Enabling Commercial PEM Fuel Cells With Breakthrough Lifetime Improvements

2005 DOE Hydrogen Program Review

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This presentation does not contain any proprietary or confidential information

Project ID # FC9

Overview

Timeline

- Project start date: 10/1/2003
- Project end date: 9/29/2006
- Percent complete: 50%

Budget

- Total project funding
  - DOE share: $6.987 MM
  - Contractor share: $1.747 MM
- Funding received in FY04
  - $2.2 MM ($2.745 MM Total Project)
- Funding for FY05
  - Released to date: $1.75 MM DOE Share ($2.187 MM Total Project)
  - FY2005 Total Cost: $2.1 MM DOE Share ($2.625 MM Total Project)

Barriers

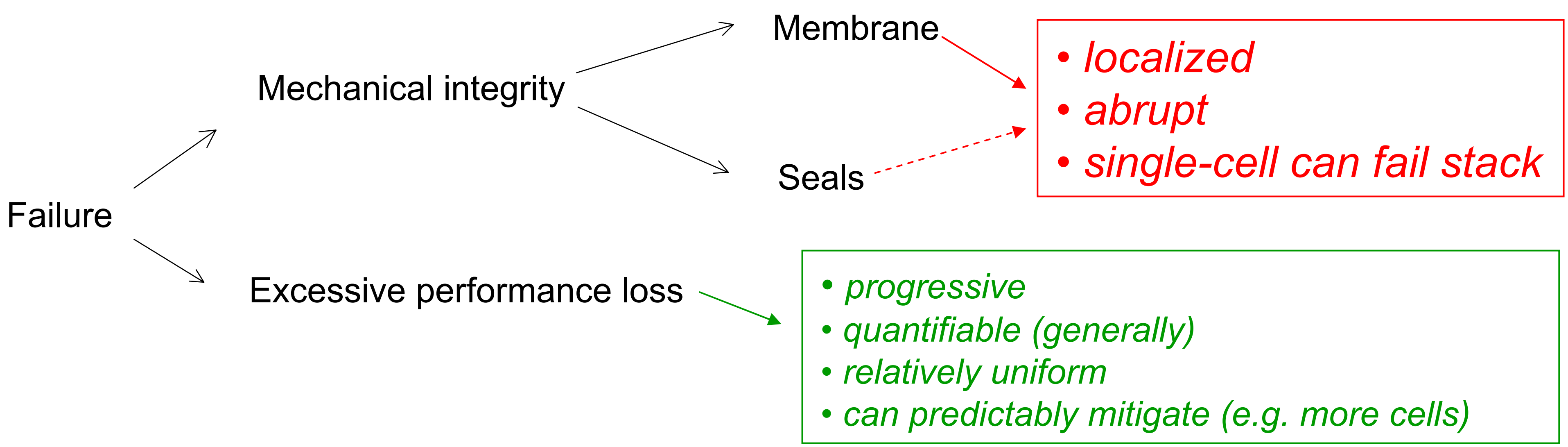
- DOE Technical Barriers for Fuel Cell components
  - A. Durability
  - B. Cost
- DOE Technical Targets for Fuel Cell Stack System for 2010
  - Durability > 40,000 hours (stationary), 5000 (hours) auto
  - Cost no greater than current Nafion® projections

Partners

- UTC
- USM

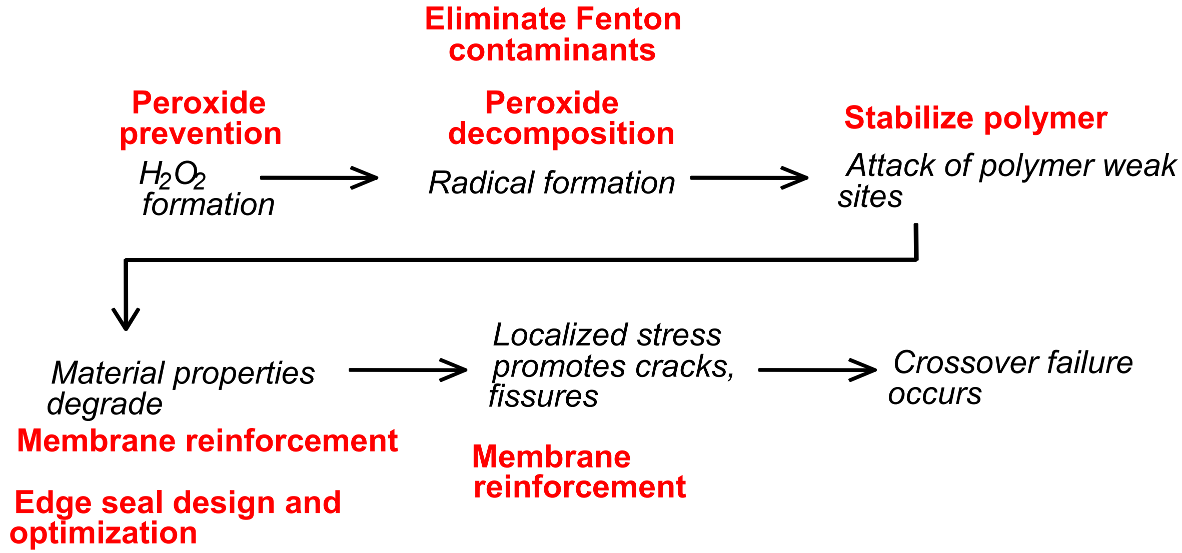
Objectives

- Through both experiments and modeling, develop an understanding of potential mechanisms than 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.



Approach

Program Scope



Program Tasks

Task 1. Materials Synthesis

Task 2. Accelerated Aging Tests

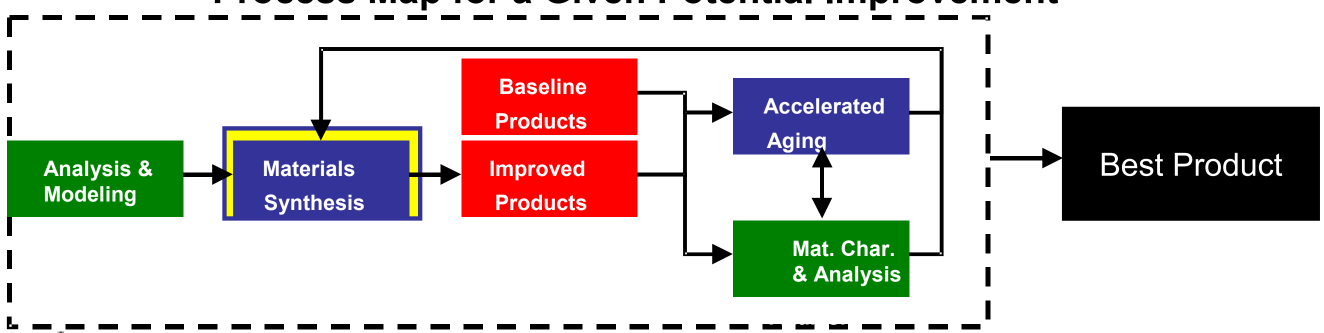
Task 3. Analysis and Modeling

Task 4. Stack Testing

Task 5. Materials Char. and Analysis

Task 6. Cost Analysis

Process Map for a Given Potential Improvement

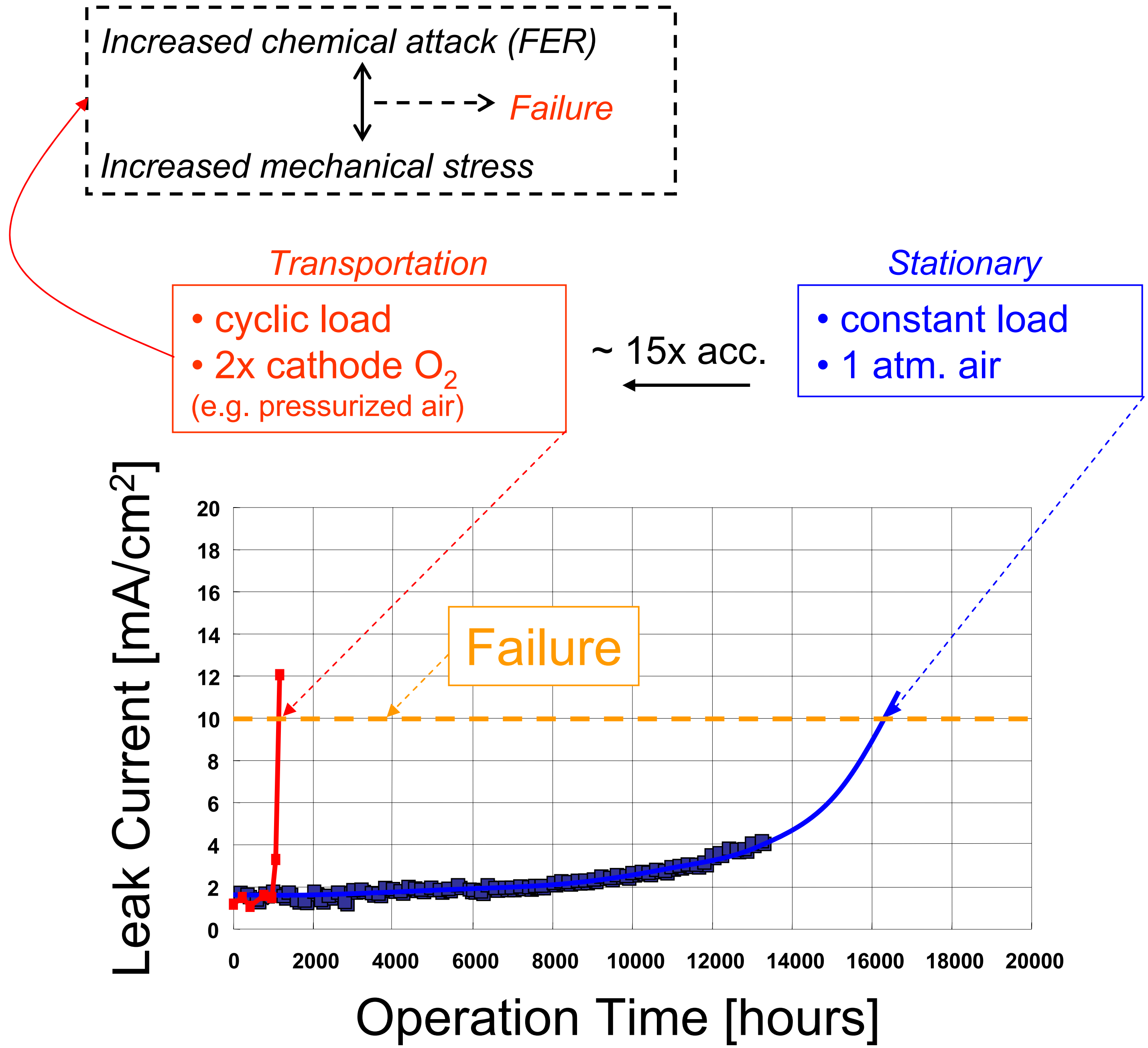


Outline: Technical Accomplishments

1. DOE goals – shift of focus to transportation goals
2. Fundamentals
    1. DuPont: PFSA degradation mechanism
    2. UTC: modeling of membrane degradation
    3. USM: molecular and morphological origins of membrane degradation
3. Mechanical durability
4. Chemical durability
    1. New DuPont membrane with increased chemical stability
    2. UTC mitigation
5. Future work

Shifted Focus to Membrane Failure in Transportation Applications

Membrane failure exacerbated by transportation conditions (cyclic load, pressurized cathode)

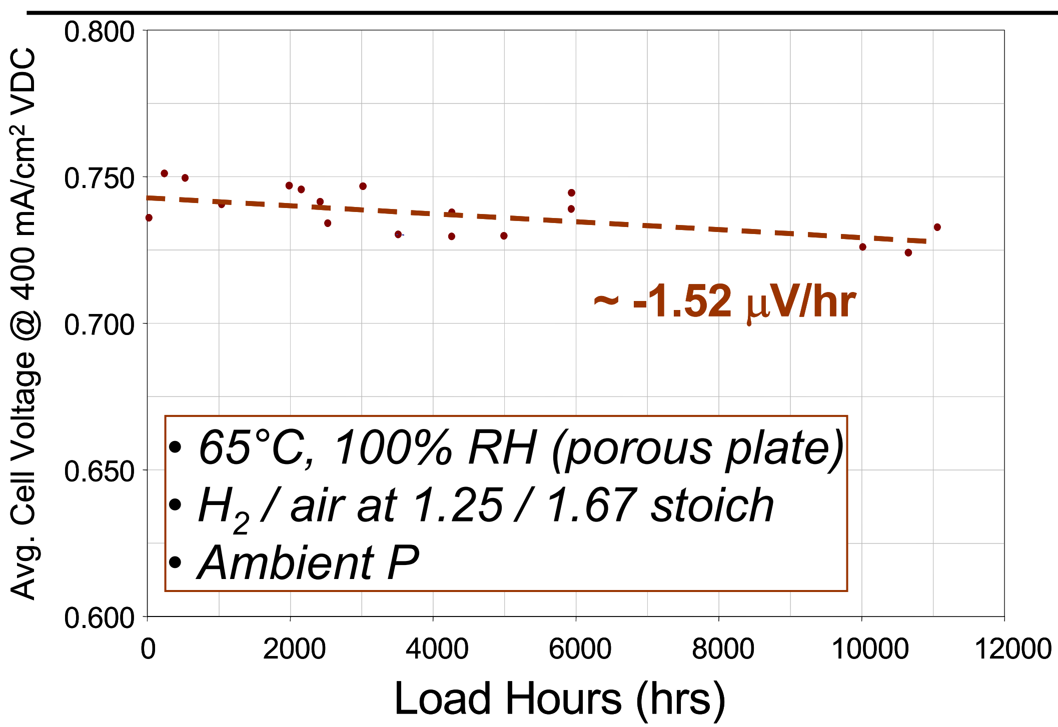


* Sub-scale, solid plate hardware

Program Shift to Transportation (cyclic) will Still Enable Stationary

Materials development and testing provide lifetime estimates through modeling

Product	UTC full-size testing	Lifetime
"Improved" MEA → Cyclic stack, Cyclic single-cell	Cyclic stack	UTRC model to predict:
Baseline MEA → Cyclic single-cell, Stationary stack	Cyclic single-cell	•5000 hr transportation
	Stationary stack	• 40,000 hr stationary



- UTC Fuel Cells short-stack (>5 kW)
- **Baseline DuPont MEA technology**

(prior to program start)

- 11,000+ hrs life (ongoing)
- Low decay rates (<2 μV/hr)

Fundamentals 1 - DuPont Expertise in PFSA Degradation

Have correlated chemical attack mechanisms to unstable end-groups in PFSA

Fragments in product H_2O

polymer-CF_2-CF-CF_2-CO_2H ——— ***H_2O_2/Fe^{+2} or fuel cell*** ———→ HO_2C-$CF(CF_3)OCF_2CF_2$-SO_3H

(side chain on the central CF: | $OCF_2CF(CF_3)OCF_2CF_2SO_3H$)

HO_2C-CF_2-SO_3H

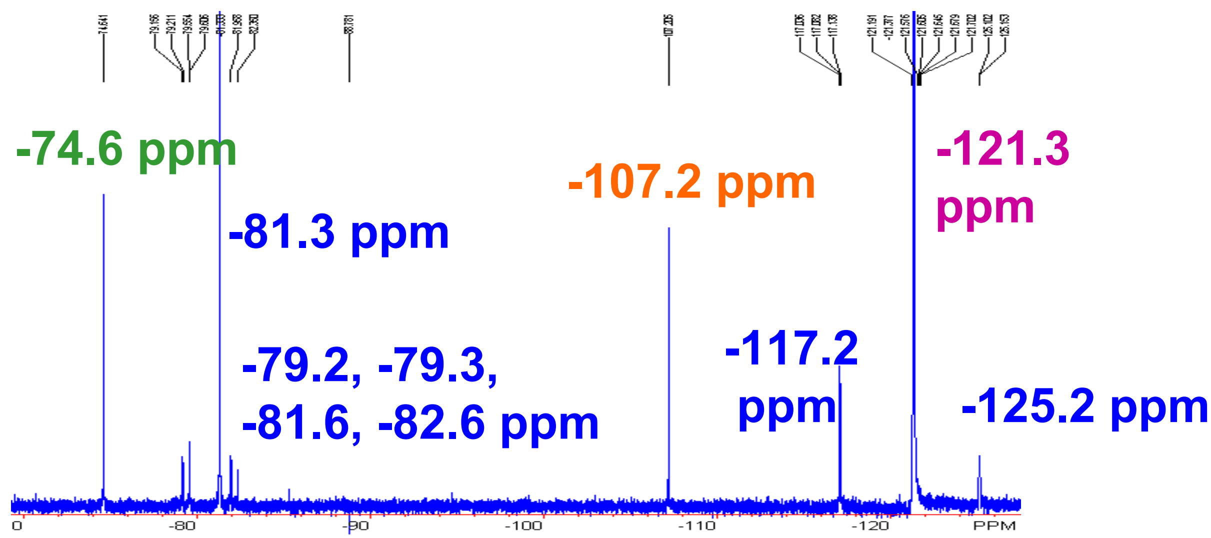
CF_3CO_2H

HF

CO_2 also formed

- Similar polymer fragments found in ex-situ Fenton's test and fuel cell test suggest similar degradation mechanisms
- Fragments are consistent with a step-wise degradation mechanism from unstable polymer end-groups

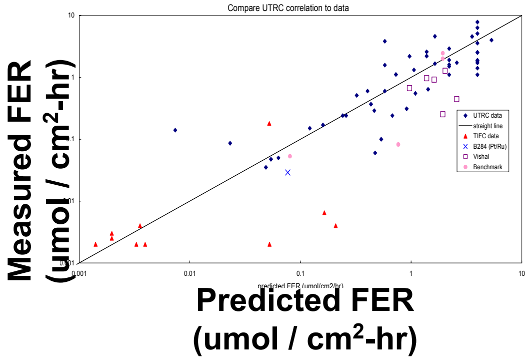
^{19}F NMR of Cathode Product Water - OCV Test



Fundamentals 2 – UTRC Membrane Degradation Modeling

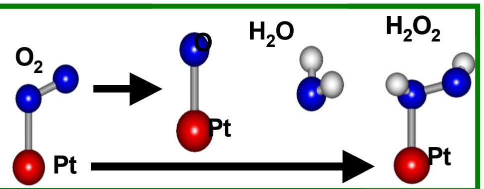
Current multi-scale physics-based model combines experimental / theoretical to yield a predictive model for membrane degradation

100+ subscale tests

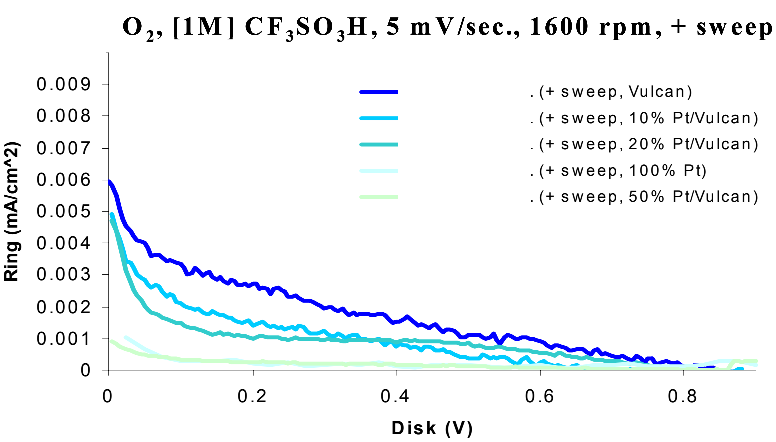


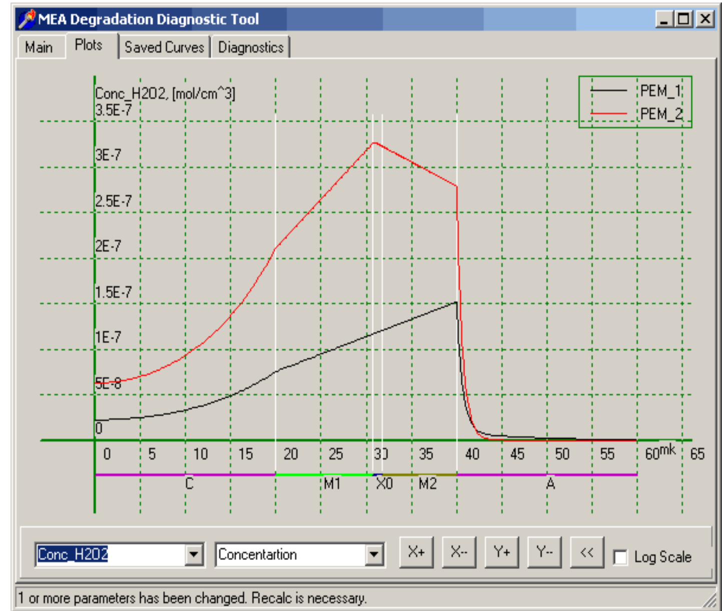
Atomistic modeling

Pt partially covered by H. One Pt site is vacant



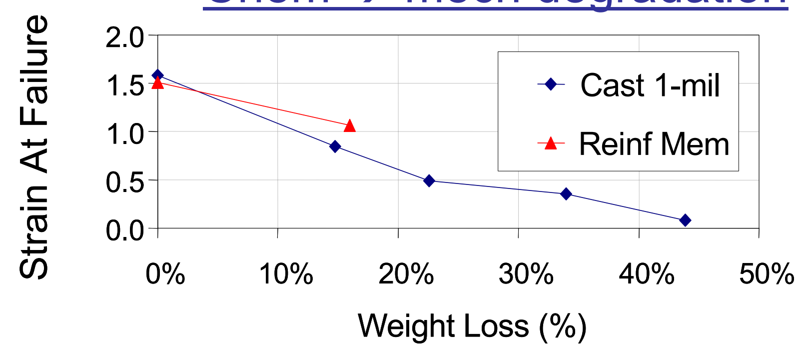
Ex-situ tests (e.g. RRDE)





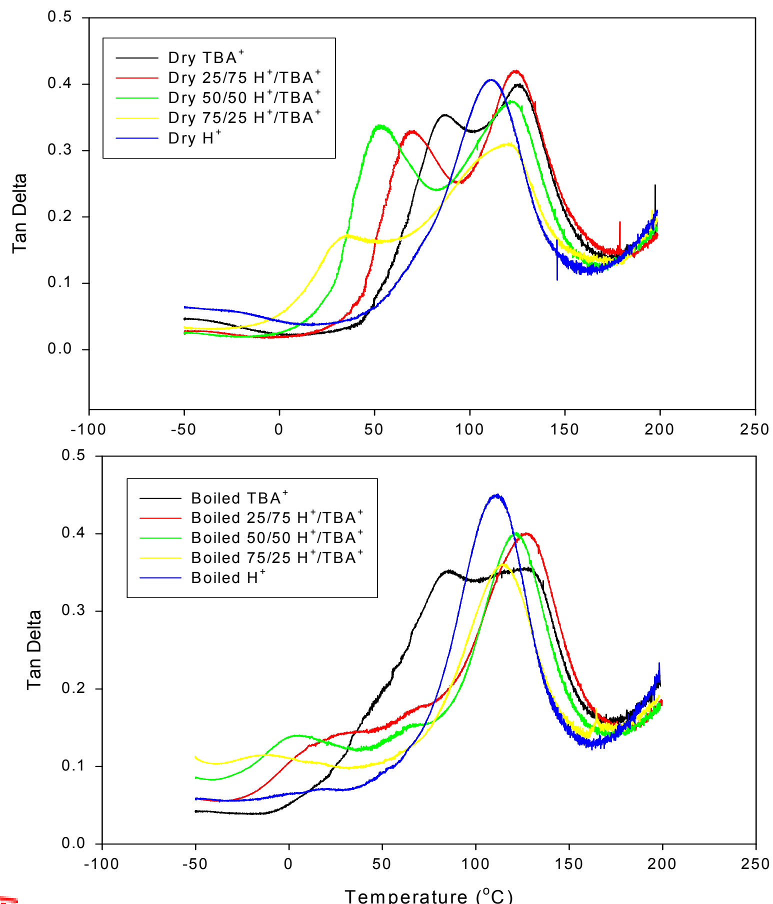
- Predicts location / extent of membrane attack
- No significant ionomer attack in electrodes
- Agreement with post-test analysis

Chem → mech degradation



Fundamentals 3 – USM Studies of the Molecular and Morphological Origins of Membrane Degradation in PEM Fuel Cell Applications

- USM efforts on this project have been focused on developing methods to accurately monitor changes in membrane structure (molecular and morphological) that occur during PEM fuel cell application.
- Through these studies, we will be able to gain a deeper understanding of the chemical and physical mechanisms of degradation and to evaluate the beneficial effects of various chemical modifications of new PEM fuel cell membranes.



Effect of Membrane Humidification on the Mechanical Properties of PEM Fuel Cell Membranes

- With humidification, the magnitude of the β–relaxation is greatly reduced. This indicates that water is significantly affecting the chain motions within the electrostatic network.
- In the static tensile test, water (at different %RH) significantly lowers the modulus of the material in agreement with the DMA data.

Integrated Technologies: Chemical / Mechanical Failure Mitigation

Fundamental understanding facilitates accurate screening methodologies

Improved MEA Strategies

Mechanical stability

- Reinforced membrane (DuPont)
- Seal design UTC

Chemical stability

- Stable (CS) ionomer (DuPont)
- Peroxide mitigation (UTC)

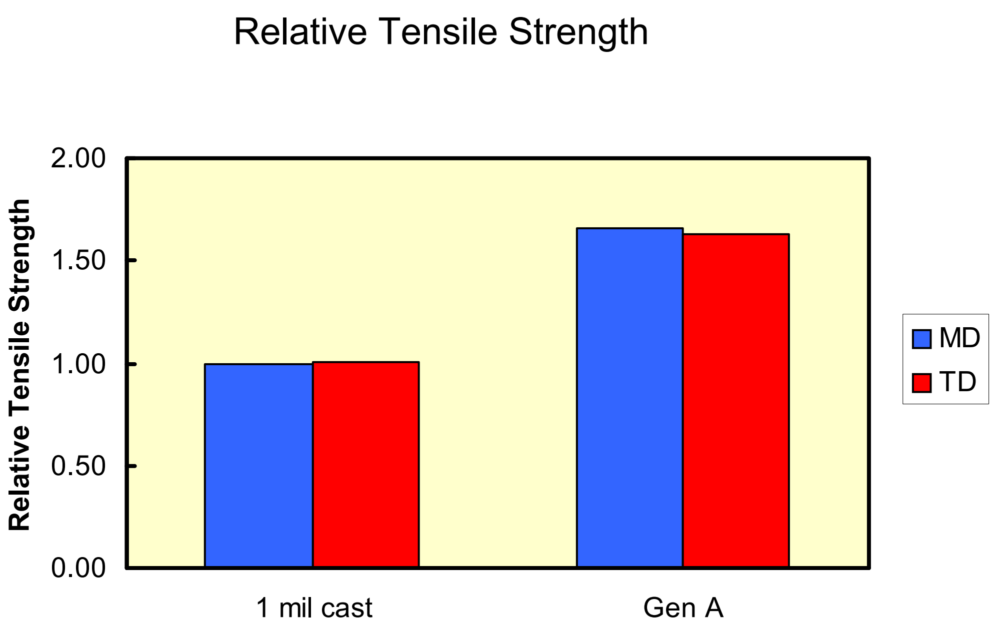
Screening Techniques

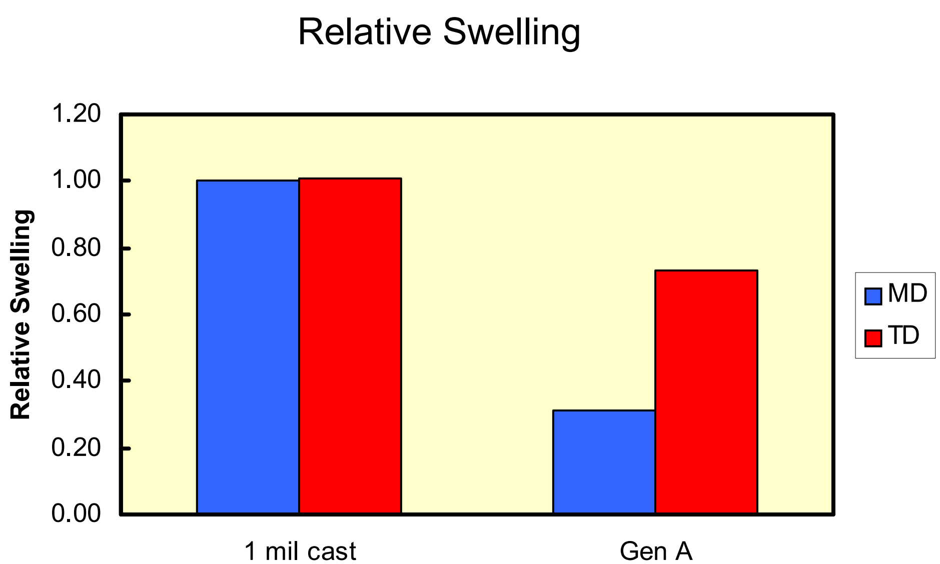
Fuel Cell | Out of Fuel Cell

- Mechanical testing
  - modulus, strain, swelling
- Accelerated Mechanical Degradation
  - lifetime, OCV decay
- RH-load cycle
  - lifetime
- Automotive cyclic
  - lifetime, fluoride release
- OCV hold
  - lifetime, fluoride release
- Fenton's test
  - wt. Loss, fluoride release

New DuPont Membrane with Increased Mechanical Stability - 1

Results of mechanical properties measurements





Mechanical testing
- modulus, strain

•We have made significant progress in membrane properties, through membrane design and process development.

•An intermediate prototype, known as Gen A membrane was selected for stack testing on 12/2004.

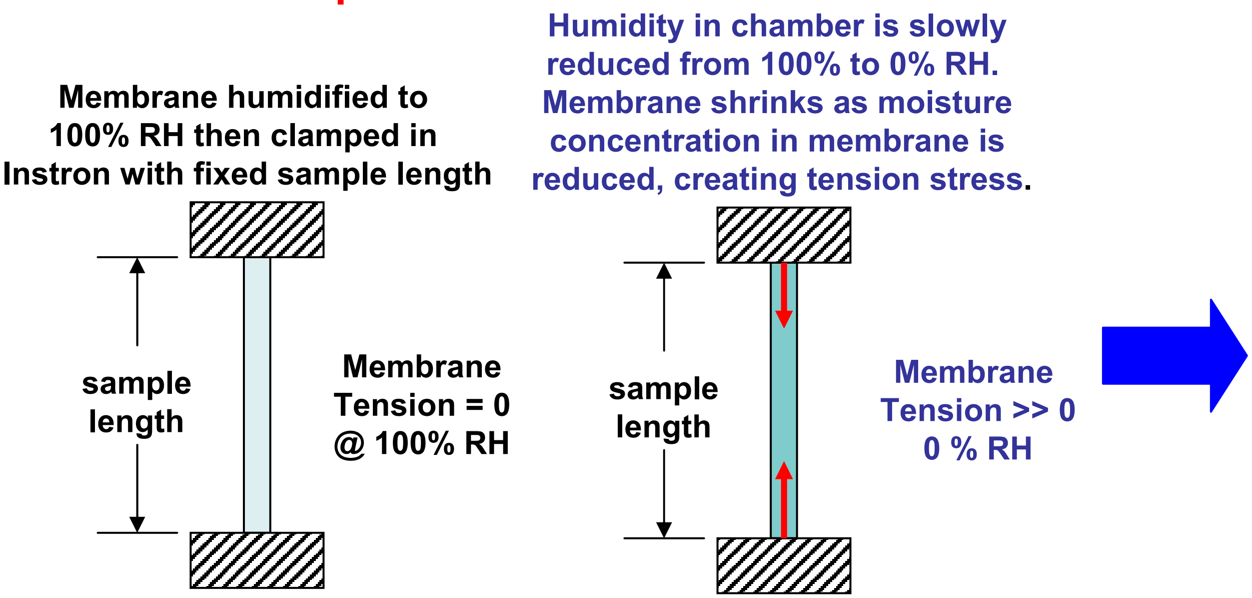
•Gen A showed remarkably good performance in our accelerated FC tests, although it does not include the chemically stabilized ionomer.

•We still see an opportunity to improve the physical properties of this membrane.

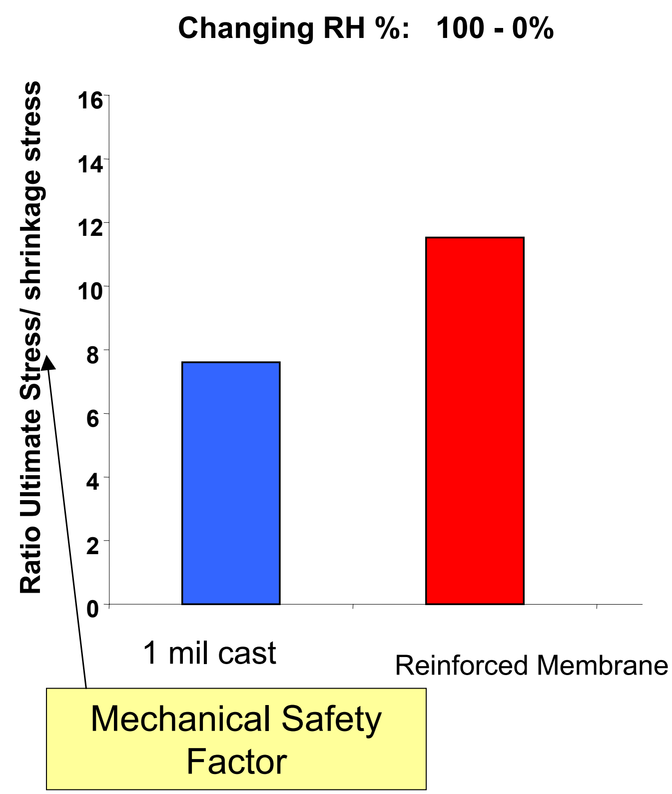
New DuPont Membrane with Increased Mechanical Stability - 2

Results of mechanical properties measurements

Shrinkage Stress tests done in a humidity and temperature controlled chamber



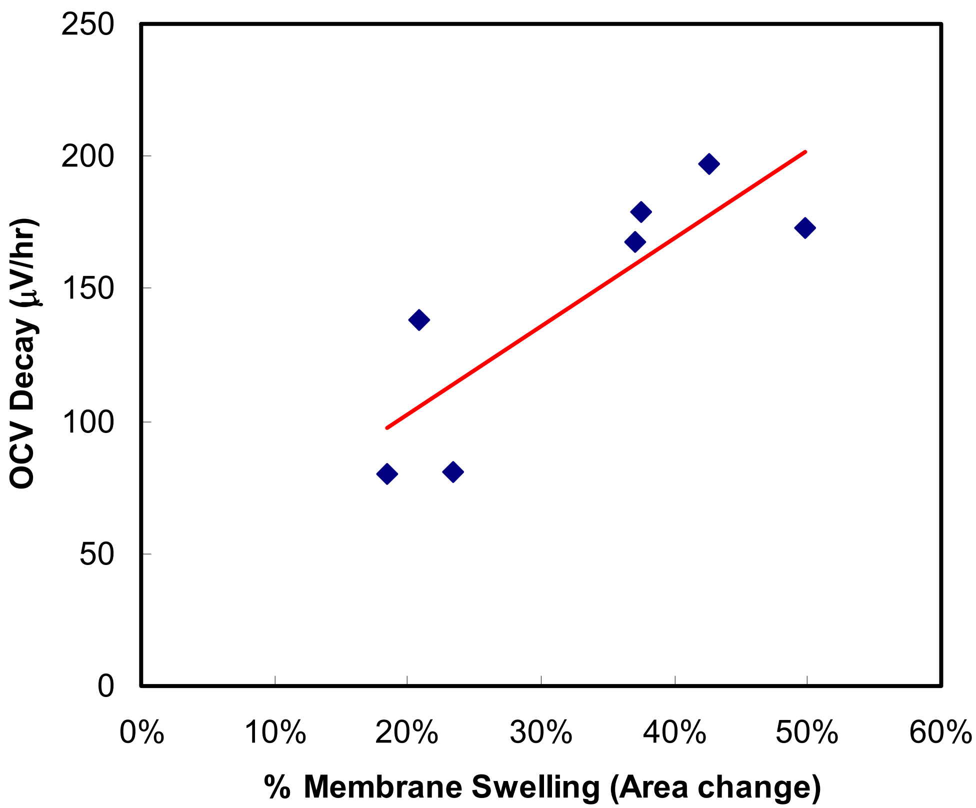
Mechanical testing
- modulus, strain



- We believe that a key membrane failure mode is fatigue caused by stresses imposed by humidity and thermal cycling, thus leading to tears and pinholes.
- Shrink tension and membrane expansion originate stress cycles in membrane during fuel cell operation.
- Our reinforced membrane shows a higher safety factor than baseline materials; therefore, we expect it to be less affected by the stresses developed during RH cycling.

Relationship Between Decay Rate and Dimensional Stability

Accelerated fuel cell and swelling test results



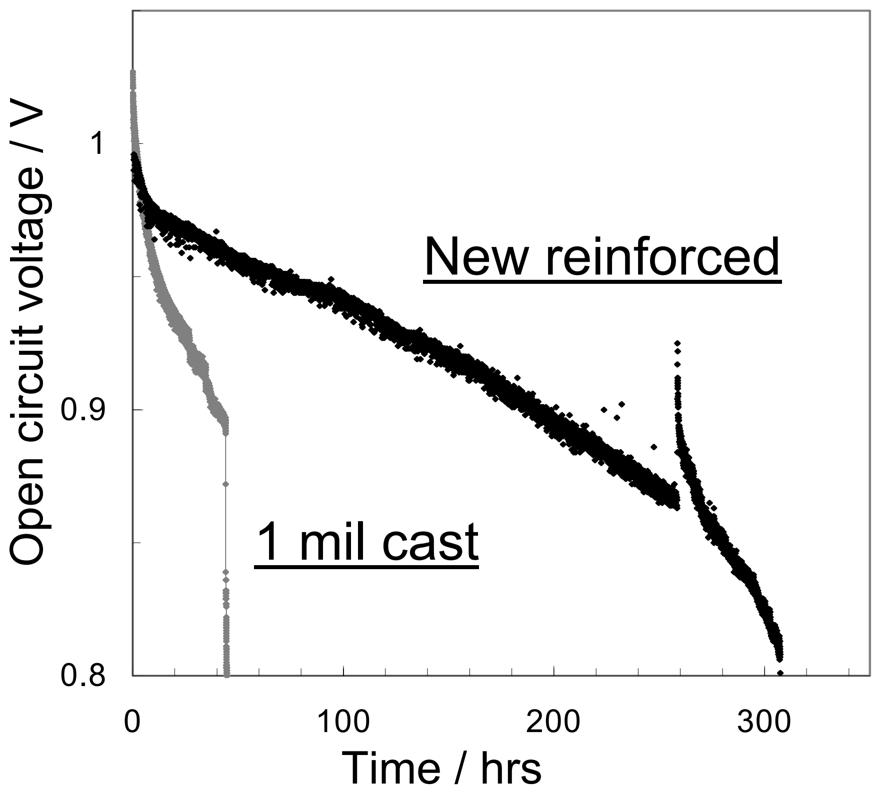
- Our data shows a relationship between the dimensional stability of the membrane and the OCV decay rate measured under accelerated conditions.
- These results provide basis to the hypothesis that durability is also enhanced through improvements in dimensional stability, presumably due to a reduction of the impact of the shrinkage stresses developed in the membrane.

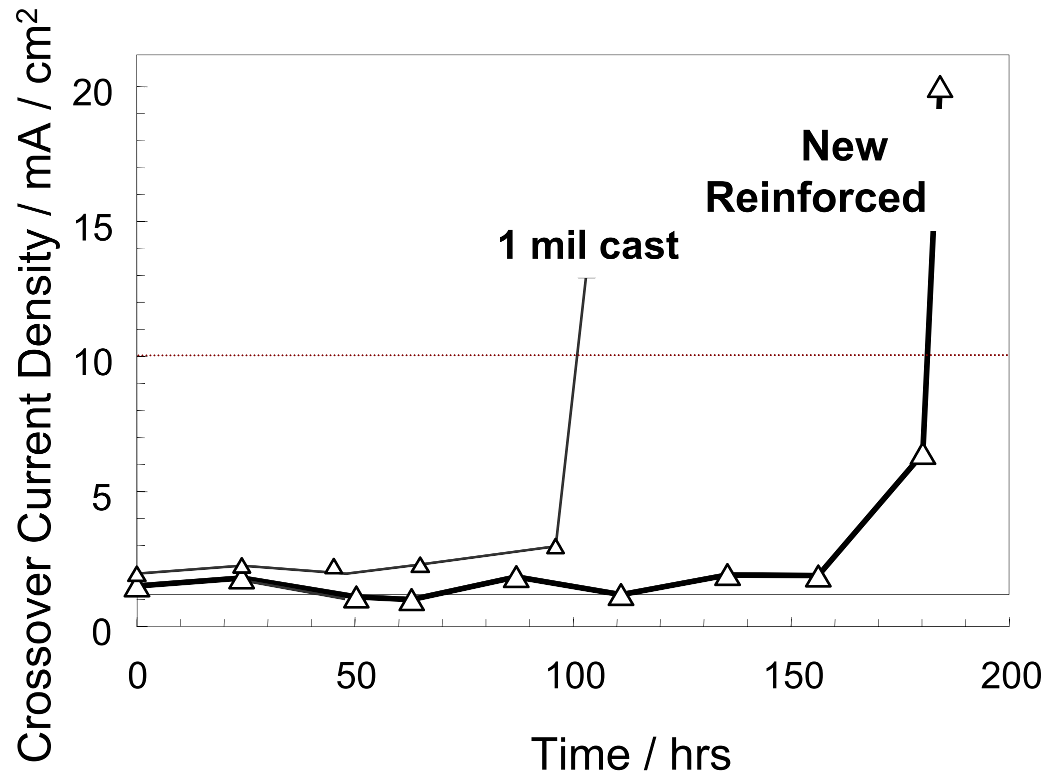
Accelerated Mechanical Degradation
- lifetime, OCV decay

Mechanical testing
- swelling

UTC Single Cell Testing of Gen A Reinforced Membrane

New membrane shows increased chemical and mechanical stability





OCV hold
- lifetime, fluoride release

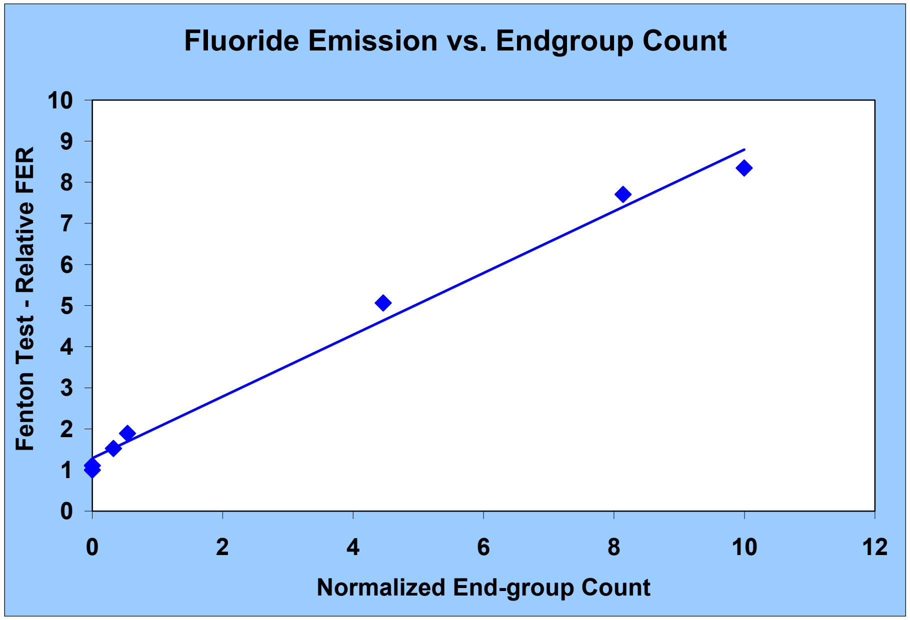
RH-load cycle
- lifetime

- 7x increase in OCV hold lifetime
- Substantial chemical stability
- Does not yet include CS ionomer, UTC peroxide mitigation

- ~2x increase in RH-load cycle lifetime
- Improved mechanical properties improve durability in a fuel cell

New DuPont membrane with increased chemical stability

Accelerated fuel cell and Fenton's test results

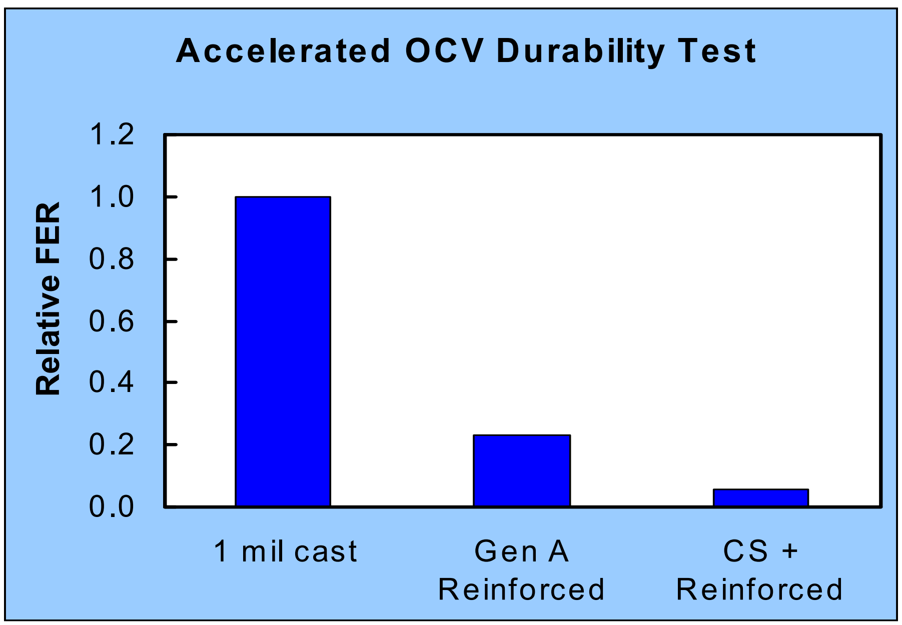


Fenton's test
- wt. Loss, fluoride release

•PFSA ionomer is stabilized by reducing reactive polymer end-groups

•Fluoride emission in the Fenton's test is 8X lower for stabilized membrane

•Stabilized membrane has lower decay and longer lifetimes in our accelerated fuel cell tests



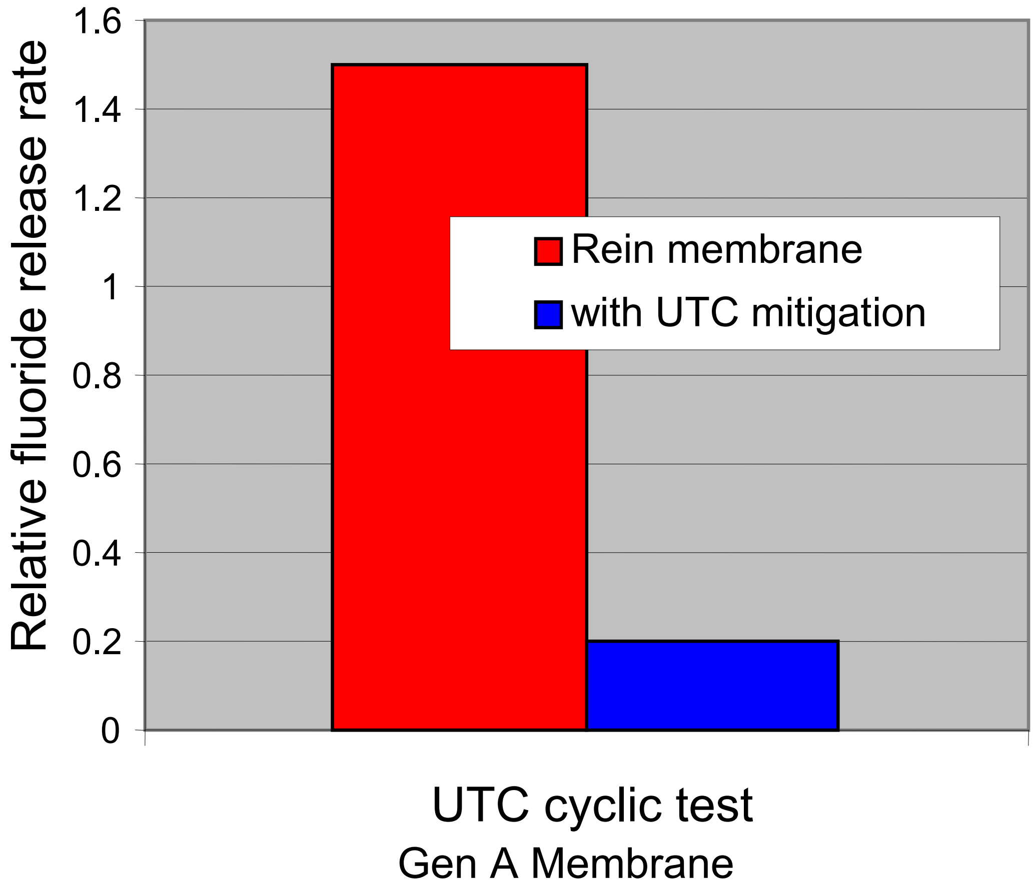
OCV hold
- lifetime, fluoride release

•We have successfully combined our mechanical and chemical stability strategies in a series of prototype membranes

•Different reinforced membrane structures including stabilized ionomer (CS) show good performance in our accelerated durability tests.

UTC Peroxide Mitigation

Provides significant fluoride emission rate reduction in load-cycle testing



Automotive cyclic
- lifetime, fluoride release

- Typically 3-7x reduction in fluoride emission
- Does not involve chemical additives
- Small performance impact, additional processing step required

Responses to Previous Year Reviewers' Comments

•Degradation factors associated with membrane/electrode/catalyst interface needs consideration.

The UTC peroxide mitigation strategy specifically enhances durability at the membrane/electrode interface. These strategies are proprietary, so no detailed information can be provided. UTC has developed in-depth understanding of the durability issues associated with these interfaces, so these are taken into account in our program.

•Establish correlation coefficients for accelerated aging to project to real life expectations

Our approach is to establish this correlation through modeling. We also plan to address this issue using the data that will be generated in the stack tests scheduled for the second part of the project. Experimentally, there are different definitions of "1x" lifetime operation to use as a baseline to quantify the acceleration factor. We are considering different reported stack data, internally and externally, (e.g. reported lifetime from an MEA vendor) to account for the different numerator.

Consolidation of Durability Technology in Cyclic Full-Size Testing

Progressively reduced risk through scale-up in durability technology

Completed | Ongoing | Planned | Milestone

2004		2005				2006		
3rd Q	4th Q	1st Q	2nd Q	3rd Q	4th Q	1st Q	2nd Q	3rd Q

Single-cell test (Completed)

- Mild cyclic conditions
- Seal failure at ~3000 hrs
- No failure of baseline membrane

→ Revise edge seal design

Single-cell test (Completed)

- Aggressive cyclic conditions
- Reinforced membrane + UTC mitigation
- Membrane failure at 1300 hrs

→ Revise hardware

Short stack test (Ongoing)

- Intermediate cyclic conditions
- Integrate durable technology :
  - Reinforced membrane
  - UTC peroxide mitigation

◆ Lock-in MEA design

Short stack test (Planned)

- Intermediate cyclic conditions
- Integrate durable technology :
  - Reinforced membrane
  - CS ionomer
  - UTC peroxide mitigation
  - Durable edge-seal

◆ Finish

Future Work

- Selection of structure to build the Second Stack: we will focus on integrating the major achievements of the program:
    - Reinforced membrane
    - CS ionomer
    - Peroxide mitigation
    - Advanced edge seal design
- We are investigating other possible chemical degradation modes in order to further improve polymer chemical stability
- DuPont team will continue developing membrane reinforcement strategies to further increase tensile strength and reduce swelling
- Post-mortem analysis in collaboration with USM team
- UTC:
    - Modeling:
        - Complete chemical degradation modeling validation
        - Incorporate mechanical stress modeling
    - Accelerated test:
        - Determine acceleration factors for single cell and stack tests
    - Mechanical:
        - Complete correlations of in-cell decay to mechanical properties degradation
    - Edge-seal:
        - Sub-scale accelerated test validation of new edge-seal concepts

Supplemental Slides

Publications and Presentations

Presentations

“Durability of Perfluorosulfonic Acid Membranes” K. Raiford at the 2004 Gordon Research Conference – Fuel Cells, July 27th 2004, Roger William University, Bristol RI

“Summary of PEM Fuel Cell Durability at the United Technologies Research Center” T. Madden at the 2004 Gordon Research Conference – Fuel Cells, July 28th 2004, Roger William University, Bristol RI

“Determination of Hydrogen Peroxide Generation/Decomposition Kinetics Using RRDE on Vulcan, 10, 20, and 50% Vulcan-Supported Pt Electrodes” H. Yehia, S. Burlatsky, D. Condit, and T. Madden at the 2004 Joint Electrochemical Society International Meeting: October 3-8, 2004 Honolulu, Hawaii

“Durability of Perfluorosulfonic Acid Membranes” K. Raiford at the Meeting of the American Chemical Society Polymer Section entitled “ Advances in Materials for Proton Exchange Fuel Cells “ - February 20-23, 2005, Asilomar Conference Grounds, Pacific Grove, CA

Hydrogen Safety

The most significant hydrogen hazard in this project is the catastrophic failure of a major hydrogen supply line that can lead to a fire or explosion.

Hydrogen Safety

Our approach to deal with this hazard is:

- Working and living safely is pervasive throughout DuPont culture. Consequently, all fabrication and testing is subject to a rigorous Safety, Health, and Environment review before commencement of any work. Any safety incidents are thoroughly investigated to capture learnings.
- Our safety record validates the effectiveness of our acute attention to detail
- DuPont Fuel Cells has never had a hydrogen-related safety incident. We attribute this to careful planning of both operating procedures and facilities installation:
- The high-pressure hydrogen supply cylinders are located outside the buildings, on a pad with appropriate warning signs.
- Only authorized personnel who are properly trained are allowed to change the cylinders.
- Pressure regulators are located outside as close to the high-pressure cylinders as reasonably possible to lower the hydrogen supply pressure, prior to entry into the building, to minimize the effects of any potential leak.
- Mechanical excess flow valves, that will automatically close the hydrogen supply to the building in the event of a large flow outside of their designed flow range, are also located outside the building in the hydrogen supply lines and need to be manually reset if they are tripped.
- All hydrogen piping in non-ventilated areas is welded and pressure tested prior to placement in service.
- Hydrogen sensors are located in both the ventilated and non-ventilated portions of each testing laboratory, and in the ventilated enclosure of each test station. Automated solenoid valves will shutdown the hydrogen supply to a whole room or test station as indicated by the sensors.

DuPont FC Test Station