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

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## Overall Objectives

- To develop low-Pt@PGM (platinum group metal)-free (LP@PF) cathode catalysts and membrane electrode assemblies (MEAs) meeting DOE fuel cell performance metrics, particularly at high current/power density region.
- To demonstrate one or more MEAs of total Pt loading  $<0.125 \text{ mg/cm}^2$  with mass activity  $>0.44 \text{ A/mg-Pt}$ , current density  $>300 \text{ mA/cm}^2$  at  $0.8 \text{ V}$ , and  $>1,000 \text{ mW/cm}^2$  rated power tested in fuel cell.
- To demonstrate MEA stability of  $<40\%$  loss in mass activity or  $<30 \text{ mV}$  loss of voltage at  $1.5 \text{ A/cm}^2$  after accelerated stress test in fuel cell.
- To gain better understanding on the synergistic catalysis between Pt and PGM-free active sites through computational modeling and advanced characterization.

## Fiscal Year (FY) 2018 Objectives

- Demonstrate a MEA containing LP@PF catalyst with current density  $>300 \text{ mA/cm}^2$  at  $0.8 \text{ V}$  and  $<40\%$  loss of mass activity when tested under one-bar air in single fuel cell.
- Demonstrate a MEA/fuel cell with mass activity  $>0.44 \text{ A/mg-PGM}$  and  $<40\%$  loss of mass activity,  $<30 \text{ mV}$  loss at  $1.5 \text{ A/cm}^2$  in durability, following the accelerated test protocol by DOE.
- Complete LP@PF catalyst structure, electronic state, and surface property characterization using conventional and advanced characterization tools.

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cell section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan<sup>1</sup>:

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

## Technical Targets

The current project status measured against the DOE 2025 catalyst/MEA performance targets is shown in Table 1.

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

## FY 2018 Accomplishments

- Argonne National Laboratory's (ANL's) new LP@PF catalysts demonstrated high Pt mass activities up to 3.30 A/mg<sub>Pt</sub> in fuel cell tests, exceeding the DOE 2025 target.
- Fuel cells containing ANL's LP@PF cathode catalyst with ultralow Pt loading demonstrated current densities >300 mA/cm<sup>2</sup> at 0.8 V and >1,000 mA/cm<sup>2</sup> at 0.65 V under one bar air, respectively, meeting the DOE 2025 target.
- Fuel cells containing ANL's LP@PF cathode catalyst with ultralow Pt loading showed 7% loss of mass activity, less than 6 mV voltage loss at 0.8 A/cm<sup>2</sup> and less than 8 mV voltage loss at 1.5 A/cm<sup>2</sup> after 30,000 voltage cycle accelerated stress test, meeting the DOE target.
- Advanced characterization and density functional theory (DFT) calculation revealed the catalyst structural properties and synergistic mechanism.

**Table 1. Current Project Status Measured Against DOE 2025 Catalyst/MEA Performance Targets**

	Units	DOE 2025 Target	Project Inception	Current Status
Pt mass activity @ 900 mV <sub>iR-free</sub>	A/mg <sub>PGM</sub>	0.44	1.77	3.30
PGM total loading	mg/cm <sup>2</sup>	<0.125 (total)	0.039 (cathode)	0.033 (cathode)
MEA performance @ 800 mV (1 bar air)	mA/cm <sup>2</sup>	≥300	273	359
MEA performance @ 675 mV (1 bar air)	mA/cm <sup>2</sup>	≥1,000	754	1,005
Loss in mass activity @ 900 mV <sub>iR-free</sub>	% loss	<40	85%	7%
Loss in performance at 0.8 A/cm <sup>2</sup>	mV	<30	50	6
Loss in performance at 1.5 A/cm <sup>2</sup>	mV	<30	62	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 porous organic precursors. It addresses a major challenge in fuel cell catalyst/MEA development—how to improve electrocatalyst/MEA activity and the durability in the full fuel cell operational span using the least possible amount of platinum. The idea stemmed from an early discovery made in our laboratory: a synergistic catalysis exists between ultralow-concentration Pt alloy and its PGM-free catalytic support, leading 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/MEA performance metrics, particularly at high current density region. The project addresses several key barriers for polymer electrolyte 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. This amount is similar to that currently used in the catalytic converter of the automobile with internal combustion engine. The success of the new catalyst potentially could smooth the transition from internal combustion 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 and MEAs also can be applied to portable tool, stationary power generation for which the cost reduction is essential to market penetration.

## APPROACH

The LP@PF catalysts are prepared using transition metal (TM) based metal-organic frameworks (MOFs) as the precursors that can be converted to PGM-free catalytic substrate upon heat activation. The monometallic or bimetallic MOF is 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 active site, TM-N<sub>x</sub>-C<sub>y</sub>, is formed through the coordination between TM ion and the carbonaceous nitrogen. Meanwhile, a fraction of TM is reduced to metallic nanoparticles under the high temperature in reducing environment, which subsequently serve as the seeds to grow Pt-TM core-shell alloy nanoparticles during the following platinum catalyzing and annealing processes. The catalytic activity and durability are tested by the rotating disk electrode (RDE) method and in a fuel cell. In addition to LP@PF catalyst, we also integrated MOFs into nanofiber using the electrospin approach to produce LP@PF catalyst support embedded in nanofiber, LP@PFNF catalysts under this program [3].

## RESULTS

During FY 2018, we designed and synthesized nearly 100 LP@PF and LP@PFNF catalysts and tested more than 70 MEAs in fuel cells. We also studied the catalyst structures, electronic states, and surface properties using high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and Brunauer-Emmett-Teller surface analysis. Figure 1 shows the HR-TEM images of a representative LP@PF catalyst. The catalyst consists of Pt-Co alloy nanoparticles situated over high-surface-area Co-N<sub>x</sub>-C<sub>y</sub> substrate (Figure 1A). The Pt-Co nanoparticles have a Pt-Co core and Pt shell of two to three layers of Pt atom (Figure 1B). Amplifying the contrast of the substrate at the background shows the individually dispersed Co atoms embedded in N/C composite (Figure 1C). The oxygen reduction reaction catalysis occurs over Pt-Co nanoparticles and PGM-free sites simultaneously and independently. Meanwhile the unconverted H<sub>2</sub>O<sub>2</sub> produced from the TM-N<sub>x</sub>-C<sub>y</sub> sites can migrate over to nearby Pt-Co nanoparticle surface to be further reduced to H<sub>2</sub>O at much faster pace, accomplishing synergistic catalysis and improving Pt utilization.

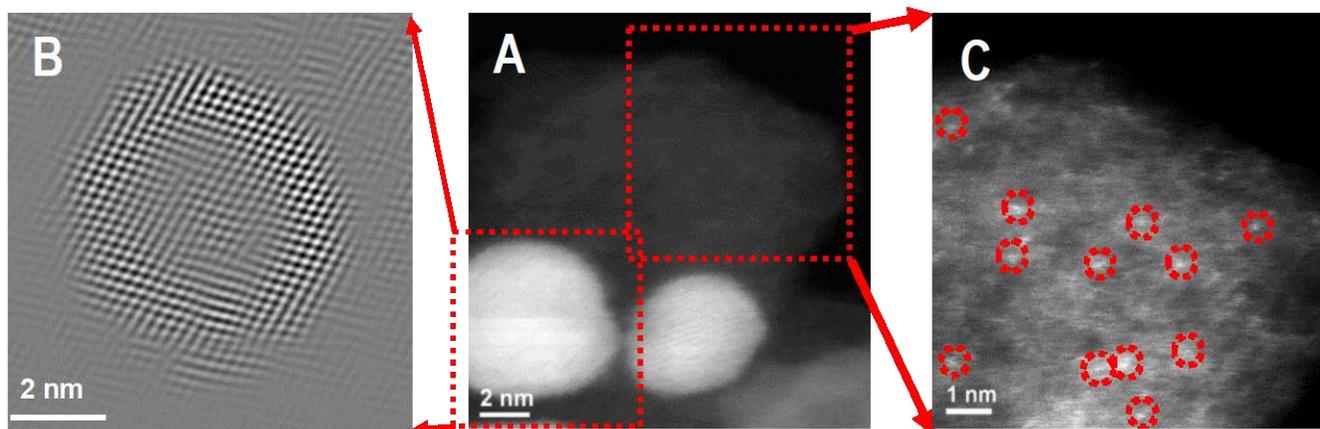


Figure 1. (A) HR-TEM showing a representative LP@PF catalyst with Pt-Co nanoparticles over PGM-free support; (B) core-shell structure of Pt-Co nanoparticles with the Pt-Co core and Pt shell; and (C) PGM-free support showing evenly distributed single Co atoms (red circles) over N/C composite

The LP@PF catalysts were incorporated into MEAs and tested under PEM fuel cell operating condition. Figure 2 shows the current-voltage polarizations tested under one-bar air of PEM fuel cells containing MEAs with LP@PF-11 and LP@PF-12 catalysts at the cathode. The cathodic Pt loadings for the catalysts were  $0.033 \text{ mg}_{\text{Pt}}/\text{cm}^2$  and  $0.035 \text{ mg}_{\text{Pt}}/\text{cm}^2$ , respectively. For comparison, the current-voltage polarizations of two commercial MEAs with 6–10 times the cathodic Pt loading also are plotted. The activity of MEAs with LP@PF cathode catalyst outperformed the commercial products at both high voltage and high current domains of the fuel cell operation, even at substantially less Pt loading.

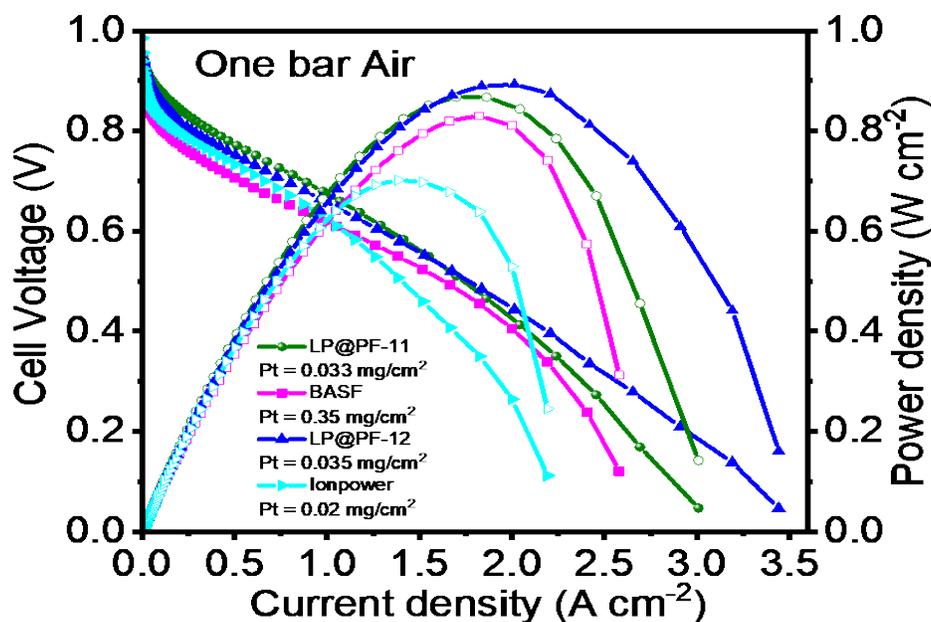


Figure 2. The current-voltage polarizations of fuel cells containing MEAs with LP@PF catalysts at cathode. For comparison, the polarization of two commercial MEAs also is shown. Test condition:  $80^\circ\text{C}$ ,  $P_{\text{air}} = P_{\text{H}_2} = 1 \text{ bar}$ , 100% relative humidity, Nafion 211 membrane, MEA area =  $5 \text{ cm}^2$ .

The LP@PF catalyst durability also was evaluated under multiple voltage cycling from 0.6 V to 1.0 V, using DOE's accelerated stress test protocol. Figure 3 shows current-voltage polarization of a MEA containing cathodic LP@PF-new catalyst. After 5,000 and 30,000 voltage cycles, the polarization voltage at any given

current density remained nearly unchanged or actually improved somewhat, indicating high stability of the LP@PF catalyst under aging conditions in a fuel cell.

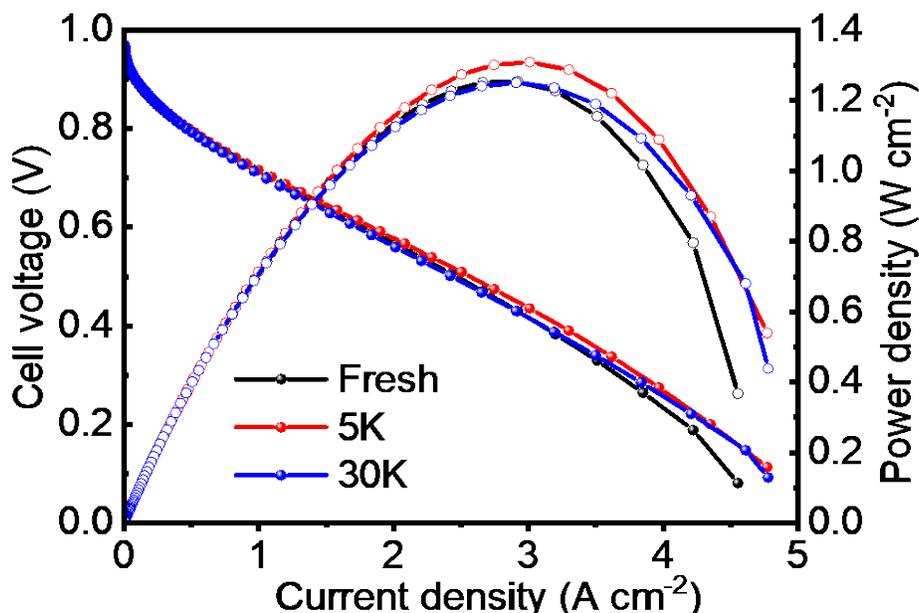


Figure 3. The current-voltage polarizations of fuel cells at different voltage cycles during the accelerated stress test. The MEA has LP@PF-new catalyst at cathode with Pt loading of 0.033 mg/cm<sup>2</sup>. Test condition: 80 °C, P<sub>air</sub> = P<sub>H<sub>2</sub></sub> = 1 bar, 100% relative humidity, Nafion 211 membrane, MEA area = 5 cm<sup>2</sup>.

## CONCLUSIONS AND UPCOMING ACTIVITIES

Argonne's LP@PF catalysts demonstrated excellent activity and durability when tested in PEM fuel cell, indicating oxygen reduction reaction catalyst performance can be improved through synergistic interaction between ultralow loading of Pt and PGM-free active sites. Further studies include:

- Complete evaluation of new membranes for LP@PF catalyst in MEA H<sub>2</sub>-air fuel cell.
- Complete exploration and evaluation of new catalysts and catalytic electrodes for LP@PF and LP@PFNF MEAs.
- Complete optimization of anode/cathode Pt distribution and demonstrate MEA with total Pt loading <0.125 mg/cm<sup>2</sup>.

## SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. "Low Platinum Catalyst and Method of Preparation," Di-Jia Liu and Lina Chong, U.S. Patent 9,825,308.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. 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* (2018), DOI:10.1126/science.aau0630.
2. Di-Jia Liu and Lina Chong, "Highly Efficient and Durable Cathode Catalyst with Ultralow Pt Loading Through Synergetic Pt/PGM-Free Catalytic Interaction," 2018 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, June 13–15, 2018, Washington, D.C.

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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.