

V.A.16 Advanced Electro-Catalysts through Crystallographic Enhancement

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

Overall Objectives

- Design and synthesize fully 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 cm² MEAs and synthesize up to a 100 g batch of carbon-supported alloy nanoparticles.

Fiscal Year (FY) 2017 Objectives

- Synthesize fully ordered face-centered tetragonal (fct)-FePt nanoparticles from FePt-Fe₃O₄ precursors and perform initial electrochemical characterization.
- Incorporate at least two distinct ordered intermetallic catalysts into MEAs and perform fuel cell testing including mass activity and high-current performance.
- Perform initial durability testing using square-wave accelerated stress test (AST) on ordered intermetallic catalysts in MEA.
- Demonstrate 5–7 nm fct-MPt with durability in electrocatalyst AST superior to baseline Pt/C.

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.

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

Technical Targets

The technical targets and status for this project are listed in Table 1.

FY 2017 Accomplishments

- fct-FePt and fct-CoPt nanoparticles were synthesized and tested.
- Mass activity of 0.46 A/mg_{PGM} and 0.43 A/mg_{PGM} demonstrated for fct-FePt and fct-CoPt, respectively.

TABLE 1. Progress towards 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	0.46
Mass activity loss after catalyst AST	%	<40	65
Loss at 0.8 A/cm ² after catalyst AST	mV	30	52
MEA performance	mA/cm ² @ 800 mV	≥300	240
MEA performance	mW/cm ² @ rated power (663 mV)	≥1,000	557

PGM – platinum group metal, iR – internal resistance



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 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.

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 fully-ordered intermetallic alloy nanoparticles, and are being developed at Los Alamos National Laboratory as well as at subcontractors Brown University and University of Pennsylvania. The advanced catalyst nanoparticles are being supported on high-performance, nitrogen-doped carbon supports as developed by subcontractor State University of New York at Buffalo, as well as on commercially-available carbon supports. Catalysts examined include PtFe, PtNi, and PtCo, with subsequent examination of ternary catalyst systems. While 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 fully-ordered intermetallic compounds with face centered tetragonal 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

Several fct catalysts were successfully synthesized in FY 2017, including fct-FePt and fct-CoPt supported on high surface area carbon. Initial fct-FePt catalysts had mass activity lower than the target, but they exhibited good stability during catalyst durability testing using the 0.6–0.95 V square wave AST, with very little change in polarization behavior (Figure 1).

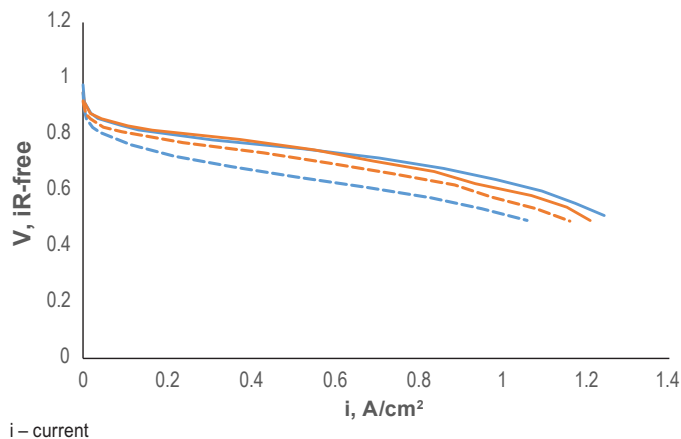
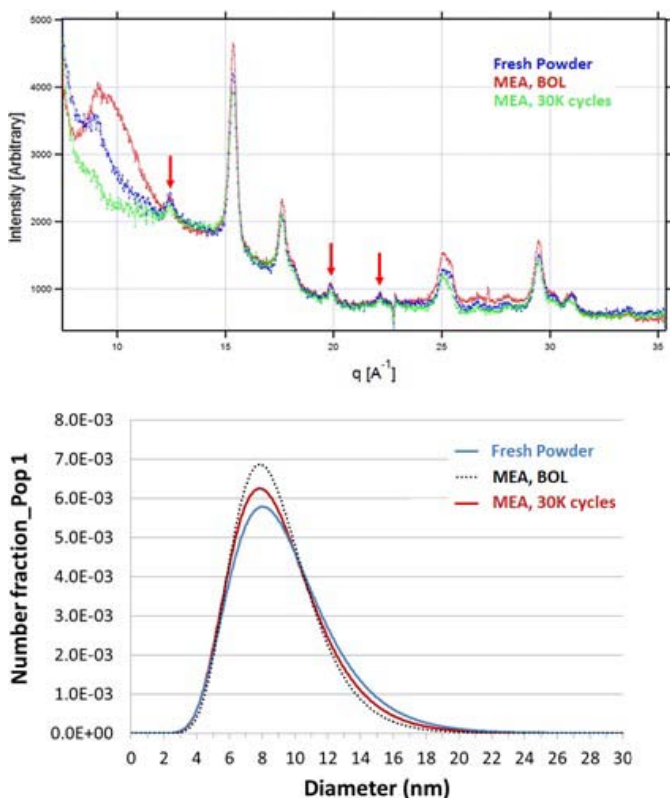


FIGURE 1. Polarization behavior of fct-FePt catalyst (orange) compared with commercial Pt/C (TKK TEC10E50, blue). Test conditions: 150 kPa_{abs}, 100% relative humidity, 500/1,000 sccm anode/cathode, 0.1/0.1 mg_{Pt}/cm² anode/cathode, NR212 membrane. Solid lines represent initial performance, while dashed lines represent performance after the 30,000 cycle AST.

Characterization including X-ray absorption spectroscopy, wide-angle X-ray scattering, and small angle X-ray scattering was performed at the Advanced Photon Source on fresh catalyst, catalyst on as-prepared MEAs, and catalyst after 30,000 cycle AST MEA testing. Little change in catalyst structure was observed. Wide-angle X-ray scattering results showed negligible change in particle size, while small-angle X-ray scattering results showed that the fct structure remains even after the AST (Figure 2). Similarly, X-ray absorption fine structure results indicated little change in bond distance. The catalysts also showed very little change in electrochemical surface area during the AST (Figure 3).

While the initial catalysts had high durability, they did not have sufficient mass activity. Synthesis of smaller fct-FePt particles (approximately 5 nm) enabled mass activity values as high as 0.46 A/mg_{PGM}, but these particles exhibited lower durability. Similarly, approximately 5 nm fct-CoPt nanoparticles with mass activity values as high as 0.43 A/mg_{PGM} were synthesized, but without sufficient durability. The small particles exhibited a lower degree of ordering, which may account for the lower durability. Work is underway to try to increase the degree of ordering of these small fct particles.

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, but efforts to match this performance in MEA testing are still underway.



BOL – beginning of life

FIGURE 2. Top: Wide-angle X-ray scattering analysis demonstrates that superlattice peaks (marked with red arrows) remain after 30,000 cycles, indicating that the fct structure survives the AST. Bottom: Small-angle X-ray scattering demonstrates negligible change in particle size due to AST.

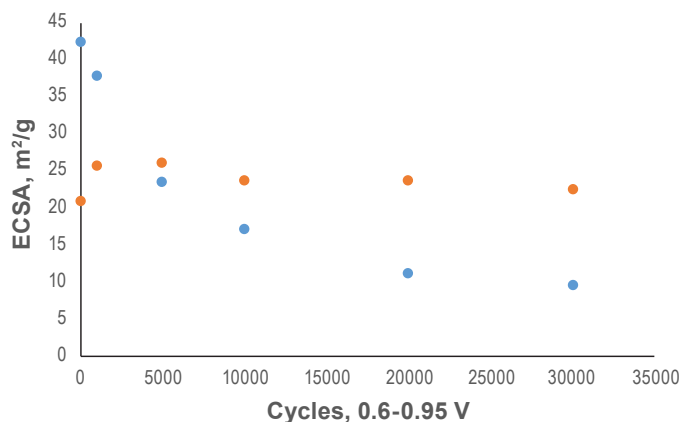


FIGURE 3. Electrochemical surface area (ECSA) change of fct-FePt (orange) during the 30,000 cycle AST is much smaller than the electrochemical surface area change of commercial Pt/C (TKK TEC10E50, blue).

CONCLUSIONS AND UPCOMING ACTIVITIES

Results from the first year of the project indicate that high durability can be achieved through formation of ordered fct-FePt nanoparticles, and that this ordering can survive even during extended durability testing. However, the relatively large particles that exhibit good ordering and high durability have a relatively low surface area and do not yet meet the mass activity target. Formation of smaller particles (around 5 nm) has been demonstrated, and these smaller particles are capable of meeting the mass activity target, but improved ordering is required to increase durability.

Upcoming activities include efforts to increase the degree of ordering through improved annealing procedures, and efforts to replace Fe content with Co or Ni. Work is also underway to improve the incorporation of these fct catalysts into high-performance MEAs. Further efforts on synthesis of nitrogen-doped graphitic carbon supports are planned to produce structures that can be more readily incorporated into MEAs. Once these structures are demonstrated as supports for Pt catalysts, they will be further developed and demonstrated as supports for the novel fct catalysts being developed in this project.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Jacob S. Spendelow and Yu Seung Kim, “Advanced Electro-Catalysts through Crystallographic Enhancement,” presentation to the Fuel Cell Tech Team, Southfield, MI, February 15, 2017.
2. Jacob S. Spendelow, “Advanced Electro-Catalysts through Crystallographic Enhancement,” presentation at the 2017 DOE Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 7, 2017.

REFERENCES

1. M. Nguyen et al., “Synthesis of carbon supported ordered tetragonal pseudo-ternary Pt₂M₃M” (M = Fe, Co, Ni) nanoparticles and their activity for oxygen reduction reaction,” *J. Power Sources* 2015, 280, 459–466.
2. D. Chung et al., “Highly Durable and Active PtFe Nanocatalyst for Electrochemical Oxygen Reduction Reaction,” *J. Am. Chem. Soc.* 2015, 137, 15478–15485.
3. Q. Li et al., “New Approach to Fully Ordered fct-FePt Nanoparticles for Much Enhanced Electrocatalysis in Acid,” *Nano Lett.* 2015, 15, 2468–2473.