PEM Fuel Cell Durability

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This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
2001: Project started as Fuel Cell Stack Durability on Gasoline Reformate
2004: Changed focus PEM H₂ Durability
2007: Ended. Restarted at $300k

Budget
- FY04: $900k
- FY05: $950k
- FY06: $1000k
- FY07: $0 → $300
- FY08: $300

Barriers
- Durability
- Cost
- Electrode Performance

Collaborators
- No Formal Partners
- ORNL (Karren More)
- LANL H₂ Storage Center
- Analysis:
  - Univ. New Mexico, Augustine Scientific, LANL MPA-MC
- Materials:
  - Gore, SGL, Cabot Fuel Cells
Objectives:
Quantify and Improve PEM Fuel Cell Durability

2010-2015 Technical Target: 5000 hours Durability (with cycling)

- Define degradation mechanisms
- Design materials with improved durability

- Identify and quantify factors that limit PEMFC Durability
  - Measure property changes in fuel cell components during life testing
    - Life testing of materials
      - Examine testing conditions, incl. drive cycle
    - Membrane-electrode durability
    - Electrocatalyst activity and stability
    - Electrocatalyst and GDL carbon corrosion
    - Gas diffusion layer hydrophobicity
    - Bipolar plate materials and corrosion products
  - Develop/apply methods for accelerated and off-line testing

- Improve durability
Approach to Durability Studies

- **Fuel Cell MEA Durability Testing and Study**
  - Constant voltage/current/power and power cycling (drive cycle)
    - VIR / cell impedance
    - Catalyst active area
    - Effluent water analysis

- **in situ and post-characterization of MEAs, catalysts, GDLs**
  - SEM / XRF / XRD (ex situ and in situ) / TEM / ICP-MS / neutron scattering / H₂ adsorption / Inverse Gas Chromatography / Contact Angle / total porosity / hydrophillic vs. hydrophobic porosity

- **Develop and test with off-line and accelerated testing techniques**
  - Potential cycling
  - Environmental component aging, testing and characterization
  - Component interfacial durability property measurements
Durability Testing Issues

• Testing times can be lengthy (and costly)
  – 5,000 hrs = ~ 7 months (automotive target)
  – 40,000 hrs = ~ 4.6 years (stationary system target)
  – *Need relevant accelerated testing*
  – *Need to close ‘field / lab gap’ or ‘transfer function’*
    • *Lab single cell → ‘real’ stacks → field data*

• Operating variables effect not fully understood
  – *Many degradation mechanisms likely yet undefined*
  – Power transients - vehicle fuel cell/battery hybridization
  – Transient power, temperature, RH
  – Shut down / start-up

• Materials still being developed and improved
  – *Need relevant accelerated testing*
Comparison of Accelerated Testing Methods

USFCC Accelerated Catalyst Test #1
Step vs. Triangle Potential Cycle

- Accelerated catalyst testing by potential cycling in H₂ / Air
- Voltage cycling: 0.6 and 0.96V (H₂/Air)

- H₂/Air requires load bank for high current (can’t use potentiostat).
- Some MEAs do not reach 0.96V OCP with standard load control
- Triangle potential sweep shows much faster degradation
Comparison of Accelerated Testing Protocols

Test #1. Voltage cycling: 0.6 and 0.96V (H₂/air)
Step vs. Triangle Potential Cycle

**Step Potential Cycle**

- OCP decreases with cycles
- Varies potential limits
- Increase in sample HFR
- H₂/Air cycling not just catalyst degradation

**Triangle Potential Cycle**

- Difficulties with this test being consistent and repeatable
- Does not separate catalyst durability from other components
Shut-down/Start-up Effects

• ‘Reverse Current’ degradation
  • Non-homogeneous mixture of H₂ on anode
  • H₂/air portion of cell drives ‘reverse current’ elsewhere

\[
\begin{align*}
O_2 + 4H^+ + 4e^- &\rightarrow 2H_2O \\
C + 2H_2O &\rightarrow CO_2 + 4H^+ + 4e^- \\
H_2 &\rightarrow 2H^+ + 2e^- \\
O_2 + 4H^+ + 4e^- &\rightarrow 2H_2O
\end{align*}
\]

Modified from: Sathya Motupally, UTC Power
Stop-Start Cycling Effect on Carbon Corrosion

**Anode Purge Rate Comparison**

- **Operation**
  - OCV and dry air (250 sccm) continuously to cathode
  - Shut-down: anode dry air purge: 5 min.
  - Start-up: flow dry H₂ to anode: 5 min.
  - Measure CO₂ (and CO) evolution at cathode by NDIR (Non-dispersive Infrared)

- **Results**
  - Increasing anode gas change-over rate decreases CO₂ evolution
  - More CO₂ evolution at start-up compared to shut-down, 25 °C
  - Small amounts of CO produced
Temperature Effect on Carbon Corrosion During Stop-Start Cycling

**CO₂ Evolution at Slow Purge Rate**

- **25 °C**
  - Higher at start-up than shut-down
  - Much lower evolution than at 60 °C

- **60 °C**
  - Greatest evolution
  - Higher evolution at shut-down

- **80 °C**
  - Non-zero steady-state evolution
  - ~ Equal shut-down/start-up evolution
GDL Durability
Contact Angle Changes

Contact angles with aging
(Single Fiber Measurements)

Contact angles with NaCl exposure
(Paper Sessile Drop Measurements)

- GDLs lose hydrophobicity with aging
- Exposure to NaCl make GDLs more hydrophobic
  - Also slows rate of water uptake
Surface Analysis of GDL Material

- Confirm –COOH surface species
  - Observe –OH and C=O IR
- Confirm acyl chloride
  - Reduction of –OH, and/or C-Cl

DRIFTS Spectra of Aged GDL
(Diffuse Reflectance Infrared Transmission Spect.)

- OH species identified
- Not yet satisfactorily identified surface species
- Using DRIFTS, will also explore Raman

MPA-MC, John Rau, Clay Macomber
Spatial Resolution of Durability: Individual Fuel Cell Segments: VIRs over Time

- Performance degradation greater at fuel cell inlet and near outlet
Crossover Current Density
Electrocatalyst Surface Area

Note: Because of segmented flowfield traversing in series, each subsequent segment cross-over is cumulative for all previous segments.

- $H_2$ cross-over per segment is ~ constant
- Unclear about segment 10

- Loss of electrocatalyst surface area (ECA) predominately at cathode outlet
  - (higher water content)
- Loss of ECA at inlet doesn’t explain significant performance loss at inlet
RH Effect on Membrane Degradation

Hydrogen Crossover

- Increase in $\text{H}_2$ crossover at medium RHs (20-60%)

Open-Circuit (OCP)

- Stable OCP at 100% RH
- OCP degrades at 20 & 60% RH
  - More $\text{H}_2$ and $\text{O}_2$ crossover results in greater $\text{H}_2\text{O}_2$ formation

H2, 500 sccm, 26psi; cathode: air/N2, 1000 sccm, 26psi.
Fluoride Emission Rate (FER)

- Highest fluoride ion emission rate at 60% RH at anode and cathode
- 20% RH rate similar to 100% RH rate

Anode: H2, 500 sccm, 26psi; cathode: air, 1000 sccm, 26psi.
Durability Test with Hydrogen from Chemical Hydride

Test #1

- Immediate decrease in cell performance upon switching to H₂ from H₂ Storage Material
- Complete failure in 3 hours
- Gas analysis suggests B-N species

Test #2

- Cell gradually recovered ~ 80% over several days
- Used carbon filter in H₂ line
- No immediate decrease in performance
- Simple filtration may work

Supporting LANL H₂ Storage COE
## Milestones: PEM Fuel Cell Durability

<table>
<thead>
<tr>
<th>Mon Yr</th>
<th>Milestone</th>
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<tbody>
<tr>
<td>May 07</td>
<td>Shut-down / start-up protocol comparison of degradation rates</td>
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<tr>
<td>Dec 07</td>
<td>Electrocatalyst particle size growth measurements performed on 2010 and 2015 DOE target loadings</td>
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<tr>
<td>Jan 08</td>
<td>Comparison of off-line potential square-wave cycling with fuel cell operation with square-wave cycling</td>
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<tr>
<td>Jun 08</td>
<td>Segmented Cell Operation</td>
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<tr>
<td>Sept 08</td>
<td>Peroxide formation results as function of Temperature, Operating potential and Electrocatalyst</td>
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- **Carbon corrosion**
- **DOE/USFCC**
  - H2/Air
  - H2/N2
- **S.S.**
Summary - Durability Testing

- Durability testing remains difficult and time intensive
  - Time constraints led to accelerated type testing
  - Decay mechanisms required to define accelerated test protocols
    - Need to understand all degradation mechanisms
    - Need to correlate accelerated testing with real fuel cell life

- Operational variables important to component durability
  - RH, temperature, potential and potential cycling
  - Shut-down / start-up variations important to corrosion

- Components
  - Electrocatalyst (Particle growth)
  - Membrane (Chemical and mechanical degradation)
  - GDL (Hydrophobicity loss/gain, porosity losses)
Future Activities

• Not sure of future funding status (>FY08)

• MEA durability measurements
  – Drive cycle testing, operating effects (shut-down), spatial distribution
  – Identification of degradation mechanisms

• Accelerated testing and durability correlation
  – Correlate accelerated durability tests to fuel cell performance
  – Continue to develop accelerated tests for degradation mechanisms

• Component interfacial durability property measurements
  – GDL / MEA catalyst layer material interfacial contact

Remainder of FY08:
  – Evaluate surface species leading to hydrophobicity changes
    • (both decreasing and increasing)
  – Evaluate mechanisms leading to change in hydrophobicity
  • Examine Nafion / PTFE degradation and carbon bonding