2007 DOE Hydrogen Program Review

MEA & Stack Durability for PEM Fuel Cells

3M/DOE Cooperative Agreement

No. DE-FC36-03GO13098

Project ID # FC10

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3M Company

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Overview

Timeline

- 9/1/2003 – 12/31/2007
- 90% complete

Budget

- Total $10.1 M
  - DOE $8.08 M
  - Contractor $2.02 M
- Funding received in FY06: $1.895 M
- Funding (estimated) for FY07: $1.604 M

Barriers & Targets

- Durability:
  - Demonstrate:2k hrs
  - Target: 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 to meet the DOE's 2010 objective of 40,000 hour system lifetime.

Goal: *Develop an MEA and System with enhanced durability*

- – Manufacturable in a high volume process
- – Capable of meeting market required targets for lifetime and cost
- – Optimized for field ready systems
- – 2,000 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
- Stack testing with intermediate developments
- Final Stack Demonstration Started

Approach

Case Western Reserve University

- Component Characterization
- Model Compounds
- Peroxide Model
- Accelerated testing (ex-situ)

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- Accelerated Testing (in-situ)
- Statistical Lifetime Analysis
- New components
- Fabricate MEAs
- Segmented Cell

Goal – Better MEA and System Durability

University of Miami

- Nonuniformity Studies
- Segmented Cell
- 3D Modeling

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- Single Cell MEA Evaluation
- Modules Evaluation
- Operating conditions
- Stack demonstration

Accomplishments ('07)

Membrane Degradation Mechanism

- Utilized ionomer model compounds to identify likely 'points of attack' and confirmed degradation pathway
- Developed initial hydrogen peroxide model to study peroxide in operating fuel cell

GDL Characterization

- Demonstrated new test equipment to measure capillary pressure in GDLs

MEA Nonuniformity Studies

- Utilized 121-channel segmented cell to investigate current uniformity as a function of load setting, flow rate and flow configuration.
- Completed a series of durability experiments with segmented cell
- Segmented cell fabricated to run in full stack

Membrane

- Developed film edge protection technology
- Ongoing monitoring of membrane properties in accelerated tests

MEA Lifetime Modeling

- Developed initial lifetime prediction model to estimate MEA lifetime relative to DOE's 2010 stationary system goals
- Related initial fluoride ion to lifetime

System Test

- Ongoing Saratoga system test with a preliminary, durable MEA design
- Initiated 'Final' MEA and system test

Membrane Degradation Model

Objective – Predict degradation pattern and Fluoride release rate

Source terms:

- H_2O_2 production rate from O_2 x-over
- ORR side reaction

} well-known from previous work

Reaction terms:

- H_2O_2 decomposition rate in electrodes (Multidecker sandwich cells)
- peroxide reaction rate with PFSAs (Model compounds w/kinetic analysis)

Transport Terms:

- H_2O_2 diffusion rate through each MEA component (GDL, CL, membrane) (Multidecker sandwich cells)

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

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

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

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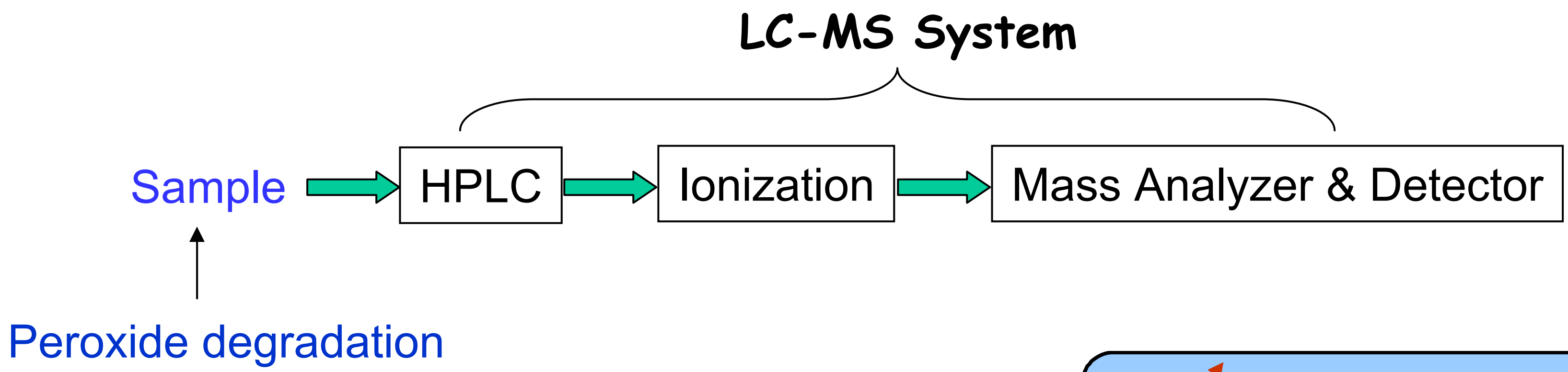
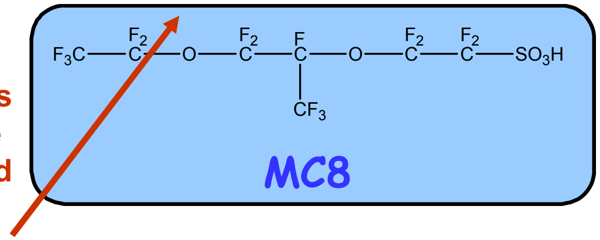
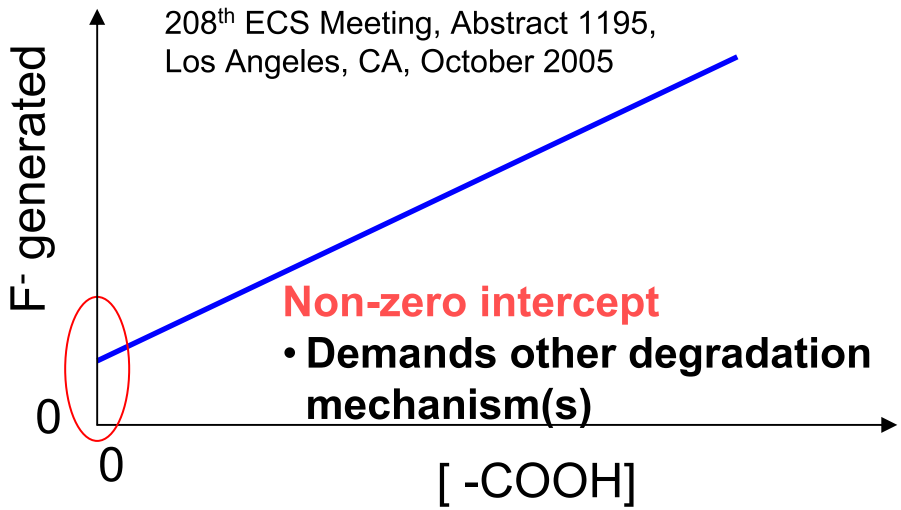
Model Compound Studies



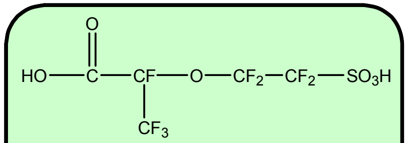
“Side chain” cleavage appears to occur with the model compound



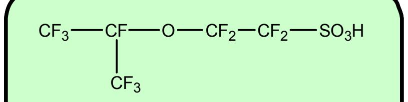


Non-zero intercept

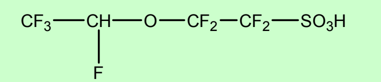
- **Demands other degradation mechanism(s)**



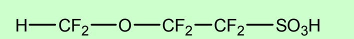
Possible Product 1
(Parent Ion: 341 Da)



Possible Product 2
(Parent Ion: 365 Da)



Possible Product 3
(Parent Ion: 297 Da)



Possible Product 4
(Parent Ion: 247 Da)

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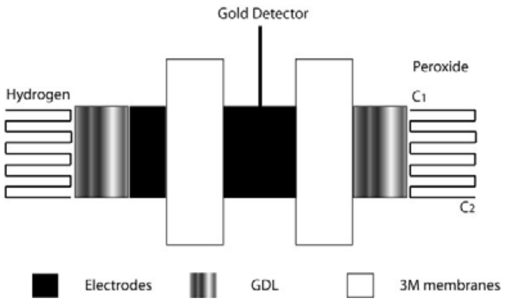
H_2O_2 Transport and Reaction Processes

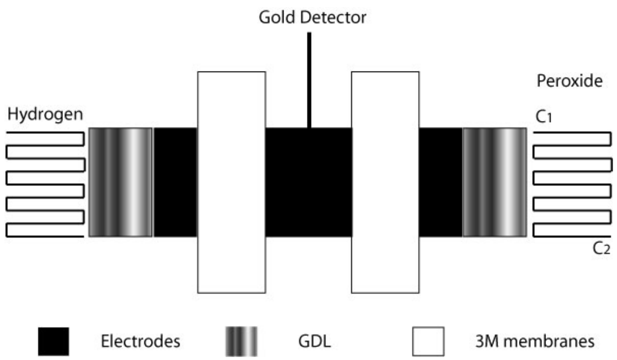
Half MEA Setup



Allows us to measure:

- H_2O_2 diffusion through GDL layer
- Diffusion+Reaction(?) through the membrane
- I_d --- for H_2O_2 redox at center electrodes

Full MEA Setup



Allows us to measure:

- Mass transfer through GDL
- Mass transfer+dis-proportionation through catalyst layer

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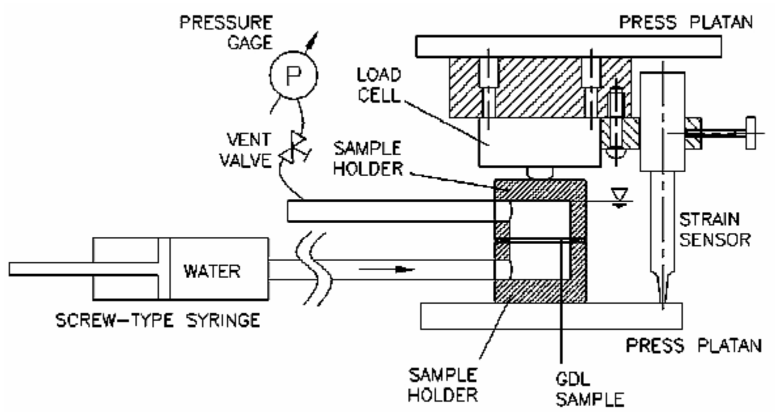
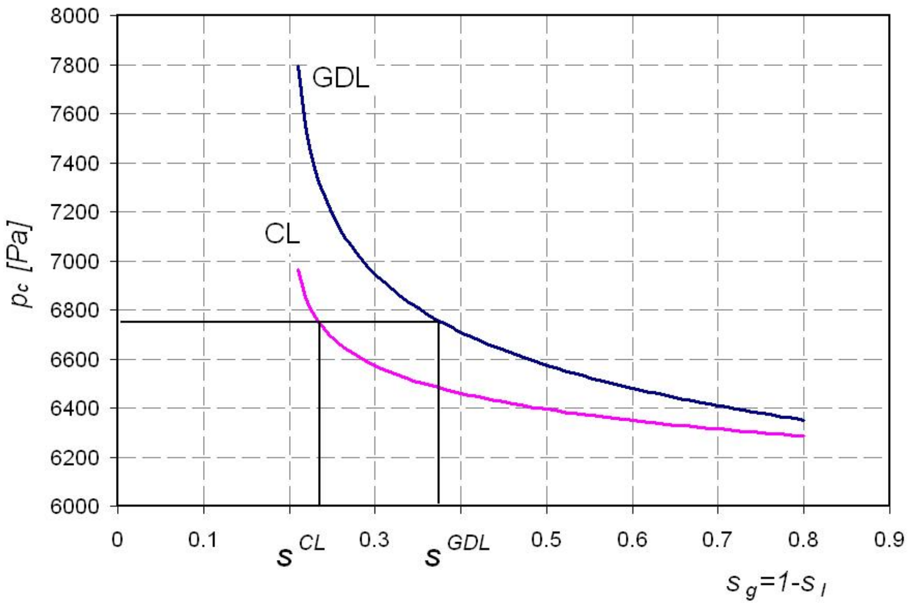
GDL Characterization – Capillary Pressure

Motivation:

- Inherently, catalyst layers lack the flexibility to control the amount of water that resides in its pores during fuel cell operation;

- GDLs may be designed to promote or inhibit water flow out of the catalyst layer pores; to achieve this, one needs to be able to assess the capillary pressure as function of water saturation $P_c(s)$ in the GDL;





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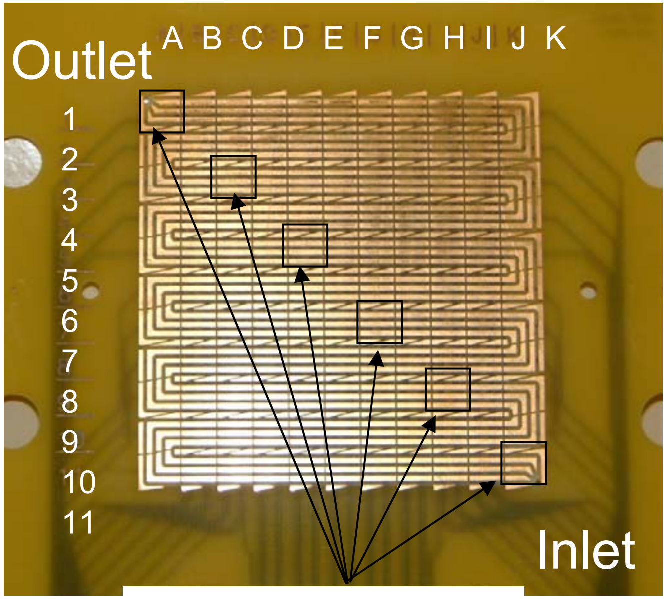
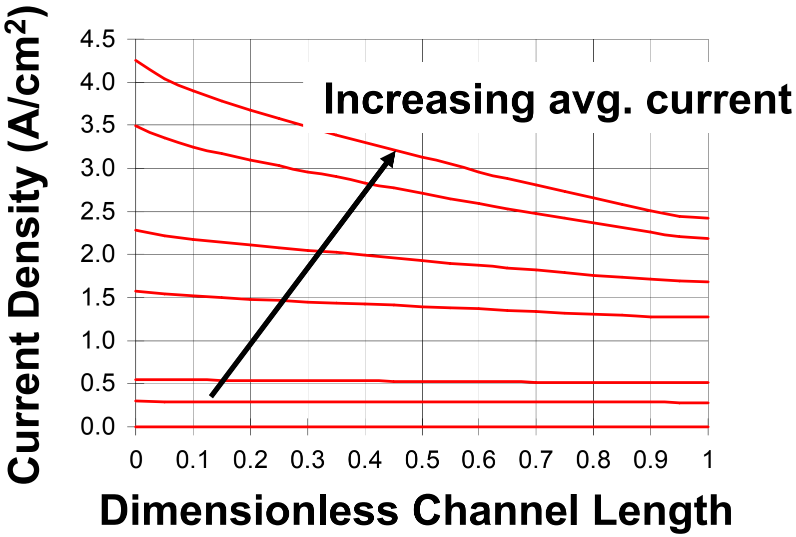
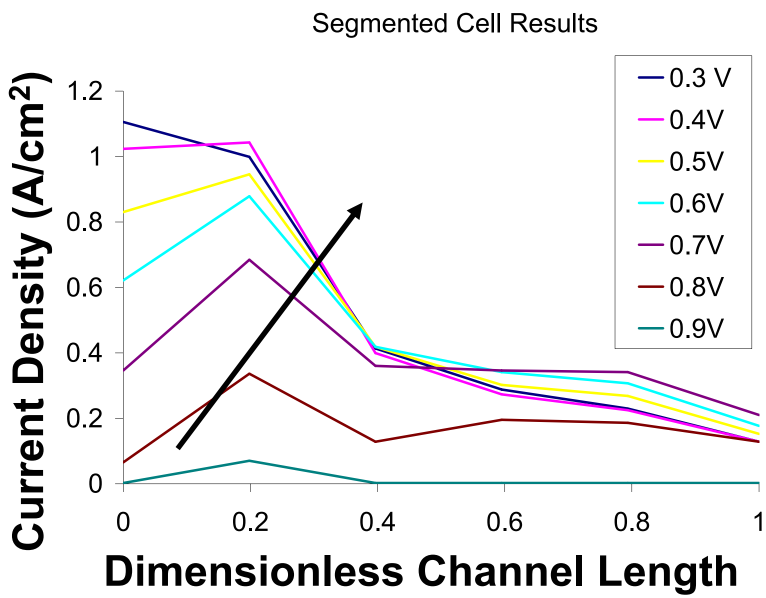
Segmented Cell - Update



Selected segments

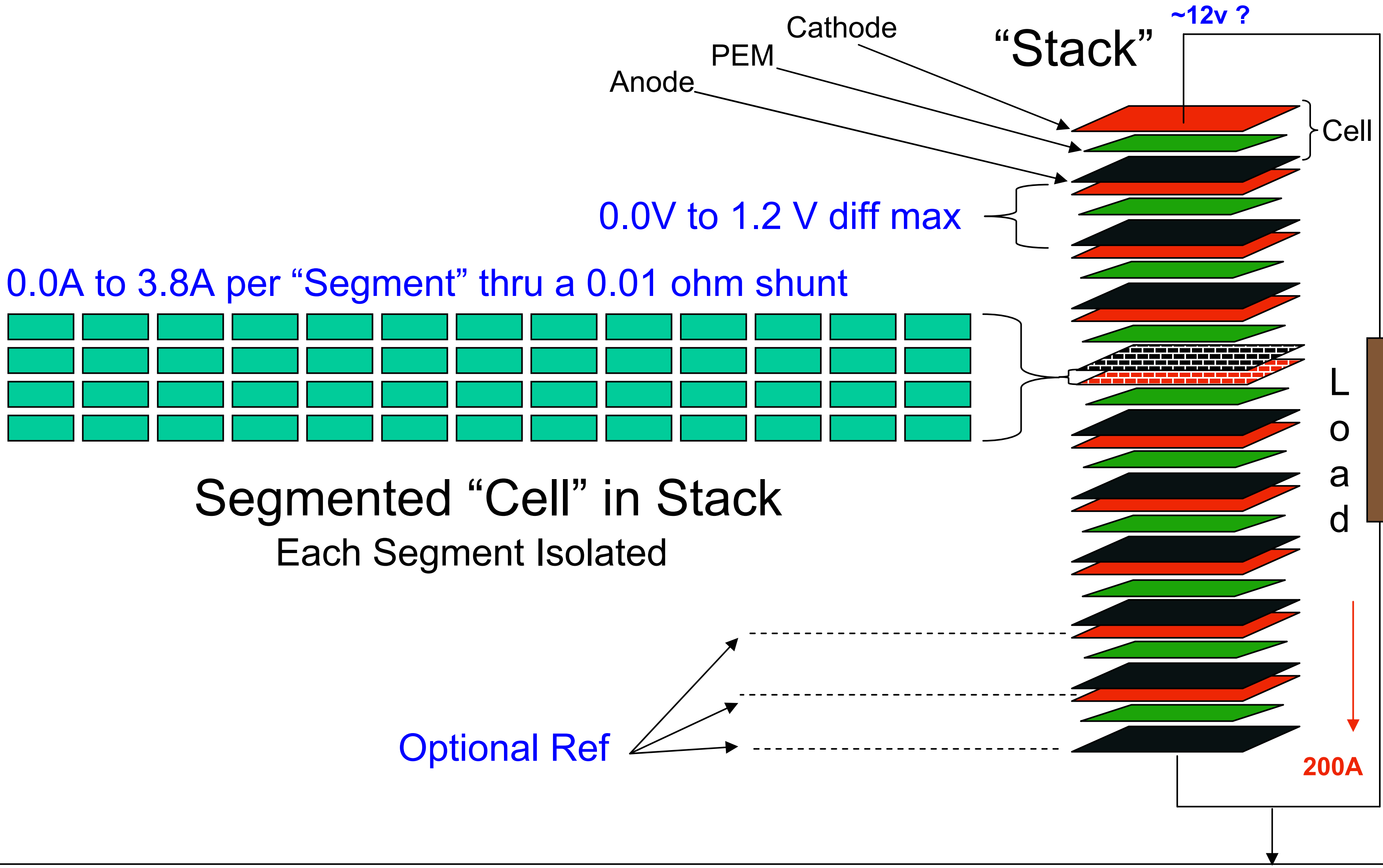
- Recently completed 121 channel load
- Cell design validated
- Design fuel cell systems to operate at high stoichiometry for uniformity
- Cell for Plug Power under fabrication





Segmented Cell for GenSys Stack

Objective – Study cell uniformity in real system. Optimize operating parameters for performance and durability



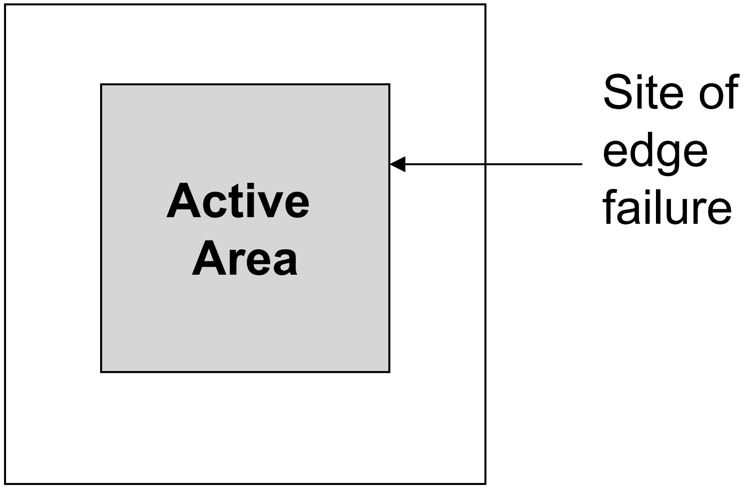
Film Edge Protection

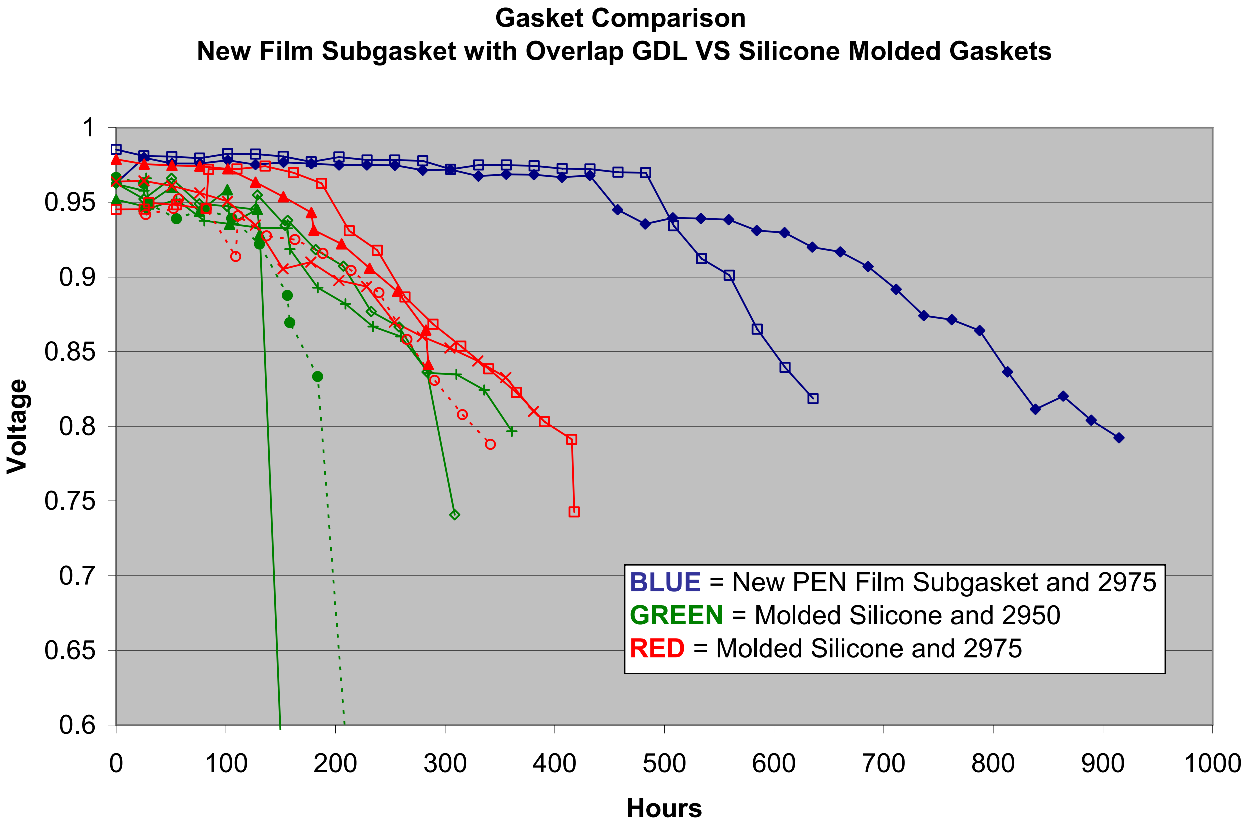
Problem

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

Solution

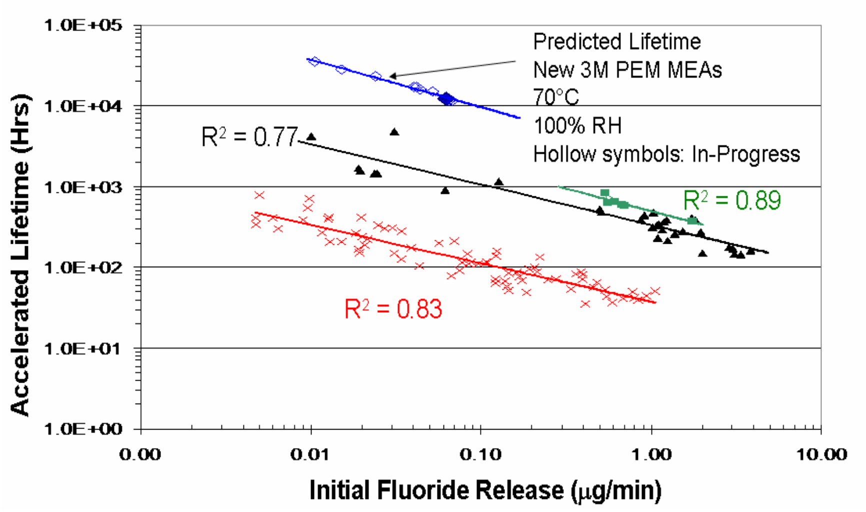
- Developed edge protection component for MEA

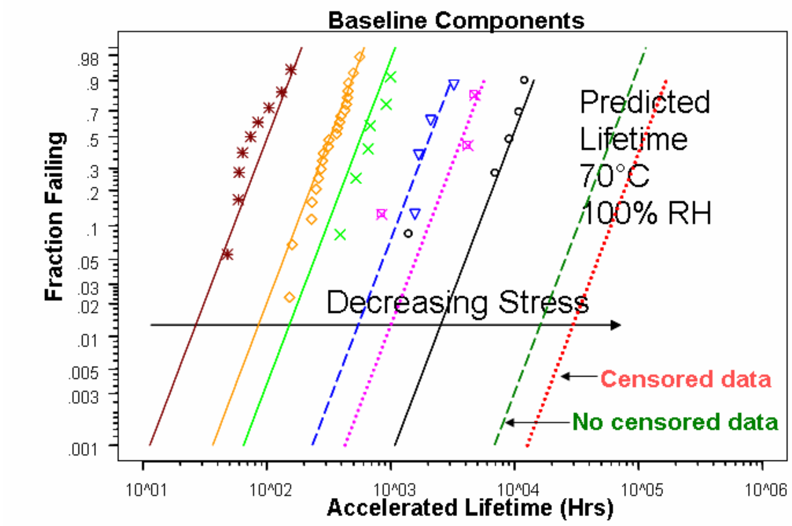




- Identified MEA failure mode
- Increased Lifetime Observed in Accelerated tests
- Reduced infant mortality in non-accelerated tests

Combine Fluoride Ion Mapping and Statistical Lifetime Modeling





Fluoride Release and Lifetime Correlation

– Uses Strong correlation for initial fluoride release

SPLIDA Statistical Modeling Using

– Lognormal distribution
– Arrhenius for temp
– Humidity model for RH

Using SPLIDA Software

Unified Prediction Equation

$$Lifetime = \frac{A}{T+273} + H * LN\left(\frac{RH}{100-RH}\right) + F * LN(FRR) + I$$

Where:

– A = Arrhenius Constant
– H = Humidity Constant
– F = Fluoride Release Constant
– I = Intercept

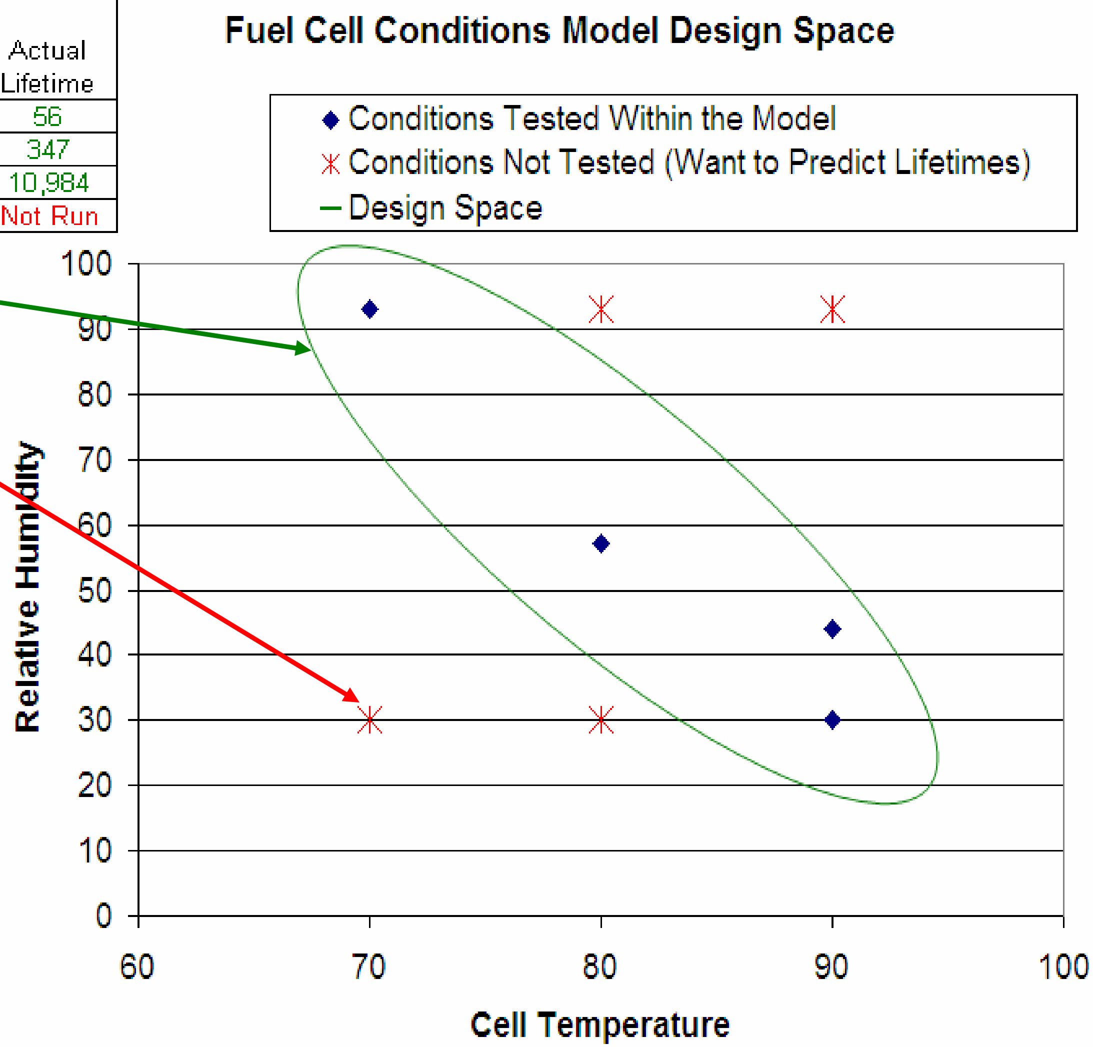
* Load cycle differences not included yet

Equation Predictions

Conditions	Fluoride Release	Equation Prediction Lifetime	95% Lower Confidence Interval	95% Upper Confidence Interval	Actual Lifetime
90°C 30%RH	0.46	63	56	70	56
90°C 44%RH	1.11	329	291	372	347
70°C 93%RH	0.04	11,314	9,272	13,817	10,984
90°C 93%RH	0.50	5,633,891	1,079,697	29,410,394	Not Run

Predictions reasonable within oval design space

Predictions unreasonable due to poor temperature correlation

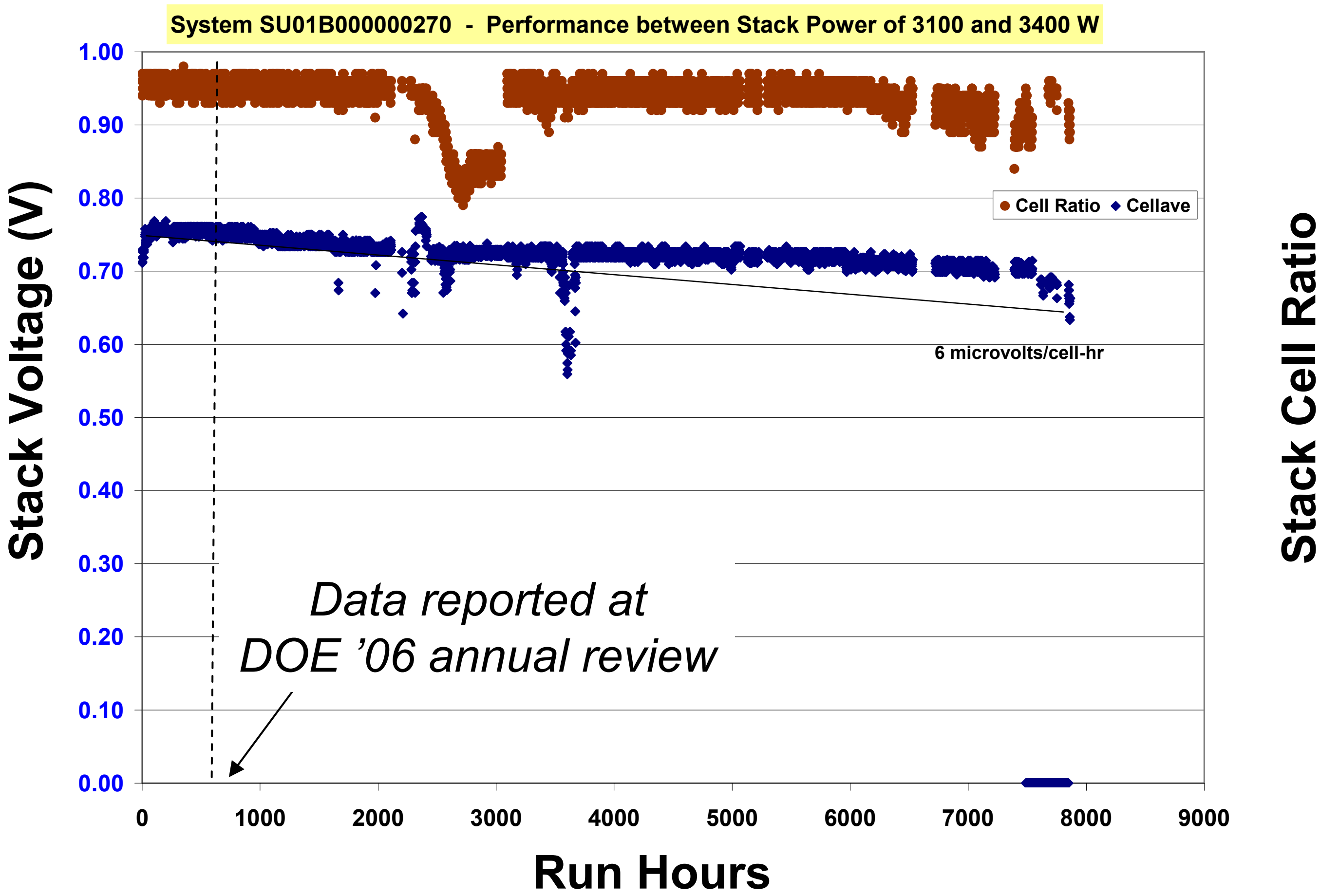


Unified Prediction Equation made by SPLIDA Software

- Reasonable predictions for data within design space that has been tested
- Unreasonable predictions outside the design space due to inaccurate temperature dependence
- Need data at different temperatures with same RH

DOE4 MEA in SU1 System

Objective – Demonstrate Intermediate advances



- New Membrane
- New Catalyst
- New GDL
- First Generation System

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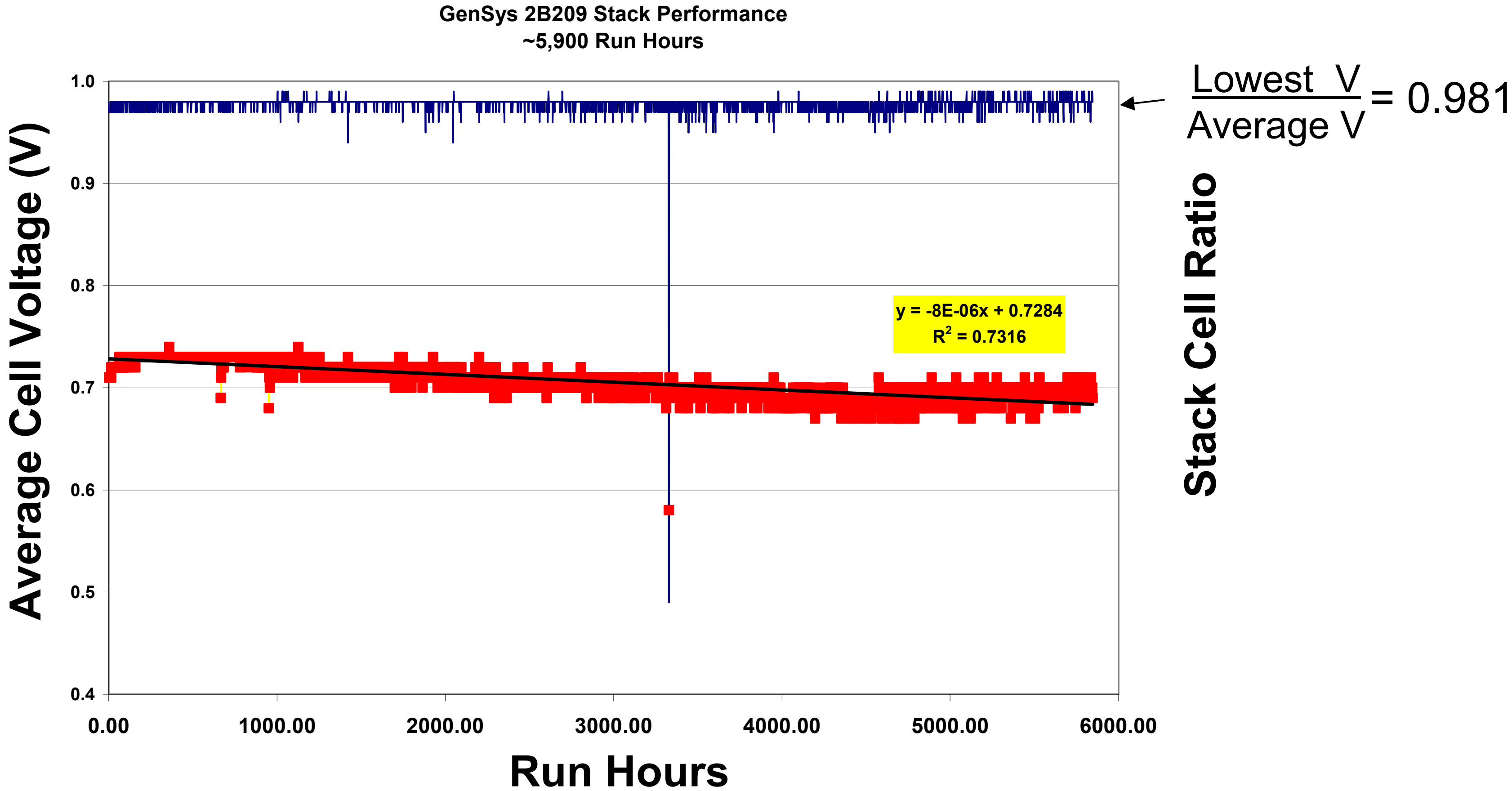
DOE4 Membrane in GenSys System

Objective – Demonstrate Intermediate Advances



- New Membrane
- Improved System
- First Generation Catalyst
- *No low cell shut downs*
- *No maintenance for 257 consecutive days*

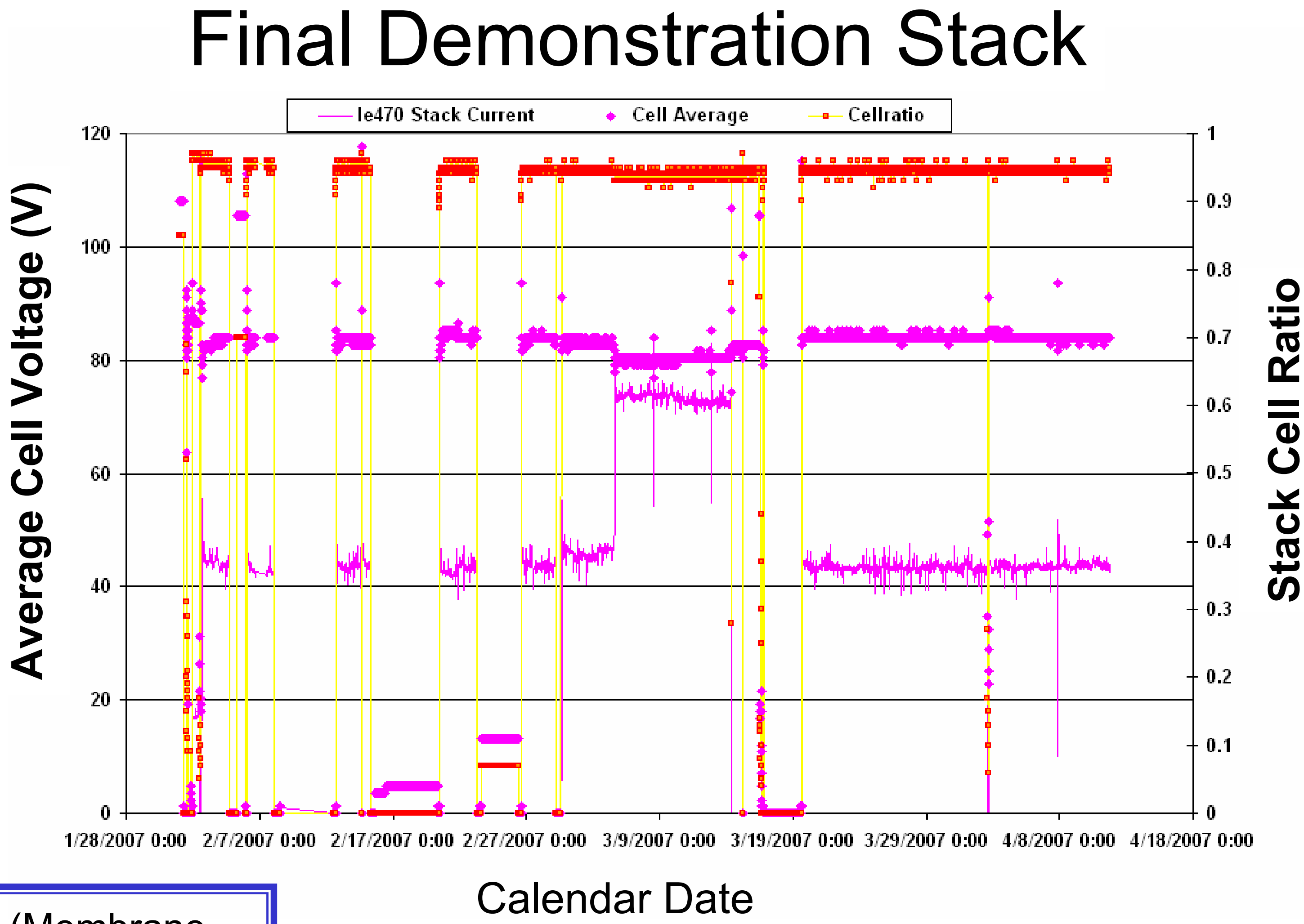
DOE4 MEA in Final GenSys System

Objective – Demonstrate Final Components and System for 2,000 hours per statement of work

- Installed DOE Final 4 stack in GenSys Unit 2B304 on 2/1/2007.
- Total stack hours as of 3/31/2007 = 996 hrs (3374 kw-hrs)
- System Efficiency actual 28.69% vs goal of 28.5 to 30%
- Low Degradation
    - - 3.02 microvolts/cell hr Entire 59 day run
    - 0.151 microvolts/cell hr last 10 days (3/20/07 to 4/3/07)
- High Number of low cell trips 10 to date vs goal of 0
- Low Cell Trips: Perform Stack Testing to confirm System Delta T Model
- ***Anticipating 2000 stack hours will be achieved by early June***

DOE4 MEA in Final GenSys System

Objective – Demonstrate Final Components and System for 2,000 hours per statement of work



- Final MEA (Membrane, Catalyst, GDL)
- Improved System

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Future Work – To the End of the Project

MEA & Stack Development & Testing

- Run until failure Saratoga stack tests – Plug Power
- Run until failure ‘Final’ stack and MEA design and test – Plug Power/3M
- Module testing on continual component improvements

MEA Degradation Studies (update based upon CASE data)

- 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

- Continue to update MEA lifetime modeling – 3M/Plug Power
- Add temperature and humidity conditions to balance model
- Final MEA design started

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**	**FY '07**	**DOE 2010 Goal (hrs)**
Accelerated Lifetime Predictions (hrs)	16,000	> 20,000	> *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: Continue system tests