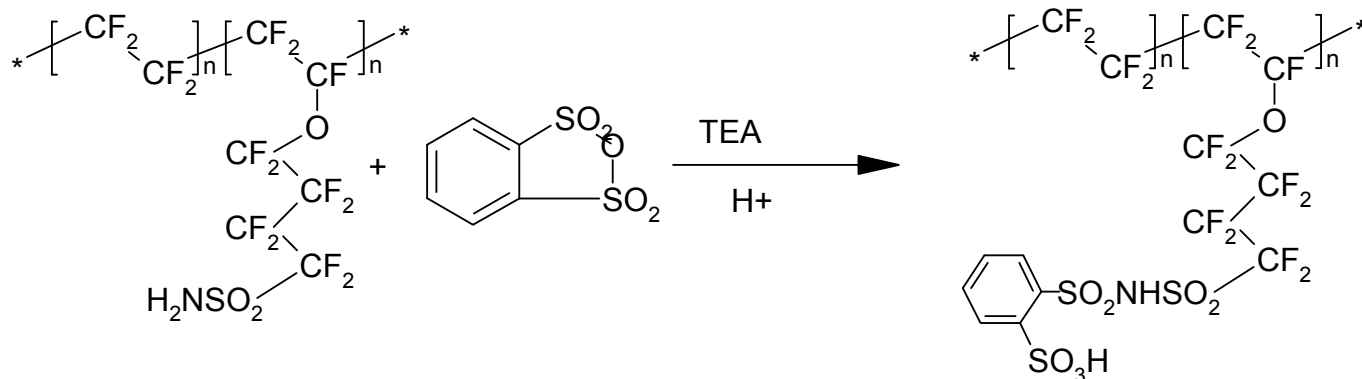


*Sulfone formation can  
result in cross-links*

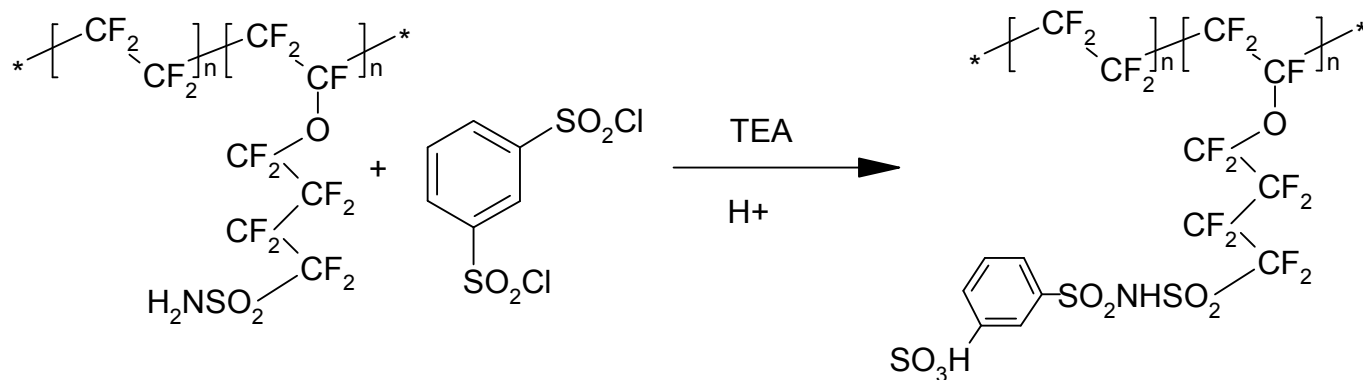
1. EE Gilbert "Sulfonation and Related Reactions" Wiley-Interscience 1965
2. A. Meyer, Ann., 433, 327 (1923),
3. B.M. Graybill, J. Org. Chem. 32 (9), 2931 (1967).



## Addition Of More Sulfonic Acids To Side Chain Polymer



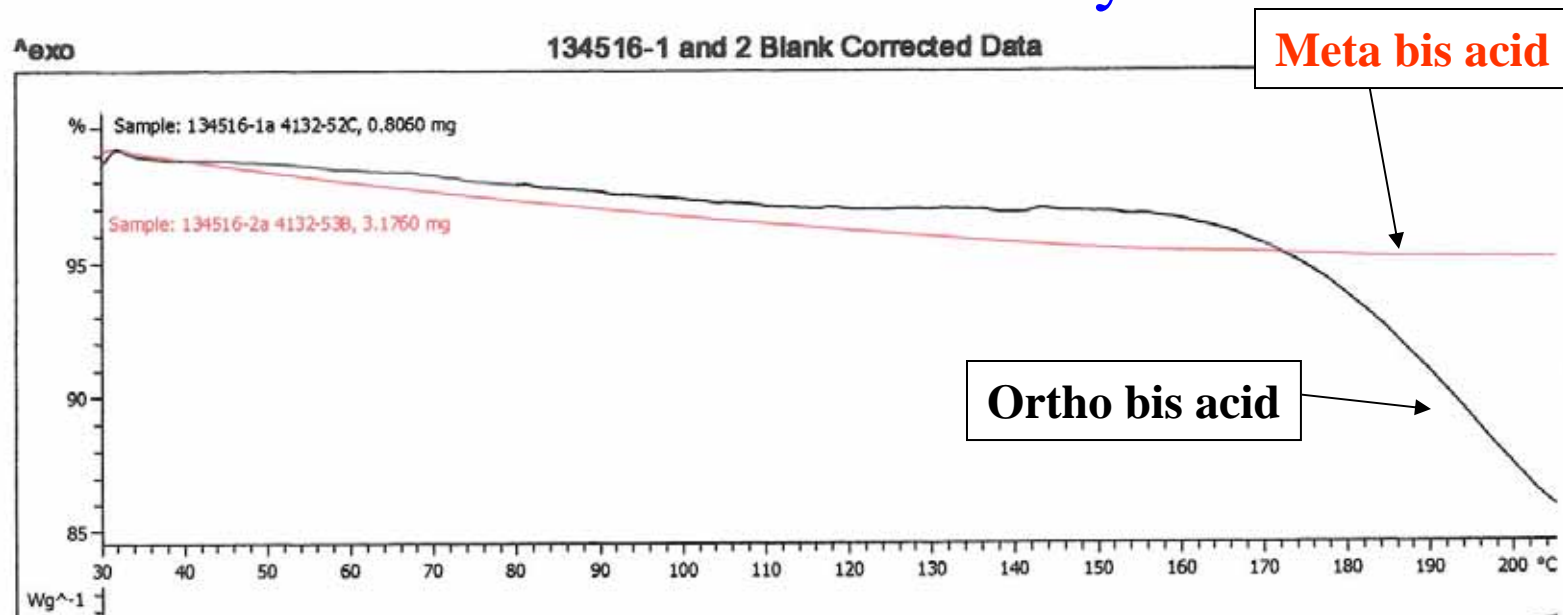
Ortho and Meta bis acids are prepared in high yield from inexpensive starting materials



Imide linkages are isoelectronic with sulfonic acids and have been shown to be stable to hydrolysis



## Thermal Gravimetric Analysis



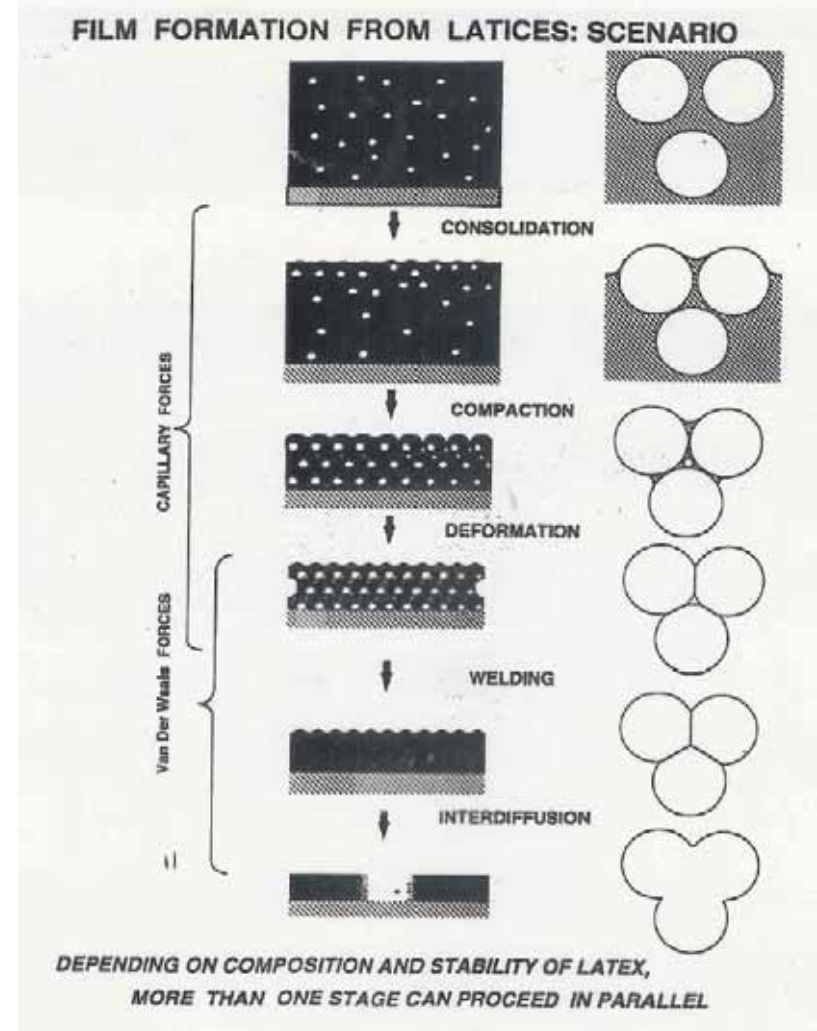
- The ortho substitution is less thermally stable than the meta, para.(1).
- This temperature range and relative reactivity is consistent with observations on other arene bis-sulfonic acids (2).
- Neutralized samples have much better stability.

1. SJ Hamrock U.S. Department of Energy Hydrogen Program 2009 Annual Merit Review Proceedings.  
2. EE Gilbert "Sulfonation and Related Reactions" p. 430 Wiley-Interscience 1965

# Why do we care about thermal stability?

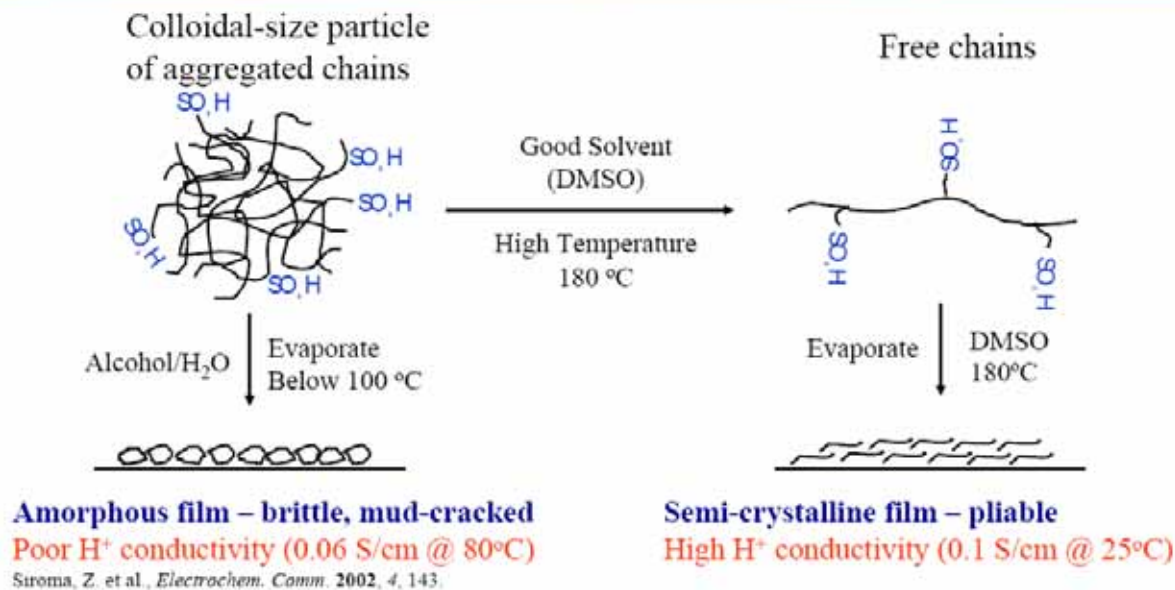
## Minimum film forming temperature (MFFT)

- Coating from a dispersion often requires heating the film above a minimum film forming temperature, or “MFFT” to get good mechanical properties. Without this, your membrane may look nice, but residual interfaces from the dispersion particles may compromise film properties.
- Not as great an issue if ionomers are cast out of “good” solvents.
- MFFT is often 40-50°C or more above  $T_g$
- Ionomers also have ionic structure which forms during drying and this phenomenon can be vastly more complex



## Thermal process can also affect conductivity

### Solution Processing of Perfluorosulfonate Ionomer Membranes

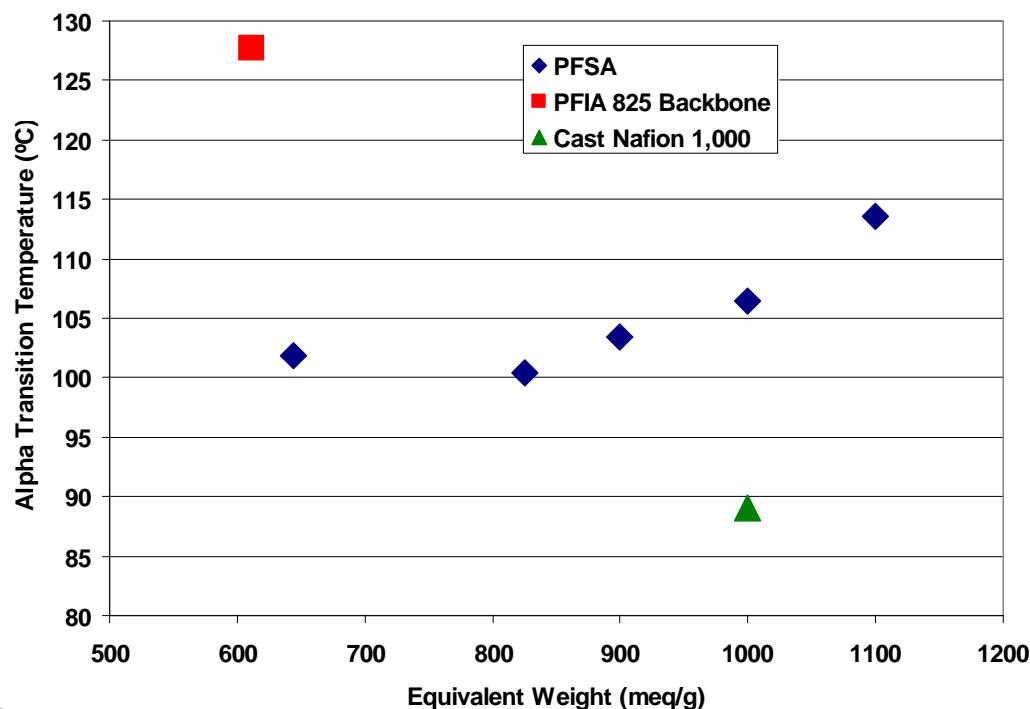
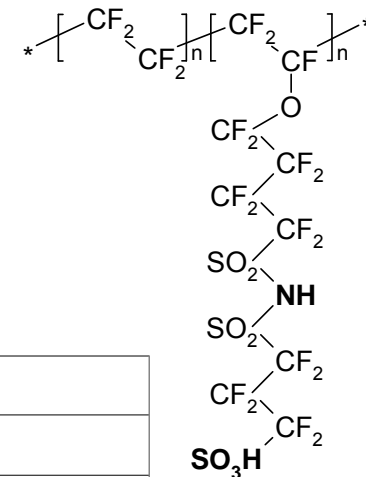


Moore, R.B.; Martin, C.R. *Macromolecules* 1988, 21, 1334.





## PFSA's soften above 100°C



- Not a sharp transition like a melting point. Coating typically must be heated a fair bit above this temp for good mechanical properties
- The PFIA ionomer has a higher  $\alpha$  transition ( $T_g$ ) than a PFSA of the same EW.
- SSC Ionomer (Dow, Solvay) has an even higher  $T_\alpha$  ( $>140^\circ\text{C}$ ).
- In semi crystalline polymers  $T_m$  must also be considered.

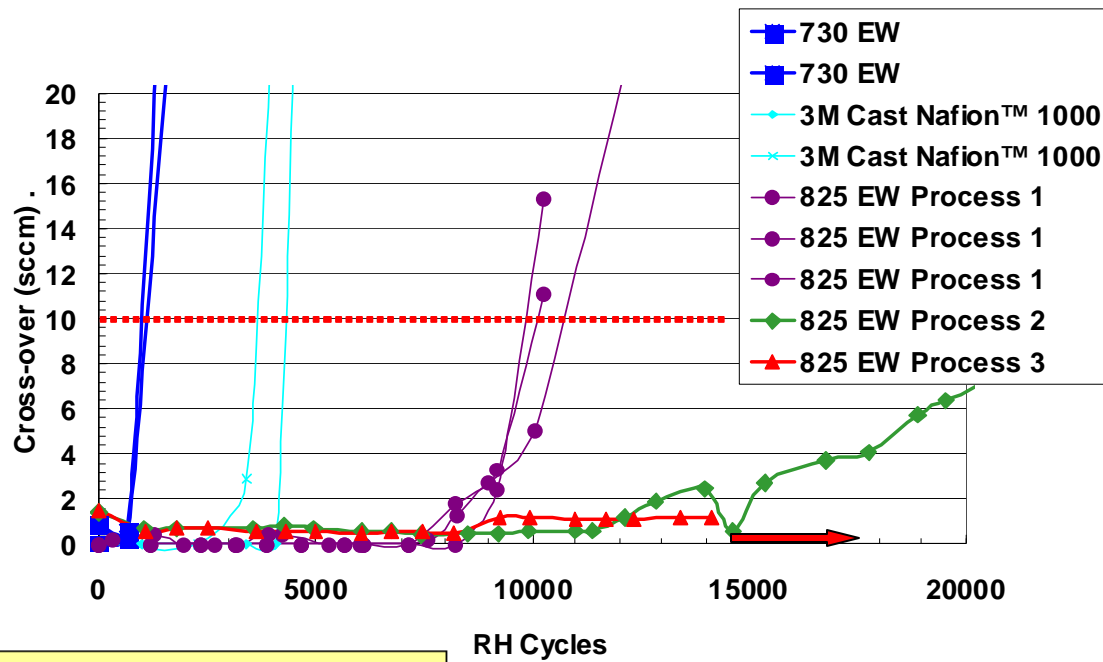
*$T_g$ 's of Hydrocarbon ionomer can be much higher.*



## 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)

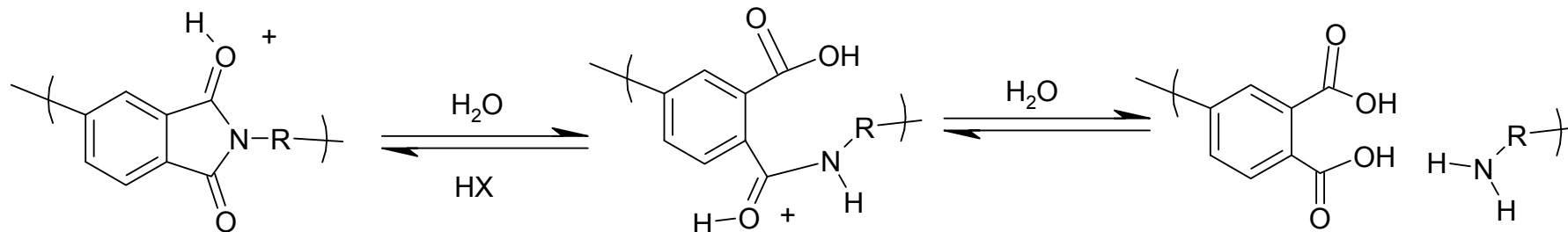
**Target:** 20000 RH cycles with no measurable crossover leak or observable mechanical damage





## Stability towards acid catalyzed hydrolysis

- There is currently no evidence that PFSA's undergo hydrolysis. If you have evidence to the contrary please let me know.
- Some aromatic hydrocarbon ionomers have been shown to hydrolyze under acidic conditions.
- Since only acid catalysis is possible, electron withdrawing groups should improve stability.
- Naphthalenic imides are thought to be more stable due to lower ring strain moving equilibrium of step 1 to the left.



# Sulfonated polyimides undergo hydrolytic cleavage.

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Meyer et. al. have shown that even naphthalenic imides are still susceptible to hydrolytic degradation

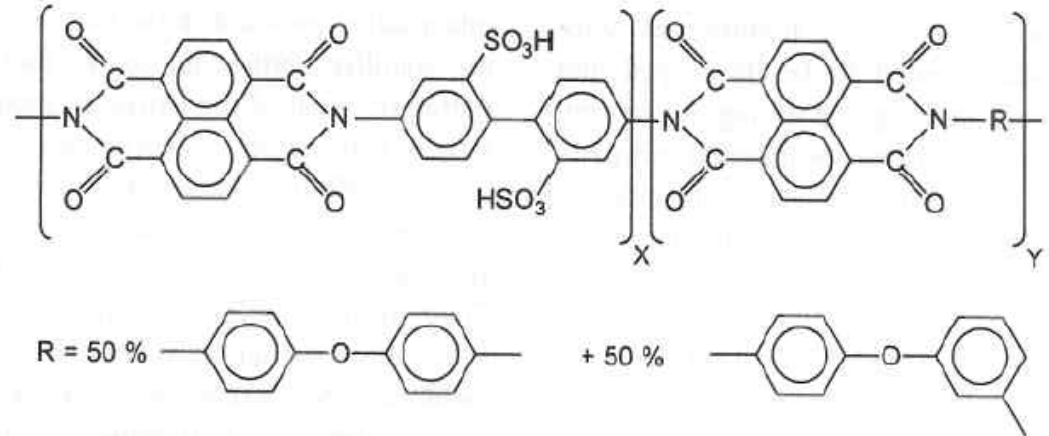


Fig. 1. General chemical formula of sulfonated polyimides.

IR, tensile measurements shows loss of cyclic imide functionality.

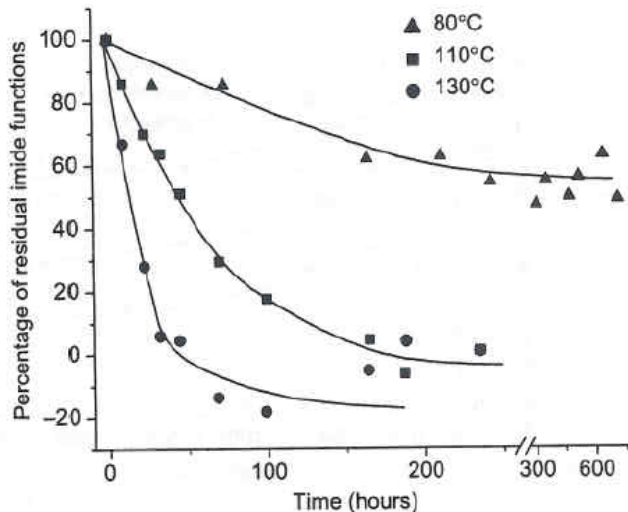


Fig. 6. Percentage of residual imide functions against ageing time in water for different temperatures ranging from 80 to 130 °C and a sPT 0.9/5–21 membrane.

G. Meyer et. al, *Polymer* 47 (2006)



## Oxidative stability

- It has been proposed that  $\text{H}_2\text{O}_2$  can be formed on the anode at higher voltages, the cathode at lower voltages and on Pt deposited within the membrane from catalyst dissolution at the cathode (1,2).
- $\text{H}_2\text{O}_2$  can decompose to form hydroxyl and hydroperoxy radicals and this reaction is catalyzed by metals such as Pt particles deposited in the membrane or Fe or other metals which can find their way into the membrane from corrosion of system components or other (?)
- Hydroxyl radical is an extremely electron deficient species and can attack any ionomer (3)
- The lifetime of  $\text{H}_2\text{O}_2$  is probably sufficiently long enough to allow to diffuse throughout the membrane before decomposition.
  - The area where the membrane sees the most degradation is not necessarily where the peroxide is formed, perhaps just where  $\text{OH}^\bullet$  is formed.

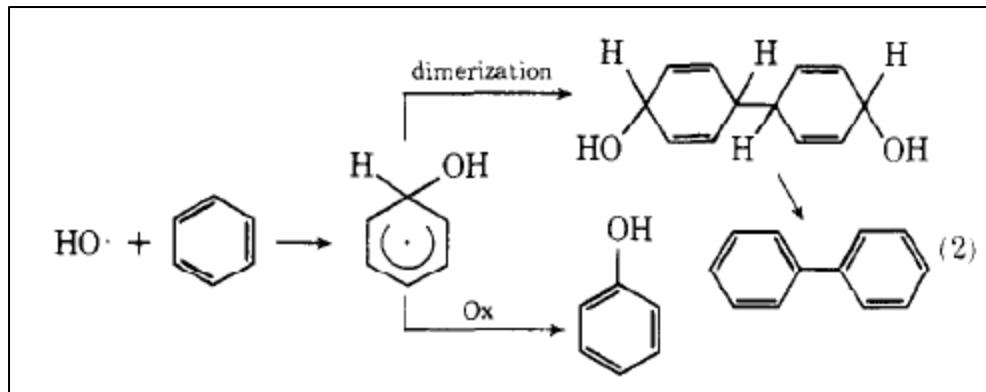
1. H. Liu in "Polymer Electrolyte Fuel cell Durability" p. 71, Springer, (2009).
2. Ohma et. al, ECS Transactions, 11(1) p.1183 (2007)
3. FD Coms, ECS Transactions, 16(2) p.235 (2008)

# Hydroxyl radicals add to aromatic rings

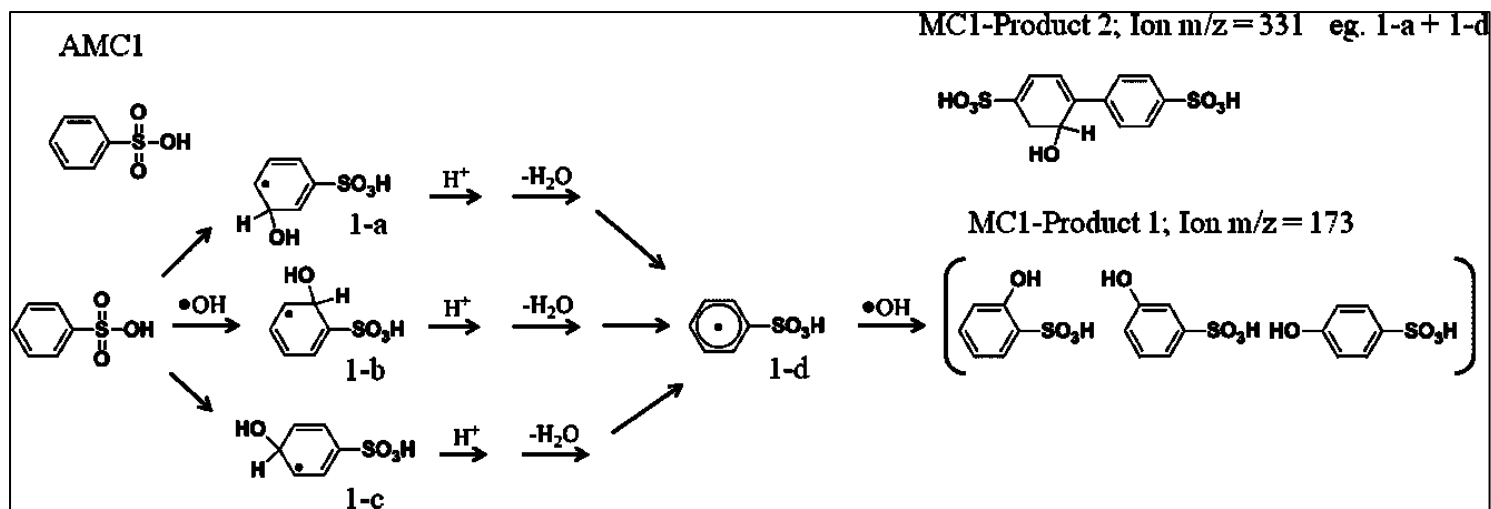
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- Aliphatic hydrocarbons degrade quickly in fuel cells and Fenton's tests.
- $\text{OH}^\cdot$  adds to aromatic rings to give hydroxyls, coupling. Reaction is:
  - Catalyzed by Fe, metals
  - Accelerated by  $e^-$  donating groups, slowed by  $e^-$  withdrawing groups (the second hydroxyl probably adds faster).



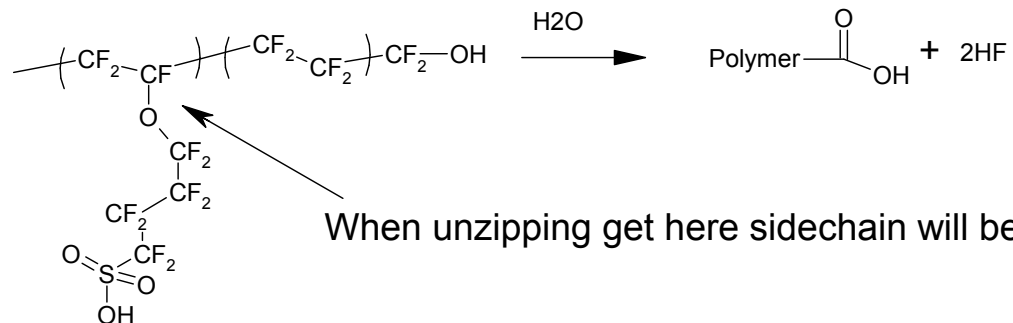
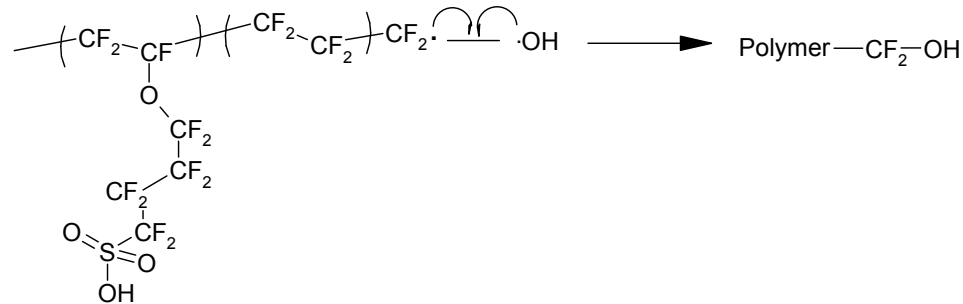
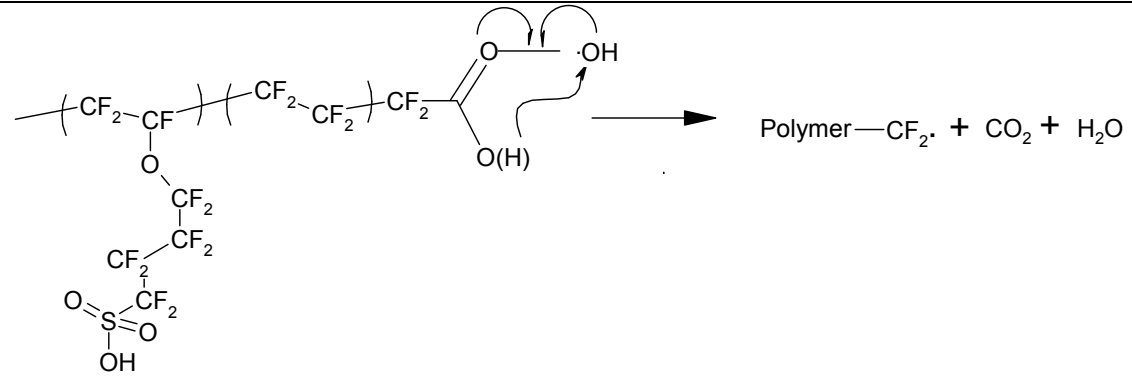
C Walling, RA Johnson, JACS 97, 363(1975)



D Schraldi et. al. in "Fuel Cell Chemistry and Operation" ACS Symposium Series, p137(2010)

# PFSAs react too. Reaction of hydroxyl radicals with polymer end groups

- Carboxylate end groups are common in many fluoropolymers and also often the product of oxidative degradation of fluoropolymers
- Fluorinated carboxylates are known to react with oxygen centered radicals.
- Ionomer is “un-zipped”, one carbon at a time.

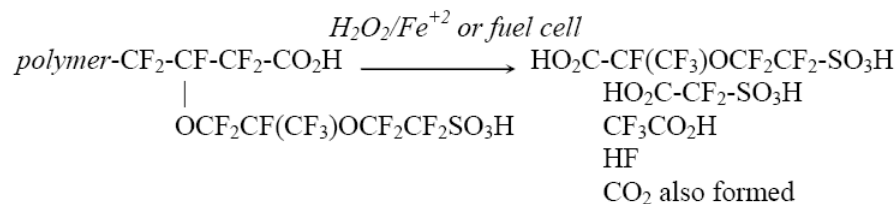


When unzipping get here sidechain will be lost



## People find other degradation products

- In addition to HF, side-chain fragments have also been identified as degradation products.
- These products are consistent with un-zipping mechanism, but could also be form side-chain cleavage.

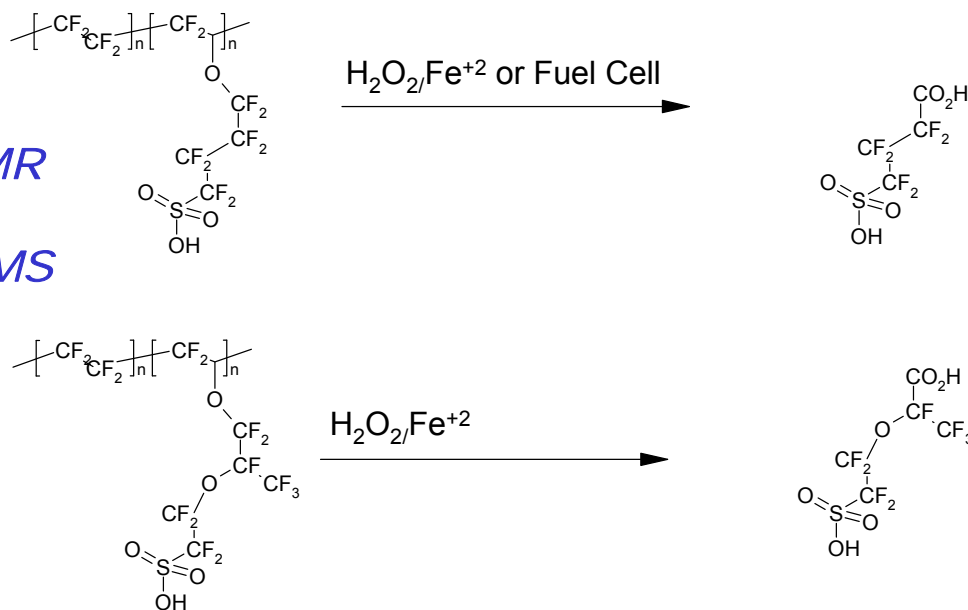


[1]

**$^{19}\text{F}$  NMR**

*KE Schwiebert, ECS Transactions, 1 (8) 303 (2006)*

**$^{19}\text{F}$  NMR  
and  
HPLC/MS**





## HF and other fragments can come from unzipping

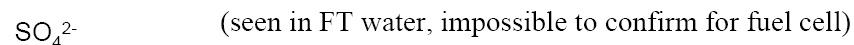
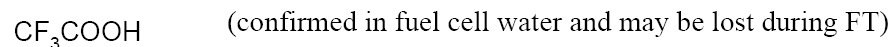
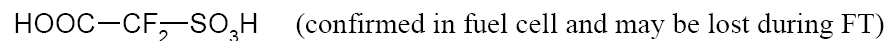
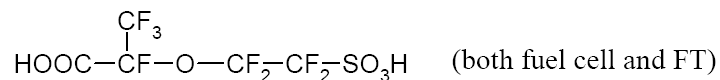
- Side-chain fragments can be lost and then further degraded.

### Degradation Products

Main products:

HF      CO<sub>2</sub>      (both fuel cell and FT water)

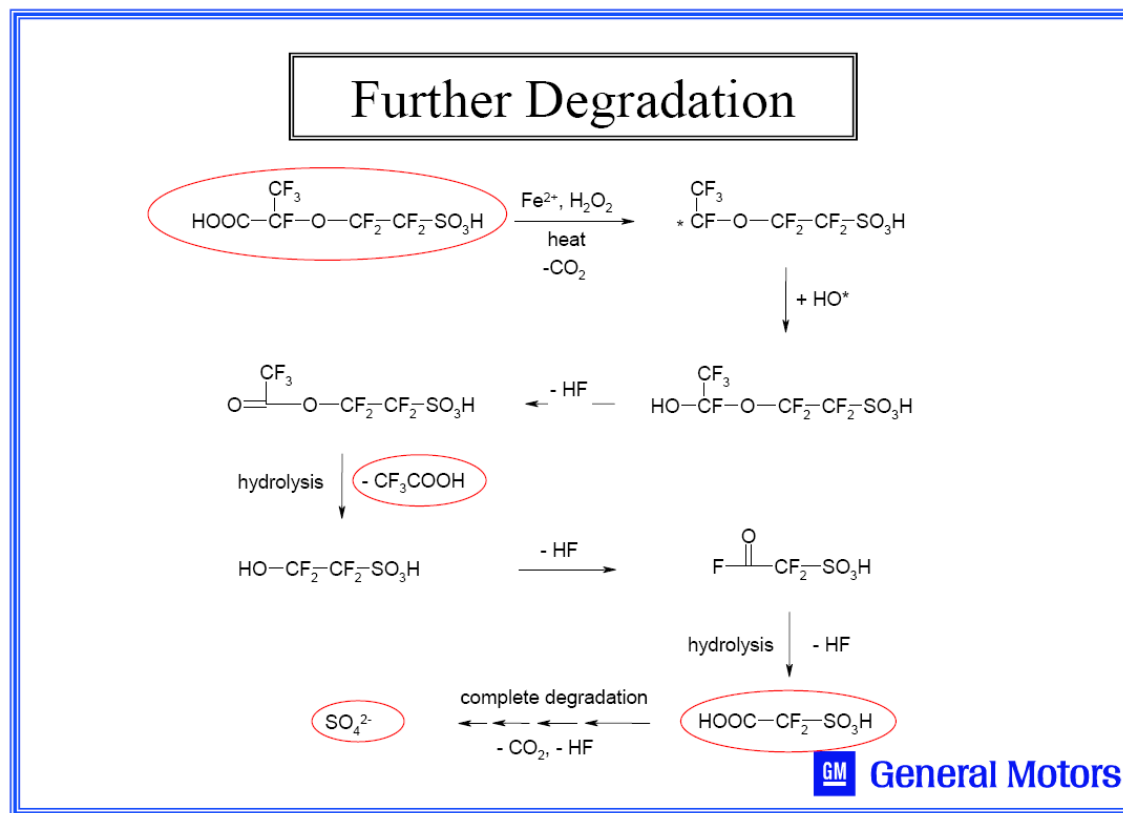
Other products:





## HF and other fragments can come from unzipping

- Side-chain fragments can be lost and then further degraded.



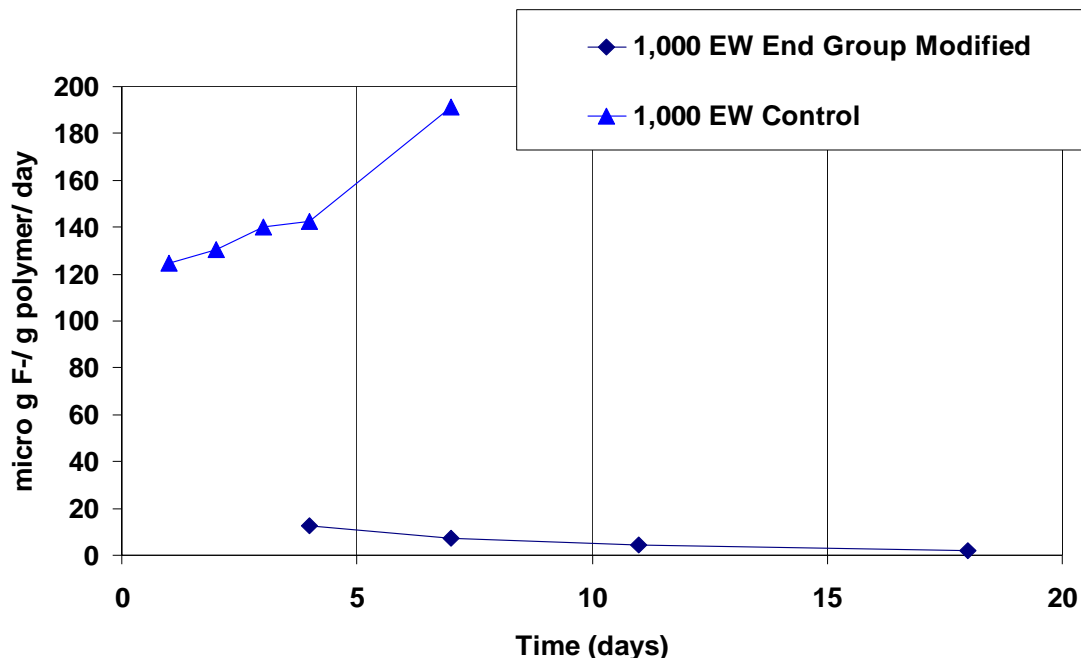
Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005





## Process allows ionomer to be made with much lower concentration of carboxylate endgroups.

- Degradation can also be followed by monitoring fluoride levels in peroxide solution.
- Run in 1M H<sub>2</sub>O<sub>2</sub> with 200 ppm Fe.
- Membrane with lower concentration of carboxylate endgroups exhibits much lower rate of degradation.
- Fuel Cell testing shows lifetime increased by almost 2x (50 cm<sup>2</sup> cell, 90C, 30%RH. Load cycled OCV-0.25-0.5 A/cm<sup>2</sup>)





## Unzipping mechanism accounts for all of the degradation products seen so far but...

DuPont - Lower end group count membranes lasted about 8x longer in OCV tests. Less of an effect at lower V?

If one believes that this is a straight line, then even with end group concentration “below the detection level”, the polymer still degrades – another mechanism or a better detection method needed?

If you remove one reactive group do radicals find another place to attach??

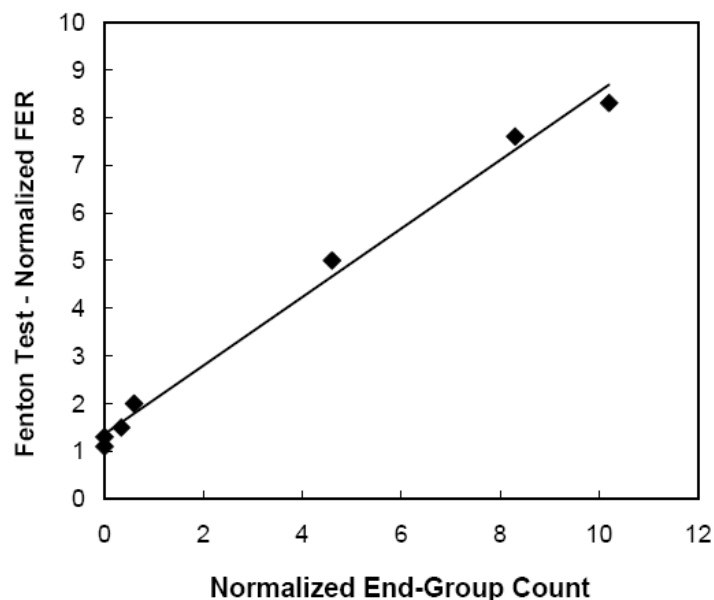


FIGURE 3. Relative Fluoride Emission vs. Normalized End-group Count for Nafion® Ionomers.  
Fenton's test conditions: 85 °C, 3 cycles with fresh reagent, 30% H<sub>2</sub>O<sub>2</sub>, 20 ppm Fe<sup>2+</sup>

# Side chain attack

Component

- Membrane and model compound studies show that side-chain functional groups can degrade when exposed to peroxide.
- It has been proposed that hydroxyl radical or hydrogen atoms generated from its reaction with  $H_2$  may attack sulfonic acid or ether linkages in the sidechain.
- Worth noting: MEAs run for 1,000s of hours under various conditions at 3M typically show a slight **decrease** in cell resistance, due at least in part to membrane thinning. No evidence of changing EW.

D Schiraldi et. al. *Macromol.* 40, 8695(2007), Schlick, Et. Al. *Fuel Cells*, 436(2008)

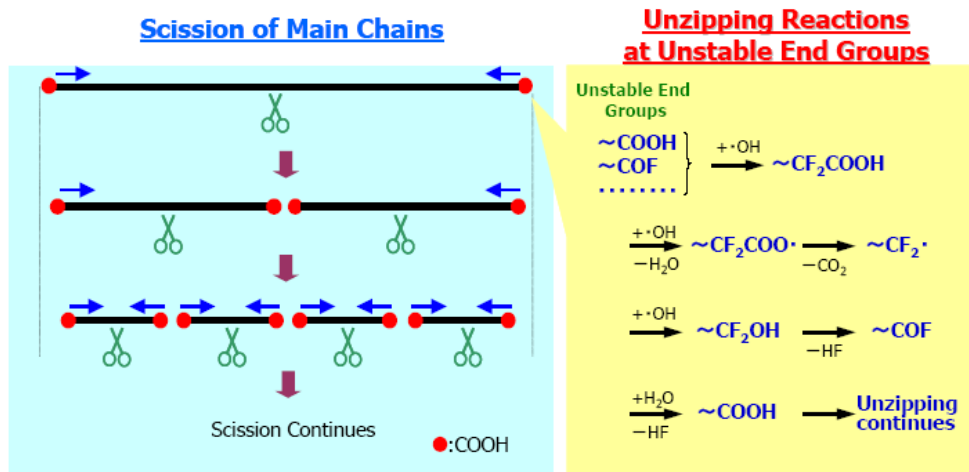


Fig.4 Degradation mechanism of perfluorinated membrane

S Hommura, *J Electrochem Soc*, 155 1 A29 (2008)

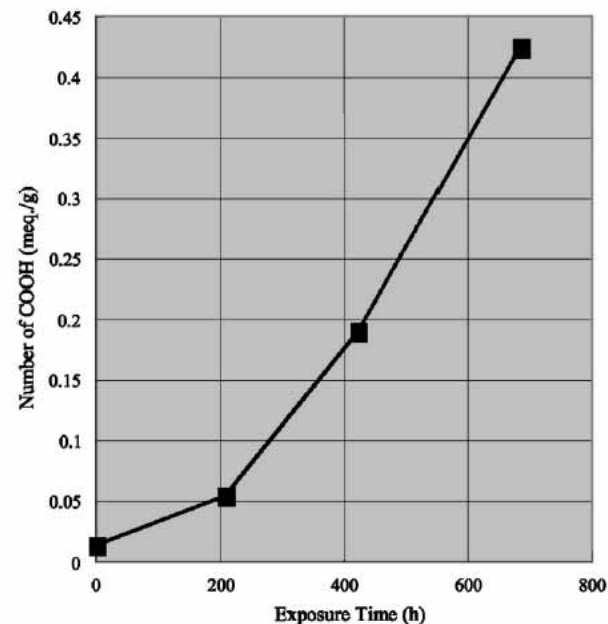


Figure 5. Number of carboxyl groups in degraded membrane.

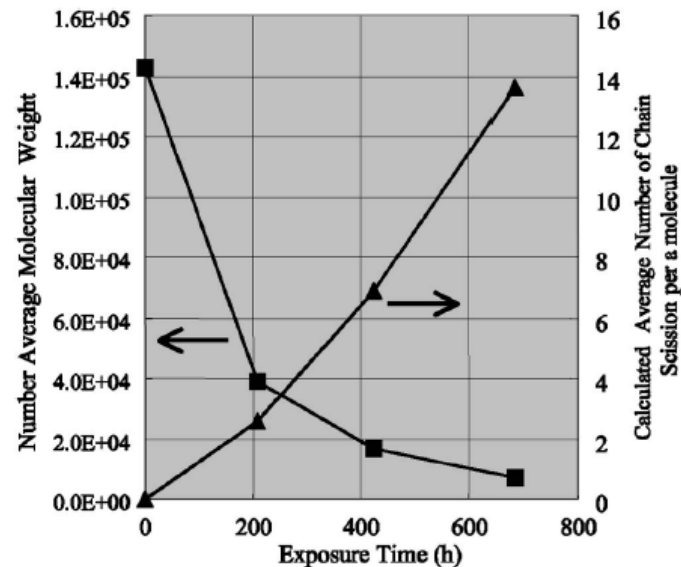
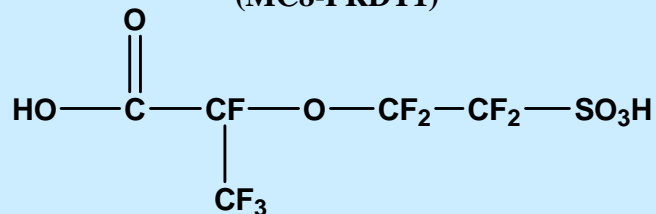


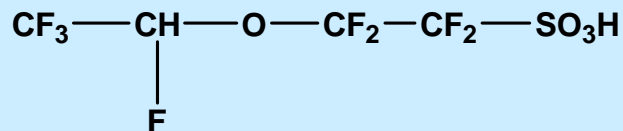
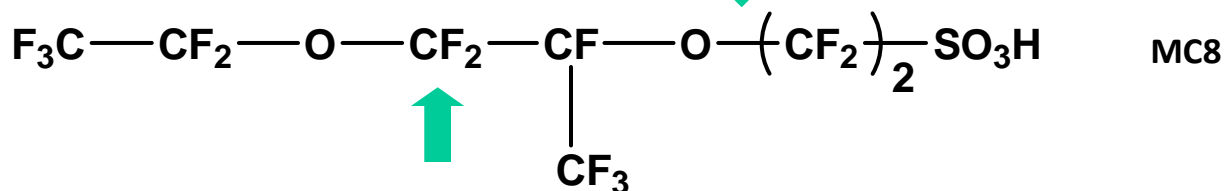
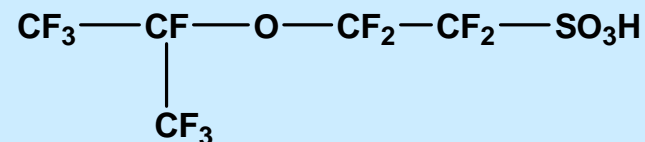
Figure 8. Molecular weight and calculated number of chain scission.

# MC8 Degradation Products

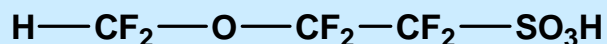
MC8, Product-1  
(MC8-PRDT1)



MC8, Product-2  
(MC8-PRDT2)



MC8, Product-3  
(MC8-PRDT3)



MC8, Product-4  
(MC8-PRDT4)



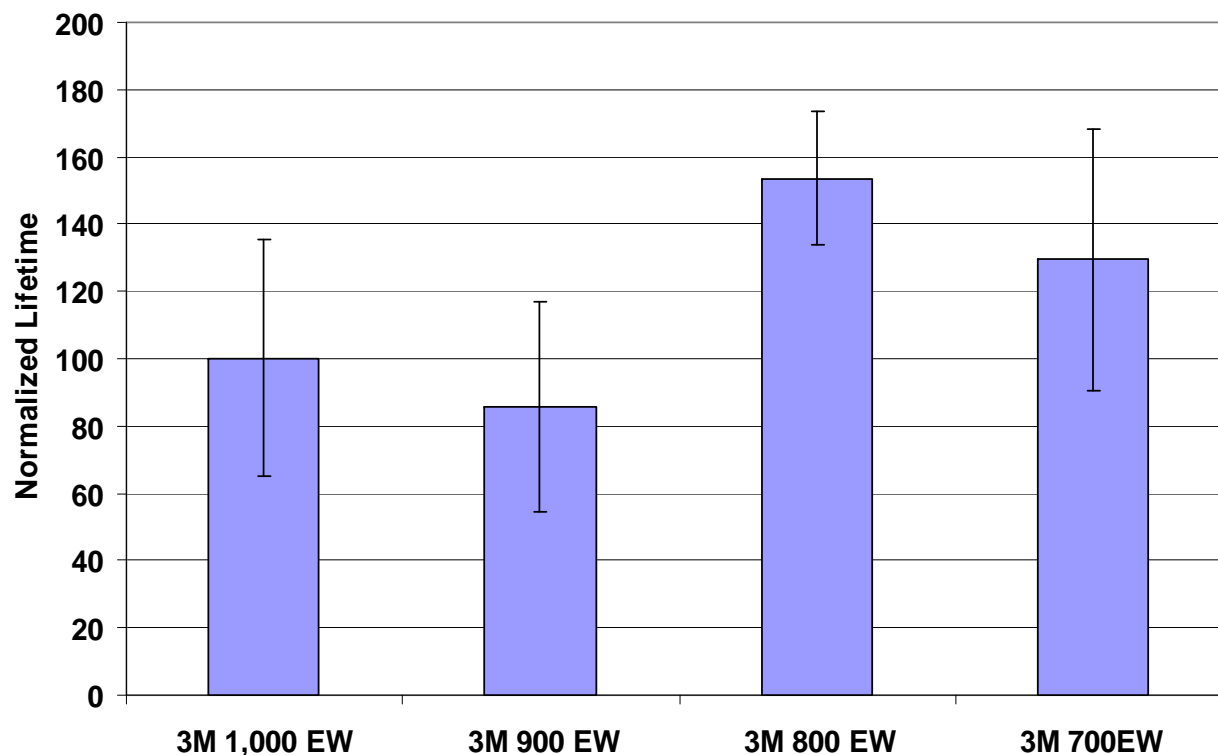
*Thanks to Dave Schiraldi*



## Normalized lifetime under accelerated testing

Normalized lifetime 5 samples each

- Test run at 90°C, 30%RH. Load cycled OCV-0.25-0.5 A/cm<sup>2</sup>
- Lifetime defined as when OCV drops below 800mV.
- No difference from 700 to 1,000 EW in this test.
- 40% increase in SO<sub>3</sub>H group concentration

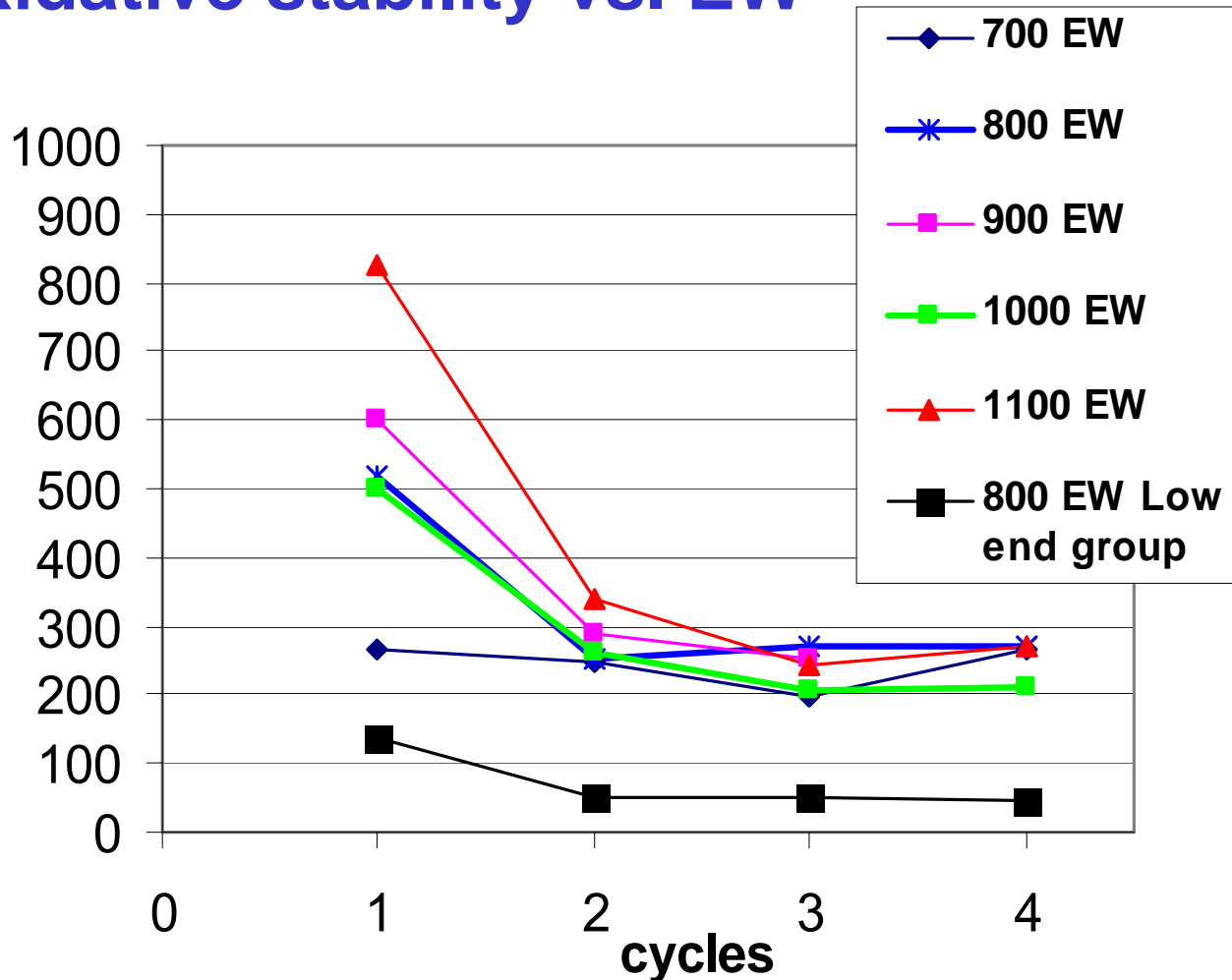




## Oxidative stability vs. EW

- Samples are heated to 70°C in 30% H<sub>2</sub>O<sub>2</sub> with 50 ppm Fe.
- H<sub>2</sub>O<sub>2</sub> is changed every 3 days.
- Degradation is followed by monitoring F- content of the solution with an ISE

**F- ppm/g membrane**



# Hydrocarbon membranes with poorer oxidative stability can last longer in FC tests

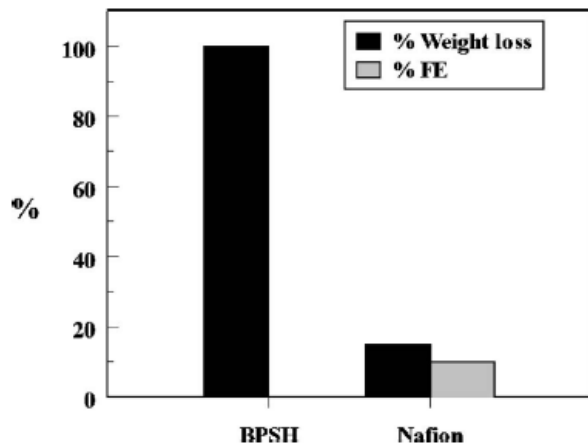


Figure 1. Percent weight loss and fluorine emission obtained from Fenton tests on BPSH and Nafion membranes after 24 and 96 h, respectively.

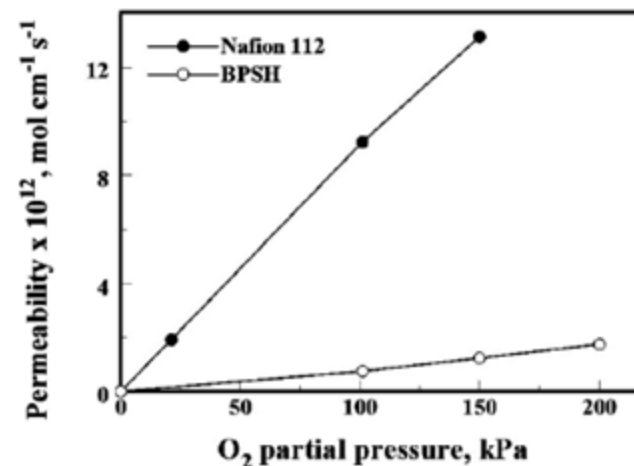
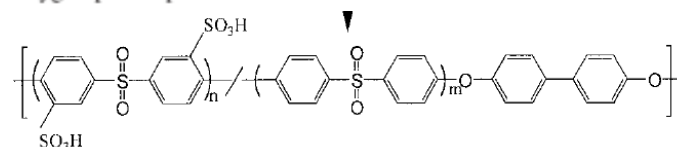


Figure 8. Oxygen permeability rates for Nafion 112 and BPSH membranes measured using the electrochemical monitoring technique at 25°C for different oxygen partial pressures.



While the BPSH degrades about 5 times faster than the Nafion membrane in a Fenton's test, it has about 11x lower O<sub>2</sub> permeability. This results in a 7x increase in lifetime in an OCV durability test. O<sub>2</sub> crossover to form H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> crossover which promotes formation of a Pt band in the membrane are thought to be important contributors to degradation at OCV.

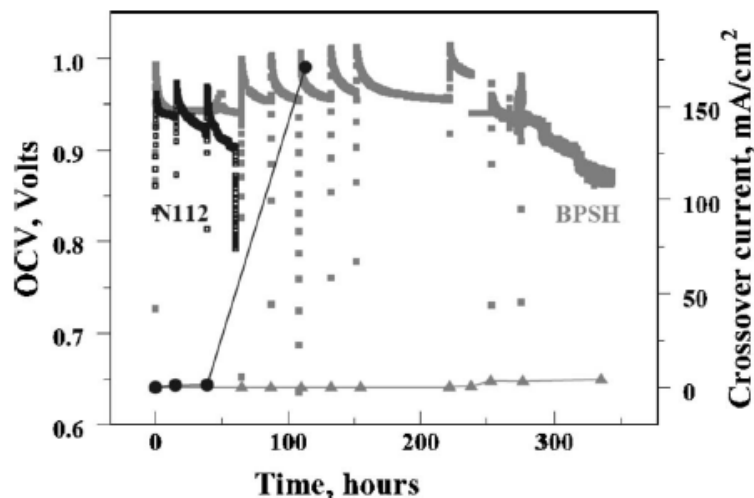


Figure 4. OCV decay (□, ■) and hydrogen crossover current (●, ▲) for Nafion 112 (□, ●) and BPSH (■, ▲) membranes at 100°C and 25% inlet gas relative humidity.



## To Fenton's test or not to Fenton's test? Steve's opinion

- Fenton's testing can give useful data on the oxidative stability of the components of a membrane **but**,
- It is not a way to predict how long a membrane or MEA will last in a fuel cell. There are too many other factors related to the membrane such as degree of in plane swelling and gas permeability which have a big impact on lifetime **but**
- The BPSH membrane that lasted 350 hours at OCV presumably failed due to oxidative degradation. Can improved resistance to hydroxyl radical attack increase this? Has anyone made a membrane that meets automotive durability requirements?
- If you're gonna do it - Tests must be run under carefully controlled conditions



# The rate at which $\text{H}_2\text{O}_2$ forms radicals is sensitive to a lot of things

- Estimates of the effective pH inside an ionomer membrane vary a lot (1,2) but it is quite acidic. At these pHs, the  $\text{H}_2\text{O}_2$  decomposition rate may be very sensitive to changes in pH or  $\lambda$  (3).
- Can changing the nature of the protogenic group or the morphology impact local pH and  $\text{H}_2\text{O}_2$  decomposition rates?
- At lower %RH more  $\text{H}_2\text{O}_2$  is formed and it can degrade to  $\text{OH}^\cdot$  faster.
- **If you are doing Fenton's tests control pH carefully, especially for model compound studies**

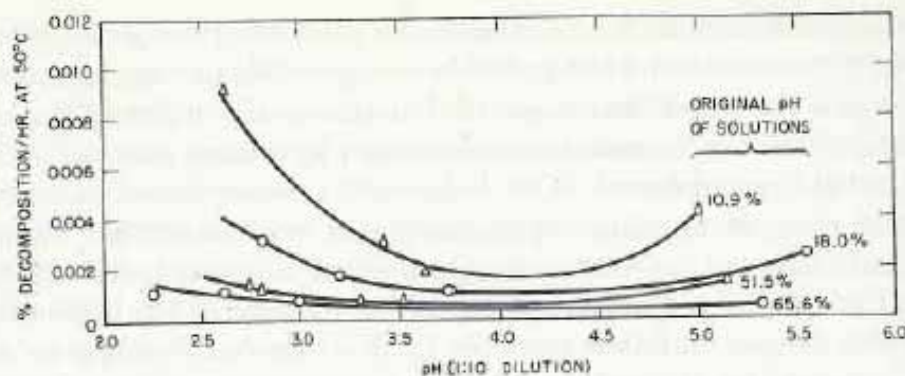


FIG. 4—Rate of decomposition of hydrogen peroxide of various concentrations with change in pH, at 50°C. (pH adjusted with sulfuric acid)

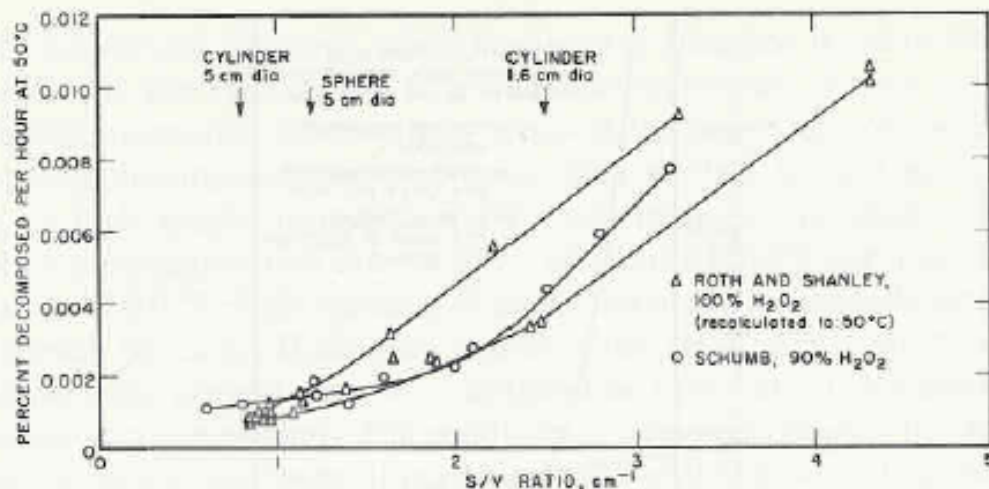


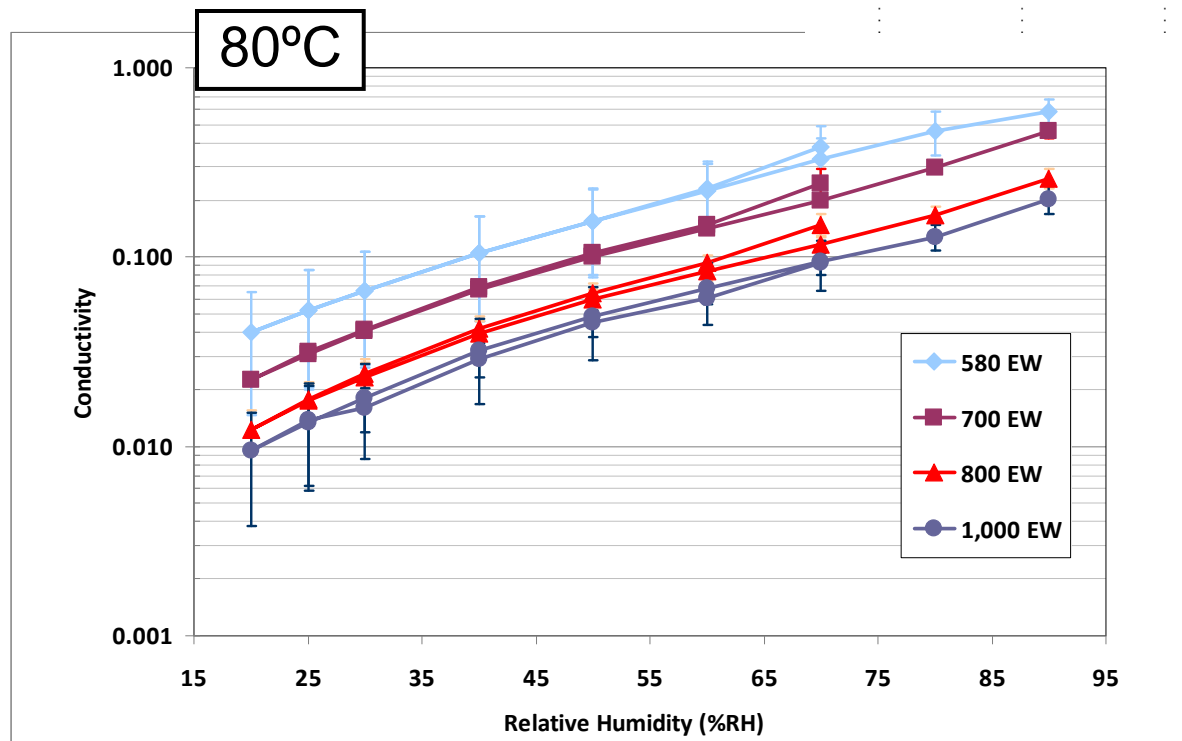
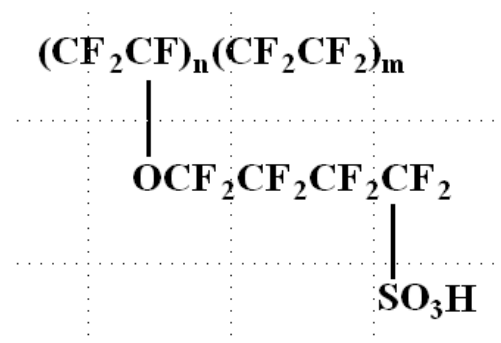
FIG. 3—Effect of surface-to-volume ratio on decomposition rate

1. DB Spry et. al. *J. Phys. Chem.* **113**, 10210 (2009)
2. VA Sethuraman et. al. *J. Electrochem. Soc.* **155**, B50 (2008)
3. WC Schumb, CN Satterfield, RL Wentworth "Hydrogen Peroxide" ACS Monograph Series, p. 522,526, 1955.



## Conductivity w/ Low EW

- These ionomers below about 700 EW, meets DOE milestones:
  - RT conductivity > 100 mS/cm at 80%RH, 30°C.
  - 80°C 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 targets at 80°C, even at 40% RH.

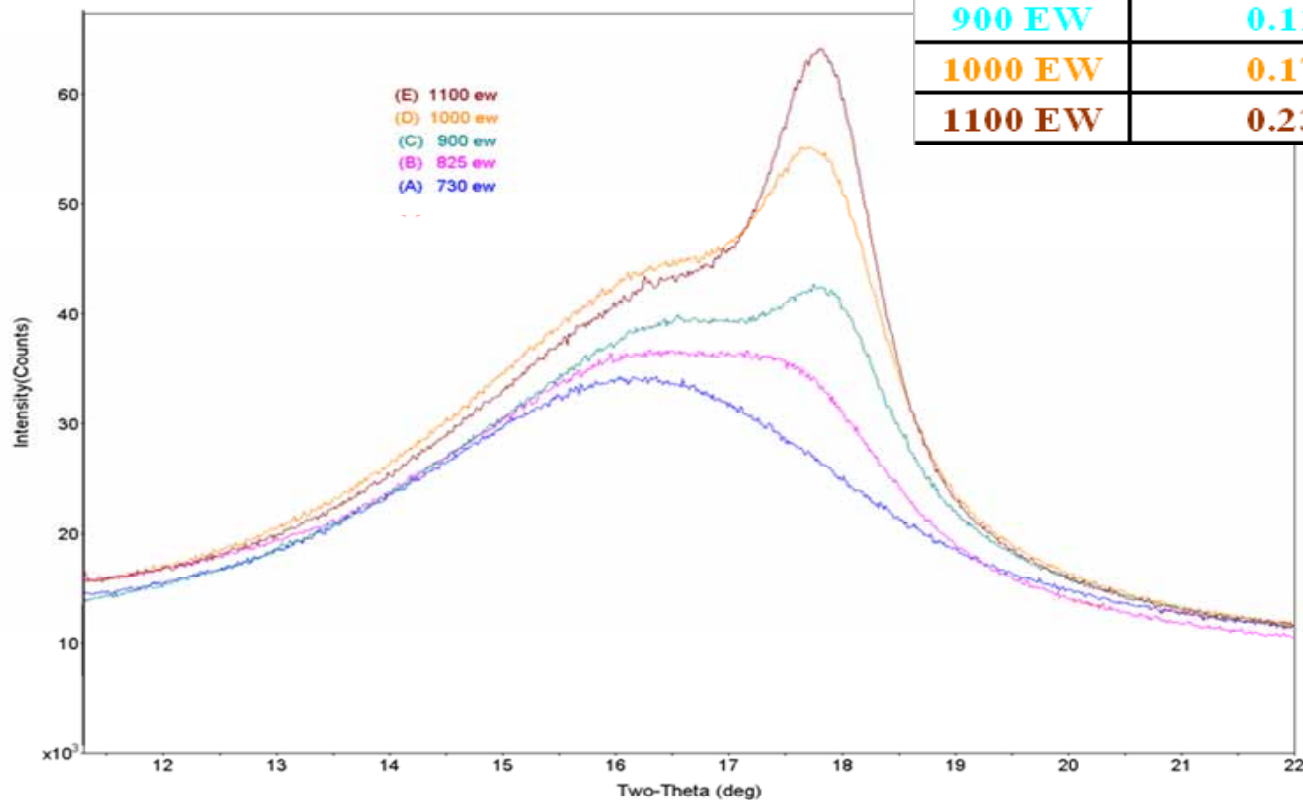


**AC 4-point probe measurement.**



## 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                |



- 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



## 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 – excessive swelling begins before dissolution.
- 
- Understanding “true” solubility helps defining possible mechanical stabilization methods
  - This experiment only works with well “processed” membranes

