Highly Accessible Catalysts for Durable High-Power Performance

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• Carnegie Mellon University (CMU), Pittsburgh, PA
• Cornell University (Cornell), Ithaca, NY
• Drexel University (Drexel), Philadelphia, PA
• National Renewable Energy Lab (NREL), Golden, CO

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Project End Date: March 31, 2020

Overall Objectives

• Reduce overall stack cost by improving high-current-density (HCD) performance in H₂/air fuel cells appropriate to meet DOE heat rejection and Pt-loading targets.
• Maintain long-term high electrocatalytic mass activities.
• Mitigate catalyst HCD degradation.

Fiscal Year (FY) 2019 Objectives

• Optimize PtCo and intermetallic ordered PtCo catalysts on accessible carbon supports for durable kinetic activity and HCD performance.
• Evaluate effects of electrolyte on electrode kinetics and transport.
• Quantify performance loss terms and degradation mechanism on developed catalysts.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:
• (B) Cost
• (C) Performance
• (A) Durability.

Technical Targets

The DOE technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

• Improved durability of accessible-PtCo with minimal performance penalty at both low current density and HCD using intermetallic ordering.
• Enhanced the power density at 150 kPa to 0.95 W/cm², approaching the DOE target of 1 W/cm².
• Increased PGM utilization (to 12.1 vs. target of 8 kW/gPGM at 150 kPa) by reducing Pt amount in both anode and cathode.

### Table 1. Progress toward Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

<table>
<thead>
<tr>
<th>Metric</th>
<th>Units</th>
<th>PtCo/KB 2016</th>
<th>PtCo/HSC-f</th>
<th>Ordered-PtCo/HSC-f</th>
<th>Ordered-PtCo/KB</th>
<th>PtCo/HSC-f</th>
<th>DOE 2025 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGM total loading (both electrodes)</td>
<td>mg/cm²</td>
<td>0.125 (0.025 + 0.10)</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>0.075 (0.015 + 0.06)</td>
<td>&lt;0.125</td>
</tr>
<tr>
<td>Mass activity @ 900 mV&lt;sub&gt;free&lt;/sub&gt;</td>
<td>A/mgPGM</td>
<td>0.62&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.7&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.53&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>&gt;0.44</td>
</tr>
<tr>
<td>Loss in catalytic (mass) activity</td>
<td>% loss</td>
<td>30%</td>
<td>59%&lt;sup&gt;b&lt;/sup&gt;</td>
<td>45%&lt;sup&gt;b&lt;/sup&gt;</td>
<td>16%</td>
<td>tbd</td>
<td>&lt;40%</td>
</tr>
<tr>
<td>Performance at 0.8 V (150 kPa, 94 °C)</td>
<td>A/cm²</td>
<td>0.304</td>
<td>tbd</td>
<td>tbd</td>
<td>0.301</td>
<td>tbd</td>
<td>&gt;0.3</td>
</tr>
<tr>
<td>Power at rated power (150 kPa, 94 °C)</td>
<td>W/cm²</td>
<td>0.8</td>
<td>0.95</td>
<td>0.94</td>
<td>tbd</td>
<td>0.91</td>
<td>&gt;1.0</td>
</tr>
<tr>
<td>Power at rated power (250 kPa, 94 °C)</td>
<td>W/cm²</td>
<td>1.01</td>
<td>1.31</td>
<td>1.29</td>
<td>1.15</td>
<td>1.23</td>
<td>-</td>
</tr>
<tr>
<td>PGM utilization (150 kPa, 94 °C)</td>
<td>kW/gPGM</td>
<td>6.4</td>
<td>7.6</td>
<td>7.5</td>
<td>tbd</td>
<td>12.1</td>
<td>&gt;8</td>
</tr>
<tr>
<td>PGM utilization (250 kPa, 94 °C)</td>
<td>kW/gPGM</td>
<td>8.1</td>
<td>10.5</td>
<td>10.3</td>
<td>9.2</td>
<td>16.4</td>
<td>-</td>
</tr>
<tr>
<td>Catalyst cycling (0.6–0.95V, 30k cycles)</td>
<td>mV loss at 0.8 A/cm²</td>
<td>24</td>
<td>39&lt;sup&gt;b&lt;/sup&gt;</td>
<td>25</td>
<td>8</td>
<td>tbd</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Support cycling (1.0–1.5V, 5k cycles)</td>
<td>mV loss at 1.5A/cm²</td>
<td>&gt;500</td>
<td>&gt;500</td>
<td>tbd</td>
<td>tbd</td>
<td>tbd</td>
<td>&lt;30</td>
</tr>
</tbody>
</table>

MEA – membrane electrode assembly; PGM – platinum group metal

Green: meets target; Red: did not meet target

<sup>a</sup> Mass activity at 0.9 V<sub>HR</sub> in cathodic direction

<sup>b</sup> Meets target in absolute terms (i.e., >0.26 A/mg<sub>PGM</sub>)

### INTRODUCTION

The amount of platinum used in the oxygen reduction reaction (ORR) catalyst in fuel cells must be lowered by at least 4-fold to enable proton exchange membrane fuel cells to be cost-competitive with other vehicular propulsion power sources. In our previous DOE-funded project, we demonstrated that carbon-supported Pt-alloy catalysts (PtNi/HSC and PtCo/HSC) exhibited very high ORR electrocatalytic activity and impressive durability, exceeding DOE targets [1]. However, their high-power performance fell short of the target.

As the Pt content is lowered in the cathode, approaching <0.1 mgPt/cm², large oxygen and proton fluxes must be supplied to the Pt surface, causing a performance loss due to a relatively high local transport resistance in the state-of-the-art electrodes. The local resistance was associated with the electrolyte-Pt interface and Pt location/distribution [2]. In addition, the non-precious transition metal in the catalyst, such as Ni or Co, could dissolve and migrate into the ionomer phase, replacing protons and consequently lowering the ionomer proton conductivity and causing hydrodynamic performance loss. As a result, although these Pt-alloy catalysts exhibit excellent durable high catalytic activity, the target performance at high power has not been realized, limiting its cost reduction benefit.

### APPROACH

The general approach for this project is to develop and select carbon supports and electrolytes that have favorable transport properties and subsequently to develop a high-performance Pt-alloy electrode using these subcomponents. The efforts can be divided into four thrusts: (1) development of carbon support, (2) selection of electrolyte (ionomer or ionic liquid), (3) development of stable highly-dispersed Pt alloy nanoparticles, and (4) understanding the effects of the transition metal on performance.

### RESULTS

Last year, we showed that the carbon support morphology has a pronounced effect on how electrocatalysts perform and degrade. Catalysts made from compact, solid carbon have most of their Pt particles on the carbon...
surface in contact with ionomer. The adsorption of ionomer onto Pt was shown to decrease its ORR activity and increase the local transport resistance. Pt particles on the carbon surface can also migrate and collide with each other leading to additional Pt surface loss mechanism. On the other hand, a majority of the deposited Pt particles on catalysts made with porous carbon are embedded inside the carbon pores. This mitigates Pt surface area loss via migration and coalescence. Residing in the carbon pores also decreases ionomer adsorption, thus increasing the ORR activity. However, it can also make it difficult for protons and O₂ to access the electrocatalyst sites.

We have continued our effort to optimize these carbon internal pores to maximize ORR activity, decrease proton and O₂ resistance, and avoid adverse effects on catalyst stability. A collective understanding from high-resolution transmission electron microscopic (TEM) tomography at Cornell, MEA diagnostics at GM and NREL, and ex situ measurements and mesoscale particle-pore modeling at CMU led us to a preliminary guideline for an ideal catalyst morphology, which was reported last year. It is preferable to have all Pt particles within the carbon shielded away from the ionomer layer to optimize ORR activity and local transport. The primary particle size and internal pore morphology of carbon particles are also important to provide sufficient/appropriate proton and O₂ conduction.

As shown in Figure 1, Cornell conducted an in-depth, high-resolution TEM tomography study comparing the carbon internal pore morphology on conventional porous carbon (PtCo/KB) and accessible porous carbon (PtCo/HSC-f). Compared to HSC-f, KB has smaller pore size (2–5 vs. 5–10 nm), smaller pore opening (1–2 vs. 3–7 nm), and likely a more tortuous path into the pores. The mean primary carbon particle of the HSC-f was also smaller (21 vs. 27 nm), which also helps reduce the path length of the reactants. These results confirm the guideline for an ideal catalyst morphology we proposed last year based on performance and characterization.

![Figure 1. Sliced images of PtCo/KB and PtCo/HSC-f catalysts showing the openings of the carbon internal pores. Sliced image analysis was reconstructed from scanning transmission electron microscopic tomography.](image)

However, using the measured carbon pore morphology, it was not sufficient to predict such large performance loss at HCD for the conventional porous carbon (PtCo/KB) when traditional transport properties were applied in CMU's mesoscale particle-pore model. Literature has indicated quickly reduced gas diffusivity in <10-nm liquid-filled micropores [3,4] as much as one-tenth depending on the gas type, channel width, and channel interaction. Simulation using this hypothetical reduced O₂ diffusivity yielded a reduction in O₂ concentration and local current density in the carbon internal pore at HCD operation (Figure 2). CMU is currently conducting an ex situ measurement of O₂ diffusivity through water-filled nanopores with controlled diameter size.
Increase in atomic level ordering of a Pt binary alloy, a so-called ordered intermetallic, was proposed to improve both ORR activity and stability of the catalyst. Last year we were able to obtain improved performance stability of PtCo/KB, our best catalyst for stability. Cornell further studied the degradation mechanism of these catalysts with TEM and found that the intermetallic appears to undergo particle size growth in a lesser degree. This result agrees with the observed Pt surface area and fuel cell performance loss. From our earlier results, catalysts made with accessible carbons—having more open pore structures than conventional porous carbon—showed increased degradation rate. Although the HCD benefit from better local transport could still be realized on accessible carbon catalysts even after the stability test, there is room for improvement. We’ve prepared ordered intermetallics on HSC-f accessible porous carbons in order to achieve both good fuel cell HCD performance and durability. As shown in Figure 3, the retention of HCD voltage after accelerated stability testing (AST) is improved for i-PtCo/HSC-f. However, the magnitude of improvement appears smaller than when the intermetallic was applied on conventional porous carbon. The origin of this discrepancy is unclear, but it may be due to the relative prominence of Ostward ripening vs. migration and coalescence. The intermetallic structure helps mitigate Pt dissolution but not migration. Therefore, it may be more effective on KB because migration and coalescence are negligible on this carbon.

**Figure 2.** Simulated O$_2$ concentration and local current density on a single catalyst aggregate. The analysis shows that reduced O$_2$ concentration and performance loss can be recreated if one uses an O$_2$ diffusivity in the water-filled carbon pores that is about 5 times lower than the bulk value.

**Figure 3.** Voltage at 2 A/cm$^2$ after a different number of accelerated stability voltage cycles for dealloyed PtCo and intermetallic ordered PtCo (i-PtCo) catalysts on different carbon supports. Pt loadings were 0.025 and 0.10 mgPt/cm$^2$ on anode and cathode, respectively. Cell operation conditions are in the order of anode/cathode: H$_2$/air, 94°C, 65%/65% RH, 250/250 kPa$_{abs,outlet}$, stoichiometries of 1.5/2. Accelerated stability test was a trapezoidal voltage cycling between 0.6 and 0.95 V at 80°C, 100% RH, in H$_2$/N$_2$. 

**Carbon Supports and Annealing Effects on HCD Stability**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Voltage at 2 A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtCo/KB</td>
<td>0.7</td>
</tr>
<tr>
<td>PtCo/AB</td>
<td>0.6</td>
</tr>
<tr>
<td>PtCo/V</td>
<td>0.5</td>
</tr>
<tr>
<td>i-PtCo/KB</td>
<td>0.4</td>
</tr>
<tr>
<td>PtCo/HSC-f</td>
<td>0.3</td>
</tr>
<tr>
<td>i-PtCo/HSC-f</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Ionic liquids were added to the PtCo/HSC-f MEA cathode. Improved electrode proton conduction and Pt accessibility under dry conditions were observed, but unfortunately a benefit on the fuel cell performance from ionic liquids was not observed. Due to a lack of available characterization techniques, it is unclear whether we were able to effectively contain ionic liquids in the cathode or not. An effort to optimize the ionic liquids application procedure is ongoing. On the other hand, Drexel evaluated the effect of ionic liquids on the Pt stability during voltage cycling AST in rotating disk electrode (RDE) (Figure 4). They found that ionic liquids helped mitigate electrochemical surface area (ECSA) loss on both Pt/V and Pt/KB catalysts. Inductively coupled plasma–optical emission spectrometry (ICP-OES) measurement showed less Pt dissolution occurred when ionic liquids were applied. TEM images of the catalysts after AST confirmed smaller Pt particle growth with ionic liquids. This result indicates that ionic liquids may help improve the stability of the catalyst in addition to the fuel cell performance enhancement.

**Figure 4. Stabilization against Pt dissolution by ionic liquids (IL). (Left) Retention of Pt surface area during the accelerated stability voltage cycling test in RDE experiments. (Right) Pt ion concentration in RDE liquid electrolyte after 10,000 voltage cycles.**

In the project “Novel Ionomers and Electrode Structures for Improved Polymer Electrolyte Membrane Fuel Cell Electrode Performance at Low Platinum Group Metal Loadings,” 3M has shown promising results using perfluoromethyl bis(sulfonyl)imide (PFMI) ionomer in the cathode, especially for H2/air HCD performance. This may be a result of a less-adsorbing acid group compared to a sulfonic acid group in a traditional perfluorosulfonic acid ionomer. Interestingly, our evaluation of the PFMI with PtCo on porous carbon in an MEA cathode showed less performance sensitivity to humidity. However, PtCo/KB with this ionomer gave lower mass activity and thus was not able to show improvement across all operating conditions in this initial testing.

To minimize the PGM amount and maximize the PGM utilization of the accessible catalyst, we also reduced the MEA Pt loading on the anode and cathode to 0.015 and 0.060 mgPt/cm², respectively. The fuel cell polarization curve showed negligible local transport-related loss up to 2 A/cm², only 17 mV lower than an MEA with 0.025 and 0.100 mgPt/cm² Pt loading. This results in a PGM utilization of 12.1 kW/gPGM at 150 kPa, surpassing the DOE 2025 target of 8 kW/gPGM (Table 1). It is noteworthy that such cathode with excellent ORR activity and transport property still cannot meet the power density target of 1 W/cm² at 150 kPa (Table 1). This will require further improvement in Ohmic resistance (both membrane and contact resistance) and ORR activity, outside the scope of this project.

**CONCLUSIONS AND UPCOMING ACTIVITIES**

In FY 2019, this project accomplished the following.

- Continued progress toward achieving DOE targets:
  - Advanced PGM utilization status by 15% by reducing Pt in both anode and cathode.
  - Narrowed gap to 1 W/cm² (150 kPa) target (now 0.95 W/cm²).
Demonstrated promising new materials provide paths to better activity and durability:
- Intermetallic ordering was effective for improving durability of accessible-PtCo with minimal performance penalty.
- While ionic liquid was beneficial for some PtCo/HSC, benefits on our best accessible-catalyst were not yet realized. Potential merit on stability awaits confirmation in MEA.
- PFMI cathode ionomer showed less performance sensitivity to humidity.

Improved understanding of low-PGM electrodes:
- 3-D TEM and modeling confirmed that internal pore size (opening) is the key factor for good ORR activity and transport properties in porous carbon catalysts.
- Ex situ tests and modeling highlighted (a) importance of high negative Pt surface charge in carbon pores on kinetic and proton transport and (b) unusually strong dependence of O₂ diffusivity on carbon pore size.
- Scanning transmission electron microscopy nanobeam diffraction allows study of how lattice strain and defects in Pt shell affect ORR activity in MEAs.

Upcoming activities include:
- DOE validation: Evaluate durability of low-loaded (0.075 mgPt/cm²) MEA and provide MEAs for DOE validation.
- Implement new ionomer on accessible-porous carbons.
- Optimize ionic liquids application and evaluate potential durability benefit of ionic liquids.
- Develop catalyst synthesis path for intermetallic ordered PtCo with well controlled size.
- Finalize catalyst particle-pore performance model and cation fundamental performance model.

FY 2019 PUBLICATIONS/PRESENTATIONS


REFERENCES


