New Membranes for PEM Fuel Cells

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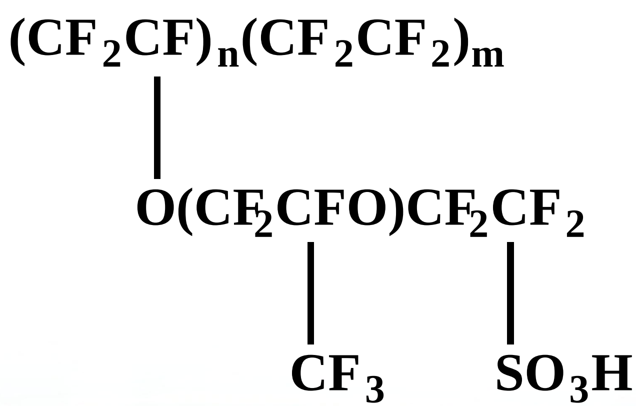
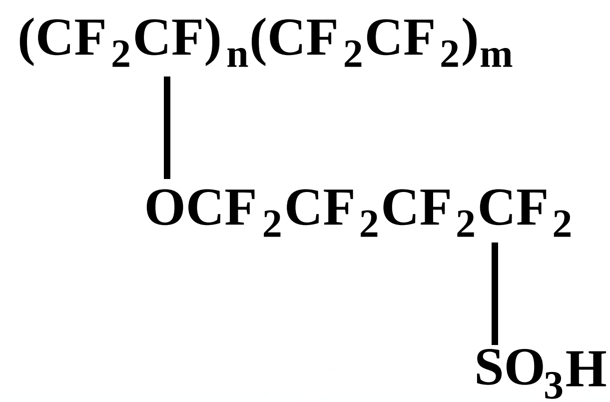
The new 3M ionomer has a slightly shorter side chain than standard PFSA Membrane ionomer without the pendant -CF3 group.

This allows a higher degree of crystallinity at a given EW.



Standard PFSA



New 3M Polymer

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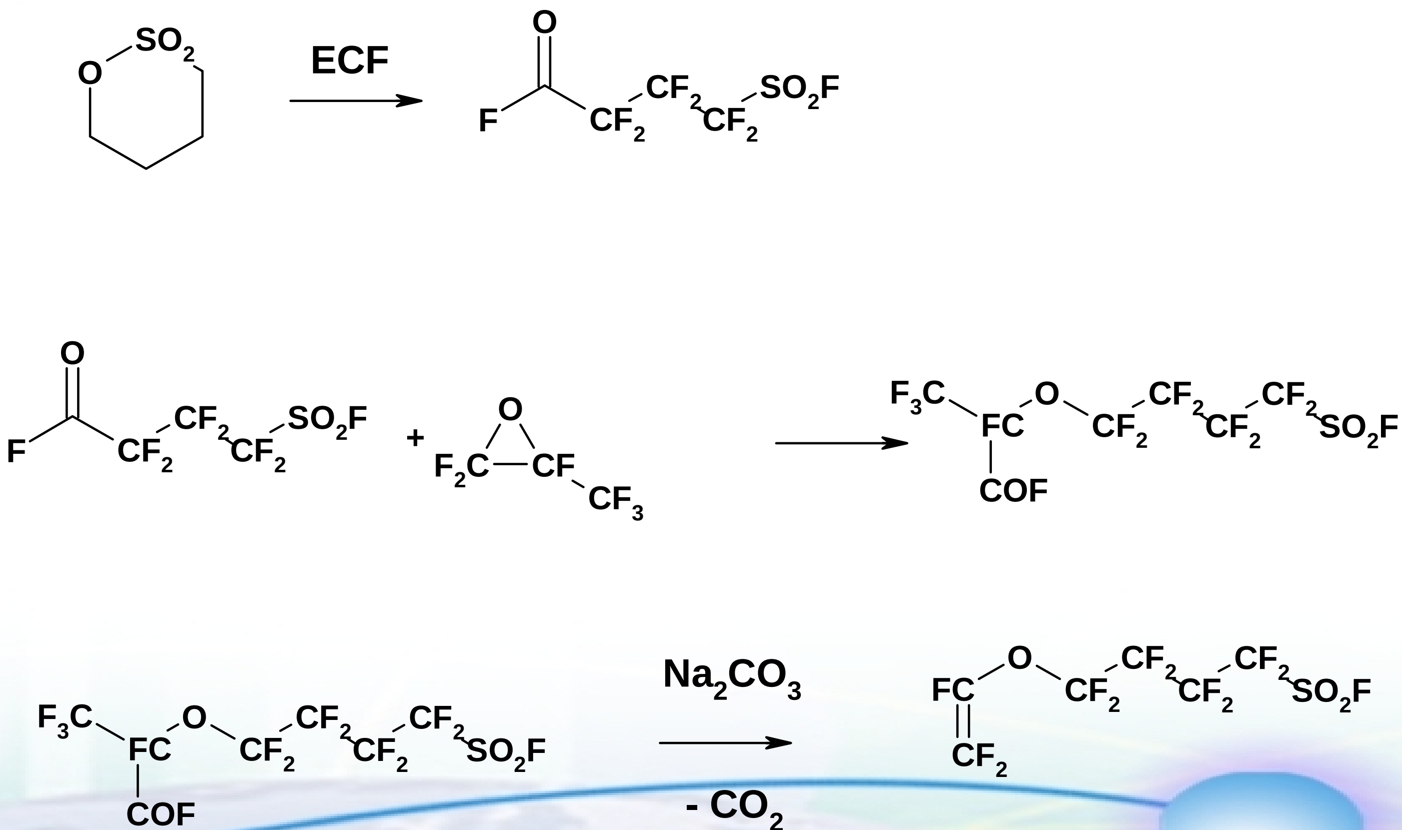
Monomer synthesis

The 3M monomer is based on electrochemical fluorination (ECF) of a hydrocarbon starting material.



3M monomer

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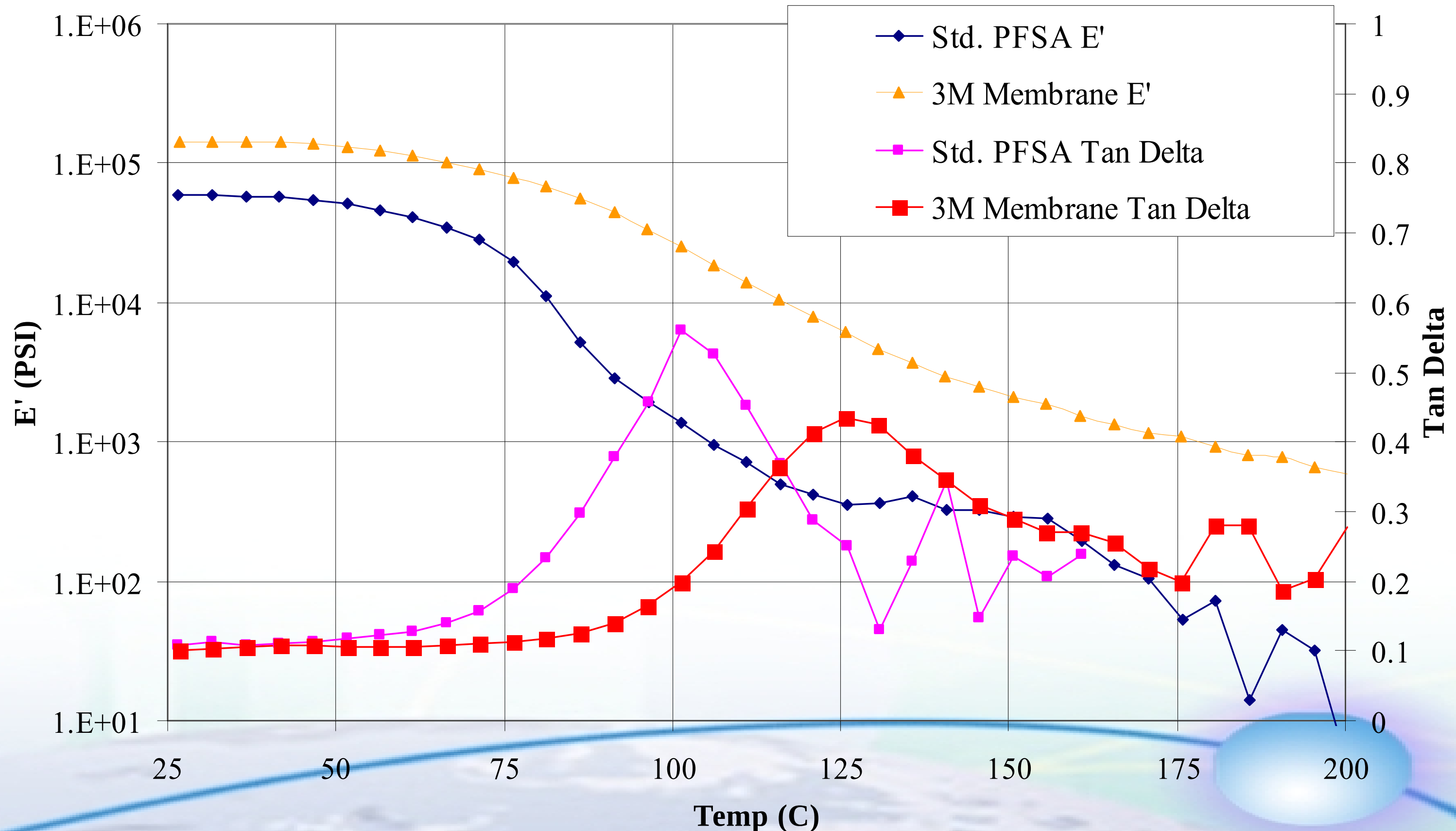
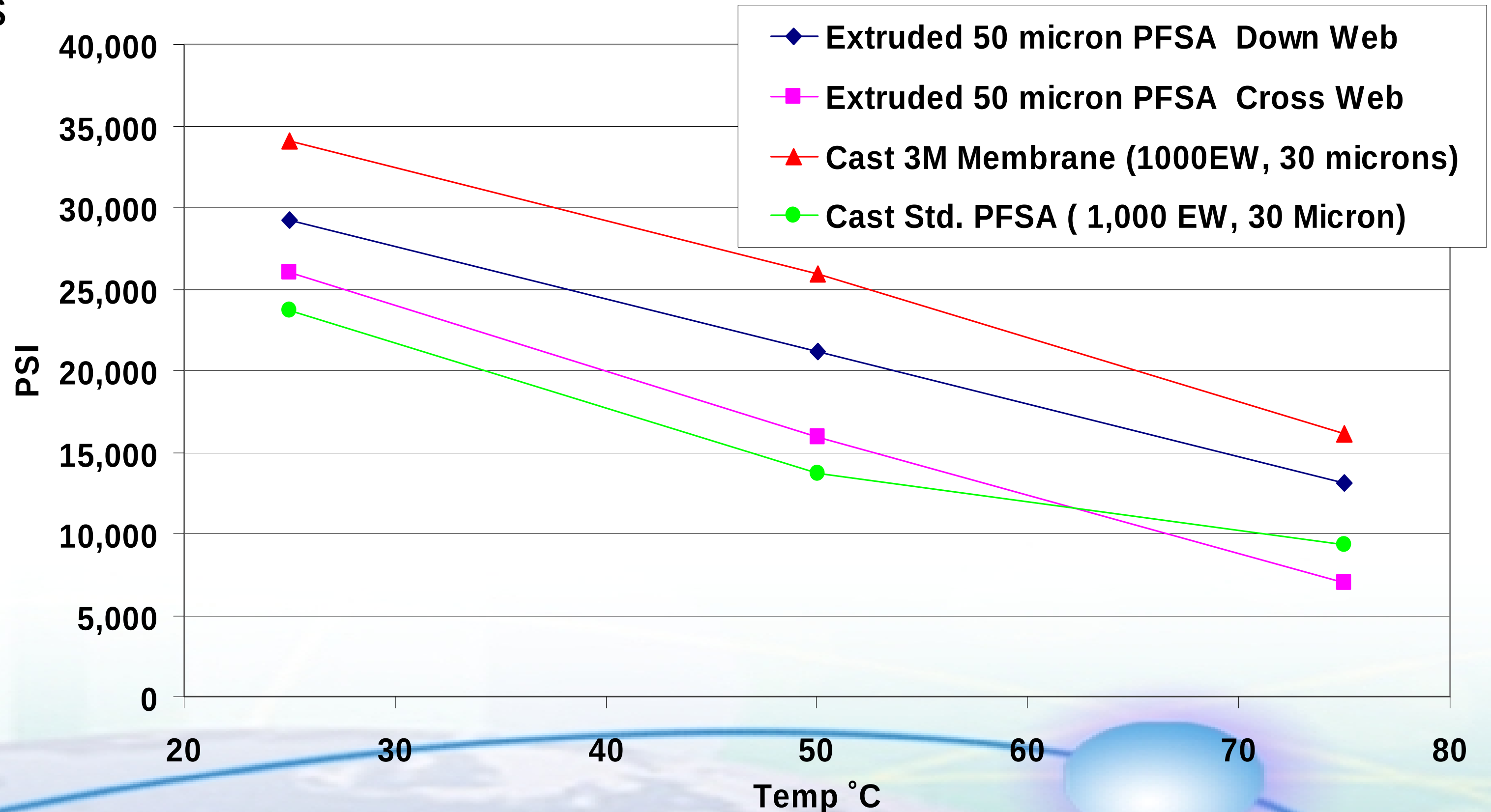
Mechanical properties of 3M ionomer

Dynamic Mechanical Analysis shows higher Tg and storage modulus than cast standard PFSA membrane at 1,000 EW



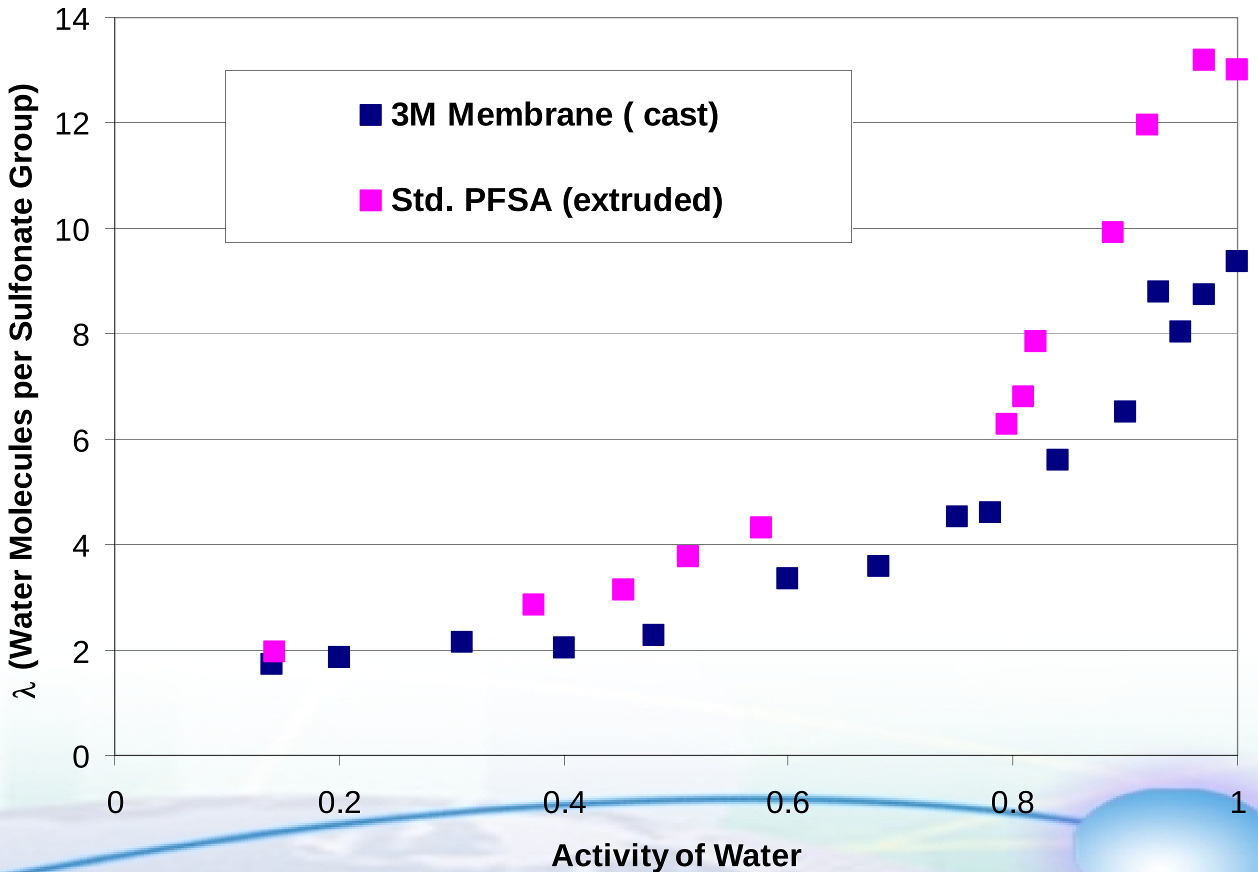
Membrane tensile test at 95% RH, vs Temp.

- Tensile tests run in a controlled humidity oven.
- 3M Membrane maintains high modulus up to 75°C



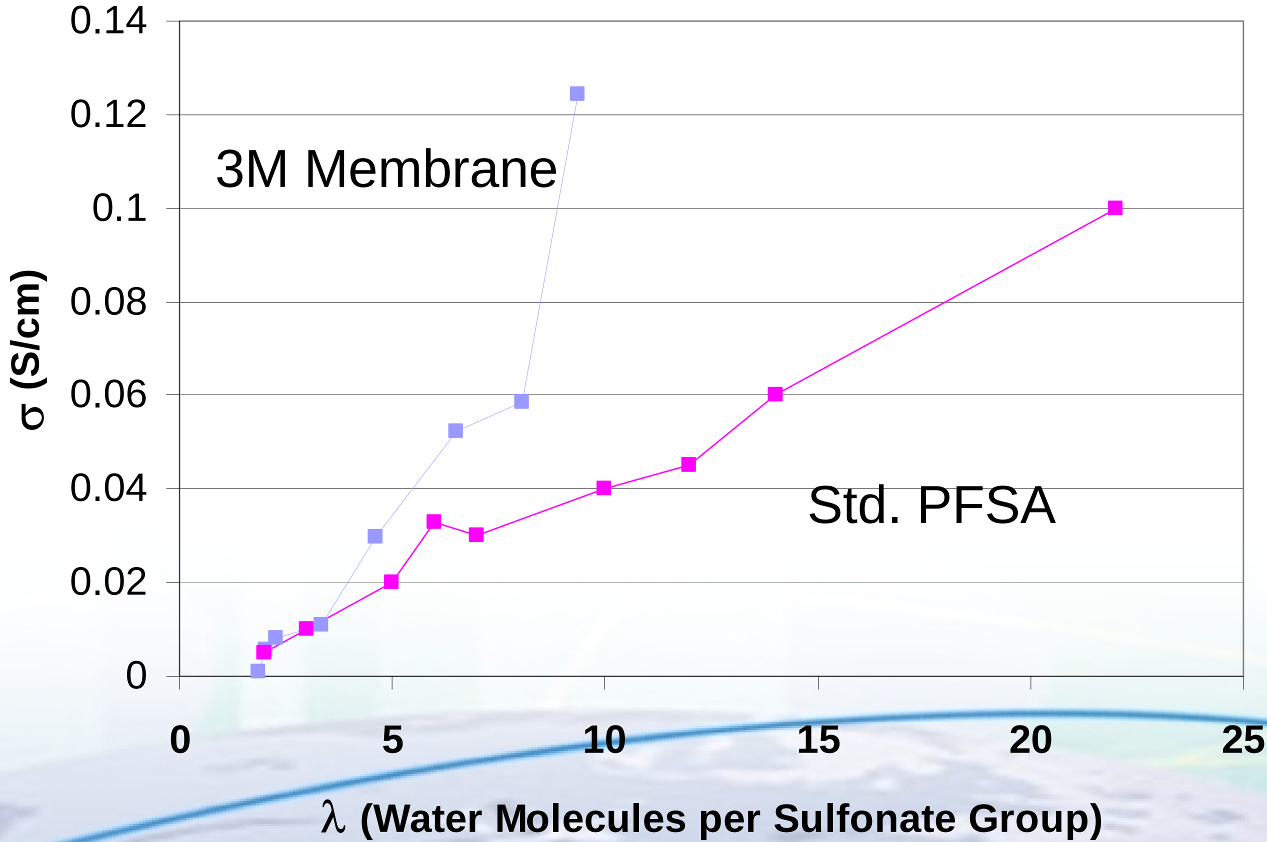
Water Sorption Isotherm for 1000 EW 3M Membrane 30°C

Note relatively lower uptake for 3M ionomer



T. Zawodzinski CWRU

Conductivity of 1000 EW 3M Membrane 30°C vs. hydration state (λ)

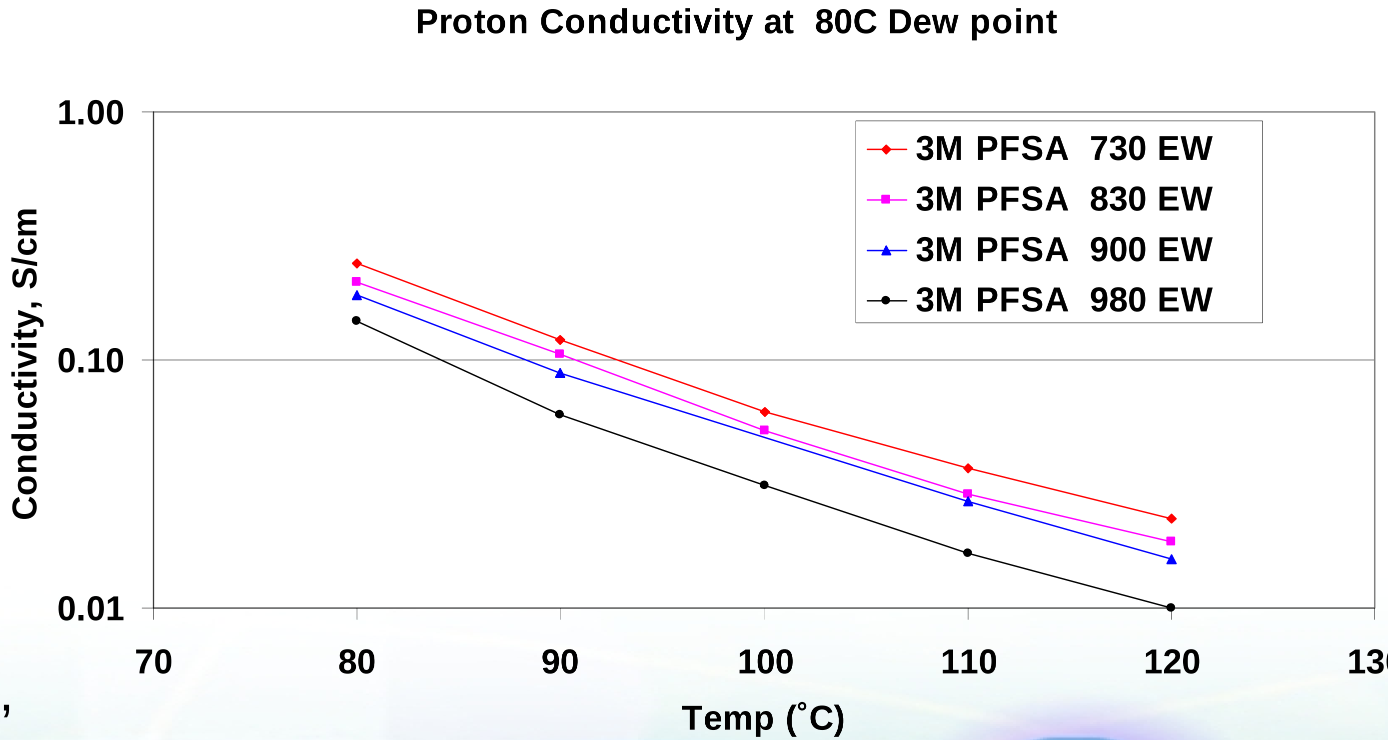


Conductivity data shows sharp increase with water content

T. Zawodzinski CWRU

Conductivity vs. temperature for different EW ionomers

- AC 4-point probe measurement, ambient pressure.
- The lowest EW ionomer tested so far is about 700. The conductivity of this material is about 25-30 mS/cm at 120° C, 80° C DP.



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Membrane chemical stability

- Peroxides generated from fuel cell operation are thought to cause membrane degradation and failure.
- The mechanism of this is thought to involve attack of peroxides or radicals from peroxides at the carboxylate endgoups. Fe accelerates this process.

$$(CF2)_n\text{-}CO_2H + H_2O_2 \longrightarrow (CF2)_n\text{-}CO_2\cdot + \cdot OH$$

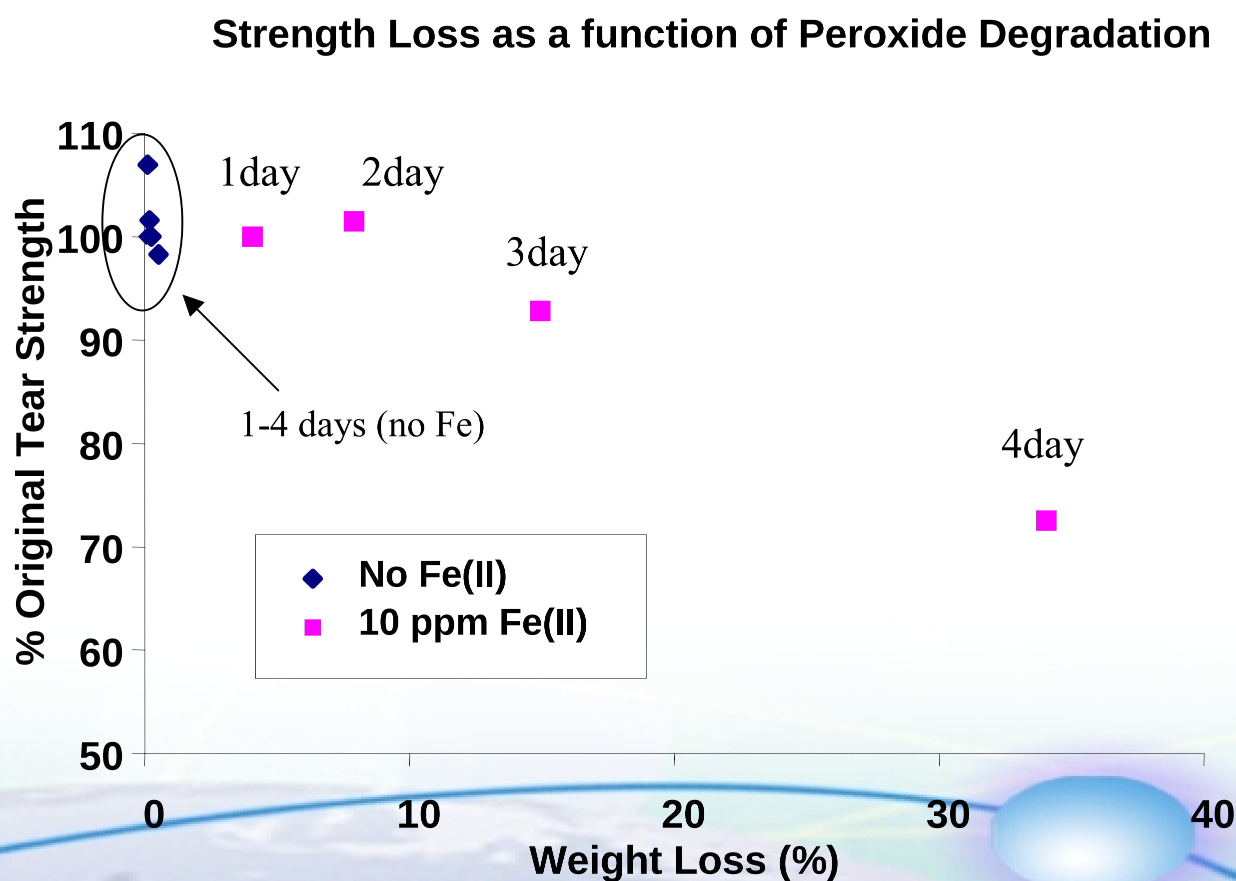
$$(CF2)_n\text{-}CO_2\cdot + \cdot OH \longrightarrow (CF2)_{n-1}\text{-}CF_2OH + CO_2\uparrow$$

$$(CF2)_{n-1}\text{-}CF_2OH \longrightarrow (CF2)_{n-1}\text{-}COF + HF$$

$$(CF2)_{n-1}\text{-}COF + H_2O \longrightarrow (CF2)_{n-1}\text{-}CO_2H + HF$$

Weight loss and decrease in tear strength during heating in H_2O_2

- Sample heated to 90° C for 4 days in 1M H_2O_2.
- H_2O_2 changed every day.
- Without Fe, no change observed.



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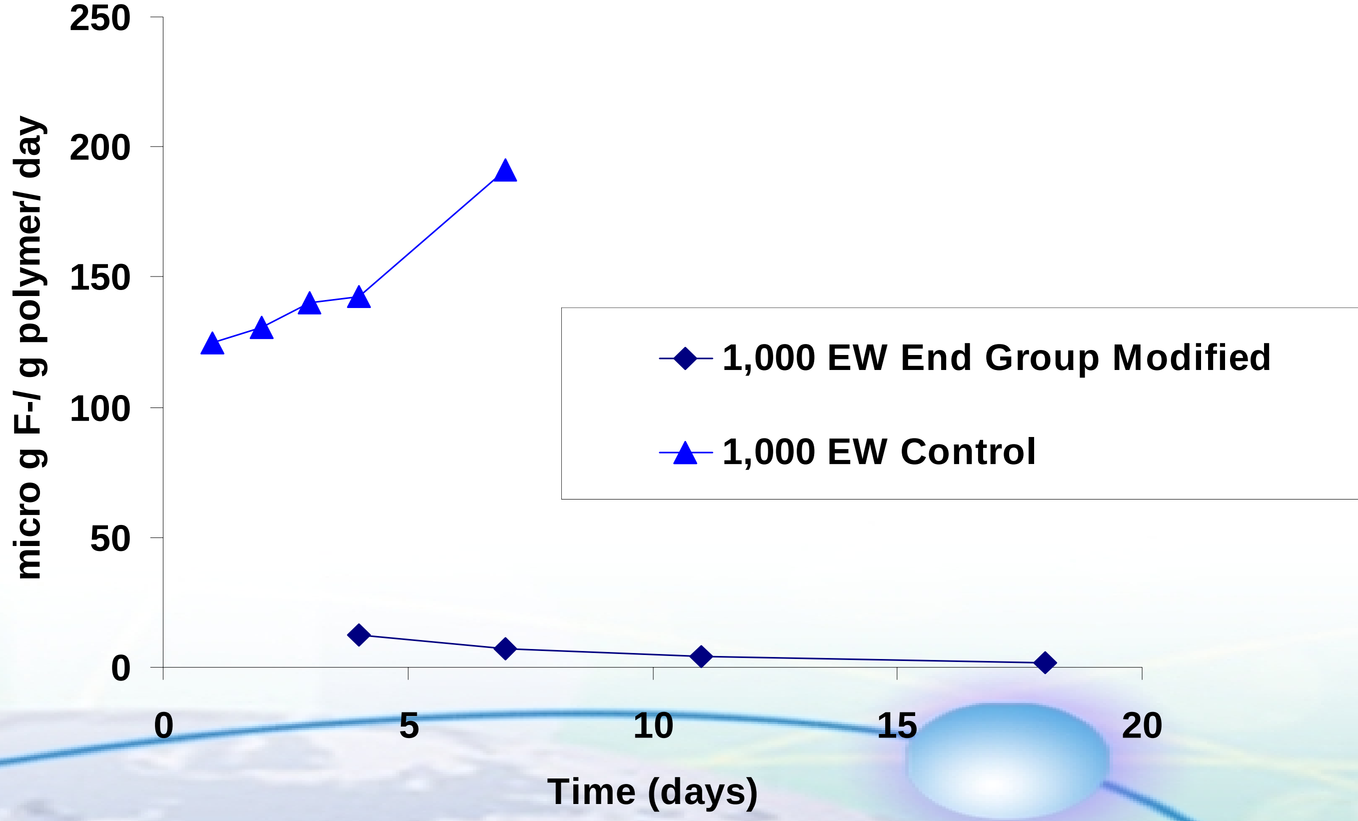
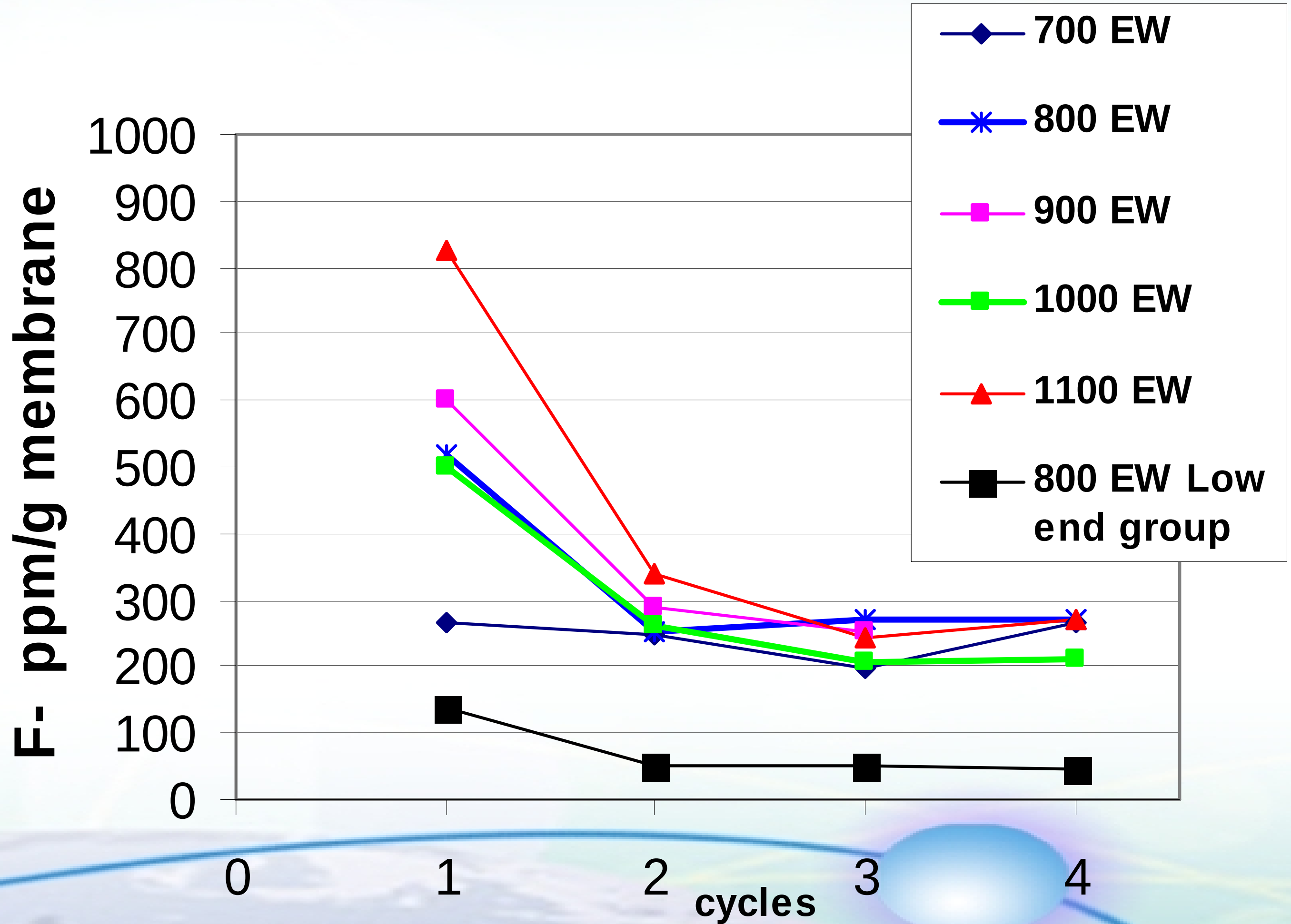
New process allows ionomer to be made with much lower concentration of carboxylate endgroups.

- Degradation can also be followed by monitoring fluoride levels in peroxide solution.
- Membrane with lower concentration of carboxylate endgroups exhibits much lower rate of degradation.



Oxidative stability vs. EW

- Samples are heated to 70°C in 30% H_2O_2 with 50 ppm Fe.
- H_2O_2 is changed every 3 days.
- Degradation is followed by monitoring F- content of the solution with an ISE



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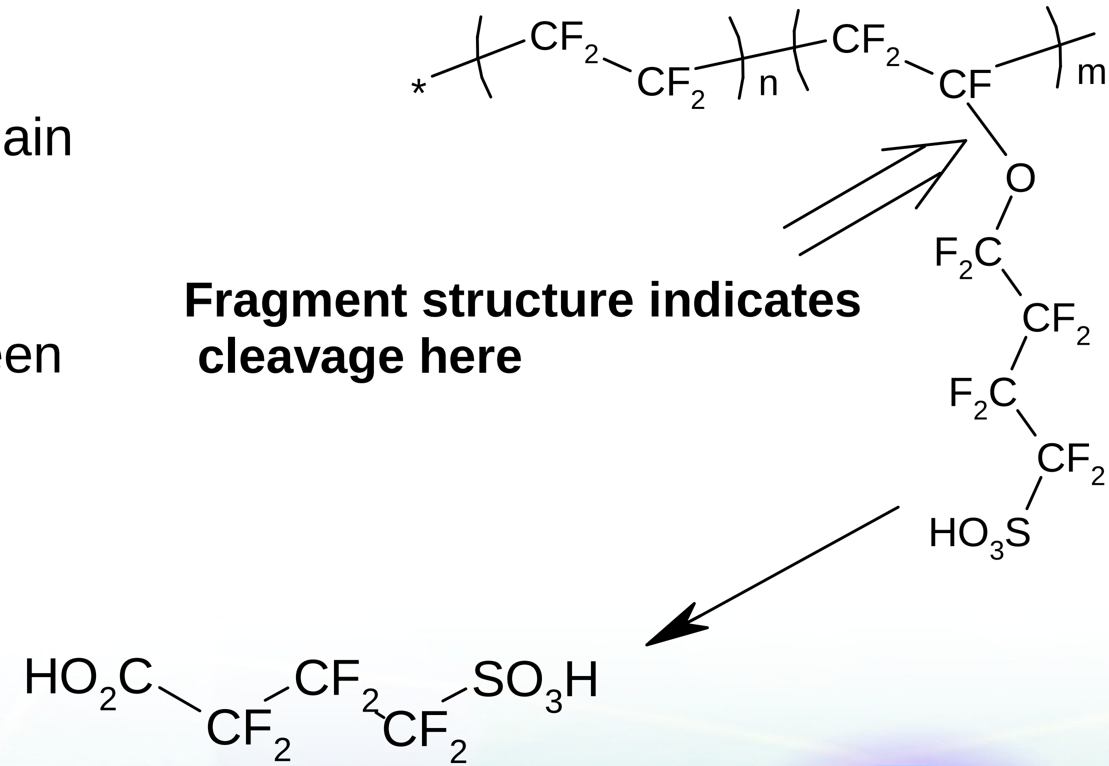
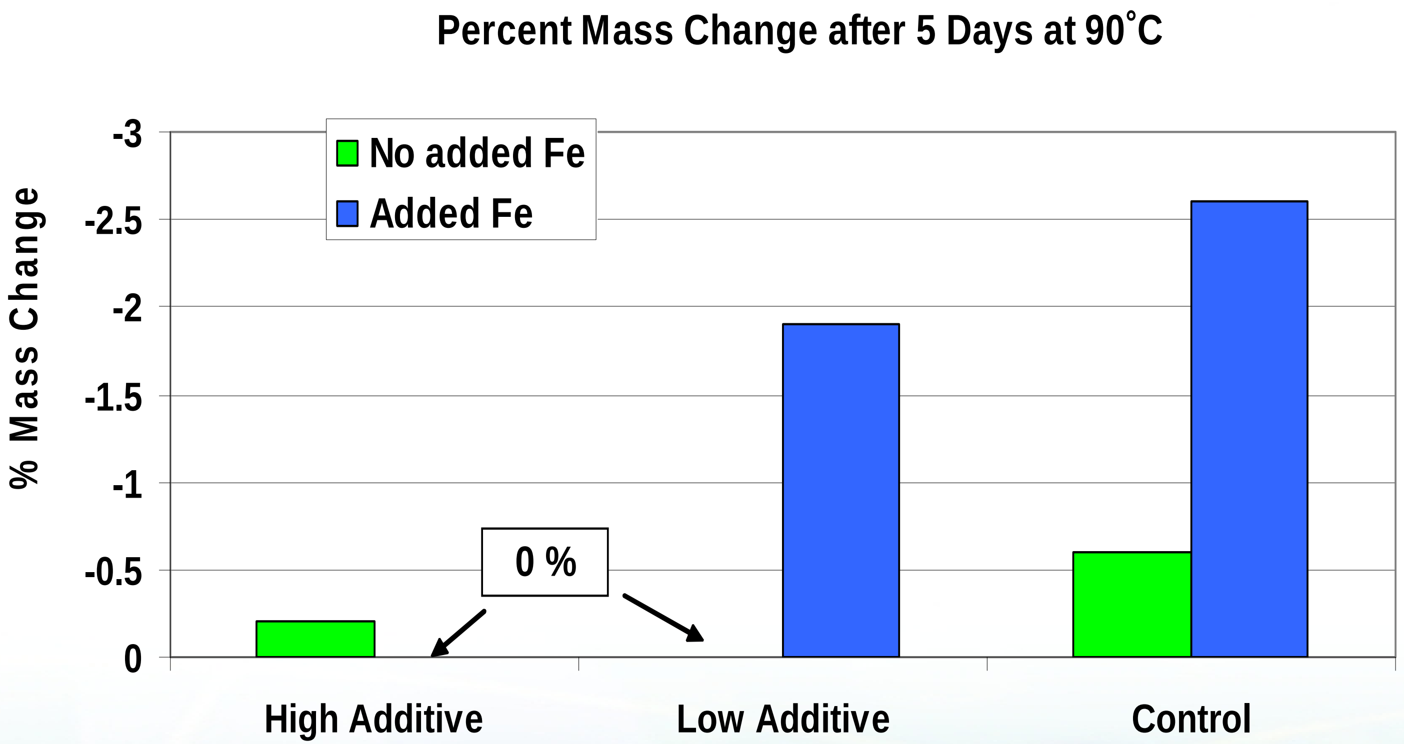
Fluorinate fragment identified during peroxide testing

- HPLC/MS analysis showed whole side-chain fragment
- No other fragments seen by this method.



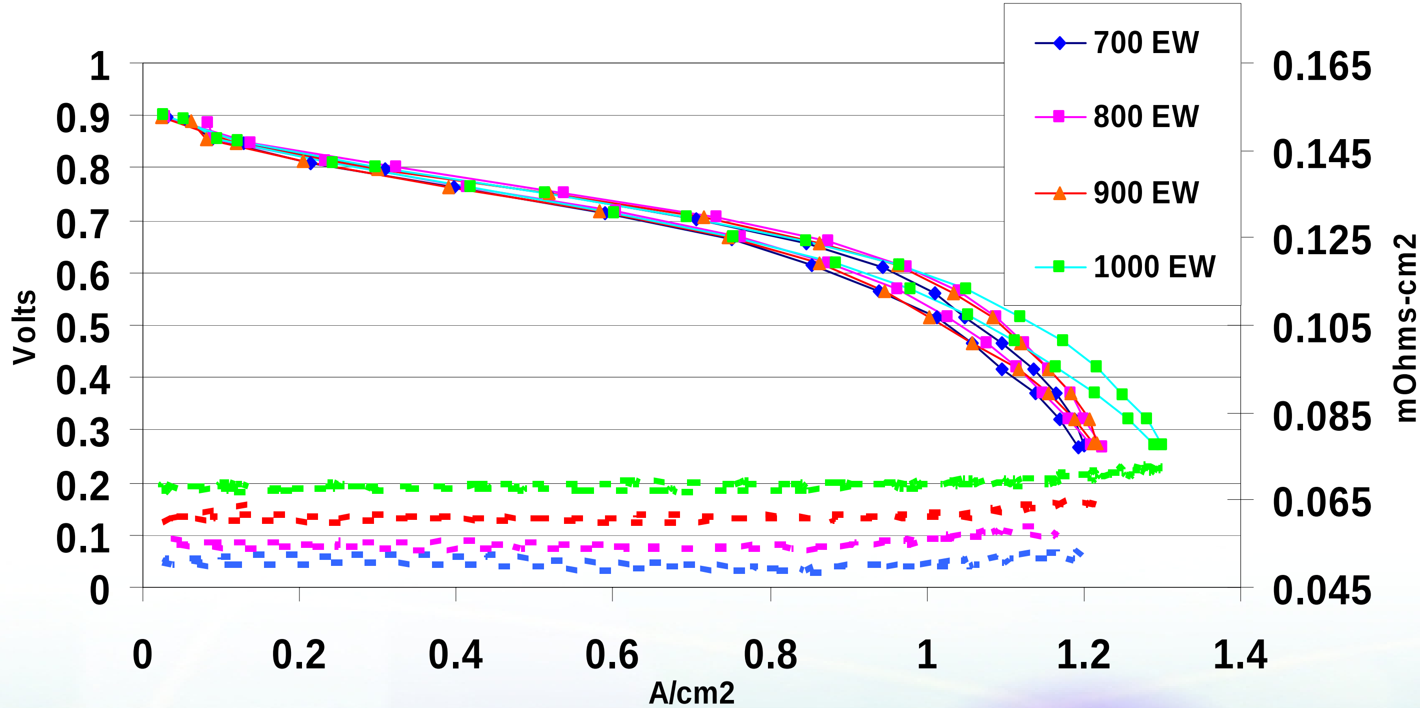
Additives improve oxidative stability and help mitigate the negative effects of Fe

- High and low levels of additive both with and without added Fe.
- At high additive level, not much difference between w/ and w/o Fe.
- At low additive level, mass loss was much higher for added Fe sample.



EW vs. performance
70˚C H_2/air, fully humidified

- Lower cell resistance with lower EW.
- No observed impact on performance at 70°C, fully humidified.
- MEA's not optimized for different EW membranes.



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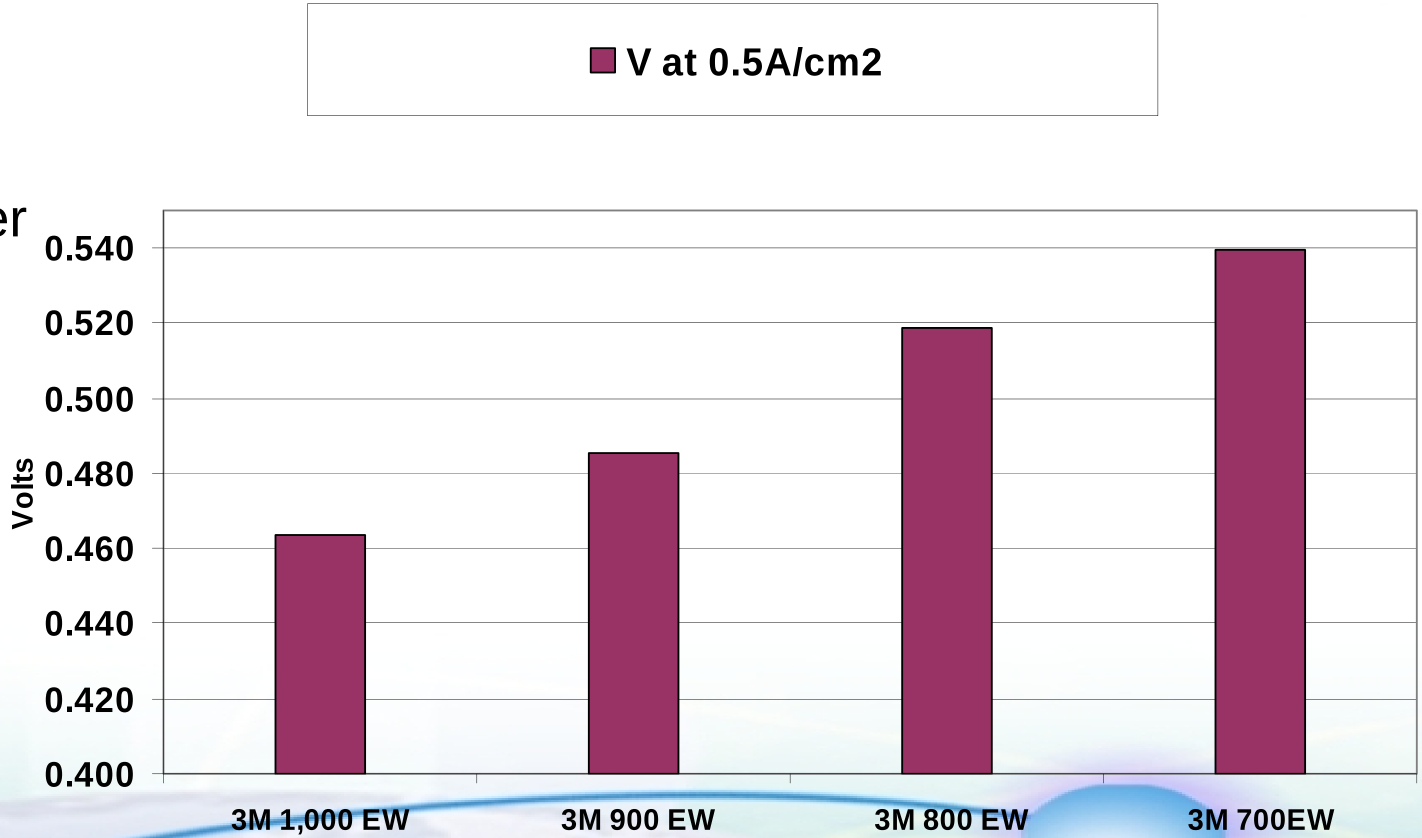
EW vs. performance constant current at 0.5 A/cm^2, 90˚C H_2/air, 28% RH

- Performance increases with lower EW under hot, dry conditions.
- MEA's not optimized for different EW membranes.



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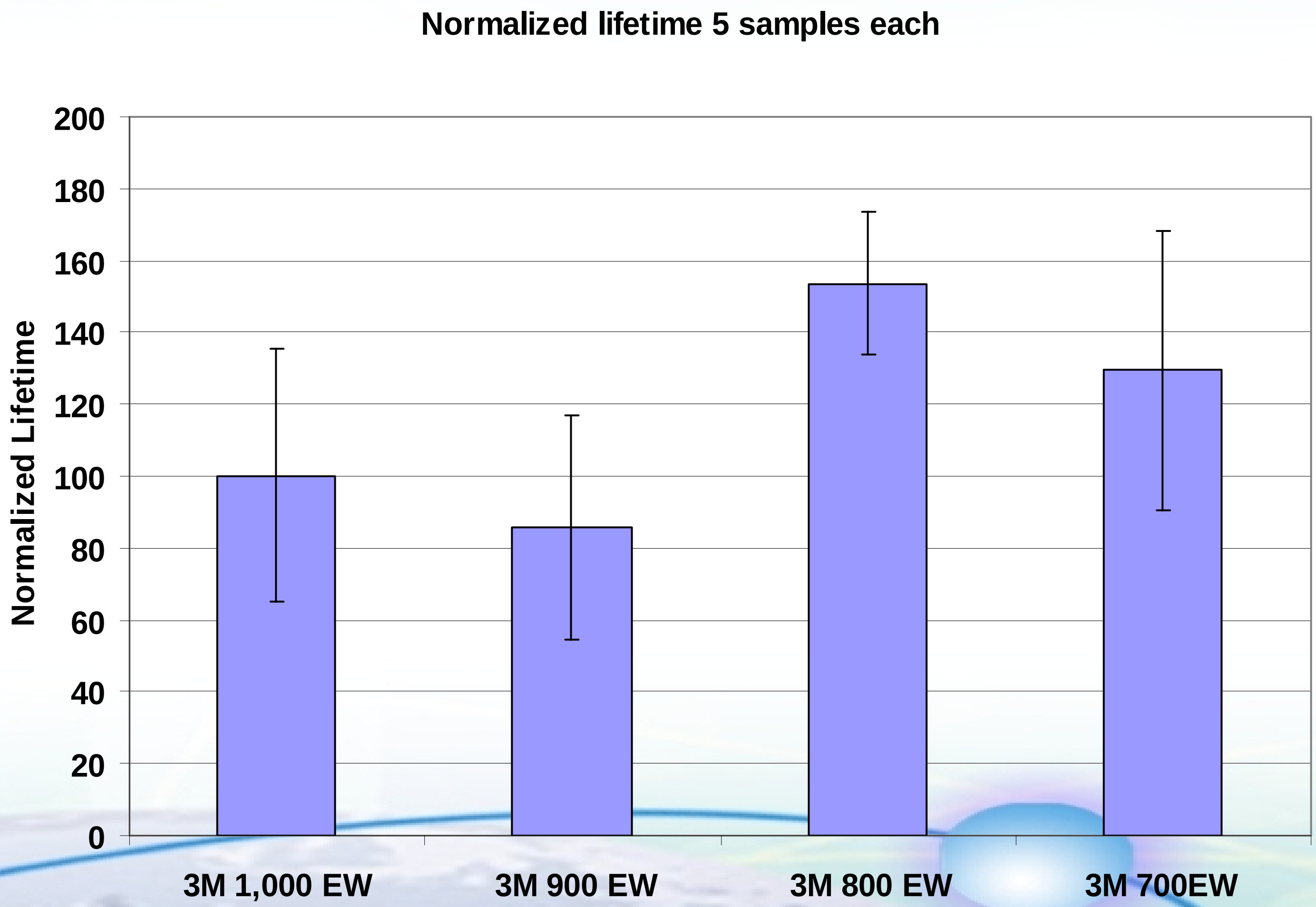
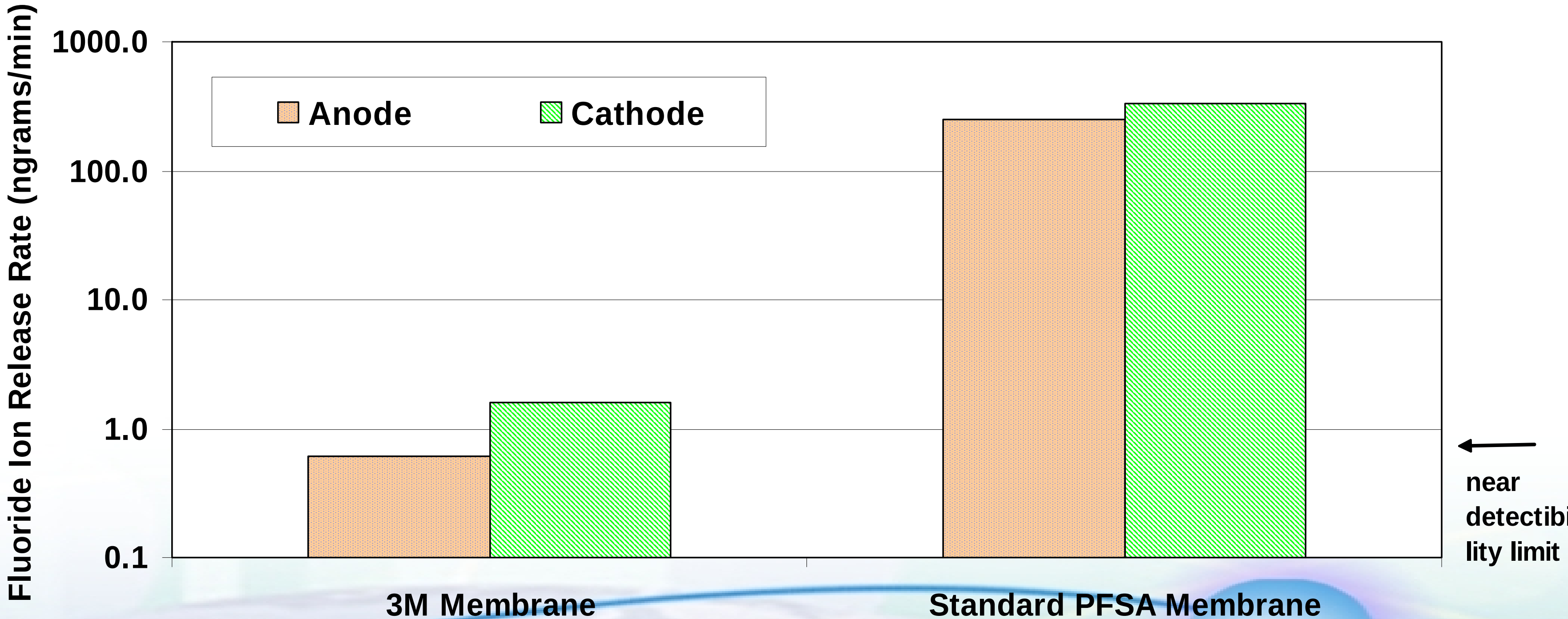
Normalized lifetime under accelerated testing –
Lifetime defined as when OCV drops below 800mV

- Test run at 90°C, 12% RH.
- Lifetime defined as when OCV drops below 800mV.
- No difference between 700 to 1,000 EW in this test.



Fluoride Release under accelerated testing conditions (90 ˚C, 12% RH). F generation rate of MEA's with new 3M membrane is about 100 times less than that of 50 micron extruded standard PFSA membrane under these conditions.



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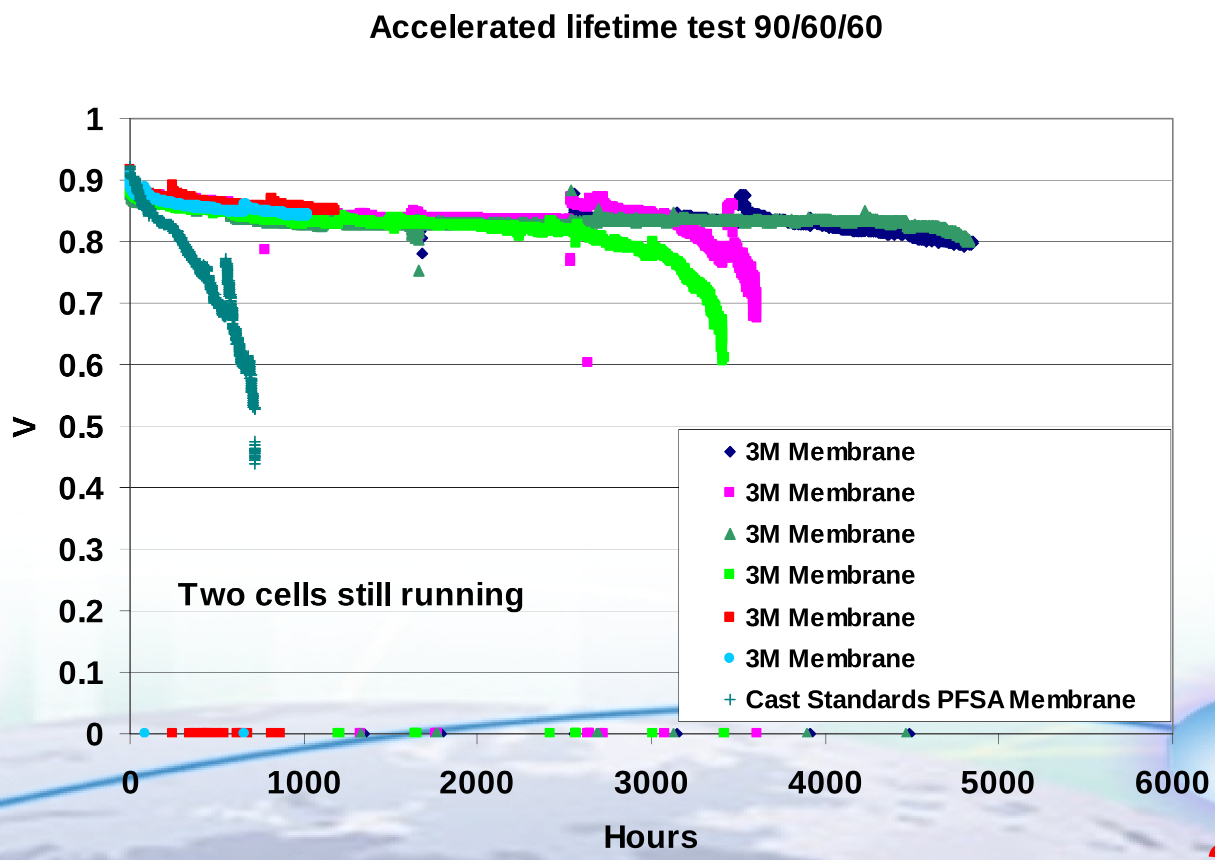
May 27th, 2005

MEA Accelerated Lifetime testing

90º C, 28% RH, Load cycled from 0 to 0.5 A/cm^2 , 50 cm^2 cell, 0.4/0.4 Pt/Pt, 7/0 PSIG. Life defined as when OCV drops below 800mV



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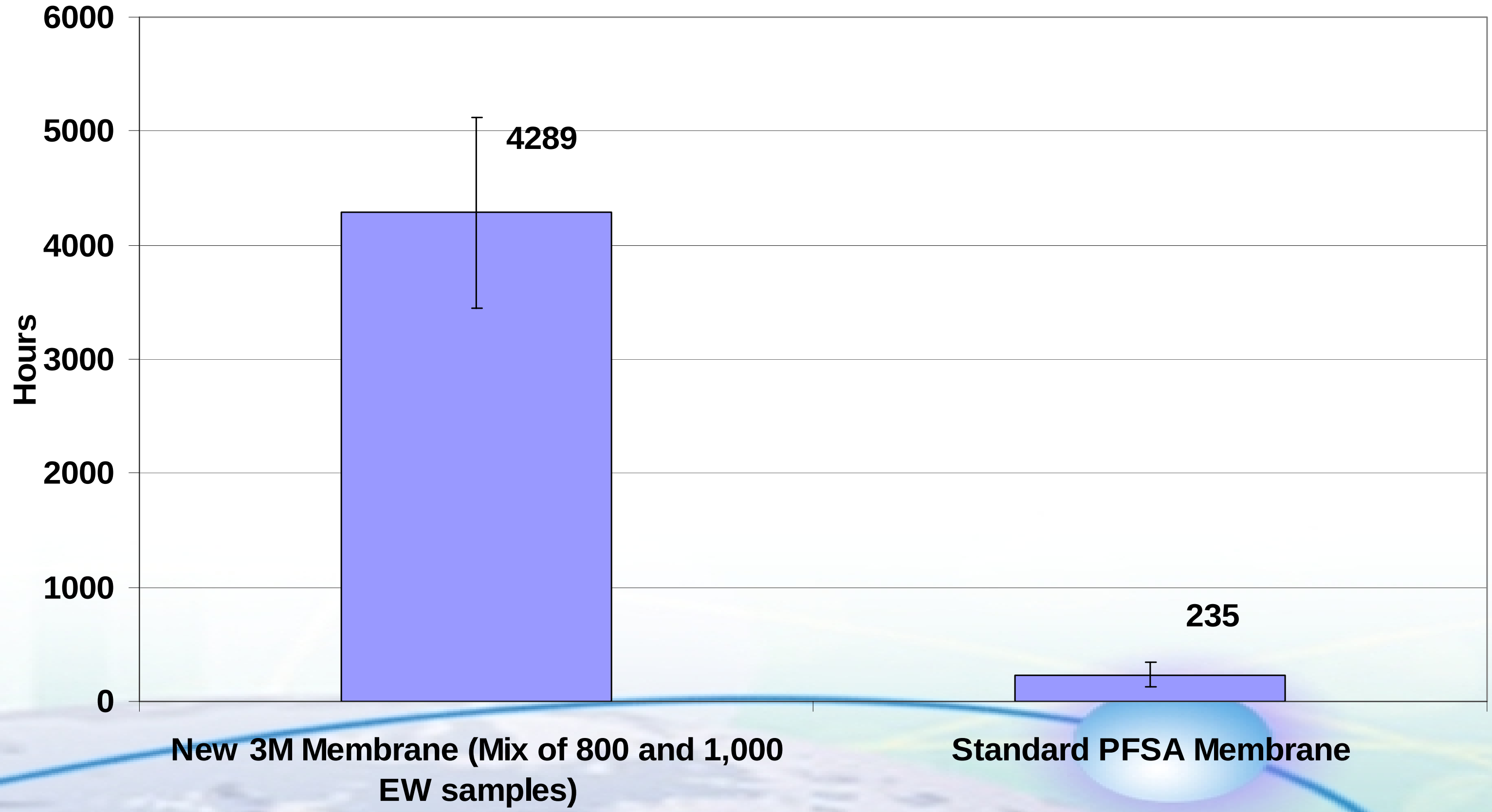
MEA Accelerated Lifetime testing

90º C, 28% RH, Load cycled from 0 to 0.5 A/cm^2 , 50 cm^2 cell, 0.4/0.4 Pt/Pt, 7/0 PSIG. Life defined as when OCV drops below 800mV

New 3M membrane shows >15 X increase in lifetime over 50 micron extruded standard PFSA membrane.



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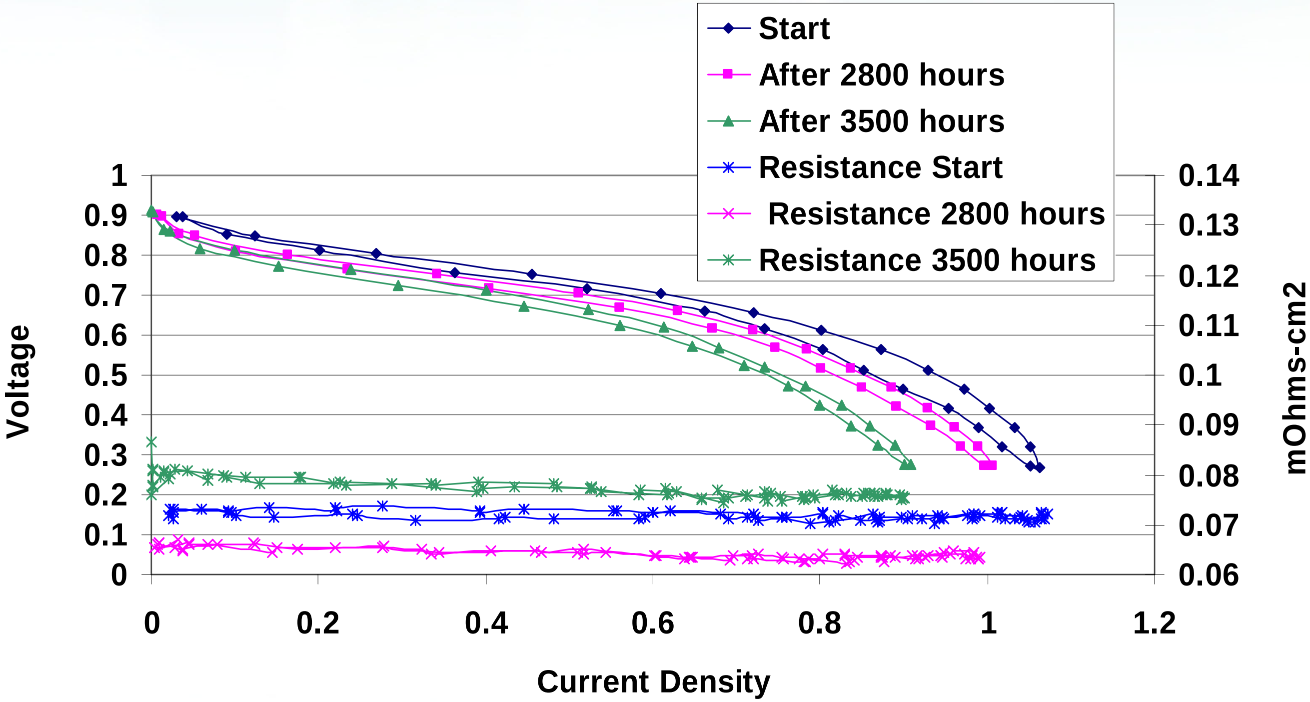
Performance during accelerated durability testing



SEF (M^2/M^2)	H2 Crossover (mA/cm^2)	Short Resistance ($OHM\text{-}CM^2$)	Testing Time
178.3	4.2	>500	0
102.9	3.4	>500	2800
78.1	17.0	>500	3500

Accelerated durability testing was stopped periodically and sample was tested at 70˚C 100%RH. No increase in crossover or shorting was detected before 3500 hours.

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Summary

- A new perfluorinated sulfonic acid ionomer (PFSA) has been developed at 3M. This polymer has:

    - High Tg (125ºC for 1,000 EW)
    - High modulus, tear and puncture resistance both dry and under use conditions.
    - Lower EW membranes have increased conductivity, providing MEA's with better performance under hotter/drier conditions.
    - Excellent oxidative stability for EW's from 700 to 1,100.
    - Low fluoride content in the water coming from the cell.
    - **Longer MEA life in accelerated testing.**