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FC-PAD Overview & Cross cutting thrusts

Objective of Thrusts 4-6

- Develop and implement characterization techniques and models to improve performance and durability of fuel cells
- Highly integrated into Thrusts 1-3

- Operando evaluation and durability is focus of this presentation
- Supported by modeling and characterization not specific to individual components
FC-PAD contributors to this presentation

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Current Collaborators

GM/W. L Gore (SOA MEAs)
IRD, Ion Power (MEAs)
Umicore (Catalyst)
SGL Carbon (GDLs)
National Physical Laboratory (Reference electrode)

Partners to be added by DOE DE-FOA-0001412
Overview - Relevance

Timeline
Project start date: 11/20/2015
Project end date: 09/30/2020

National Labs
• ANL, LANL, LBNL, NREL, and ORNL

External Collaborators
• IRD, New Mexico
• Umicore, Germany
• GM, USA
• W. L. Gore, USA
• Ion Power, USA
• Tanaka Kikinzoku Kogyo (TKK), Japan
• National Physical Laboratory, United Kingdom

Barriers
• Durability of PEMFC stacks, which must include tolerance to impurities and chemical and mechanical integrity, has not been established
• Sufficient durability of fuel cell systems operating over automotive drive cycles has not been demonstrated
• Development and implementation of accelerated stress tests (ASTs) are needed to shorten the time required to address durability issues
• MEA Targets:
  • 300mA @ 0.8V
  • 1W/cm² @ rated power
  • 5000 hour durability
Overview - Approach (Operando Evaluation/Durability)

- Refine ASTs
  - Proposed new membrane and electrocatalyst ASTs
- Evaluate durability of Pt-alloy catalyst based MEAs and propose methods to improve durability
  - Operando evaluation, Characterization and Modeling
- Impurity effects on fuel cell performance
  - Reversible/Recoverable degradation (membrane degradation fragments)
  - Sulfate anion poisoning
- Benchmark SOA MEA
  - Obtained MEA with membrane from Gore and SOA catalyst from GM
- Develop/Apply advanced electrochemical characterization techniques
  - Reference electrodes
Accomplishments: Adoption of Membrane AST

Severe degradation of DuPont XL® after 307 hours @ OCV

No degradation of DuPont XL® 20098 RH Cycles

Degradation of DuPont XL® 9934 RH Cycles in OCV

- 30sec wet and 45sec dry cycles in H₂/Air
- Similar RH stresses as determined by HFR
- Cycling time needs to be adjusted based on HFR

See additional slide for FCTT adopted AST
Accomplishments: Adoption of Electrocatalyst AST

- **0.6 to 1.0V cycles**: Target = 133 hours
- **0.6 to 0.95V cycles**: Target = 50 hours

- **New AST 20X faster than old AST** and **100X faster than FCTT durability protocol**

Higher N$_2$ flow rates (200sccm vs 75sccm)

See additional slide for FCTT adopted AST
Accomplishments: Refined catalyst AST

- Acceleration factor can be increased with increasing N₂ flow rate
- High N₂ flow (200 sccm) results in 100X acceleration while low N₂ flow (75 sccm) results in 25X acceleration
- Spatial variation in degradation is greater at the higher flow rate
- Use 75sccm N₂: 5X acceleration over old AST
Accomplishments: Alloy catalyst durability

- The 3 alloy catalysts tested met the BOL mass activity criteria (Thrust 2)
- Surface area and beginning catalyst particle sizes are different
- The smaller particle size catalysts grew from 4.4 nm to 5.5 nm
- The larger particle size catalyst showed no increase (5.5 nm) after AST
- ECSA loss of 40% can be met by starting with larger catalyst particle (> 4.5 nm)

Note: Loading not identical
IRD = 0.21 mg\(_{Pt}\)/cm\(^2\) and Umicore/NREL = 0.1 mg\(_{Pt}\)/cm\(^2\)
Accomplishments : Alloy catalyst durability

- Fuel cell performance decreases even though ECSA can be constant
- Kinetic losses observed and seem to be independent of ECSA losses
- Losses > 30mV @ 0.8 A/cm²
Accomplishments: Alloy catalyst durability

- Loss in fuel cell performance mainly due to de-alloying of Co from the PtCo electrocatalyst
- Significant and uniform Co present across entire membrane thickness (no Co in anode)
- Pt enrichment at Cathode Catalyst Layer (CCL)/membrane interface (1.5 μm in CCL) and large Pt particles form in the membrane
Accomplishments : Alloy catalyst durability

- Co loss uniform across CCL thickness
- Average Co content in CCL decreases by ≈ 60-70%
- Separated Pt and Co formed in the CCL during AST
- Significant and separate Pt and Co present in membrane
Accomplishments: Modeling

3-D Differential Cell Model

- Model Parameters to be Determined from Limiting Current Density
  - GDL resistance to $O_2$ transport
  - CCL pore resistance to $O_2$ transport
  - Ionomer film resistance to $O_2$ transport

Impedance @ 1.6 A/cm²
Before and After Catalyst AST

- Blue: Air (BOT: 0.35V)
- Black: Air (BOT: 0.16V)
- Red: HelOx (BOT: 0.50V)
- Orange: HelOx (EOT: 0.39V)

Cathode half-cell model extending from gas channel to CCL

- Nearly uniform ORR flux in CCL for $R_c/R_f = 0.05$
- Non-uniform ORR flux in CCL for $R_c/R_f = 5$
Accomplishments: Modeling

**O₂ Transport Resistances in Saturated Alloy catalyst**
- \( R_g \): Gas channel resistance
- \( R_d \): GDL resistance
- \( R_{cf} \): Combined resistance of CCL pores and ionomer
- \( R_c \): CCL pore resistance
- \( R_f \): Ionomer resistance

**Assumptions**
- O₂ transport in GDL is by molecular diffusion: diffusivity is inversely proportional to pressure
- O₂ transport in 20-100 nm CCL macros is by Knudsen diffusion: diffusivity weakly dependent on pressure
- O₂ transport in ionomer film and micro pores is independent of pressure
- Water breaks through GDL because gas channel RH is 100%: \( R_d = R_d(P, i) \)
- Ionomer is saturated with water and CCL pores contain liquid water: \( R_{cf} = R_{cf}(i) \)

Cathode catalyst layer pore resistance and GDL resistance are primary contributors at high current density (100% RH)
Recoverable Degradation

- From various developers and notable #’s of presentations (e.g. ECS), interest is increasing in understanding recoverable degradation
- Losses noted during long periods of uninterrupted operation\(^1,2\)

**Known and suggested mechanisms:**

- Pt-Ox formation and Pt reduction
  - (e.g. Pt-Ox have reduced kinetics)\(^1,2\)
- Adsorbed species
  - Cathode\(^1,3\) – SOx / membrane fragments
  - Anode\(^1\) – CO or other adsorbed species
- Transport
  - Flooded catalyst layer/GDL\(^1\)

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\(^1\) S.J.C. Cleghorn, et al, Journal of Power Sources, 158, 1, 2006, 446–454
Accomplishments – Sulfate ORR Inhibition (Ex situ)

- Noticeable poisoning effect by sulfates in RDE
- PtCo alloy catalyst shows a larger decrease in performance with sulfate anions
  - 10 mV shift for Pt/C; 30 mV shift for PtCo/C
- Pt and PtCo alloy catalyst show full recovery after removal of the anions
- Onset of OH ads. shifts to higher potentials
- ORR inhibition affected by scan rate and direction (anodic vs cathode scan)
Sulfate infusion causes degradation in fuel cell performance at 0.6 A/cm² when the cathode loading is 0.1 mg<sub>Pt</sub>/cm² (no effect at 0.2 A/cm² and 0.4 mg<sub>Pt</sub>/cm²).

The adsorption of sulfate anions on the cathode catalyst resulted in performance loss of $\Delta V_1 = 24$ mV.

Membrane resistance (HFR) was not affected by sulfate contaminant.

Voltage loss not recovered when infusion was stopped ($\Delta V_2 = 28$ mV).

Sulfate caused degradation appears to be reversible after potential cycling recovery step.

Low voltages and high RH’s have been reported to result in recovery.
Accomplishments – Sulfate Anion Contamination (recovery)

- After infusion, Pt CV shows a decrease in ECSA
- After several CVs from low (0.085V) to high (1V) potentials, ECSA was partially recovered and performance almost fully recovered
- Recovery potential needs to be <= 0.3V for sulfate anions
- Cathode environment irrelevant between: N₂ or Air
- Liquid water injection observed to hurt recovery

OCV tests

Recovery in H₂-N₂ at 0.4V

Recovery in H₂-N₂ at 0.2V

Recovery of Pt-Ox
Accomplishments – Recoverable Degradation

- Degradation effect decreases with increasing levels of membrane chemical stabilization and cathode catalyst loading
- Greater effect at outlets

**MEA 1:** Membrane with no additives: \( \approx 0.04 \text{mg}_{\text{Pt}}/\text{cm}^2 \)

**MEA 2:** Membrane with no additives: \( 0.4 \text{mg}_{\text{Pt}}/\text{cm}^2 \)

**MEA 3:** Chemically stabilized membrane: \( 0.4 \text{mg}_{\text{Pt}}/\text{cm}^2 \)
Benchmarking

• W. L. Gore provided 18 μm membrane to GM
• GM applied SOA catalyst layer of $0.1\text{mg}_{\text{Pt}}/\text{cm}^2$ @ cathode
• MEA meets DOE BOL Mass activity target (FC 137)
• Will be used in durability protocol, membrane AST protocols, and catalyst/support AST protocols to benchmark SOA MEA
Accomplishments: Spatially distributed Reference Electrodes

Luis Castanheira, Gareth Hinds

- Nafion salt bridge contacts directly the anode catalyst layer through small holes in the GDL
- 6 of the 9 RE positions were used (numbered in direction of hydrogen flow)
- 3 unused holes were sealed with a PEEK rod (diameter 0.9 mm) inside the PTFE tubing
Collaborations

<table>
<thead>
<tr>
<th>Institutions</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC-PAD Consortium</td>
<td>ANL, LBNL, ORNL, LANL, NREL</td>
</tr>
<tr>
<td>Umicore, TKK</td>
<td>Supply SOA catalysts for evaluation</td>
</tr>
<tr>
<td>IRD, Ion Power</td>
<td>Supply SOA catalysts and/or MEAs for evaluation</td>
</tr>
<tr>
<td>GM/W.L. Gore</td>
<td>Supply SOA MEA for Benchmarking</td>
</tr>
<tr>
<td>NPL</td>
<td>Reference electrode Setup</td>
</tr>
</tbody>
</table>
Proposed Future Work

• Plans for the remainder of FY16
  o Complete durability evaluation of PtCo alloy catalyst based MEAs
  o Complete development of reference electrode setup
  o Systematically evaluate effect of sulfate infusion as a function of potential and during durability cycling protocol
  o Quantify effect of reversible degradation under durability cycling protocol

• Plans for FY 17
  o Evaluate durability of PtNi and advanced carbon based MEAs
  o Use segmented/reference cell to evaluate effect of operating parameters on durability
  o Model durability of MEAs under both AST and durability cycling protocols
  o Benchmark durability of SOA MEA (durability cycling, membrane AST, and support AST)
  o Adopt a differential cell for single cell durability testing
  o Evaluate effect of system contaminants on low loaded SOA MEAs
Summary

• **Relevance:** Evaluate durability of SOA MEAs, determine degradation mechanisms, propose mitigation strategies to meet DOE 2020 durability targets for MEAs that can meet the DOE 2020 Pt loading and BOL performance targets. Refine ASTs to evaluate the durability of MEAs.

• **Approach:** Our approach involves developing advanced diagnostics, modeling and characterization techniques to evaluate SOA MEAs and provide insights to improve the durability of the MEA components to meet DOE 2020 performance and durability targets.

• **Accomplishments and Progress:** 2 new ASTs have been adopted by the DOE. Durability studies of SOA MEAs meeting BOL targets have been initiated. Benchmarking of SOA MEA initiated. Reference electrode setup being developed for durability studies.

• **Future work:** Identify all degradation mechanisms in SOA alloy catalysts and quantify voltage losses (especially in the mass transport region). Develop mitigation strategies. Complete the development of advanced tools and models.
Supplemental Slides
# New Catalyst AST (Square Wave)

## Table A1 Electro catalyst Cycle and Metrics

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Square wave cycle: steps between 0.6 V (3 s) and 0.95 V (3 s) with rise time of ~0.5 s or less; run polarization curve and ECSA at specified intervals. Single cell 25-50 cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>30,000 cycles</td>
</tr>
<tr>
<td>Cycle time</td>
<td>6 s</td>
</tr>
<tr>
<td>Temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>Anode/Cathode 100/100%</td>
</tr>
<tr>
<td>Fuel/Oxidant</td>
<td>Hydrogen/N₂ (H₂ at 200 sccm and N₂ at 75 sccm for a 50 cm² cell)</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric pressure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic Mass Activity</td>
<td>At beginning and end of test minimum</td>
<td>&lt;40% loss of initial catalytic activity</td>
</tr>
<tr>
<td>Polarization curve from 0 to &gt;1.5 A/cm²</td>
<td>After 0, 1k, 5k, 10k, and 30k cycles</td>
<td>&lt;30 mV loss at 0.8 A/cm²</td>
</tr>
<tr>
<td>ECSA/Cyclic Voltammetry</td>
<td>After 10, 100, 1k, 3k, 10k, 20k and 30k cycles</td>
<td>&lt;40% loss of initial area</td>
</tr>
</tbody>
</table>

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**a.** A protocol such as the one in Table A9 should be used to recover reversible losses prior to measurement of metrics.

**b.** Mass activity in A/mg @ 150 kPa abs backpressure at 900 mV iR-corrected on H₂/O₂, 100% RH, 80°C, anode stoichiometry 2, cathode stoichiometry 9.5. A minimum hold time of 15 min is recommended, with the mass activity calculated based on the average current during the last 1 min. Multiple points should be measured at low current, and the 0.9 V iR-free potential should be determined based on these measurements. Measured ORR current may be corrected for H₂ crossover. Based on the protocol published by Gasteiger et al., Applied Catalysis B: Environmental, 56 (2005) 9-35.

**c.** Polarization curve per protocol in Table A6.
Table A5 Membrane Chemical/Mechanical Cycle and Metrics (Test Using a MEA)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Frequency</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total time</td>
<td>Until crossover &gt;15 mA/cm² or 20,000 cycles</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>90°C</td>
<td></td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>Cycle from 0% RH (30 s) to 90°C dewpoint (45 s)</td>
<td></td>
</tr>
<tr>
<td>Fuel/Oxidant</td>
<td>H₂/Air at 40 sccm/cm² on both sides</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>Ambient or no back-pressure</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻ release or equivalent for non-fluorine membranes</td>
<td>At least every 24 h</td>
<td>No target – for monitoring</td>
</tr>
<tr>
<td>Hydrogen crossover (mA/cm²)ᵇ,c</td>
<td>Every 24 h</td>
<td>&lt;15 mA/cm²</td>
</tr>
<tr>
<td>OCVᵈ</td>
<td>Continuous</td>
<td>Initial wet OCV ≥ 0.95 V, &lt;20% OCV decrease during test</td>
</tr>
<tr>
<td>High-frequency resistance</td>
<td>Every 24 h at 0.2 A/cm²</td>
<td>No target – for monitoring</td>
</tr>
<tr>
<td>Shorting resistanceᵉ</td>
<td>Every 24 h</td>
<td>&gt;1,000 ohm cm²</td>
</tr>
</tbody>
</table>

a. Step durations of 30 s dry and 45 s wet were selected in testing at LANL so that the HFR at the end of the dry step was 2.5 times the HFR at the end of the wet step, which is approximately equal to the HFR ratio that occurs when running the mechanical test (Table A4). Depending on hardware used, these step times may need to be adjusted to achieve the same HFR variation.
c. Hydrogen crossover and OCV targets should be achieved at 0 kPa pressure differential and at 50 kPa anode overpressure, providing sensitivity to global membrane thinning and to hole formation, respectively.
d. A protocol such as the one in Table A9 should be used to recover reversible losses at least once every 24 h and prior to each measurement of metrics.
e. Measured at 0.5 V applied potential, 80°C, 100% RH N₂/N₂. Compression to 20% strain on the GDL.