
Advanced Electrocatalysts Through Crystallographic Enhancement

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Subcontractors:

- Brown University, Providence, RI
- University of Pennsylvania, Philadelphia, PA
- State University of New York at Buffalo, Buffalo, NY
- EWII Fuel Cells, Albuquerque, NM

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

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/mg_{Pt} mass activity in MEA testing with an Fe-free system at 0.9 V, H₂/O₂, 150 kPa_{abs}.
- 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/mg_{Pt} in MEA testing with small L1₀-CoPt nanoparticles (4-nm particle size).
- Demonstrated mass activity as high as 0.56 A/mg_{Pt} 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).

¹ <https://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-free}	≥0.44	0.67
Mass activity loss after catalyst AST	%	<40	54
Loss at 0.8 A/cm ² after catalyst AST	mV	30	34
MEA performance	mA/cm ² @ 800 mV	≥300	420
MEA performance	mW/cm ² @ rated power (670 mV)	≥1,000	830

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 $L1_0$ 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 the catalyst development.

RESULTS

The team developed several high-performance, durable intermetallic PtCo catalysts in the project in FY 2018. An $L1_0$ -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 $Pt_{50}Co_{50}$ core after the AST (total particle composition $Pt_{70}Co_{30}$). 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.

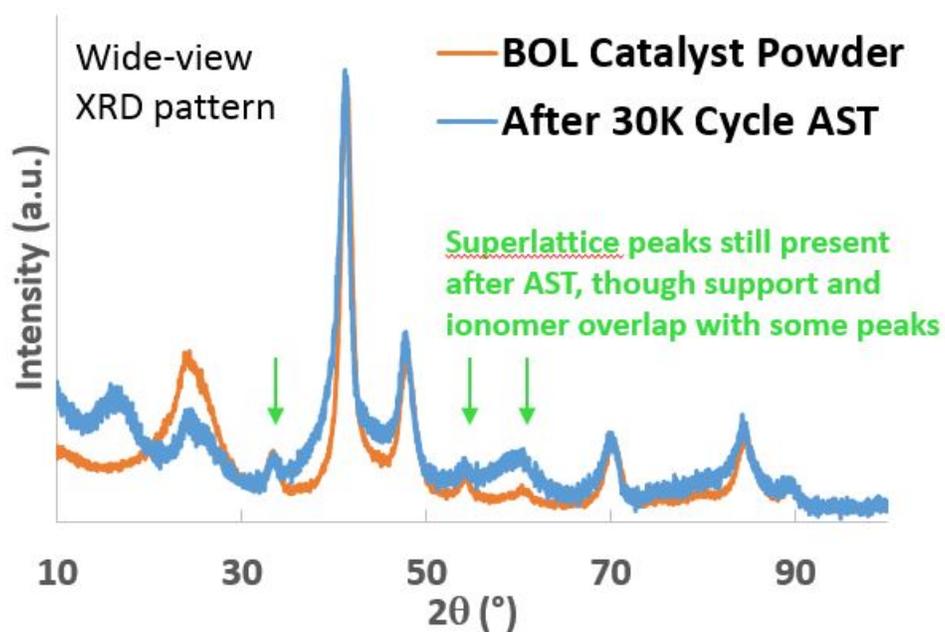


Figure 1. XRD patterns recorded on fresh L1₀-CoPt catalyst powder and on catalyst that had been subjected to the 30,000-cycle catalyst AST reveal similar superlattice peaks, indicating that the ordered structures remain intact even after durability testing

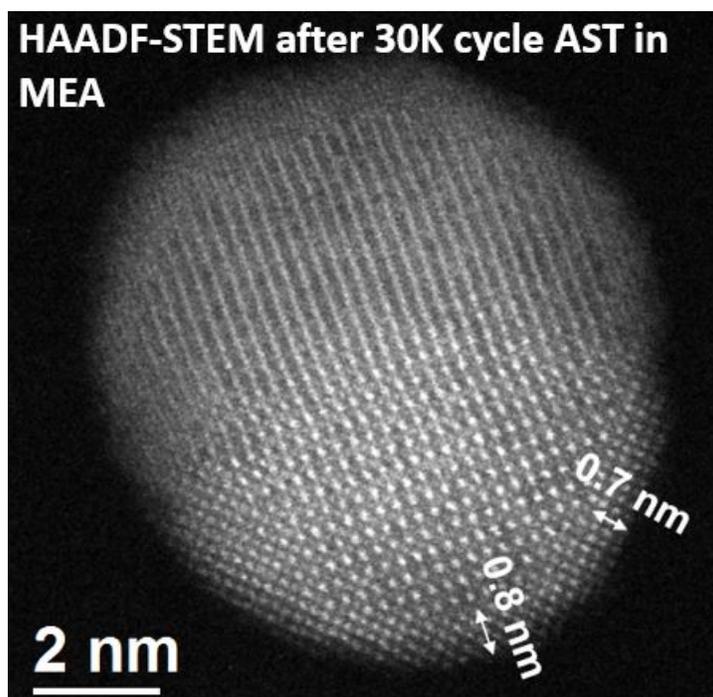


Figure 2. HAADF-STEM image of a particle showing the ordered L1₀-CoPt structure after MEA testing

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/mg_{PGM}—well above the 0.44 A/mg_{PGM} 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.

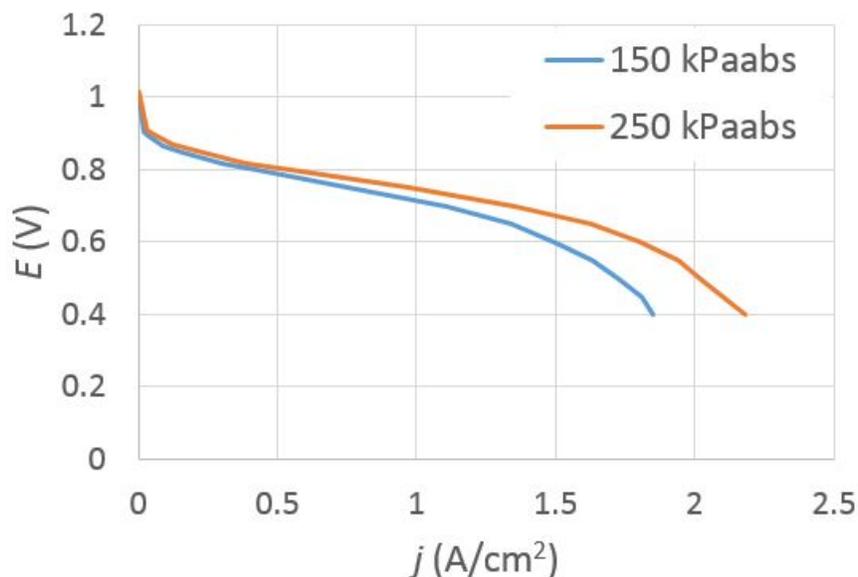


Figure 3. Small particle L1₀-CoPt catalysts provide high performance in fuel cell testing. Test conditions: H₂/air, 80 °C, 150 kPa_{abs}, 100% RH, 0.1 mgPt/cm² on cathode and anode

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

1. Dave Cullen, Brian Sneed, Karren More, Gang Wu, Jacob Spendelow, Hoon Chung, Ted Holby, Piotr Zelenay, “Electron Microscopy Observations of Catalyst-Support Interactions in Polymer Electrolyte Membrane Fuel Cells,” 232nd ECS Meeting, National Harbor, MD, October 2017.
2. J. Li and S. Sun, “Atomically Thin Pt Coated over Intermetallic FePt Nanoparticles for Efficient Oxygen Reduction Catalysis in Fuel Cells,” 255th ACS National Meeting, New Orleans, LA, March 2018.
3. J. Li, Z. Xi, Y.-T. Pan, J. S. Spendelow, P. N. Duchesne, D. Su, Q. Li, C. Yu, Z. Yin, B. Shen, Y. S. Kim, P. Zhang, S. Sun, “Fe Stabilization by Intermetallic L10-FePt and Pt Catalysis Enhancement in L10-FePt/Pt Nanoparticles for Efficient Oxygen Reduction Reaction in Fuel Cells,” *J. Am. Chem. Soc.* 40 (2018): 2926–2932.
4. Yung-Tin Pan, Yu Seung Kim, Junrui Li, Shouheng Sun, Jacob S. Spendelow, “Fuel Cell Performance and Durability of Intermetallic Oxygen Reduction Catalysts,” 233rd ECS Meeting, Seattle, WA, May 2018.
5. Yung-Tin Pan, Yu Seung Kim, Junrui Li, Shouheng Sun, Jacob S. Spendelow, “Fuel Cell Testing of Intermetallic Oxygen Reduction Catalysts,” 232nd ECS Meeting, National Harbor, MD, October 2017.
6. Shubham Sharma and Andrew Peterson, “Predictions of Oxygen Reduction Reaction (ORR) on Face-Centered Tetragonal (FCT) Platinum-Iron Alloy Surface Using Density Functional Theory,” 10th World Congress of Chemical Engineering, Barcelona, Spain (WCCE 2017).
7. Shubham Sharma and Andrew Peterson, “Predictions of Oxygen Reduction Reaction (ORR) on Face-Centered Tetragonal (FCT) Platinum-Iron Alloy Surface using Density Functional Theory,” Materials Research Society (MRS) Fall Meeting 2017, Boston, MA.
8. Shouheng Sun, “Synthetic Tuning of Nanoparticles to Achieve High Efficiency in Electrocatalysis,” MRS Spring Meeting, Phoenix, AZ, April 2–6, 2018.
9. Xiao Xia Wang, David Cullen, Yung-Tin Pan, Sooyeon Hwang, Maoyu Wang, Zhenxing Feng, Jingyun Wang, Mark Engelhard, Hanguang Zhang, Yuyan Shao, Dong Su, Karren More, Jacob Spendelow, Gang Wu, “Nitrogen Coordinated Single Cobalt Atom Catalysts for Oxygen Reduction in Proton Exchange Membrane Fuel Cells,” *Advanced Materials* 30, no. 11 (2018): 1706758.
10. Gang Wu, “Oxygen-Reduction Active Carbon Supports for Pt Cathode Catalysts in Polymer Electrolyte Fuel Cells,” 231st ECS Meeting, May 2017, New Orleans, LA.

REFERENCES

1. Minh T. Nguyen, Ryo H. Wakabayashi, Minghui Yang, Héctor D. Abruña, and Francis J. DiSalvo, “Synthesis of Carbon Supported Ordered Tetragonal Pseudo-Ternary $Pt_2M'M$ (M = Fe, Co, Ni) Nanoparticles and Their Activity for Oxygen Reduction Reaction,” *J. Power Sources* 280 (2015): 459–466.
2. Dong Young Chung, Samuel Woojoo Jun, Gabin Yoon, Soon Gu Kwon, Dong Yun Shin, Pilseon Seo, Ji Mun Yoo, Heejong Shin, Young-Hoon Chung, Hyunjoong Kim, Bongjin Simon Mun, Kug-Seung Lee, Nam-Suk Lee, Sung Jong Yoo, Dong-Hee Lim, Kisuk Kang, Yung-Eun Sung, and Taeghwan Hyeon, “Highly Durable and Active PtFe Nanocatalyst for Electrochemical Oxygen Reduction Reaction,” *J. Am. Chem. Soc.* 137 (2015): 15478–15485.
3. Q. Li, Liheng Wu, Gang Wu, Dong Su, Haifeng Lv, Sen Zhang, Wenlei Zhu, Anix Casimir, Huiyuan Zhu, Adriana Mendoza-Garcia, and Shouheng Sun, “New Approach to Fully Ordered Cct-FePt Nanoparticles for Much Enhanced Electrocatalysis in Acid,” *Nano Lett.* 15 (2015): 2468–2473.