2006 DOE Hydrogen Program Review

MEA & Stack Durability for PEM Fuel Cells

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

Project ID # FC8

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This presentation does not contain any proprietary or confidential information
### 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
**Hypothesis** - Need reinforcing member to carry stress to eliminate mechanical failure or reduce mechanical failure rate

**RH Cycle Test to Evaluate Hypothesis**

**Test Conditions:**
80°C

Cycle equally between 0 and 150% RH

<table>
<thead>
<tr>
<th>MEA (electrode and GDL) made with:</th>
<th>Time to failure (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DuPont™ Nafion® (NR-111)¹</td>
<td>260 – 330</td>
</tr>
<tr>
<td>Ion Power™ Nafion® (N111-IP)¹</td>
<td>1330 +</td>
</tr>
<tr>
<td>Gore™ Primea®¹</td>
<td>400 – 470</td>
</tr>
<tr>
<td>3M Cast Nafion® (1000 EW)</td>
<td>1200 +</td>
</tr>
</tbody>
</table>

**Evaluation of Various Reinforcing Members**

- Lines – 3M Cast Nafion® Membrane
- Symbols – Various reinforced membranes with 3M Ionomer

- Desired Result – stronger and higher conductivity than neat Nafion

- **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

![Graph showing relative MEA failure rate with and without edge protection]

- No Failures with edge protection
- Significant increase in failure rate without edge protection

Site of edge failure
**Membrane Aging Procedure**

1. **Received Membrane**
   - H⁺ Form

2. **Pre-condition**
   - Ion exchange with H₂SO₄ (0.1M)
   - 70°C, 1 hour

3. **H⁺ Form**
   - Ion exchange with FeSO₄ (0.1M)
   - 70°C, 2 hours

4. **Fe(II) Form**
   - Ion exchange with H₂O₂ (0.1M)
   - 70°C, ~35 hours

5. **Degraded Membrane**
   - Fe(II) Form

- **Measure degraded membrane properties over time**

**Dynamic Mechanical Analysis**

- ‘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$_2$O$_2$ 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)

Non-zero intercept
- Demands other degradation mechanism(s)

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

MEA & Stack Durability for PEM Fuel Cells
Model Compounds Relative Degradation Rates

**MC3 > MC1 ≈ MC2 > MC4 > MC7 & MC8**

- **MC3**
  - $\text{HO} - \text{C} - \text{C} - \text{C} - \text{C} - \text{SO}_3\text{H}$
- **MC1**
  - $\text{HO} - \text{C} - \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{CF}_3$
- **MC2**
  - $\text{HO} - \text{C} - \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{SO}_3\text{H}$
- **MC4**
  - $\text{F}_3\text{C} - \text{C} - \text{O} - \text{C} - \text{F}_2$
- **MC7**
  - $\text{F}_3\text{C} - \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{SO}_3\text{H}$
- **MC8**
  - $\text{F}_3\text{C} - \text{C} - \text{O} - \text{C} - \text{C} - \text{SO}_3\text{H}$

- 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**

- $\text{F}_3\text{C} - \text{C} - \text{O} - \text{C} - \text{C} - \text{OH}$
- $\text{F}_3\text{C} - \text{C} - \text{O} - \text{C} - \text{C} - \text{CF}_2$

**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:

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

\[
+ \text{Rate of consumption} \left( \text{Ionomer degradation} + \text{catalytic disproportionation} + \text{electrochemical reduction} \right)
\]

\[
+ \text{Transport through the electrode} \left( \text{Diffusion} + \text{Convection} \right)
\]

Geometry

O₂ inlet
No peroxide

\[ Z = 0 \quad \text{Peroxide to membrane} \quad Z = 1 \]

Experiments to Determine Input Parameters

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

Model Output

Peroxide Concentration Profile as f(L)

0.75 V = \eta

\[ \frac{C}{C_0} \]

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

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


Approach

• Measure experimentally – segmented cell
• Theoretical modeling
Segmented Cell

Validation of Cell Design

- Filled Symbols – Sum of Individual Segments
- Hollow Symbols – Fuel Cell (Segments shorted together)

Effect of Air Flow Rate on Current Distribution

- O₂ Utilization = 0.99 0.96 0.56 0.31

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

MEA & Stack Durability for PEM Fuel Cells
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
**Objective** – Investigate possible interaction between system design and durable MEA design

- No negative MEA – System interaction
- Program approach validated
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

Baseline MEAs

New 3M PEM MEAs

~ 4x

Baseline Components

- Predicted Lifetime
- 70°C
- 100% RH

0.001 0.003 0.005 0.007 0.01

10^01 10^02 10^03 10^04 10^05 10^06

Accelerated Lifetime (Hrs)

Fraction Failing

Decreasing Stress

Censored data

No censored data

- 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

**Graph Details:**
- **Predicted Lifetime**
  - New 3M PEM MEAs
  - 70°C
  - 100% RH
- **R² Values:**
  - R² = 0.77
  - R² = 0.89
  - R² = 0.83

**Near-OCV Load Cycle**
- I (A/cm²)
- Time
- Initial Fluoride Release (μg/min)
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.

<table>
<thead>
<tr>
<th>Accelerated Lifetime Predictions (hrs)</th>
<th>FY ’05</th>
<th>FY ’06</th>
<th>DOE 2010 Goal (hrs)</th>
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<tbody>
<tr>
<td></td>
<td>16,000</td>
<td>&gt; 20,000</td>
<td>40,000</td>
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**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

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

• 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

MEA & Stack Durability for PEM Fuel Cells

3M Fuel Cell Components
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