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
To develop an MEA with enhanced durability ….

- 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
Reinforced Membrane Activities

Membrane Stress Model

Evaluation of Various Reinforcing Members

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>

• 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?

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

Relative MEA Failure Rate

<table>
<thead>
<tr>
<th></th>
<th>w/o Edge Protection</th>
<th>w/ Edge Protection</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Failures</td>
<td>0</td>
<td>120</td>
</tr>
<tr>
<td>w/o Edge Protection</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>w/ Edge Protection</td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

Site of edge failure

• Identified MEA failure mode
• Implemented a solution to significantly reduce infant mortality failure rate
**3M Ionomer Membrane Properties vs Decay**

**Membrane Aging Procedure**

- Pre-condition w/ $\text{H}_2\text{SO}_4$ (0.1M) at 70°C, 1 hour
- Ion exchange w/ FeSO$_4$ (0.1M) at 70°C, 2 hours
- Ion exchange w/ $\text{H}_2\text{SO}_4$ (0.1M) at 70°C, 1 hour
- $\text{H}_2\text{O}_2$ (0.1M) at 70°C, ~ 35 hours

- Measure degraded membrane properties over time

**Graphs:**
- **Dynamic Mechanical Analysis**
  - ‘As Received’
  - ‘$\text{H}^+$ Form’
  - ‘Degraded Sample @ 125 hrs’
  - Aging experiments in progress
  - No change after 125 hrs

- **Thermal Gravimetric Analysis**
  - MEA & Stack Durability for PEM Fuel Cells
Membrane Decay Mechanism Via Model Compounds

‘Conventional Wisdom’:
- H$_2$O$_2$ generated during fuel cell operation
- HO$^\cdot$ 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

\[
\text{HO-C-F-O-C-F}_2\text{CF}_3
\]

MC2

\[
\text{HO-C-F-O-C-F}_2\text{F}_2\text{SO}_3\text{H}
\]

MC3

\[
\text{HO-C-C-C-C-SO}_3\text{H}
\]

MC4

\[
\text{F}_3\text{C}
\]

MC7

\[
\text{F}_3\text{C-C-O-C-F}_2\text{F}_2\text{SO}_3\text{H}
\]

MC8

\[
\text{F}_3\text{C-C-O-C-F}_2\text{F}_2\text{SO}_3\text{H}
\]
Model Compounds Relative Degradation Rates

\[ \text{MC3} > \text{MC1} \approx \text{MC2} > \text{MC4} > \text{MC7 & MC8} \]

- 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:
\[
\frac{d}{dt}(C_{H_2O_2}) = \text{Rate of production (electrochemical + Chemical recombination)}
+ \text{Rate of consumption (Ionomer degradation + catalytic disproportionation)}
+ \text{Transport through the electrode (Diffusion + Convection)}
\]

Geometry
- \(O_2\) inlet
- No peroxide
- \(Z = 0\)
- Peroxide to membrane
- \(Z = 1\)

Experiments to Determine Input Parameters
1. Rate of Peroxide Production
2. Rate of Peroxide Disproportionation

Model Output
- Peroxide Concentration Profile as \(f(L)\)

- 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

Effect of Air Flow Rate on Current Distribution

- 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
**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 more durable

Baseline Components

- Predicted Lifetime
  - 70°C
  - 100% RH

Decreasing Stress

- Censored data
- No censored data

Accelerated Lifetime (Hrs)

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

MEA & Stack Durability for PEM Fuel Cells
Fluoride Ion Mapping of Accelerated Test Data

Predicted Lifetime
New 3M PEM MEAs
70°C
100% RH
Hollow symbols: In-Progress

R² = 0.77
R² = 0.89
R² = 0.83

Initial Fluoride Release (μg/min)

• 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.

<table>
<thead>
<tr>
<th>Accelerated Lifetime Predictions (hrs)</th>
<th>FY ’05</th>
<th>FY ’06</th>
<th>DOE 2010 Goal (hrs)</th>
</tr>
</thead>
<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
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