
HydroGEN Seedling: High-Performance Ultralow-Cost Non-Precious-Metal Catalyst System for Anion Exchange Membrane Electrolyzer

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Subcontractor:
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Project Start Date: October 1, 2017
Project End Date: Project continuation and
direction determined annually by DOE

Overall Objectives

- Develop low-cost, active, and durable platinum-group-metal-free (PGM-free) oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) catalysts to achieve high performance in a pure water-feeding anion exchange membrane (AEM) water electrolyzer.
- Demonstrate AEM electrolyzer performance of 500 mA/cm² at 2.1 V with unlimited anode or cathode.
- Produce 25 g batch of the best-performing PGM-free catalyst.

Fiscal Year (FY) 2018 Objectives

- Demonstrate OER activity of 5.1 mA/cm² at 1.65 V_{RHE} and the same degradation rate as that of IrO₂ with 5,000 cycles durability test in the potential range of 0.6 and 2.1 V_{RHE} in rotating disk electrode (RDE) measurements.
- Demonstrate HER activity of 34 mA/cm² at a 200 mV overpotential and a durability of less than 20% current density loss at a 200 mV

overpotential with 5,000 cycles in the potential range of 0.2 and -0.25 V_{RHE} in RDE measurements.

Technical Barriers

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

- Capital Cost: develop lower-cost materials with improved efficiency and durability.

Technical Targets

This project is conducting PGM-free OER and HER catalyst development in conjunction with fundamental studies of phenomena occurring at the interface of PGM-free catalyst and ionomer. The results gained from these studies will be applied toward the design and synthesis of PGM-free catalysts that meet the DOE hydrogen production cost target:

- Cost: <\$2/kg of H₂.

FY 2018 Accomplishments

- Carbon-free perovskite oxide OER catalysts demonstrated 87% improved current density of 5.6 mA/cm² in 0.1 M KOH and 177% improved current density of 8.3 mA/cm² in 0.1 M benzyltrimethylammonium hydroxide (BTMAOH) at 1.65 V_{RHE} compared to the initial state-of-the-art (SOA) current density of 3.0 mA/cm² at 1.65 V_{RHE} in 0.1 M KOH. Cyclic and constant voltage durability tests of the carbon-free perovskite oxide catalyst exhibited comparable durability to that of IrO₂ in RDE tests.
- In pure-water-feeding AEM electrolyzer tests, carbon-free perovskite oxide OER catalysts demonstrated better performance and durability than IrO₂.

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

- $\text{Ni}_{0.95}\text{La}_{0.05}$ HER catalyst demonstrated 110% improved current density of 42 mA/cm^2 at a 200 mV overpotential in 1.0 M NaOH compared to the initial SOA current density of 20 mA/cm^2 at a 200 mV overpotential with 19% current density loss at a 200 mV overpotential in cyclic durability tests.

INTRODUCTION

Precious-metal catalysts (i.e., platinum for cathode and iridium oxide for anode) are SOA catalysts for acidic polymer electrolyte membrane (PEM) electrolyzers and contribute in a major way to the cost of the PEM electrolyzers. Alternatively, alkaline AEM electrolyzers can take advantage of utilizing low-cost PGM-free catalysts for both anode and cathode. In preliminary experiments we have developed PGM-free OER and HER catalysts exhibiting promising performance in terms of activity and durability in an electrochemical cell. We will further develop these OER and HER catalysts for AEM electrolyzer applications. If successful, this project will overcome the cost barrier of hydrogen production technology associated with electrocatalysts, required to meet the DOE-established hydrogen production target of $< \$2/\text{kg H}_2$.

APPROACH

The chosen OER catalysts are perovskite oxides for the anode and bimetallic NiLa HER catalysts for the cathode. Specifically $(\text{La}_{0.85}\text{Sr}_{0.15})\text{CoO}_{3-\delta}$ (i.e., a perovskite with higher lanthanide and lower alkaline earth metal contents) was chosen to control the valence state of the transition metals. Bimetallic NiLa and Ni(Zn)La will be synthesized via spray pyrolysis as alternatives to Pt catalysts for the AEM electrolyzer cathode. The primary responsibilities of Pajarito Powder, LLC, the partner in this project, are to make 25-cm² membrane electrode assemblies (MEA), test the electrolyzer performance, and ultimately produce a 25-g batch of the best-performing PGM-free OER and/or HER catalysts. Four nodes are involved in this project: (1) “Separator for Hydrogen Production” (Cy Fujimoto, Sandia National Laboratories) for AEM synthesis; (2) “Hydrogen in situ Testing Capabilities for Hydrogen Generation” (Guido Bender, National Renewable Energy Laboratory) for AEM electrolysis testing; (3) “Surface Analysis Cluster Tool” (Glenn Teeter, National Renewable Energy Laboratory) for composition analyses; and (4) “Density Functional Theory and Ab initio Calculations” (Lin-Wang Wang, Lawrence Berkeley National Laboratory) for theoretical understanding of electrochemical reactions.

RESULTS

Figure 1a shows the RDE HER activity of $\text{Ni}_{0.95}\text{La}_{0.05}$ catalyst. The initial current density measured at a 200 mV overpotential is 42 mA/cm². This exceeds the go/no-go decision current density of 34 mA/cm² by 8 mA/cm². The RDE 5,000 cyclic durability test was performed with a triangle sweep cycling with a sweep rate of 200 mV/s between 0.2 V and $-0.25 V_{\text{RHE}}$. The current density measured at a 200 mV overpotential after the cyclic durability test is 34 mA/cm² (i.e., the loss in current density is 19%). This loss meets the go/no-go decision criterion loss of less than 20% current density. Figure 1b is scanning electron microscopy (SEM) images of the $\text{Ni}_{0.95}\text{La}_{0.05}$ catalysts before and after the cyclic durability test. No noticeable particle growing is observed, attesting stability of the catalyst.

The current densities of carbon-free perovskite oxide-F and -G in 0.1 M KOH, the most active two catalysts among the seven developed catalysts, are 5.2 mA/cm² and 5.6 mA/cm² at 1.65 V_{RHE} , respectively (Figure 2a). Both these current densities exceed the go/no-go decision current density of 5.1 mA/cm². The RDE 1,000 cyclic durability result (the 5,000 cyclic durability test cannot be done due to catalyst detachment from the RDE electrode) with perovskite oxide-F demonstrates nearly the same durability as that of IrO_2 (Figure 2b), thus the durability target of the go/no-go decision has also been met. Figure 2b is a comparison of OER activity of perovskite oxide-F in 0.1 M KOH and 0.1 M BTMAOH. Higher OER activity is obtained in 0.1 M BTMAOH than in 0.1 M KOH. Figure 2c is a pure-water-feeding (no added electrolyte) electrolyzer test result with IrO_2 and perovskite oxide-F and -G. Perovskite oxide-F and -G demonstrate higher OER activity (higher current densities at lower voltage) and better durability (lower voltage increase during the test) compared to IrO_2 . OER activities of IrO_2 , perovskite oxide-F, and perovskite oxide-G in 0.1 M KOH are almost the same when gauged by the current density at 1.65 V_{RHE} (Figure 2a). However, in pure-water-feeding AEM electrolyzer measurements (Figure 2c), perovskite oxide-F and -G demonstrated higher OER activity than IrO_2 . This indicates that OER activity measured in 0.1 M KOH does not properly reveal the OER activity in the water electrolysis test.

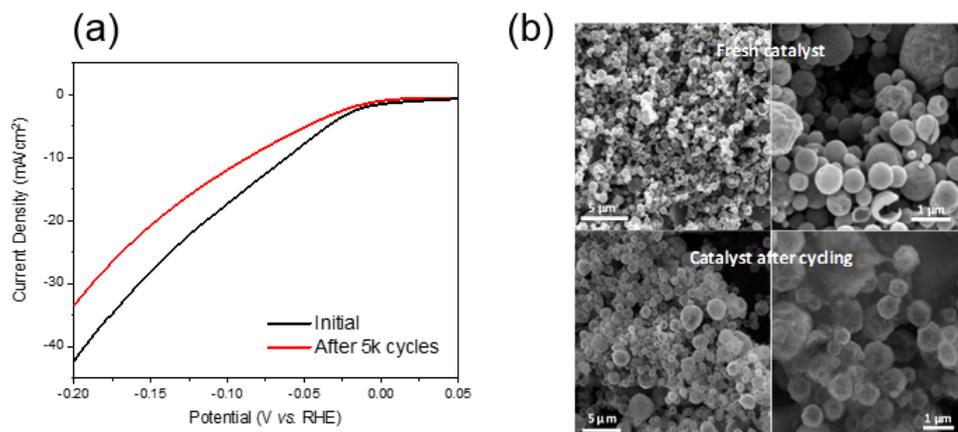


Figure 1. (a) Linear scan voltammetry plots of $\text{Ni}_{0.95}\text{La}_{0.05}$ HER catalyst. Electrolyte: N_2 -saturated 1.0 M NaOH; cell temperature: 60°C ; 1,600 rpm; scan rate: 2 mV/s. **(b)** SEM images of $\text{Ni}_{0.95}\text{La}_{0.05}$ HER catalysts before and after cyclic durability tests.

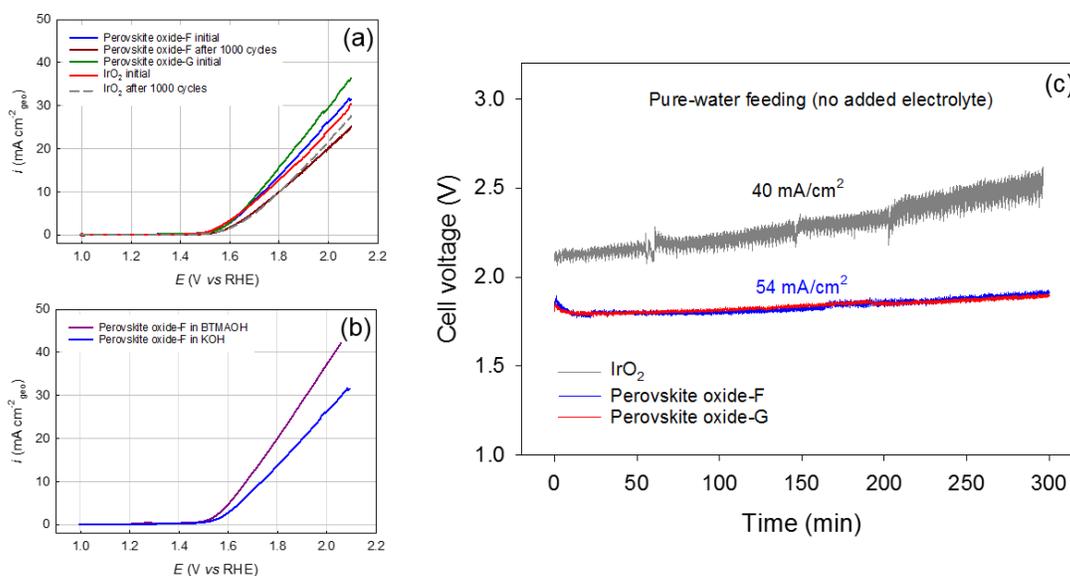


Figure 2. (a) RDE OER activities of IrO_2 , perovskite oxide-F, and perovskite oxide-G. Electrolyte: N_2 -saturated 0.1 M KOH; cell temperature: 25°C ; 1,600 rpm; scan rate: 10 mV/s. **(b)** RDE OER activity of perovskite oxide-F in 0.1 M KOH and BTMAOH. N_2 -saturated electrolytes; cell temperature: 25°C ; 1,600 rpm; scan rate: 10 mV/s. **(c)** 5- cm^2 electrode area MEA electrolysis test under water-feeding (no added electrolyte) condition: cell temperature 60°C ; anode catalysts: $\sim 1.0 \text{ mg}/\text{cm}^2$ for IrO_2 and perovskite oxide-F and -G; cathode: $0.35 \text{ mg}_{\text{Pt}}/\text{cm}^2 \text{ Pt}/\text{C}$.

We tested the effect of electrolyte on RDE OER activity measurements. Besides the commonly used inorganic KOH electrolyte, we also chose the organic BTMAOH electrolyte. The ammonium group in BTMA^+ is a typical functional group in AEMs and a phenyl group also is usually found in the backbone of AEMs, thus BTMAOH electrolyte contains the elements constituting the AEMs. Figure 3a shows the structure of AEM used in our AEM electrolysis tests. As shown, both an ammonium group and phenyl group exist in this AEM. Comparing the electrochemical cell OER activities measured in 0.1 M KOH (Figure 3b) and 0.1 M BTMAOH (Figure 3c) with the pure-water electrolysis results (Figure 3d), the electrochemical cell result obtained with

0.1 M BTMAOH more closely reflects the water electrolysis result. This tells us that BTMAOH solution is a more appropriate electrolyte than the KOH to gauge the activity in AEM water electrolysis.

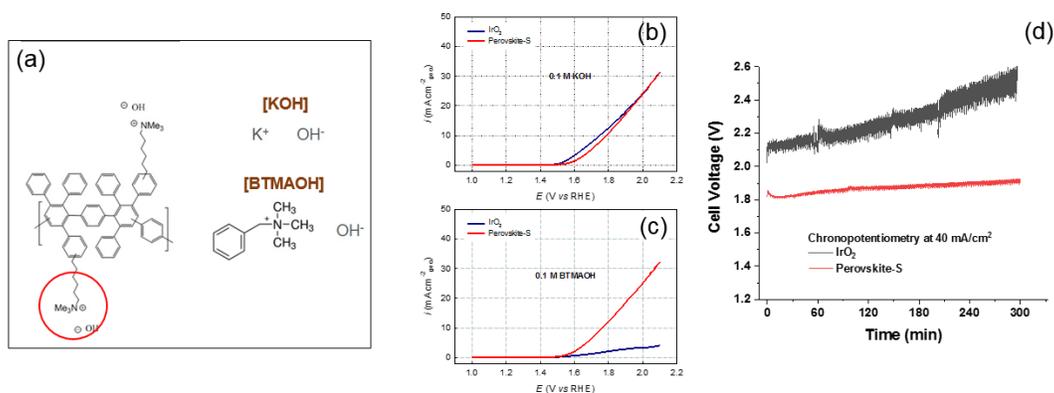


Figure 3. (a) Structures of poly(phenylene)-based anion exchange membrane with fully alkylated ammonium group cation and BTMAOH; RDE OER activity of IrO₂ and perovskite-S in (b) 0.1 M KOH and (c) 0.1 M BTMAOH. N₂-saturated 0.1 M KOH; cell temperature: 25 °C; 1,600 rpm; scan rate: 10 mV/s. (d) 5-cm² electrode area MEA electrolysis test under water-feeding (no added electrolyte) condition: cell temperature 60 °C; anode catalysts: ~1.0 mg/cm² both for IrO₂ and perovskite-S; cathode: 0.35 mg_{Pt}/cm² Pt/C.

CONCLUSIONS AND UPCOMING ACTIVITIES

We have successfully developed PGM-free OER and HER catalysts that exceeds the first year's go/no-go decision performance. In particular, carbon-free perovskite oxide OER catalysts demonstrated better activity and durability in a pure-water-feeding AEM electrolyzer test than IrO₂. In addition, BTMAOH solution is found as a more appropriate electrolyte than KOH solution in gauging AEM water electrolysis activity. Understanding the interfacial phenomena that occur at the catalyst-membrane-electrolyte in conjunction with analysis tools such as X-ray absorption spectroscopy is crucial for further improving the activity and durability of PGM-free OER and HER catalysts. Based on these findings, advanced PGM-free OER and HER catalysts will be developed in the next year. Four nodes have contributed to achieving the progress in this year; in particular, the AEM supply from Sandia National Laboratories is crucial in AEM electrolysis tests.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Hoon T. Chung, "High-Performance Ultralow-Cost Non-Precious Metal Catalyst System for AEM Electrolyzer," Poster presentation at the DOE Hydrogen and Fuel Cell Program Annual Merit Review, Washington, D.C., June 2018.
2. Hoon T. Chung et al., "Carbon-free Perovskite Oxide OER Catalysts for AEM Electrolyzer," 233rd ECS Meeting, Seattle, WA, May 2018.