2006 DOE Hydrogen Program Review

MEA & Stack Durability for PEM Fuel Cells

3M/DOE Cooperative Agreement
No. DE-FC36-03GO13098

Project ID # FC8

Mike Hicks
3M Company
May 16, 2006

Powered by 3M

Overview

Timeline

- 9/1/2003 – 6/30/2007*
- 70% complete

* Revised end date subject to DOE approval

Budget

- Total $10.1 M
  - DOE $8.08 M
  - Contractor $2.02 M
- Funding received in FY05: $2.43 M
- Funding for FY06: $2.60 M

Barriers & Targets

- A. Durability: 40k hrs

Team Members

- Plug Power
- Case Western Reserve University
- University of Miami

Consultant

- Iowa State University

Objectives

Develop a pathway/technology for stationary PEM fuel cell systems for enabling DOE's 2010 objective of 40,000 hour system lifetime to be met

Goal: *Develop an MEA with enhanced durability*

- Manufacturable in a high volume process
- Capable of meeting market required targets for lifetime and cost
- Optimized for field ready systems
- 2000 hour system demonstration

Focus to Date

- MEA characterization and diagnostics
- MEA component development
- MEA degradation mechanisms
- MEA nonuniformity studies
- Hydrogen peroxide model
- Defining system operating window
- MEA and component accelerated tests
- MEA lifetime analysis

Approach

To develop an MEA with enhanced durability ….

Optimize MEAs and Components for Durability ⟷ Optimize System Operating Conditions to Minimize Performance Decay

- Utilize proprietary 3M Ionomer
  - Improved stability over baseline ionomer
- Utilize ex-situ accelerated testing to age MEA components
  - Relate changes in component physical properties to changes in MEA performance
  - Focus component development strategy
- Optimize stack and/or MEA structure based upon modeling and experimentation
- Utilize lifetime statistical methodology to predict MEA lifetime under ‘normal’ conditions from accelerated MEA test data

Accomplishments

GDL Characterization

- Developed new test equipment to measure capillary pressure in GDLs

Membrane

- Completed investigation of reinforced membranes – reinforcement may not be necessary for membrane durability
- Identified membrane failure mode and implemented solution to mitigate it
- Ongoing monitoring of membrane properties in accelerated tests

Membrane Degradation Mechanism

- Analyzed experimental and literature data – more than just end group degradation
- Utilized ionomer model compounds to identify likely ‘points of attack’ and provide insight into ionomer degradation mechanism
- Developed initial hydrogen peroxide model to study peroxide in operating fuel cell

MEA Nonuniformity Studies

- Completed 121-channel segmented cell and investigated the effects of flow rate, load setting and GDL type; determined high gas stoichiometry yields current uniformity
- Utilized theoretical 3D fuel cell model to investigate effects of catalyst, membrane and GDL nonuniformity; determined that electrode defects result in highly, nonuniform current distribution

System Test

- Initiated Saratoga system test with a preliminary, durable MEA design

MEA Lifetime Modeling

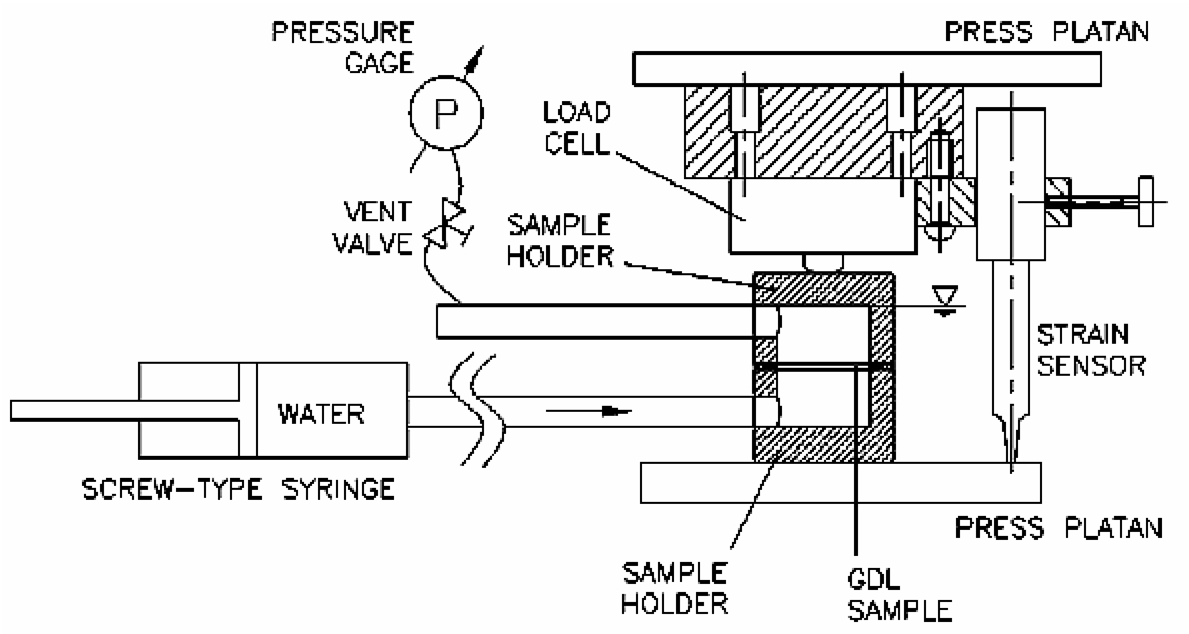
- Demonstrated that load profile affects MEA durability
- Developed initial lifetime prediction model to estimate MEA lifetime relative to DOE’s 2010 stationary system goals
- Related initial fluoride ion to lifetime – method to increase sample throughput

GDL Characterization – Capillary Pressure

Background
- Measured GDL permeability in humid and dry air
- Humid air yields lower gas permeability
  - Pores fill with water

Problem
- Need technique to characterize water transport in GDL pores
- There are no available instruments for measuring capillary pressures for hydrophobic porous media

Solution
- Design your own instrument
- *CWRU* has designed, machined and assembled the sample holders, load cell and strain sensor
- *CWRU* collaborated with *Porous Materials Inc*, Ithaca, NY to fabricate the instrument
- *PMI* will integrate the syringe pump, the press and automation

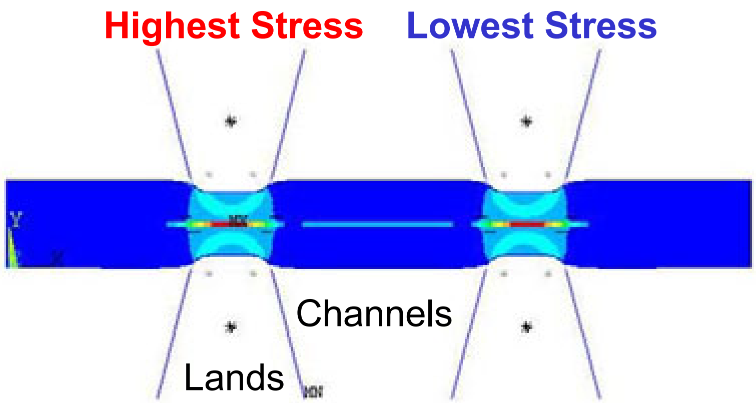


- Developed an instrument for measuring Capillary Forces in hydrophobic GDLs
- New method to characterize GDLs

CASE
CASE WESTERN RESERVE UNIVERSITY

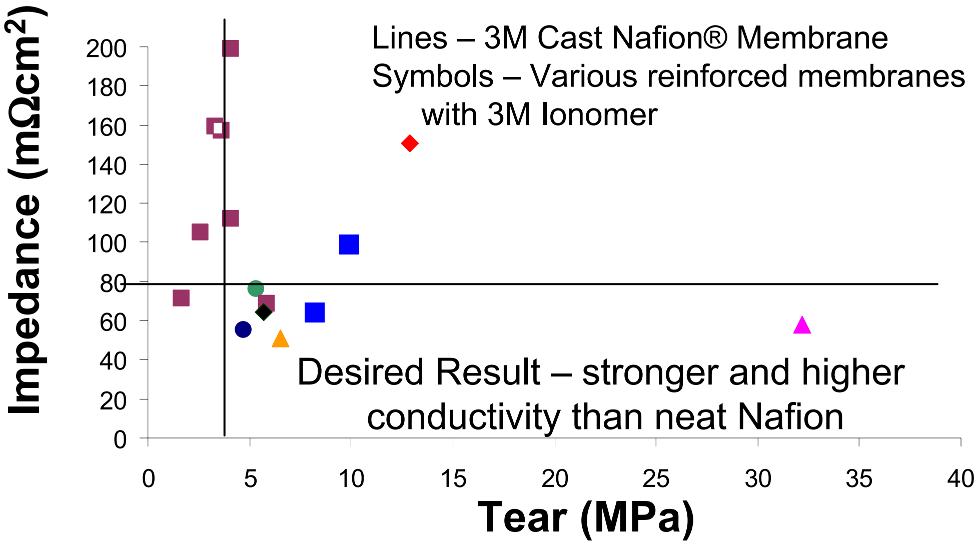
Reinforced Membrane Activities

Membrane Stress Model



Hypothesis - Need reinforcing member to carry stress to eliminate mechanical failure or reduce mechanical failure rate

Evaluation of Various Reinforcing Members



RH Cycle Test to Evaluate Hypothesis

Test Conditions:

80°C

Cycle equally between 0 and 150% RH

MEA (electrode and GDL) made with:	Time to failure (hours)
DuPont™ Nafion® (NR-111)[1]	260 – 330
Ion Power™ Nafion® (N111-IP)[1]	1330 +
Gore™ Primea®[1]	400 – 470
3M Cast Nafion® (1000 EW)	1200 +

- **Neat membrane most durable**
- No relationship between mechanical props and durability
  - Tensile test does not predict mechanical durability
  - Tear resistance does not predict mechanical durability
  - Less shrinking does not correlate to more mechanical durability
- What is the benefit of reinforcement?

1. Gittleman et al, Fall AIChE Meeting, October 2005.

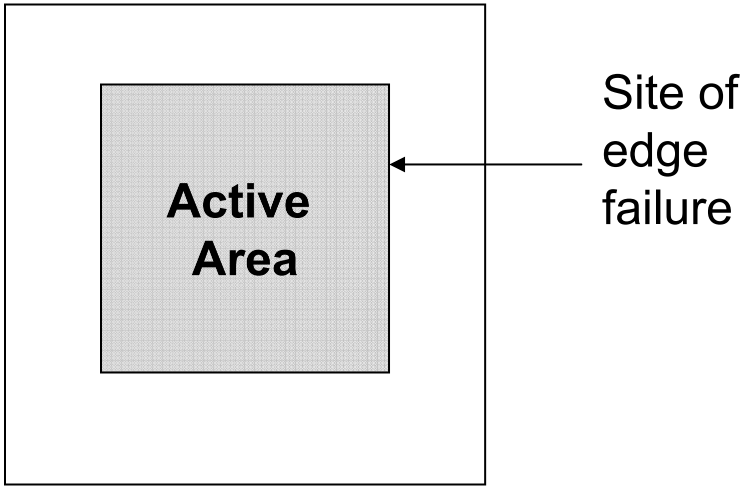
Mitigation of Membrane Edge Failure in Modules

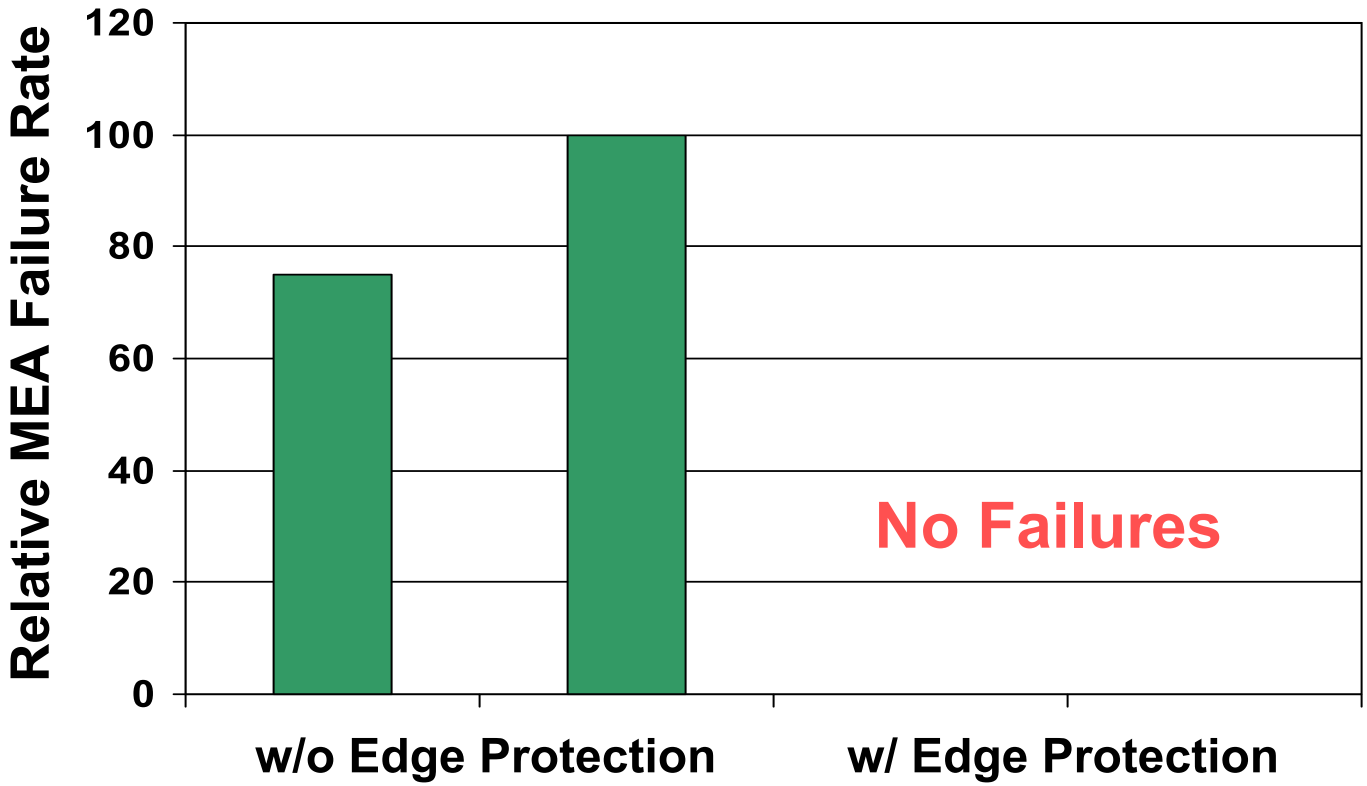
Problem

- In module testing, observe infant mortality of MEAs due to edge failure at the membrane – catalyst interface

Solution

- Developed edge protection component for MEA

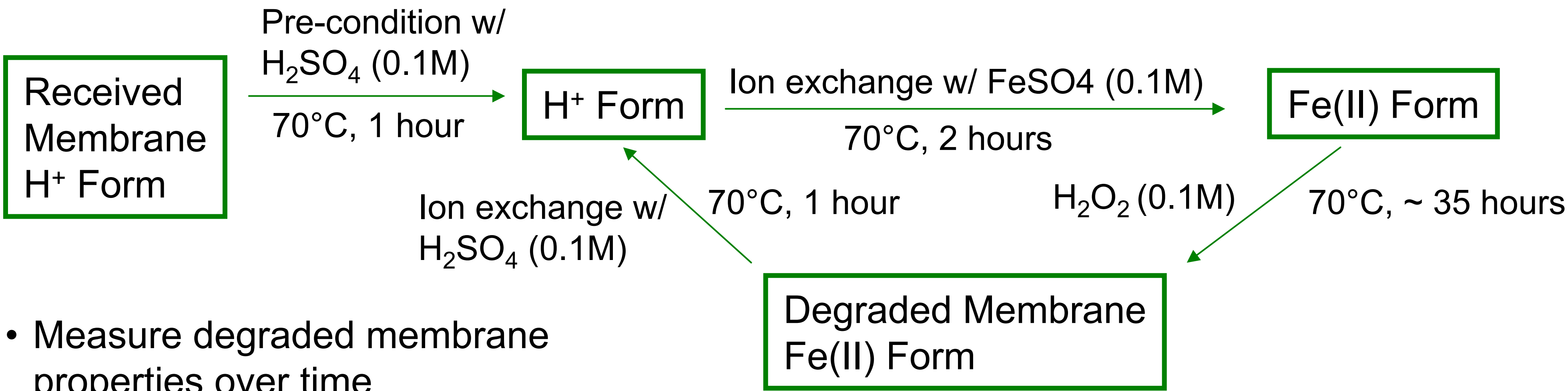




- Identified MEA failure mode
- Implemented a solution to significantly reduce infant mortality failure rate

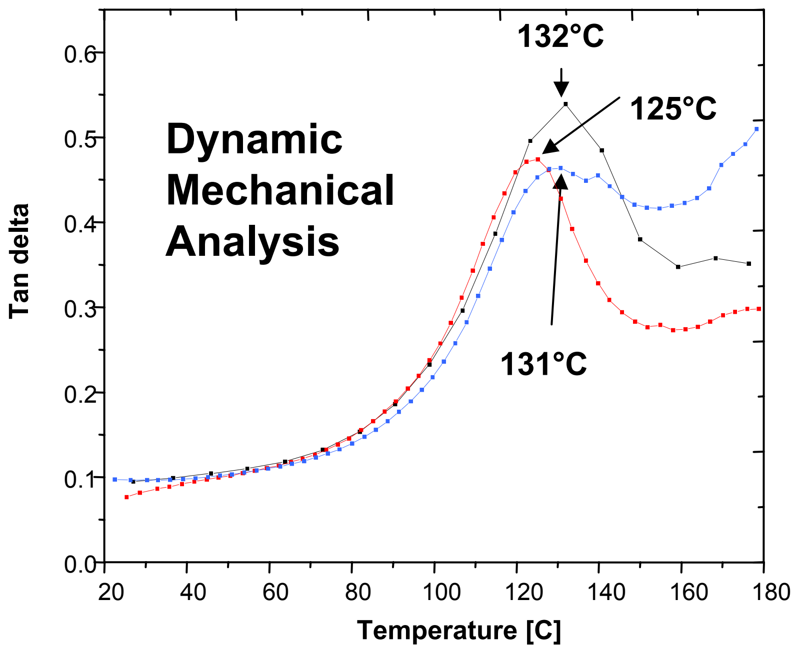
3M Ionomer Membrane Properties vs Decay

Membrane Aging Procedure

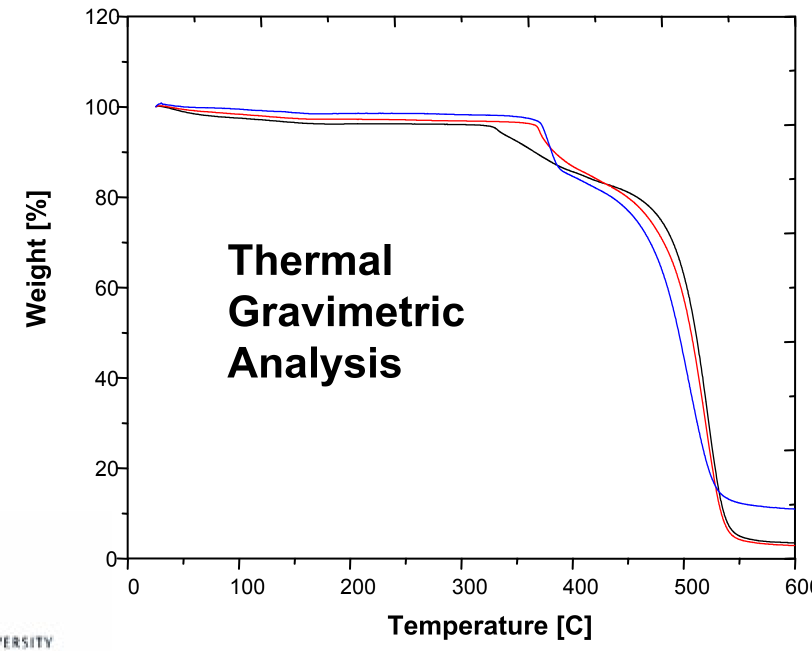


- Measure degraded membrane properties over time

'As Received' **'H+ Form'** **'Degraded Sample @ 125 hrs'**



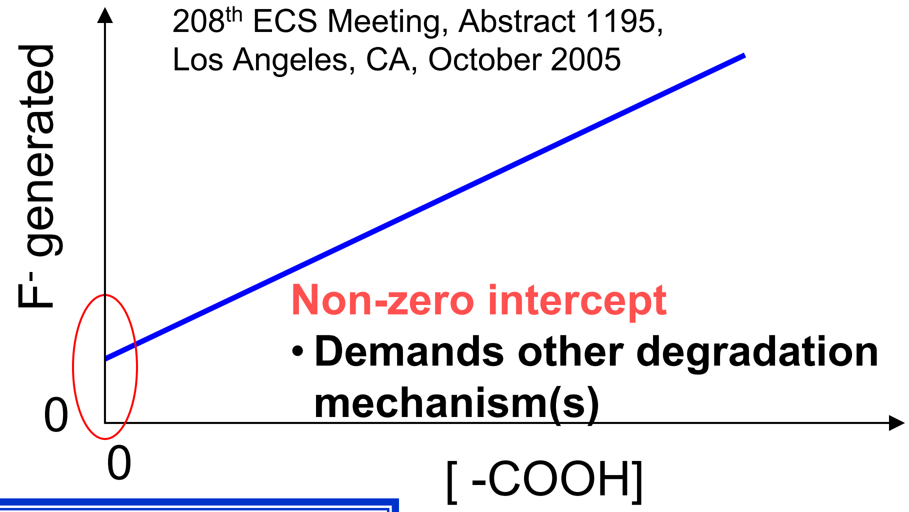
- Aging experiments in progress
- No change after 125 hrs



Membrane Decay Mechanism Via Model Compounds

‘Conventional Wisdom’:

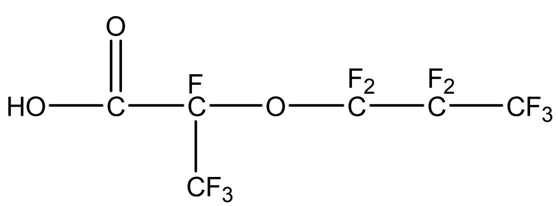
- H_2O_2 generated during fuel cell operation
- HO· or other radicals are attacking species
- -COOH end group unzipping primary route



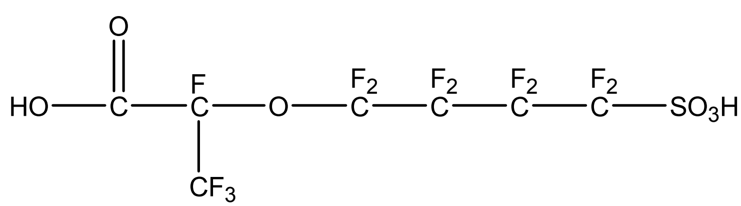
Investigate alternative degradation mechanism(s) via model compounds

- Utilize analytical capabilities
- Better isolation of effect from different reactive sites
- Age MCs via Fenton’s test or UV light (200 - 2400 nm @ 100W)

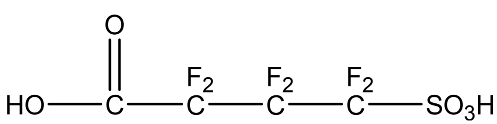
MC1



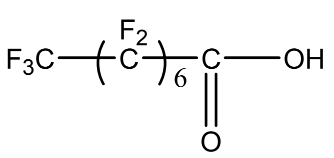
MC2



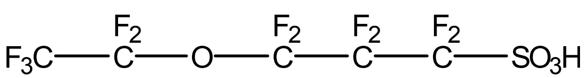
MC3



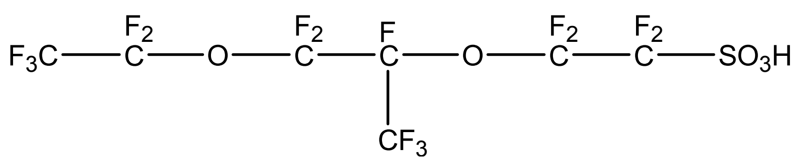
MC4



MC7



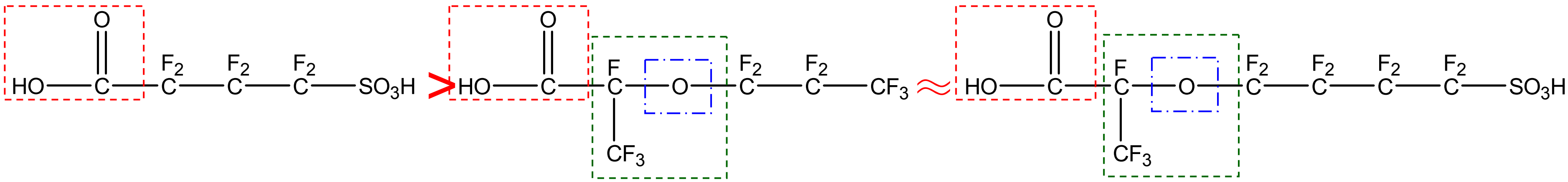
MC8



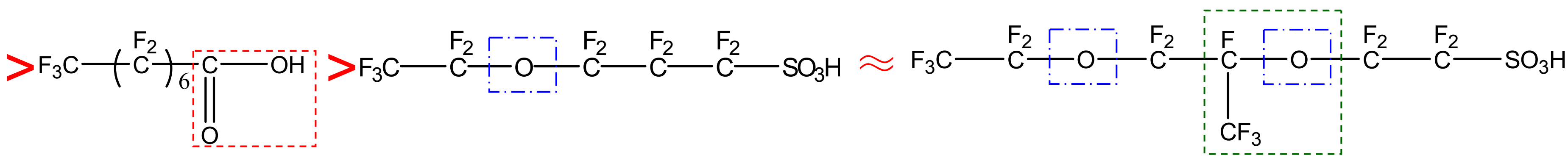
Model Compounds Relative Degradation Rates

MC3 > MC1 ≈ MC2 > MC4 > MC7 & MC8

MC3 **MC1** **MC2**

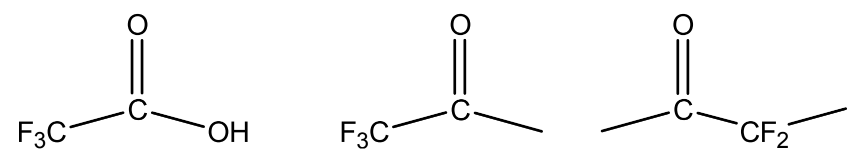


MC4 **MC7** **MC8**

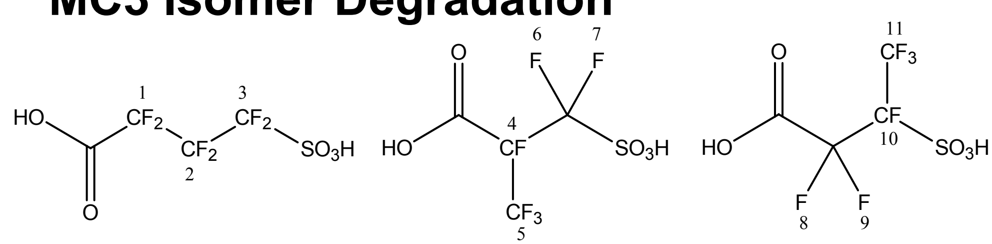


- COOH containing MCs exhibit low stability
- Comparison of MC3 & MC4
  - Is it really a reactivity effect or solubility effect
- Is there a change in reactivity hydrolysis products?
  - Hydrolysis observed (by NMR) for MC1 & MC2
  - Need to evaluate MC7 & MC8 for hydrolysis

Identified MC1 & MC2 Reaction Products



MC3 Isomer Degradation



- Same degradation rate
- Decarboxylation is rate determining step

Membrane Decay Mechanism – Hydrogen Peroxide Model

Objective

- To define simple model to study peroxide behavior in an MEA

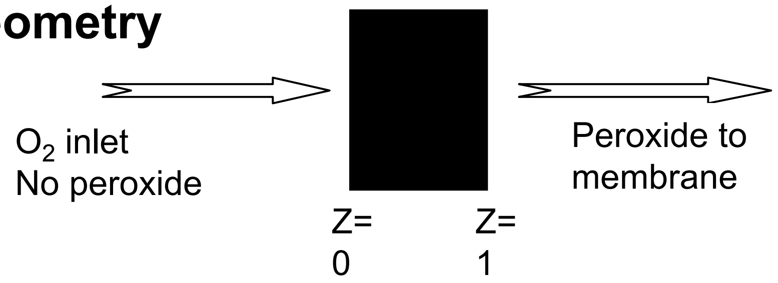
Equations:

$$\frac{d}{dt}\left(C_{H_2O_2}\right) = Rate\ of\ \ production\left(electrochemical + Chemical\ recombination\right)$$

$$+ Rate\ of\ \ consumption\begin{pmatrix} Ionomer\ degradation + catalytic\ disproportionation \\ + electrochemical\ reduction \end{pmatrix}$$

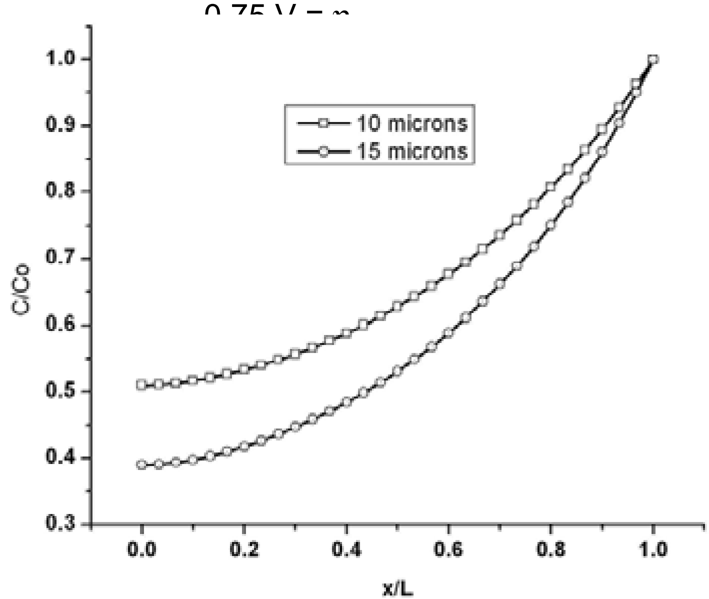
$$+ Transport\ through\ the\ electrode\left(Diffusion + Convection\right)$$

Geometry



Model Output

Peroxide Concentration Profile as f(L)



Experiments to Determine Input Parameters

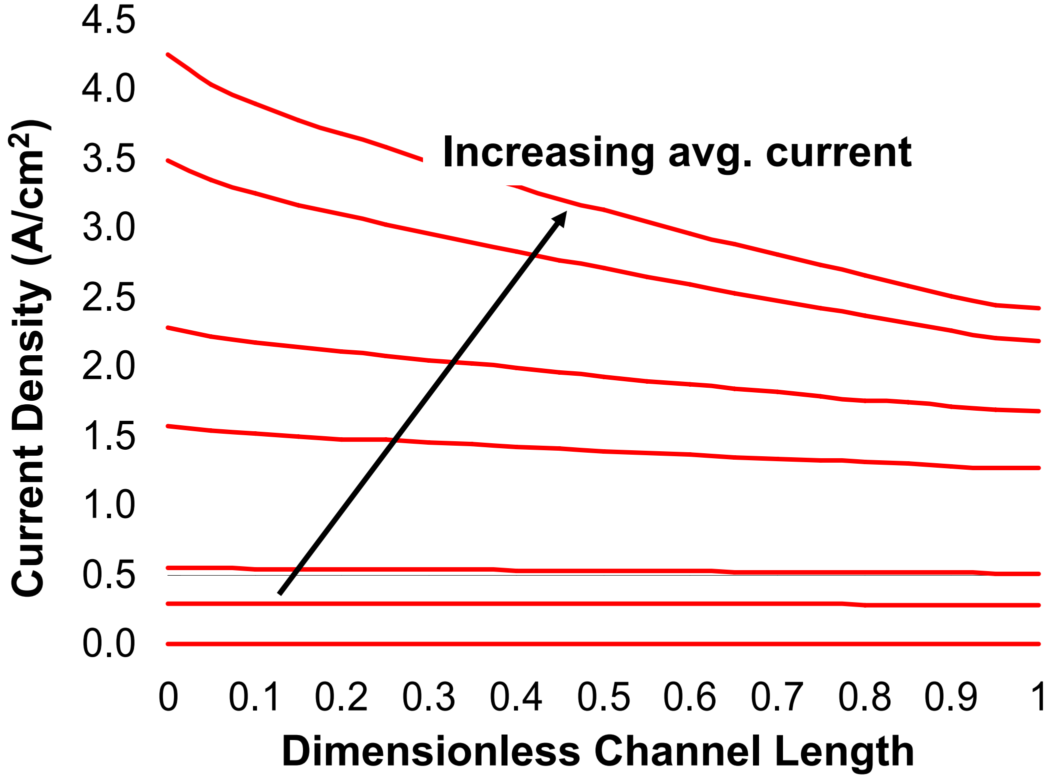
1. Rate of Peroxide Production
2. Rate of Peroxide Disproportionation

- Model provides insight into hydrogen peroxide distribution in an operating fuel cell and the degradation of ionomer by hydrogen peroxide

MEA Nonuniformity Studies

Motivation - MEA Durability

- Is MEA durability a function of current distribution/uniformity?

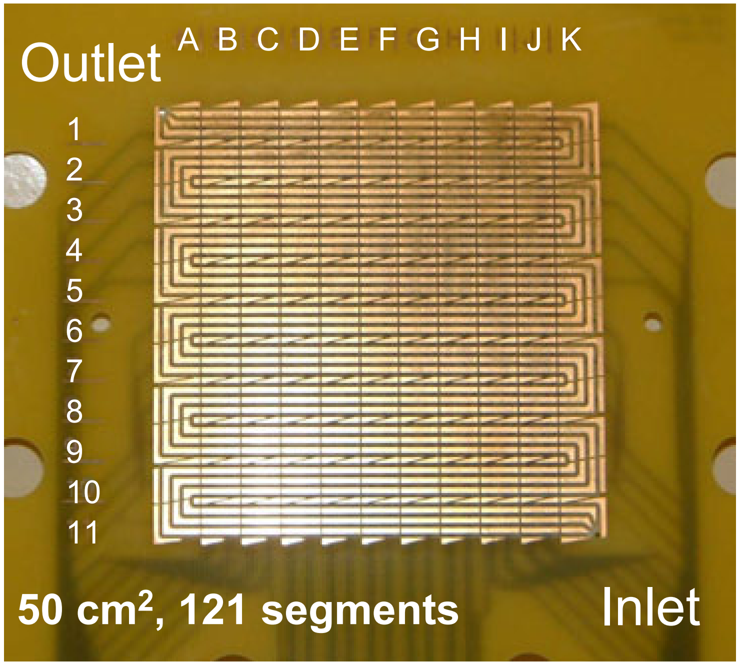


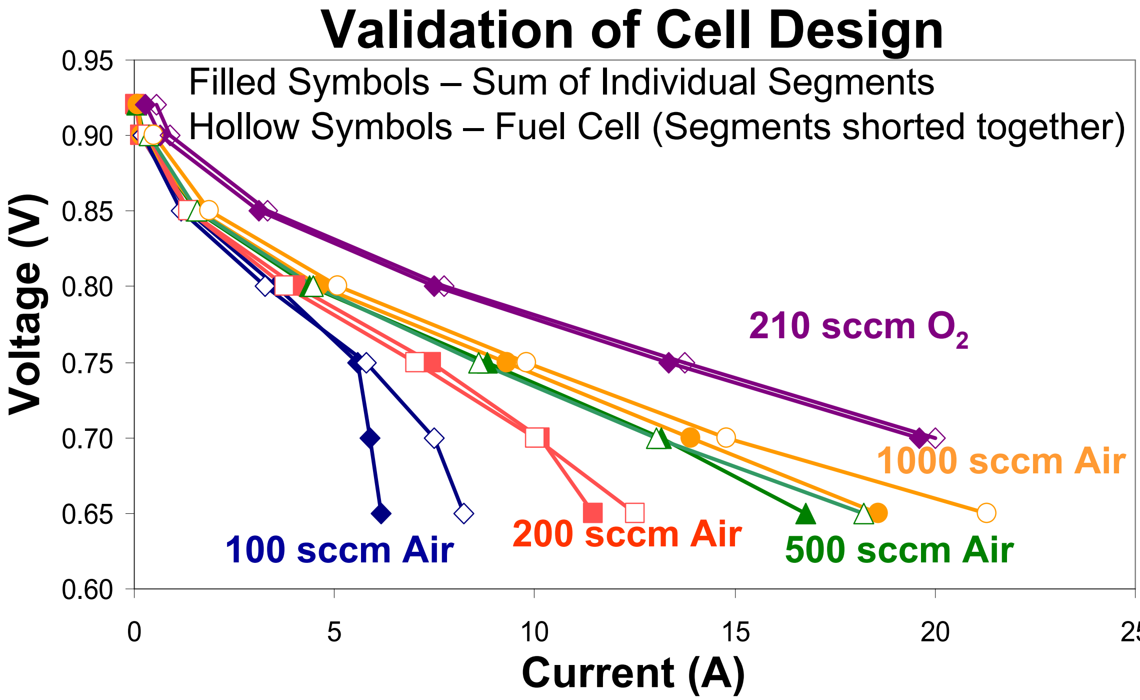
V. Gurau, H. Liu and S. Kakac, “A Two Dimensional Non-Isothermal Mathematical Model for Proton Exchange Membrane Fuel Cells,” ***AIChE Journal***, Vol. **44** (11), pp. 2410 – 2422, 1998

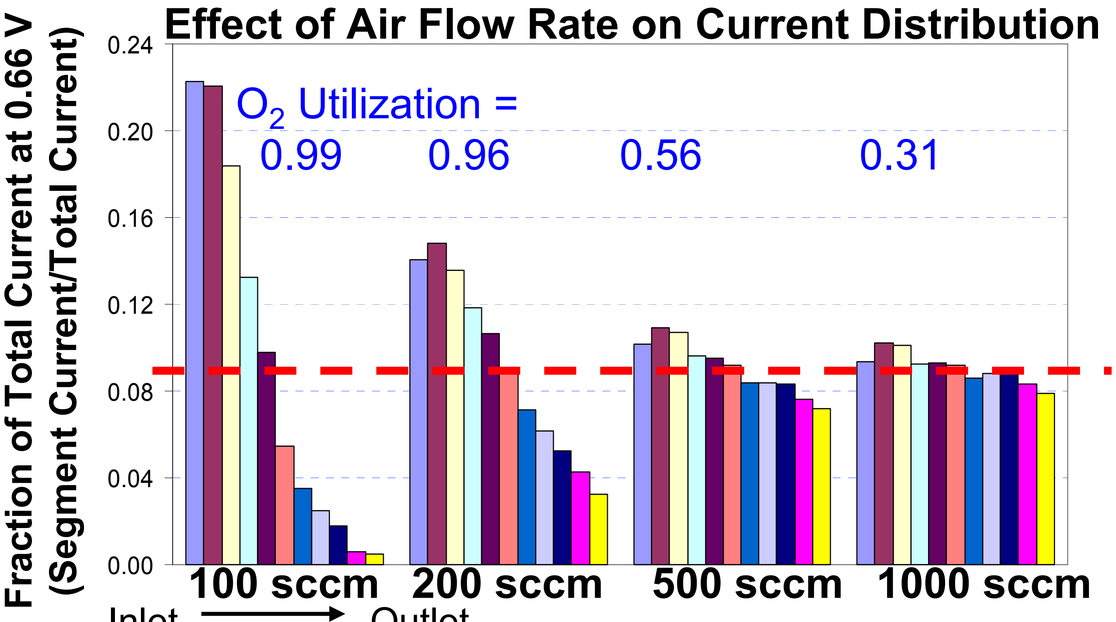
Approach

- Measure experimentally – segmented cell
- Theoretical modeling

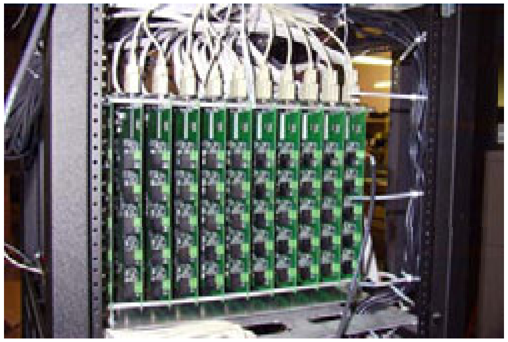
Segmented Cell



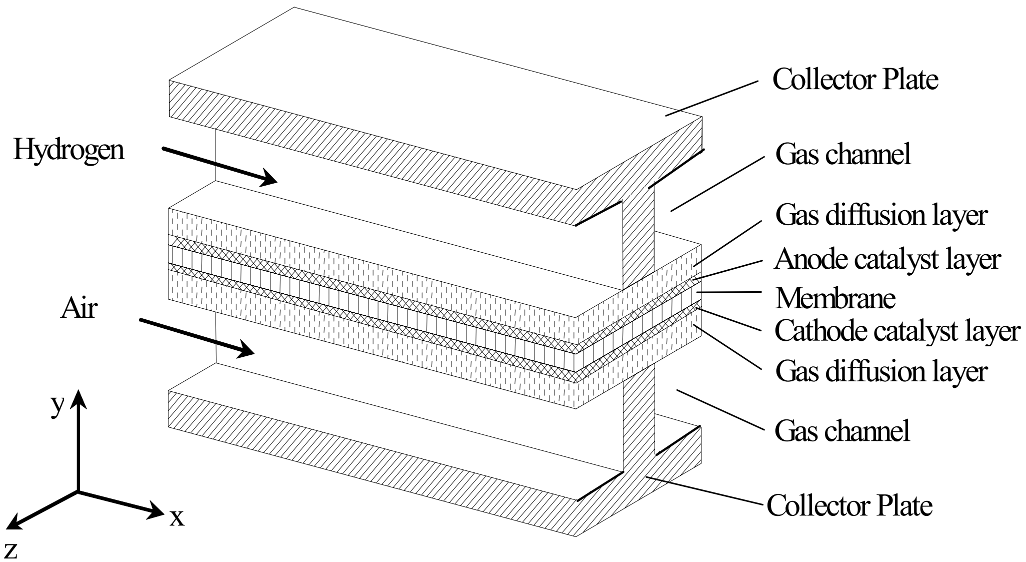




- Cell design validated
- Design fuel cell systems to operate at high stoichiometry for uniformity
- Recently completed 121 channel load

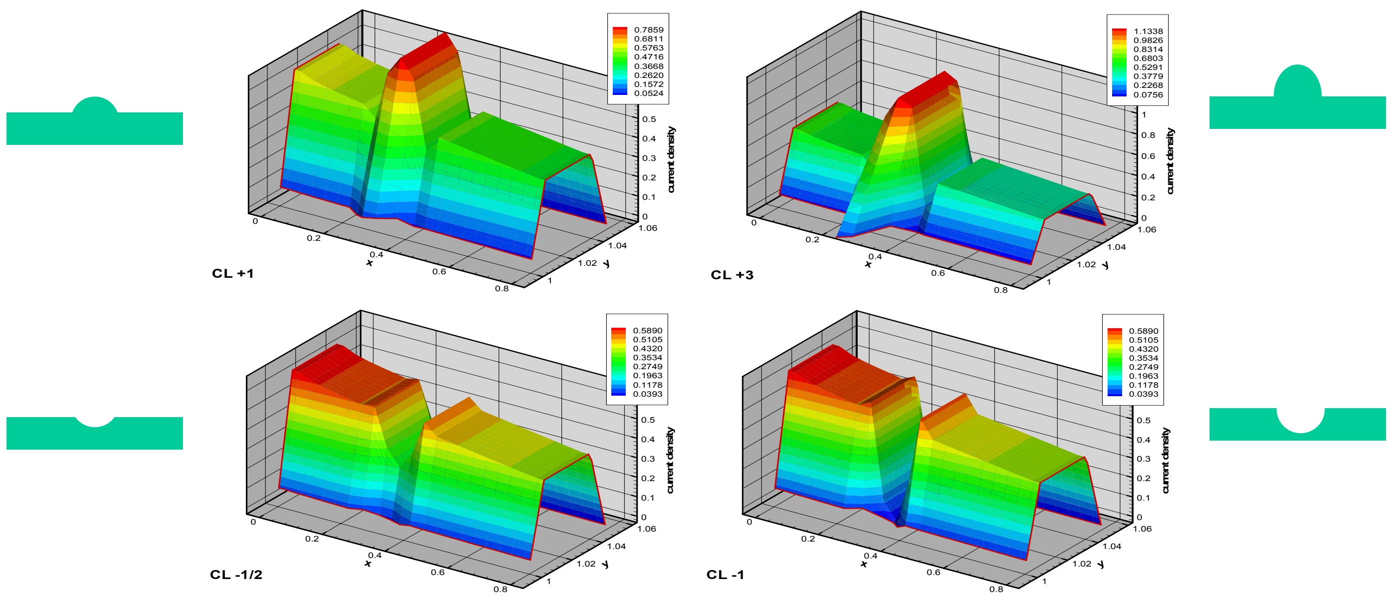


MEA Nonuniformity Studies



Variables Investigated
- Ionic Conductivity
- Catalyst Loading
- GDL Porosity
- Electrode Thickness
- Membrane Thickness
- GDL Thickness

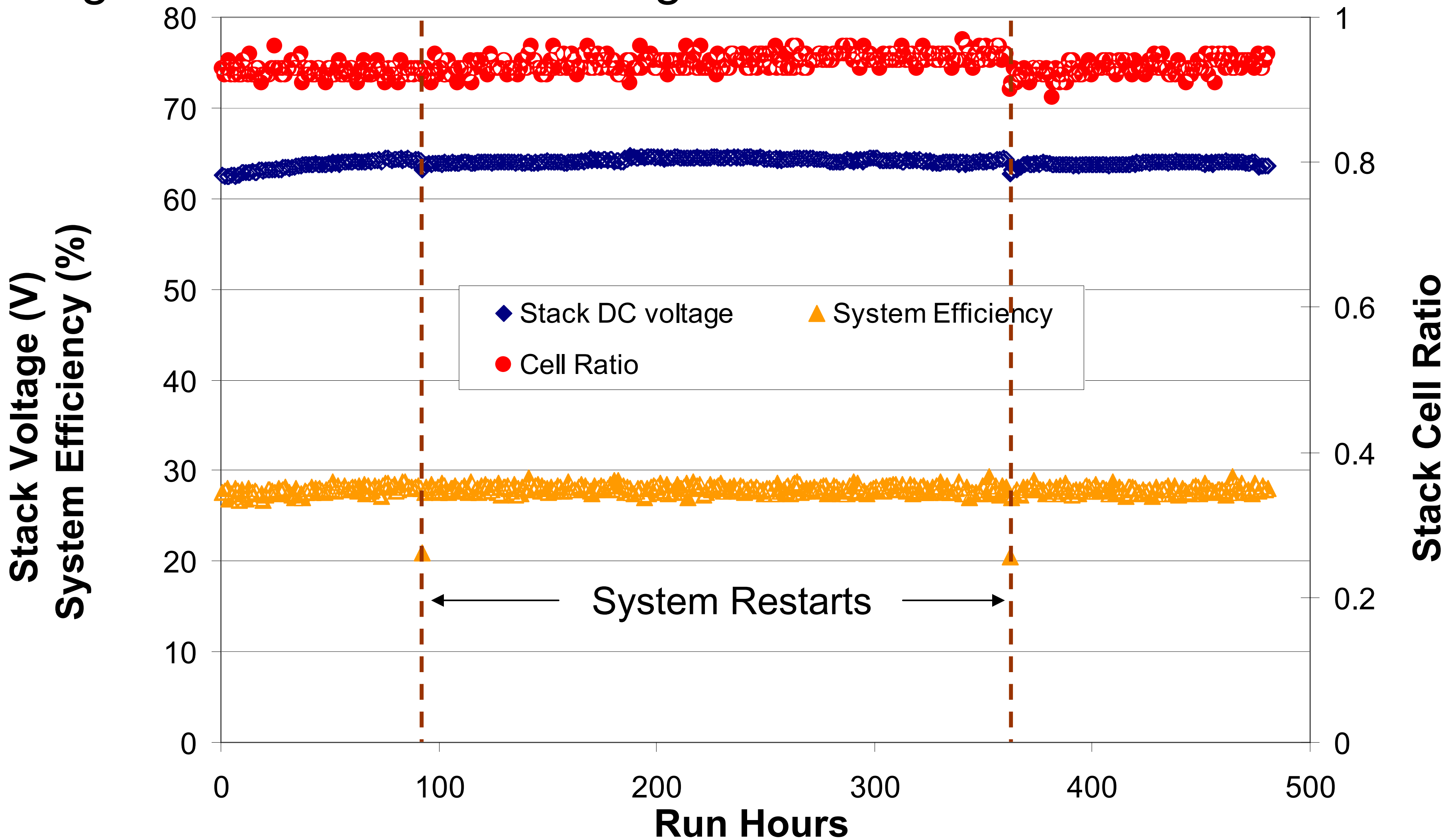
Electrode Thickness



- Surface defects resulted in highly non-uniform current distribution

Saratoga System Test – First Durable MEA Testing

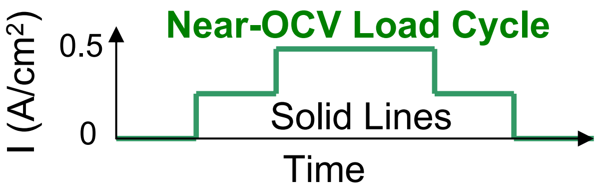
Objective – Investigate possible interaction between system design and durable MEA design

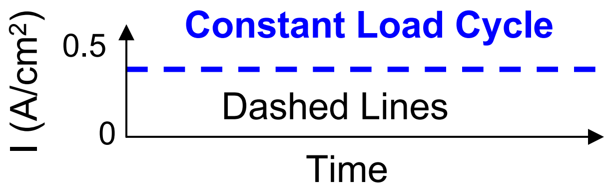


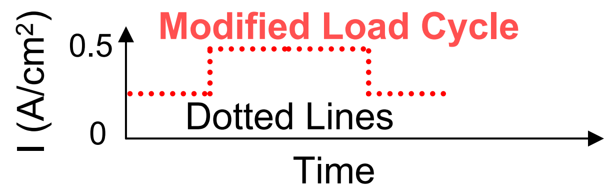
- No negative MEA – System interaction
- Program approach validated

plug power

Statistical MEA Lifetime Predictions from Accelerated Test Data

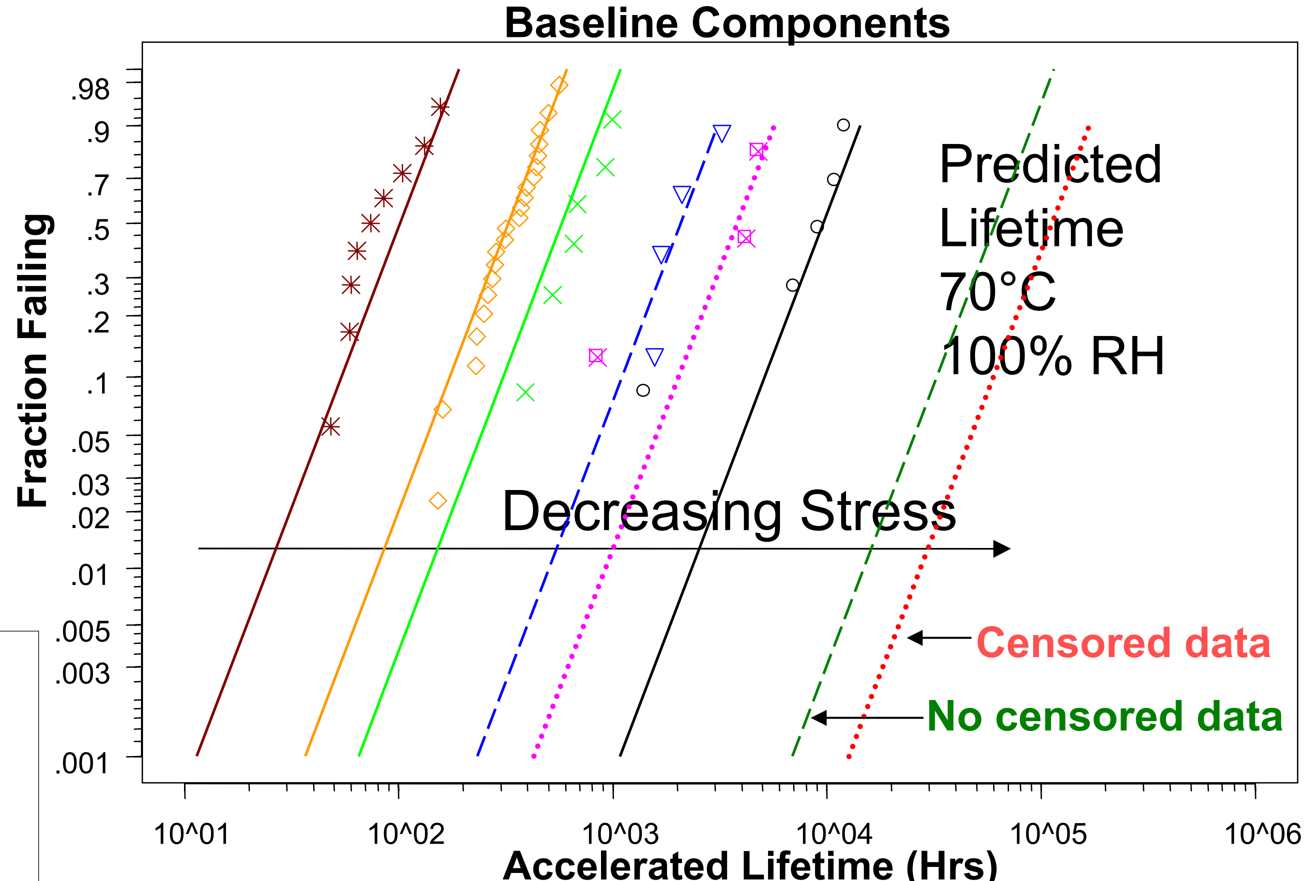




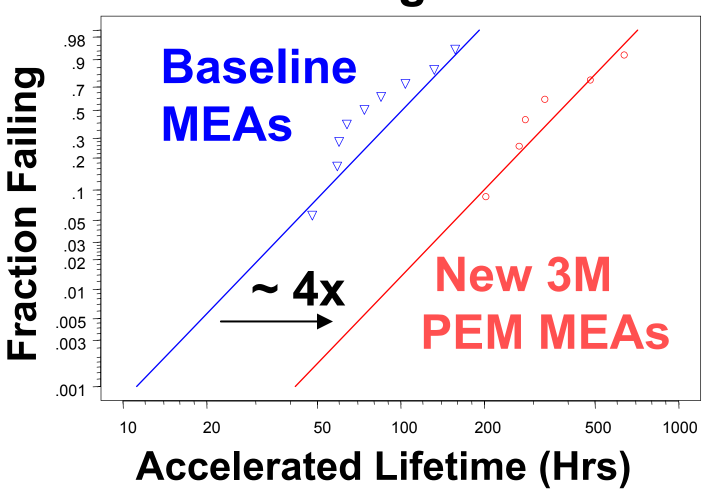


Model Assumes

- Weibull distribution
- Arrhenius for temp
- Humidity model for RH
- Class model load profiles

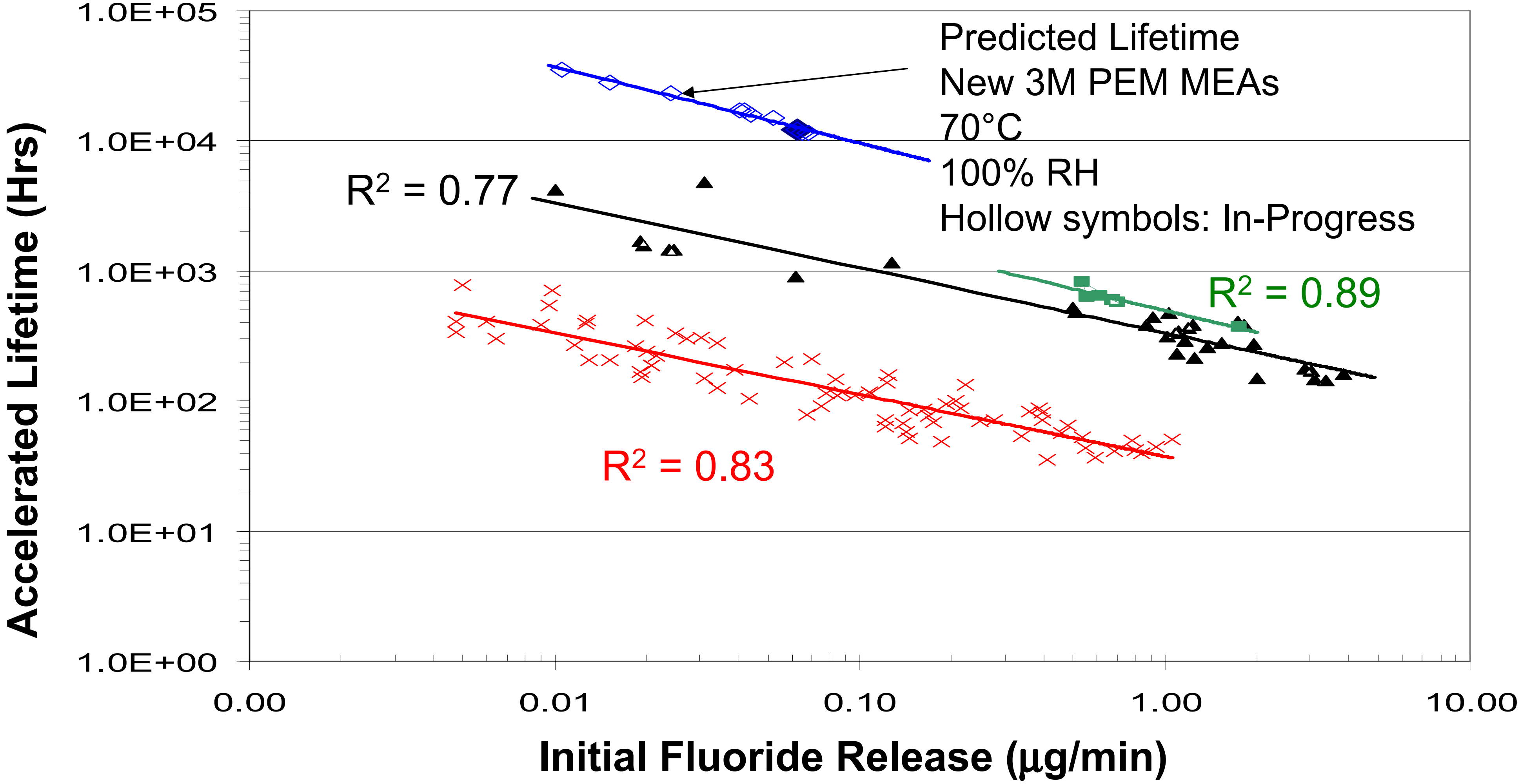


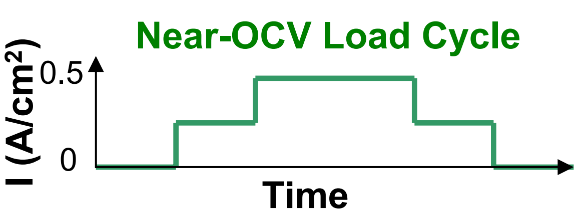
Comparison of MEA Designs



- Lifetime probability distribution
- Reasonable predictive values
- No OCV load cycle offers ~ 13X lifetime improvement
- New MEAs with 3M ionomer ~ 4x more durable

Fluoride Ion Mapping of Accelerated Test Data





- Pathway towards ~ 20,000 hour MEA lifetime with 3M PEM MEAs under accelerated, near-OCV load cycle test conditions
- Means to increase sample throughput

Future Work – To the End of the Project

MEA & Stack Development & Testing

- MEA Component optimization & integration – 3M
- Saratoga stack tests – Plug Power
- Complete MEA evaluation in modules/single cells – Plug Power
- Select 'Final' stack and MEA design and test – Plug Power/3M

MEA Degradation Studies

- Peroxide model – CASE
  - Incorporate realistic kinetic and transport parameters
- Model compounds – CASE
  - Determine degradation kinetic constants
- MEA nonuniformity studies – 3M/Plug/University of Miami
  - Determine operating conditions/MEA designs that yield current distribution uniformity
- Post mortem analysis – CASE/Plug Power
- Mechanical properties-morphology relationship – CASE

MEA Statistical Lifetime Predictions

- MEA lifetime modeling – 3M/Plug Power

Project Summary

Relevance: Developing MEA and system technologies to meet DOE's year 2010 stationary durability objective of 40,000 hour system lifetime. Providing insight to MEA degradation mechanisms.

Approach: Two phase approach (1) optimize MEAs and components for durability and (2) optimize system operating conditions to minimize performance decay.

Progress: Demonstrated pathway towards 20,000 hour MEA lifetime with 3M PEM MEAs under accelerated 'near-OCV' load cycle test conditions. Initiated durable MEA-stack system tests.

	FY '05	FY '06	DOE 2010 Goal (hrs)
Accelerated Lifetime Predictions (hrs)	16,000	> 20,000	40,000

Technology Transfer/Collaborations: Active partner with CWRU, Plug Power and the University of Miami. Presented 9 presentations and 2 papers on work related to this project in last 12 months.

Future Work: Complete studies on MEA degradation mechanism. Select 'final' MEA and stack design and test system for 2,000 hours.

Publications and Presentations

- M. Yandrasits, "Mechanical property measurements of PFSA membranes at elevated temperatures and humidities," 2nd International Conference on Polymer Batteries and Fuel Cells, Las Vegas, NV, June 2005.
- D. Stevens, M. Hicks, G. Haugen, J. Dahn, "Ex situ and in situ stability studies of PEMFC catalysts: Effect of carbon type and humidification on degradation of the carbon," *J. Electrochem. Soc.*, 152 (12), A2309 (2005).
- D. Schiraldi and C. Zhou, "Chemical durability studies of PFSA polymers and model compounds under mimic fuel cell membrane conditions," 230th ACS Meeting, Washington, D.C., August 2005.
- M. Hicks, D. Pierpont, P. Turner, T. Watschke, M. Yandrasits, "Component Accelerated Testing and MEA Lifetime Modeling," 2005 Fuel Cell Testing Workshop, Vancouver, BC, September 2005.
- J. Dahn, D. Stevens, A. Bonakdarpour, E. Easton, M. Hicks, G. Haugen, R. Atanasoski, M. Debe, "Development of Durable and High-Performance Electrocatalysts and Electrocatalyst Support Material," 208th Meeting of The Electrochemical Society, Los Angeles, CA, October 2005.
- D. Pierpont, M. Hicks, P. Turner, T. Watschke, "Accelerated Testing and Lifetime Modeling for the Development of Durable Fuel Cell MEAs," 208th Meeting of The Electrochemical Society, Los Angeles, CA, October 2005 (presentation and paper).
- M. Hicks, K. Kropp, A. Schmoeckel, R. Atanasoski, "Current Distribution Along a Quad-Serpentine Flow Field: GDL Evaluation," 208th Meeting of The Electrochemical Society, Los Angeles, CA, October 2005 (presentation and paper).
- G. Haugen, D. Stevens, M. Hicks, J. Dahn, "Ex-situ and In-situ Stability Studies of PEM Fuel Cell Catalysts: the effect of carbon type and humidification on the degradation of carbon supported catalysts," 2005 Fuel Cell Seminar, Palm Springs, CA, November 2005.
- D. Pierpont, M. Hicks, P. Turner, T. Watschke, "New Accelerated Testing and Lifetime Modeling Methods Promise Development of more Durable MEAs," 2005 Fuel Cell Seminar, Palm Springs, CA, November 2005.
- M. Hicks, R. Atanasoski, "3M MEA Durability under Accelerated Testing," 2005 Fuel Cell Durability, Washington, DC, December 2005.
- Z. Qi, Q. Guo, B. Du, H. Tang, M. Ramani, C. Smith, Z. Zhou, E. Jerabek, B. Pomeroy, J. Elter, "Fuel Cell Durability for Stationary Applications - From Single Cells to Systems," 2005 Fuel Cell Durability, Washington, DC, December 2005.

Response to 2005 Reviewer's Comments

- **Need to evaluate catalyst degradation; how does catalyst degradation affect overall MEA durability?**
  - Reported results of 'commercial' Pt/C catalyst durability and degradation at 2004 HFCIT Review
  - Project not focused on development of Pt/C catalyst; separate 3M/DOE project focused on catalyst durability (3M NSTF catalyst)
- **Need additional characterization of membrane physical properties and effect of aging on these properties**
  - Initiated task on measuring membrane mechanical properties & morphology as a function of aging
- **Need to relate effect of component improvements to overall MEA improvements. What component improvement added most value to MEA lifetime?**
  - Integration of components is critical in terms of obtaining good MEA durability
  - Considering possible patent applications
- **Need to work on reinforced membranes.**
  - Have evaluated reinforced membranes; results to be presented in the future
  - Development out of scope of project – some work done at expense to 3M
- **Better description of lifetime model**
  - Using std lifetime statistical analysis techniques; see W.Q. Meeker and L.A. Escobar, Statistical Methods for Reliability Data, John Wiley and Sons, Inc. (1998)
- **Need to address other targets (cost/performance) in concert with durability**
  - Reported performance at the 2005 DOE Hydrogen Program Review
  - Cost not a primary objective; it is used as a metric when deciding options
- **Too much emphasis on fluoride ion release.**
  - Disagree
  - Very strong relationship between fluoride release and MEA lifetime

Critical Assumptions and Issues

- Validation of lifetime model analysis method
  - Testing baseline samples at 'normal' test conditions
  - Comparison to field test data
- Increasing sample throughput of improved durability MEAs
  - New, durable MEAs last too long
  - Use initial fluoride ion release as metric (reduces test time)
  - Plug Power test equipment online (adds more test equipment)
- Understanding role of peroxide
  - Initial peroxide lifetime model established
- Demonstrate benefit of new, more durable MEAs
  - Start lifetime accelerated tests of new MEAs
  - Apply lifetime model to new MEAs