
HydroGEN Seedling: Platinum-Group-Metal-Free Oxygen Evolution Reaction Catalysts for Proton Exchange Membrane Electrolyzers

Di-Jia Liu (Primary Contact), Lina Chong, Hao Wang, Haiping Xu
Argonne National Laboratory
9700 South Cass Avenue
Lemont, IL 60439
Phone: 630-252-4511
Email: djliu@anl.gov

DOE Manager: David Peterson
Phone: 240-562-1747
Email: David.Peterson@ee.doe.gov

Subcontractors:

- Gang Wu, The State University of New York (SUNY-Buffalo), Buffalo, NY
- Hui Xu, Giner, Inc., Newton, MA

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

Overall Objectives

- Reduce proton exchange membrane (PEM) electrolyzer capital cost by developing transition-metal-based catalysts as the replacements for platinum group metal (PGM) materials for oxygen evolution reaction (OER) in the PEM electrolyzer.
- Reduce the low-temperature water electrolyzer operating cost to meet the DOE hydrogen production target of <\$2/kg of hydrogen while maintaining the system efficiency at 43 kWh/kg of hydrogen.

Fiscal Year (FY) 2019 Objectives

- To prepare and test multiple bimetallic PGM-free OER catalysts and to integrate selected catalysts into a membrane electrode assembly (MEA) and tested by PEM electrolyzer.
- To complete a structural analysis of PGM-free OER catalysts using conventional and advanced analytical tools to better understand their activity and aging mechanism in the acidic environment.

- To complete the synthesis and preparation MEAs containing Co-based porous nanonetwork electrode (PNNE) OER catalyst or Fe-MOF based OER catalyst to be tested under proton exchange membrane water electrolyzers (PEMWE) operating condition.
- To demonstrate the MEAs containing PGM-free anode catalyst in operating PEMWE with a current density >400 mA/cm² measured at 1.80 V, and a voltage loss <100 mV measured at 200 mA/cm² after 100 voltage cycles from 1.4 V to 1.7 V.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Cost: low-cost PGM-free OER catalyst as the replacement for Ir in PEM electrolyzer
- Footprint: lower hydrogen production footprint with PEM electrolyzer of high ion conductivity
- Renewable energy integration: remove the capital cost barrier of PEM electrolyzer for broadly implemented distributed renewable energy applications.

Technical Targets

This project aims at developing anodic PGM-free OER catalyst for PEM electrolyzer that meets the following DOE hydrogen production targets:

- Cost: \$2/kg of H₂
- System efficiency: 43 kWh/kg of H₂

FY 2019 Accomplishments

- Argonne National Laboratory (ANL) continued to improve two series of MOF-derived PGM-free catalysts, ANL-A and ANL-B. Both were incorporated into PNNE

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

and demonstrated excellent OER activity approaching to that of Ir black.

- Multi-metallic OER catalysts developed by ANL have demonstrated improved activity and durability in Real Driving Emissions test.
- Carbon nanotube added, ZIF-derived single atom and multi-metallic M-N-C OER catalysts developed at SUNY-Buffalo have shown consistent improvement in activity.
- MEAs integrated with ANL-A anodic catalyst have shown continuous improvement under

the operating PEMWE, reaching current density of 320 mA/cm² at cell voltage of 1.8 V without any internal resistance (iR) correction when using Nafion 115 membrane.

- MEAs integrated with ANL-B anodic catalyst have demonstrated current density of 400 mA/cm² at cell potential of 1.78 V. After 2000 voltage cycles from 1.4 V to 1.7 V, the cell voltage at the current density of 200 mA/cm² increased only 25 mV, exceeding Phase 2 go/no-go decision targets.

INTRODUCTION

This project aims at developing the next-generation, high-efficiency, and durable PGM-free OER catalysts for the PEM electrolyzer through collaboration between Argonne National Laboratory (ANL), SUNY-Buffalo, and Giner Inc. (Giner) leveraging the multiple capability nodes at HydroGen. It is based on initial success in demonstrating a highly active PGM-free electro-catalyst in the acidic medium at ANL [1],[2],[3]. The new catalysts are composed of porous yet stable transition metal composite incorporated in a 3D nano-network electrode architecture with the potential to be inexpensive, highly active, and resistant to the oxidation corrosion during OER. The project goal is to produce one or more durable PGM-free OER catalysts with the performance approaching that of Ir-based catalysts but at <1/20 of the cost, demonstrated through the operating PEM electrolyzer.

APPROACH

This project focuses on the design and synthesis of a new class of PGM-free OER catalysts for PEM electrolyzers. The new catalysts consist of a highly porous, yet stable transition metal composite derived from the metal-organic-frameworks (MOFs). The new catalysts will be integrated into a porous nano-network electrode architecture to further improve the conductivity, mass transport, and durability against oxidative corrosion. The catalyst development was carried out at both ANL and SUNY-Buffalo. The activity and durability of the new catalysts are first evaluated by the rotating disk electrode (RDE) method in the acidic electrolyte. The catalysts that demonstrate promising performance will be integrated into the membrane electrode and tested under the operating PEM electrolyzer at Giner.

As a seedling project under HydroGEN Seedling, this project leverages the consortium expertise in catalyst development. The specific nodes include computational modeling, surface property characterization cluster tool, advanced electron microscopy, ex-situ electrocatalyst characterization, and scaling new PEM electrolysis electrode.

RESULTS

This project entered Phase 2 in FY 2019. ANL is to continue developing cobalt MOF-derived OER catalysts (ANL-A and ANL-B) and incorporate both catalysts into PNNE architecture via the electrospin method. Furthermore, second and third transition metal elements are incorporated into the catalyst during MOF synthesis to improve overall OER activity and durability. SUNY-Buffalo focused on OER catalysts derived from heat-treated zeolitic imidazolate frameworks (ZIFs) containing various combinations of Fe, Co, Mn, and Ni. The OER activities were measured by the catalyst coated rotating disk or carbon paper in the strong acidic media (pH = 1 or 2). Figure 1 shows the RDE test of several ANL-B catalysts incorporated with different transition metals in a stepwise approach. After the addition of the first transition metal, M₁, OER potential at the current density of 10 mA/cm² was clearly improved. Adding a second transition metal, M₂, further reduced the OER overpotential with the onset voltage approaching to that of Ir, revealing the function of M₂ in promoting water splitting catalysis.

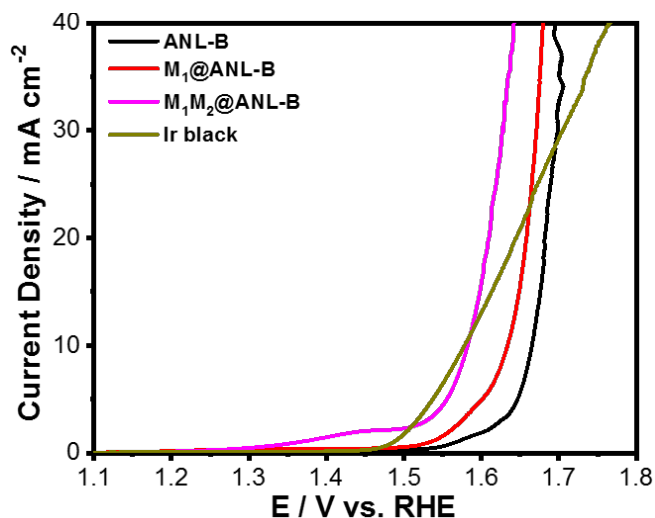


Figure 1. RDE investigation of a group of ANL-B catalyst with stepwise addition of 2nd and 3rd transition metal elements.

Parallel to catalyst development, the team also carried out a structural study using conventional and advanced characterization tools. Figure 2 (top row) shows the high-angle annular dark-field imaging (HAADF) of a scanning transmission electron microscopy (STEM) of an ANL catalyst. It shows that the catalyst nearly maintained the morphology of the original MOF with different elements evenly distributed throughout the catalyst. The addition of the second and third elements, however, could result in different distributions within the catalyst depending on their dimensions, as is shown by Figure 2 (bottom row). The element M_1 tends to stay on the catalytic particle surface, while M_2 embeds more uniformly throughout the crystallite. They each promote different catalytic functions during OER.

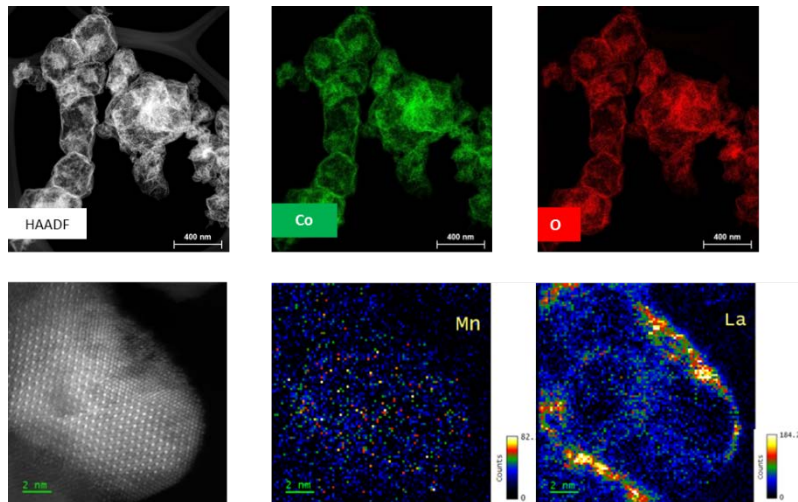


Figure 2. (Top row) HAADF images of a representative ANL catalyst. (Bottom row) OER catalyst particle, together with 2nd and 3rd transition metal distributions of a representative ANL-B catalyst.

Several ANL-A and ANL-B catalysts have been fabricated into the MEA's anode and evaluated in the operating PEMWE at Giner after several rounds of preparation optimization. New processing parameters were improved, tailoring different conductivity and morphology of the PGM-free OER catalyst, which is different from the conventional Ir based catalyst. Figure 3 shows the PEMWE current-voltage polarizations over two MEAs containing the same ANL-A catalyst at anode but after MEA process improvement from October 2018 to February 2019. The current density at 1.8 V was enhanced significantly from 250 mA/cm² to 320 mA/cm² when tested at 60°C in deionized water as the anode feed. The improved processing parameter also supported the preparation and testing of MEA containing ANL-B catalyst. Figure 4 shows multiple PEMWE

polarizations during an accelerated stress test (AST). The MEA in PEMWE cell was under voltage cycling from 1.4 V to 1.7 V up to 2000 cycles. Before the AST, the PEMWE cell current density reached 400 mA/cm² at 1.78 V, and cell voltage was 1.670 V at the current density of 200 mA/cm². After 2000 voltage cycles, the cell voltage was 1.695 V at the same current density, a merely 25 mV increase over that at the beginning of AST, exceeded go/no-go decision point of <100 mV increase after 100 cycles.

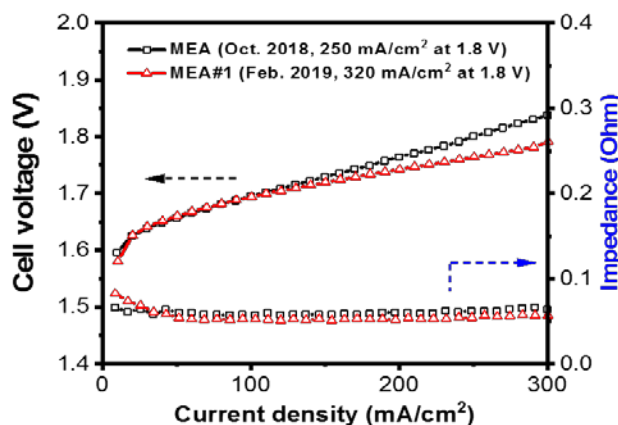


Figure 1. The improvement of current-voltage polarization of MEAs containing a representative anodic ANL-A catalyst in an operating PEMWE.

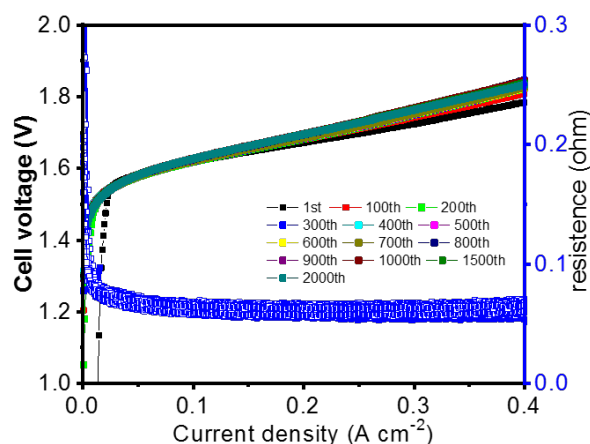


Figure 2. The current-voltage PEMWE polarization containing a representative anodic ANL-B catalyst during multiple voltage cycling AST.

CONCLUSIONS AND UPCOMING ACTIVITIES

ANL's PGM-free OER anodic catalyst delivered the state-of-the-art PEMWE current density at 60°C in DI water. Furthermore, it demonstrated a promising stability during voltage cycling AST. However, the PGM-free OER catalyst performance is still significantly lower than that of precious metal-based catalyst. There is clearly a need to continually improve the catalyst and MEA. The PGM-free OER catalyst requires different MEA processing conditions from that of PEM fuel cell due to difference of the catalyst (surface area, conductivity, operating environment, etc.), and therefore needs to be optimized accordingly. The stability under acidic operating condition remains to be the key challenge for PGM-free catalyst. In addition to catalyst/MEA development, improved fundamental understanding on OER process over PGM-free catalyst is critical to material development.

We will focus on the following area during the next phase project development:

- Further improve PGM-free catalyst activity and durability with more emphasis on the durability through catalyst surface protection enhancement
- Continue to optimize MEA composition and fabrication to maximize the PEMWE performance
- Address the catalyst durability at MEA level through new synthesis and processing
- Evaluate MEA under constant potential in the operating PEMWE
- Collaborate with HydroGen in fundamental understanding & catalyst characterization through modeling (LLNL/BNL), Imaging (SNL), Material characterization/MEA development (NREL).

SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED

1. “Nanofiber Electrocatalyst” Di-Jia Liu and Lina Chong, US patent application 20190060888

FY 2019 PUBLICATIONS/PRESENTATIONS

1. D.J. Liu, “PGM-free OER Catalysts for PEM Electrolyzer Application” Invited presentation at Electrochemical Society Spring Meeting, Dallas, TX, May 26–30, 2019
2. D.J. Liu, L. Chong, H. Wang, G. Wu, H. Xu, “PGM-free OER Catalysts for PEM Electrolyzer” 2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, April 30–May 1, 2019, Washington, D.C.
3. D.J. Liu, “Rational Design of PGM-free catalysts for ORR & 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 25–29, 2019

REFERENCES

1. D. Zhao, J.L. Shui, L.R. Grabstanowicz, C. Chen, S.M. Commet, T. Xu, J. Lu, D.J. Liu, “Highly Efficient Non-Precious Metal Electrocatalysts Prepared from One-Pot Synthesized Zeolitic Imidazolate Frameworks (ZIFs),” *Advanced Materials*, 26 (2014): 1093–1097
2. S. Ma, G. Goenaga, A. Call, D.J. Liu, “Cobalt Imidazolate Framework as Precursor for Oxygen Reduction Reaction Electrocatalyst,” *Chemistry: A European Journal*, 17 (2011): 2063–2067
3. J. Shui, C. Chen, L.R. Grabstanowicz, D. Zhao, D.J. Liu, “High-efficiency non-precious metal catalyst containing metal-organic framework precursor inside of carbon nano-network,” *Proceedings of National Academy of Sciences*, vol. 112, no. 34, (2015): 10629–10634