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

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Subcontractors:
- State University of New York at Buffalo, Buffalo, NY
- 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.
- Support the low-temperature water electrolyzer system cost reduction to meet the DOE hydrogen production target of \$2/kg H_2 while maintaining the system efficiency at 43 kWh/kg H_2.

Fiscal Year (FY) 2018 Objectives

- Design and test at least 10 PGM-free OER catalysts derived from transition metal metal-organic frameworks (MOFs).
- Design and test at least four PGM-free OER catalysts with porous nano-network electrode architecture.
- Prepare at least 10 membrane electrode assemblies (MEAs) containing PGM-free anode catalyst and evaluate them under PEM electrolyzer operating conditions.
- Demonstrate one or more PGM-free OER catalysts with potential of <15 mV higher than commercial Ir black measured at current density of 10 mA/cm^2 or MEA electrolyzer with current density >200 mA/cm^2 at 1.80 V.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- 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 capital cost barrier of PEM electrolyzer for broadly implemented distributed renewable energy application.

Technical Targets

This project aims to develop anodic PGM-free OER catalysts for PEM electrolyzers that meet the following DOE hydrogen production targets:

- Cost: \$2/kg H_2
- System efficiency: 43 kWh/kg H_2.

FY 2018 Accomplishments

- Argonne National Laboratory (ANL) developed two series of MOF-derived PGM-free OER catalysts, ANL-Cat-A and ANL-Cat-B; both demonstrated less than 15 mV difference from Ir black (at 0.1 mg/cm^2 loading) when tested in acidic electrolyte.
- The University at Buffalo developed several OER catalysts derived from Fe, Co, Mn, and Ni

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

doped ZIF-8 and demonstrated improved performance.

- ANL-Cat-A and -Cat-B showed only minor activity loss (24 mV and 22 mV at 10 mA/cm^2) after 10,000 voltage cycles from 1.2 to 2.0 V by rotating disk electrode (RDE) in strong acidic electrolyte. Both catalysts showed better catalyst stability than low-loading Ir black (at 0.1 mg/cm^2 loading) tested under the same cycling condition.
- Both ANL-Cat-A and -Cat-B were incorporated into the anode of a PEM electrolyzer and achieved 250 mA/cm^2 and 300 mA/cm^2 at 1.8 V under the operating condition at Giner, respectively, meeting go/no-go decision criteria.

INTRODUCTION

This project aims to develop next-generation, high-efficiency, and durable PGM-free OER catalysts for the PEM electrolyzer through the collaboration between ANL, University at Buffalo, and Giner, Inc. (Giner) leveraging the multiple capability nodes at the HydroGEN consortium. It is based on an initial success in demonstrating highly active PGM-free electrocatalyst in an acidic medium at Argonne National Laboratory [1–3]. The new catalysts are composed of porous yet stable transition-metal composite incorporated in a 3-D nano-network electrode architecture with 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 current Ir-based catalysts at <1/20 of the cost, demonstrated through the operating PEM electrolyzer.

APPROACH

This project focuses on design and synthesis of a new class of PGM-free OER catalyst for PEM electrolyzers. The new catalysts consist of highly porous yet stable transition-metal composite derived from the MOFs. The new catalysts will also be integrated into a porous nano-network electrode architecture to further improve the conductivity, mass transport, and durability against oxidative corrosion (Figure 1). The catalyst development was carried out at both ANL and University at Buffalo. The activity and durability of the new catalysts are first evaluated by the RDE method in the acidic electrolyte. The catalysts that demonstrate promising performance will then be integrated into the membrane electrode and tested under the operating PEM electrolyzer at Giner.

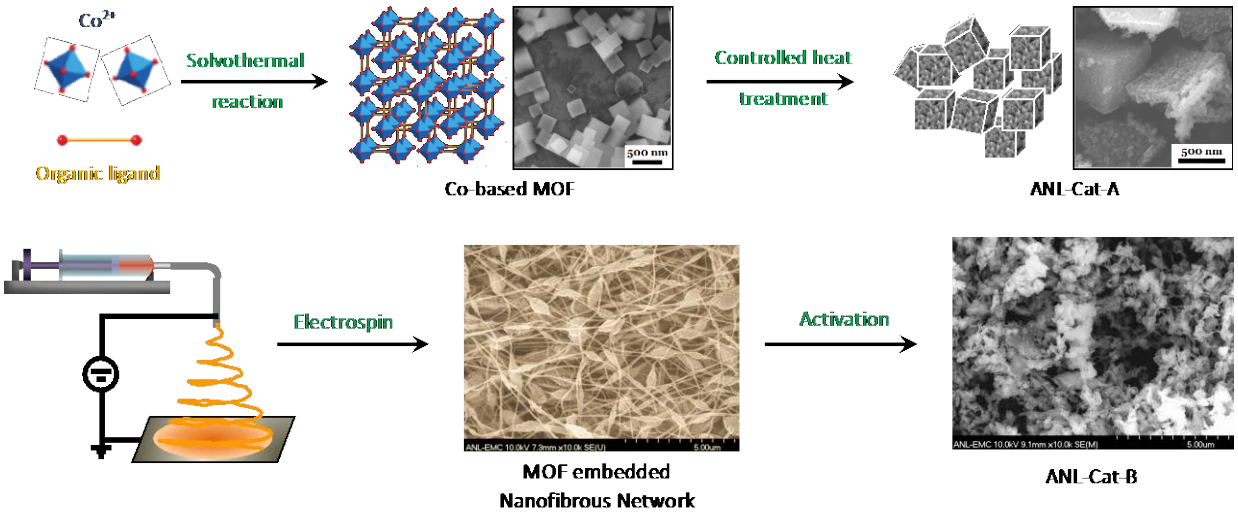

Figure 1. Synthesis scheme of ANL-Cat-A OER catalyst and ANL-Cat-B OER catalyst

As a seedling project under HydroGEN, this project leverages the expertise in the consortium in supporting the catalyst development. The specific nodes include Lawrence Berkeley National Laboratory's (LBNL's) "DFT and Ab Initio Calculations for Water Splitting Including Real-Time Time-Dependent Density Functional Theory," Lawrence Livermore National Laboratory's (LLNL's) "Multiscale Modeling of Water-Splitting Devices," National Renewable Energy Laboratory's (NREL's) "Surface Analysis Cluster Tool," Sandia National Laboratories' (SNL's) "Advanced Electron Microscopy," and NREL's "Electrolysis Catalyst Synthesis, Ex Situ Characterization, and Standardization."

RESULTS

This seedling project started in FY 2018. The tasks at ANL focused on developing cobalt-based OER catalysts derived from MOFs through facile solvothermal or solid-state syntheses. Two catalyst series—ANL-Cat-A and ANL-Cat-B—were developed and investigated in parallel using MOFs as sacrificial precursors through thermal activation. Meanwhile, the University at Buffalo team focused on OER catalysts derived from zeolitic

imidazolate frameworks (ZIFs) containing various combination of Fe, Co, Mn, and Ni after heat treatment. The OER catalyst activities were measured by the catalytic layer coated over rotating disk or carbon paper in strongly acidic media. Figure 2A shows the OER current density as the function of the polarization potential of a representative ANL-Cat-A with the catalyst loading of 2 mg/cm^2. For comparison, the same polarization was performed over Ir-black catalyst at the loading of 0.2 mg/cm^2. The OER potential measured at current density of 10 mA/cm^2 typically served as the gauge of activity. In this case, ANL-Cat-A achieved an OER potential of 1.584 V vs. reversible hydrogen electrode (RHE), which is only 29 mV higher than that of the Ir black benchmark.

The catalyst durability was measured through the multiple potential cycling from the voltage of 1.2 V to 2.0 V (vs. RHE) in the acidic electrolyte. Figure 2B shows the percentage of current density retention measured against the initial value at 1.8 V and 2.0 V during 2,000 voltage cycles. For ANL-Cat-A catalyst, the current density retentions of 90% and 80% were achieved at 1.8 V and 2.0 V, respectively. In contrast, the percentage of the current density retention for Ir black was dramatically decreased to 10% after only 1,000 voltage cycles. Both ANL catalysts demonstrated excellent activity and durability over most of the PGM-free catalysts in acidic medium reported in the literature so far.

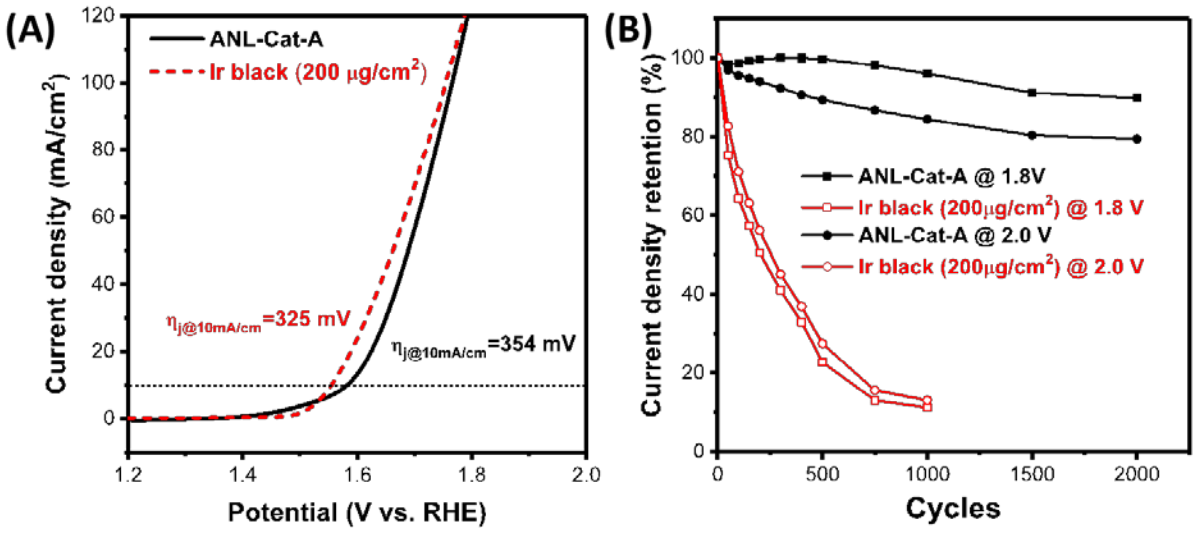

Figure 2. (A) OER current density as the function of polarization voltage measured over ANL-Cat-A catalyst and Ir black in 0.5 M H_2SO_4 electrolyte solution. (B) The retention of OER current densities measured at 1.8 V and 2.0 V for ANL-Cat-A catalyst and benchmark Ir black during 2,000 voltage cycles from 1.2 V to 2.0 V.

Several catalysts from the ANL-Cat-A and -Cat-B series were selected for evaluation in the operating PEM electrolyzer at Giner. A significant amount of effort was first devoted to the MEA optimization at ANL due to the limited knowledge in integrating the catalysts of different conductivity and morphology than the conventional electrocatalyst. Important processing parameters, such as anode catalyst loading, ionomer-to-catalyst ratio, pretreatment, and application methods, have been systematically studied. Fifteen MEAs with ANL's PGM-free OER catalysts were sent to Giner and evaluated under PEM electrolyzer operating conditions (60°C and ambient pressure). Several MEAs demonstrated OER current density >200 mA/cm^2 at 1.8 V. Figure 3 shows the current-voltage polarization curve of a representative MEA with anode containing ANL-Cat-B catalyst. The current density reached 300 mA/cm^2 at 1.8 V, exceeding the DOE Phase I go/no-go decision criteria.

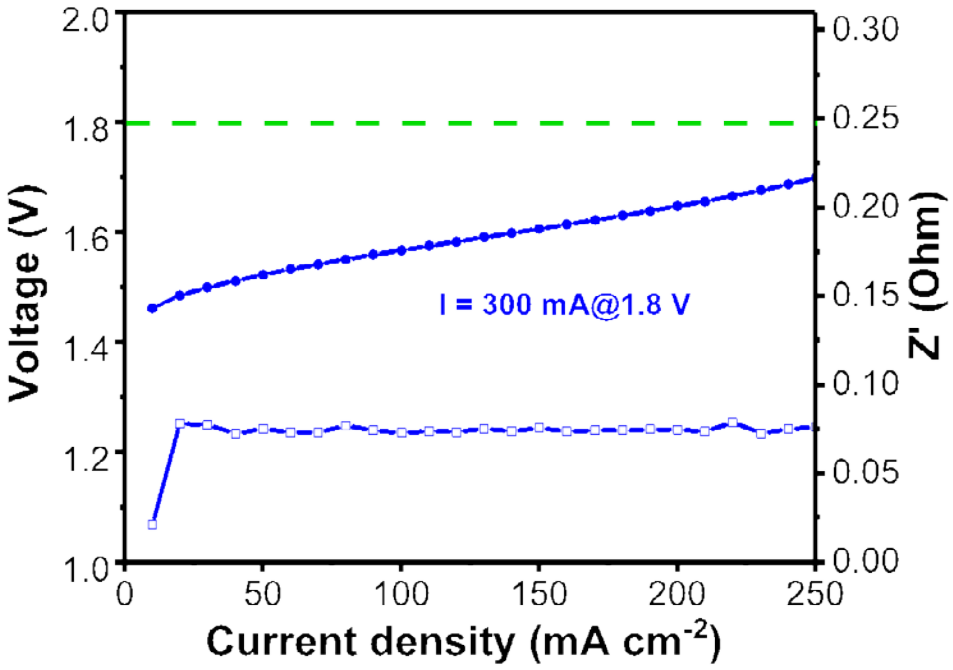

Figure 3. The current-voltage polarization of an MEA containing a representative ANL-Cat-B catalyst at anode in a PEM electrolyzer

CONCLUSIONS AND UPCOMING ACTIVITIES

ANL's PGM-free OER catalyst delivered promising performance in a PEM electrolyzer for the first time. The study clearly indicates the need to continually improve catalyst and MEA in order to compete with Ir catalyst. A PGM-free OER catalyst requires different MEA processing conditions than that in a PEM fuel cell due to the different nature of the catalyst (surface area, conductivity, operating environment, etc.) and therefore needs to be optimized accordingly. Similar to the oxygen reduction reaction catalyst, the PGM-free OER catalyst also faces stability challenges although the deactivation mechanisms are unlikely to be the same.

The project now moves to Phase II with the following research focuses:

- Improvement of OER activity through catalyst design and refinement by reprioritizing the synthesis approach and formulation, with more focus on durability and conductivity.
- MEA fabrication and testing through optimizing catalyst loading, ionomer-to-catalyst ratio, and application techniques.
- Exploration of new synthesis techniques and catalyst material with higher stability and acid resistance.
- Collaboration with HydroGEN in fundamental understanding and catalyst characterization through modeling (LLNL/Brookhaven National Laboratory), imaging (SNL), and material characterization and MEA development (NREL).

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. "Nanofiber Electrocatalyst," Di-Jia Liu and Lina Chong, U.S. patent application filed in 2018.
2. "Prussian Blue Analogue-Derived Catalysts for PEM Electrolyzer," Di-Jia Liu and Hao Wang, U.S. patent application filed in 2018.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Di-Jia Liu, Lina Chong, Hao Wang, Gang Wu, and Hui Xu, "PGM-free OER Catalysts for PEM Electrolyzer," Poster presentation at the 2018 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, June 13-15, 2018, Washington, D.C.

REFERENCES

1. 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.
2. 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.
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.