DOE Hydrogen Program

2007 DOE Hydrogen Program Review

MEA & Stack Durability for PEM Fuel Cells

3M/DOE Cooperative Agreement

No. DE-FC36-03GO13098

Project ID # FC10

3M

Mike Yandrasits

3M Company

May 16, 2007

Powered by 3M

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.

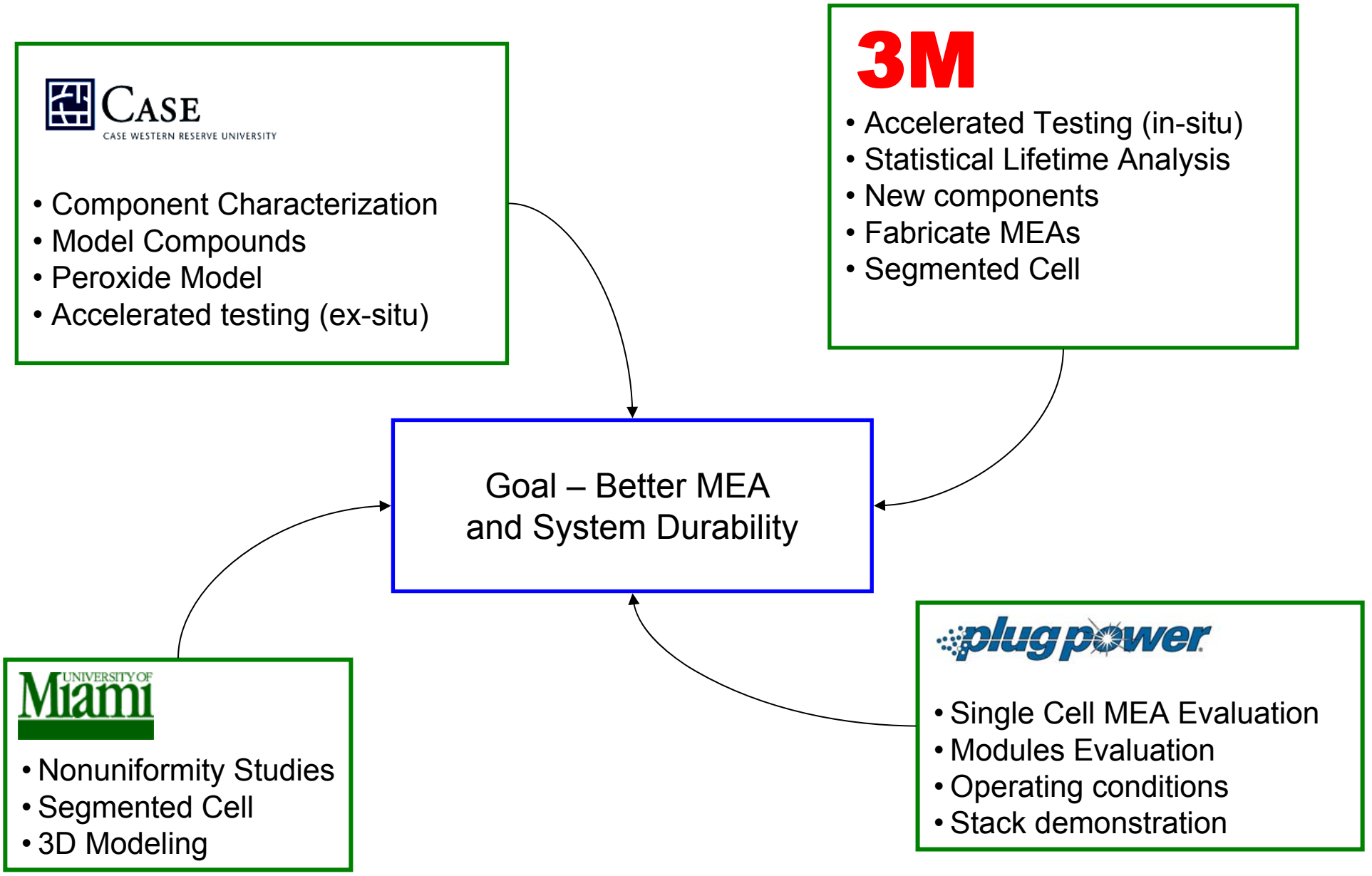
Goal: *Develop an MEA and System with enhanced durability*

- 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
CASE WESTERN RESERVE UNIVERSITY
• Component Characterization
• Model Compounds
• Peroxide Model
• Accelerated testing (ex-situ)
3M
• 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
plug power
• 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

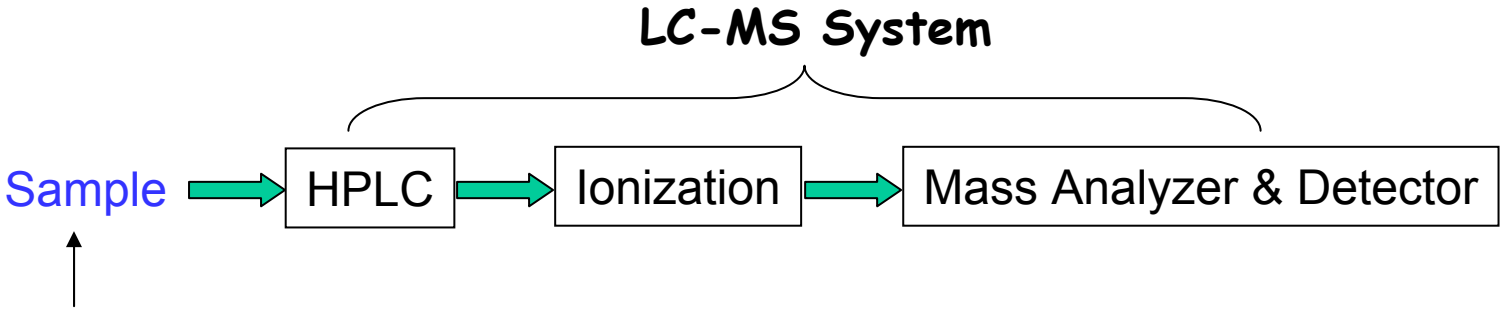
Reaction terms:
- H_2O_2 decomposition rate in electrodes (Multidecker sandwich cells)
- peroxide reaction rate with PFSAs (Model compounds w/kinetic analysis)

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

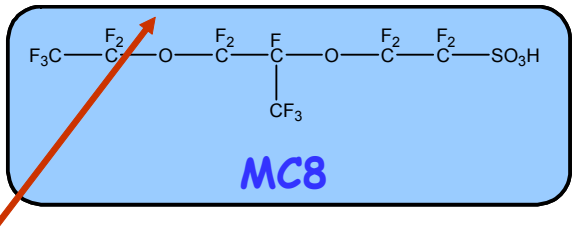
$$\frac{d}{dt}\left(C_{H_2O_2}\right) = Rate\ of\ \ production\left(electrochemical + Chemical\ recombination\right)$$
$$+ Rate\ of\ \ consumption\begin{pmatrix} Ionomer\ degradation + catalytic\ disproportionation \\ + electrochemical\ reduction \end{pmatrix}$$
$$+ Transport\ through\ the\ electrode\left(Diffusion + Convection\right)$$

CASE
CASE WESTERN RESERVE UNIVERSITY

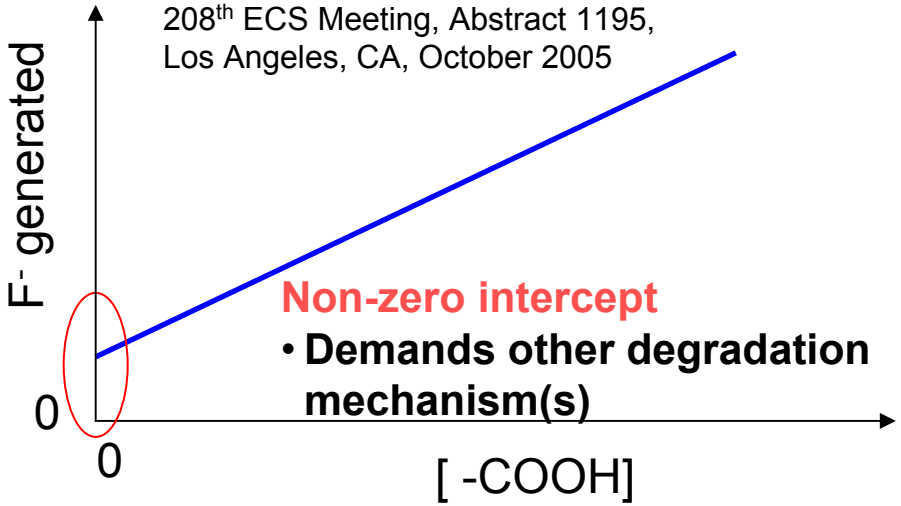
Model Compound Studies

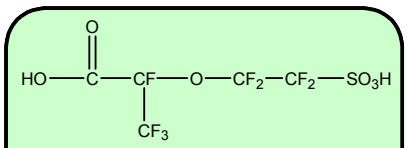


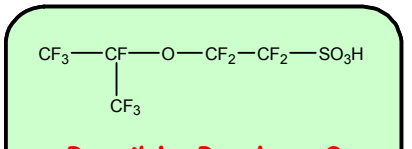
"Side chain" cleavage appears to occur with the model compound

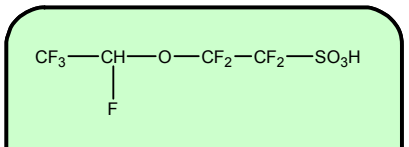


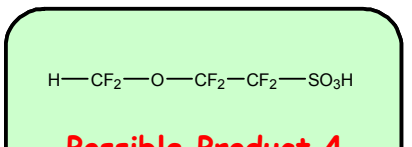
208th ECS Meeting, Abstract 1195, Los Angeles, CA, October 2005







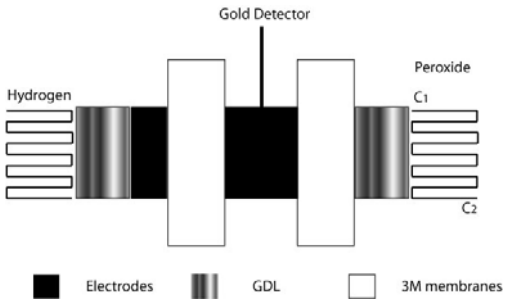




CASE
CASE WESTERN RESERVE UNIVERSITY

H_2O_2 Transport and Reaction Processes

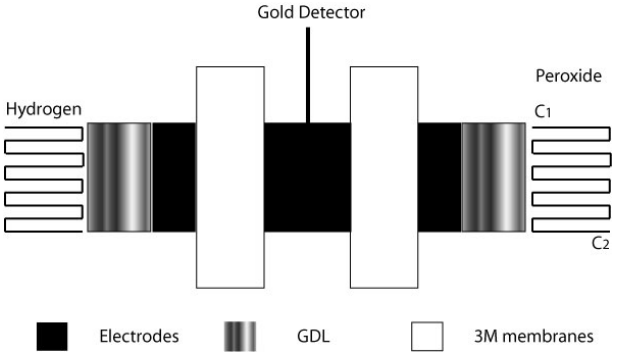
Half MEA Setup



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:

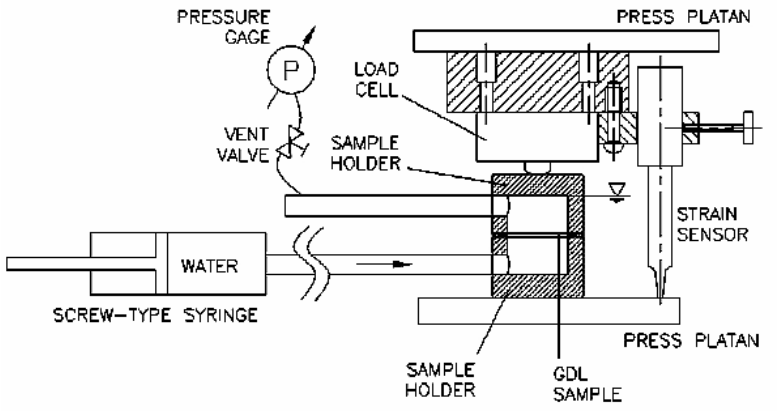
- Mass transfer through GDL
- Mass transfer+dis-proportionation through catalyst layer

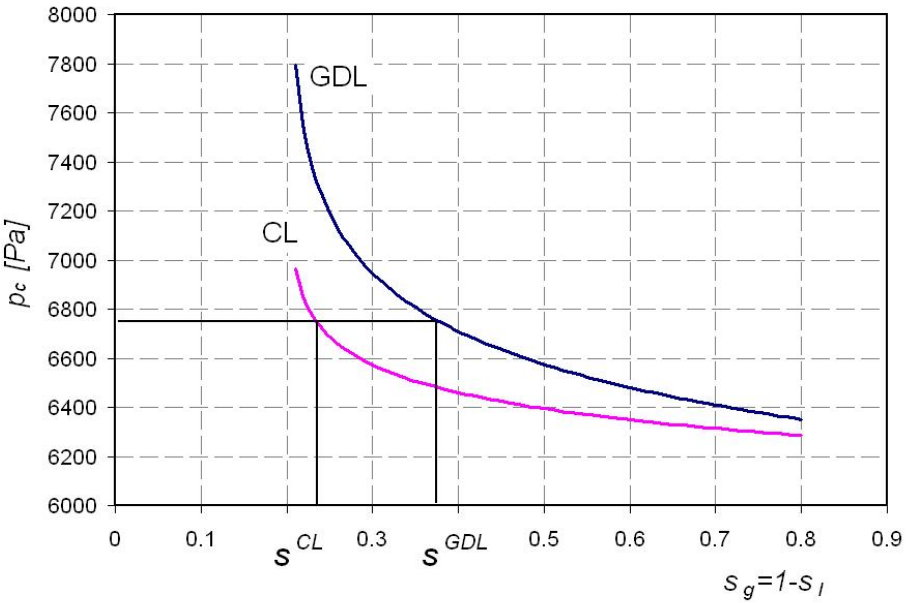
CASE
CASE WESTERN RESERVE UNIVERSITY

GDL Characterization – Capillary Pressure

Motivation:

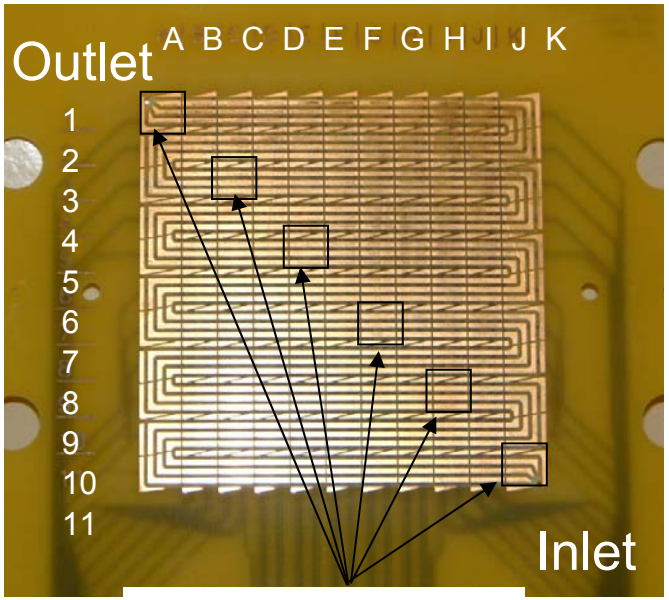
- Inherently, catalyst layers lack the flexibility to control the amount of water that resides in its pores during fuel cell operation;
- GDLs may be designed to promote or inhibit water flow out of the catalyst layer pores; to achieve this, one needs to be able to assess the capillary pressure as function of water saturation $P_c(s)$ in the GDL;





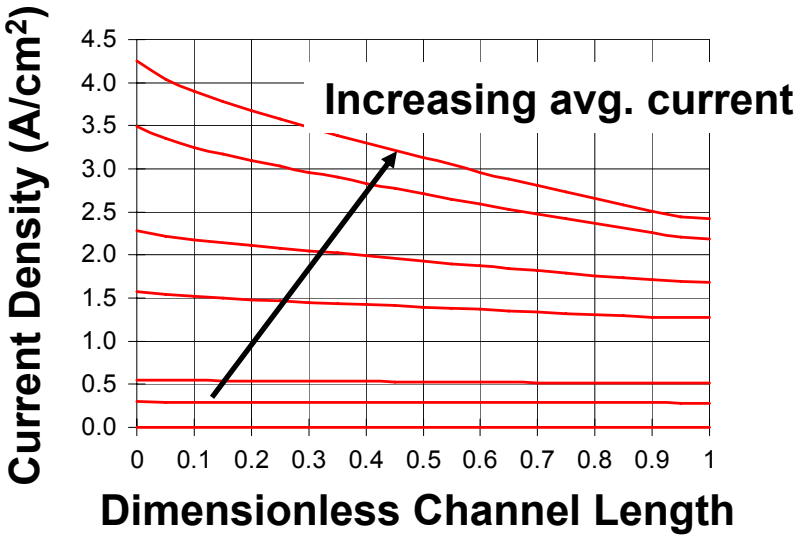
CASE
CASE WESTERN RESERVE UNIVERSITY

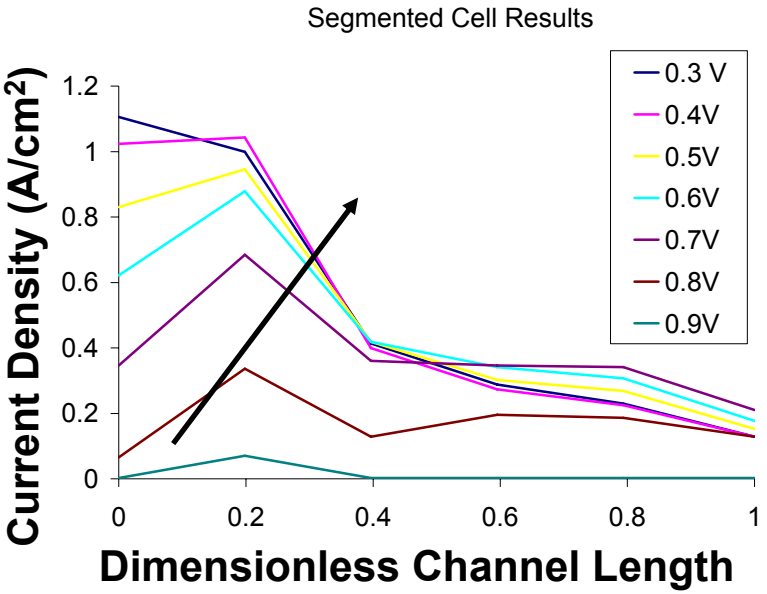
Segmented Cell - Update



Selected segments

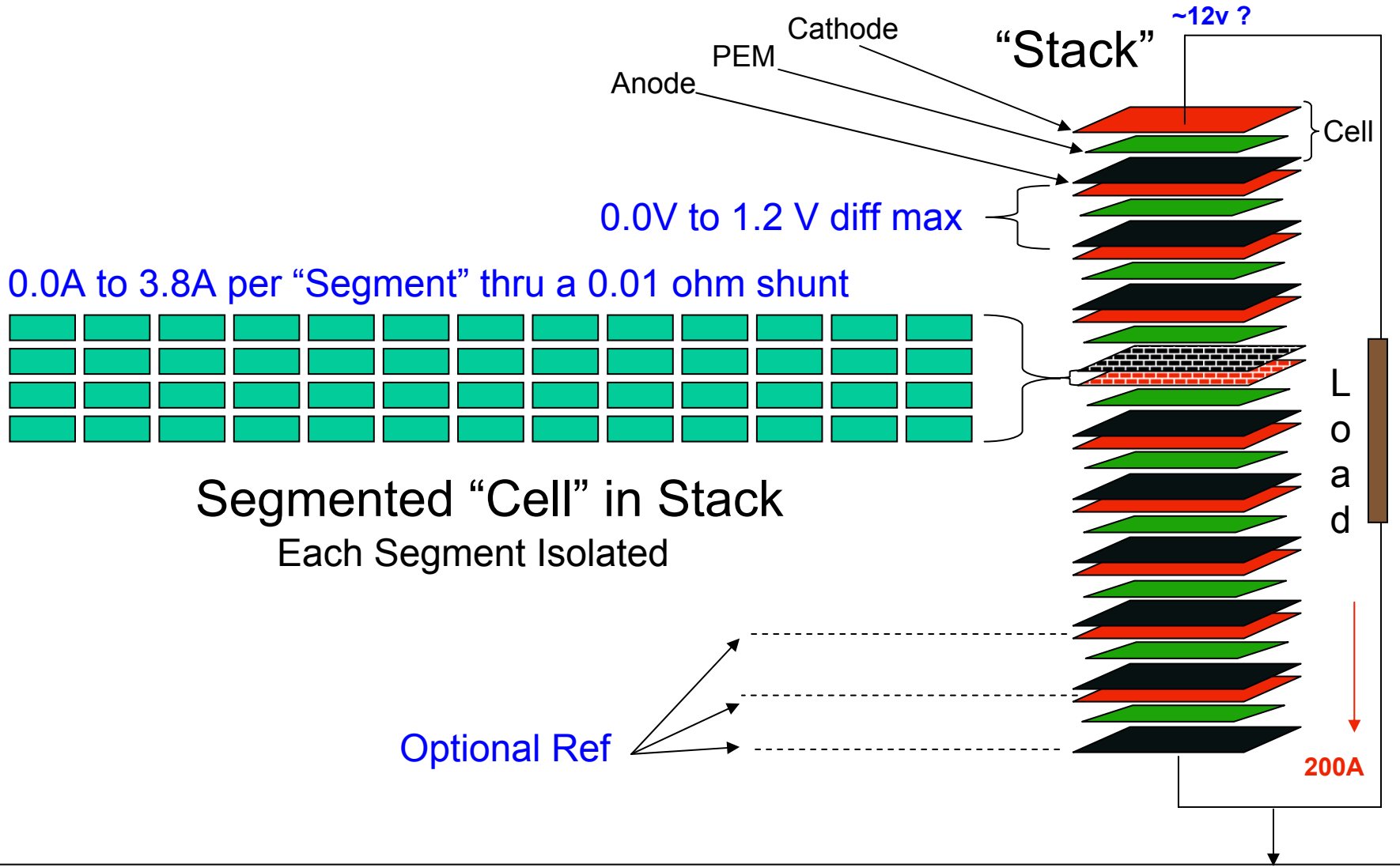
- Recently completed 121 channel load
- Cell design validated
- Design fuel cell systems to operate at high stoichiometry for uniformity
- Cell for Plug Power under fabrication





Segmented Cell for GenSys Stack

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



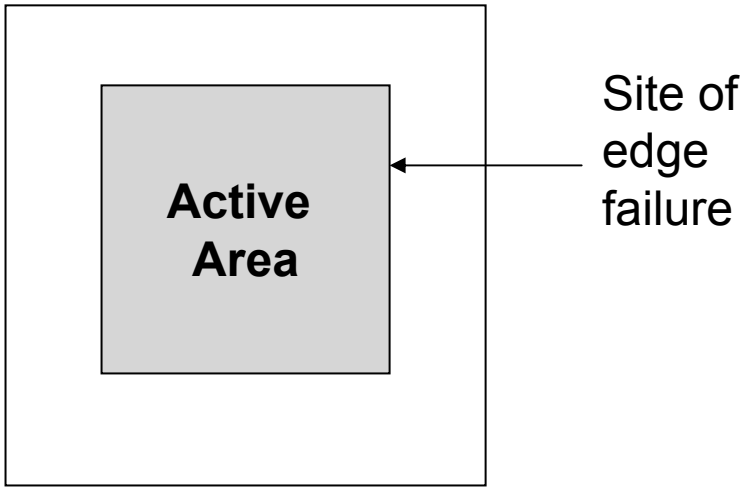
Film Edge Protection

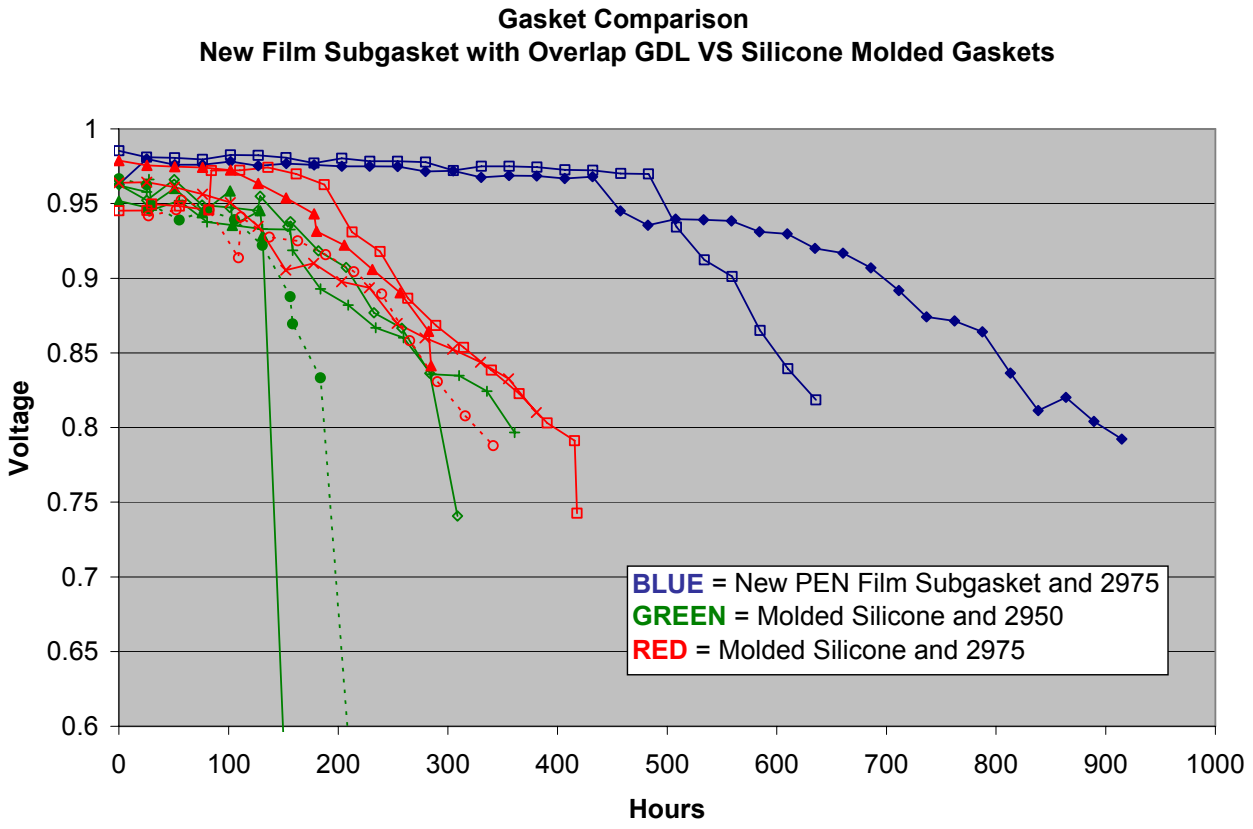
Problem

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

Solution

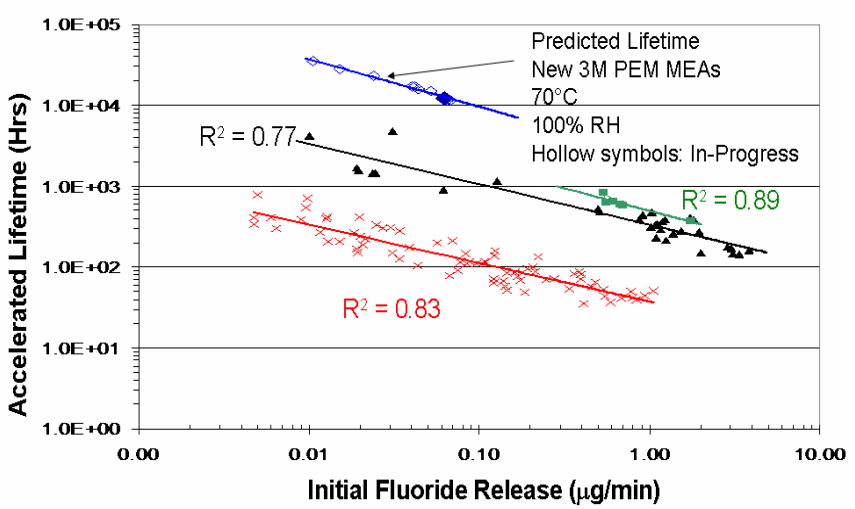
- Developed edge protection component for MEA

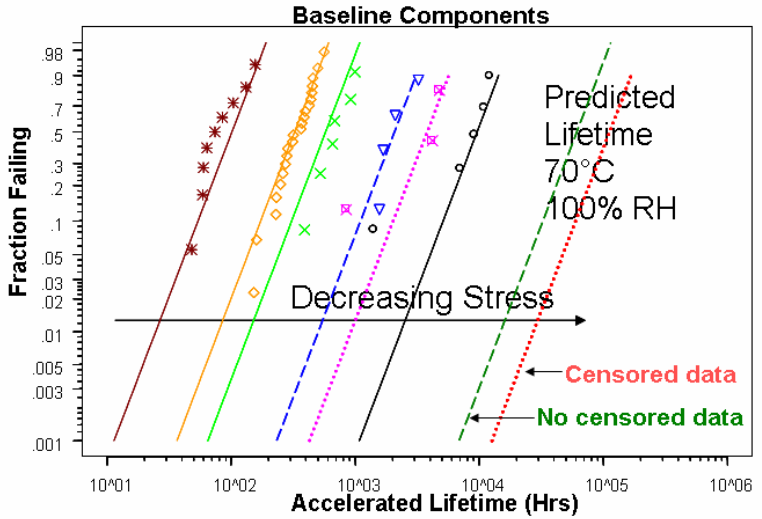




- Identified MEA failure mode
- Increased Lifetime Observed in Accelerated tests
- Reduced infant mortality in non-accelerated tests

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

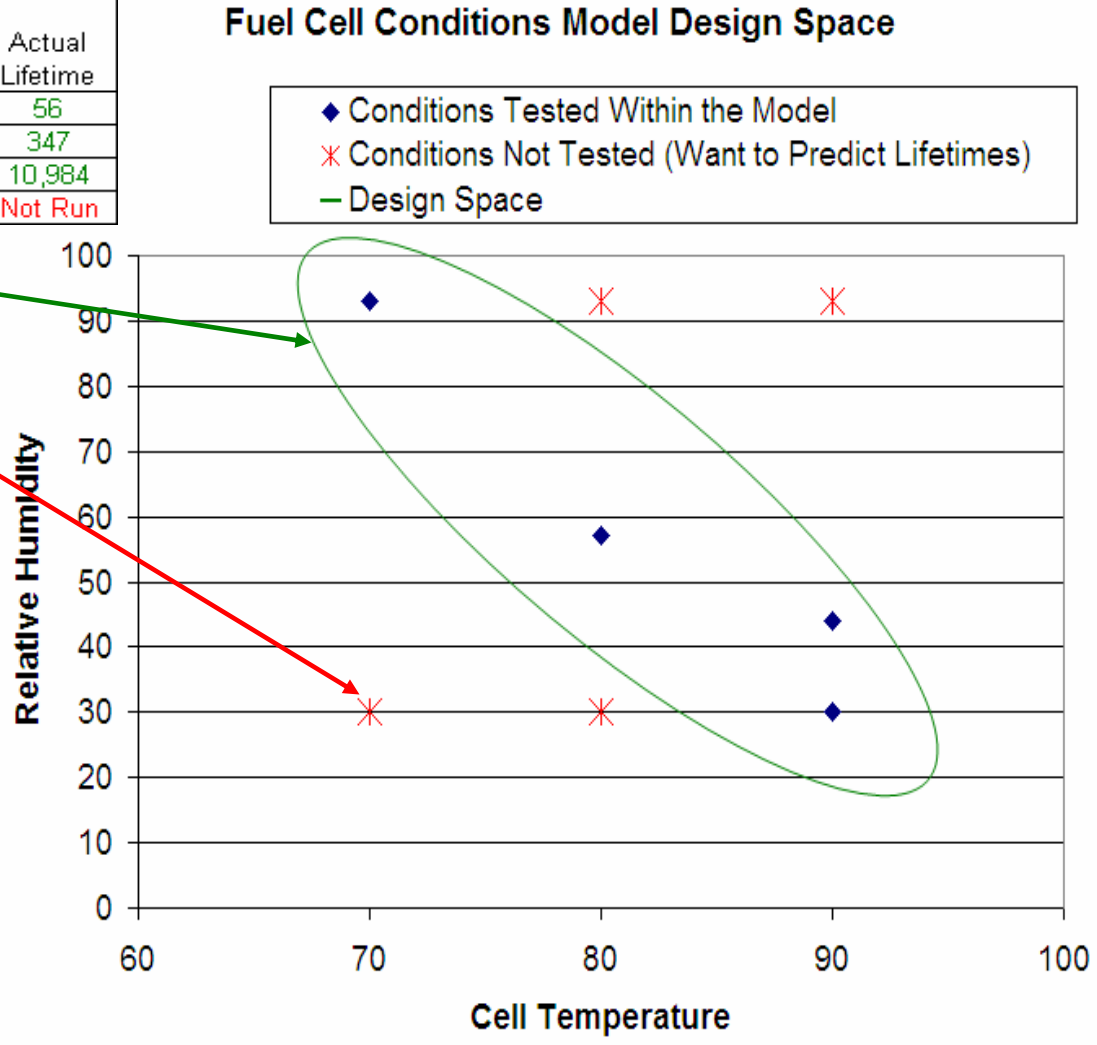
Statistical MEA Lifetime Model Unified Equation

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

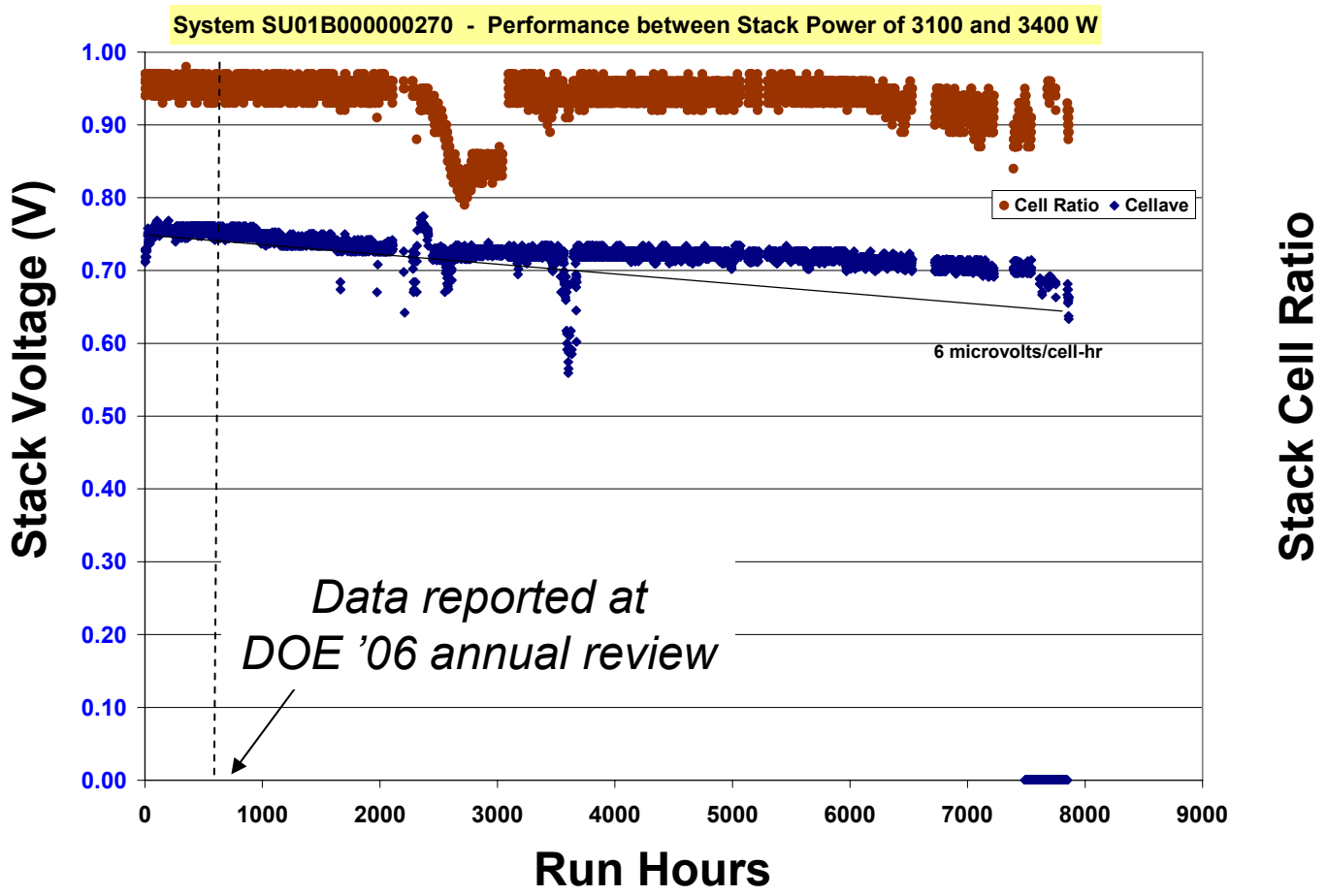


Unified Prediction Equation made by SPLIDA Software

- 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

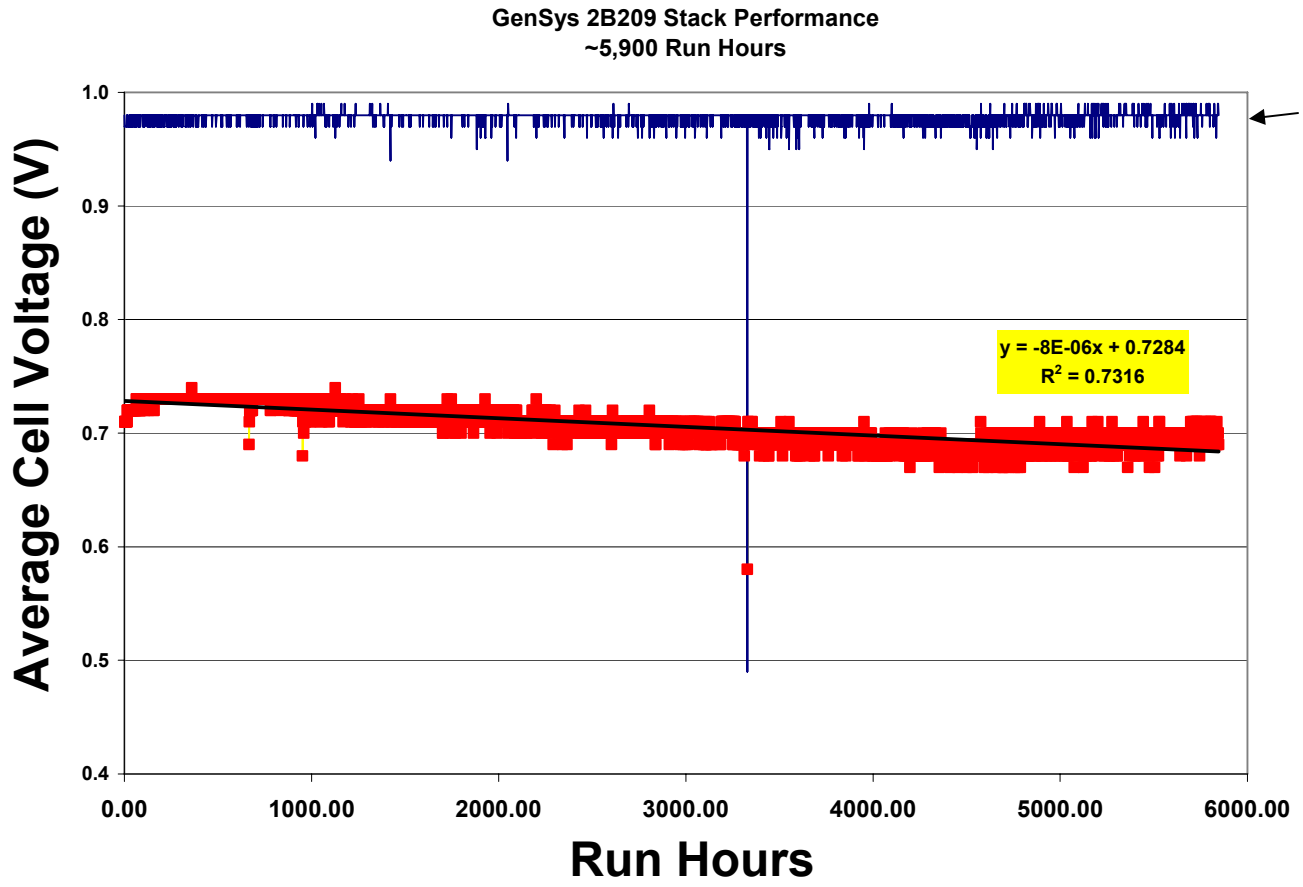
Objective – Demonstrate Intermediate advances



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

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

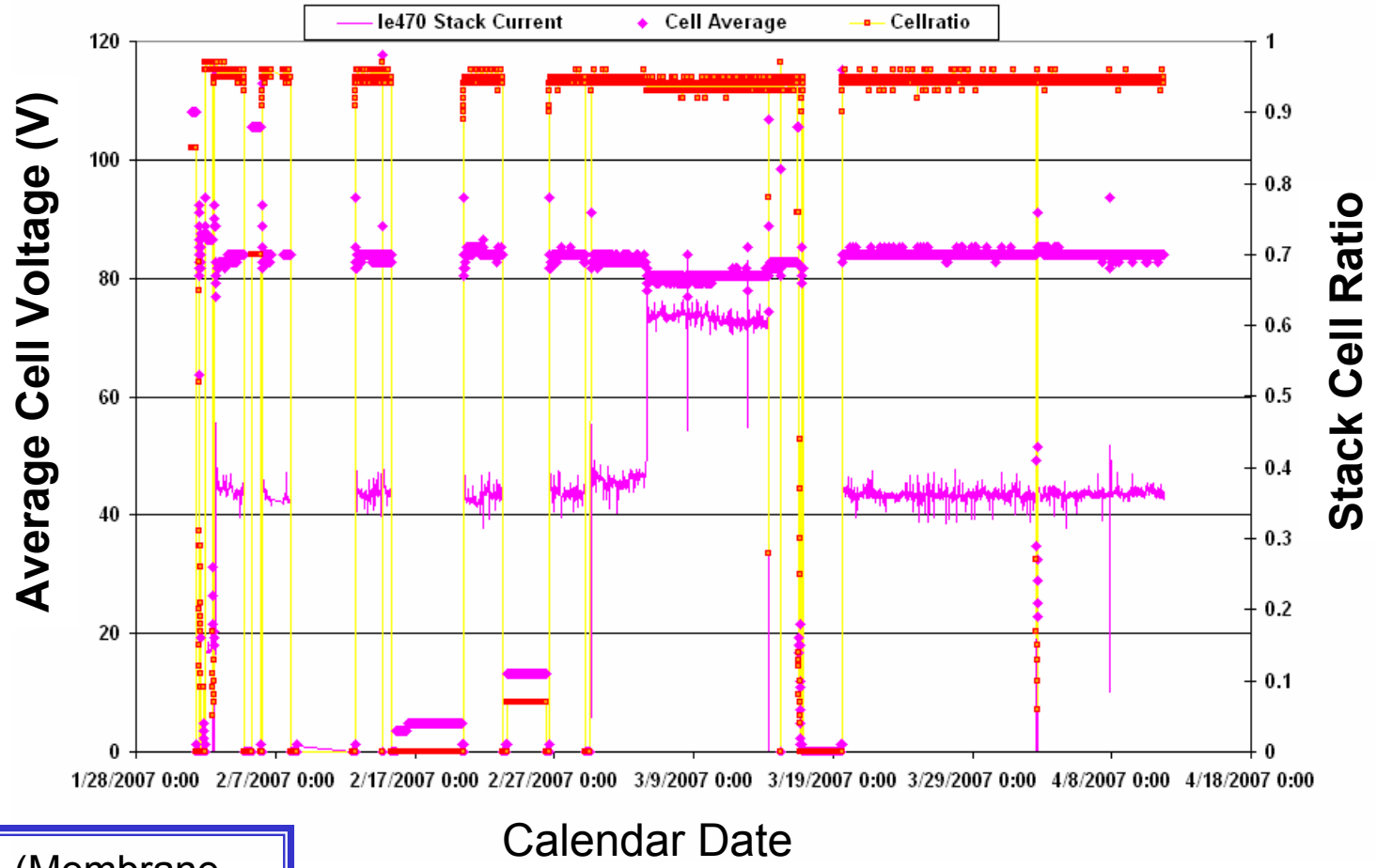
- Installed DOE Final 4 stack in GenSys Unit 2B304 on 2/1/2007.
- Total stack hours as of 3/31/2007 = 996 hrs (3374 kw-hrs)
- System Efficiency actual 28.69% vs goal of 28.5 to 30%
- Low Degradation
    - - 3.02 microvolts/cell hr Entire 59 day run
    - 0.151 microvolts/cell hr last 10 days (3/20/07 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***

plug power

DOE4 MEA in Final GenSys System

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

Final Demonstration Stack



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

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