Advanced Electrocatalysts Through Crystallographic Enhancement

Overall Objectives

- Design and synthesize fully ordered intermetallic MPt (M represents non-precious metals other than iron) nanoparticles.
- Optimize the Pt-support interaction to maximize the catalyst activity and durability.
- Establish effective material interfaces in membrane electrode assemblies (MEAs).
- Scale-up to 50 cm² MEAs and synthesize gram-scale batches of carbon-supported alloy nanoparticles.

Fiscal Year (FY) 2018 Objectives

- Synthesize ordered L1₀-CoPt nanoparticles from Co and Pt precursors and perform initial electrochemical characterization.
- Synthesize at least two distinct nitrogen-doped supports and compare their properties as catalyst supports.
- Demonstrate 0.44 A/mgPGM mass activity in MEA testing with an Fe-free system at 0.9 V, H₂/O₂, 150 kPaabs.
- Develop alternative fct-CoPt synthetic pathway using deposition on Pt nanoparticle seeds.
- Develop atomistic models that attribute reactivity changes to strain, ligand, and crystal structure for L1₀-CoPt system.

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 Plan¹:

(A) Durability
(B) Cost
(C) Performance.

Technical Targets

Technical targets are detailed in Table 1.

FY 2018 Accomplishments

- Synthesized and tested several classes of L1₀-CoPt nanoparticles.
- Demonstrated mass activity as high as 0.67 A/mgPGM in MEA testing with small L1₀-CoPt nanoparticles (4-nm particle size).
- Demonstrated mass activity as high as 0.56 A/mgPGM and less than 20% loss in mass activity after catalyst accelerated stress test (AST) in MEA testing with large L1₀-CoPt nanoparticles (9-nm particle size).

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

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>DOE 2020 Electrocatalyst and MEA Targets</th>
<th>Project Status (5 cm² cell, differential conditions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass activity</td>
<td>A/mg PGM @ 0.9 mV&lt;sub&gt;iR-free&lt;/sub&gt;</td>
<td>≥0.44</td>
<td>0.67</td>
</tr>
<tr>
<td>Mass activity loss after catalyst AST</td>
<td>%</td>
<td>&lt;40</td>
<td>54</td>
</tr>
<tr>
<td>Loss at 0.8 A/cm² after catalyst AST</td>
<td>mV</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>MEA performance</td>
<td>mA/cm² @ 800 mV</td>
<td>≥300</td>
<td>420</td>
</tr>
<tr>
<td>MEA performance</td>
<td>mW/cm² @ rated power (670 mV)</td>
<td>≥1,000</td>
<td>830</td>
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INTRODUCTION
Platinum intermetallic nanoparticles recently have been demonstrated as promising catalytic materials for fuel cells and other electrochemical energy technologies [1–3], with initial results suggesting that these intermetallic structures can have greater performance and durability than disordered alloys in electrochemical applications such as fuel cells. Most work to date, however, has used partially-ordered nanoparticles. Scalable synthesis of fully-ordered intermetallics with high surface-to-volume ratio is a key challenge preventing advancement of this field. The goal of this project is to develop novel synthetic routes to prepare monodisperse, highly-ordered, high surface area intermetallics in large quantities with high quality control and with good performance and durability.

APPROACH
The overall approach is to synthesize advanced fuel cell catalysts based on intermetallic alloys and subject them to performance and durability testing in MEAs. The targeted catalysts consist of ordered intermetallic alloy nanoparticles, and they are being developed at Los Alamos National Laboratory (LANL) as well as at the subcontractor facilities, Brown University and University of Pennsylvania. The advanced catalyst nanoparticles are being supported on high-performance nitrogen-doped carbon supports as developed by subcontractor the State University of New York (SUNY) at Buffalo, as well as on commercially-available carbon supports. Catalysts examined include PtFe, PtNi, and PtCo, with subsequent examination of ternary catalyst systems. Although PtFe is being examined as a model catalyst, the project team is working to remove all Fe from the catalyst system to alleviate durability concerns.

By forming ordered intermetallic compounds with L10 structure, the project team seeks to produce catalysts that retain high activity during durability testing with reduced leaching of base metal components when compared with conventional non-ordered alloys. Theory-based design principles based on a machine-learning technique developed at Brown University are being used to guide the catalyst development.

RESULTS
The team developed several high-performance, durable intermetallic PtCo catalysts in the project in FY 2018. An L10-CoPt catalyst with relatively large particle size (9 nm) was the first catalyst developed that met the DOE targets for mass activity and durability. This promising catalyst exhibited highly ordered structure even after the 30,000-cycle DOE catalyst AST, as demonstrated by comparison of X-ray diffraction (XRD) patterns before and after testing (Figure 1). This remarkable stability of the ordered structure and high resistance to Co leaching leads to excellent retention of catalytic activity. High-resolution scanning transmission electron microscopy–energy-dispersive spectroscopy (STEM-EDS) (shows an approximately 1-nm Pt shell surrounding a Pt50Co50 core after the AST (total particle composition Pt70Co30). High-resolution high angle annular dark field–scanning transmission electron microscopy (HAADF-STEM) shown in Figure 2 reveals that a highly ordered core remains after AST, coated with a ~0.7–1.0 nm Pt shell (3 to 4 atoms thick), in agreement with the STEM-EDS results. This observation is significant because it demonstrates that atomic-level ordering can be maintained even after durability testing. Co leaching occurs only from surface, forming a Pt shell that protects the particle interior from further leaching. This Pt shell is too thick for significant Co-induced ligand enhancement of oxygen reduction reaction kinetics after the AST, but the kinetic enhancement due to strain remains even after 30,000 cycles.
Figure 1. XRD patterns recorded on fresh L1₀-CoPt catalyst powder and on catalyst that had been subjected to the 30,000-cycle catalyst AST reveal similar superlattice peaks, indicating that the ordered structures remain intact even after durability testing.

Figure 2. HAADF-STEM image of a particle showing the ordered L₁₀-CoPt structure after MEA testing.
Though the mass activity and durability were promising, the large particle size of this L10-PtCo catalyst leads to low electrochemical surface area and poor performance at high current density. To get around this problem, L10-CoPt with smaller particle size is under development in the project. Initial results with 4-nm L10-CoPt developed using a novel seed-mediated synthesis and heat treatment approach are highly promising. Mass activity as high as 0.67 A/mgPGM—well above the 0.44 A/mgPGM target—has been demonstrated. More importantly, these catalysts exhibit good performance at high current density (Figure 3). Further work to improve the durability of these catalysts is underway.

![Graph](image)

**Figure 3.** Small particle L10-CoPt catalysts provide high performance in fuel cell testing. Test conditions: H₂/air, 80°C, 150 kPaabs, 100% RH, 0.1 mgPt/cm² on cathode and anode

Computational modeling of base metal leaching using density functional theory calculations to predict the energetics of the diffusion process has been used to build understanding of the factors governing catalyst stability. Results from this work help guide design of more durable catalysts. A key finding in FY 2018 was that formation of a Pt skin on top of an L10-CoPt surface can slow down the rate of vacancy-mediated diffusion, leading to a 53-times increase in predicted stability. This improved understanding has guided synthetic efforts, including a greater focus on formation of high-quality Pt skins encapsulating L10-CoPt nanoparticles.

Several novel supports based on nitrogen-doped graphitic carbon were synthesized and used as supports for Pt nanoparticles. These catalysts exhibited good activity and stability in rotating disk electrode testing. Pt on carbon support from polyaniline hydrogel precursor was found to provide good polarization performance in MEA testing. Accelerated testing of these materials using the DOE support AST demonstrated little performance loss during the first 500 cycles, and better electrochemical surface area retention than Pt/Vulcan, but further improvement is needed to meet the 5,000-cycle durability target at 80°C.

**CONCLUSIONS AND UPCOMING ACTIVITIES**

Results from FY 2018 have demonstrated the viability of the intermetallic L10 nanoparticle approach to achieve simultaneous improvements in performance and durability. Highly ordered L10 structures have greater resistance to base-metal leaching as compared to random alloys, and this improved leaching resistance is instrumental in providing good MEA durability.

The focus of the project in FY 2019 is on further developing the promising synthetic methods developed in FY 2018 and scaling up the most successful approaches to produce gram-scale batches. These larger batches will
be used to enable further MEA optimization and achievement of good high-current performance along with high mass activity and durability.

**FY 2018 PUBLICATIONS/PRESENTATIONS**


**REFERENCES**

