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

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Project End Date: September 30, 2020

## Overall Objectives

- Develop low-cost, active, and durable platinum-group-metal-free (PGM-free) hydrogen evolution reaction (HER) and PGM- and carbon-free oxygen evolution reaction (OER) catalysts for pure water (no added electrolytes) anion exchange membrane (AEM) electrolyzers.
- Develop HER and OER catalysts based on (Ni, La) alloys and (La, Sr)CoO<sub>3</sub> perovskites.
- Scale-up synthesis of Los Alamos National Laboratory (LANL) developed catalysts by Pajarito Powder, LLC.

## Fiscal Year (FY) 2019 Objectives

- Demonstrate current density of 100 mA/cm<sup>2</sup> at 1.8 V in pure water feed AEM electrolyzer
- Demonstrate 100-hour durability with the same degradation rate as PGM-catalysts at 100 mA/cm<sup>2</sup> (at 1.8V) in pure water feed AEM electrolyzer.

## Technical Barriers

### INTRODUCTION

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<sup>1</sup>:

- Reduce the cost of hydrogen production.

## Technical Targets

This project is conducting fundamental studies of (Ni, La) alloy HER and (La, Sr)CoO<sub>3</sub> perovskite OER catalysts for AEM electrolyzers. Insights gained from these studies will be applied toward the hydrogen production from water electrolysis to meet the following DOE hydrogen production target.

- Cost: <\$2/kg of H<sub>2</sub>.

## FY 2019 Accomplishments

- Demonstrated no performance loss during 100 h durability test at a current density of 100 mA/cm<sup>2</sup> in pure water feed AEM with (La, Sr)CoO<sub>3</sub> perovskite catalyst.
- Achieved five times improvement in current density at 1.8 V since 2018 (243 mA/cm<sup>2</sup> vs 48 mA/cm<sup>2</sup>).
- Demonstrated that AEM ionomer greatly suppresses the OER activity of perovskite (La, Sr)TiO<sub>3</sub> catalyst.
- Discovered that phenyl oxidation on the anode is proportional to the phenyl adsorption onto the catalysts and causes AEM electrolyzer performance degradation during operation.
- Discovered that perovskite (La, Sr)CoO<sub>3</sub> exhibits negligible phenyl adsorption and accordingly marginal phenyl oxidation.

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

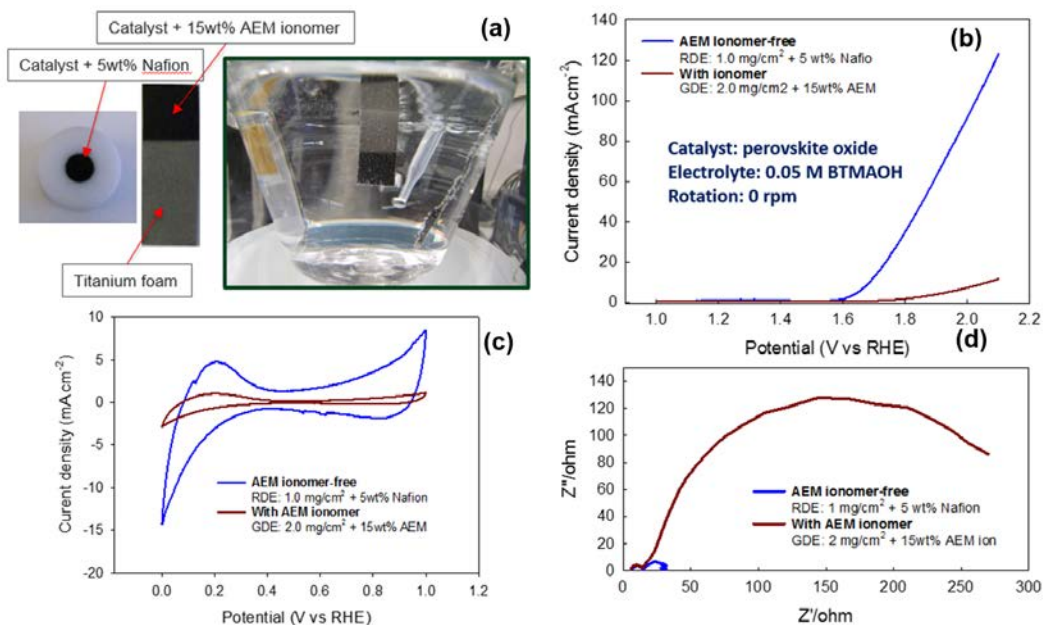
Hydrogen is an energy carrier that can deliver or store a tremendous amount of energy and produce electricity, heat, and water when consumed in fuel cells. Electrolyzers produce hydrogen by splitting water into oxygen and hydrogen using electricity. Currently, alkaline solution electrolysis and proton exchange membrane (PEM) electrolysis are commercialized water electrolysis technologies. Alkaline solution electrolysis operates in highly corrosive concentrated 30–40 wt % potassium hydroxide (KOH) solution, and its purity of hydrogen is relatively low, and its massive hydrogen production is limited by low current density ( $\sim 0.4 \text{ A/cm}^2$ ). Alkaline solution electrolysis has the advantage of utilizing PGM-free catalysts for the anode and cathode. PEM electrolysis can produce high purity hydrogen through pure water splitting, and high current density ( $>2 \text{ A/cm}^2$ ) hydrogen can be generated by PEM electrolysis. This allows efficient hydrogen generation even with a small system size. However, PEM electrolysis requires a high loading of PGM catalysts and expensive titanium bipolar assembly, which leads to an increase in hydrogen production cost. Compared to these technologies, AEM water electrolysis is a new technology and possesses combined advantages of both alkaline solution and PEM electrolysis systems. The working mechanism of AEM electrolysis is similar to PEM electrolysis, as both of them use ion-conducting membranes as electrolytes. But hydrogen production cost can be significantly reduced with AEM electrolysis, as the expensive PGM catalysts and titanium bipolar assembly can be replaced by PGM-free catalysts and inexpensive bipolar assembly. In spite of such advantages, performance and durability of AEM water electrolysis is still inferior to those of PEM electrolysis. To make AEM electrolysis viable, advancement in AEM electrolysis technology is needed.

## APPROACH

The main goal of the proposed work is to develop an entirely precious-metal-free complete catalyst system for the AEM electrolyzers. At the anode, perovskite-oxide ( $\text{La}_{1-x}\text{Sr}_x$ ) $\text{CoO}_{3-\delta}$  catalysts for the OER will be developed. At the cathode, bimetallic La-doped Ni alloy will be developed for the HER. In addition to assuring very high performance, which will approach that of precious metal catalysts, this proposed complete catalyst system promises to be ultralow cost, required to meet the DOE-established hydrogen production target of  $< \$2/\text{kg}$  of  $\text{H}_2$ . Precious metal catalysts contribute in a major way to the cost of the PEM electrolyzer. Alternatively, AEM electrolyzers can take advantage of using low-cost PGM-free catalysts for both anode and cathode reactions. In addition, the cost, activity, and durability of PGM-free OER and HER catalysts are crucial factors for the performance of AEM electrolyzers. In this project, we are developing the PGM-free catalysts that exhibit higher activity and durability than those of PGM-catalysts. Besides the development of catalysts, diverse HydroGEN nodes are being used in this project to confirm AEM electrolyzer performance and to study catalyst-ionomer interaction: (i) AEM membranes and ionomers from Sandia National Laboratory (SNL); (ii) AEM electrolyzer performance test from National Renewable Energy Laboratory (NREL); (iii) catalyst-ionomer interaction studies with ambient pressure x-ray absorption spectroscopy from SNL and with in situ x-ray absorption spectroscopy from Lawrence Berkeley National Laboratory (LBNL). If successful, this project will overcome the durability, performance, and cost barriers of AEM electrolyzer technology associated with electrocatalysts.

## RESULTS

Understanding how catalysts work in the AEM electrolyzer is critical to catalyst development. To this end, we fabricated the titanium foam gas diffusion electrode (GDE), on which perovskite OER catalyst was deposited with 15 wt % AEM ionomer, with which we can figure out the effect of AEM ionomer on the catalyst (**Figure 1(a)**). As a comparison, the catalyst was also deposited onto a rotating disk electrode (RDE), on which the perovskite OER catalyst was deposited with just 5 wt % of Nafion® ionomer that is working just like a binder (**Figure 1(a)**). This will show the AEM ionomer-free catalyst performance. There is a stark difference in the performance of GDE and RDE (**Figure 1(b)**). The OER activity measured with the titanium GDE is much lower than with the RDE, even though two times higher catalyst loading was deposited onto the GDE. This clearly indicates that the AEM ionomer depresses the catalyst activity significantly. Cyclic voltammetry shows significantly reduced electrochemically accessible active area (**Figure 1(c)**), and the mass transfer resistance is also greatly increased with the addition of AEM ionomer (**Figure 1(d)**). To improve the performance of the AEM electrolyzer, it is very important to understand the activity and durability of the catalysts as well as the catalyst/ionomer interaction that causes catalyst performance loss.



**Figure 1.** (a) Comparison of RDE and GDE electrode; (b) Linear scan voltammetry (LSV) of perovskite (La, Sr)TiO<sub>3</sub> OER; (c) Cyclic voltammetry of (La, Sr)TiO<sub>3</sub> OER catalyst; (d) Electrochemical impedance spectroscopy of (La, Sr)TiO<sub>3</sub> OER catalyst.

The catalyst/ionomer interaction was studied by using the benzyl trimethyl ammonium hydroxide (BTMAOH) as an electrolyte. The BTMAOH is composed of benzyl and ammonium cation. Both of these chemicals are also key elements in constituting the AEM membrane and ionomer. Thus, we can get some idea about catalyst/ionomer interaction using the BTMAOH as an electrolyte rather than using the commonly used KOH or NaOH electrolyte. Chronoamperometry tests were performed with four different catalysts at 1.6 V in the 0.1 M BTMAOH electrolyte to measure the performance (**Figure 2(a)**). Two commercial IrO<sub>2</sub> catalysts, IrO<sub>2</sub>-A and IrO<sub>2</sub>-S, were tested. The IrO<sub>2</sub>-A shows much higher activity than the IrO<sub>2</sub>-S, due to difference in size and in exposed facets [1]. In the AEM electrolyzer tests, we used the highly active IrO<sub>2</sub>-A as a reference catalyst. Pt/C catalyst was also chosen to understand the benzyl oxidation more deeply with diverse catalysts. Perovskite oxide (La, Sr)TiO<sub>3</sub> was compared with these PGM-catalysts. The catalytic activity of perovskite is next to that of the IrO<sub>2</sub>-A catalyst, and Pt/C shows the lowest OER activity. Phenyl oxidation was measured with these four catalysts. The order of phenyl oxidation is Pt/C to IrO<sub>2</sub> to perovskite oxide (**Figure 2(b)**). The adsorption energy of phenyl onto the catalysts was calculated with density functional theory (DFT) (**Figure 2(c)**). The adsorption energy of phenyl onto the catalysts exactly follows the order of the phenyl oxidation, i.e., Pt/C to IrO<sub>2</sub> to perovskite oxide, indicating that the degree of phenyl oxidation is proportional to the extent of phenyl adsorbed onto the catalysts. To achieve the durable AEM electrolyzer performance, catalysts immune to the phenyl adsorption are to be developed. Phenyl oxidation at the benzene ring of the ionomers converts the phenyl into acidic phenol. This acidic phenol decreases the pH in the vicinity of the catalyst and ionomer, and in turn, decreases the OER activity of the catalyst in AEM electrolyzers (**Figure 2(d)**).

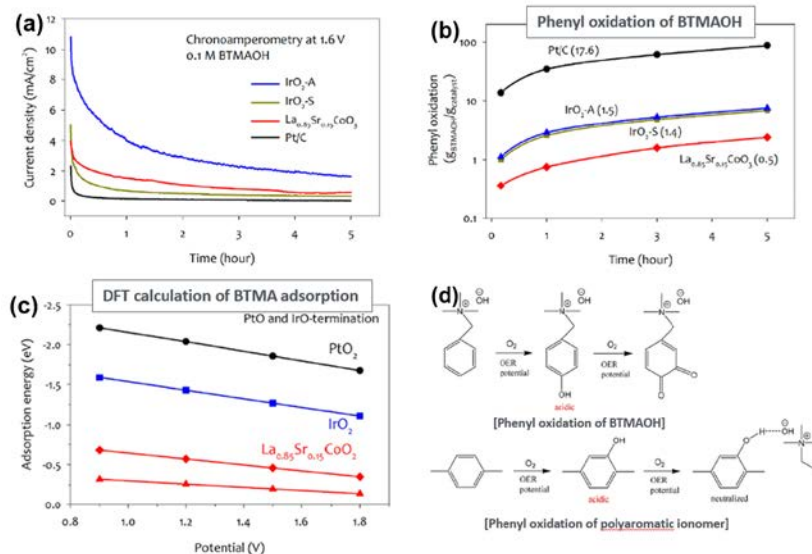


Figure 2. (a) Chronoamperometry of IrO<sub>2</sub>-A, IrO<sub>2</sub>-S, (La, Sr)TiO<sub>3</sub>, Pt/C at 1.6 V. (b) DFT calculation of BTMA adsorption on IrO<sub>2</sub>-A, IrO<sub>2</sub>-S, (La, Sr)TiO<sub>3</sub>, Pt/C; (c) Measured phenyl oxidation of BTMAOH at 1.6 V with IrO<sub>2</sub>-A, IrO<sub>2</sub>-S, (La, Sr)TiO<sub>3</sub>, Pt/C catalysts; (d) Phenyl oxidation process during chronoamperometry. LSV of Li<sub>0.95</sub>La<sub>0.05</sub> HER catalyst. Electrolyte: N<sub>2</sub>-saturated 1.0 M KOH; Cell temperature: 60 °C; scan rate: 2 mV/s. (b) SEM images of Li<sub>0.95</sub>La<sub>0.05</sub> HER catalysts before and after durability test.

The AEM electrolyzer durability tests were performed with IrO<sub>2</sub>-A and perovskite (La,Sr)CoO<sub>3</sub> at 60°C for 100 hours in pure water feed condition (**Figure 3(a)**). The constant current density of 100 mA/cm<sup>2</sup> was applied, and voltage was measured to estimate the durability. In this test, the higher voltage indicates the lower activity. The perovskite OER catalysts show nearly no voltage change, which indicates very good durability, while the IrO<sub>2</sub>-A shows a lower voltage at the beginning, which indicates the higher activity than the perovskite (La,Sr)CoO<sub>3</sub>. However, the voltage increases very rapidly within 1 hour and shows a much higher voltage than the perovskite (La,Sr)CoO<sub>3</sub>. This clearly indicates that perovskite (La,Sr)CoO<sub>3</sub> exhibits a much higher durability than IrO<sub>2</sub>-A. The polarization plots were measured before and after the durability test. As shown in **Figure 3(b)**, there is no performance degradation with the perovskite (La,Sr)CoO<sub>3</sub>, but IrO<sub>2</sub>-A shows huge degradation, as shown in **Figure 3(c)**. These results attest that phenyl oxidation shown in Figure 2 is a critical factor in determining the AEM electrolyzer durability. With the optimization of the catalyst/ionomer ratio and gas diffusion layer, we can also largely improve the performance. Figure 4 demonstrates that a 500% improvement in current density at 1.8 V in pure water feed condition has been achieved since 2018.

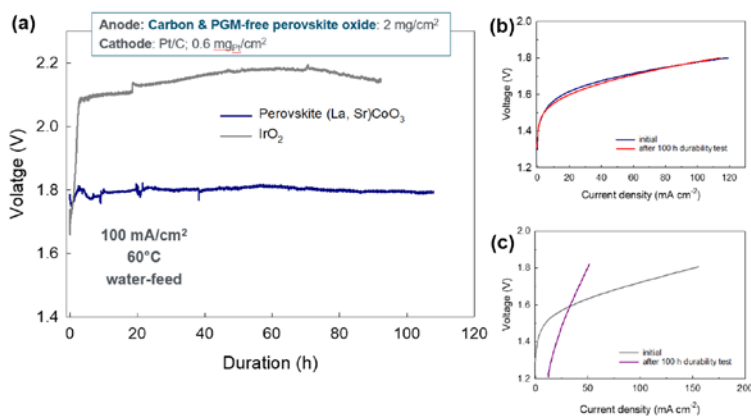


Figure 3. (a) Durability test of perovskite (La, Sr)TiO<sub>3</sub> OER catalyst at 100 mA/cm<sup>2</sup> at 60 °C in pure water feed; (b) Polarization plots of perovskite OER catalyst before and after the 100 hours durability test; (c) Polarization plots of IrO<sub>2</sub> before and after the 100 hours durability test.

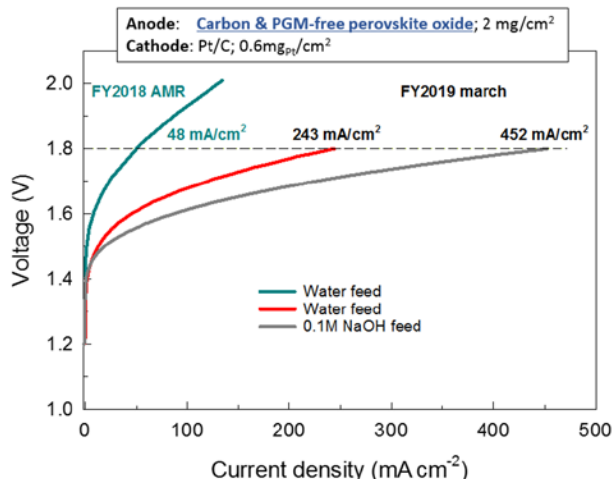


Figure 4. Performance improvement since 2018.

## CONCLUSIONS AND UPCOMING ACTIVITIES

We demonstrated 500% improved AEM water electrolyzer performance at 1.8 V since FY 2018. The most important achievement in this year is the demonstration of excellent AEM electrolyzer durability with the perovskite OER (La, Sr)CoO<sub>3</sub> catalyst. No performance degradation has been achieved for 100 hours durability test at 60°C in pure water feed AEM electrolyzer test. Understanding the catalyst-ionomer interaction is the key for improving the AEM water electrolyzer performance up to level of PEM water electrolyzer. Currently atmospheric pressure x-ray photoelectron spectroscopy and in situ x-ray absorption spectroscopy studies are being performed to understand the electrochemical phenomena occurring at the interface of catalyst/ionomer.

## FY 2019 PUBLICATIONS/PRESENTATIONS

1. D. Lee, I. Matanovic, A.S.S. Lee, E.J. Park, C.H. Fujimoto, H.T. Chung, Y.S. Kim, “Phenyl Oxidation Impacts the Durability of Alkaline Membrane Water Electrolyzer,” *ACS Appl. Mater. Interfaces*, 11 (2019): 9696-9701.
2. H.T. Chung, “High Performance Ultra Low-Cost Non-Precious Metal Catalyst System for AEM Electrolyzer,” Poster presentation to the DOE Hydrogen and Fuel Cell Program Annual Merit Review, Washington, D.C., April 2019

## REFERENCES

1. D. Lee, I. Matanovic, A.S.S. Lee, E.J. Park, C.H. Fujimoto, H.T. Chung, Y.S. Kim, “Phenyl Oxidation Impacts the Durability of Alkaline Membrane Water Electrolyzer,” *ACS Appl. Mater. Interfaces*, 11 (2019): 9696-9701.