# Advanced Electrocatalysts through Crystallographic Enhancement

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Subcontractor(s):
- Brown University, Providence, RI
- University of Pennsylvania, Philadelphia, PA
- State University of New York at Buffalo, Buffalo, NY
- IRD Fuel Cells, Albuquerque, NM

Project Start Date: October 1, 2016
Project End Date: September 30, 2019

## Overall Objectives

- Design and synthesize ordered intermetallic MPt (M represents non-precious metals other than Fe) 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 $cm^2$ MEAs and synthesize gram-scale batches of carbon-supported alloy nanoparticles.

## Fiscal Year (FY) 2019 Objectives

- Optimize synthesis of ordered $L1_0$-CoPt nanoparticles from Co and Pt precursors, perform characterization, and test in fuel cells.
- Compare the performance of $L1_0$-CoPt/C on N-doped supports vs. commercial carbon supports, and compare their performance in fuel cell testing.
- Demonstrate mass activity of at least 0.55 $A/mg_{PGM}$ in MEA testing with an Fe-free system at 0.9 V, $H_2/O_2$, 150 $kPa_{abs}$, 25% higher than the 0.44 $A/mg_{PGM}$ DOE target.
- Further develop the $L1_0$-CoPt synthetic pathway using deposition on Pt nanoparticle seeds.
- Develop atomistic models that attribute reactivity changes to strain, ligand, and crystal structure for the $L1_0$-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 Plan[1]:

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

## Technical Targets

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

## FY 2019 Accomplishments

- Synthesized and tested several new kinds of $L1_0$-CoPt nanoparticles.
- Demonstrated mass activity as high as 0.60 $A/mg_{PGM}$, with a 40% loss after 30,000 accelerated stress test (AST) cycles, using MEA testing with small $L1_0$-CoPt nanoparticles (4 nm particle size).
- Demonstrated mass activity as high as 0.79 $A/mg_{PGM}$, with a 37% loss after 30,000 AST cycles, using MEA testing with $L1_0$-CoPt nanoparticles supported on N-doped hydrogel carbon.

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

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

| Characteristic | Units | DOE 2020 Electrocatalyst and MEA Targets | Project Status (5 $cm^2$ cell, differential conditions) |
|---|---|---|---|
| Mass activity | $A/mg_{PGM}$ @ 0.9 $mV_{iR\text{-}free}$ | ≥0.44 | 0.60 |
| Mass activity loss after catalyst AST | % | <40 | 40 |
| Loss at 0.8 $A/cm^2$ after catalyst AST | mV | <30 | 26 |
| MEA performance | $mA/cm^2$ @ 800 mV | ≥300 | 410 |
| MEA performance | $mW/cm^2$ @ rated power (670 mV) | ≥1,000 | 890 |

AST – accelerated stress test
PGM – platinum group metal

## INTRODUCTION

Platinum intermetallic nanoparticles have recently 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 higher performance and durability than disordered alloys in electrochemical applications such as fuel cells. However, most work to date has used nanoparticles with a low degree of order, and most testing has been performed in aqueous rotating disk electrodes. Scalable synthesis of highly-ordered intermetallics with a high surface-to-volume ratio is a key challenge preventing the 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 to test and demonstrate these catalysts in MEAs

## APPROACH

The overall approach is to synthesize advanced fuel cell catalysts based on intermetallic structures and subject them to performance and durability testing in MEAs. The targeted catalysts consist of ordered intermetallic alloy nanoparticles and are being developed at Los Alamos National Laboratory as well as at subcontractors Brown University, University of Pennsylvania, and State University of New York at Buffalo (SUNY Buffalo). The advanced catalyst nanoparticles are being supported on high-performance nitrogen-doped carbon supports as developed by subcontractor SUNY Buffalo, as well as on commercially available carbon supports. Catalysts examined focus on PtCo, with a subsequent examination of ternary catalyst systems including PtCoNi.

By forming ordered intermetallic compounds with $L1_0$ 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 catalyst development.

## RESULTS

Several new $L1_0$-CoPt catalysts were developed in the project in FY 2019. An $L1_0$-CoPt/Vulcan catalyst with small particle size (4 nm) met or approached all DOE catalyst and MEA targets. This promising catalyst exhibited a highly ordered structure even after the 30,000 cycle DOE catalyst AST, as demonstrated by the 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 high-angle annular dark field–scanning transmission electron microscopy shown in Figure 2 reveals that a highly ordered core remains after AST, coated with a ~0.7–1.0 nm Pt shell (3–4 atoms thick), in agreement with the scanning transmission electron microscopy–energy-dispersive X-ray spectroscopy results. This observation is significant because it demonstrates that atomic-level ordering can be maintained even after durability testing in small $L1_0$-CoPt nanoparticles. Co leaching occurs only from the 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.

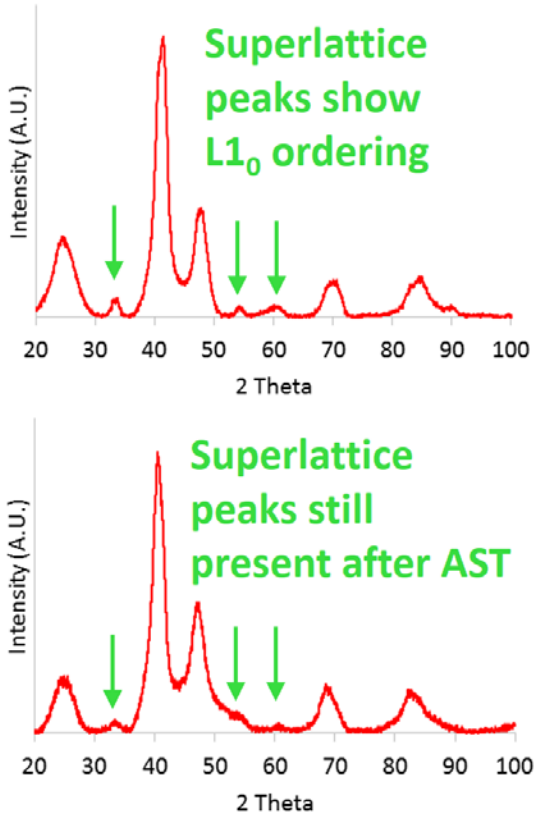


Figure 1. XRD pattern of 4 nm L1$_0$-CoPt/Vulcan before (top) and after (bottom) 30,000 AST cycles in a 50 cm$^2$ MEA. Superlattice peaks reveal that the ordered L1$_0$ structure survives the durability test.

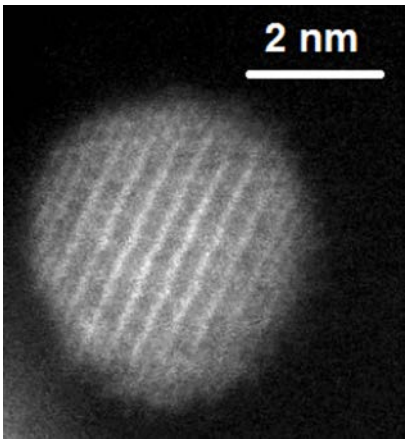


Figure 2. Scanning transmission electron micrograph of a 4 nm ordered L1$_0$-CoPt particle on Vulcan carbon support.

Fuel cell testing results demonstrate that this 4 nm L1$_0$-CoPt/Vulcan catalyst meets mass activity and durability targets. Indeed, this catalyst meets or approaches all DOE catalyst and MEA targets. The only target remaining to be met is the power density at 150 kPa$_{abs}$, for which the current status of 0.89 W/cm$^2$ is slightly lower than the target of 1.0 W/cm$^2$.

Several nitrogen-doped graphitic carbon supports synthesized from hydrogel precursors were developed and used as supports for Pt and CoPt nanoparticles. These catalysts exhibited good activity and stability in MEA testing. Pt on carbon support from polymer hydrogel precursor was found to provide good polarization performance and durability in MEA testing. Accelerated testing of these materials using the DOE support AST demonstrated low performance loss during 5,000 cycles, with only 9 mV loss in performance at 1.5 A/cm$^2$, meeting the DOE target of less than 30 mV loss (Figure 3).

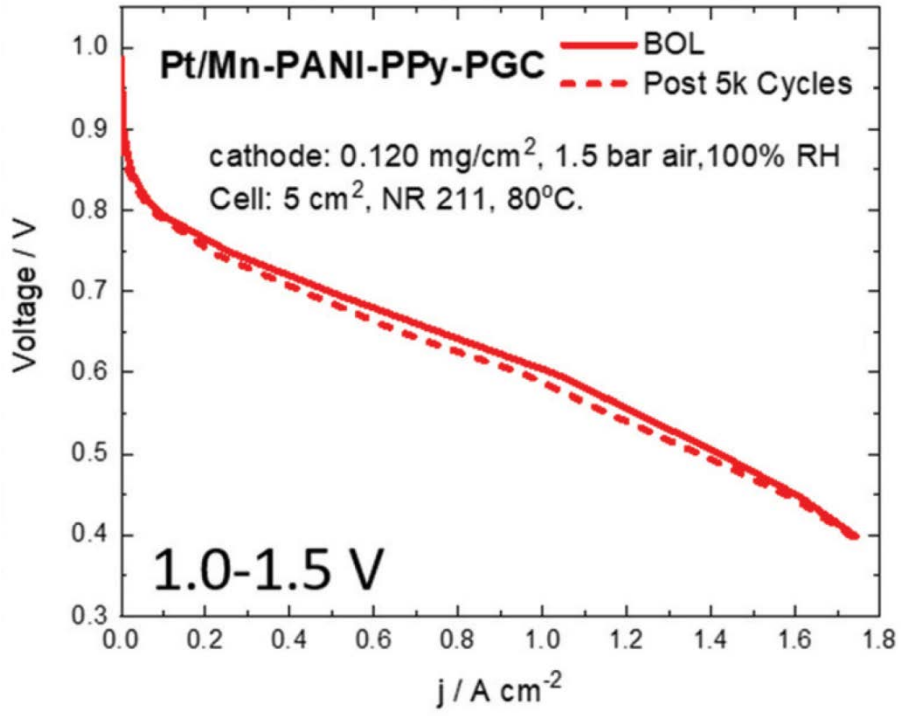


Figure 3. A Pt/C catalyst synthesized using a novel N-doped graphitic carbon support based on a polymer hydrogel precursor was developed in FY 2019. This novel support meets the DOE support durability targets, with only 9 mV loss in performance at 1.5 A/cm$^2$ after 5,000 1.0–1.5 V AST cycles (target: less than 30 mV loss).

## CONCLUSIONS AND UPCOMING ACTIVITIES

Results from FY 2019 have demonstrated the viability of the intermetallic $L1_0$ nanoparticle approach to achieve simultaneous improvements in performance and durability. Highly ordered $L1_0$ structures have greater resistance to base metal leaching compared to random alloys, and this improved leaching resistance is instrumental in providing good MEA durability. Graphitic nitrogen-doped carbon supports have also been shown to meet DOE support durability targets. The combination of new intermetallic catalysts and new n-doped graphitic supports has resulted in catalysts that can meet or approach all DOE catalyst and MEA targets, though further work is needed to meet the 1.0 W/cm$^2$ power density target at 150 $kPa_{abs}$.

This project reached its scheduled end date in FY 2019. If additional funding becomes available, future work would focus on tailoring the ordering the process to provide improved $L1_0$-CoPt dispersion, enabling the 1.0 W/cm$^2$ power density target to be met in an MEA that simultaneously meets all DOE catalyst and MEA targets. With a recent increase in emphasis on heavy-duty transportation applications, ordered intermetallic structures will become even more important to satisfy the higher efficiency and higher durability requirements. Therefore, future work would also include tailoring of mid-range (5–7 nm) $L1_0$-CoPt catalysts capable of providing the required improvements in efficiency and durability.

## SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

The improvements in fuel cell catalyst performance and durability achieved in this project were recognized at the FY 2019 Annual Merit Review and Peer Evaluation Meeting, in which the project principal investigator received a Fuel Cell R&D Award for his leadership of this project.

## FY 2019 PUBLICATIONS/PRESENTATIONS

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8. S. Sharma, "Face-Centered Tetragonal Pt Alloys of Fe & Co As Potential Catalysts for ORR," AIChE, Oct. 30, 2018.

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3. Q. Li et al., "New Approach to Fully Ordered fct-FePt Nanoparticles for Much Enhanced Electrocatalysis in Acid," *Nano Lett.* 15 (2015): 2468−2473.