2005 DOE Hydrogen Program Review

MEA & Stack Durability for PEM Fuel Cells

3M/DOE Cooperative Agreement

No. DE-FC36-03GO13098

Project ID # FC12

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3M Company
May 24, 2005

Overview

Timeline

- 9/1/2003 – 8/31/2006
- 40% complete

Budget

- Total $10.1 M
  - DOE $8.08 M
  - Contractor $2.02 M
- FY04 – $1,650,000 from DOE (47% of FY04 PMP)
- FY05 – Projected $2,350,000 from DOE (88% of FY05 PMP)

Barriers & Targets

- A. Durability: 40k hrs
- B. Cost: $400 - 750/kW

Partners

- Plug Power
- Case Western Reserve University

Subcontract

- University of Miami

Consultant

- Iowa State University

Objectives

Develop a pathway/technology for stationary PEM fuel cell systems for enabling DOE to meet its year 2010 objective of 40,000 hour system lifetime

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
- Degradation mechanisms
- 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

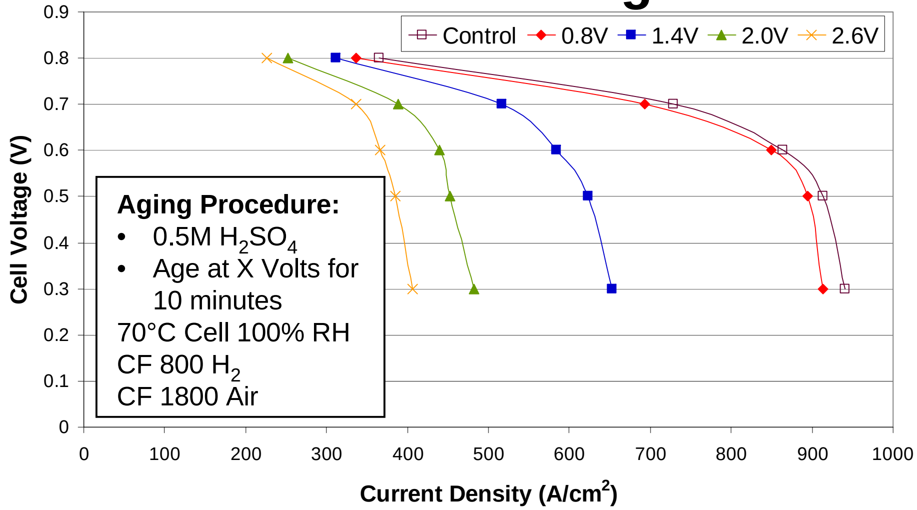
- Utilize proprietary 3M Ionomer
  - Improved stability over baseline ionomer
- Utilize ex-situ accelerated testing to age MEA components
  - Relate changes in component physical properties to changes in MEA performance
  - Focus component development strategy
- Optimize stack and/or MEA structure based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

Accomplishments

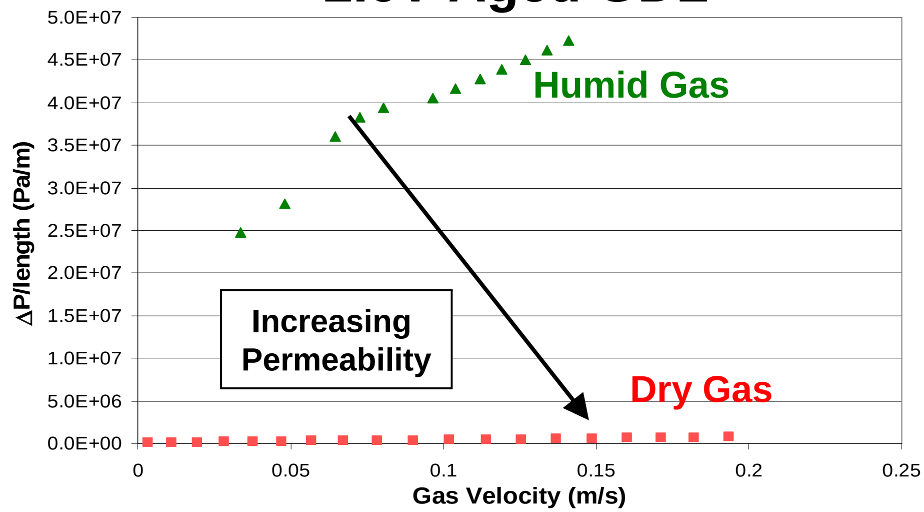
- Component Characterization
  - GDL permeability
  - Membrane properties vs decay
  - Segmented cell
- Model Compound Study – Membrane Decay Mechanism
- Component Development
  - Membrane (improved oxidative stability)
    - End group modified
    - Additive studies
  - GDL (improved oxidative stability)
    - Stability factor
  - Electrode design – Start-up, performance and fluoride release
- System Study – CO and Air Bleed
- MEA Accelerated Testing
  - Effect of load settings
  - Relationship between fluoride release and MEA lifetime
  - Statistical analysis of accelerated test data
  - New MEAs with significant durability improvement

GDL Permeability Measurements

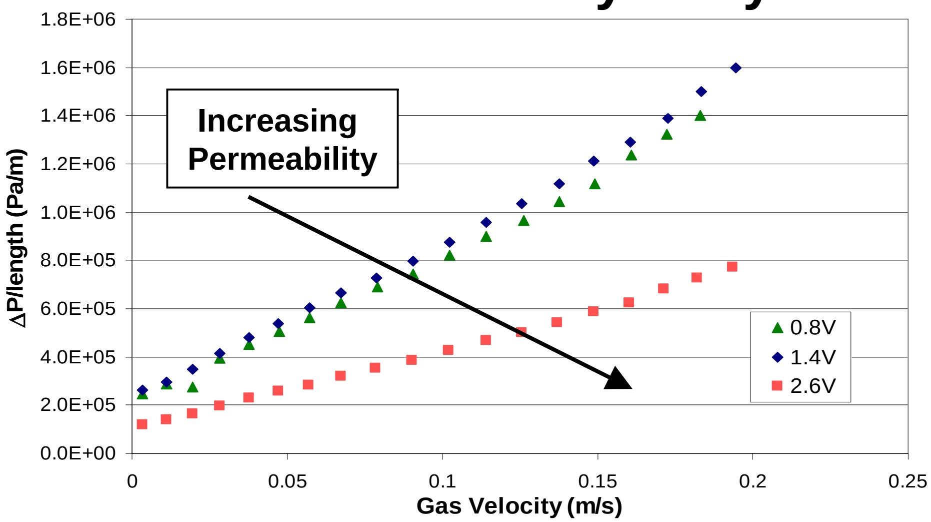
Performance of Aged GDLs



GDL Permeability – Humid Gas 2.6V Aged GDL



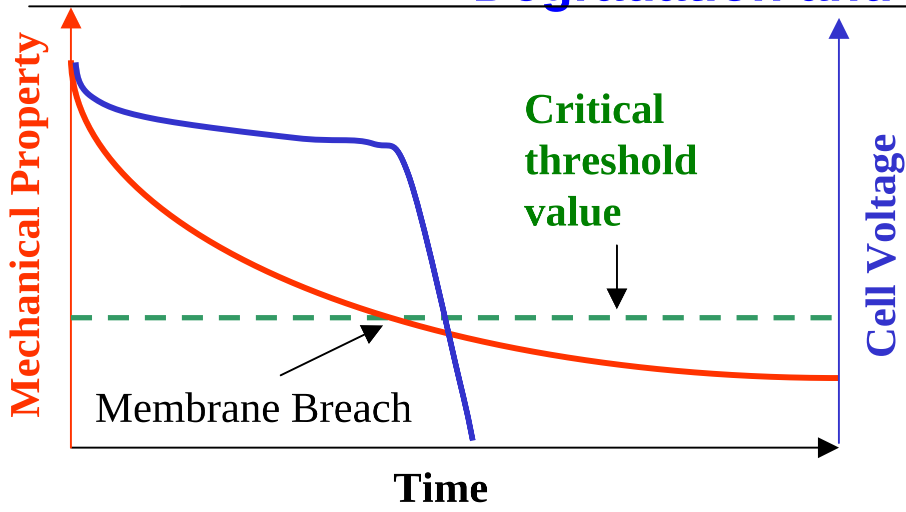
GDL Permeability – Dry Gas



- Measure GDL permeability under both humid and dry air
- Humid permeability lower than dry
  - Pores fill with water
- Humid conditions represent fuel cell conditions

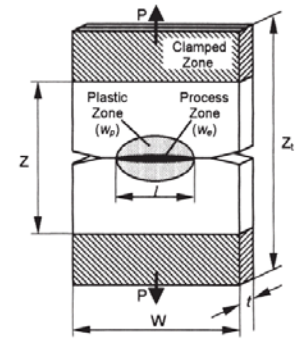
3M Fuel Cell Components

Relationship Between Membrane Chemical Degradation and Mechanical Failure

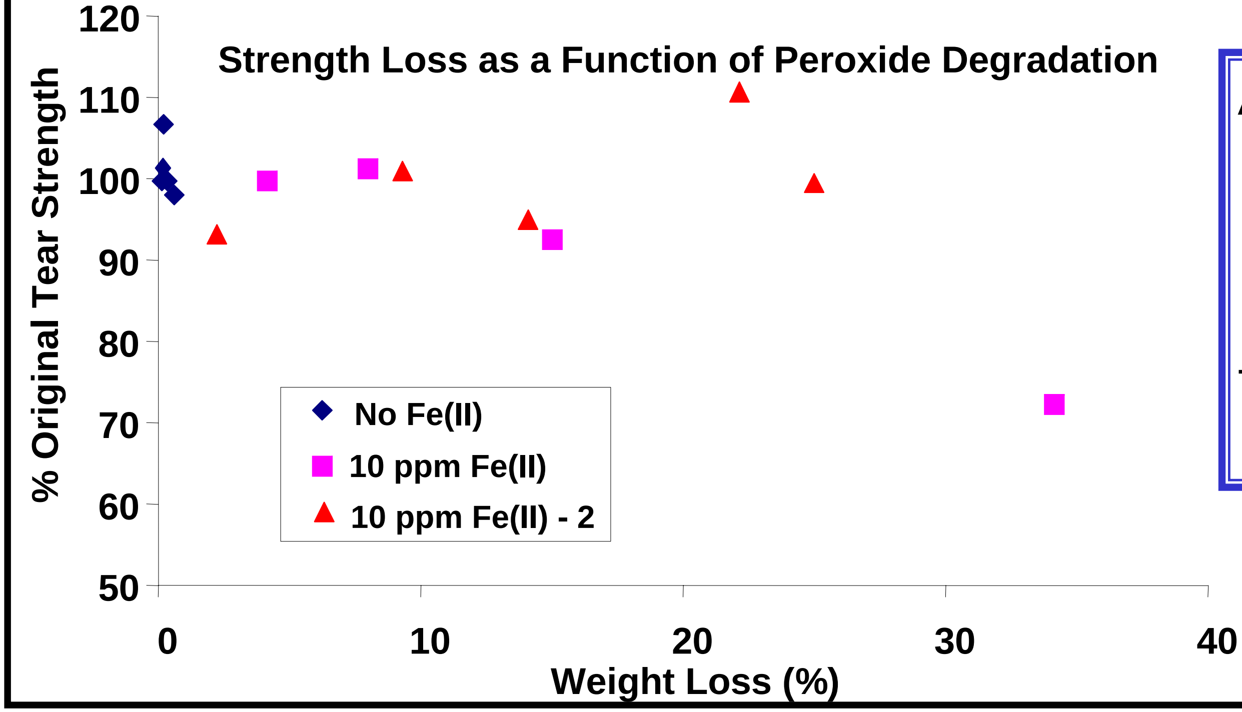


Peroxide Test
- 1M H_2O_2
- 90ºC

Strength Test
- Double notch tear test
- 50ºC
- 95% RH



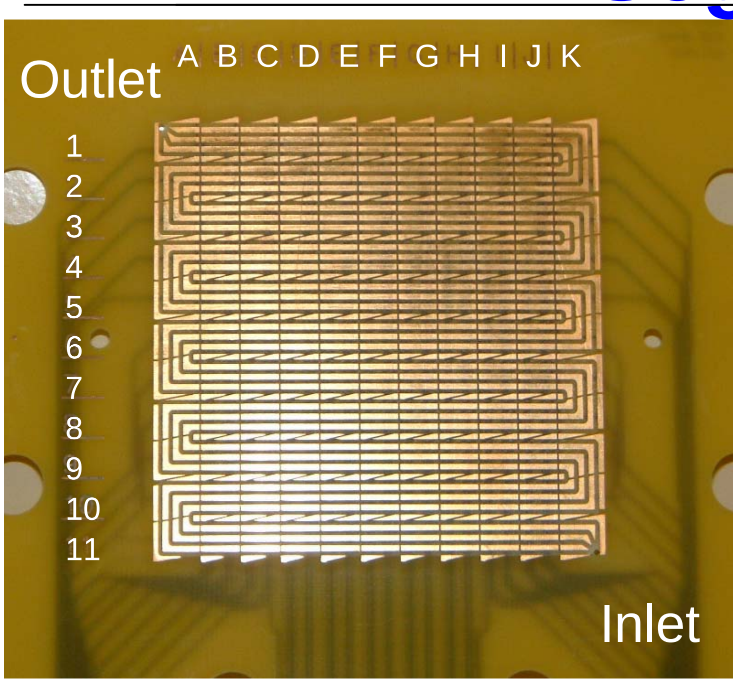
John Nairn, *Polymer Engineering and Science*, **38** (1998) 186-193.

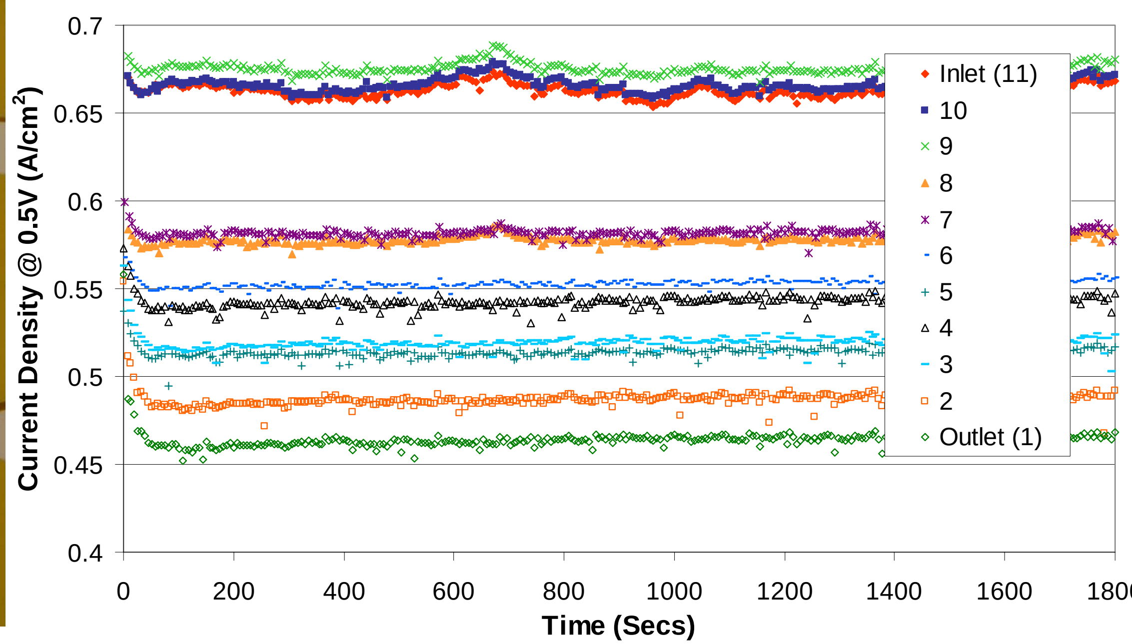


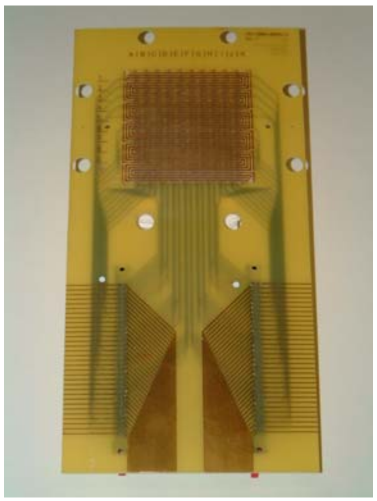
A method of aging membrane in a way that degrades mechanical properties is under development

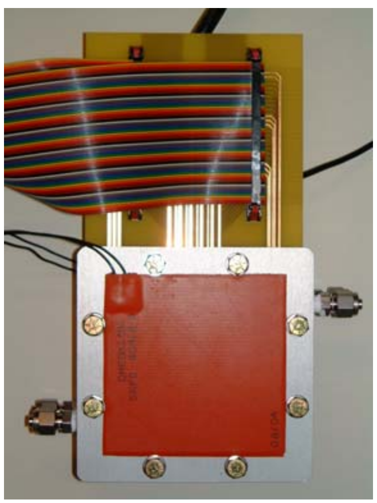
Tear strength constant up to 25% membrane weight loss

Segmented Cell





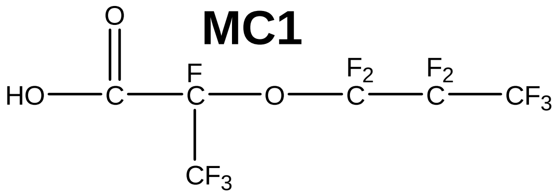




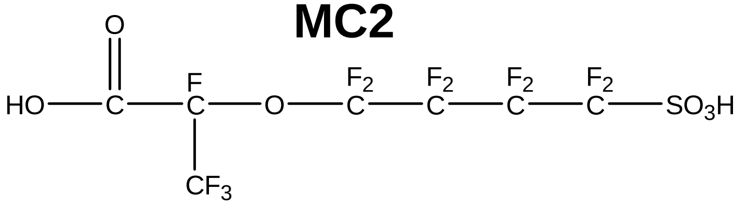
- Printed circuit board technology
- Divides 50cm^2 active area into 121 segments which follow flow field
- Quad serpentine flow field
- Inlet current 30% higher than outlet
- 121 channel load under development

Model Compound (MC) Study – Membrane Decay Mechanism

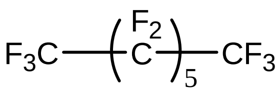
MC1



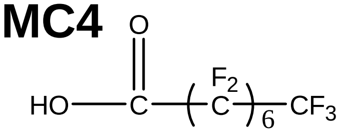
MC2



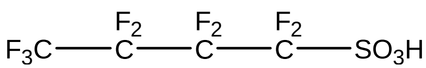
MC3



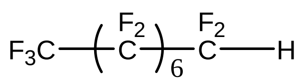
MC4



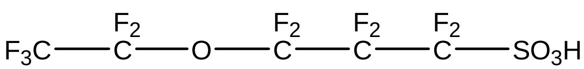
MC5



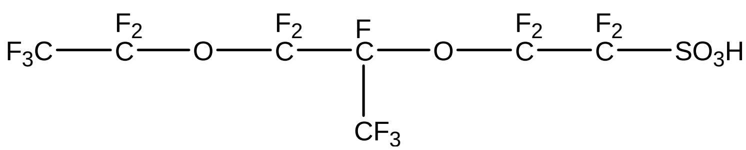
MC6

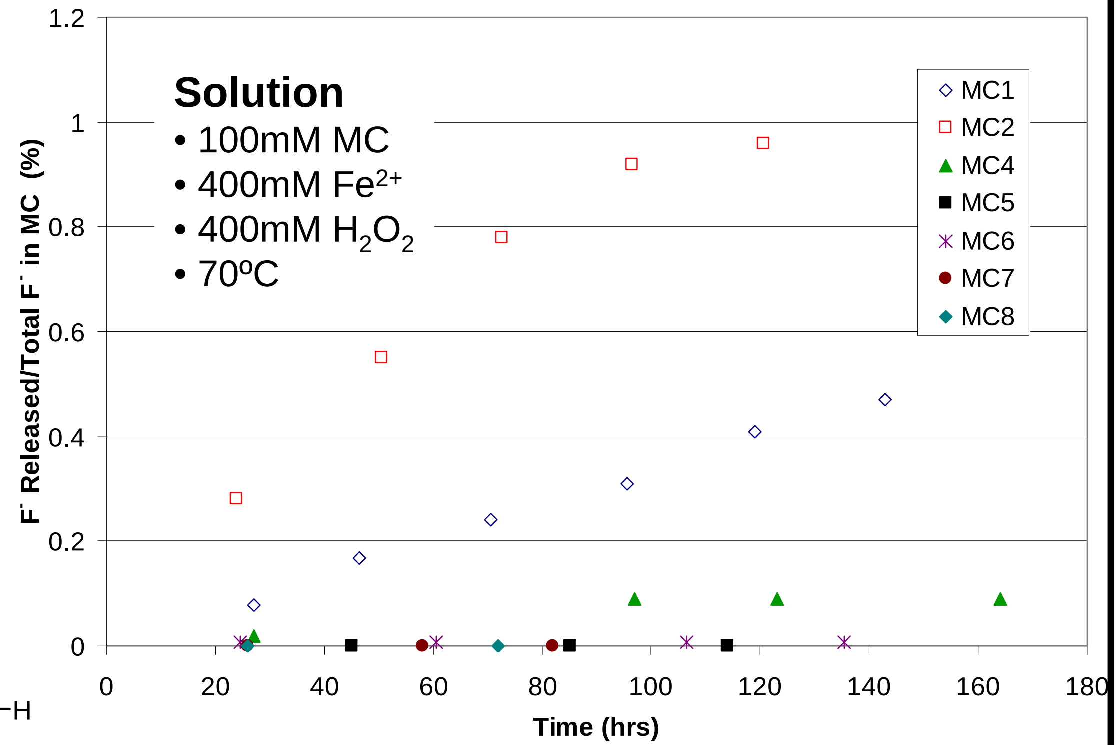


MC7



MC8

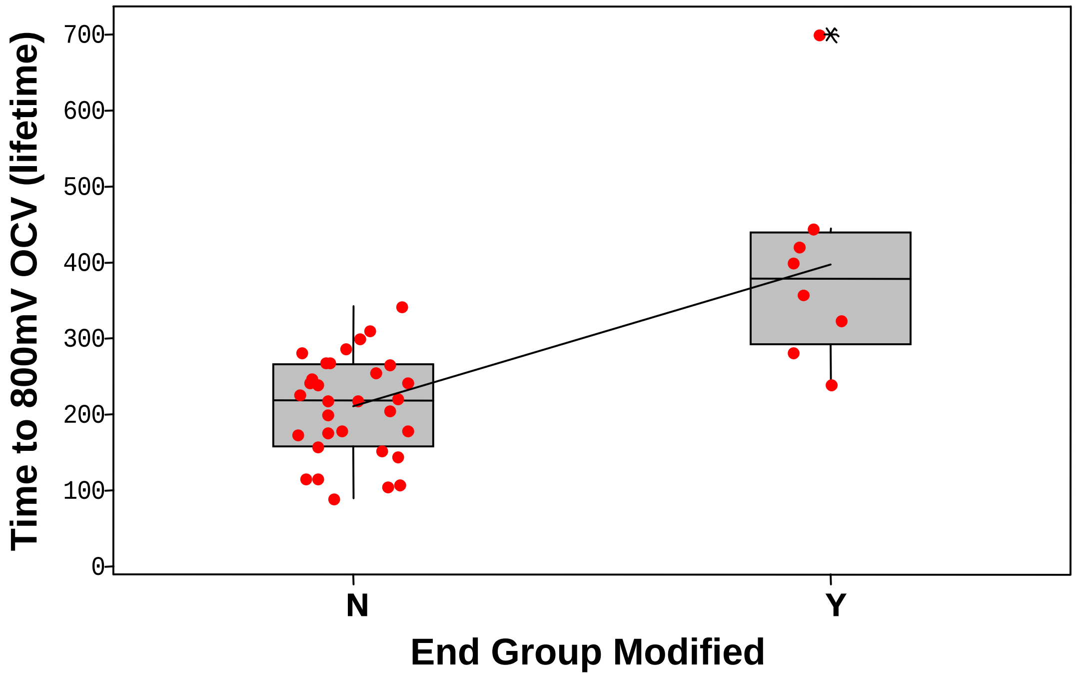




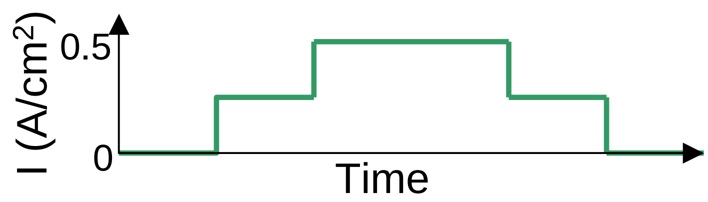
- –SO_3H stable
- –COOH unstable
  - Ether linkages & tertiary C–F positions alpha to –COOH accelerate decay

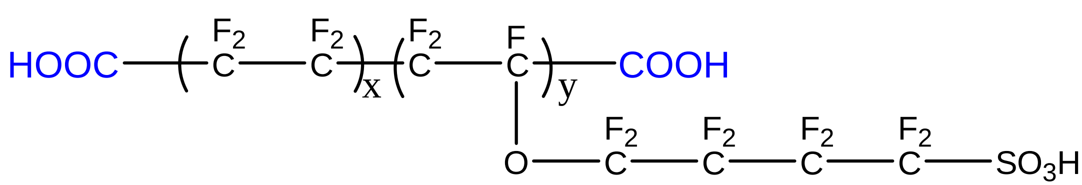
Stability of End Group Modified 3M Ionomer

Lifetime under accelerated conditions



Accelerated Test Conditions:
90ºC cell
70ºC gas dew points
H_2/Air
Anode over pressure
Load Profile:



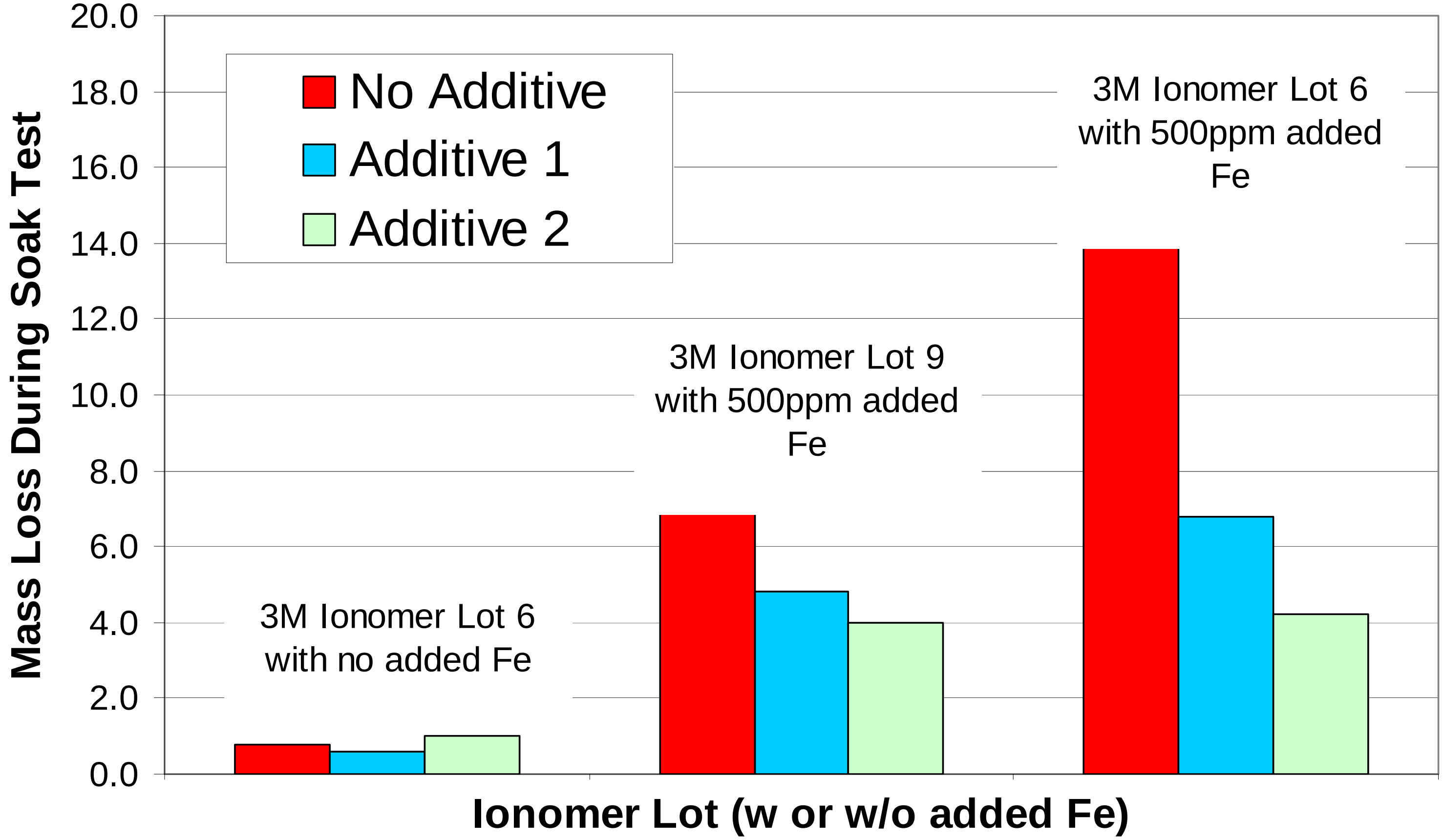


End Group Modification
- Eliminates –COOH groups

Statistically significant difference
- ANOVA => p=0.000 @ 90% confidence interval

Accelerated lifetime test
- 89% improvement
- 396hrs vs 210hrs

3M Membrane Stability – Ex-situ Tests

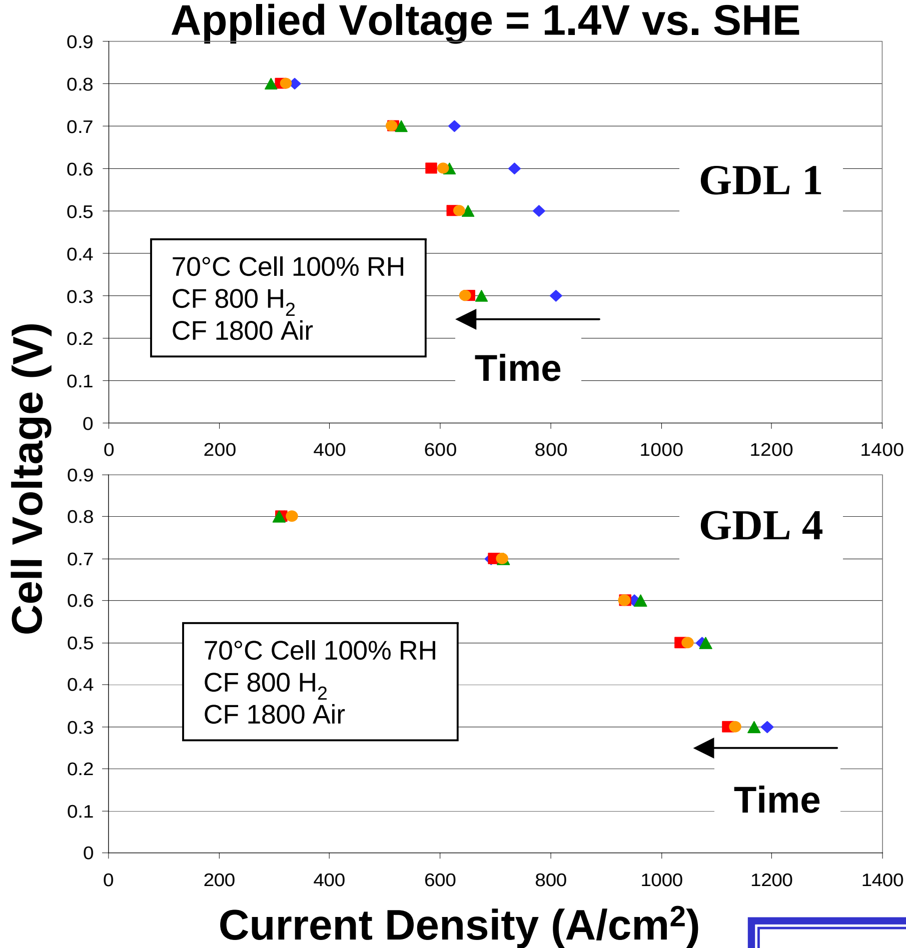


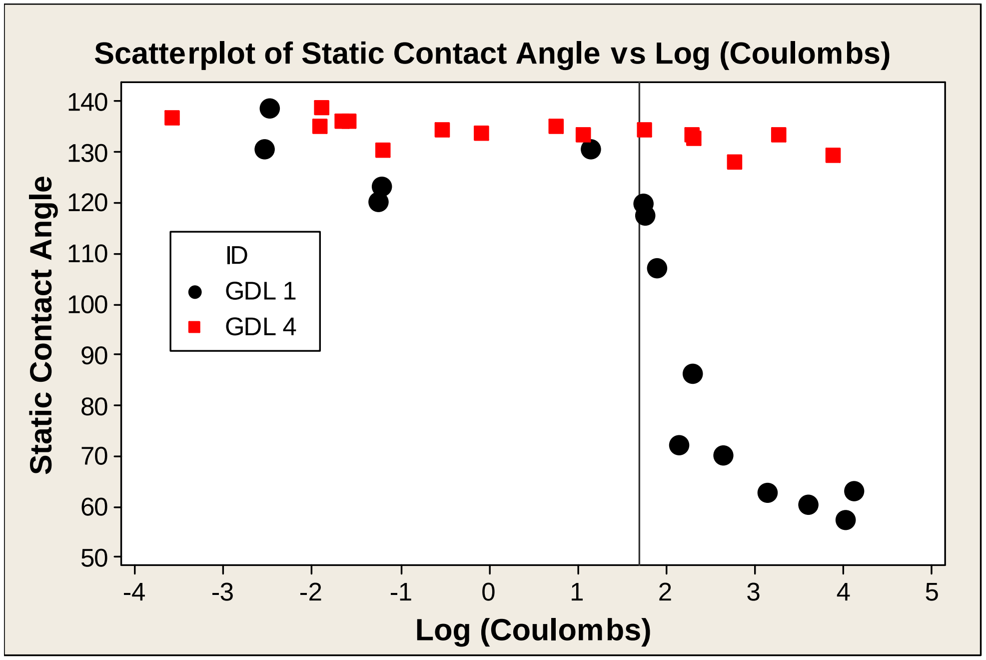
Procedure:
- 1M H_2O_2
- 90°C
- 5 days

Additives significantly mitigate membrane degradation via hydrogen peroxide

3M Fuel Cell Components

GDL Stability Improvements





Stability Factor (SF) = *f*(GDL, Voltage)

$$= \frac{\text{Time to 50 C [GDL X, Volts]}}{\text{Time to 50 C [GDL 1, Volts]}}$$

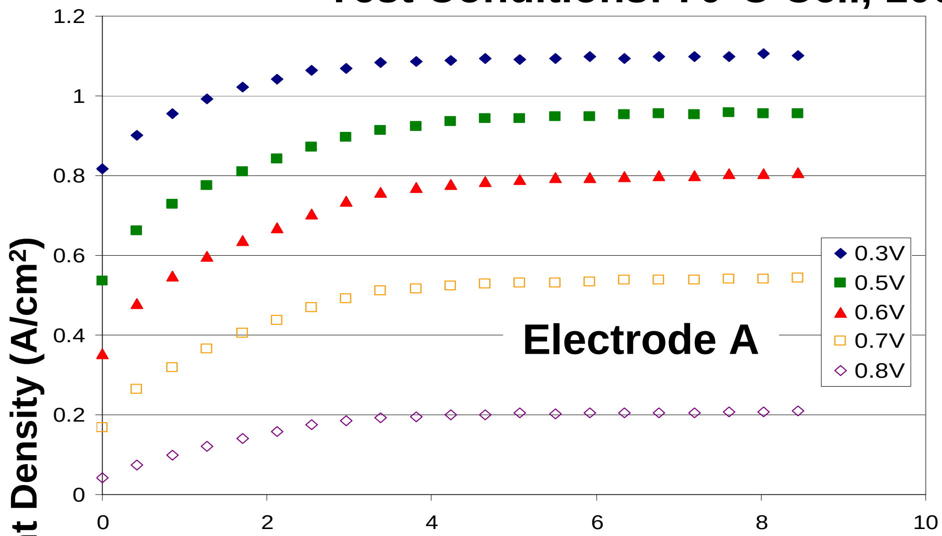
Voltage (V)	GDL 5 SF
2.5	6
2.3	13
2.0	87
1.6	1549

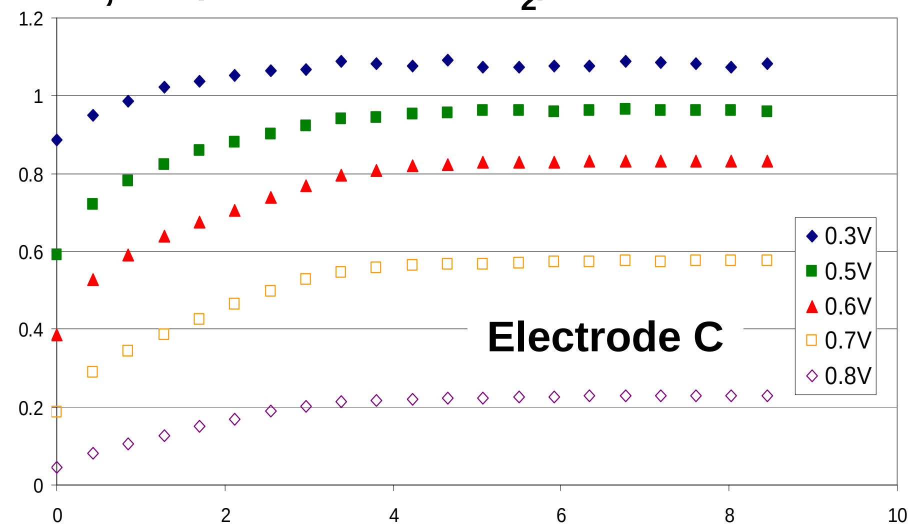
Aging Procedure:
- 0.5M H_2SO_4
- Age at voltage for 1, 10, 100 or 1000 minutes

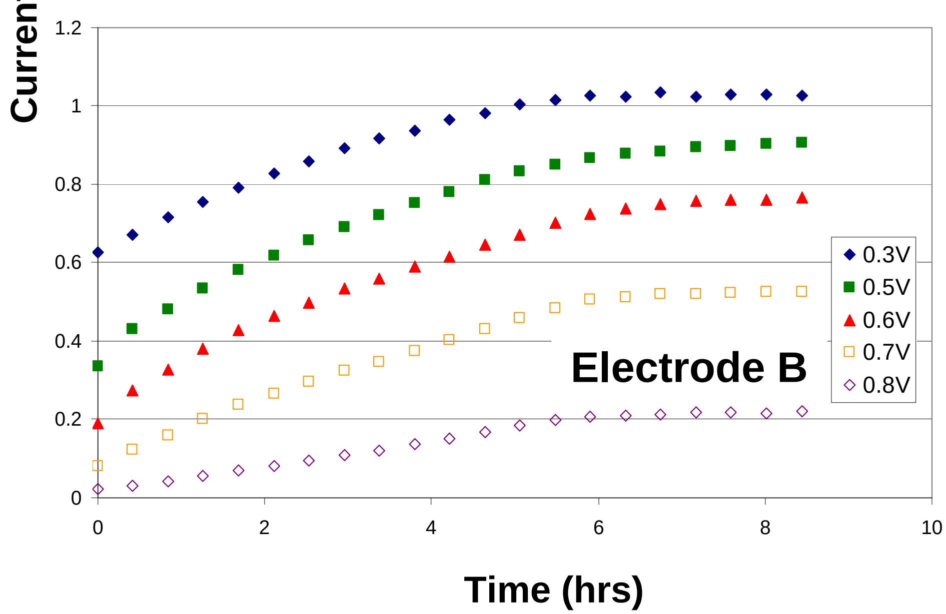
New GDLs more stable
- GDL5 > 1500X improvement

Electrode Design – Start-up, Performance and Fluoride Release

Test Conditions: 70°C Cell, 100% RH, 800/1800 sccm of H_2/Air





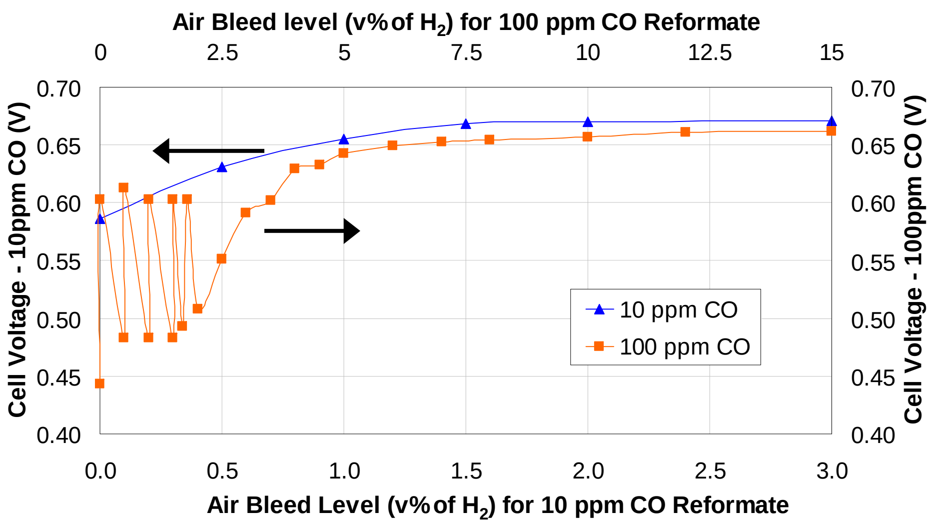


Electrode	A	B	C
I (A/cm^2) @ 0.6V 80°C, 100% RH, 260/850 sccm H_2/Air	0.571	0.535	0.563
F^- Release (µg/day/cm^2)	0.10 ±0.02	0.17 ±0.02	0.16 ±0.02

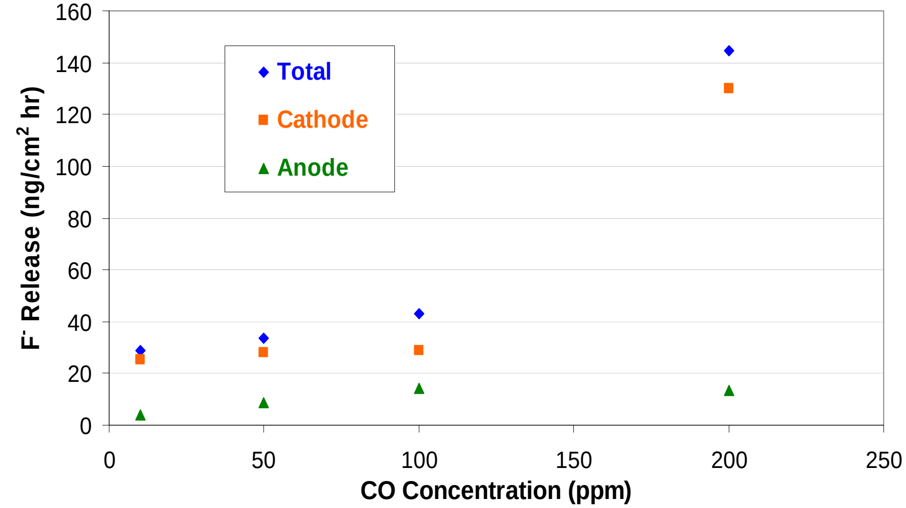
Need to balance start-up, performance & fluoride release when selecting electrode design

System Studies – CO/Air Bleed and Their Effect on F^- Release

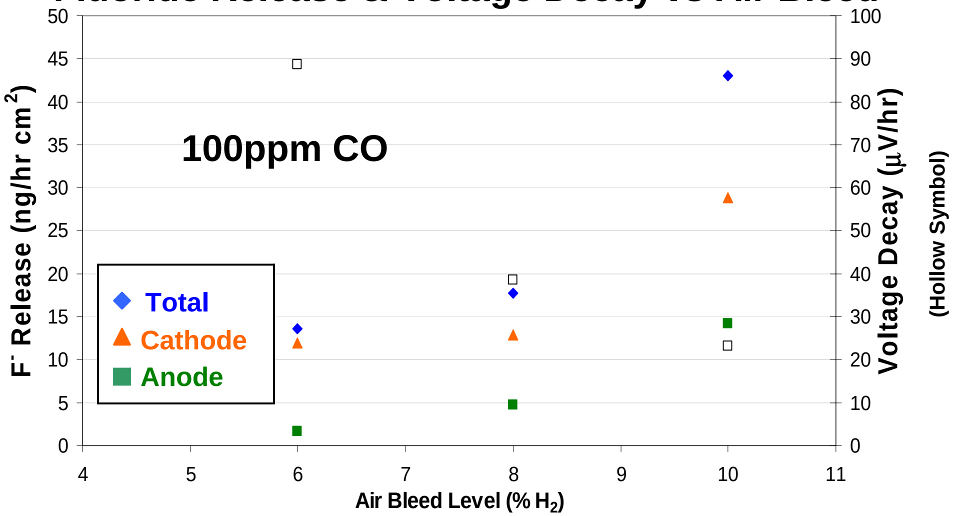
Typical Cell Performance vs Air Bleed



Fluoride Release vs CO Level

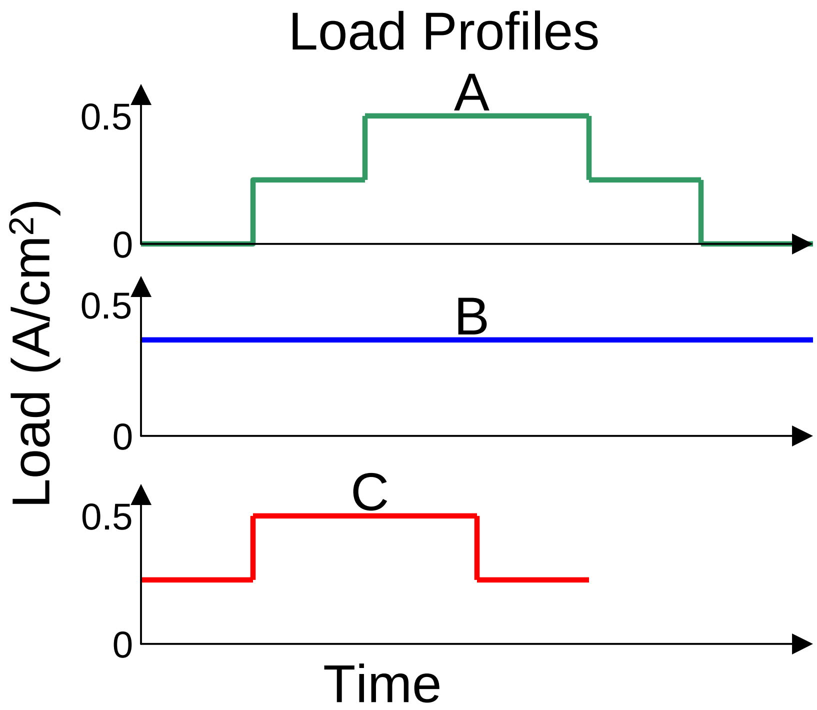


Fluoride Release & Voltage Decay vs Air Bleed



- Fluoride release increases with CO level
  - Both anode and cathode
- Performance and fluoride release increase with air bleed
- System design must account for these competing factors

Accelerated Testing: Effect of Load on Lifetime

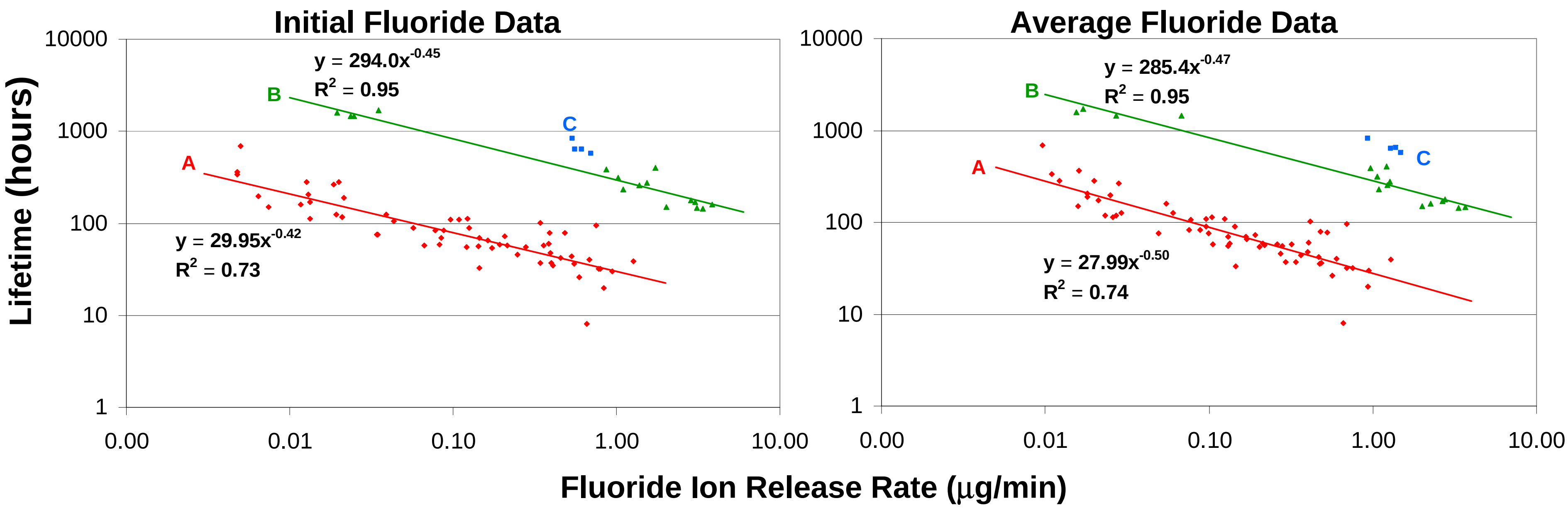


Load Profile	Lifetime (hrs)	Average F^- Ion Release (µg/min)
A (14 samples)	260 +/- 110	2 +/- 1
B (4 samples)	1548 +/- 120	0.13 +/- 0.1
C (2 samples)	> 2500 (ongoing)	< 0.04

Accelerated Test Conditions:
90ºC cell
70ºC gas dew points
H_2/Air
Anode over pressure
Same MEA construction

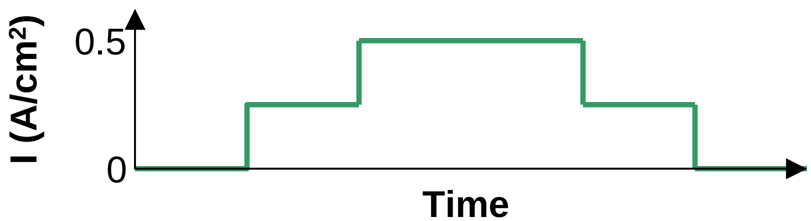
Load profile significantly affects lifetime
- OCV setting results in a > 8X reduction in MEA lifetime under accelerated conditions
- Systems should be designed to reduce total time spent at OCV

Relationship Between F^- Release & MEA Lifetime



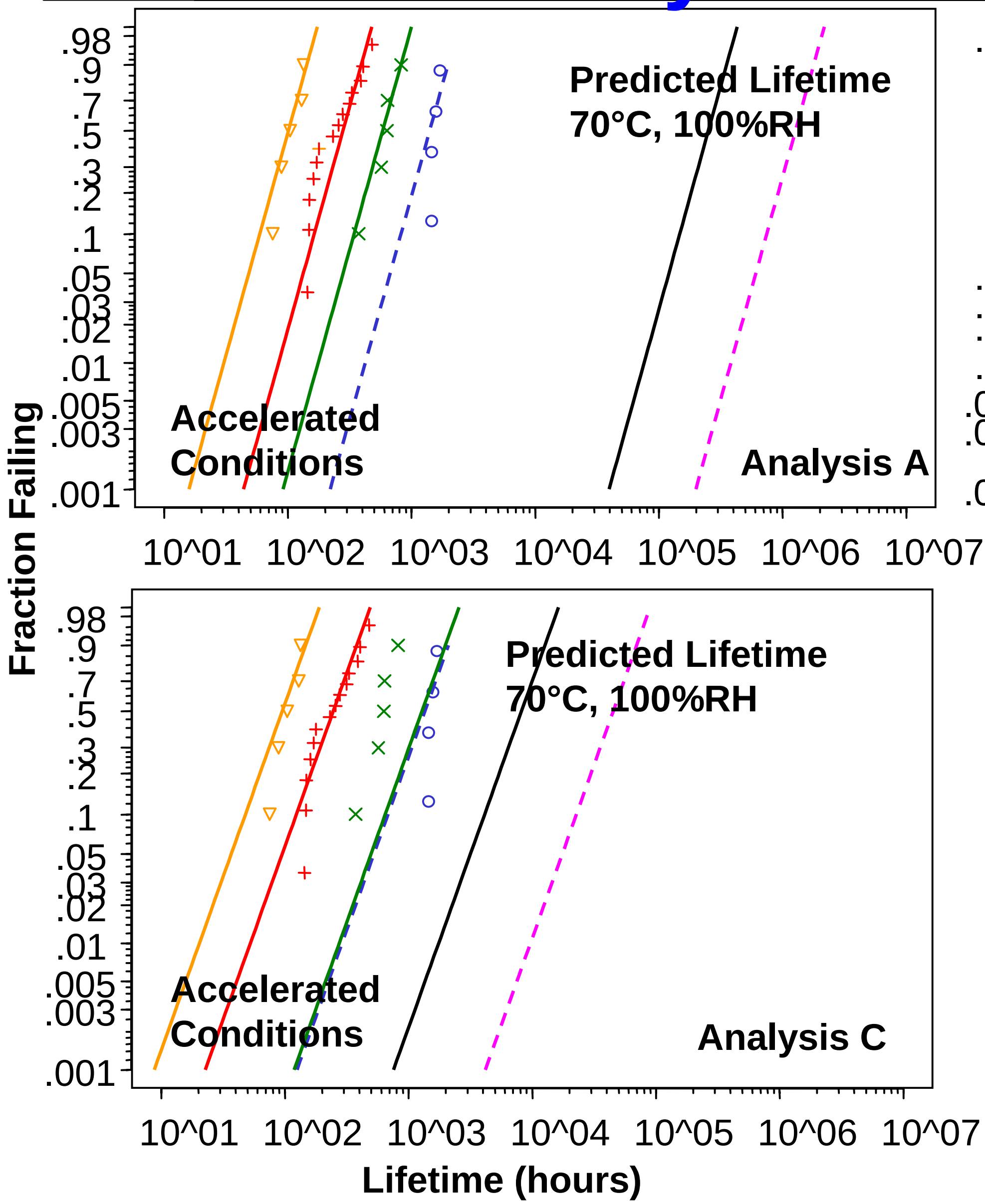
Accelerated Test Conditions:

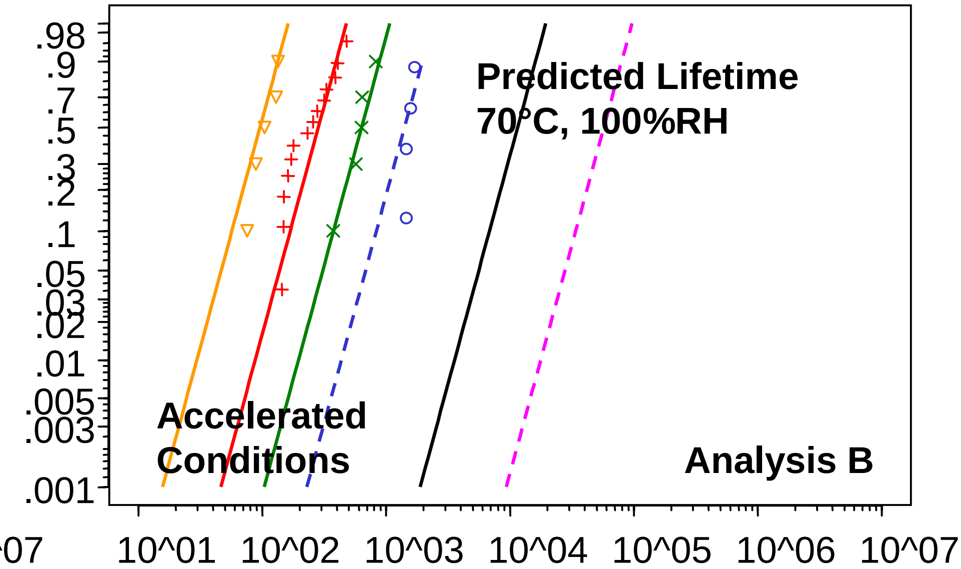
H_2/Air
Anode over pressure
Various membranes
Load profile:

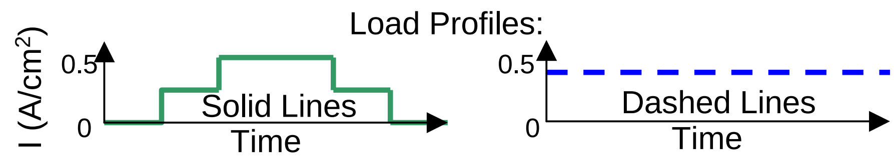


- Strong relationship between fluoride release rate and MEA lifetime
- Relationship independent of membrane type

Statistical Analysis of Accelerated Test Data





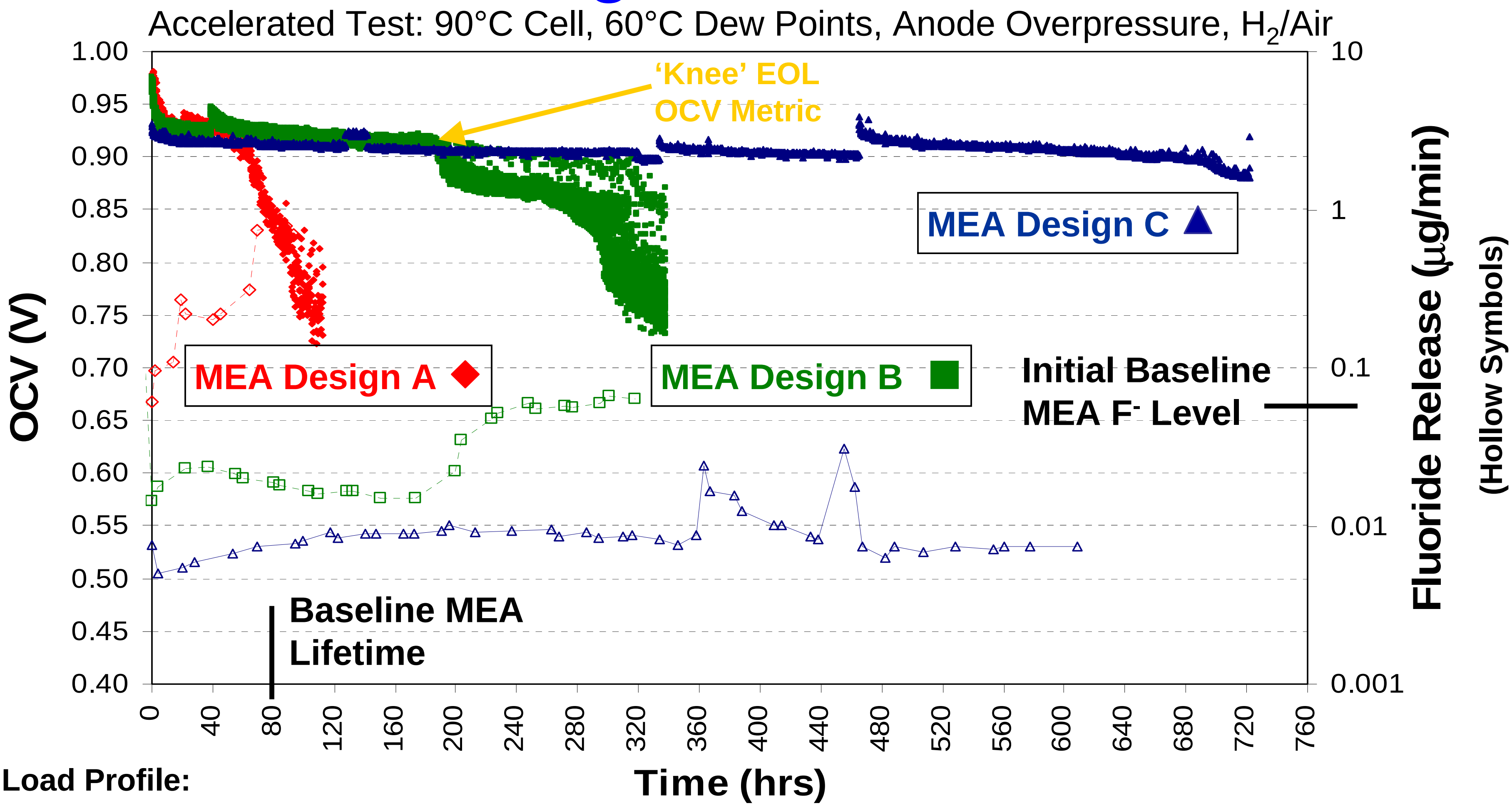


Baseline MEAs

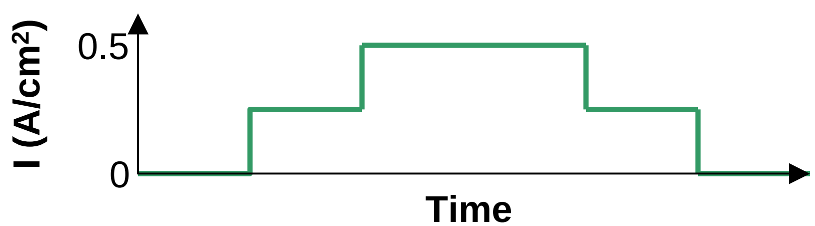
- no newly developed components

- Predicted lifetime depends on analysis methodology
- Analysis C worst fit to data
- Need to determine correct analysis method by comparing predicted lifetime to real data

New 3M MEA Designs with Enhanced Lifetime



Load Profile:



Significant improvement in MEA lifetime

- Design C 775% Improvement
  - 700hrs vs 80hrs

Response to 2004 Reviewers' Comments

- Incorporate automotive conditions; define durability requirements for automotive operation.
  - Accelerated stationary MEA tests are close to actual automotive operating conditions
  - Accelerated component tests valid for both stationary and automotive
- No collaboration outside of team members. Program only valuable to 3M and Plug Power.
  - "Critical mass" of collaboration established with CASE, Plug Power, and 3M as required in the solicitation
    - Subcontract with University of Miami
    - Working with consultant from Iowa State University
  - R&D addresses fundamental issues
  - Knowledge gained and successful demonstration of progress will benefit entire fuel cell industry
- Need MEAs and systems less sensitive to operating conditions.
  - Only reported results with baseline materials and system in 2004
  - New designs are still under development
    - First system test w/new MEAs underway in 2005
- Catalyst support degradation critical barrier. How will it be solved?
  - Not a critical barrier; commercially available catalysts address this issue

Future Work

- Remainder of 2005
  - Ongoing MEA component development
  - Pilot scale-up of new components
    - MEA component integration
  - Ongoing accelerated MEA lifetime testing
    - Initiate MEA accelerated testing with new components
  - Ongoing 3D model and segmented cell work
  - Ongoing studies on interactions between system parameters and MEA durability
  - Start system testing using newly developed MEAs
- 2006
  - Complete activities started in 2005
  - Select MEA components for final system tests
  - Final system demonstration

Publications and Presentations

- C. Zhou, T. Zawodzinski, Jr., D. Schiraldi, "Chemical changes in Nafion® membranes under simulated fuel cell conditions," 228th ACS Meeting, Philadelphia, PA, August 2004.
- M.T. Hicks, "Accelerated testing – Application to fuel cells", 2004 Fuel Cell Testing Workshop, Vancouver BC, Canada, September 2004.
- A. Agarwal, U. Landau and T. Zawodzinski, Jr., "Hydrogen peroxide formation during oxygen reduction on high surface area Pt/C catalysts," 206th ECS Meeting, Honolulu, HI, October 2004. (Presentation and Paper)
- C. Zhou, T. Zawodzinski, Jr., D. Schiraldi, "Chemical changes in Nafion® membranes under simulated fuel cell conditions," 206th ECS Meeting, Honolulu, HI, October 2004.
- M. Pelsozy, J. Wainright and T. Zawodzinski Jr., "Peroxide production and detection in polymer films," 206th ECS Meeting, Honolulu, HI, October 2004. (Presentation and Paper)
- J. Frisk, W. Boand, M. Hicks, M. Kurkowski, A. Schmoeckel, and R. Atanasoski, "How 3M developed a new GDL construction for improved oxidative stability," 2004 Fuel Cell Seminar, San Antonio, TX, November 2004.
- D. Schiraldi, "Chemical durability studies of model compounds and Nafion® under mimic fuel cell conditions," Advances in Materials for Proton Exchange Membrane Fuel Cells, Pacific Grove, CA, February 2005.
- S. Hamrock, "New membranes for PEM fuel cells", Advances in Materials for Proton Exchange Membrane Fuel Cells, Pacific Grove, CA, February 2005
- C. Zhou, T. Zawodzinski, Jr., D. Schiraldi, "Chemical durability studies of model compounds and Nafion® under mimic fuel cell conditions," 229th ACS Meeting, San Diego, CA, March 2005.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Accidental H_2 release in cylinder closet leading to ignition from:
  - H_2 line or manifold breach
  - Accident during replacement of tank cylinders

Hydrogen Safety

Our approach to deal with this hazard is:

- Design
  - Hydrogen cylinder closet and gas distribution system adhere to codes.
  - Reduction in number of cylinders in the tank closet
  - 2-step regulators (less susceptible to failure and designed to fail closed)
  - H_2 sensors in all labs and tank closet, alarm system
  - Automatic shut-off of H_2 gas supply if sensors detect H_2 release
- Procedures
  - SOP's for tank changing, alarm responses, test station operation
  - Tank changing restricted to highly trained personnel
  - Regular maintenance checks – sensors, leak check of valves etc.
- Installing H_2 Generator (in non-inhabited mechanical room) to significantly reduce total volume of H_2 in facility