
Highly Efficient and Durable Cathode Catalyst with Ultralow Platinum Loading through Synergetic Platinum/Platinum-Group-Metal-Free Catalytic Interaction

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Project End Date: December 31, 2019

Overall Objectives

- Develop low-platinum@platinum group metal (PGM)-free (LP@PF) cathode catalysts and membrane electrode assemblies (MEAs) meeting DOE 2025 fuel cell catalyst performance metrics.
- Demonstrate catalyst stability of <40% loss in mass activity or <30 mV loss of voltage at 1.5 A/cm² after accelerated stress test (AST) in fuel cell.
- Gain better understanding on the synergistic catalysis between Pt and PGM-free active sites through computational modeling and advanced characterization.

Fiscal Year (FY) 2019 Objectives

- Complete synthesis and evaluation of at least three trimetallic catalysts and catalytic electrodes for LP@PF MEAs.
- Complete the optimization of anode/cathode Pt distribution and demonstrate an MEA with total Pt loading <0.125 mg/cm².
- Demonstrate an MEA with total Pt loading <0.125 mg-Pt/cm² with improved activity (mass activity >0.44 A/mg-PGM) and durability (<40% loss of mass activity, <30

mV loss at 1.5 A/cm²). The new MEA/catalyst will be delivered to the National Renewable Energy Laboratory for evaluation.

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:

- Insufficient fuel cell cathode catalyst durability
- High cost due to high Pt loading in fuel cell cathode
- Low performance at high fuel cell current density due to insufficient catalytic sites.

Technical Targets

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

FY 2019 Accomplishments

- We achieved platinum mass activity of ~2 A/mg_{Pt} at 0.9 V_{IR-free} in a MEA/fuel cell test over Argonne National Laboratory's (ANL's) nanofibrous low Pt@PGM-free nanofiber (LP@PFNF) using DOE test protocols, exceeding the DOE 2025 target.
- We prepared MEAs with total Pt loading <0.125 mg_{Pt}/cm² and demonstrated their performance in an operating fuel cell.
- Fuel cells containing ANL's LP@PFNF cathode catalyst with ultralow Pt loading showed excellent durability under a newly established DOE AST protocol, meeting the DOE 2025 target.
- We carried out conventional and advanced structural characterizations and density functional theory (DFT) calculation in

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

understanding the mechanism of the synergistic catalysis.

Table 1. Current Project Status Measured Against DOE 2025 Fuel Cell Catalyst Performance Targets

	Units	DOE 2025 Target	Current Status
Pt mass activity @ 900 mV _{iR-free}	A/mg _{PGM}	0.44	1.91
PGM total loading	mg/cm ²	<0.125	<0.12
Loss in mass activity @ 900 mV _{iR-free}	% loss	<40	7%
Loss in performance at 0.8 A/cm ²	mV	<30	30
Loss in performance at 1.5 A/cm ²	mV	<30	8

INTRODUCTION

This project applies a new approach of preparing highly efficient and stable cathode catalysts containing ultralow Pt on PGM-free catalytic substrate derived from metal-organic frameworks (MOFs). It addresses a major challenge in fuel cell catalyst development—that is, how to improve electrocatalyst activity and durability in fuel cells using the lowest possible amount of platinum. The idea stems from an early discovery at ANL that a synergistic catalysis between ultralow concentration Pt alloy and its PGM-free catalytic support can lead to high specific activity and stability. The goal of this project is to deliver one or more such catalysts that can meet DOE fuel cell catalyst performance metrics. The project addresses several key barriers for proton exchange membrane (PEM) fuel cell technology including cost, efficiency, and durability, aiming at reducing the fuel cell Pt usage to <0.125 g/kW, or <10 g/vehicle, the amount similar to that in the automobile catalytic converter. The success of the new catalyst could potentially smooth the transition from internal combustion engine to fuel cell vehicles without interrupting Pt price and supply. The research also has broader impact to fuel cell technology beyond the transportation sector. The same catalysts can also be applied to portable tool, stationary power generation where the cost reduction is essential to market penetration.

APPROACH

The LP@PF catalysts are prepared using transition metal (TM)-based MOFs as the precursors that can be converted to PGM-free catalytic substrate upon heat activation. The monometallic or bimetallic MOFs are synthesized by either solvothermal or solid-state reaction between the TM ions and nitrogen-containing organic ligands [1, 2]. Upon high-temperature pyrolysis, the ligands are converted to charge-conducting N/C graphitic composite on which the oxygen reduction reaction (ORR) active site, TM-N_x-C_y, is formed through the coordination between TM ion and the nitrogen. Meanwhile, a fraction of TM is reduced to metallic nanoparticles (NPs) under the high temperature in the reducing environment, which serve as the seeds to grow Pt-TM core-shell alloy NPs during the subsequent Pt catalyzing and annealing processes. In addition to LP@PF catalyst, we also integrated MOF into nanofiber using electrospinning to produce catalyst of low Pt@PGM-free active sites embedded in nanofiber, LP@PFNF [3]. The catalytic activity and durability were tested by the rotating disk electrode method and in a fuel cell.

Figure 1a shows the schematic representation of catalytic active sites inside a cobalt MOF-derived LP@PF, which consists of Pt₃Co core shell NPs, Co-N_x-C_y, and Co NP encapsulated by layer of graphene; all are known active toward ORR. Figure 1b shows the energy diagram of stepwise ORR over Pt and Co-N_x-C_y sites. Sequential proton and electron transfers occur in parallel over Pt and PGM-free active sites to complete the four-electron process to reduce O₂ to H₂O. For Co-N_x-C_y, however, there exists a branching reaction where H₂O₂ is formed and detached from the active site due to the weak binding. The peroxide thus formed can migrate to a nearby Pt site to be converted to water through O-O bond breaking and OH conversion to H₂O by combining with H⁺ and e⁻, completing the synergistic catalysis.

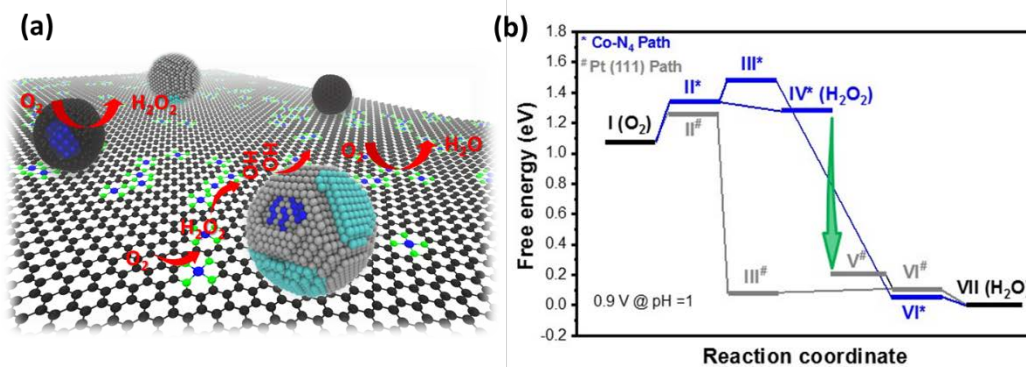


Figure 1. (a) Schematic presentation of different ORR active sites in LP@PF catalyst; (b) ORR free energy as the function of reaction coordinate over Pt and PGM-free active sites

RESULTS

The primary focus of our FY 2019 activity included continually improving the LP@PF catalyst and its nanofibrous form LP@PFNF to evaluate their compatibility with thin and high-temperature membranes and to reduce and rebalance anode/cathode platinum loadings so that the total loading is less than 0.125 mg/cm². We also continued our investigation on the synergistic interaction between Pt-Co alloy and PGM-free active sites through advanced structural characterization and computational modeling. Our preliminary study encountered some challenges in adopting our catalyst with a high-temperature membrane. This is presumably due to the water management issue although more thorough investigation is needed. We also found that reducing anodic platinum loading to <0.035 mg/cm² lowered the cathodic performance in the fuel cell test, although a more comprehensive anode optimization should be carried out to confirm the observation.

During the development of LP@PF and LP@PFNF, we found that we could reach higher batch-to-batch performance consistency for the nanofiber catalyst. This could be attributed to a better control on the alloy particle size by minimizing platinum/transition metal agglomeration through segregation by fibers. Furthermore, we found that both LP@PF and LP@PFNF catalysts offer excellent and consistent stability when tested in MEA/fuel cell using an updated DOE AST protocol. Figure 2 shows the representative current-voltage polarizations of a fuel cell containing ANL's LP@PFNF at cathode with the total platinum loading less than 0.1 mg/cm². The fuel cell test was conducted at one-bar pressure in a fully humidified H₂-air cell. We further studied the catalyst stability through a 30,000 voltage cycle AST (0.6 V to 0.95 V, step-function) and found that the MEA/catalyst showed remarkable stability compared to commercial state-of-the-art catalyst. Such stability has been observed consistently for both LP@PF and LP@PFNF catalysts.

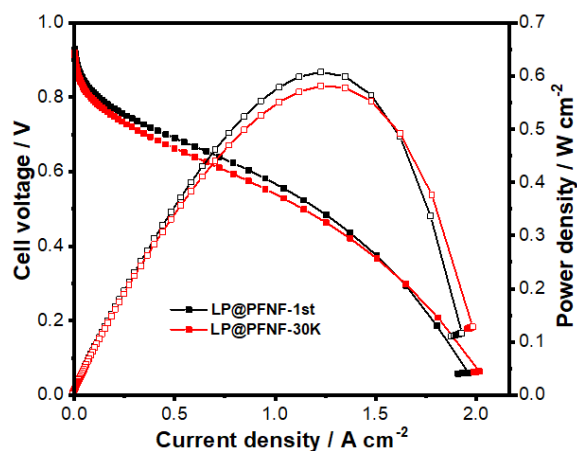


Figure 2. The current-voltage polarizations of fuel cells containing a LP@PFNF catalyst at cathode before and after 30,000 voltage cycle AST. Test condition: 80 °C, $P_{\text{air}} = P_{\text{H}_2} = 1$ bar (backpressure = 0.5 bar), 100% relative humidity, Nafion 211 membrane, MEA area = 5 cm², anode Pt loading = 0.035 mg/cm², cathode Pt loading = 0.06 mg/cm².

To better understand the catalyst stability, we also performed high-resolution transmission electron microscopy and DFT calculation. Figure 3 shows that Pt-Co nanoparticles in LP@PF catalyst are partially covered by “terraces” of layered materials. Electron energy loss spectroscopy indicates that the layered materials consist of CoC and CoN. DFT calculation shows that these terraces grow preferentially over the Pt (100) plane, which is more prone to acidic corrosion, while leaving Pt (111), which is more ORR active, exposed. The protective cover for Pt alloy, combined with facile removal of peroxide by Pt and PGM-free site, could potentially explain the enhanced stability of LP@PF catalyst.

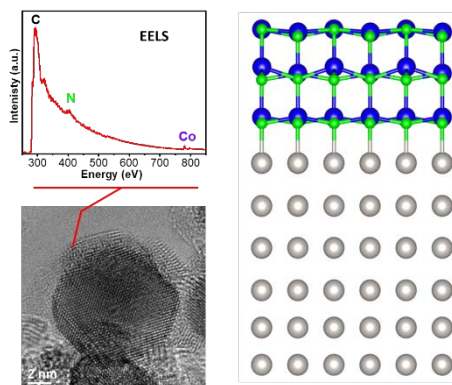


Figure 3. Transmission electron microscopy image shows Pt-Co nanoparticles are covered by layered material (bottom left), which is composed of Co, C and N measured by electron energy loss spectroscopy (top left). DFT shows preferential growth of CoN layer over Pt (100) lattice (right).

CONCLUSIONS AND UPCOMING ACTIVITIES

Argonne’s LP@PF and LP@PFNF catalysts demonstrated very promising activity and excellent durability when tested in a PEM fuel cell. Computational modeling and advanced characterization identified a synergistic mechanism that promotes the utilization of Pt and improves its stability during the ORR catalysis. Further studies should include:

- Design multi-metallic LP@PF catalysts by taking advantage of MOF’s porous structure for infiltration and exchangeable framework for metal substitution.
- Improve the structural and mass transport robustness by controlling graphitization level and optimizing protection coating and nano-network for better activity and durability.
- Gain fundamental knowledge on Pt and PGM-free active site interaction through a systematic design, synthesis, and investigation on PGM-free substrate type, site density, peroxide/transport, water management, etc.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. “Fuel Cell Catalyst with Ultralow Pt Loading,” by Di-Jia Liu and Lina Chong, was selected for a 2019 R&D 100 Award by R&D Magazine.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. “Highly Efficient and Durable Cathode Catalyst with Ultralow Pt Loading through Synergetic Pt/PGM-Free Catalytic Interaction,” Slide presentation at the 2018 US Drive Fuel Cell Tech Team October Meeting, Southfield, MI, October 17, 2018.
2. Lina Chong, Jianguo Wen, Joseph Kubal, Fatih G. Sen, Jianxin Zou, Jeffery Greeley, Maria Chan, Heather Barkholtz, Wenjiang Ding, and Di-Jia Liu, “Ultralow-Loading Platinum-Cobalt Fuel Cell Catalysts Derived from Imidazolate Frameworks,” *Science* 362 (2018): 1276–1281.

3. Di-Jia Liu, “Rational Design and Synthesis of Electrocatalysts for Fuel Cells,” Invited departmental seminar at University of South Florida, Tampa, Florida, October 18, 2018.
4. Lina Chong and Di-Jia Liu, “High Active Ultra-Low Pt Content Oxygen Reduction Reaction Catalyst Derived from Metal Organic Framework for PEMFC,” Presentation at Electrochemical Society Spring Meeting, Dallas, TX, May 26–30, 2019
5. Di-Jia Liu, “Highly Efficient and Durable Cathode Catalyst with Ultralow Pt Loading through Synergetic Pt/PGM-Free Catalytic Interaction,” 2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC, April 30–May 1, 2019.
6. Di-Jia Liu, “Rational Design of PGM-Free Catalysts for ORR and Beyond,” Invited presentation at the 2019 Platinum Group Metal-free Electrocatalysts: Structure-to-Property Relations, Materials Synthesis and Integration in Catalysts Layers, Telluride, CO, June 25–June 29, 2019.

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1. Shengqian Ma, Gabriel Goenaga, Ann Call and Di-Jia Liu, “Cobalt Imidazolate Framework as Precursor for Oxygen Reduction Reaction Electrocatalyst,” *Chemistry: A European Journal* 17 (2011): 2063–2067.
2. Dan Zhao, Jiang-Lan Shui, Lauren R. Grabstanowicz, Chen Chen, Sean M. Commet, Tao Xu, Jun Lu, and Di-Jia Liu, “Highly Efficient Non-Precious Metal Electrocatalysts Prepared from One-Pot Synthesized Zeolitic Imidazolate Frameworks (ZIFs),” *Advanced Materials* 26 (2014): 1093–1097.
3. Jianglan Shui, Chen Chen, Lauren R. Grabstanowicz, Dan Zhao and Di-Jia Liu, “High-Efficiency Non-Precious Metal Catalyst Containing Metal-Organic Framework Precursor Inside of Carbon Nano-Network,” *Proceedings of National Academy of Sciences* 112, no. 34 (2015): 10629–10634.