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

Project Start Date: October 1, 2017
Project End Date: September 30, 2020

Overall Objectives

- Design and fabricate high-performance platinum group metal (PGM)-free oxygen reduction catalysts with increased oxygen reduction active site density and improved mass transport property.
- Design and fabricate highly active H_2O_2 decomposers to decrease H_2O_2 formation in catalyst layer (50%).
- Demonstrate dual active site catalysts (O_2 reduction active sites and H_2O_2 decomposition sites) for improved durability (by 2 times).

Fiscal Year (FY) 2018 Objectives

- Develop two stable H_2O_2 decomposers.
- Identify pathways to produce 200 mg catalysts using thermal shock activation technique.
- Develop two O_2 reduction catalysts with $\Delta E_{1/2}$ <65 mV (vs. Pt/C) under rotating ring disk electrode (RRDE) test.
- Develop dual-site catalysts with H_2O_2 generation no more than 4% under RRDE test.
- Annual milestone: Demonstrate a PGM-free catalyst ≥20 mA/cm^2 at 0.90 V (iR-corrected) in an H_2-O_2 fuel cell and 100 mA/cm^2 at 0.80 V in an H_2-air fuel cell (measured); maintain partial pressure of $O_2 + N_2$ 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[1]:

- 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 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^2 at 0.90 V in a polymer electrolyte fuel cell membrane electrode assembly (MEA) by 2020 (Table 1).

FY 2018 Accomplishments

- Developed two H_2O_2 decomposition catalysts that decrease H_2O_2 formation on PGM-free catalysts by up to 50%.
- Developed a PGM-free, Fe-free, atomically dispersed Co catalyst that demonstrated a half-wave potential above 0.81 V (reversible hydrogen electrode [RHE]) (0.6 mg/cm^2 loading).

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

- Identified one key degradation mechanism of PGM-free catalysts by H_2O_2 (radical) attacking of carbon (in collaboration with the Electrocatalysis Consortium (ElectroCat), Los Alamos National Laboratory [LANL]).

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^2 @ 0.9 $mV_{iR\text{-}free}$	≥44	13

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 incomplete reduction of O_2 and formation of H_2O_2 (and radicals). The formation of destructive H_2O_2 (and radicals) not only decreases the activity and stability of PGM-free catalysts, it also damages the membrane and ionomers in the catalyst layer (particularly in the existence of Fe ions that catalyze radical formation from H_2O_2 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/eliminate H_2O_2 formation.

APPROACH

This project is designed to increase PGM-free ORR catalyst activity and improve its durability. Our technical approaches to accomplish these goals include the dual-active site synergy approach, which integrates O_2 reduction active sites and H_2O_2 decomposition active sites, and the unique thermal shock activation technique with extremely fast heating/cooling (16,000 K/s to 400,000 K/s for up to 3,000 K) to increase active site density. The dual-active site synergy approach will minimize or eliminate H_2O_2, which is believed to be a major source of activity loss [1, 2]. Our close collaboration with the ElectroCat consortium by using advanced capabilities will enable deep understanding of the function mechanisms and degradation mechanisms of the catalysts.

RESULTS

We have developed a PGM-free, Fe-free, atomically dispersed Co catalyst that demonstrated a half-wave potential of ~ 0.81 V (RHE) (Figure 1), which is among the highest ones reported so far for this class of ORR catalyst. We have also demonstrated an MEA ORR activity of 13 mA/cm^2 at 0.90 V in an H_2-O_2 fuel cell (Figure 1c).

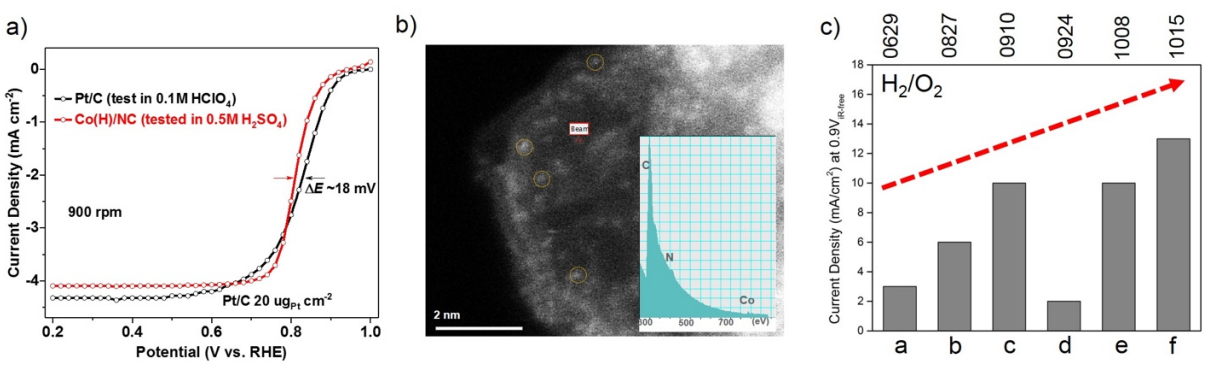

Figure 1. Performance and characterization of Co catalyst. a) RRDE test of Co catalyst (0.6 mg/cm² loading) in comparison with Pt/C, b) Scanning transmission electron microscopy image (taken at Oak Ridge National Laboratory) of Co catalyst showing atomic dispersion and the colocation of Co and N, indicating the formation of CoN_4 moieties, c) ORR activity of Co catalyst in MEA showing the progress enabled by MEA optimization.

Through integrating H_2O_2 decomposition catalyst and PGM-free catalyst, we were able to decrease H_2O_2 formation significantly. Figure 2 shows one example of our nitrogen-doped ceria (N-CeO_x) with PGM-free catalysts. In collaboration with ElectroCat consortium core team member LANL, we demonstrated significant decrease in CO_2 and F emission in the MEA with the H_2O_2 decomposition catalyst in the catalyst layer (Figure 3). The formation of CO_2 at the cell voltage as low as 0.3 V indicates prominent carbon oxidation by H_2O_2 (radicals) rather than the electrochemical oxidation of carbon, which occurs at electrode potential of 0.9 V and higher. The CO_2 emission measurement confirms that H_2O_2 (radicals) attacking on PGM-free catalysts is one key degradation mechanism that can be controlled using H_2O_2 decomposition catalysts. The decreased F emission (from the degradation of membrane and/or ionomers by H_2O_2 [radicals]) indicates the protection of membrane/ionomers by H_2O_2 decomposition catalysts.

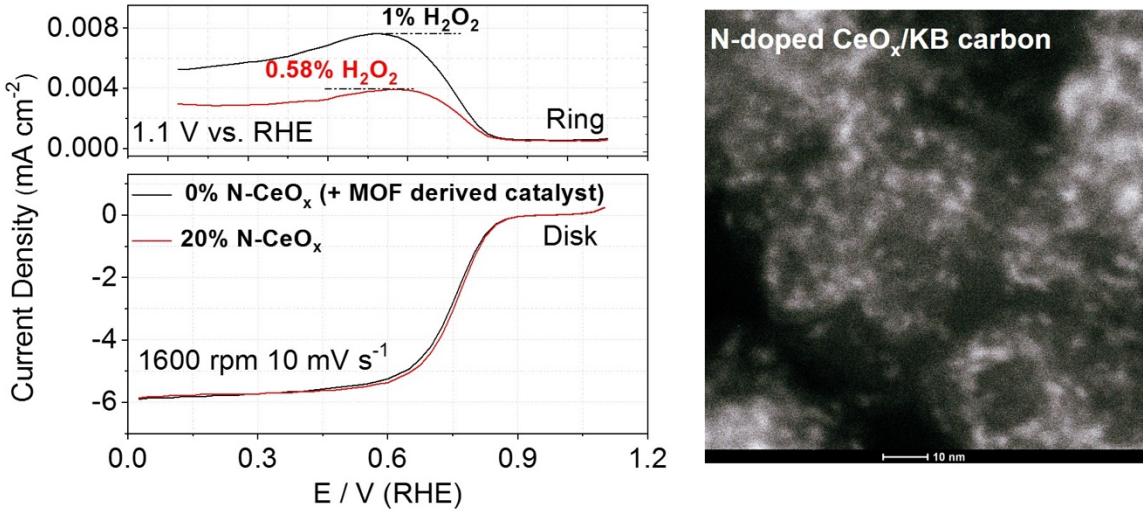

Figure 2. Dual-active site catalysts with decreased H_2O_2 formation and transmission electron microscopy image of an H_2O_2 decomposition catalyst

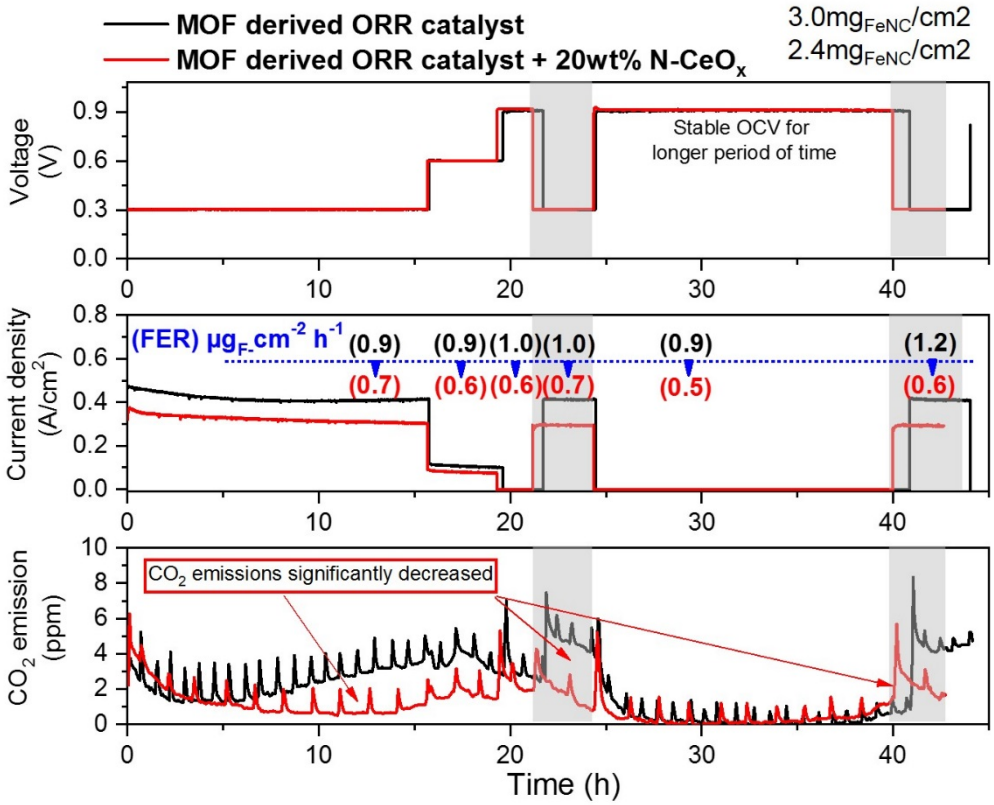

Figure 3. In Situ measurement of CO_2 and F emission in MEA with/without H_2O_2 decomposition catalysts (in collaboration with LANL)

Thermal shock synthesis has been explored to achieve the improved active site density of ORR and H_2O_2 decomposition catalysts. We have synthesized uniformly dispersed, small metal oxide nanoparticles (Figure 4a–b), which will be further functionalized for H_2O_2 decomposition catalysts. Through optimization of thermal shock synthesis, we were able to increase the activity of metal-organic-framework-derived catalysts (Figure 4a), but further improvement is still needed (Figure 4c).

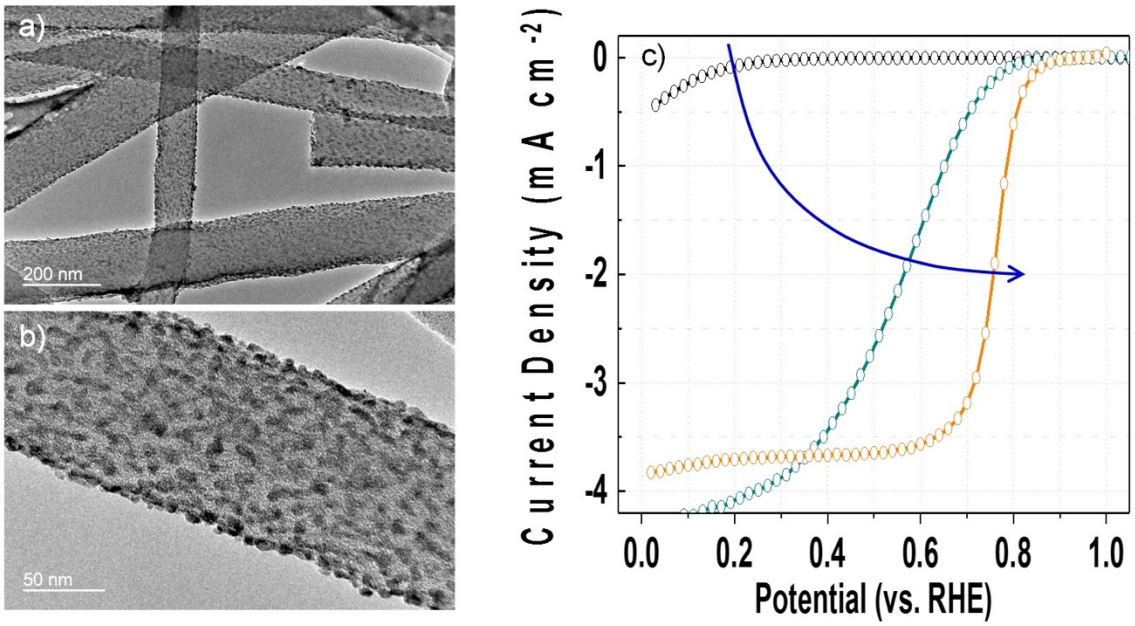

Figure 4. Thermal shock synthesis of H_2O_2 decomposition catalysts and ORR catalysts

CONCLUSIONS AND UPCOMING ACTIVITIES

We have developed a PGM-free, Fe-free Co catalyst that demonstrated a half wave potential of above 0.81 V (RHE) (loading 0.6 mg/cm^2) and 13 mA/cm^2 ORR activity in an H_2-O_2 cell. We, in collaboration with ElectroCat, identified that H_2O_2 (radical) attack on PGM-free catalysts is one key mechanism for its degradation. With the dual-active sites catalysts (O_2 reduction and H_2O_2 decomposition), we demonstrated the decreased CO_2/F emission, indicating the protection of catalyst and membrane/ionomer by the dual-active site catalysts.

Our upcoming activities include:

- Optimization of catalysts and MEA to achieve activity and performance target of 20 mA/cm^2 @ 0.90V (IR-free) in H_2-O_2 and 100 mA/cm^2 @ 0.80 V in H_2-air, including catalyst morphology (e.g., particle size, porosity) and ionomer content/distribution in catalyst layer.
- Optimization of thermal shock synthesis to demonstrate its advantages in producing active sites and uniform, smaller particles.
- Integration of dual-active sites for better dispersion of H_2O_2 decomposition catalysts and closer match between ORR sites and H_2O_2 sites.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Clarivate Analytics "Highly Cited Researchers." Yuyan Shao, November 2017.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Y. Shao, "Materials Electrochemistry for Energy Conversion and Storage @Scale," Invited seminar, University of California, Riverside, Department of Chemistry, April 2, 2018.
2. Y. Shao, "Electrochemical Materials and Interface Studies for Improved Activity and Durability in Chemical Transformation Processes," Invited talk, 39th Symposium on Applied Surface Analysis, Richland, Washington, June 19–22, 2018.
3. Y. Shao, X. Xie, V. Prabhakaran, and J. Liu, "Instability of Fuel Cell Catalysts: Precious Metal and PGM-Free Catalysts," Invited talk, ACS 2018 Fall Meeting, Boston, Massachusetts, August 19–23, 2018.

REFERENCES

1. Xi Yi and Piotr Zelenay, "Kinetic Models for the Degradation Mechanisms of PGM-Free ORR Catalysts," *ECS Transactions* 85, no. 13 (2018): 1239-1250.
2. Chang Hyuck Choi, Hyung-Kyu Lim, Min Wook Chung, Gajeon Chon, Nastaran Ranjbar Sahraie, Abdulrahman Altin, Moulay Tahar Sougrati, Lorenzo Stievano, Hyun Seok Oh, Eun-Soo Park, Fang Luo, Peter Strasser, Goran Dražić, Karl Mayrhofer, Hyungjun Kim, and Frederic Jaouen, "Achilles' Heel of Iron-Based Catalysts During Oxygen Reduction in Acidic Medium," *Energy Environ. Sci.* (2018).