Durability Improvements Through Degradation Mechanism Studies

DOE 2011 Annual Merit Review Meeting
May 14 - 18, 2012

Presented by: Rod Borup

National Labs: Los Alamos National Lab (LANL), Argonne National Lab (ANL), Oak Ridge National Lab (ORNL), Lawrence Berkeley National Lab (LBNL)
Industry: Ballard Fuel Cells, Ion Power
University: University of New Mexico

This presentation does not contain any proprietary or confidential information
Organizations / Partners / Collaborators

- **Los Alamos National Lab (LANL)**
  - R. Mukundan, J. Davey, Bo Li, D. Spernjak, J. Fairweather, K. Rau, R. Lujan, D. Langlois, J. Chlistinoff; Applied Science Task; Christina Johnston, Yu Seung Kim, Nate Mack

- **Argonne National Laboratory (ANL)**
  - Rajesh Ahluwalia, Xiaohua Wang

- **Lawrence Berkeley National Laboratory (LBNL)**
  - Adam Weber, Ahmet Kusoglu

- **Oak Ridge National Laboratory (ORNL)**
  - Karren More, Mike Brady

- **Ballard Power Systems (BPS)**
  - Paul Beattie, Sylvia Wessel, G. James, D. Ramrus, S. Loif, W. Williams

- **Ion Power**
  - Steve Grot, Walter Grot

- **University of New Mexico (UNM)**
  - Kateryna Artyushkova, Plamen Atanassov, Anant Patel

- **University of Nancy, Lorraine France**
  - Gaël Maranzana, Adrien Lamibrac, Jérôme Dillet, Sophie Didierjean, Olivier Lottin

- **Nuvera, Ballard, ANL, LANL-AST, UTC-AST Durability projects**
## Budget

<table>
<thead>
<tr>
<th>DOE Cost Share</th>
<th>Recipient Cost Share</th>
<th>Total</th>
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<tbody>
<tr>
<td>$8,225k</td>
<td>$501k</td>
<td>$8,726k</td>
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<td>94%</td>
<td>6%</td>
<td>100%</td>
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<table>
<thead>
<tr>
<th>Yr 1</th>
<th>Yr 2</th>
<th>Yr 3</th>
<th>Yr 4</th>
<th>Cumulative</th>
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<tbody>
<tr>
<td>$2000k</td>
<td>$2000k</td>
<td>$2175k</td>
<td>$2050k</td>
<td>$8225k</td>
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</table>

**Approximately 2/3 through project: 18 months left**

<table>
<thead>
<tr>
<th>Participant</th>
<th>FY11 (Year 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LANL</td>
<td>$1000k</td>
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<tr>
<td>Industrial + Univ. Partners (Ballard, Ion Power, UNM)</td>
<td>$425k</td>
</tr>
<tr>
<td>Other National Labs (ANL, LBNL, ORNL)</td>
<td>$850k</td>
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</tbody>
</table>
Relevance and Objectives

• **Relevance**
  – Increase fuel cell durability; not at the expense of component cost

• **Objectives**
  • Identify and Quantify Degradation Mechanisms
    – Degradation measurements of components and component interfaces
    – Elucidation of component interactions, interfaces, operating conditions leading to degradation
    – Development of advanced in situ and ex situ characterization techniques
    – Quantify the influence of inter-relational operating environment between different components
    – Identification and delineation of individual component degradation mechanisms
  
  • **Understand Electrode Structure Impact - Applied Science Subtask**
    – Better understand the electrode structural and chemical reasons for differences in durability
    – Understand impact of electrode structure on durability and performance
    – Correlate different electrode structures to fuel cell tests and durability
    – Define different fabrication effects (esp. solvents) on electrode structure
  
  • **Develop Models Relating Components and Operation to Fuel Cell Durability**
    – Individual degradation models of individual fuel cell components
    – Development and public dissemination of an integrated comprehensive model of cell degradation
  
  • **Methods to mitigate degradation of components**
    – New components/properties, designs, operating conditions
### Table 3.4.3 Technical Targets for Automotive Applications: 80-kW\textsubscript{e} (net) Integrated Transportation Fuel Cell Power Systems Operating on Direct Hydrogen\textsuperscript{a}

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2011 Status</th>
<th>2017 Targets</th>
<th>2020 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy efficiency\textsuperscript{b} @ 25% of rated power</td>
<td>%</td>
<td>59</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Power density</td>
<td>W / L</td>
<td>400\textsuperscript{c}</td>
<td>650</td>
<td>850</td>
</tr>
<tr>
<td>Specific power</td>
<td>W / kg</td>
<td>400\textsuperscript{c}</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>Cost\textsuperscript{d}</td>
<td>$ / kW\textsubscript{e}</td>
<td>49\textsuperscript{e}</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Durability in automotive drive cycle</td>
<td>hours</td>
<td>2,500\textsuperscript{h}</td>
<td>5,000\textsuperscript{i}</td>
<td>5,000\textsuperscript{i}</td>
</tr>
<tr>
<td>Assisted start from low temperatures\textsuperscript{j}</td>
<td>°C</td>
<td>–</td>
<td>-40</td>
<td>-40</td>
</tr>
<tr>
<td>Unassisted start from low temperatures\textsuperscript{j}</td>
<td>°C</td>
<td>-20\textsuperscript{f}</td>
<td>-30</td>
<td>-30</td>
</tr>
</tbody>
</table>

### Table 3.4.5 Technical Targets: 1–10 kW\textsubscript{e} Residential Combined Heat and Power and Distributed Generation Fuel Cell Systems Operating on Natural Gas\textsuperscript{a}

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>2011 Status</th>
<th>2015 Targets</th>
<th>2020 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degradation with cycling\textsuperscript{h}</td>
<td>&lt;2% / 1,000 h</td>
<td>0.5% / 1,000 h</td>
<td>0.3% / 1,000 h</td>
</tr>
<tr>
<td>Operating lifetime\textsuperscript{i}</td>
<td>12,000 h</td>
<td>40,000 h</td>
<td>60,000 h</td>
</tr>
</tbody>
</table>
Approach

• **Understand Degradation Mechanisms**
  • Measurements of degradation ex situ and in situ
  • Analysis to define individual component contributions to loss in performance

• **Characterization of Component Degradation**

• **Understand and Correlate Electrode Structure to Durability**
  • Understand connection between structure and performance/durability
    • Vary the ionomer and catalyst with different solvents to assess impact

• **Modeling**
  • Fundamental degradation mechanisms (LBNL)
  • Integrated degradation model – kinetic/rate based (ANL)
  • Coordinate activities with other efforts via DOE Modeling Working Group

• **Coordinate activities with other durability projects**
  • DOE Durability Working Group
  • Current coordination includes: ANL, Nuvera, Ballard, UTC-AST, LANL-AST
    • Data from ANL on Pt dissolution used for modeling effort
    • Joint material testing with AST projects (esp. LANL)
    • Extend characterization (Neutron Imaging) to benefit Ballard
<table>
<thead>
<tr>
<th>Mon Yr</th>
<th>Milestone</th>
<th>Status</th>
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</thead>
<tbody>
<tr>
<td>Nov 2011</td>
<td>Complete OCV tests for 200 hr on improved LANL cathodes and compare the performance drop to LANL standard and commercial MEAs</td>
<td>Experiments complete</td>
</tr>
<tr>
<td>Dec 2011</td>
<td>Compare carbon corrosion due with GDL variations (SGL 24BC-24BC and 24BC-24BA cells) by measuring performance in 10x10 segmented cell during carbon corrosion AST</td>
<td>Experiments complete</td>
</tr>
<tr>
<td>Jan 2012</td>
<td>Calculate a relative activation energy for metal plate corrosion comparing FE-20Cr-4V and 904L metals by measuring relative corrosion rates between 20C and 80C</td>
<td>Experiments complete</td>
</tr>
<tr>
<td>Feb 2012</td>
<td>Compare water bonding with new (stabilized, non-stabilized) and aged ionomer by DSC (Differential Scanning Calorimetry) to identify changes in water bonding with age.</td>
<td>Incomplete; Lost Student</td>
</tr>
<tr>
<td>Mar 2012</td>
<td>Determine the impact of catalyst loading over the range 0.05 mg/cm² to 0.20 mg/cm² on the durability of improved LANL cathodes to potential cycling tests from 0.60-1.0 V for 30,000 cycles at 50 mV/s</td>
<td>Experiments complete</td>
</tr>
<tr>
<td>May 2012</td>
<td>Complete microscopy on improved LANL cathodes and compare to durability results from potential cycling (0.60-1.0 V, 30,000 cycles) and OCV tests (200 hr)</td>
<td>On-going; microscopy complete on baseline</td>
</tr>
<tr>
<td>June 2012</td>
<td>Measure and compare changes in catalyst layer and GDL surface energies/hydrophobicity due to operation with shutdown/startup (using durability working group protocol)</td>
<td>SD/SU Experiments complete</td>
</tr>
<tr>
<td>Sept 2012</td>
<td>Compare cathode catalyst loading effect on catalyst electrode layer durability examining loadings of 0.15, 0.2, 0.25, 0.4 and 0.5 mg/cm²</td>
<td>Partially complete, MEAs received</td>
</tr>
</tbody>
</table>
Durability of Low Loading Pt/C Cathode during Potential Cycling

- Performance of ultra-low loading cathode (0.05 mg/cm²) increased with potential cycling
- Performance of MEA with “high” loading decreased; with “low” loading stayed the same
- ECSA decreased with potential cycling for all MEAs; does not correlate with performance change

Electrode milestone (Determine the impact of catalyst loading on the durability of LANL cathodes to potential cycling tests) - Achieved

**Anode:** 0.2 mg cm² Pt/C (BASF), **Cathode:** 0.06-0.25 mg cm² Pt/C (BASF); **Membrane:** Nafion® 212; **Cell:** 80°C, 30 psig backpressure, Potential cycling: 0.6 – 1.0 V under H₂/N₂

**Typical LANL decal process using water/alcohol/glycerol mixture in the ink was used.**

<table>
<thead>
<tr>
<th>Pt (mg/cm²)</th>
<th>0 K</th>
<th>10 K</th>
<th>30 K</th>
<th>50 K</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>50</td>
<td>35</td>
<td>28</td>
<td>22</td>
<td>-55</td>
</tr>
<tr>
<td>0.11</td>
<td>49</td>
<td>28</td>
<td>24</td>
<td>22</td>
<td>-56</td>
</tr>
<tr>
<td>0.05</td>
<td>52</td>
<td>29</td>
<td>21</td>
<td>14**</td>
<td>-74**</td>
</tr>
</tbody>
</table>

* Determined by the H₂ desorption of CV; **very low surface areas with higher error

**ECSA change***
Electrode Structural Change during Potential Cycling

- Enhanced performance and impedance behavior of low loading cathode with potential cycling have similarity with performance improvement with heliox (or air flow increase)

Electrode structural change that occurs during potential cycling in favor of oxygen diffusion, lower Mass Transport Resistance
Electrode Performance and Durability of Processed Low Loading Cathode

• Highlight: Introduce new electrode processing technologies that generate better electrode structure for low loading Pt/C cathode -- Electrode processing time reduced from 5.5 days, ca. 30,000 cycles to 2 h

• Highlight: High power density achieved with low Pt loading and pre-processed Pt/C (i.e. $P_{0.5V} = 540$ mW/cm² for 0.05 mg/cm² vs. $P_{0.5V} = 840$ mW/cm² for 0.25 mg/cm²)
  
  • Not yet optimized for CL ionomer and membrane

• Processed electrode shows excellent stability with potential cycling from 0.6-1.0 V; cell performance was slightly improved after first 10,000 cycles then remained same after further 20,000 cycles

• ECSA decreased from 58.5 to 35.8 m²/g_{Pt} after 30,000 cycles; the reduction of ECSA does not impact fuel cell performance

Anode: 0.2 mg cm⁻² Pt/C (BASF), Cathode: 0.05 mg cm⁻² Pt/C (Commercially available), ionomer: Nafion® 1100; Membrane: Nafion® 212; Cell: 80ºC, H₂/air under 30 psig backpressure, Potential cycling: 0.6 – 1.0 V under H₂/N₂ condition
Impact of Cathode Structure on Membrane Degradation

- Durability of MEAs to OCV test depends both on electrode ionomer choice and solvent used in inks.
- OCV durability ranking:
  - WIN < NMP < Gly
  - LSC < SSC
- Hydrogen crossover after OCV test affected by cathode electrode structure; implies membrane is indirectly affected by the electrode.
- Hydrogen crossover after OCV test correlates well with electrode porosity; perhaps oxygen diffuses into membrane faster and accelerates its degradation when the electrode is more porous.

*Slit pore QSDFT model used assuming carbon surfaces; results provide qualitative comparison.

**Anode:** 0.2 mg cm⁻² Pt/C (BASF) LANL standard processing, **Cathode:** 0.2 mg cm⁻² Pt/C (BASF) processed with different dispersing solvent; **Membrane:** Nafion® 212; **Cell:** 80°C, 30 psig backpressure; OCV test: H₂/Air at 90°C, 30% RH, no backpressure; H₂ crossover measured at 70°C, 50/50 sccm of H₂/N₂.
Rate of Platinum Agglomeration Depends → Loading & Mechanism

Catalyst Degradation Comparison for Catalyst Layers with Similar Carbon Loadings

Loadings of 0.2 mg/cm² (20 wt%Pt) and 0.4 mg/cm² (40 wt%Pt)

- Pt PSD shows no difference after potential cycling
- Dissolution/re-precipitation kinetics/particle growth kinetic unaffected by Pt particle concentration

- Greater Pt coarsening for cathode with higher Pt loading
- Higher concentration of Pt particles led to higher agglomeration
Pt Dissolution Model

- Completed initial development of Pt dissolution model
  - Dissolution thermodynamics from aqueous potentiostatic data
  - Oxide growth thermodynamics from the measured reduction charge after long hold at different CV potentials
  - Oxide growth kinetics from CV oxidation and reduction scans
  - Dissolution kinetics from constant potential and potential cycling data
  - Size evolution driven by dissolution of small Pt particles and growth of large particles through re-deposition and coalescence (primary)
  - Growth in average size more significant for initial distributions with small mean diameter and potential cycles with higher UPL (more dissolution), lower LPL (more re-deposition), and faster scan rates

Collaboration with ANL (D. Myers) and Nuvera durability projects Discusses Earlier by (D. Myers)
Understanding Changes to Hydrogen Crossover During MEA Aging

- Measuring OCV as a function of H₂ pressure and relating OCV to H₂ crossover to cathode
- Cell aged for more than 1500 h using DOE Drive Cycle Protocol:
  - Deposits Pt particles inside the membrane
  - Measured OCV is less than the Nernst potential and close to mixed potential typical of ORR and HOR
    - Suggests H₂ crossing from anode does not completely react inside membrane
    - Data for unequal anode and cathode pressures not meaningful because of H₂ leaks around the seals and gaskets in aged MEA
Our OCV data show that the Pt particles deposited in an aged membrane promote reaction between H₂ crossing over from the anode (i_{xa}) and O₂ crossing over from the cathode (i_{xc}).

Only a fraction of the H₂ that crosses over from the anode reacts in the membrane (i_{xm}), and this fraction decreases as P(H₂) is reduced.

H₂ crossover from anode is weakly affected by H₂ reaction in the membrane (i_{xa}), but O₂ crossover from cathode (i_{xc}) can increase markedly and be consumed completely inside the membrane.

\[ i_{xa}(H_2) : \text{H}_2 \text{ crossover from anode} \]
\[ i_{xc}(H_2) : \text{H}_2 \text{ crossover to cathode} \]
\[ i_{xc}(O_2) : \text{O}_2 \text{ crossover from cathode} \]
\[ i_{xm}(H_2) : \text{Reaction between H}_2 \text{ and O}_2 \text{ inside membrane} \]
Evidence of Ionomer Electrode Degradation

XPS Chemical Analysis shows Changes in Fluorine, Carbon, Oxygen

- Correlation between ECSA and particle size normally observed
- Not for tests using OCV hold (AST) designed to accelerate membrane degradation through formation of radicals
  - No effect on catalyst particle size (XRD)
  - Reduced ECSA measured

- New Fluorine Binding Energy species detected after testing
- Twice as much for nonstabilized system vs stabilized

- Carbon changes more pronounced for nonstabilized system

- Increase in Oxygen high BE component due to oxygen connected to teflon
Local currents during Shut-down / Start-up Transients
University of Nancy Collaboration

Measure carbon corrosion by linear series segments and CO₂ by NDIR

Shut-down
Anode purge with air
~ 0.05 s exchange residence time

Start-up
Anode H₂ feed
~ 0.2 s exchange residence time

The difference between the calculated residence time and the measured residence time (from internal currents) is due to the GDL volume and diffusion times.
GDLs Effect Localized Performance Degradation:
GDLs with and without MPL

- Current density at 0.4 V reduced by:
  - factor of 3 for the MPL case (BC cell)
  - factor of 3.7 without the MPL (BA cell)

Top portion (upstream):
Current increased (negative difference).

Bottom portion (downstream):
Current decreased (positive difference).
Small portions of the central lower region decreased more.
Ex Situ Characterization Post-Carbon Corrosion Shows Non-Uniform Carbon Corrosion Due to GDL / Water Content

New MEA (without GDL)

New MEA (with GDL, cathode on top)

Area ~ 1 x 1 mm

X-Ray Computed Tomography

SEM Images

MPL

Uniform cathode thinning (~30% remains)

Anode thickness unchanged

Nonuniform cathode thinning

Membrane ‘flows’ under pressure

Anode thickness unchanged
Carbon Structure shows Localized Structure Changes

Loss of meso-graphitic structure in catalyst layer – No structural change in MPL

Interface between Pt/High Surface Area Carbon (HSAC) cathode and MPL is distinct – MPL carbon retains its meso-graphitic structure and porous network (even adjacent to the cathode surface) whereas the HSAC directly at the interface is fully oxidized.

AST1.2V hold for 100hr in H₂/N₂
Carbon Structure shows Localized Structure Changes

1.2V hold for 100hr in H₂/N₂

Loss of meso-graphitic structure in catalyst layer – No structural change in MPL

Interface between Pt/High Surface Area Carbon (HSAC) cathode and MPL is distinct – MPL carbon retains its meso-graphitic structure and porous network (even adjacent to the cathode surface) whereas the HSAC directly at the interface is fully oxidized.

Note distinct interface between meso-graphitic carbon particle in MPL (A) and densified and oxidized Pt/HSAC cathode (B).
Kinetics of Carbon Corrosion: Model Development

- Carbon corrosion measured shows multiple potentials producing CO₂

- Multiple reaction pathways

![Graph showing corrosion rate vs. potential with peaks labeled for different reactions.]

Peak I  Peroxide reaction 1 and CO₂ holdup
Peak II  Reactions 2 and 3
Peak III  Reactions 3 and 4
Peak IV  Reaction 2

- Initial Model for Corrosion of High-Surface Area Carbon

1. \( C + H₂O₂ \rightarrow CO₂ + 2 H^+ + 2e^- \)  (Peroxide attack, low potentials)
2. \( C + H₂O \leftrightarrow C-O + 2 H^+ + 2e^- \)  (Active surface oxide)
3. \( C-O + H₂O \rightarrow CO₂ + 2 H^+ + 2e^- \)  (Electrochemical corrosion)
4. \( x C + H₂O \leftrightarrow Cₓ-O + 2 H^+ + 2e^- \)  (Passive surface oxide)

Current is not a good indication of CO₂ production; measured by NDIR
Parametric Results on Carbon Corrosion

- **Effect of cell temperature**
  - At higher T, Peak I shifts to lower potentials and decreases in magnitude; Peak IV corrosion rate also increases

- **Effect of scan rate**
  - At higher scan rates, the corrosion rates are generally higher and the curves lose their fine structure (Peaks II and III disappear)

- **Effect of relative humidity**
  - At higher RH, the corrosion rates are higher
Water Content is Reduced During Carbon Corrosion AST

Dramatic reduction in water retention at constant current density

0.8 A/cm², 80°C, 100%RH

*x-axis enlarged 250% to show detail
Post-mortem Characterization: XPS + SEM
Cathode Materials Become More Hydrophillic → Heat Generation dominates

Surface oxides increase → more hydrophillic

New cathode

Corroded cathode

Species:

<table>
<thead>
<tr>
<th></th>
<th>C-OH/C-OC</th>
<th>C=O</th>
<th>COOH</th>
<th>C(O)_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>New cathode</td>
<td>1.9</td>
<td>3.7</td>
<td>5.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Corroded cathode</td>
<td>3.6</td>
<td>5.4</td>
<td>8.6</td>
<td>18.4</td>
</tr>
</tbody>
</table>

• PEM ~ 18 μm
• Anode CL ~ 7 μm

MPL

Cathode CL ~ 3.5 μm

Waste heat

Heat generation dominates changes in hydrophilicity during carbon corrosion AST conditions
**Metal Bipolar Plate Anodic Polarization Corrosion Results**

- Examine effects for model development:
  - Different metals (316L S.S., NiCr, Hastelloy)
  - Temperature effect
  - Fluoride anion content effect
  - Contact resistance increase
  - Metal cation poisoning of proton conduction

- Temperature increases corrosion rate
  - Decreases Free Corrosion Potential (OCV)
- Other testing in progress

---

**Temperature Effect on Ni50Cr Polarization**

- Potential (V vs. SHE) vs. Current density (A/cm²)
- Ni50Cr 40C
- Ni50Cr 80C

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**Contact Resistance after Fuel Cell Operation**

- R (Ω cm²) vs. Torque (lb-in)
- Before FC operation
- After 300+ h drive cycle
- After 300+ h drive cycle and plate cleaning

---

**Post-MEA Analysis**

<table>
<thead>
<tr>
<th>Component</th>
<th>Total metal content (μg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endplate</td>
<td>∞</td>
</tr>
<tr>
<td>MEA before FC testing</td>
<td>0.71</td>
</tr>
<tr>
<td>MEA after FC testing</td>
<td>0.11</td>
</tr>
<tr>
<td>Cathode GDL</td>
<td>0.22</td>
</tr>
<tr>
<td>Anode GDL</td>
<td>0.41</td>
</tr>
</tbody>
</table>

- No Measureable Increase in MEA Metal Cations

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**Increase in plate contact resistance observed at low contact force**
# Carbon Bipolar Plates

## Overview

<table>
<thead>
<tr>
<th>Group</th>
<th>Testing</th>
<th>AST Data</th>
<th>Sampling</th>
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</thead>
<tbody>
<tr>
<td><strong>Mechanical Change</strong></td>
<td>Instron</td>
<td>Flexural strength</td>
<td>To 20K hours</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Flexural modulus</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Strain to failure</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dynamic Mechanical Analysis (DMA)</td>
<td>Glass transition temperature</td>
<td></td>
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<tr>
<td><strong>Chemical Change</strong></td>
<td>Thermo-gravimetric Analysis (TGA)</td>
<td>Thermal degradation onset T</td>
<td>To 20K hours</td>
</tr>
<tr>
<td></td>
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<td>Isothermal weight loss</td>
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<tr>
<td><strong>Contamination</strong></td>
<td>Extraction</td>
<td>Metals and organics</td>
<td>BOL</td>
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<tr>
<td></td>
<td>Leachate Analysis</td>
<td>Metals and organics</td>
<td>To 4K hours</td>
</tr>
<tr>
<td></td>
<td>Rotating Disc Electrode</td>
<td>Performance vs. concentration (isolated)</td>
<td>BOL</td>
</tr>
<tr>
<td><strong>Surface Change</strong></td>
<td>Tensiometry</td>
<td>Advancing / receding forces</td>
<td>To 1K hours</td>
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<tr>
<td></td>
<td>Goniometry</td>
<td>Advancing / receding CA's</td>
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<tr>
<td></td>
<td>Laser Microscopy</td>
<td>Surface roughness</td>
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<tr>
<td><strong>Intrinsic Property Change</strong></td>
<td>Electrical Conductivity</td>
<td>Bulk electrical conductivity</td>
<td>To 1K hours</td>
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<tr>
<td></td>
<td></td>
<td>Electrical contact resistances</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thermal Conductivity</td>
<td>Bulk thermal conductivity</td>
<td>BOL, EOL</td>
</tr>
</tbody>
</table>

- Levels of contaminants established for different material classes
Investigating separation of bulk properties and contact resistances

Method distinguishes different material types

Goniometry
- Dynamic method to capture key properties relating to water management
- Measureable properties include: advancing / receding contact angle, removal angle (force), droplet size / shape
- Concentrating on moment of initial water movement
Summary

• **Project Goals are to:**
  – Understand Degradation Mechanisms
  – Develop Integrated model of Degradation

• Material variants include: ionomer, membrane, catalyst, support, electrodes, GDL, metal plates, carbon plates, seal materials
  • > 30 MEA variants, > 6 AST tests, > 3 fuel cell durability tests

• Components
  – Electrode Structure
  – Catalyst
  – Catalyst Support
  – GDL
  – GDL/Catalyst Layer Interface
  – Metal Plates
  – Carbon Plates
  – Seals

• Operational Variables
  – Shut-Down / Start-Up
  – Temperature, RH, etc.
Selected Technical Conclusions - 1

• Catalyst
  – Rate of platinum agglomeration has dependency on loading & mechanism
    – Agglomeration independent of loading for dissolution / reprecipitation
    – Agglomeration dependent on loading during carbon corrosion

• Electrode structural changes occur
  – During potential cycling favor of oxygen diffusion result in lower MT Resistance
  – New electrode processing technologies generate better electrode structure for low loading Pt/C cathode
  – Cathode electrode structure effects membrane degradation

• Catalyst layer ionomer degrades
  – ECSA loss without particle size change, Pt particles agglomerating in ionomer
  – Chemical Analysis/Binding Energy changes more pronounced for non-stabilized ionomer, including development of a new fluorine binding energy species

• Carbon structure shows localized structure changes
  – Loss of meso-graphitic structure in catalyst layer
  – No structural change in MPL (meso-graphitic structure remains across interface)
  – Rate of carbon oxidation decreases with each potential hold
  – Portion of the evolved CO$_2$ originates from the MPL, not the catalyst layer
Selected Technical Conclusions - 2

- **Hydrogen crossover affected by catalyst layer degradation**
  - OCV test affected by cathode electrode structure; implies membrane is indirectly affected by the electrode
  - OCV data show that the Pt particles deposited in an aged membrane promote reaction between $H_2$ crossing over from the anode ($i_{xa}$) and $O_2$ crossing over from the cathode ($i_{xc}$)
  - Pt particle degradation and migration effects the membrane $H_2$ crossover

- **GDL effects Catalyst layer Performance Degradation**
  - Surface oxides of carbon of catalyst layer and GDL increase
  - Hydrophillicity increase effect on water transport overwhelmed by overpotential increases
  - Mass transport losses during carbon corrosion are due to collapse of pore space, not increased flooding

- **Bipolar plate primary effect on degrading performance appears to be contact resistance increase**
  - No Measureable Increase in MEA Metal Cations from Metal Plate corrosion,
  - Increases in contact resistance
Future Work

Identify and Quantify Degradation Mechanisms
- Vary MEA materials to better define ionomer degradation
  - Expand mixed hydrocarbon and PFSA materials for unambiguous chemical analysis

Electrode Structure
- Identify structural change of electrodes during potential cycling and operation
- Identify causes behind ionomer and solvent impact on MEA durability
  - Establish correlation of electrode structure durability to mechanical strength

Start-up / Shut-down
- Series Segmented Cell SU/SD measurements comparing catalyst support materials
- Compare CO$_2$ during SU/SD to 1.2V AST holds
- Compare the degradation mechanisms from the SU/SD to the ASTs

Component Interactions
- Metal bipolar plate evaluation and evaluation of interactions with MEA/GDL
  - Fuel cell testing of metal materials to correlate corrosion rate to metal cation contamination of membrane and proton conduction
- Composite (graphite) bipolar plate evaluation
  - Standardize surface evaluation improving data consistency to evaluate surface properties

Modeling
- Incorporate parametric studies of components into integrated model
- Water profile modeling during carbon corrosion comparing overpotential and hydrophobicity changes to water transport
Future Plans: Parametric Studies (on-going)
Parametric Studies Feed the Final Integrated Model Development

Membrane Degradation

<table>
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<tr>
<th>Pressure (150 kPa)</th>
<th>Fuel/Oxidant</th>
<th>H₂/air</th>
<th>Measurement Times for F &amp; TER Rates</th>
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<tbody>
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<td>T</td>
<td>RH</td>
<td>Time</td>
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Catalyst Support Cycle

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Vary Catalyst Loading
Vary Carbon Types: High Surface Area, Low Surface Area, Vulcan Carbon

- PO₂, RH and Temp dependence of membrane degradation
- Data for Pt dissolution from ANL study (D. Myers)
- Carbon corrosion RH, Temp, Loading, Carbon type, V)
Future Work: Carbon Corrosion

- Characterize corrosion rates of carbon supports with higher degree of graphitization during the aging process
- Measure and model the effect of ageing on carbon corrosion rates
  - Initial observations: ECSA dropped by ~90%, carbon mass decreased by ~47%, yet the cell capacitance increased and the carbon corrosion rate did not slow down
- Measure and model the effects of carbon corrosion on growth of Pt particles, loss in ECSA and mass transfer overpotentials

![Graph](image)

- Define the hysteresis, age effect on the studies (i.e. degradation rates new vs. rates from aged samples)
Thanks to

• U.S. DOE -EERE Fuel Cell Technologies Program for financial support of this work
  – Technology Development Manager: Nancy Garland

• All project partners and personnel

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• SANS beam time provided by
  – Los Alamos Neutron Science Center: LQD beam line
  – NIST: NG3, NG7 beam lines
• Neutron imaging beam time provided by
  – National Institute of Standards and Technology: BT-2
• Other materials provided by:
  – W.L. Gore
  – Solvay
  – SGL Carbon GmbH
Technical Backup Slides
Morphology changes upon aging (OCV Test)

- Water domain spacing reduces when membrane is equilibrated in water
- Crystalline peak formation is observed for XL100 at ~ 0.06 Å⁻¹
- Aging results in a similar domain region for both XL and N212
- Initial slope also suggests change in morphology, where aged sample reach similar structure
Chemical Analysis of Ionomer Degradation: Carbon 1s

- Stabilized ionomer has more of CF₂ ends/no CO
- Increase in graphitic C is detected for both nonstabilized and stabilized
  - Larger graphitic C increase for NS system
- Amount of CₓOᵧ species decreased after testing
- CFₓ species is unchanged
- Overall trend during testing
  - Decrease in high BE C
  - Increase in low BE C
  - More pronounced for nonstabilized system
Fresh NS, F 1s

Fresh S, F 1s

AST NS, F 1s

AST S, F 1s

- New F BE species detected after testing
  - BE similar to Teflon®-like species.
  - Twice as much for nonstabilized system vs stabilized
- Analysis of Teflon®-less GDL MEA is planned to rule out migration from these species from GDL
Chemical Analysis of Ionomer Degradation: Oxygen 1s

- Fresh NS and S systems have similar O 1s speciation
- Decrease in CO*CF / COCF species from testing
- Increase in high BE component due to oxygens connected to Teflon®-like species detected for both
  - Slightly bigger increase for NS
FC Tech Team Action items

- **NREL Contamination**
  - Contacted Huyen Dinh
  - Gave general input on their approach
  - Provided specific input on durability testing
  - Suggested material types for their investigations
  - Will establish regular dialogue

- **Thermal conductivity plan**
  - Investigated off-site measurement tool
  - ASTM E1530 – Guarded Heat Flow Meter Technique
  - Testing planned for later this year on BOL and EOL samples

- **Normalized water management noise signal**
  - Internal group measured pressure drop in a channel with various geometries and surface treatments
  - As water was produced and moved through the channel, the pressure drop signal fluctuated
  - This was called a “water management noise signal”
  - The uncoated plate showed a 4:1 ratio in this signal compared to the hydrophilic plate, meaning it fluctuated 4x as much.

- **Hydrogen permeance**
  - No plan to investigate at this time