

2006 DOE Hydrogen Program Review

Enabling Commercial PEM Fuel Cells With Breakthrough Lifetime Improvements

DuPont/DOE Cooperative Agreement
No. DE-FC36-03GO13100

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Project ID# FC5



The miracles of science™

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date: 10/1/2003
- Project end date: 3/31/2007
- Percent complete: 90%

Budget

- Total project funding: \$8.74 M
 - DOE share: \$6.99 M
 - Contractor share: \$1.75 M
- DOE funding received in FY05: \$2.25 M
- DOE funding for FY06: \$2.04 M

Barriers

- DOE Technical Barriers for Fuel Cell components
 - A. Durability
 - B. Cost
- DOE Technical Targets for Fuel Cell Stack System for 2010
 - Durability > 40,000 hours (stationary), 5000 (hours) auto
 - Cost no greater than current Nafion® projections

Partners

- United Technologies Corporation
- University of Southern Mississippi



Objectives

Overall:

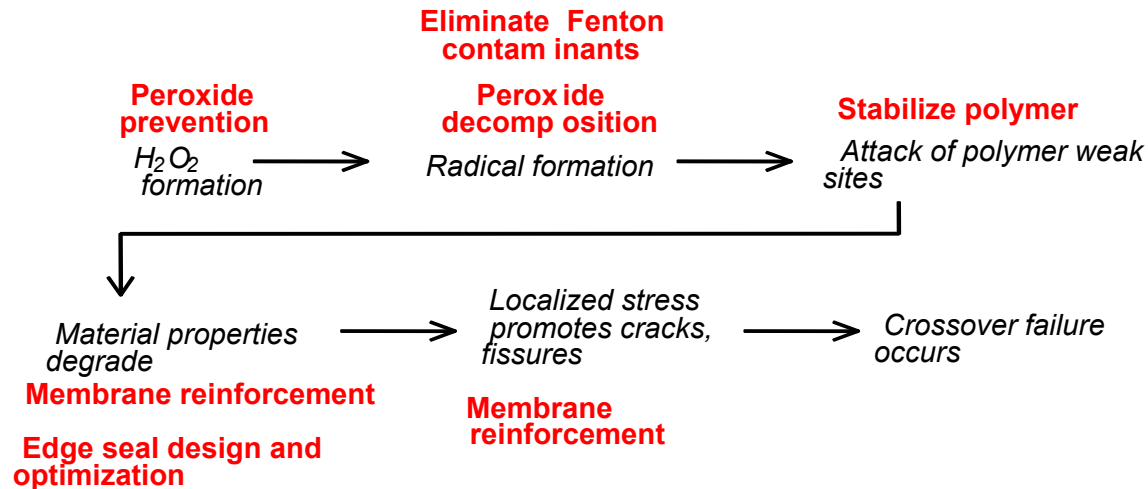
- Through both experiments and modeling, develop an understanding of potential mechanisms that can lead to membrane failure
- Identify and implement mitigation strategies to address the root causes of membrane failure
- Individually, each of these strategies are expected to improve membrane durability. This program will optimize each and integrate them, into more durable fuel cell products
- Due to the unpredictable and catastrophic nature of membrane failure, we are addressing this problem first in advance of performance loss

Focus in 2005:

- Validate mechanical reinforcement, chemical stability and peroxide mitigation strategies in accelerated single cell and stack tests
- Investigate other possible chemical degradation modes in order to further improve polymer chemical stability
- Validate the chemical degradation model
- Complete correlations of membrane degradation and mechanical properties degradation

Approach

Program Scope



Program Tasks

Task 1. Materials Synthesis

Task 2. Accelerated Aging Tests

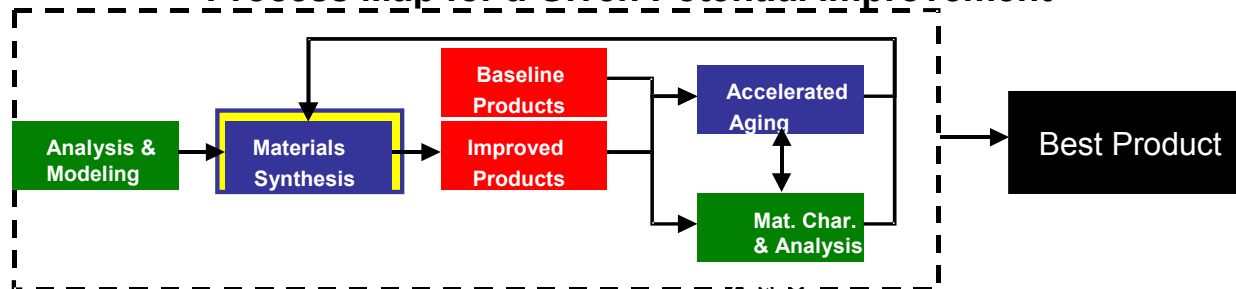
Task 3. Analysis and Modeling

Task 4. Stack Testing

Task 5. Materials Char. and Analysis

Task 6. Cost Analysis

Process Map for a Given Potential Improvement



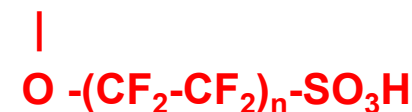
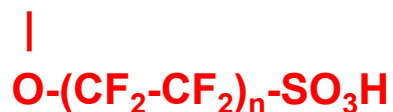
Technical Accomplishments

- Fundamentals
 - DuPont: PFSA degradation mechanism
 - USM: molecular and morphological origins of membrane degradation
 - UTC: modeling of membrane degradation
- Chemical durability
 - New DuPont membrane with increased chemical stability
 - UTC peroxide mitigation strategy
- Durability Testing
 - Single cell accelerated test results
 - Stack test results

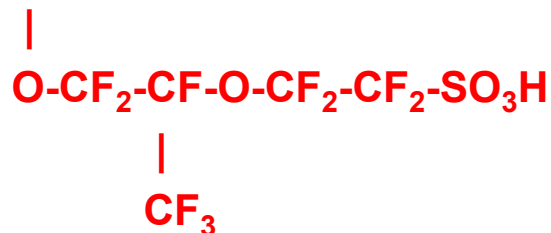
DuPont - New Model Compound Studies

- DuPont has proposed that the primary mode of chemical attack is on reactive polymer end-groups
- DuPont has shown that PFSA ionomer is chemically-stabilized by reducing reactive polymer end-groups
- Stabilized membrane has lower decay and longer lifetimes in our accelerated fuel cell tests
- We conducted a new series of model compound studies to compare the stability of of PFSA ionomers with linear and branched perfluoroether side-chains

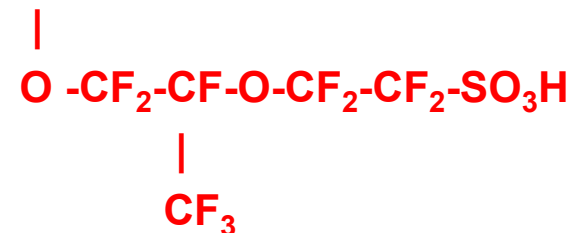
Short side chain Ionomer with acid end-group DuPont Model Compound #3 (n=1)



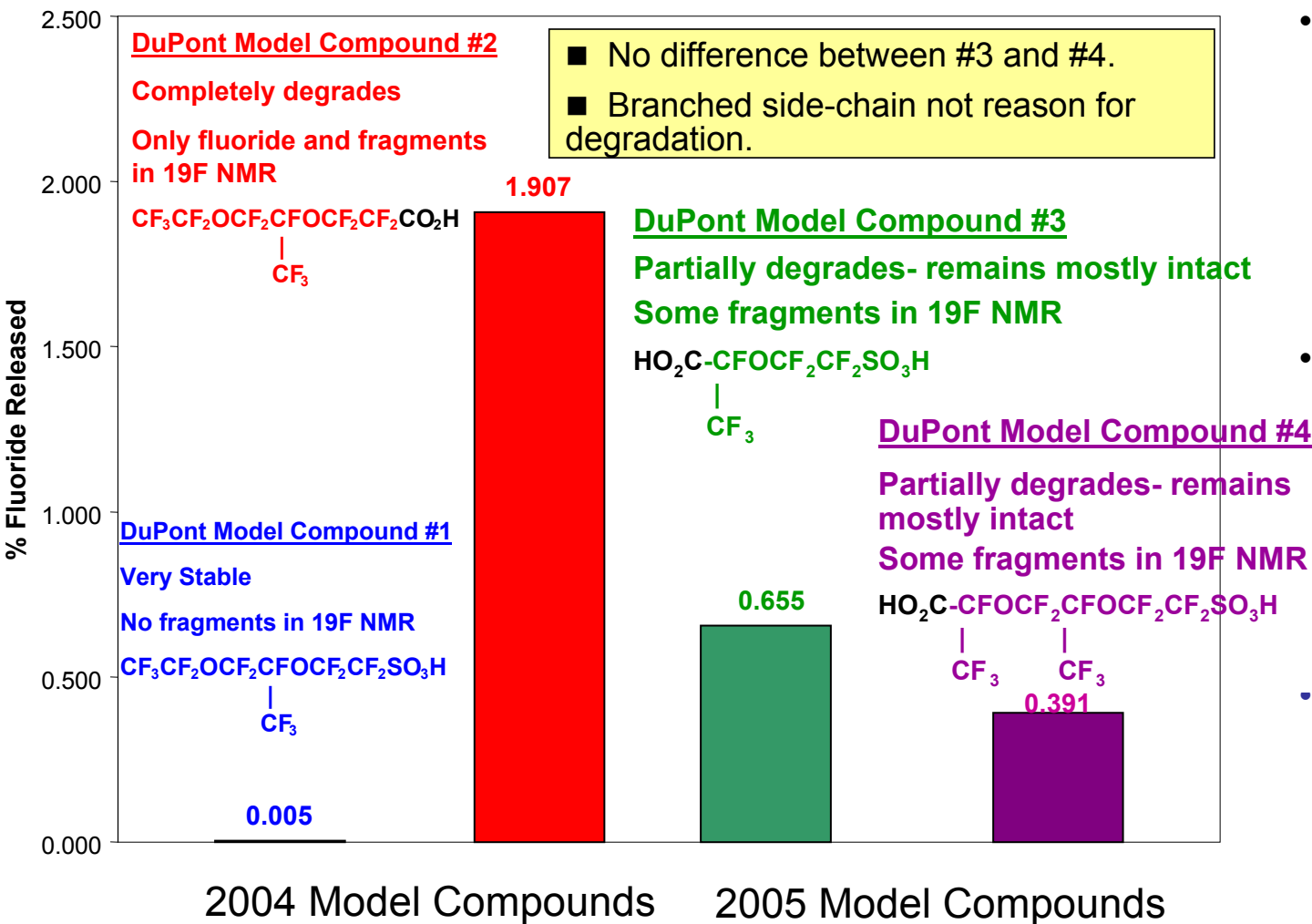
Nafion® Ionomer with acid end-group



DuPont Model Compound #4



Model Compound Test Results



- In the Fenton's test, PFSA model compounds with carboxylic acid end-groups degrade; whereas PFSA model compounds without acid end-groups are completely stable
- PFSA model compounds with linear and branched side-chains that also contain a carboxylic acid group degrade to a similar extent in the Fenton's test (DuPont Model Compounds 3 & 4)
- **Our studies show that carboxylic acid groups, not branched side-chains make PFSA compounds susceptible to attack by peroxy radicals**



USM: Degradation of Cast Nafion®

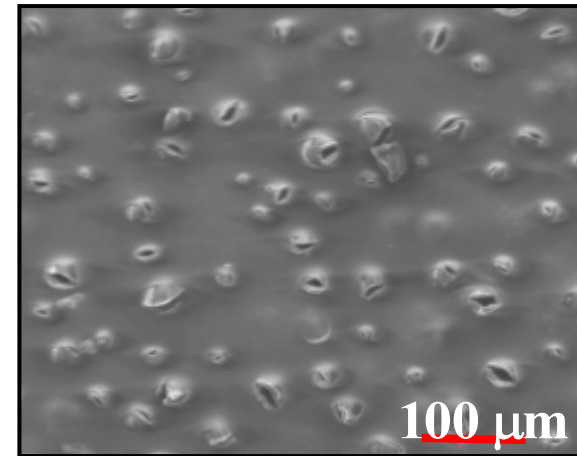
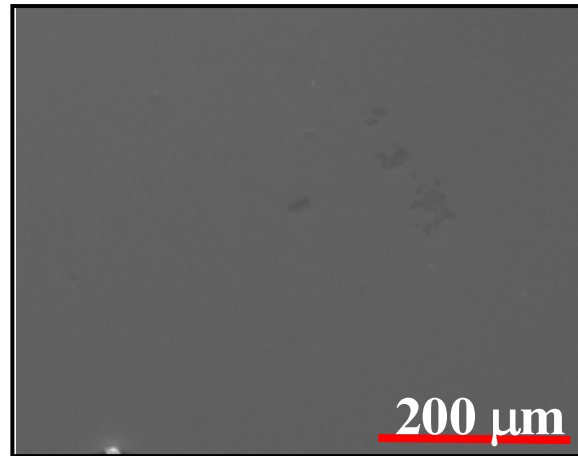
Scanning Electron Microscopy

2 mil Cast non-CS Nafion® Membrane

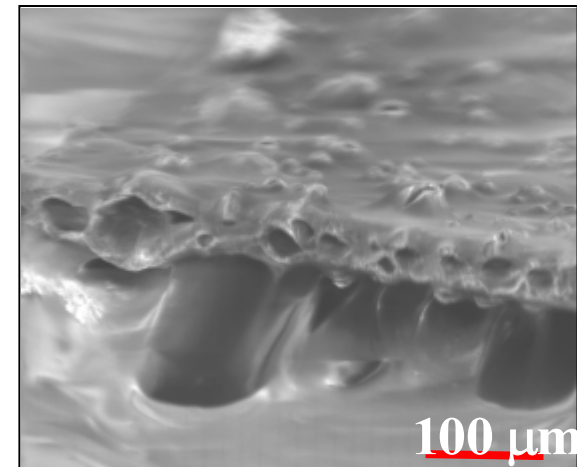
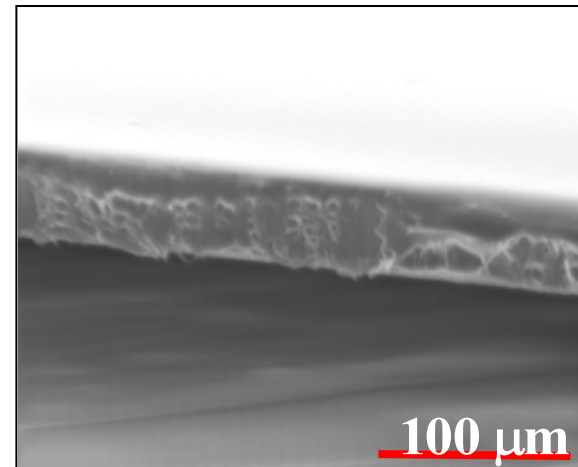
As Received

Fenton's Degradation

Top View

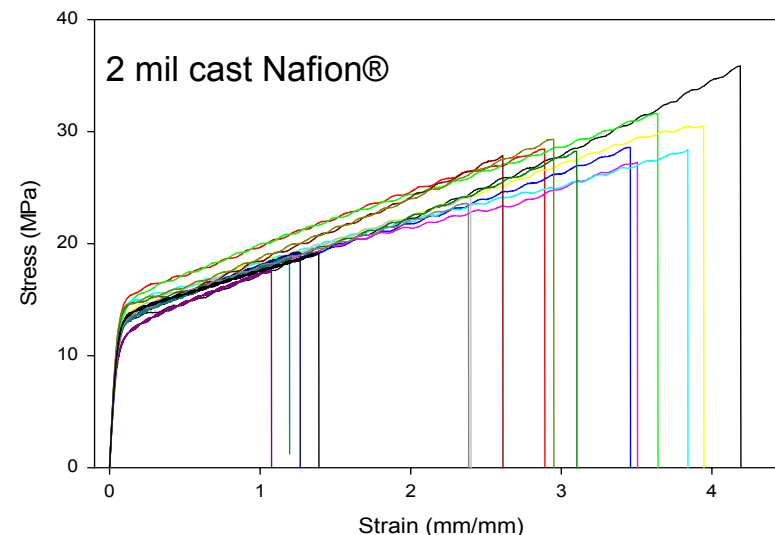
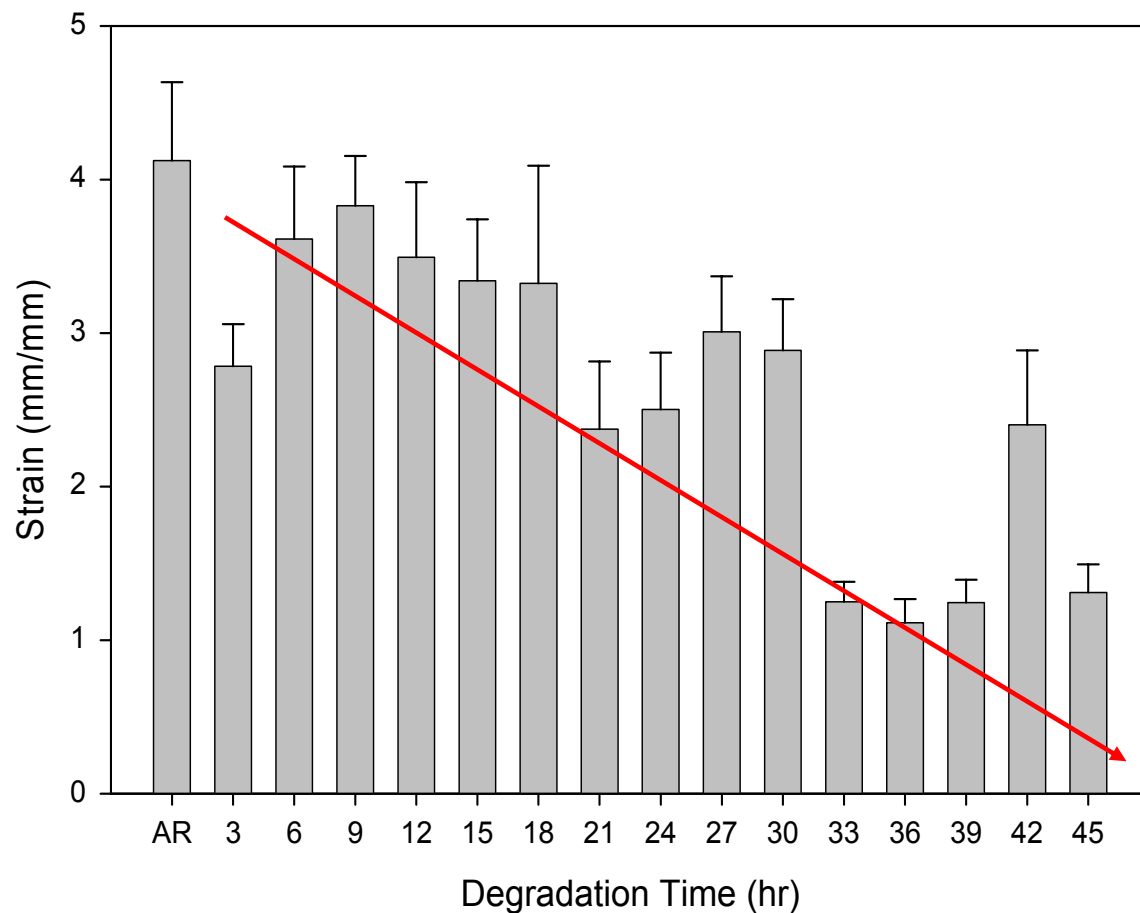


Cross-section view



- As-received samples are smooth
- Degraded samples are rough
 - Ruptured bubbles (gas origin?)
 - Crack in bubble (mechanical failure nuclei?)
- Bubble formation is not prevented by chemically stable (CS) ionomer

Effects of Chemical Degradation on the Tensile Properties of Cast Nafion® Membrane

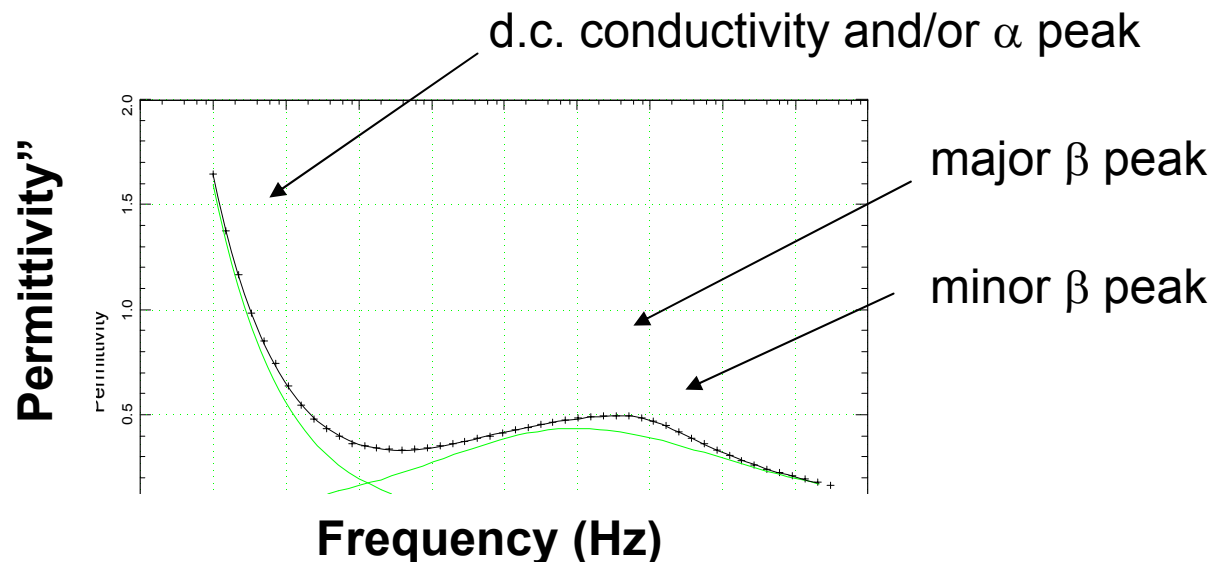
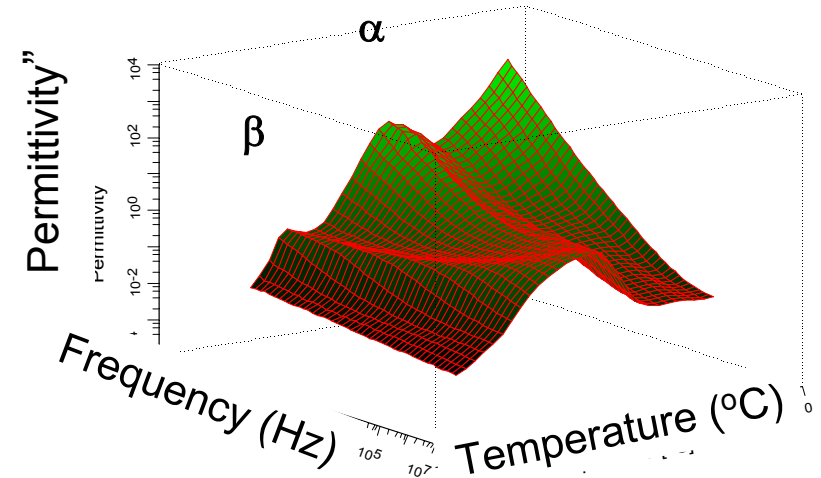


- As degradation time increases a general trend of decreasing strain at break is observed.
- A loss of toughness through chemical degradation may be attributed to a change in the molecular weight distribution.

Dielectric Spectra: Signature of Molecular Motions

Relaxation Peaks:

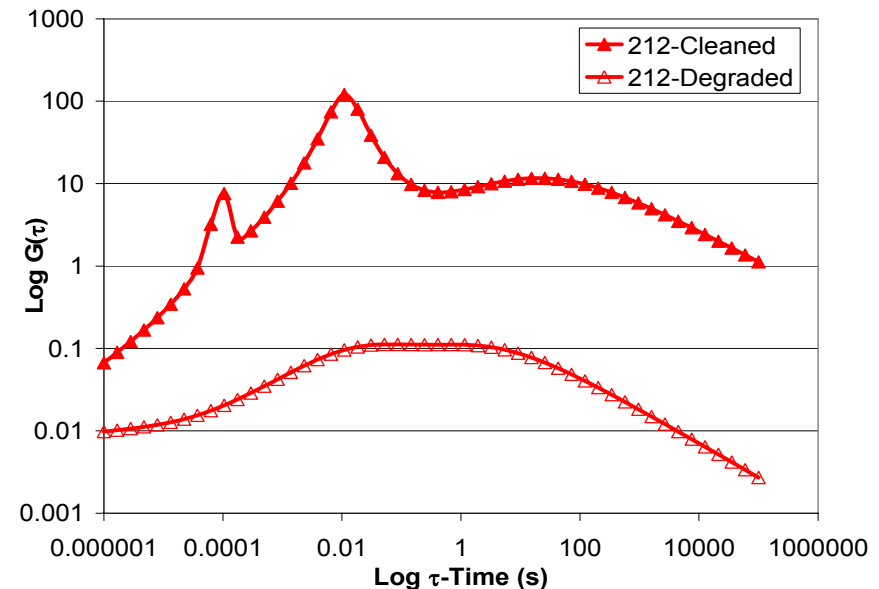
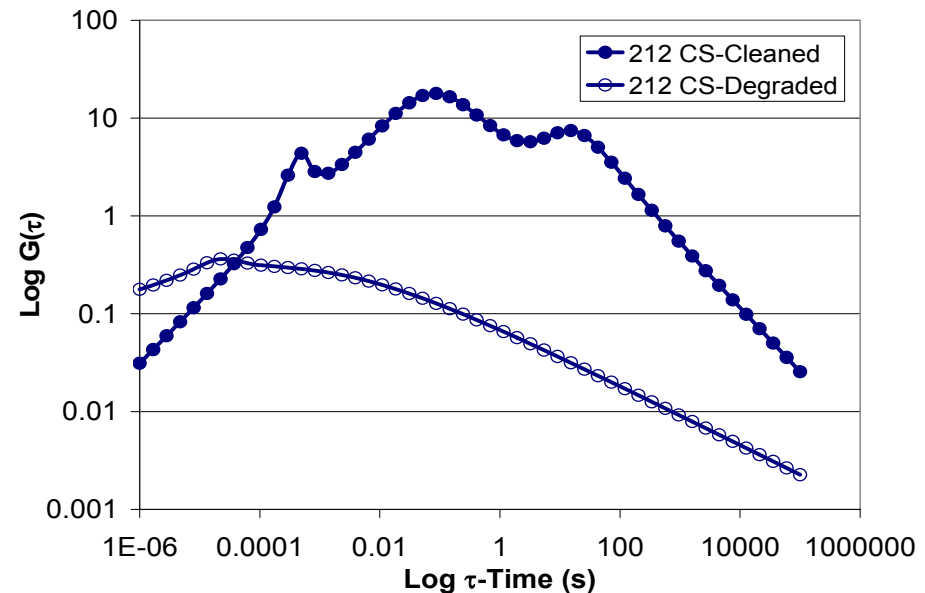
- 2 β peaks at lower temp.
Major and minor β peak components change with moisture
- α peak at higher temp.
- d.c. conductivity at high T and low f



Relaxation Time (τ) Distributions = $G(\tau)^*$

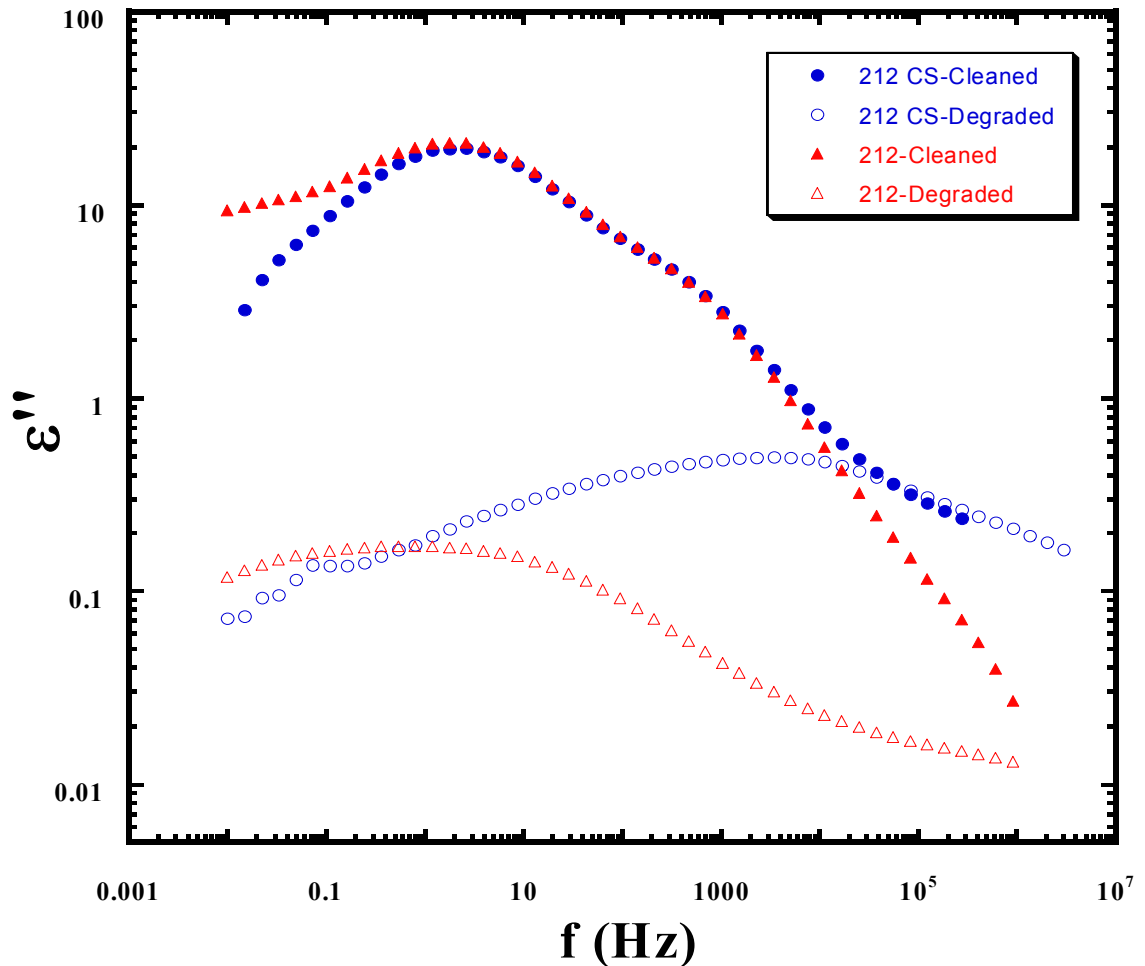
- Multi-modal due to different relaxation processes operative in Nafion®
- Degradation broadens distribution - modes become less distinct – shift toward faster motions
- Results are commensurate with *broadened molecular weight distribution of **shorter** chain lengths*
- Overall: Spectra is a very diagnostic of chemical degradation

* *Note:* $G(\tau)$ is corrected for dc conduction at low frequencies.



Degraded vs. Non-degraded Nafion® Samples

- CS vs. non-CS β peak:
No difference in f_{\max}
- Degraded CS vs. degraded non-CS β peak:
Upward shift in f_{\max} w/
degradation
- Commensurate with a
broader distribution of
smaller chain lengths upon
degradation

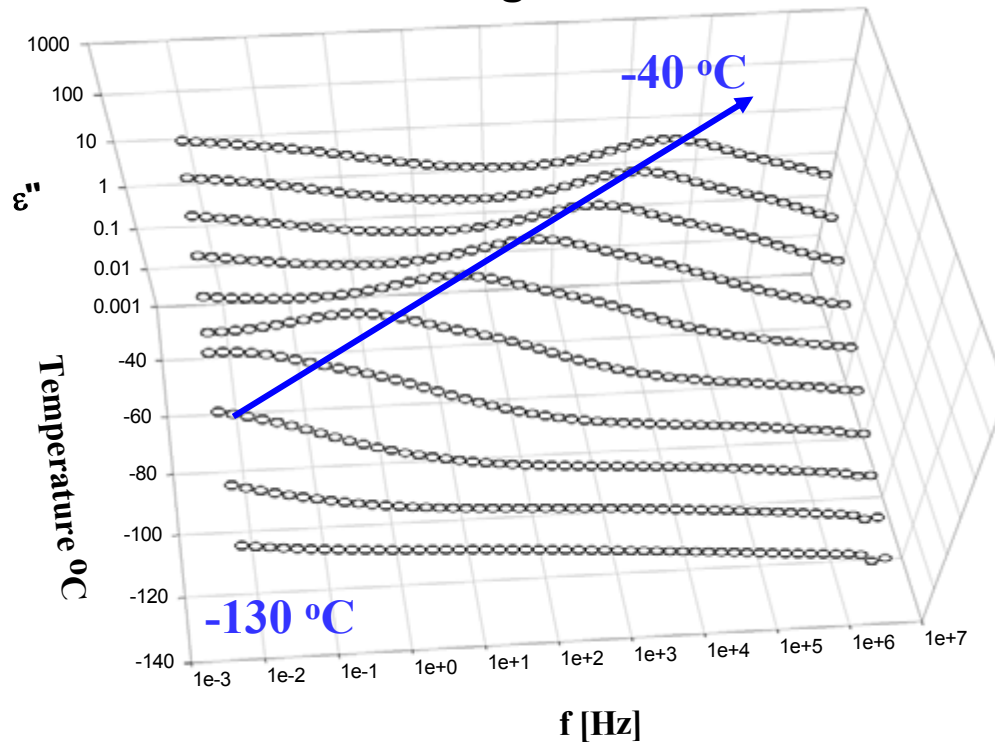


Dielectric Spectra

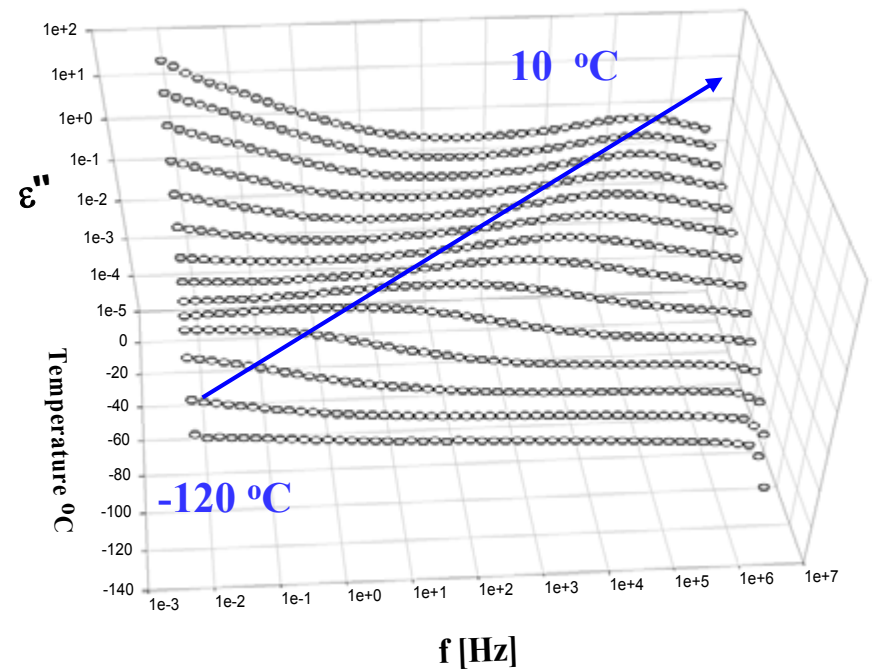
Degraded vs. Non-degraded Cast Nafion® Samples

Major peak shifts to higher frequencies with increased temperature

Non-degraded



Degraded



Illustrates relaxation broadening w/ degradation

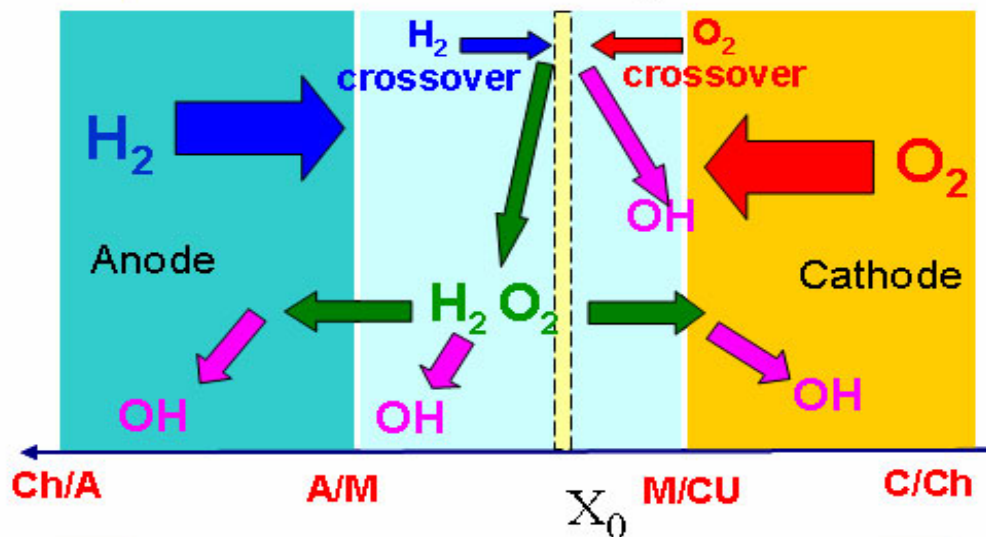
Curves separated by 10°C increments starting at the lowest temperature

USM: General Conclusions

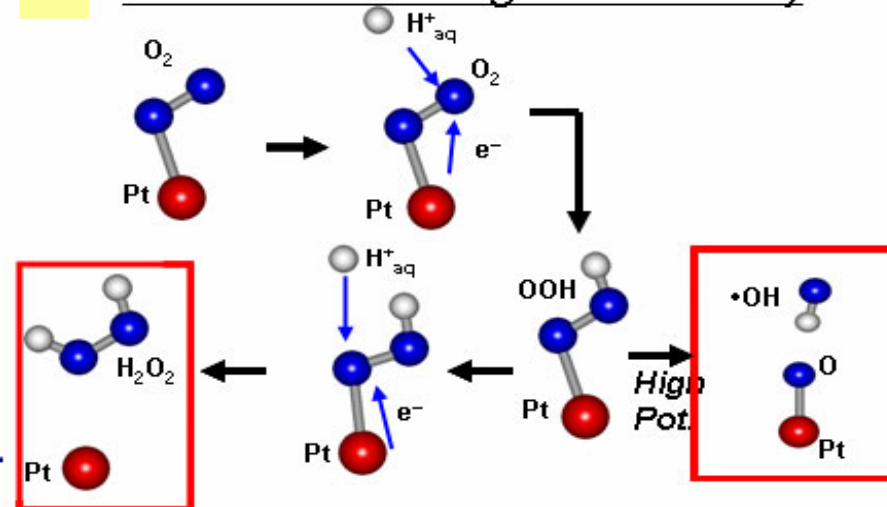
- SEM shows chemical degradation which produces bubbles that become cracked – mechanical failure nuclei
- Bubble formation not prevented by CS ionomer
- DMA displays increase in alpha relaxation temperature with chemical degradation
- Strain at break decreases with degradation time
- Dielectric spectroscopy (DS) is diagnostic of chemical degradation
- Multi-modal distribution of relaxation times due to different molecular motions
- Degradation broadens distribution - modes less distinct – shift toward faster motions
 - *Interpretation: broadened molecular weight distribution of shorter chain lengths.*

UTC: Modeling Overview

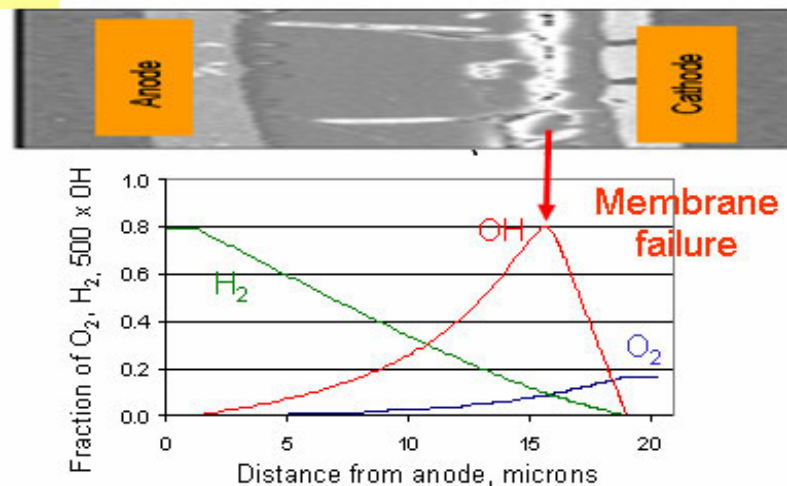
a Observation based hypothesis



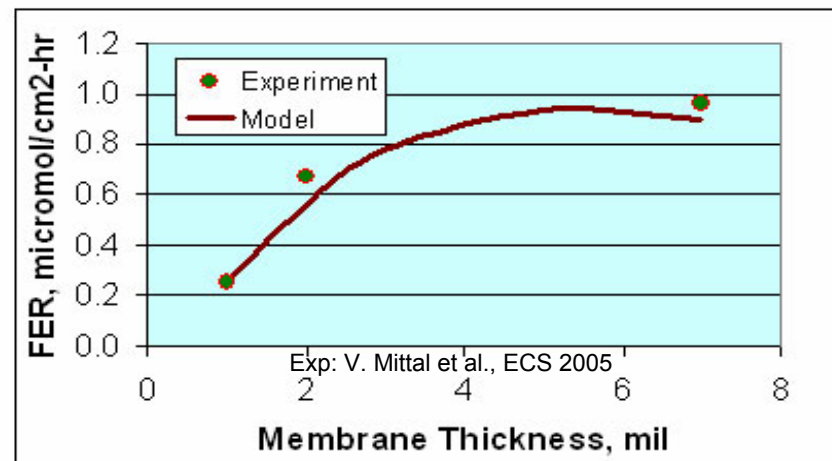
b Ab-initio modeling for feasibility



c MEA Model development

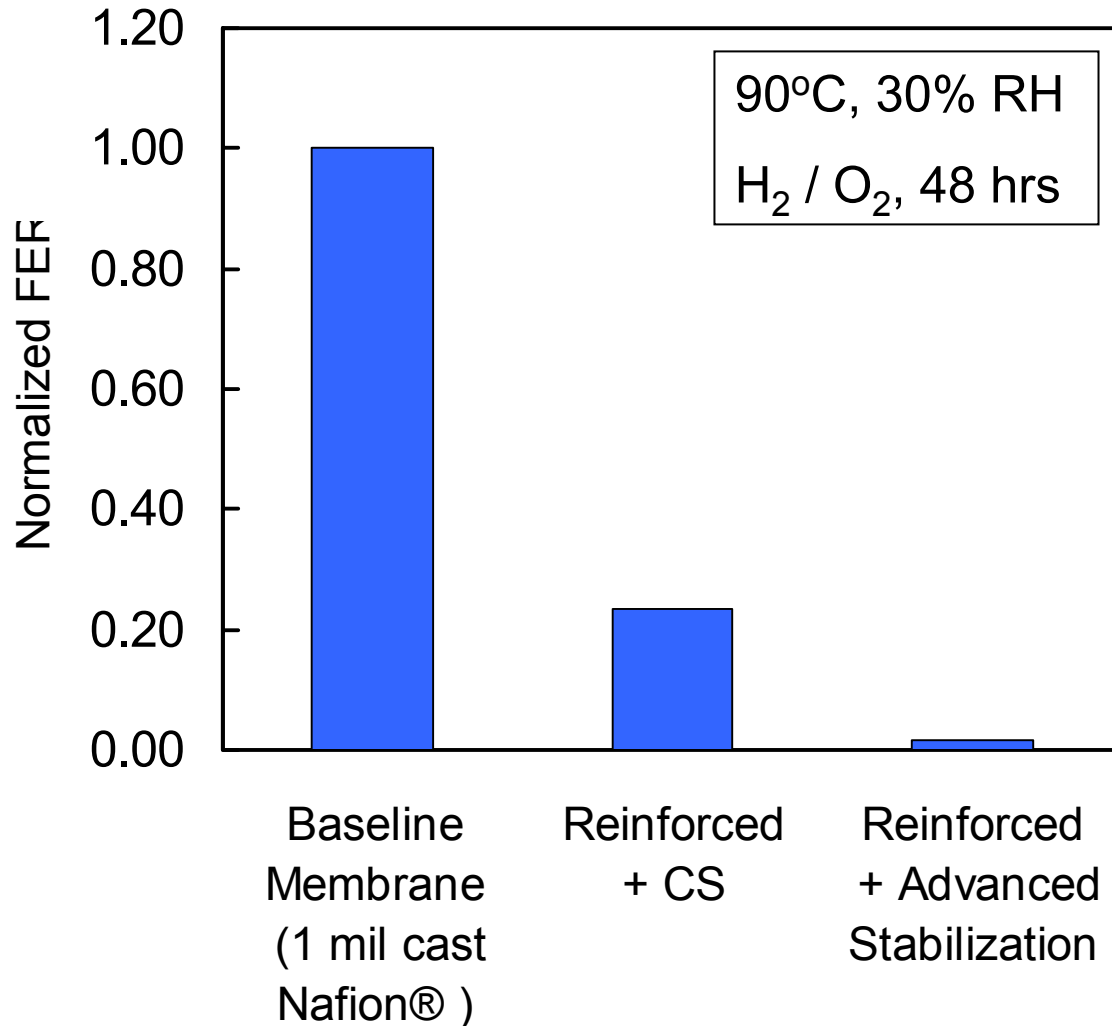


d MEA model verification



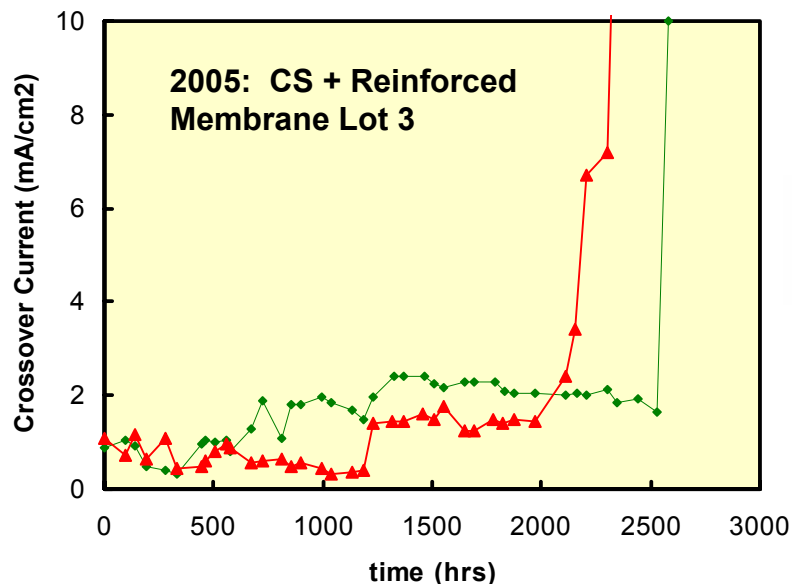
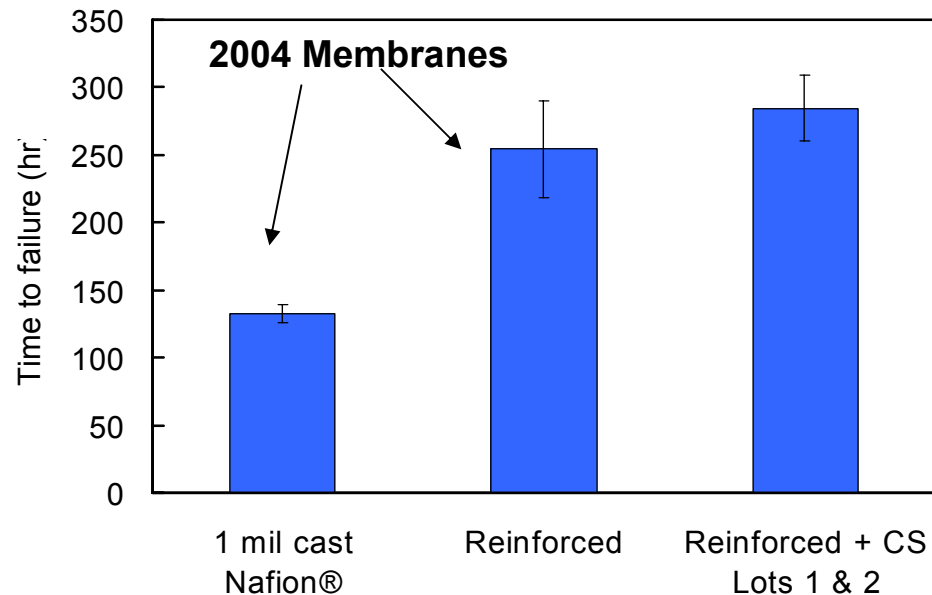
DuPont Durable Membrane

Fluoride Emission in OCV Accelerated Test



- We have successfully combined our chemically stable (CS) ionomer and our mechanical reinforcement
 - No significant change in physical properties by use of chemically stable ionomer
 - 4 to 5 X improvement in FER by combining chemically stable ionomer + mechanical reinforcement
- DuPont advanced stabilization:
 - Technology developed at DuPont in parallel to the program
 - Based on initial promising results we decided to integrate it into the program
 - 40 to 50 X reduction in FER

Performance in Load + RH Cycle Test *



- Reinforced membrane (non-CS) shows about 2x improvement over baseline materials

- Membrane degradation (thinning) observed in the area surrounding the cell outlet

- Combination of CS ionomer and mechanical reinforcement has enabled us to demonstrate up to 10x improvement

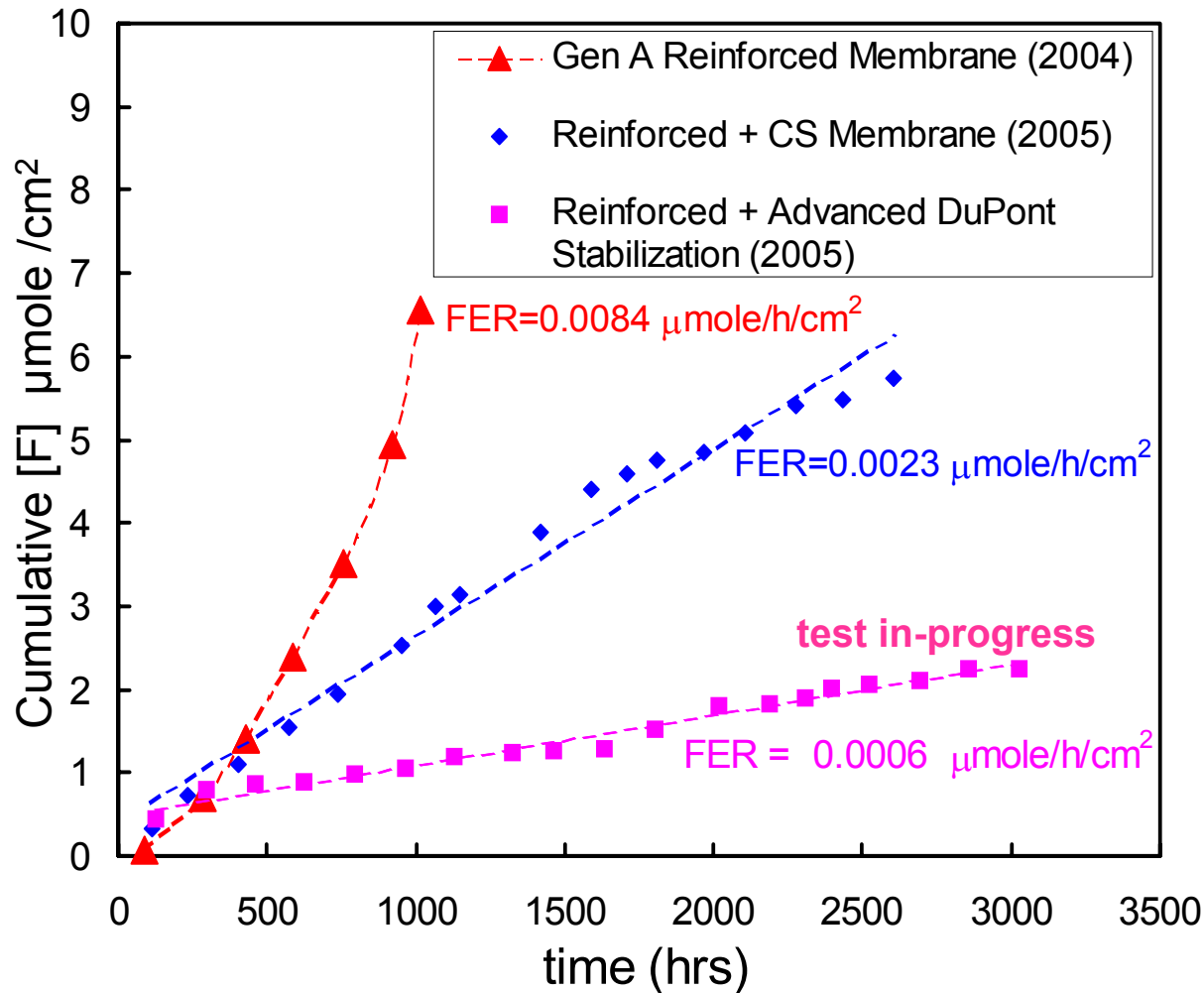
- Samples A & B of lot # 3 endured > 2000 hrs

- These are exceptional results that are not well understood yet

- No membrane thinning or localized failure detected in post-mortem analysis

* Note: Test Conditions: Humidity cycle (24 h): N₂ / N₂, 80 °C; RH of inlet gases is cycled between 0 and 100% every 30 mins. Load cycle (24 h): H₂ / O₂; 50%RH, 80 °C; the load is cycled between 10 and 800 mA/cm² (7min/3 min)

Performance in Drive Cycle Test



- The drive cycle test is aimed at replicating conditions typical of automotive applications, at a single cell level

- Membrane is exposed to load and relative humidity cycling conditions
- Combination of CS ionomer and membrane reinforcement has enabled us to demonstrate:

- ~3x longer Life time
- ~3.5 x lower FER

- Further improvements are achieved by using DuPont's advanced stabilization

- 14 x lower FER
- Sample has been on test > 3000 hrs - **test still in progress**



UTC: Durable MEA Technology Testing: “Rainbow” 20-Cell Stack

Goal

- Accelerate membrane and edge-seal failure
- Stack test of reinforced membrane (non-CS)
- Understand UTC peroxide mitigation (PM) benefit

Stack facts

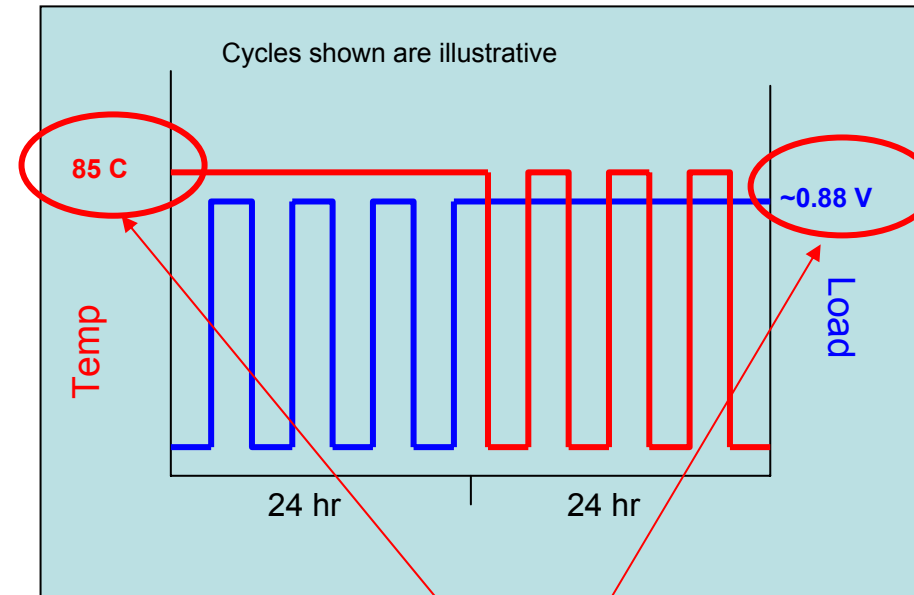
- “Rainbow” stack means mixed parts:
 - DuPont MEA's (6 of 20)
 - UTC MEA's no PM (7 of 20)
 - UTC MEA's with PM (7 of 20)
- Each membrane 410 cm² - DuPont reinforced

Conditions

- H₂ / O₂ constant Load for 1000 hr;
- H₂ / O₂ for 800 hr;
- H₂ / Air for 3200 hr
- Alternate load / thermal cycling
- Repeat until failure (crossover failure or 10% loss)

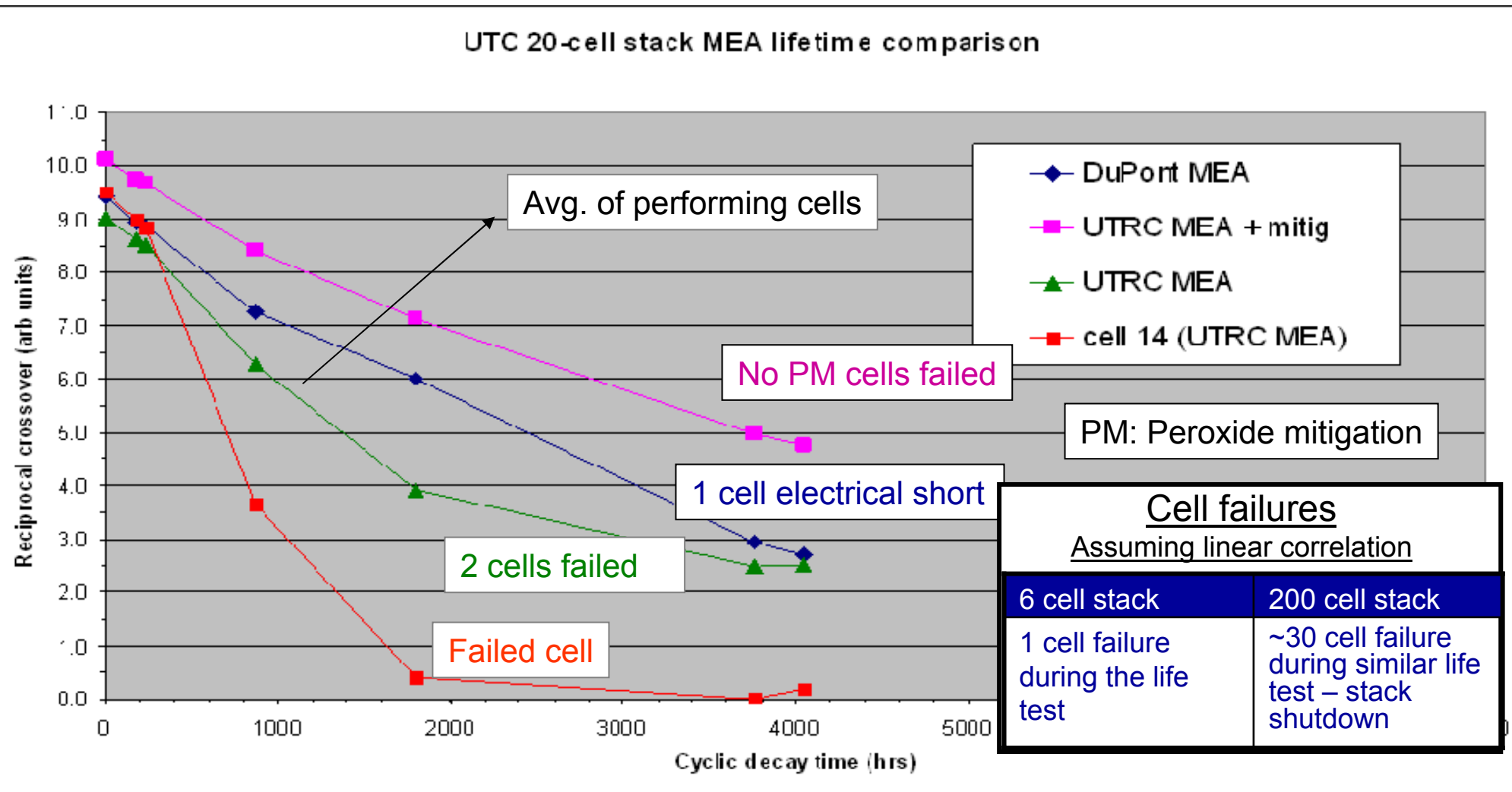
Failure criteria

- Fall-off time <<1min
- [Note: fall-off t ~ (crossover current)⁻¹]
- Performance decay >10% of BOL

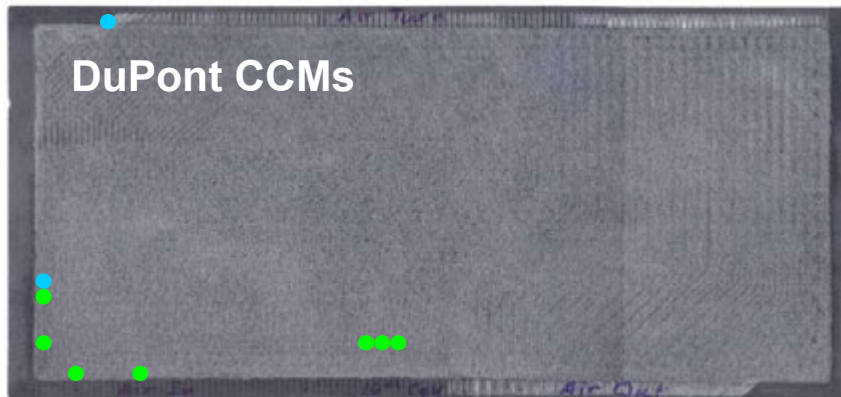


Highly accelerating for:
-membrane failure
-performance decay

20 Cell Stack Diagnosis: Fall-off Time (~4000 hrs Accelerated Cycling Testing)



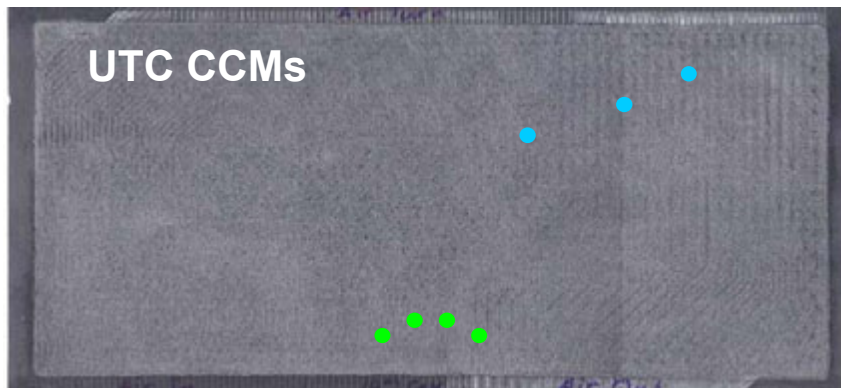
20-Cell *UEA/Stack* Leak Test Results



Cell-leaks

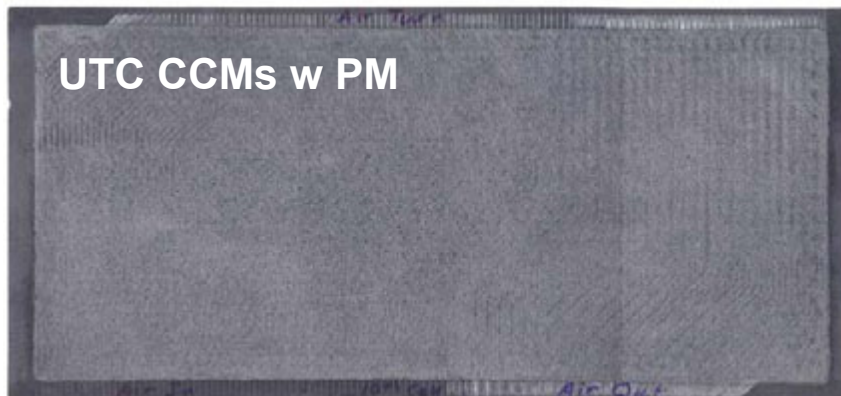
- 3-7
- 18-2

No *stack* leaks detected
Only ***UEA*** leaks detected at
edges/near corners of
active area



- 13-4
- 14-3

Stack leaks detected
from bubbles exiting
gas flow channels
consistent with ***UEA*** leaks



- 7
- 8

No *Stack* leaks nor ***UEA***
leaks detected

Future Work

- Conclude postmortem analysis to get understanding of degradation mechanisms (DuPont- USM)
- Mitigation Strategy (DuPont - UTC)
 - Verification of manufacturability of peroxide mitigation strategy in sub-scale and full size cell tests
- Continue development of reinforced membrane to improve overall dimensional stability (DuPont)
- Theoretical Modeling (UTC)
 - Establish the correlation between mechanical and chemical degradation
 - Estimate the acceleration factor for the conditions used in the 1st 20-cell stack validation
- Edge Seal (UTC)
 - Completion of sub-scale accelerated tests of new edge-seal concepts to verify design improvements
- Finalize Cost Analysis for improved membrane (DuPont)

Summary

- Our studies indicate that carboxylic acid groups, not branched side-chains make PFSA compounds susceptible to attack by peroxy radicals
- DuPont membrane with advanced stabilization has enabled a 50x reduction in Fluoride emission in the OCV test. This membrane also shows other significant improvements: 14x lower FER and more than 3x longer life times in the drive cycle test
- UTC has demonstrated 4000 hrs in stack test under accelerated cyclic conditions
 - Combination of DuPont reinforced membrane and UTC mitigation strategy showed best durability - no failures observed
 - The 2010 Technical target is 5000 hrs durability with cycling at $<80^{\circ}\text{C}$
- UTC has made significant progress in their modeling effort
 - Physics based chemical degradation model developed and validated
 - Model is able to predict FER for non-reinforced membranes
 - Model is able to predict the membrane failure location
- USM has developed analytical techniques to investigate the effects of degradation on the morphology of the membrane
 - SEM shows chemical degradation which produces bubbles that can become mechanical failure nuclei
 - Dielectric spectroscopy reveals changes in the MW distribution as a result of chemical degradation

Back up slides

Responses to Previous Year Reviewers' Comments

Comment 1: “Improved Durability and Performance required to meet the life time goals”.

Towards this, the UTRC mitigation strategy and DuPont MEA fabrication have been implemented on the same MEA and have enabled the realization of dramatic improvements in performance and durability.

Comment 2: “Lack of publications for this project”.

Towards addressing this, four presentations have been made and two extended abstracts have been submitted to Electrochemical Society and Materials Research Society in Q4, 2005. We also presented a paper at the KFTCA International Symposium on Fuel Cells Durability. The USM group has also been generating a number of publications. A continued effort to publish will be made.

Comment 3: “The UTRC mitigation strategy and DuPont MEA fabrication need to be merged”.

In the last quarter of '05, DuPont has successfully integrated their electrode application process with membranes treated with the UTC peroxide mitigation. These have been tested under sub-scale conditions.

Comment 4: “Clear strategies for UTC and DuPont, unclear future collaboration with USM.”

USM has been working in close collaboration with DuPont developing techniques to assess the effects of chemical and mechanical degradation on the morphology of the Nafion® ionomer. This collaboration has yielded a better understanding of the degradation mechanisms. Furthermore, USM is currently doing post-mortem analysis of samples tested under accelerated fuel cell conditions.



Publications and Presentations

Presentations by DuPont Team Members:

- 1) "Strategies for Mitigation of Perfluorosulfonic Acid Degradation in PEM Fuel Cells", K. Schwiebert, K. Raiford, G. Escobedo, F. Principe, and G. Nagarajan, 208th meeting of the Electrochemical Society, Oct 16-21, 2005, Los Angeles, CA
- 2) "Strategies to Improve the Durability of Perfluorosulfonic Acid Membranes for PEM Fuel Cells", G. Escobedo, KFTCA International Symposium, December 8 -9 2005 - Washington, D.C

Two extended abstracts have also been submitted for publication to the above conferences during the reporting period.

Presentations by UTC Team Members:

- 1) Membrane Degradation in PEMFC's, 208th meeting of the Electrochemical Society, Oct 16-21, 2005, Los Angeles, CA
- 2) Attack of the Killer radicals, MRS 2005 Fall Meeting, Nov 27-Dec 1, Boston MA.

Two extended abstracts have also been submitted to the above conference during the reporting period.

Presentations by R.B. Moore (USM):

- 1) "Correlations between Spectroscopic, Morphological, and Dynamic Mechanical Information to Determine the Molecular Origins of Thermal Relaxations in Perfluorosulfonate Ionomer Membranes," Department of Chemistry, University of North Carolina, Chapel Hill, NC, September 21, 2005.
- 2) "Alteration of membrane properties of Perfluorosulfonate Ionomers using Solution and Melt Processing Procedures," 2005 Fall ACS Meeting, Washington, DC, September 1, 2005.
- 3) "Influence of Electrostatic Interactions on Chain Dynamics and Morphological Development in Perfluorosulfonate Ionomer Membranes," 2004 MRS Fall Meeting, Boston, MA, December 1, 2004. Trophy Award for best paper.

External publications by R.B. Moore (USM):

- 1) Page, K.A.; Cable K.M.; Moore, R.B. "Molecular Origins of the Thermal Transitions and Dynamic Mechanical Relaxations in Perfluorosulfonate Ionomers," *Macromolecules* 2005, 38, 6472.

Two other papers recently submitted.



Critical Assumptions and Issues

“Durability and life improvements are being demonstrated on stack with porous plate technology and not solid plate”.

While, the full size stack testing has been done with porous plates, degradation modes are accelerated considerably, with automotive load cycle. Additionally, subscale tests with solid plates have been performed, to demonstrate the life improvements. Furthermore, DuPont is collaborating with an external testing partner in a solid plate stack test of the reinforced CS membrane. As we reported in the previous quarterly report, this test is being done outside of the project in partnership with an automotive OEM that has agreed to cooperate with DuPont, and make available the results for the purposes of this program.