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

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Subcontractors:
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• National Renewable Energy Laboratory, Golden, CO

Project Start Date: October 1, 2015
Project End Date: September 30, 2018

Overall Objectives

• Develop and deliver advanced low-PGM (platinum group metal) cathode catalysts for use in polymer electrolyte membrane fuel cells (PEMFCs) with increased mass activity at high electrode potentials and enhanced performance at high current density.

• Improve durability while reducing the total loading of PGM and cost.

• Reduce PGM loading in the catalyst through alloying of Pt with other transition metals.

• Synthesize low-PGM materials in the form of nanomaterials deployed on high surface area supports.

• Develop and evaluate durable high surface area supports for tailored nanomaterials.

• Implement scalable chemistry that would allow synthesis of tailored nanomaterials at the gram scale.

• Provide insight into the differences and similarities between rotating disk electrode (RDE) and membrane electrode assembly (MEA) performance.

• Optimize catalyst layers by studying ionomer-catalyst interaction.

• Fabricate MEAs with a total PGM loading of <0.125 mgPGM/cm² and 0.125 gPGM/kW with mass activity greater than 0.44 A/mgPGM.

• Demonstrate total loss of electrochemical mass activity that is less than 40% after 30,000 voltage cycles.

Fiscal Year (FY) 2018 Objectives

• Develop active and durable catalysts for fuel cell cathodic reaction.

• Synthesize and evaluate structural and electrochemical properties of Pt-alloy nanoparticles with controlled physical parameters such as size, compositional profile, and topmost surface.

• Develop scalable process to produce larger quantities of catalysts.

• 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 mgPGM/cm² and mass activity >0.44 A/mgPGM.

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 (MYRDD) Plan¹:

• Durability
• Cost
• Performance.

Technical Targets

The project aims to develop nanoparticles with tailored architectures and composition based on Pt-alloys with transition metals PtM (M = Ni, Co, Cr,

V, Ti), including alloys with Au, to improve performance for the fuel cell cathodic oxygen reduction reaction (ORR). The design principles focus on producing systems that have low PGM content and exhibit highly active and durable electrochemical properties evaluated in MEAs that will meet or exceed the DOE 2020 targets (Table 1).

**FY 2018 Accomplishments**

- Utilized unique RDE-inductively coupled plasma mass spectrometry (RDE-ICP-MS) capabilities to establish stability-structure relationships of two-dimensional and nanoparticle Pt catalysts.
- Synthesized PtCo and Pt₃Co intermetallic nanoparticles that show improved Pt and Co stability over the disordered alloy phase.
- Tested activity and durability of intermetallic PtCo nanoparticles in 50 cm² MEA.
- Synthesized Au@Pt core-shell nanoparticles with Pt₃Au composition and monodisperse size distribution.
- Demonstrated effect of Au core on Pt shell in complete mitigation of Pt dissolution for 3 nm and 5 nm nanoparticles up to 1 V with RDE-ICP-MS.
- Scaled up synthesis of advanced architecture nanocage, nanoframe, and nanopinwheel catalysts to more than 0.4 grams catalyst per batch.

**Table 1. Hydrogen Dispenser Targets Compared to Corresponding MYRDD Plan Targets**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>DOE 2020 Electro catalyst Targets</th>
<th>Project Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass activity</td>
<td>A/mg PGM @ 0.9 mV ir-free</td>
<td>≥0.44</td>
<td>0.70</td>
</tr>
<tr>
<td>PGM total loading</td>
<td>mg PGM/cm² geo</td>
<td>≤0.125</td>
<td>0.120</td>
</tr>
<tr>
<td>Mass activity loss</td>
<td>%</td>
<td>&lt;40</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>
INTRODUCTION
To establish fuel cell vehicles as a major portion of the U.S. automotive market, the platinum-catalyst content in PEMFCs must be significantly reduced [1]. This requires improving the activity of the platinum catalyst such that low loadings can be used, reducing the cost of the PEMFC [2]. Additionally, the PEMFC must be able to perform up to standard for the lifetime of the vehicle, requiring an improvement in durability of the platinum catalyst [3]. These requirements necessitate development of new nanostructures to provide materials solutions to the challenges facing platinum catalyst performance. The composition, size, and architecture of Pt-alloy nanocatalysts are variables with great influence on their activity and durability. The research strategy is guided by fundamental studies on well-defined surfaces and in situ electrochemical ICP-MS for detection of instability trends [4]. New nanostructured catalysts are tested in MEAs to determine their performance standards. The goals of the project are to develop catalysts that demonstrate greater than 0.44 A/mgPt activity at 0.9 V and less than 40% loss in mass activity after standard accelerated stress tests at less than 0.125 mgPt/cm² loading in MEAs. The catalysts should also be synthesized in gram-scale batches to demonstrate promise towards scalability and commercialization.

APPROACH
This is a multi-performer project led by Argonne National Laboratory and supported by inter-lab collaborations with the National Renewable Energy Laboratory and Oak Ridge National Laboratory. Argonne leads and coordinates this applied research effort with other national laboratories; defines project scope, topics, milestones; and is responsible for deliverables as well as quarterly and annual reports to the Fuel Cell Technologies Office. The National Renewable Energy Laboratory fabricates and tests the MEAs. Oak Ridge National Laboratory characterizes synthesized materials and catalysts deployed in an MEA before and after testing protocols by electron microscopy. The approach of this project is based on the knowledge obtained from well-defined systems that will be used to tailor functional properties of corresponding nanoscale materials, with the desired shape, size, structure, and compositional profile. Integration of engineered nanomaterials in electrochemical systems requires integration of a broad range of scientific disciplines such as solid-state physics, surface science, physical chemistry, and electrochemistry. This effort also includes 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 five tasks throughout the duration of the project: Task 1—Well-Defined Systems, Task 2—Synthesis of Nanoscale Materials, Task 3—Electrochemical and Structural Characterization of Catalyst, Task 4—Advanced Supports for Novel Catalysts, and Task 5—Scaling Up of Catalysts.

RESULTS
In the case of the Pt-Co system, the formation of intermetallic phases at compositions of Pt₃Co or PtCo can be utilized to induce stability in the bimetallic nanoparticle. This research has combined Task 1, Task 2, and Task 3 to develop catalysts with enhanced durability. Both PtCo and Pt₃Co compositions were studied in thin-film and nanoparticle geometry as sputtered or as synthesized, and after annealing at 700°C to induce intermetallic formation. Formation of the intermetallic phase creates an ordered structure with Pt and Co existing on specific lattice points, as opposed to randomly in a solid solution. The formation of the intermetallic phase was proven by X-ray diffraction, in which extra diffraction peaks, such as (100) and (110), are observed for intermetallic phases (Figure 1a).
In situ RDE-ICP-MS was used for the first time to probe the stability of Pt and Co within a given composition and phase under specific electrochemical conditions. The intermetallic phase demonstrated an approximate order-of-magnitude decrease in the dissolution rate of Co versus that of the solid solution alloy (Figure 1b). Pt was also stabilized by formation of the intermetallic, and the intermetallic nanoparticles demonstrated consistently higher specific activity than the random alloy nanoparticles (Figure 1c). By stabilizing Co against electrochemical dissolution from PtCo and Pt₃Co nanoparticles, the ORR catalyst is expected to maintain higher specific and mass activity throughout operation of a PEMFC by sustaining the beneficial effects of Co to the performance of the catalyst. The process of scaling up the synthesis of the intermetallic nanoparticles is underway and will lead to thorough evaluation in MEAs to determine this catalyst’s ability to overcome the technical barriers of performance, durability, and cost.

Scale Up of Catalyst Synthesis

Task 2 within the project focused on applying advanced strategies to synthesis of electrocatalysts with enhanced properties due to their precise composition, architecture, or surface control. This type of exploratory synthesis typically occurs on the scale of producing milligrams of catalyst powder for electrochemical evaluation in Task 3. This scale is suitable for evaluation by RDE and in situ ICP-MS, and in some cases 5-cm² MEA testing. To demonstrate commercial potential, however, the synthesis of the catalyst must be scaled up and the catalyst must be tested in at least 50 cm² MEAs. Therefore, significant effort was devoted through Task 5 to scale up of the advanced catalysts developed in Task 2. The proof-of-concept was performed on 5-nm PtNi nanoparticles with multilayered Pt-skin [5]. Through a multiphase scale up strategy and fine-tuning of various synthetic variables, this rather “simple” catalyst was scaled to be produced in a five-gram batch. More recently, scale up of more “complex” catalysts such as PtNi nanoframes, nanopinwheels, and nanocages is underway [6, 7]. These architectures are more complex than spherical nanoparticles because the location of Pt and Ni within the nanomaterial must be controlled to maintain the structure. They rely on creating Ni-rich and Pt-rich regions so that the Ni-rich regions can be removed by a corrosion process to expose certain Pt-rich surfaces. This type of non-uniform Pt and Ni growth typically requires careful control of metal precursor reduction rates and reaction temperature, which are very difficult variables to tune as batch size increases. However, the synthesis of these advanced architectures is currently progressing towards the scale of hundreds of milligrams (Figure 2a–c). This will enable a broader range of MEA evaluations to be performed on these architectures, which so far rarely has been explored within the catalyst development field.

Simultaneously, a second strategy for nanoparticle scale up is being developed. A continuous process for nanoparticle synthesis will use a flow reactor (Figure 2d) to produce small quantities of nanoparticles nonstop. There are many benefits to developing nanoparticle synthesis in a flow reactor. The continuous nature allows for the product quality to be monitored online, with reaction variables such as precursor concentration and reaction temperature tuned in real time. Additionally, the difficulties of batch scale up are avoided because each “individual” reaction is maintained on a small scale similar to how the synthesis originally was.
discovered. As the flow reactor is further characterized, the speed of nanoparticle scale up increases rapidly due to the continuous information feedback inherent to the process. The PtNi nanoparticles with multilayer Pt-skin already have demonstrated proof-of-concept of this nanoparticle flow reactor (Figure 2e).

![Figure 2. Scale up is now possible to the hundreds of milligram batches of (a) nanoframes, (b) nanopinwheels, and (c) nanocages. A flow reactor also is being established to study continuous flow synthesis (d), and PtNi nanoparticles have been synthesized by this process (e).](image)

**MEA Testing of Pt-Based Catalysts**

To overcome the technical barriers of performance, durability, and cost, ORR catalysts must be evaluated in MEAs. Advanced architectures such as PtNi nanopinwheels are being tested in 5 cm² MEAs at Argonne National Laboratory to optimize catalyst and MEA preparation strategies (Figure 3a). Previously, PtNi nanoparticles—which was the first catalyst to be scaled up—also had been evaluated in 5 cm² MEAs. Now, the same catalyst has been evaluated in 50 cm² MEAs in collaboration with National Renewable Energy Laboratory. The tests were performed with a Nafion 211 membrane with anode and cathode catalyst deposited by ultrasonic spray coating. The ionomer-to-carbon ratio used was 0.9 with a cathode loading of 0.046 mgPt cm⁻², well below the DOE 2020 target of 0.125 mgPt cm⁻². The MEA was tested at 150 kPa, 100% relative humidity, and 80°C, with hydrogen flowing through the anode and oxygen flowing through the cathode. At 0.9 V operating potential, the PtNi nanoparticles with multilayer Pt-skin demonstrated 0.5 A/mgPt, above the DOE 2020 target of 0.44 A/mgPt (Figure 3b). This success demonstrated the tremendous power of the fundamental strategies employed in this project, starting from well-defined surfaces on which careful study yields insight that influences design of nanoparticles that can be similarly characterized by precise RDE techniques before transitioning to scale up and MEA testing.
CONCLUSIONS AND UPCOMING ACTIVITIES

The RDE-ICP-MS technique developed within this project continued to yield critical information about electrochemical degradation of ORR catalyst materials. Intermetallic Pt-Co phases were shown to dramatically protect against the dissolution of Co, a critical feature to maintaining the specific activity of the Pt surface. Insights from well-defined surfaces studied under high-purity electrochemical conditions guided nanomaterial synthesis of novel PtNi, PtCo, and other promising advanced architectures of ORR catalysts. These highly tuned and complex architectures—such as nanoframes and nanopinwheels—demonstrated initial promise in scale up towards gram-scale batches to enable widespread testing in MEAs. MEA evaluation was performed on PtNi nanoparticles that provided the major success of eclipsing the DOE 2020 target for mass activity at very low Pt loading, reducing cost of the catalyst layer within the PEMFC. This work is ongoing to further scale up and MEA testing of intermetallic and advanced architecture catalysts and demonstrate durability of these catalysts in 50-cm² MEAs. The effort will generate new publications and patent applications in the upcoming year, and drive the field of ORR catalyst development forward in overcoming the performance, durability, and cost technical barriers.

SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED


FY 2018 PUBLICATIONS/PRESENTATIONS


Figure 3. The performance of PtNi nanopinwheels was evaluated in a 5-cm² MEA (a) while that of PtNi multilayer skin nanoparticles was evaluated in a 50-cm² MEA (b).


REFERENCES


