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# Tailored High-Performance Low-Platinum-Group-Metal Alloy Cathode Catalysts

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## Subcontractors:

- National Renewable Energy Laboratory, Golden, CO
- Argonne National Laboratory, Argonne, IL
- Oak Ridge National Laboratory, Oak Ridge, TN

Project Start Date: October 1, 2015

Project End Date: September 30, 2019

## Overall Objectives

- Deliver advanced low-PGM (platinum group metal) cathode catalysts for use in polymer electrolyte membrane fuel cells (PEMFCs).
- Increase mass activity at high electrode potentials and enhance performance at high current density, targeted toward high-duty vehicles.
- Improve durability while reducing the total PGM loading and cost.
- Alloy Pt with other transition metals to reduce PGM content.
- Develop and evaluate durable high-surface-area supports for tailored nanomaterials.
- Synthesize low-PGM materials in the form of alloy nanomaterials deployed on high-surface-area supports.
- Leverage scalable chemistry that will allow gram-scale synthesis of tailored nanomaterials.
- Assess relationships between rotating disk electrode and membrane electrode assembly (MEA) performance and the effect of ionomer-catalyst interactions.

- Fabricate MEAs with a total PGM loading of  $<0.125 \text{ mg}_{\text{PGM}}/\text{cm}^2$  and  $<0.125 \text{ g}_{\text{PGM}}/\text{kW}$  with mass activity higher than  $0.44 \text{ A}/\text{mg}_{\text{PGM}}$ .
- Demonstrate total loss of electrochemical mass activity less than 40% after 30,000 voltage cycles.

## Fiscal Year (FY) 2019 Objectives

- Develop electrocatalysts that are both active and durable for the cathode reaction of a PEMFC.
- Synthesize Pt-alloy nanoparticles with controlled physical parameters such as size, compositional profile, and topmost surface as guided by studies of well-defined systems.
- Evaluate correlations between structural and electrochemical properties of nanoscale catalysts.
- Develop scalable processes to produce gram-scale quantities of catalysts for extensive MEA evaluation.
- Integrate and evaluate novel carbon supports with tailored Pt-alloy nanoparticles.
- Reproducibly measure MEA performance for tailored Pt-alloy catalysts with total PGM loading of  $<0.125 \text{ mg}_{\text{PGM}}/\text{cm}^2$  and mass activity  $>0.44 \text{ A}/\text{mg}_{\text{PGM}}$ .

## 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<sup>1</sup>:

- Durability
- Cost
- Performance.

## Technical Targets

The DOE 2020 technical targets and our current project status are listed in Table 1 for comparison.

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

## FY 2019 Accomplishments

- Established dissolution rates of Pt for different particle sizes and loadings on carbon.
- Proved and resolved mechanism of non-existent Pt distribution from Pt<sub>3</sub>Au nanoparticles.
- Demonstrated superior durability of intermetallic systems (PtCo, PtNi) to their solid-solution counterparts.
- Scaled synthesis of multiple nanostructures with advanced architecture to gram-scale quantity.
- Evaluated differences in activity and durability for high-surface-area and low-surface-area carbon supports.
- Developed 5-nm PtNi nanoparticles that achieve 0.50 A/mg<sub>Pt</sub> at 0.9 V (iR-free).
- Developed 2-nm Pt<sub>3</sub>Co nanoparticles that achieve 0.52 A/mg<sub>Pt</sub> at 0.9 V (iR-free).
- Developed 9-nm PtNi intermetallic nanoparticles that achieve 0.60 A/mg<sub>Pt</sub> at 0.9 V (iR-free).
- Developed 8-nm PtCo intermetallic nanoparticles that achieve 0.70 A/mg<sub>Pt</sub> at 0.9 V (iR-free).
- Developed a series of highly durable PtAu nanoparticles with projected compositional gradient.

**Table 1. Primary Technical Targets for Electrocatalysts and MEAs for Transportation Applications**

Characteristic	Units	DOE 2020 Electrocatalyst Targets	Project Status
Mass activity	A/mg <sub>Pt</sub> @ 0.9 mV <sub>iR-free</sub>	≥0.44	0.70
PGM total loading (both electrodes)	mg <sub>PGM</sub> /cm <sup>2</sup> <sub>geo</sub>	≤0.125	0.120
Loss in initial catalytic activity	% mass activity loss	<40	<25

## INTRODUCTION

To penetrate the transportation market and reduce reliance on internal combustion engine vehicles, fuel cell vehicles must become cheaper and longer lasting. The primary cost barrier to cheaper fuel cell vehicles is the platinum group metal elements required for efficient catalysis in the PEMFC. Therefore, PGM content must be significantly reduced by using low loading of Pt-based catalysts in the cathode and anode of the PEMFC [1, 2]. This goal can only be achieved by improving both the activity and durability of the electrocatalysts such that fuel cell performance is maintained at low loadings and throughout the lifetime of the vehicle [3]. The technical targets to achieve for this project are greater than 0.44 A/mg<sub>Pt</sub> activity at 0.9 V and less than 40% loss in mass activity after standard accelerated stress tests at less than 0.125 mg<sub>Pt</sub>/cm<sup>2</sup> loading in MEAs. Electrocatalysts must also be designed with application in heavy-duty vehicles in mind by improving their performance at high current densities.

These challenges are addressed in this project through design of nanoscale systems influenced by catalyst design themes learned from well-defined systems. Single crystal, two-dimensional surfaces that can be characterized at the atomic scale with ultra-high vacuum techniques provide great insight into surface characteristics required to obtain advanced catalytic performance. High-precision techniques such as in situ inductively coupled plasma mass spectrometry (ICP-MS) yield information on microscopic levels of catalyst dissolution to determine how the catalyst surface is transforming under catalytic conditions [4]. This information fuels the development of real-world nanoscale catalysts that are synthesized in gram-scale batches for widespread evaluation in MEAs. By tuning elements of the catalyst's size, structure, shape, and surface composition along with its interactions with supports and electrolyte, major advances in activity and durability at low loading have been made.

## APPROACH

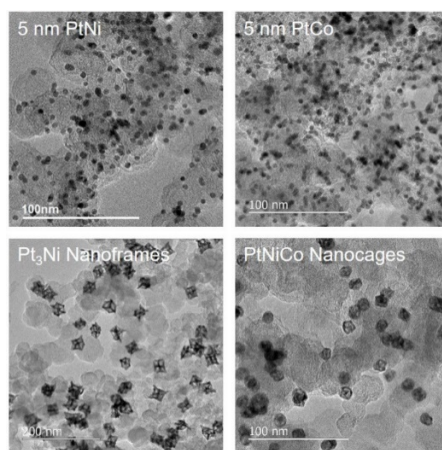
Argonne National Laboratory leads this project with support from inter-lab collaborations with National Renewable Energy Laboratory (NREL) and Oak Ridge National Laboratory. Argonne coordinates this applied research effort, defines project scope, topics, milestones, and is responsible for deliverables as well as quarterly and annual reports to the Fuel Cell Technologies Office. NREL fabricates and tests the MEAs with state-of-the-art facilities and procedures. Oak Ridge National Laboratory uses electron microscopy to characterize materials and catalysts synthesized by Argonne before and after being deployed for MEA testing protocols at NREL. The approach of this project begins with well-defined systems that are used as models of functional properties required for catalysis in PEMFCs. These properties are extended to corresponding nanoscale materials with desired shape, size, structure, and compositional profile through high-precision synthetic techniques. Nanoscale materials are first characterized through fundamental, well-defined electrochemical techniques before integration into applied MEA systems. Correlating the engineering of these materials with their performance in both fundamental and applied systems requires a combination of highly diverse experimental tools supported by state-of-the-art synthesis and characterization strategies, together with the fabrication and testing capabilities. The project is executed simultaneously in three tasks throughout the duration of the project: Task 1—electrochemical characterization, Task 2—durability evaluations (in situ ICP-MS), and Task 3—synthesis of advanced catalyst-support systems.

## RESULTS

### Synthesis Scale Up of Advanced Architectures

High-quality, solution-synthesized nanoparticles have demonstrated immense promise as cathode catalysts in PEMFCs. However, these syntheses are typically limited to fundamental discovery of new materials at which the scale of production is only tens of milligrams or less. To potentially transfer some of these highly engineered nanostructures to commercial reality, 50-cm<sup>2</sup> MEAs must be fabricated to demonstrate proof-of-performance of the catalyst. Ideally, multiple parties could perform MEA testing as there are a wide variety of variables to tune during ink formulation, MEA fabrication, and testing protocols. This process requires catalyst production on the gram scale to characterize sufficiently the activity and durability of the catalyst.

Solution-phase synthesis of nanoscale catalysts at the gram scale has different limitations and requirements than small-batch synthesis. Therefore, small-batch synthesis is ideally designed with a transition to larger batches in mind, or else significant evaluation must be performed to tune the synthesis protocol without affecting the final product. This project has allowed discovery of many high-performing catalyst structures including multilayer Pt skins, multiple alloys and compositions (PtNi, PtCo, PtNiCo, PtAu), and advanced architectures (nanoframes, nanocages, nanopinwheels) [5–7]. A few examples are shown in Figure 1.



**Figure 1. Various nanoscale catalysts that have been scaled to more than 1 gram of production**

All of the examples shown in Figure 1, in addition to others, have been scaled to greater than 1 gram of catalyst in either a batch or flow reactor system. Both systems require fine tuning of various synthetic

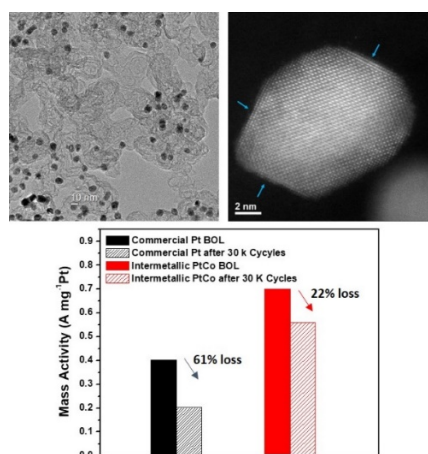
parameters because of the differences in heat and mass transfer when scaling up in batch volume or transitioning to a flow reactor. The major advantage of a flow reactor is that the synthetic parameters can be tuned continuously and the product can be checked with multiple combinations of synthetic conditions in a short time. Scale up in a flow reactor system simply requires an increase in time and/or the number of operating lines.

The great challenge in scale up of advanced architectures is the necessary precise control of shape and elemental distribution or two or more elements within the nanostructure. Architectures such as nanoframes or nanocages are created by having a shape with certain symmetry that has Pt and a less noble element distributed unevenly throughout the shape. This requires kinetic control over the reduction rate of the two (or more) elements during the synthesis to create the desired elemental segregation pattern. The less noble element (often Ni or Co) is then removed by chemical or electrochemical corrosion, leaving behind a Pt-rich, three-dimensional architecture with high surface area and activity. The ability to scale these advanced architectures, as well as spherical nanoparticles with multilayer Pt skin surfaces, has allowed for more thorough MEA evaluation of their catalytic performance to select catalysts most likely to reach DOE 2020 activity and durability technical targets.

### Improving Durability through Atomic Structure Control

There are many examples of catalysts that have met the DOE 2020 mass activity technical target of 0.44 A/mg<sub>Pt</sub> in MEA testing. However, it is much more difficult to demonstrate the catalyst durability required to maintain PEMFC performance such that consumers do not notice a decrease in the performance of their vehicle. There are many reasons for catalyst activity and structural degradation, including Pt dissolution, alloying transition metal dissolution, carbon corrosion, and nanoparticle Ostwald ripening. Through nanoparticle design, Pt and transition metal dissolution can be thoroughly mitigated. A critical role of transition metals that have been alloyed with Pt, such as Co or Ni, is that as smaller atoms, they induce some contraction of the Pt lattice that will decrease the Pt dissolution potential. However, it is very important that Pt protect the subsurface Co or Ni because otherwise their beneficial effects on activity and durability will be lost.

One strategy for protecting against both Pt and Co or Ni dissolution is to finely tune the structure to an intermetallic phase. This project has yielded both PtCo (Figure 2) and PtNi intermetallic nanoparticles. To obtain intermetallic nanoparticles, the proper composition must be obtained in the solution-phase synthesis step. Then, strategic distribution of the particles over a carbon support enables them to be annealed at high temperature without sintering, converting from a disordered solid solution to an ordered intermetallic phase. The ordered layers present in intermetallic PtCo are visible in Figure 2, with bright atomic columns representing Pt and dimmer columns representing Co.



**Figure 2.** PtCo nanoparticles distributed over carbon support (top left) are determined to be intermetallic, based partially on the alternating atomic rows of Pt and Co observed in scanning transmission electron microscope high-angle annular dark-field imaging (top right). Intermetallic PtCo nanoparticles exhibit high mass activity in MEA testing with impressive durability (bottom).

PtCo and PtNi intermetallic nanoparticles demonstrated high activity as a cathode catalyst in MEA testing with mass activity reaching 0.70 and 0.60 A/mg<sub>Pt</sub>, respectively. The high activity is primarily due to the Pt skin the forms in the first two or three layers of surface atoms on each nanoparticle. The subsurface Ni or Co contributes to the electronic structure of the surface that is optimized for catalysis of the oxygen reduction reaction. More importantly, these intermetallic nanoparticles are able to maintain high activity over the course of an accelerated stress test of 30,000 cycles because of the stability of their intermetallic structure. Ordered, intermetallic bonding provides an extremely stable phase, supporting the Pt surface atoms that protect subsurface Co or Ni atoms. In the case of PtCo, in situ ICP-MS demonstrates that Co dissolution is greatly reduced in the intermetallic compared to the solid solution nanoparticles, and Pt dissolution is close to eliminated for the intermetallic catalyst.

### MEA Screening of Diverse Catalyst Library

Through collaboration with NREL, this project has conducted a thorough evaluation of a diverse catalyst library. All catalysts were synthesized with high-precision techniques to obtain the desired characteristics, such as surface composition profile, inspired by studies on well-defined systems. Select catalyst systems were chosen based on preliminary electrochemical characterization and scaled up to gram-scale batches as described previously. The collaboration with NREL allows for these catalysts to be evaluated in 50-cm<sup>2</sup> MEAs, providing great insight into their potential for commercialization. Tests are performed with a Nafion 211 membrane coated with anode and cathode catalyst by ultrasonic spray coating (Figure 3).

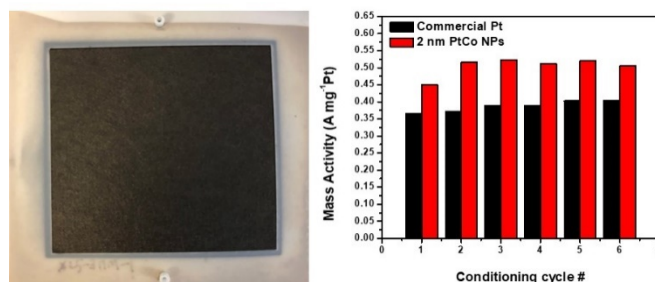


Figure 3. An example MEA (left) and performance of 2-nm PtCo nanoparticles in MEA testing (right)

The systems that have been evaluated in MEAs to date include: 5-nm PtAu nanoparticles, PtNi nanoframes, 5-nm PtNi and PtCo nanoparticles, intermetallic PtNi and PtCo nanoparticles, and 2-nm PtCo nanoparticles. Each system has specific catalyst engineering principles that could potentially benefit its activity or durability to reach the DOE 2020 technical targets. All tests are performed with low loading, less than the 0.125 mg<sub>Pt</sub>/cm<sup>2</sup> technical target. Five of the catalyst systems—PtCo intermetallic 8-nm and 2-nm, PtNi intermetallic 9-nm, PtNi with multilayered Pt skin, and PtAu 5-nm nanoparticles—have met and exceeded the DOE 2020 mass activity technical target of 0.44 A/mg<sub>Pt</sub>, and two of these systems, PtCo intermetallic 8-nm and PtAu 5-nm nanoparticles, have undergone extensive accelerated stress testing to confirm that they meet the durability technical target of <40% loss in mass activity and electrochemical surface area. Other evaluation is ongoing, as each type of catalyst architecture may require special optimization of variables such as carbon support, catalyst loading, ionomer content, and MEA fabrication methods to obtain peak activity and durability. Oak Ridge National Laboratory is supporting this effort with characterization of MEA catalyst layers after testing to evaluate the forms of catalyst evolution.

## CONCLUSIONS AND UPCOMING ACTIVITIES

This project has demonstrated the effectiveness of harvesting fundamental knowledge from well-defined systems into nanoscale catalysts applied in prototype PEMFCs. From ultra-high-vacuum, surface-sensitive techniques on model two-dimensional systems and high-precision, parts per trillion level in situ ICP-MS, many guiding principles were developed to enable high activity and electrochemical stability. This directed the search for catalytic nanostructures that could mimic the ideal surfaces, and at least four systems were developed that meet the 2020 DOE technical targets for this project. This project will evolve toward further development of high-durability systems, and heavy reliance on the MEA evaluation will continue to lead to



optimized catalyst layer formulations. In addition, current and new catalytic systems will be developed with insight from ever-advancing characterization tools.

## SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

V.Stamenkovic, N.M.Markovic, and Y. Kang, “Multimetallic Core/Interlayer/Shell Nanoparticles,” US Patent 10,099,207, October 16, 2018.

In addition, six patents are pending from this work.

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3. R. Wang, H. Lv, N. Becknell, P. Papa Lopes, P. Bergamo, N. Markovic, and V. Stamenkovic, “Scale Up of Advanced Fuel Cell Catalysts in Batch and Flow Reactors,” (Invited) 258<sup>th</sup> American Chemical Society Fall National Meeting, San Diego, CA (August 2019).
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5. P. Papa Lopes, D. Strmcnik, N. Markovic, and V. Stamenkovic, “Materials for Fuel Cells and Batteries in Hybrid Vehicles,” (Invited) 258<sup>th</sup> American Chemical Society Fall National Meeting, San Diego, CA (August 2019).
6. R. Wang, K. Pupek, T. Dzwiniel, N. Becknell, P. Lopes, H. Lv, N. Markovic, G. Krumdick, and V. Stamenkovic, “Process Engineering for Scalable Synthesis of Advanced Fuel Cell Catalyst,” 2019 TechConnect World Innovation Conference and Expo, Boston, MA (June 2019).
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12. V. Stamenkovic, “Electrocatalysts for Fuel Cell Cathodes,” (Plenary Lecture) 234<sup>th</sup> Electrochemical Society Meeting, Cancun, Mexico (October 2018).

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