Durability Improvements Through Degradation Mechanism Studies

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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 Power Systems, 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)**

- **Argonne National Laboratory (ANL)**
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- **Lawrence Berkeley National Laboratory (LBNL)**
  - Adam Weber, Ahmet Kusoglu, Kyle Clark

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

- **Ballard Power Systems (BPS)**
  - Paul Beattie, Silvia 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 (Federal Portion)

As Proposed 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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<tr>
<td>94%</td>
<td>6%</td>
<td>100%</td>
</tr>
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</table>

<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>
</tr>
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</table>

Approximately 90% through project: ~ 4 months left

<table>
<thead>
<tr>
<th>Participant</th>
<th>FY13 (Year 4)</th>
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</thead>
<tbody>
<tr>
<td>LANL</td>
<td>$1400k</td>
</tr>
<tr>
<td>Industrial + Univ. Partners (Ballard, Ion Power, UNM)</td>
<td></td>
</tr>
<tr>
<td>Other National Labs (ANL, LBNL, ORNL)</td>
<td>$1250k</td>
</tr>
</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
### Technical Targets/Barriers

**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{\circ}</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
Modeling Development Schematic

Two sets of models are under development: component-specific durability models and combined reaction-diffusion model for performance degradation.

**Support Durability (ANL, LANL)**
- Kinetics of carbon corrosion
- Performance degradation due to carbon corrosion

**Membrane Durability (LBNL, LANL)**
- OCV, FER, and pinhole formation/growth
- Water uptake of degraded samples
- Mechanical Properties, crystallinity

**Integrated Model (ANL)**
- Single Component Models (ANL, LBNL)

**Catalyst Stability (ANL, LANL, Nuvera)**
- Pt dissolution
- Particle growth
- Pt Transport
- ECSA loss
- ORR activity loss
- Mass transfer losses

**Material Characterization**
- TEM (ORNL)
- XPS (UNM)
- Performance testing, Electrochemical, Materials (LANL)
- Carbon Plates (Ballard)
- Seals (Ballard)
- Membrane properties, GDLs, MEAs (LBNL)

**Bipolar Plate Durability (ANL, LANL, NREL, ORNL)**
- Kinetics of protective oxide growth and metal dissolution
- Interfacial contact resistance

**Membrane/Electrode Durability (ANL, LANL)**
- Electrode degradation correlation
- Performance degradation due to ionomer degradation

**MEA Design (Ion Power, LANL)**
- Pt loading
- Electrode thickness
- Pt/C/I ratios
- Ionomer and membranes

Others:
- SGL Carbon
- W.L. Gore
- Tanaka
- DuPont
- Solvay
- ETEK
Modeling of ECSA loss: Particle Growth and Pt Utilization

Modified catalyst durability model to account for changes in Pt size distribution due to carbon corrosion

- Growth in size of Pt particles: coalescence kernel derived from BOT and EOT size distributions (TEM data)
- Loss of electrical contact with Pt particles: decrease of Pt utilization determined from measured ECSA and Pt size distribution
- Densification of cathode catalyst layer (TBD)
- ECSA loss is due to the combined decrease of Pt utilization and coalescence with V-type carbon, and is primarily due to decrease in Pt utilization with E-type carbon

![Graph showing ECSA and Pt utilization vs. carbon loss for V-type and E-type carbons](image)
**Carbon Corrosion: CO₂ via NDIR**

**High Surface Area (E), Intermediate (V), Low (graphitized - EA)**

80°C, 100%RH, H₂/N₂, 5 mV/s scan

- High surface area (Pt on Tanaka E)
- Intermediate (Pt on Vulcan XC-72)
- Graphitized (Pt on Tanaka EA)

Rxn 1

1. C + H₂O₂ → CO₂ + 2 H⁺ + 2e⁻
2. C + H₂O ↔ C-O + 2 H⁺ + 2e⁻
3. C-O + H₂O → CO₂ + 2 H⁺ + 2e⁻
4. x C + H₂O ↔ Cₓ-O + 2 H⁺ + 2e⁻

Completed models for Pt catalyzed corrosion of Ketjen black (E-type), Vulcan® XC-72 (V-type) and graphitized carbon (EA-type) supports:

- Determined rate constants from CO₂ emission data for potentiostatic and cyclic potentials at different T, RH and scan rates
- Related Peak I to corrosion by peroxide, Peak II to surface coverage by active oxides, and Peaks III and IV and hysteresis to Pt and surface coverage by passive oxides
Support Aging Effects: Variety in Carbon Surface Oxides

High surface area (Pt on Tanaka E)

- Surface oxides increase as bulk carbon and Pt decrease

Intermediate (Pt on Vulcan XC-72)

- All surface and bulk signals drop with aging

Graphitized (Pt on Tanaka EA)

- Low initial corrosion rate \(\Rightarrow\) small changes only

- Activation process occurs at OCV, and may be somewhat independent of potential
  \(\Rightarrow\) chemical reduction of passive oxides, or chemical attack leading to active oxides
Microscopic Characterization of Degradation During DOE/FC Tech Team Drive Cycle

~30% compression/thinning of cathode layer due to “localized” HSAC corrosion

Gore® “fresh” vs. Drive Cycle Tested (389 hr wet/dry drive cycle)

Elemental Analysis by XPS

- Graphitic content increases (as %)
- Likely → decrease of amorphous carbon
- Oxygen content increases
- Likely → increasing oxygen content on carbon surface
- Changing hydrophobicity effects transport

HAADF-STEM images
Microscopic Characterization of Carbon Corrosion
(After DOE Drive Cycle Test)

- “localized bands” of HSAC corrosion (green arrow), which are correlated to increased Pt particle sizes and closer Pt-Pt interparticle spacings. Typically, these oxidized regions of carbon surround non-oxidized regions (inside yellow outline).
- Regions of non-oxidized HSAC retain graphitic structure and are correlated with smaller Pt particle sizes.

TEM images
Modeling Carbon Corrosion: Effect of Aging

Determined the effect of aging on the specific surface area of carbon ($S_C$, m$^2$-C/g-C) for the three supports:

- $S_C$ increases with aging of E-type carbon, consistent with the observed increase in double-layer capacitance.
- Smaller increase in $S_C$ of V-type carbon.
- Data for EA-type carbon in progress.

<table>
<thead>
<tr>
<th>Carbon Loss (%)</th>
<th>E-Type</th>
<th>V-Type</th>
<th>EA-Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>735</td>
<td>250</td>
<td>236 (TBD)</td>
</tr>
<tr>
<td>25%</td>
<td>1250</td>
<td>390</td>
<td></td>
</tr>
<tr>
<td>50%</td>
<td>1840</td>
<td>410</td>
<td></td>
</tr>
<tr>
<td>75%</td>
<td>2135</td>
<td>625</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specific Surface Area of Carbon (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Loss</td>
</tr>
<tr>
<td>0%</td>
</tr>
<tr>
<td>25%</td>
</tr>
<tr>
<td>50%</td>
</tr>
<tr>
<td>75%</td>
</tr>
</tbody>
</table>

[Graph showing corrosion rate vs. carbon loss for different types of carbon]
Catalyst Degradation: E vs. EA (Bilayer)

~10X compression/thinning of E-carbon surface layer due to carbon corrosion

No change to EA-carbon layer

% change in Pt particle size much greater for Pt supported on E-carbon in surface layer than Pt particles supported on EA-carbon in inner layer
Comparison of Carbon Corrosion – Potential Mitigation of Transport Losses \(\xrightarrow{\text{Mixing Stable Materials to Keep CL Structure}}\)

**Waterfall Plot of Mass Activity and ECSA**

- E - Carbon
- V - Carbon
- EA - Carbon Mix (EA+E)

**Polarization Curves after Time at 1.2 V Hold**

- EA Carbon - 0hrs
- EA Carbon - 20hrs
- EA Carbon - 400hrs
- E Carbon - 0hrs
- E Carbon - 20hrs
- E Carbon - 100hrs
- Mix (E + EA) - 0hrs
- Mix (E + EA) - 24 hrs
- Mix (E + EA) - 400 hrs

**Impedance @ 1.0 A/cm²**

- EA Carbon (Initial)
- EA Carbon (400 hours)
- E+EA Carbon Mix (400 hours)
- E+EA Carbon Mix (Initial)
- E Carbon (Initial)
- E Carbon (100 hours 0.2A/cm²)

**Impedance @ 0.02 A/cm²**

- E-Carbon (Initial)
- E-Carbon (100 hours)
- E+EA Mix (Initial)
- E+EA Mix (400 hours)
- Mix (E + EA) - 0hrs
- Mix (E + EA) - 24 hrs
- Mix (E + EA) - 400 hrs

Note: MEA Pt loadings were: 0.15 mg/cm² (E) / 0.15 mg/cm² (Ea+E) / 0.25 mg/cm² (EA)
Comparison of Carbon Corrosion – Potential Mitigation of Transport Losses

Mixing Carbon Support Materials to Keep CL Structure and Activity

- High Surface Area Carbon shows 10x decrease in CL thickness ~ 1 µm after test
- Mixed with graphitized carbon shows ~ 50% decrease in CL thickness
  - Keeps porosity available for transport
- Pt particle size growth observed for both types of carbon

Carbon Corrosion AST – 1.2 V potential hold

Note: MEA Pt loadings were: 0.15 mg/cm² (E) / 0.15 mg/cm² (EA+E) / 0.25 mg/cm² (EA)
Mixed Catalysts (E + EA) – Fresh vs. Carbon AST

- E-carbon regions (yellow) are distinct and separate from EA-carbon regions (green)
- Regions remain distinct and separate
- Note “directional” banding of oxidized E-carbon vs. non-oxidized EA-carbon parallel to membrane

- **EA mixed with E maintains pore structure of CL – maintains transport**
- Show preferential oxidation of E-carbon forming bands of dense "graphite-oxide" encapsulating large Pt nanoparticles
- The bands are oriented parallel to membrane surface in compression direction.
- EA-carbon shows essentially *NO* oxidation, retaining its graphitic structure - Pt particle size changes are significant for E-carbon and little for EA-carbon.
Mixed Catalysts (E + EA) – Fresh vs. Carbon AST

Fresh MEA

Aged MEA

~ 50% compression/thinning due to E-carbon corrosion
Modeling Aged/Degraded Membranes

- **Model Parameters**
  
  We continue measuring properties for model

- **Structural** (see below)

- **Chemical** (EW)

- **Mechanical** (modulus)

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**Sorption Model (in-progress)**

- **Structural**
  - Domains
  - Phase-Separation

- **Chemical**
  - Interactions
  - EW (IEC)

- **Mechanical**
  - Backbone Modulus
  - Crystallinity

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Nanostructure of Degraded Membrane

SAXS (Small Angle X-Ray Scattering)
Results for membranes degraded by different protocols

Nafion® 212 Membrane
- Upon boiling of aged membrane, d-spacing increases
- Still lower than fresh membrane

Nafion® 212 Membrane
- Upon boiling of aged membrane, d-spacing increases
- Becomes higher than fresh membrane
- Break-up of reinforcement allows more water uptake
Degradation Affects Structure & Crystallinity

- Wide-Angle X-Ray Scattering
- Crystallinity of Degraded samples

XL100 (LANL AST Tests)
- As-processed
- H₂/Air
- Air/Air
- OCV

- Increased crystallinity upon degradation (OCV is highest)
- Consistent with TEM

TEM Images: Oak Ridge National Laboratory. Rod Borup (LANL), DoE 2011 AMR Meeting
Initial test completed on chemical stability of Ion Power MEA with chemically stabilized and mechanically reinforced DuPont XL membrane, and 0.23 mg/cm²(c) and 0.034 mg/cm²(a) Pt loading

- At 90°C and 30% RH, FER from XL membrane is generally 1/50th the FER from non-stabilized PFSA membranes
- FER from cathode is generally higher than from anode
- XL membrane shows weaker RH, P(O₂) and cell V dependence than literature data for non-stabilized membranes
- FER from XL membrane correlated with RH, T, V, and P(O₂) but more accurate analytics needed to reduce the error band
Membrane/Electrode Performance Degradation Model

Modeling of experimental data indicates that ionomer loss from electrodes rather than membrane degradation is the primary cause of $F^-$ release in the initial test – to be further verified

- Small change in $H_2$ crossover over the test duration
  - ECSA loss attributed to the decrease in Pt utilization caused by ionomer degradation at the three-phase boundary
- Pt particle size in TEM is not affected by ionomer loss
- Higher ECSA loss in the anode than in the cathode
- ECSA loss correlated with cumulative $F^-$ release per unit volume of the catalyst layer
Point defect model (PDM) developed for passive films in SS 316L

- ORNL electrochemical cell and LANL ICP data: the steady-state current density and metal dissolution rates independent of cell V.
- Rate controlling step assumed to be at the metal/film interface
- Consistent with ORNL XPS measurements 316L is assumed to form protective Cr-rich oxide layer up to 1 V (Fe-rich oxide at higher V)
- PDM calculates the change in oxide thickness due to cyclic potentials and metal (Cr, Fe, Mn and Ni) dissolution rates as a function of oxide thickness
Bipolar Plate Corrosion Model: Nitrided G35

Developed a 2-step lumped surface reaction model for corrosion of nitrided G35 at 0 to 1.5 V

- Rate controlling step assumed to be at the surface/electrolyte interface
- ICP and polarization data used to determine the contributions of individual species (Cr, Ni, Fe, Mn, Mo) to the dissolution current
- In the passive region (0 - 0.5 V), Fe and Ni dissolve preferentially at rates that are function of surface coverage and are weakly dependent on applied potential.
- In the trans-passive region (0.8 - 1.5 V), Ni and Cr dissolve preferentially at rates that depend on surface coverage and potential.
Bipolar Plate Interfacial Contact Resistance

Derived ICR from NREL 2XICR data for ORNL specimens exposed at different potentials, and correlated with compaction force and potential

- ICR inferred as a function of potential (0.2 – 1 V) for 316L correlates well with the modeled thickness of the protective oxide film (passive film).
- Inferred ICR for nitrided G35 shows more complex behavior that may depend on surface properties (roughness, phases). Reduction in ICR between 0.5 - 1 V may be correlated with surface coverage (preliminary analysis). More work needed to correlate ICR above 1 V.
Carbon Bipolar Plates

- **Plate Electrical Conductivity**
  - Measure bulk and contact resistances for different plate chemistries and surface treatments, and integrate into electrical modeling work

- **Water Management**
  - Measurement of dynamic surface properties to try to link ex-situ characterization (including models) to in-situ performance

**Through-Plane Voltage Drop**

- Epoxy 1
- Epoxy 4
- Epoxy 5
- Vinyl Ester 1

**Predicted 2D Drag Force vs. Measured 2D Drag Force**

- In-situ testing in development to validate ex-situ characterization work to date
All Materials – Contamination

Examples of potential contaminants by component

- Acid leach of non-aged materials
  - Plate adhesive data highlights potential extractable Fenton’s reagents
  - Film laminates data comparing total metals and total organics
- De-ionized water leachate analysis over time at 100°C
  - Sampling at 500, 1000, 2000, 3000 and 4000 hours
  - Cumulative concentrations presented
Impact of Electrode Structure on Cathode Durability

**Electrode from Water/IPA**
- Nafion®: dispersion
- Pt/C: poorly dispersed
- Mechanical property: poor
- Polymer relaxation: fast
- TYPE I degradation:
  - Fast degradation:
    - Major contributions – Decreasing ECSA
    - Decreasing transport

**Electrode from NMP**
- Nafion®: solution
- Pt/C: well dispersed
- Mechanical property: good
- Polymer relaxation: intermediate
- TYPE II degradation:
  - Moderate degradation:
    - Major contributions – Effects of decreasing ECSA

**Electrode from Glycerol**
- Nafion®: dispersion
- Pt/C: well dispersed
- Mechanical property: moderate
- Polymer relaxation: slow
- TYPE III degradation:
  - Slow/little degradation:
    - Effects of increasing transport counter decreasing ECSA

Other solvents with similar effects: water/methanol, water ethanol, water/n-propanol

Other solvents with similar effects: DMAc, DMF, DMSO, water/glycerol

Other solvents with similar effects: propylene glycol, butanediol
Ionomer Relaxation by Contacting 100°C Water Vapor Measured by AFM

- **Water/low alcohol (water/IPA 1:1)**
  - After casting
  - After 100°C H₂O vapor/1h
  - After 100°C H₂O vapor/3h
  - Relaxation rate: Fast

- **Aprotic polar (NMP)**
  - After casting
  - After 100°C H₂O vapor/1h
  - After 100°C H₂O vapor/3h
  - Relaxation rate: Intermediate

- **High alcohol (propylene glycol)**
  - After casting
  - After 100°C H₂O vapor/1h
  - After 100°C H₂O vapor/3h
  - Relaxation rate: Slow

TM-AFM (500 × 500 nm scale) measured under ambient conditions
Impact of Cathode Pt Loading on Durability and Degradation Modes

<table>
<thead>
<tr>
<th>Cathode Pt Loading (mg/cm²)</th>
<th>ECSA (m²/gPt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 K</td>
</tr>
<tr>
<td>0.25</td>
<td>50</td>
</tr>
<tr>
<td>0.11</td>
<td>49</td>
</tr>
<tr>
<td>0.05</td>
<td>52</td>
</tr>
</tbody>
</table>

- **0.25 mg/cm² cathode:** TYPE II Degradation
- **0.11 mg/cm² cathode:** TYPE III Degradation
- **0.05 mg/cm² cathode:**
  - Significant mass transport issue initially but improved over time
  - Slightly faster Pt particle growth & ECSA change
  - Need to improve the poor initial performance

**Dispersing Solvent:** commercial Nafion+glycerol/propanol/H₂O; **Ionomer:** Nafion; **Ionomer to Pt/C composition:** 30wt.%; **Anode:** 0.2 mgPt cm⁻² (20 wt.% Pt/C, BASF), **Cathode:** 0.05-0.25 mg Pt·cm⁻² (20 wt.% Pt/C, BASF); **Membrane:** Nafion® 212; **Operating conditions:** cell temperature: 80°C, backpressure: 30 psi, Potential cycling conditions: 0.6 – 1.0 V under H₂/N₂ at 80°C
Approaches to Improve Durability of Low Pt Loaded Cathodes

**Approach 1**
Reduce ionomer to Pt/C ratio

*Dispersing Solvent:* Water/glycerol; *ionomer:* Nafion; *ionomer content:* 22wt.%;
*Cathode:* 0.05 mgPt cm⁻² (20 wt.% Pt/C, BASF);

- Poor initial performance with flooding
- Improved performance after 30K
- TYPE III degradation

**Approach 2**
Use water/IPA dispersion

*Dispersing Solvent:* Water/IPA; *ionomer:* Nafion; *ionomer content:* 30wt.%;
*Cathode:* 0.05 mgPt cm⁻² (20 wt.% Pt/C, BASF);

- Improved initial performance
- No flooding issue
- TYPE III degradation

**Approach 3**
Lowered Pt to carbon ratio

*Dispersing Solvent:* Water/glycerol; *ionomer:* Nafion; *ionomer content:* 30wt.%;
*Cathode:* 0.05 mgPt cm⁻² (10 wt.% Pt/C, BASF);

- Excellent initial performance
- Performance decrease after 30K
- TYPE I degradation

**Approach 4**
MEA Pre-treatment

*Dispersing Solvent:* Water/glycerol; *ionomer:* Nafion; *ionomer content:* 30wt.%;
*Cathode:* 0.05 mgPt cm⁻² (20 wt.% Pt/C, BASF);

- Improved initial performance
- Catalyst sintering (and ECSA reduction only affects at very high potential (~ 0.9 V)
- TYPE III degradation

<table>
<thead>
<tr>
<th>No. potential cycles</th>
<th>0 K</th>
<th>10 K</th>
<th>30 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECSA (m²/gPt)</td>
<td>48</td>
<td>27</td>
<td>23</td>
</tr>
<tr>
<td>i₀.90V (mA/cm²)</td>
<td>1.47</td>
<td>1.03</td>
<td>0.78</td>
</tr>
<tr>
<td>i₀.86V (mA/cm²)</td>
<td>12.2</td>
<td>10.3</td>
<td>7.3</td>
</tr>
<tr>
<td>i₀.80V (mA/cm²)</td>
<td>84</td>
<td>75</td>
<td>58</td>
</tr>
<tr>
<td>i₀.4V (A/cm²)</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Selected Technical Conclusions/Summary - 1

• **Model Development**
  – Completed initial development of Pt dissolution model in 2012
  – 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)
  – Completed initial development of carbon corrosion model
  – Modified catalyst durability model to account for changes due to carbon corrosion
  – Completed models for Pt catalyzed corrosion of Ketjen black (E-type), Vulcan XC-72 (V-type) and graphitized carbon (EA-type) supports
  – Determined the effect of aging on the specific surface area of carbon (S_C, m²-C/g-C)
  – Modeled gas crossover
  – 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})
  – Pt particle degradation and migration affects the membrane H₂ crossover
  – Developed component model for combined chemical/mechanical membrane durability
  – Component model for combined chemical/mechanical membrane durability – combined sorption model can predict change in H₂O uptake based on nanostructure degradation
  – Aging effects on crystallinity effecting water uptake
  – Catalyst layer ionomer degradation modeled as contributing cause to ECSA loss
  – Bipolar Plates
  – Model developed for SS 316L and G35 metal bipolar plates
• **Catalyst**
  – % change in Pt particle size much greater for Pt supported on E-carbon in surface layer than Pt particles supported on EA-carbon in inner layer
  – Significant Pt growth/coarsening observed ONLY in E-carbon surface layer due to pronounced carbon corrosion throughout entire thickness of this layer.

• **Carbon corrosion ubiquitous over cathode potentials**
  – Loss of meso-graphitic structure in catalyst layer
  – Structure shows localized structure changes
  – Structure change mass transport
  – Mixing more stable materials retains structures with transport properties
  – Elemental changes
    • Catalyst Layer shows increasing graphitic content
    • Increasing oxygen concentration
Selected Technical Conclusions/Summary - 3

• **Ionomer Degradation**
  – Modeling of experimental data indicates that ionomer loss from electrodes rather than membrane degradation is the primary cause of F\(^-\) release in the initial test – to be further verified
  – 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\(_{xc}\))

• **Membrane Degradation**
  – Cycling in the absence of chemical effects does not cause failure (SOA reinforced membranes)
    • Combined chemical/mechanical degradation leads to early failure
  – Increased crystallinity upon degradation (OCV is highest)
    • Aging reduces uptake & domain size
  – Nanostructure to characterize degradation
    • Reinforced membrane could lose its integrity

• **MEAs**
  – Low loaded cathodes (0.05 mg/cm\(^2\)) durability response different than > (0.10 mg/cm\(^2\))
  – Nafion\(^\circledR\) relaxation in catalyst layer

• **Mitigation**
  – Electrode structure can be maintain by mixing stable support materials
  – Different solvent approaches can strengthen the Nafion\(^\circledR\)/catalyst layer
Future Work (this project)

Modeling:
- Incorporate component membrane model into integrated model
- Modeling of transport losses due to carbon corrosion
- Incorporate transport of dissolved cations through catalyst ionomer and membrane from carbon plates, seals and metal bipolar plates

Component Interactions:
- Measure transport of dissolved cations through catalyst ionomer and membrane
- Further quantitate relationship between carbon corrosion and resulting changes in CCL structure (Pt/pore distributions, Pt utilization, ECSA)
  - Quantification of E vs. EA carbon structures and mixed formulations
- Refined analytics and test protocols for reproducible FER measurements for chemically-stabilized membranes
Future Work

- **Understand Carbon/Nafion®/Catalyst structure and durability effects**
  - Understand structure of catalyst layer effect on durability; different methods of forming catalyst layers
  - Improve durability/performance of low loaded MEAs (0.05 mg/cm²)
  - Identify ionomer degradation source for FER (CL vs membrane)

- **Define effect of carbon corrosion on CL structure and transport losses**
  - Quantitate relationship between carbon corrosion and changes in CL structure
  - Identify uniform methodology for measuring real durability impact of start-up/shut-down, air cycling
  - Spatial/areal performance variations over aging remain largely undetermined

- **Catalyst durability**
  - Reduce solubility of Pt via increasing support interactions, alloying
  - Understand/model dissolution of Pt at elevated temperatures and in oxygen
  - Understand effect of Pt transport and band formation

- **Component surface properties**
  - Understand effects of changing surface chemistry on: bipolar plates, catalyst support, GDL

- **Mitigation of Degradation**
  - Increasing CL transport, stability through use of structure and stable materials
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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  - NIST: NG3, NG7 beam lines
- Neutron imaging beam time provided by
  - National Institute of Standards and Technology: BT-2
- Other materials provided by:
  - SGL Carbon
  - W.L. Gore
  - Tanaka
  - DuPont
  - Solvay
  - ETEK
Technical Backup Slides
## Approach - FY2013 Milestones

<table>
<thead>
<tr>
<th>Mon Yr</th>
<th>Milestone</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<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>Completed</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>Completed</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>Completed - at lower loadings; from 0.05 to 0.4</td>
</tr>
<tr>
<td>July 2013</td>
<td>Quantify carbon surface oxidation of GDL carbon by newly proposed GDL AST by titrimetric technique. Complete correlation between AST and in situ fuel cell operation. Determine if method is applicable to carbon catalyst supports by finishing evaluation of 3 different catalyst support carbons by identical techniques (Vulcan, Ketjen and EA (highly graphitized carbon).</td>
<td>Completed on GDLs</td>
</tr>
<tr>
<td>Sept 2013</td>
<td>Demonstrate H₂/air fuel cell performance of 0.05 mg/cm² cathode &gt; 0.6 A/cm² at 0.7 V</td>
<td>Completed</td>
</tr>
<tr>
<td>March 2013</td>
<td>Develop models for platinum transport in the membrane, and the resulting reactions between crossover H₂ and O₂ and fluoride emission rates</td>
<td>Completed</td>
</tr>
<tr>
<td>June 2013</td>
<td>Develop model for effect of carbon corrosion on cell performance for different carbon structures</td>
<td>Partially completed</td>
</tr>
<tr>
<td>Sept 2013</td>
<td>Integrate the models for degradation of MEA components and evaluate the potential of reaching 5000-h durability target for automotive fuel cells</td>
<td>Pending</td>
</tr>
<tr>
<td>March 2013</td>
<td>Determination of the change in lambda vs. d-spacing for membranes aged 4 different ways.</td>
<td>Completed</td>
</tr>
<tr>
<td>March 2013</td>
<td>Deliver a total of 20 catalyst layers on PTFE membrane with different ionomer:carbon ratio, carbon type, Pt/C ratio, and ionomer equivalent weight.</td>
<td>Completed (at least to satisfaction)</td>
</tr>
<tr>
<td>Sept 2013</td>
<td>Characterize aged bipolar plates in terms of changes in water balance and water-management related performance as a function of different surface modifications.</td>
<td>Nominally completed</td>
</tr>
</tbody>
</table>
Mixed Catalyst Layer E + EA – Fresh

Aged MEA
“localized bands” of HSAC corrosion observed, which are correlated with regions of increased Pt particle sizes and closer Pt-Pt interparticle spacings (yellow arrows)
Degradation Mechanisms of Pt/C Cathode during Potential Cycling

<table>
<thead>
<tr>
<th>Degradation</th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical processing solvent</td>
<td>Water/low alcohol</td>
<td>Aprotic polar or water/high alcohol</td>
<td>Single high alcohol</td>
</tr>
<tr>
<td>Porosity (^a)</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Degradation mechanism</td>
<td>Pt particle growth(^b)</td>
<td>Pt particle growth(^b)</td>
<td>Pt particle growth(^b)</td>
</tr>
<tr>
<td></td>
<td>\textbf{Electrode disintegration} due to poor mechanical properties</td>
<td>\textbf{Ionomer relaxation} due to continuous contact with saturated water</td>
<td></td>
</tr>
<tr>
<td>Features</td>
<td>Good initial mass transfer \textbf{Sudden drop} of fuel cell performance</td>
<td>Good initial and long-term mass transfer \textbf{Reasonable reflection} of Pt particle growth</td>
<td>Poor initial but good long-term mass transfer Performance could be improved overtime</td>
</tr>
</tbody>
</table>

\(^a\) BET measurement; \(^b\) The degree of Pt particle aggregation during potential cycling is comparable

Commercial MEAs exhibited Type II degradation behavior during potential cycling test. LANL developed novel electrode processing which showed Type III degradation behavior. Under severe fuel cell operation (e.g. start-stop cycling, high potential holding), all electrodes can show Type I degradation.
The conductivity of Nafion® was high at low RH with short equilibrium time.

The low RH conductivity of Nafion® gradually decreased → impossible to run fuel cell at extended dry conditions.

Slowing down the relaxation rate of Nafion® and water management are two key parameters for low RH fuel cell operations.