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# ElectroCat: Highly Active and Durable Platinum-Group-Metal-Free Oxygen Reduction Reaction Electrocatalysts through the Synergy of Active Sites

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## Subcontractors:

- Washington University in St. Louis, St. Louis, MO
- University of Maryland, College Park, MD
- Ballard Power Systems, Burnaby, BC, Canada
- Oregon State University, Corvallis, OR

Project Start Date: October 1, 2017  
Project End Date: March 31, 2021

## Overall Objectives

- Design and fabricate high-performance platinum group metal (PGM)-free oxygen reduction catalysts with increased O<sub>2</sub> reduction active site density and improved mass transport property.
- Design and fabricate highly active H<sub>2</sub>O<sub>2</sub> decomposers to decrease H<sub>2</sub>O<sub>2</sub> formation in the catalyst layer (50%).
- Demonstrate dual-active-site catalysts (O<sub>2</sub> reduction active sites and H<sub>2</sub>O<sub>2</sub> decomposition sites) for improved (2X) durability.

## Fiscal Year (FY) 2019 Objectives

- Demonstrate improved stability of PGM-free catalysts using dual active sites in a membrane electrode assembly (MEA).
- Year 1 go/no-go milestone: Demonstrate a PGM-free catalyst  $\geq 20$  mA/cm<sup>2</sup> at 0.90 V (iR-

corrected) in an H<sub>2</sub>-O<sub>2</sub> fuel cell and 100 mA/cm<sup>2</sup> at 0.80 V in an H<sub>2</sub>-air fuel cell (measured); maintain partial pressure of O<sub>2</sub> + N<sub>2</sub> at 1.0 bar (cell temperature 80°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<sup>1</sup>:

- Durability (catalyst)
- Cost (catalyst)
- Performance (catalyst).

## Technical Targets

This project focuses on the development of high-performing and durable PGM-free oxygen reduction reaction (ORR) catalysts for polymer electrolyte fuel cells with the potential to meet DOE targets (Table 3.4.7 in the Fuel Cells section of the Multi-Year Research, Development, and Demonstration Plan). Our goal is to achieve an activity of 30 mA/cm<sup>2</sup> at 0.90 V in a polymer

## FY 2019 Accomplishments

- Demonstrated improved stability of PGM-free catalysts using dual active sites in an MEA.
- Met the project's Year 1 go/no-go milestone: Demonstrate a PGM-free catalyst  $\geq 20$  mA/cm<sup>2</sup> at 0.90 V (iR-corrected) in an H<sub>2</sub>-O<sub>2</sub> fuel cell and 100 mA/cm<sup>2</sup> at 0.80 V in an H<sub>2</sub>-air fuel cell (measured); maintain partial pressure of O<sub>2</sub> + N<sub>2</sub> at 1.0 bar (cell temperature 80°C). The project achieved 30 mA/cm<sup>2</sup> at 0.9 V in H<sub>2</sub>/O<sub>2</sub> and 101.5 mA/cm<sup>2</sup> at 0.8 V in H<sub>2</sub>/air with dual-active-site catalyst.
- Further confirmed radical attack of carbon as one degradation mechanism of PGM-free catalysts.

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

**Table 1. Progress toward Meeting Technical Targets for Electrocatalysts for Transportation Applications**

Characteristic	Units	DOE 2020 Electrocatalyst Targets	Project Status
PGM-free catalyst activity	mA/cm <sup>2</sup> @ 0.9 mV <sub>iR</sub> -free	≥44	30

## INTRODUCTION

Developing PGM-free ORR catalysts has been an important strategy to decrease the cost of polymer electrolyte fuel cells. One big challenge of PGM-free ORR catalysts is the poor stability of the catalysts, partially due to the incomplete reduction of O<sub>2</sub> and formation of H<sub>2</sub>O<sub>2</sub> (and radicals). The formation of destructive H<sub>2</sub>O<sub>2</sub> (and radicals) not only decreases the activity and stability of PGM-free catalysts but also damages the membrane and ionomers in the catalyst layer (particularly in the presence of Fe ions, which catalyze radical formation from H<sub>2</sub>O<sub>2</sub> through the Fenton reaction). The other challenge of PGM-free ORR catalysts is their low active site density. Therefore, the pathway forward is to significantly increase the number of active sites and to decrease or eliminate H<sub>2</sub>O<sub>2</sub> formation.

## APPROACH

This project is designed to improve PGM-free ORR catalyst stability and activity. Our technical approaches to accomplish these goals includes the dual-active-site synergy approach, which integrates O<sub>2</sub> reduction active sites and H<sub>2</sub>O<sub>2</sub> decomposition active sites. The dual-active-site synergy approach will minimize or eliminate H<sub>2</sub>O<sub>2</sub>, which is believed to be a major source of activity loss [1, 2]. Our close collaboration with the Electrocatalysis (ElectroCat) consortium and use of its advanced capabilities will enable deep understanding of the function mechanisms and degradation mechanisms of the catalysts.

## RESULTS

In FY 2019, we focused on FeNC catalysts and applying our dual-active-site concept to FeNC catalysts. Meanwhile, we further studied the degradation of PGM-free catalysts, particularly degradation by radical attack (in collaboration with ElectroCat core lab teams).

We developed an atomically dispersed FeNC catalyst. Figure 1 shows the physical characterization of FeNC catalyst. The scanning transmission electron microscopy/electron energy loss spectroscopy (STEM/EELS) of FeNC shows atomically dispersed Fe and its co-existence with N, indicating the formation of FeN<sub>x</sub> moieties (Figure 1a and 1b); the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra reveal Fe valence between 2+ and 3+, and FeN<sub>x</sub> bond (with some Fe-O bonds), but free of Fe-Fe and Fe-C, further confirming atomic dispersion of Fe.

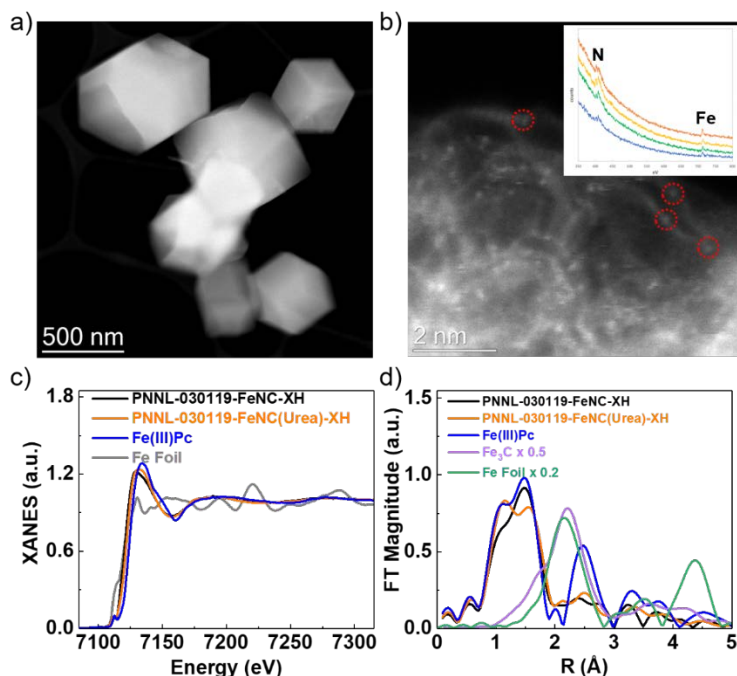


Figure 1. Physical characterization of atomically dispersed FeNC catalyst. (a, b) STEM/EELS of FeNC. (c, d) XANES and EXAFS of FeNC. In collaboration with Oak Ridge National Laboratory and Argonne National Laboratory.

Electrochemical measurements reveal activity dependence on synthesis (Figure 2a). By tuning the synthesis parameters including nitrogen precursors, a half-wave potential of  $E_{1/2} = 0.84$  V is obtained (catalyst loading on rotating disk electrode is  $0.6 \text{ mg/cm}^2$ ). We further tested the catalyst in MEAs, which show a current density of  $35 \text{ mA/cm}^2$  at  $0.9$  V in  $\text{H}_2/\text{O}_2$  and  $138 \text{ mA/cm}^2$  at  $0.8$  V in  $\text{H}_2/\text{air}$ , but these values decreased with cycling, indicating instability of FeNC.

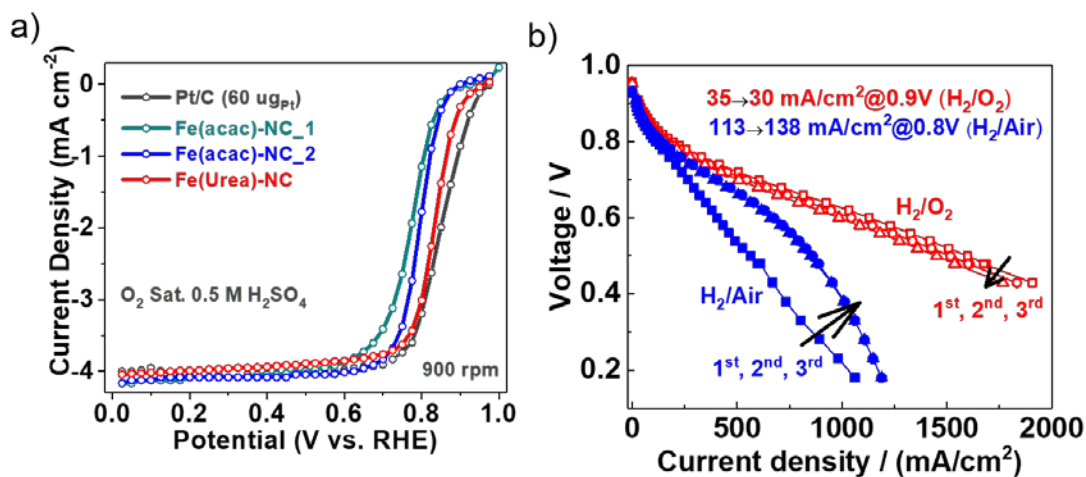


Figure 2. Activity and MEA performance measurements of FeNC. (a) ORR polarization curves on various catalysts. (b) MEA performance of FeNC in  $\text{H}_2/\text{O}_2$  and  $\text{H}_2/\text{air}$ .

With direct loading of  $\text{NCeOx}$  onto FeNC, we obtained dual-active-site catalysts FeNC\_NCeOx. Figure 3a shows the initial MEA activity ( $\text{H}_2/\text{O}_2$ ) and performance ( $\text{H}_2/\text{air}$ ) of FeNC\_NCeOx. The dual-active-site catalyst delivered  $30 \text{ mA/cm}^2$  at  $0.9$  V in  $\text{H}_2/\text{O}_2$  and  $101.5 \text{ mA/cm}^2$  at  $0.8$  V in  $\text{H}_2/\text{air}$ , both exceeding the Year 1 go/no-go milestone of the project. We further tested the stability of FeNC\_NCeOx and compared it with baseline FeNC. Figure 3b shows improved stability of the dual-active-site catalyst. We used the stability test

protocol modified from a literature one [1], which maximizes the negative effect of  $\text{H}_2\text{O}_2$ /radicals: we ran the cell in  $\text{H}_2/\text{O}_2$  at 0.4 V for 55 min and recorded the current density at 0.85 V for 5 min, and repeated the test.

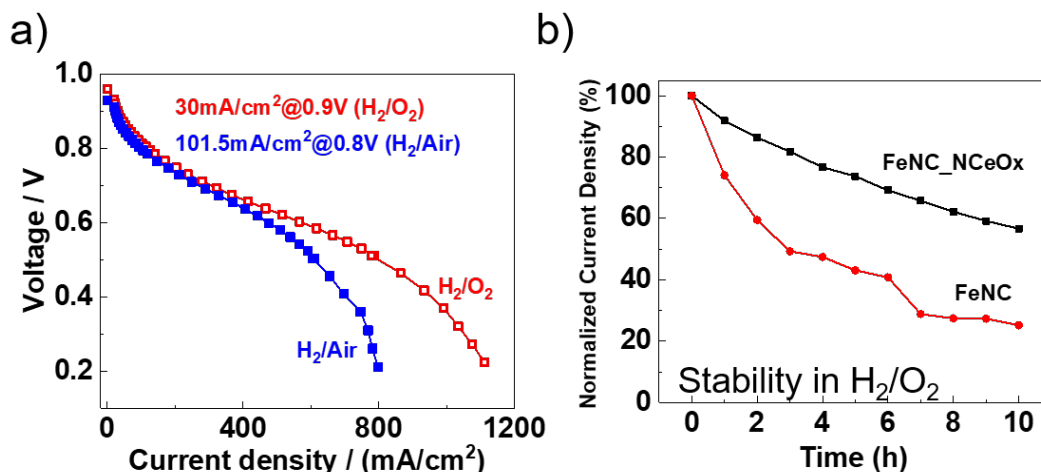


Figure 3. MEA performance and stability. (a) Dual-active-site FeNC\_NCeOx catalyst shows good initial performance in  $\text{H}_2/\text{O}_2$  and  $\text{H}_2/\text{air}$ . (b) Improved stability of dual-active-site catalyst FeNC\_NCeOx in comparison with baseline FeNC.

We further investigated the degradation of catalysts with a focus on radical attack. Figure 4 shows the online  $\text{CO}_2$  emission measurement in response to cell voltage and gas environment change. At low cell voltage of 0.3 V,  $\text{CO}_2$  concentration increases dramatically when  $\text{N}_2$  is switched to  $\text{O}_2$  at the cathode, indicating  $\text{CO}_2$  formation by chemical oxidation of carbon (by oxygen radicals). When cell voltage increases to 0.8 V, average  $\text{CO}_2$  concentration decreases, further indicating chemical oxidation of carbon instead of electrochemical oxidation. Switching to low cell voltage leads to higher  $\text{CO}_2$  concentration, and switching to  $\text{N}_2$  leads to lower  $\text{CO}_2$  concentration, confirming radical attack of carbon.

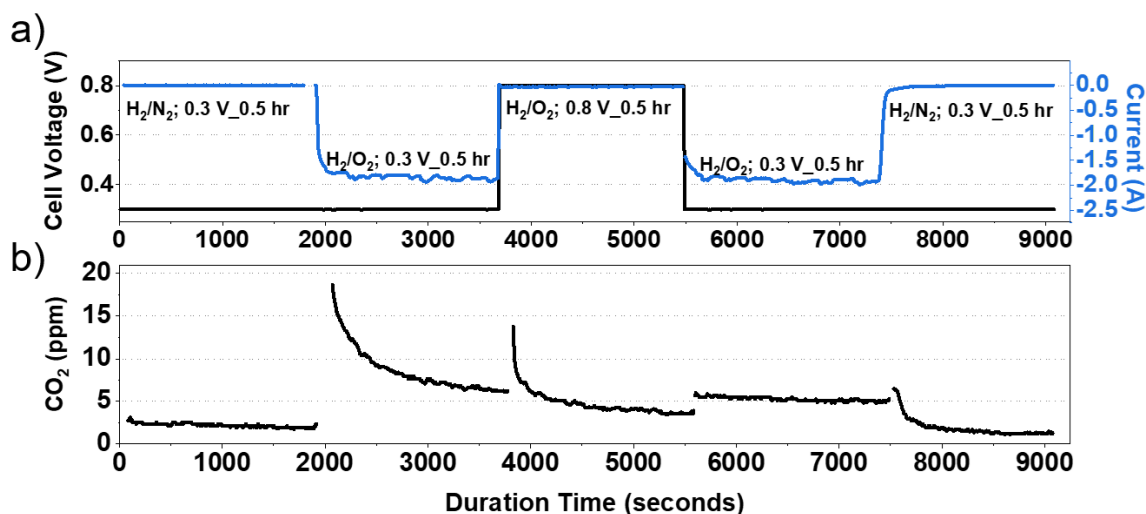


Figure 4. Online  $\text{CO}_2$  emission test. (a) Cell voltage and gas environmental change. (b)  $\text{CO}_2$  emission corresponding to cell voltage and gas environmental change. In collaboration with Los Alamos National Laboratory.

## CONCLUSIONS AND UPCOMING ACTIVITIES

We have developed a dual-active-site catalyst that delivered  $30 \text{ mA}/\text{cm}^2$  at 0.9 V in  $\text{H}_2/\text{O}_2$  and  $101.5 \text{ mA}/\text{cm}^2$  at 0.8 V in  $\text{H}_2/\text{air}$ , both exceeding the Year 1 go/no-go milestone of the project. More importantly, the dual-

active-site catalyst shows significant improvement in stability in comparison with the baseline that has no radical scavenger.

Our upcoming activities include:

- Identify key degradation mechanisms besides radical attack of carbon in order to develop a more effective technical strategy to address the instability issue of PGM-free catalysts.
- Optimize catalysts and MEA to achieve activity/performance targets.
- Develop new methods for the integration of dual active sites to better disperse radical scavenger for improved stability and performance.

## SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Clarivate Analytics “Highly Cited Researchers,” Yuyan Shao, Nov. 2018.

## FY 2019 PUBLICATIONS/PRESENTATIONS

1. Yuyan Shao, Xinliang Feng, Liming Dai, and Jean-Pol Dodelet, “Advancing Materials Electrochemistry for Chemical Transformation,” *Advanced Materials* (2019); <https://doi.org/10.1002/adma.201903622>.
2. Yuyan Shao, Jean-Pol Dodelet, Gang Wu, and Piotr Zelenay, “PGM-Free Cathode Catalysts for PEM Fuel Cells: A Mini-Review on Stability Challenges,” *Advanced Materials* (2019); <https://doi.org/10.1002/adma.201807615>.
3. Xiao Xia Wang, Venkateshkumar Prabhakaran, Yanghua He, Hui Liu, Yuyan Shao, and Gang Wu, “Advanced PGM-Free and Iron-Free Cathode Catalysts for Proton Exchange Membrane Fuel Cells: Cobalt Catalyst Approach and Peroxide Mitigation,” *Advanced Materials* (2019); <https://doi.org/10.1002/adma.201805126>.
4. Y. Shao, “Stability and Its Improvement of PGM-free ORR Catalysts,” presented at Platinum Group Metal-Free Electrocatalysts: Structure-to-Property Relations, Materials Synthesis and Integration in Catalysts Layers, Telluride, Colorado, June 25–29, 2019.
5. Y. Shao, “Identify Atomic-to-Nano Structures and Structure Evolution of Pt and PGM-Free Electrocatalysts for Oxygen Reduction Reaction,” presented at MRS Spring Meeting, Phoenix, AZ, April 22–26, 2019, Phoenix AZ.
6. Y. Shao, “Carbon-Based Materials for Electrochemical Transformation in Energy Conversion and Storage: Defects or Not?” presented at MRS Spring Meeting, Phoenix, AZ, April 22–26, 2019.
7. Y. Shao, “Electrochemical Transformation: An Energy Storage Perspective, Examples on Earth-Abundant Materials for Hydrogen, Biomass and Fuel Cells,” presented at ACS Fall Meeting, San Diego, CA, August 25–29, 2019.
8. Y. Shao, “Electrocatalyst Stability and Improvement for Oxygen Reduction Reactions,” presented at ACS Spring Meeting, Orlando FL, March 31–April 4, 2019.

## REFERENCES

1. X. Yi and P. Zelenay, “Kinetic Models for the Degradation Mechanisms of PGM-Free ORR Catalysts,” *ECS Transactions* 85, no. 13 (2018): 1239–1250.
2. C.H. Choi, H.-K. Lim, M.W. Chung, G. Chon, N.R. Sahraie, A. Altin, M.T. Sougrati, L. Stievano, H.S. Oh, E.-S. Park, F. Luo, P. Strasser, G. Dražić, K. Mayrhofer, H. Kim, and F. Jaouen, “Achilles’ Heel of Iron-Based Catalysts During Oxygen Reduction in Acidic Medium,” *Energy Environ. Sci.* (2018).