



Energy Materials Network  
U.S. Department of Energy



**HydroGEN**  
Advanced Water Splitting Materials

# High-Performance Ultralow-Cost Non-Precious Metal Catalyst System for AEM Electrolyzer

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**Los Alamos National Laboratory**  
**6-14-2018**

Project ID PD158

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# Project Overview

## Project Partners

Hoon Chung, Los Alamos National Laboratory  
Barr Zulevi, Pajarito Powder, LLC

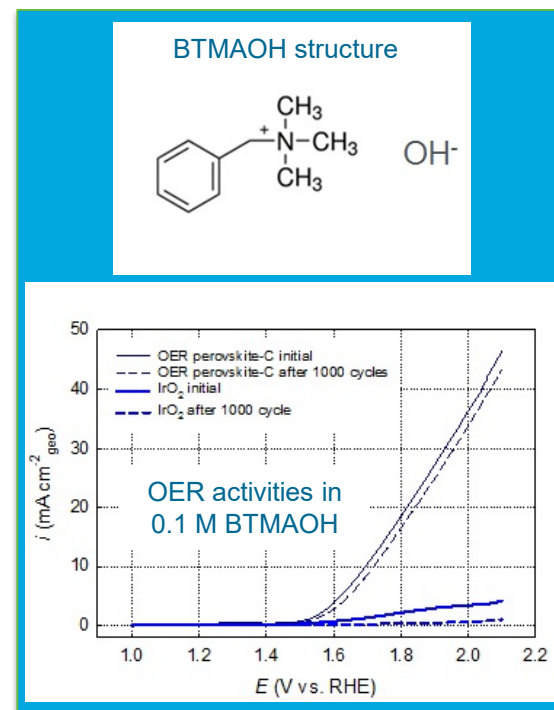
## Project Vision

The key challenge in anion exchange membrane (AEM) electrolyzer is to achieve high performance without feeding alkaline solution to the electrodes. In this project, we are developing PGM-free OER and HER catalysts with high performance in the alkaline solution-free AEM water electrolyzer.

## Project Impact

By eliminating most expensive PEM electrolyzer components AEM technology offers > 50% reduction in cost. This opens a pathway to meeting the DOE H<sub>2</sub> production cost target of < \$2/kg.

Award #	2.2.0.402
Start Date	10/1/2017
Year 1 End Date	09/30/2018
Project End Date	09/30/2020
Total DOE Share	\$1.0M
Total Cost Share	\$0.1M
Year 1 DOE Funding	\$0.25M



\* this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)



# Approach- Summary

## Project Motivation

The need for low-cost, active and durable PGM-free OER and HER catalysts for AEM electrolyzer. Perovskite oxides were chosen as OER catalysts and porous Ni-La alloys as HER catalysts.

## Barriers

- High PEM electrolysis cost:
  - ✓ Expensive PGM catalysts
  - ✓ Expensive titanium flow fields
  - ✓ Expensive Nafion® membrane

## Key Impact

Metric	State of the Art	Proposed
OER activity	5.0 mA/cm <sup>2</sup> at 1.65 V with carbon addition	5.1 mA/cm <sup>2</sup> at 1.65 V without carbon addition
HER activity	20 mA/cm <sup>2</sup> at a 0.20 V overpotential	34 mA/cm <sup>2</sup> at a 0.20 V overpotential
Durability	Performance durability of IrO <sub>2</sub>	The same degradation rate compared with IrO <sub>2</sub>

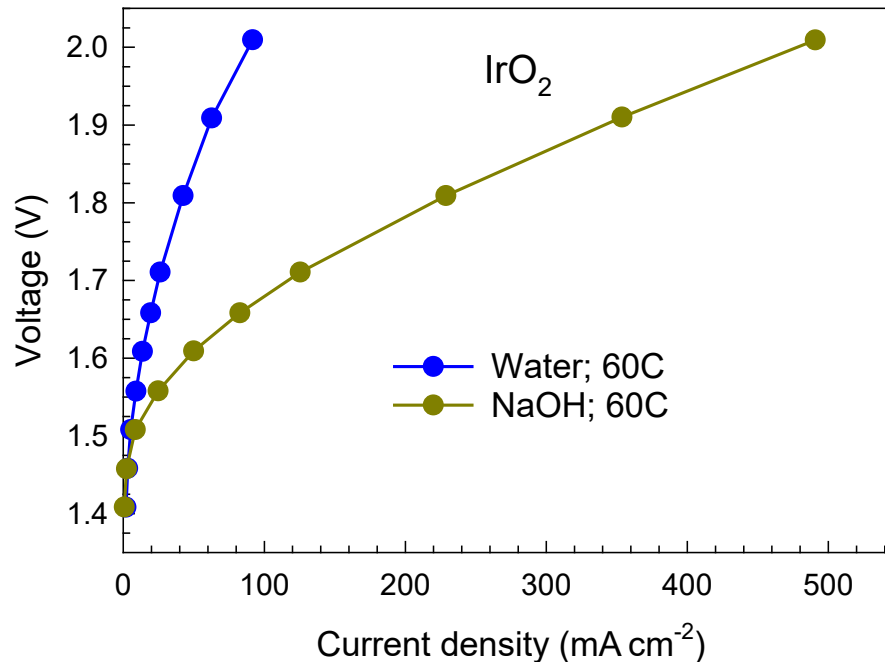
## Partnerships

Pajarito Powder, LLC (PPC) is a partner of this project. Their expertise is in (i) mass-production of catalysts, (ii) fabrication of MEAs, and (iii) AEM electrolyzer testing. Catalysts developed by LANL will be tested by PPC in AEM electrolyzer tests and their production scaled-up of 25 g/batch.



# Approach- Innovation

**Barrier:** The barrier, the need of alkaline solution feeding to achieve high performance in AEM technology, is demonstrated. With alkaline solution feeding, this technology can be considered a kind of alkaline water electrolysis, not the AEM water electrolysis technology by definition.



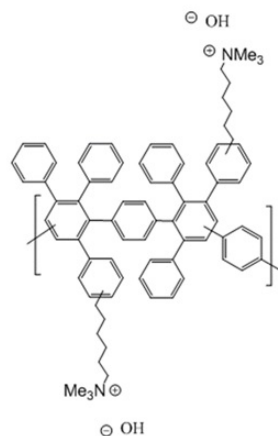
This test was performed with the help of HydroGEN consortium nodes:

- Cy Fujimoto from SNL provided AEM
- Guido Bender from NREL fabricated MEA and performed electrolyzer test

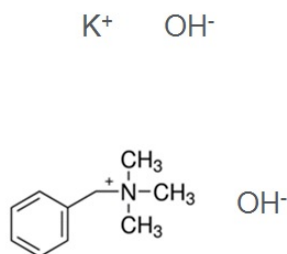


# Approach- Innovation

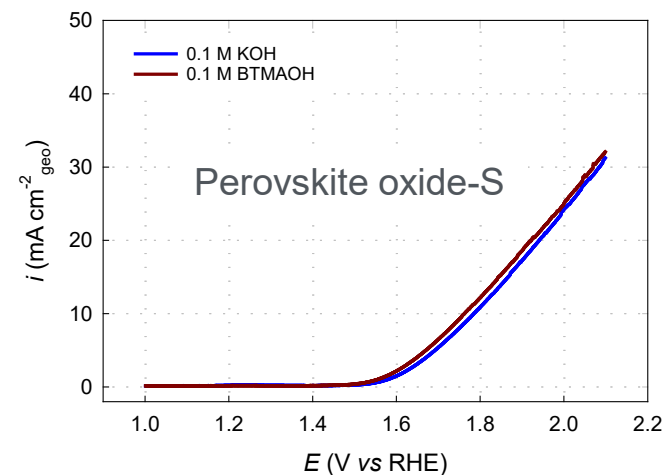
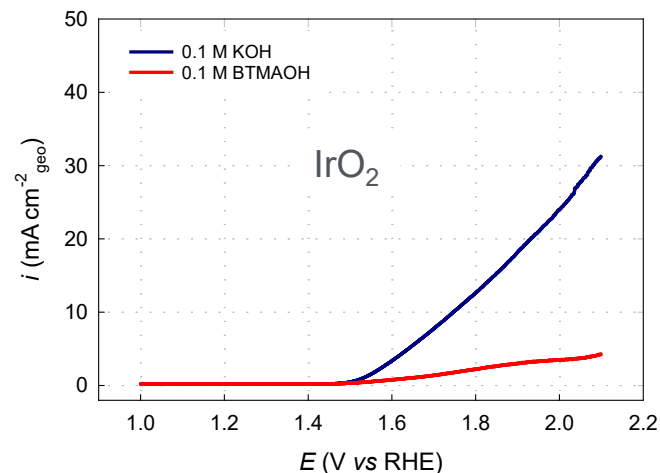
Poly(phenylene)-based anion exchange membrane with fully alkylated ammonium group cation



KOH vs BTMAOH



- Organic cation, e.g., BTMA<sup>+</sup>, represents more closely to AEM cationic group than inorganic cation, e.g., K<sup>+</sup>
- Electrolyte significantly affects OER activity of catalysts



**Understanding phenomena at the interface of a catalyst and organic alkaline electrolyte interface is key to developing AEM water electrolysis technologies**



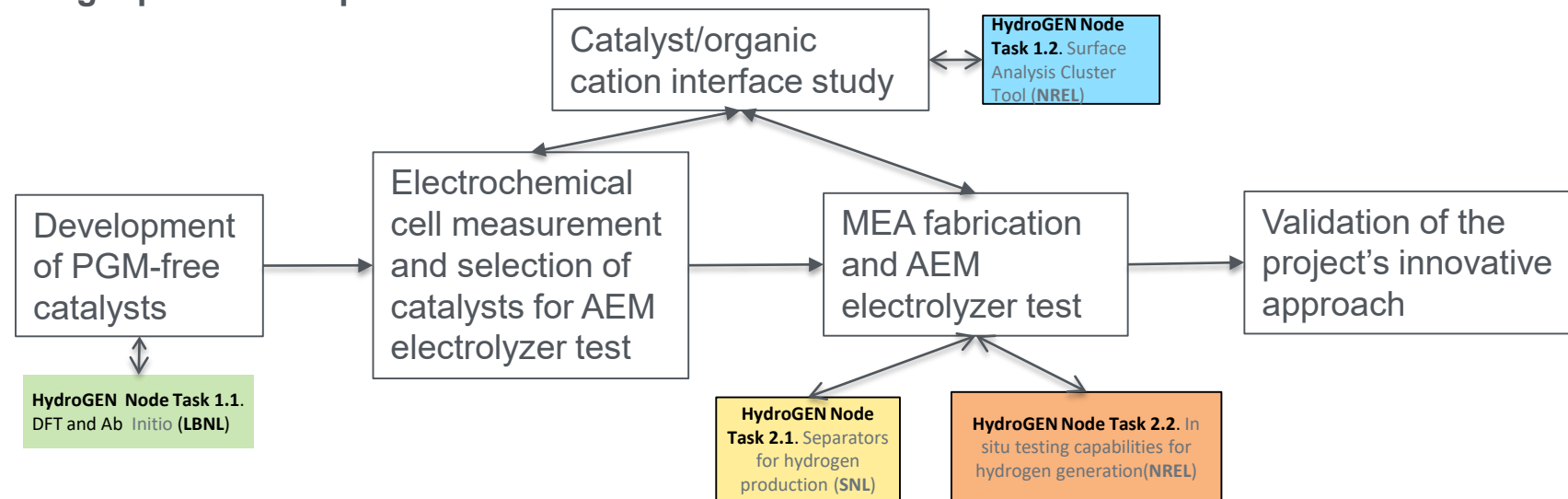
# Approach- Innovation

**Previous studies:** Significant interference of benzene and organic cations with catalysts that inhibits catalyst activity has been studied by this presenter:

- ✓ H. Chung, U. Martinez, I. Matanovic, Y. S. Kim, "Cation-hydroxide-water coadsorption inhibits the alkaline hydrogen oxidation reaction" *J. Phys. Chem. Lett.* **7**, 4464 (2016)
- ✓ H. Chung, Y. Choe, U. Martinez, J. H. Dumont, A. Mohanty, C. Bae, I. Matanovic, Y. S. Kim, "Effect of organic cations on hydrogen oxidation reaction of carbon supported platinum" *J. Electrochem. Soc.*, **163**, F1503 (2016)
- ✓ I. Matanovic, H. Chung, Y. S. Kim, "Benzene adsorption: A significant inhibitor for the hydrogen oxidation reaction in alkaline conditions" *J. Phys. Chem. Lett.* **8**, 4918 (2017)

**Innovative approach:** Implementation of PGM-free catalysts to eliminate detrimental effect of adsorption of benzene and organic cations and thus enhance AEM water electrolyzer performance.

**Budget period 1 scope of work:**

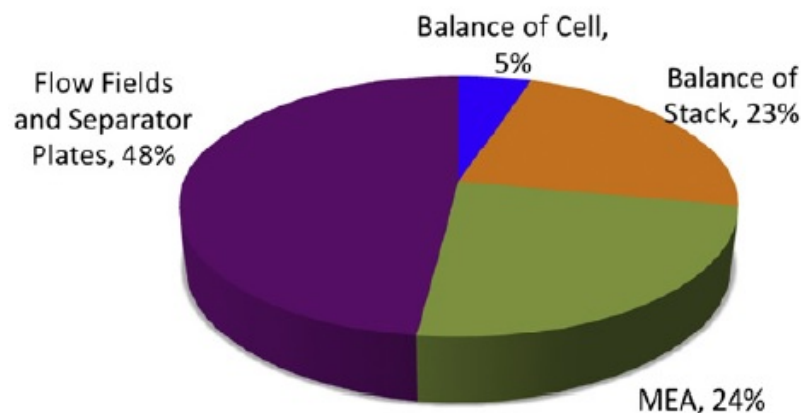


**Validation of the project's innovative approach will be demonstrated in Accomplishments**



# Relevance & Impact

In PEM water electrolyzer, titanium flow fields/separators, PGM IrO<sub>2</sub> and Pt catalysts, and Nafion® perfluorinated membrane account for more than 70% of the stack cost. If PGM-free catalyst development for AEM water electrolysis is successful, in addition to PGM catalyst replacement by PGM-free catalysts, titanium flow fields/separators and Nafion® perfluorinated membrane can be replaced by stainless steel and cheaper hydrocarbon membrane. This is expected to reduce the stack cost by more than 50% and facilitate reaching the DOE Hydrogen and Fuel Cells Program cost target of sustainably produced hydrogen of < \$2/kg.



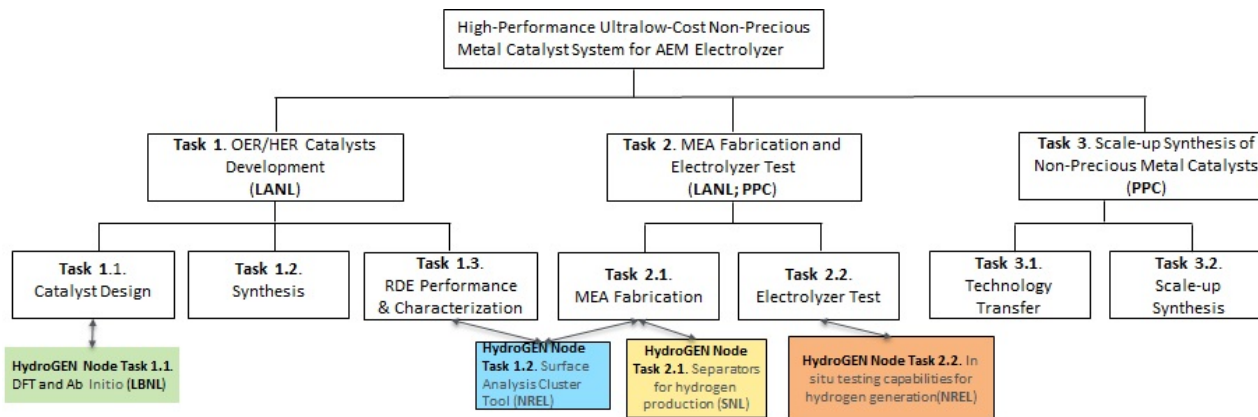
**Stack cost breakdown**

Carmo *et al.*, "A comprehensive review of PEM water electrolysis" *Int. J. Hydro. Energy* **38**, 4901 (2013)





# Relevance & Impact



Node	PI	Task
Hydrogen in situ testing capabilities for H <sub>2</sub> generation	Guido Bender (guido.bender@nrel.gov)/NREL	AEM electrolyzer test
Surface analysis cluster tool	Glenn Teeter (glenn.teeter@nrel.gov)/NREL	Surface analyses of the catalysts
DFT and Ab Initio Calculations	Lin-Wang Wang (lwwang@lbl.gov)/LBNL	Descriptor study for OER catalysts
Separators for hydrogen production	Cy Fujimoto (chfujim@snadia.gov)/SNL	Alkaline membrane synthesis

This project is a good fit for the HydroGEN consortium R&D model. As shown in the project structure flow chart, four key nodes are utilized in project to facilitate R&D and achieve the project goals. **DFT and ab initio calculations node** guides catalyst design and helps with electrochemical test result interpretation. **Surface analysis cluster node** offers a variety of surface composition/valence state analysis tools for catalysts. **Separators for hydrogen production node** supplies state-of-the-art alkaline membrane and ionomer. **Hydrogen *in situ* test capabilities for H<sub>2</sub> production node** provides MEA fabrication and in situ electrolyzer test.





# Accomplishments

Date	LANL Quarterly Progress Measures and Go/No-Go	Status
December 31 2017 (FY18 Q1)	<b>QPM 1:</b> Establishment of catalyst synthesis equipment, including spray pyrolysis, with La-doped Ni HER and LSC OER catalysts successfully fabricated as verified by XRD.	Completed
March 31 2018 (FY18 Q2)	<b>QPM 2:</b> Alkaline electrolyzer system set-up at LANL with first experiments with PGM-free catalysts complete.	Completed
June 30 2018 (FY18 Q3)	<b>QPM 3:</b> Base line LANL OER and HER materials shipped to PPC for MEA fabrication.	On track
September 30 2018 (FY18 Q4)	<b>Go/No-Go Decision:</b> <b>OER catalysis:</b> Demonstrate 70% improvement from our current SOA (with no carbon), for a target of <u>5.1 mA/cm<sup>2</sup> at 1.65 V</u> which is close to the current SOA with carbon, (but little durability) of 5.0 mA/cm <sup>2</sup> . RDE cyclic durability: triangle sweep cycle: 500 mV/s between 0.6 and 2.1 V; cycle number: 5,000 cycles; <u>the same degradation rate compared with IrO<sub>2</sub> catalyst.</u> <b>HER catalysis:</b> 70% improvement from our current SOA current density of (20 mA/cm <sup>2</sup> ) for a target of <u>34 mA/cm<sup>2</sup> at a 200 mV overpotential.</u> RDE cyclic durability: triangle sweep cycle: 200 mV/s between 0.2 and -0.25 V; cycle number: 5,000 cycles; <u>less than 20% current density loss at a 200 mV overpotential.</u>	On track

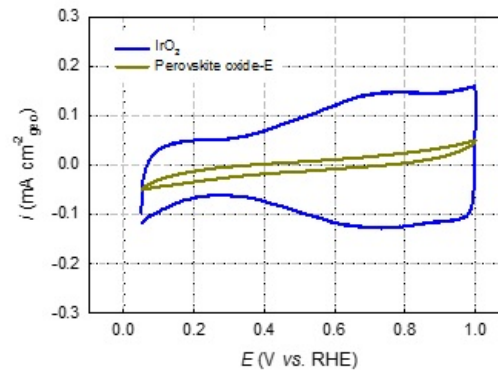
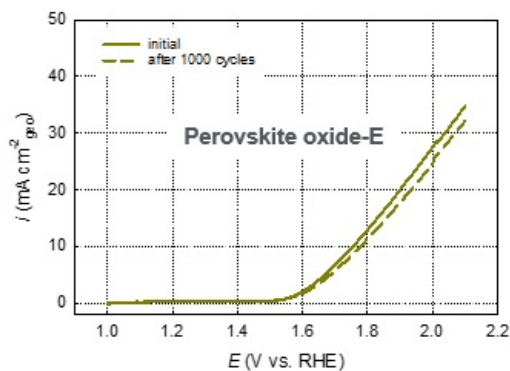
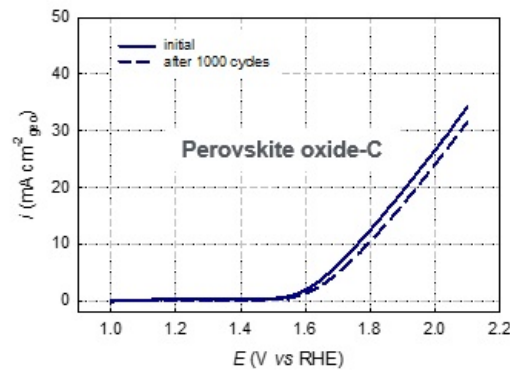
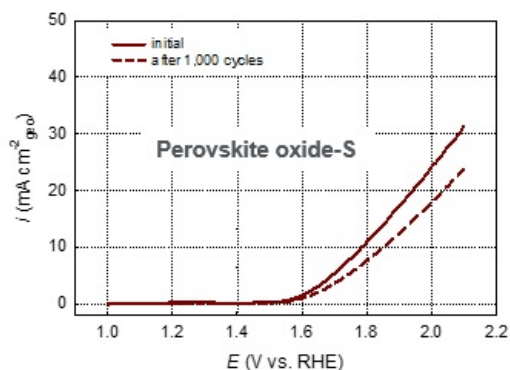
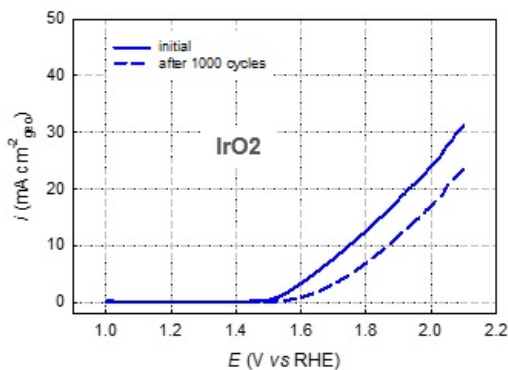
- The 1<sup>st</sup> budget year milestones and go/no-go decision are expected to be **met and possibly exceeded**
- Project is predicted to result in **significant AEM water electrolysis technology progress already in its first year**



# Accomplishments

## PGM-and carbon-free perovskite catalyst OER activity in 0.1 M KOH

RDE: catalyst loading:  $800 \mu\text{g cm}^{-2}$ ; 0.1 M KOH; 1600 rpm; room temperature; Hg/HgO (1.0 M KOH) reference electrode; LSV 10 mV/s;  $\text{N}_2$ -saturated solution.



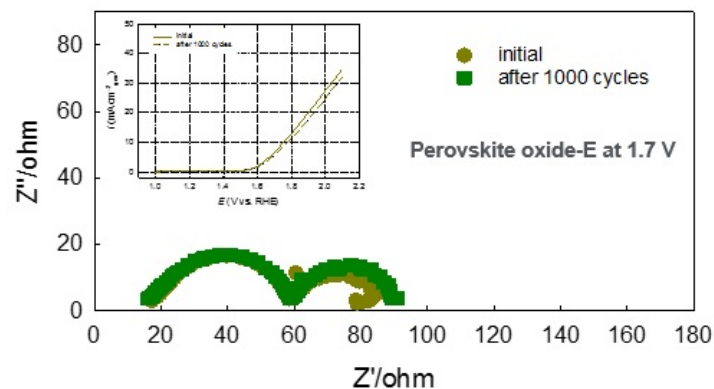
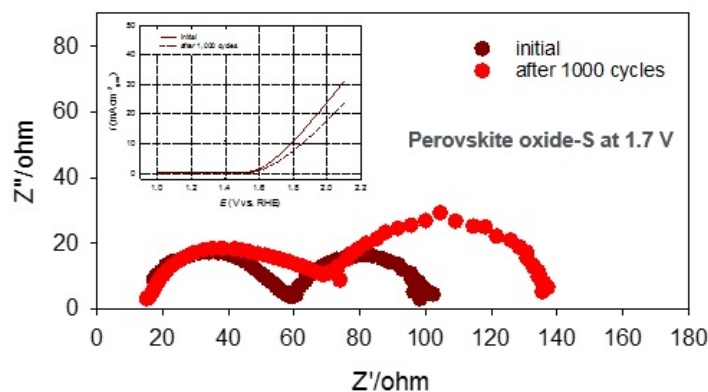
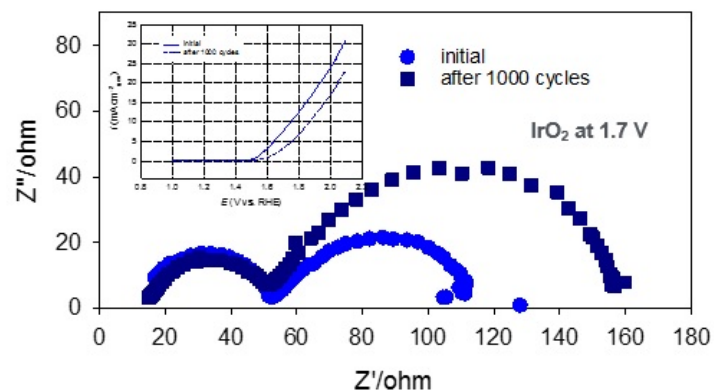
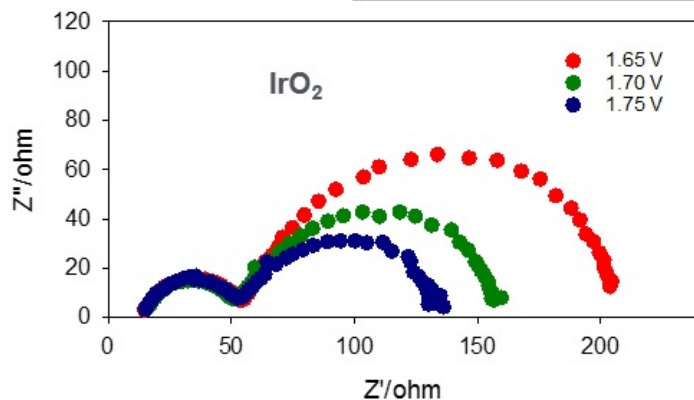
Perovskite oxide-C and -E show improved activity and durability compared with perovskite-S, and better durability than IrO<sub>2</sub>



# Accomplishments

## Impedance analysis

RDE: catalyst loading:  $800 \mu\text{g cm}^{-2}$ ; 0.1 M KOH; 1600 rpm; room temperature; Hg/HgO (1.0 M KOH) reference electrode; LSV 10 mV/s;  $\text{N}_2$ -saturated solution.



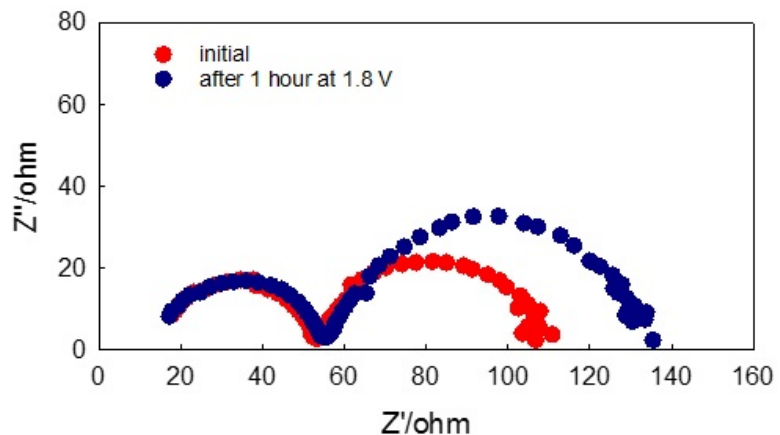
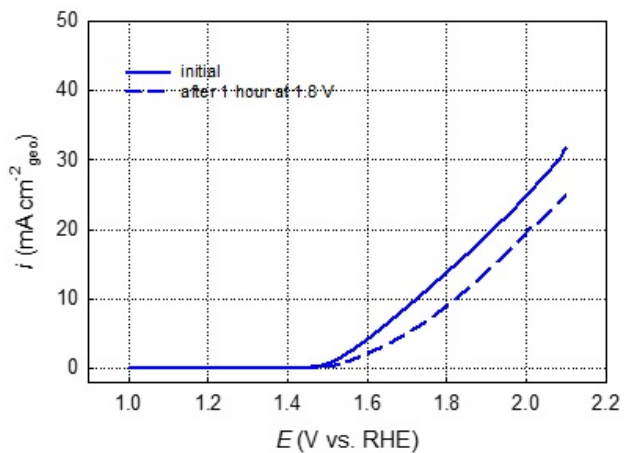
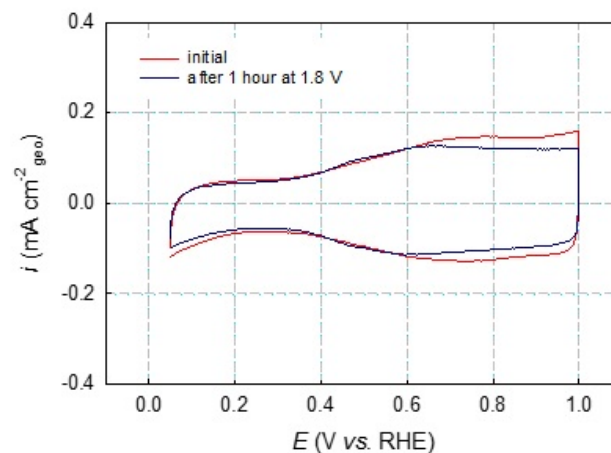
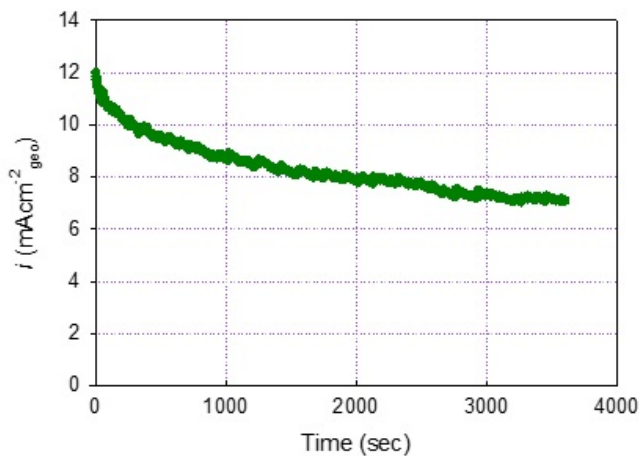
Impedance of each catalyst layer was measured before and after durability testing to gauge electrolyte and charge-transfer resistance changes



# Accomplishments

## IrO<sub>2</sub> durability test at 1.8 V in 0.1 M KOH

RDE: catalyst loading: 800  $\mu\text{g cm}^{-2}$ ; 0.1 M KOH; 1600 rpm; room temperature; Hg/HgO (1.0 M KOH) reference electrode; LSV 10 mV/s; N<sub>2</sub>-saturated solution.

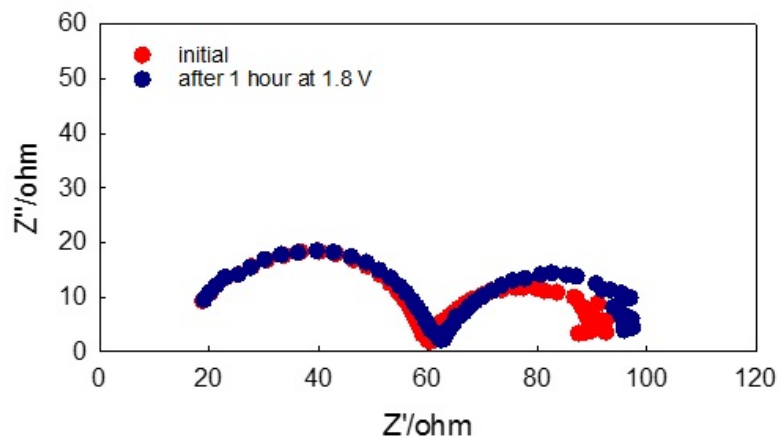
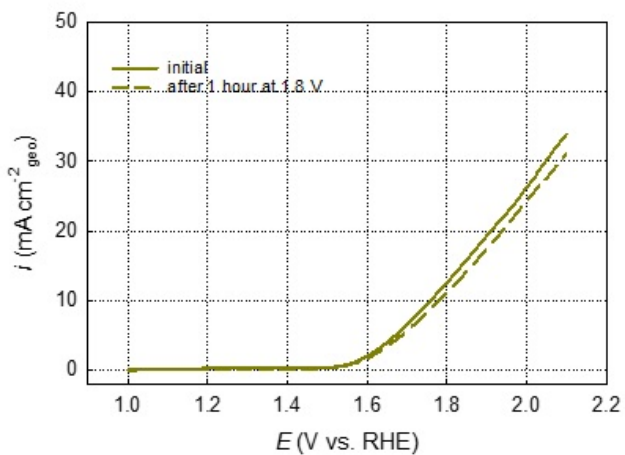
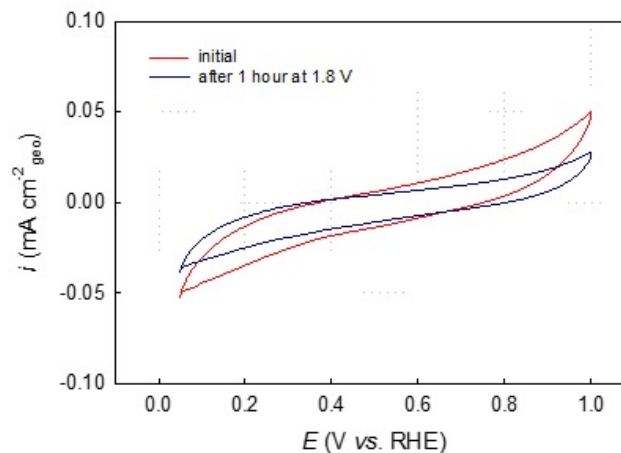
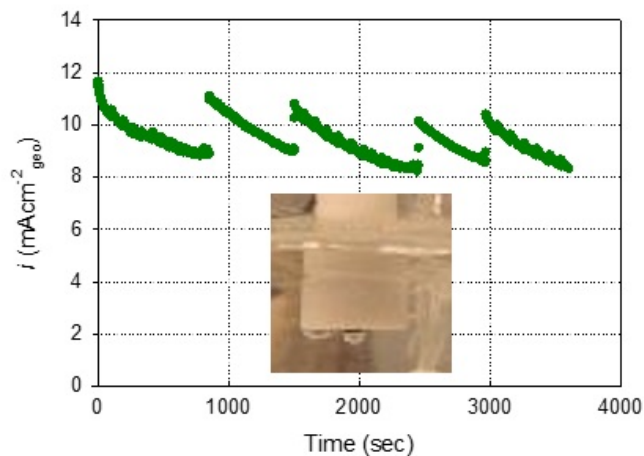




# Accomplishments

## Perovskite oxide-E durability test at 1.8 V in 0.1 M KOH

RDE: catalyst loading:  $800 \mu\text{g cm}^{-2}$ ; 0.1 M KOH; 1600 rpm; room temperature; Hg/HgO (1.0 M KOH) reference electrode; LSV 10 mV/s;  $\text{N}_2$ -saturated solution.

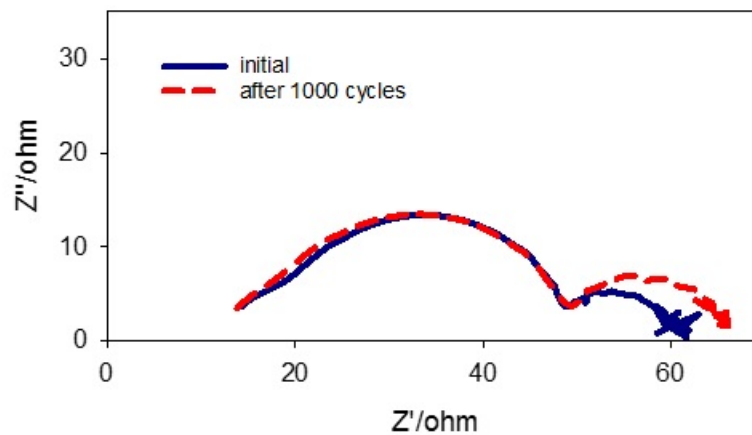
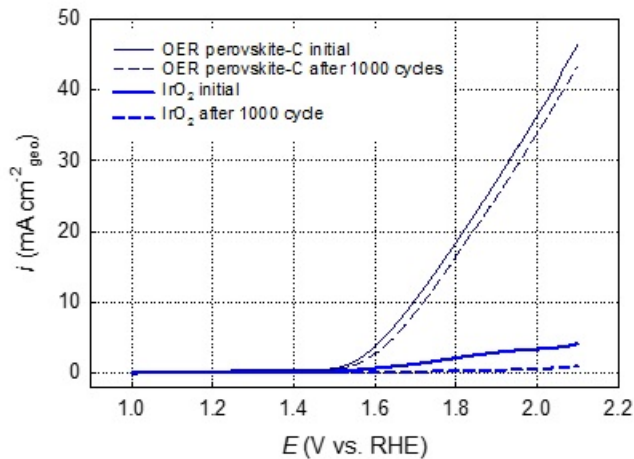
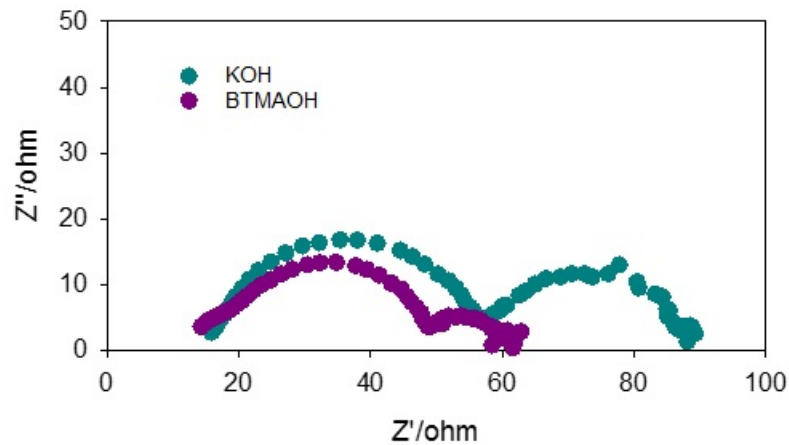
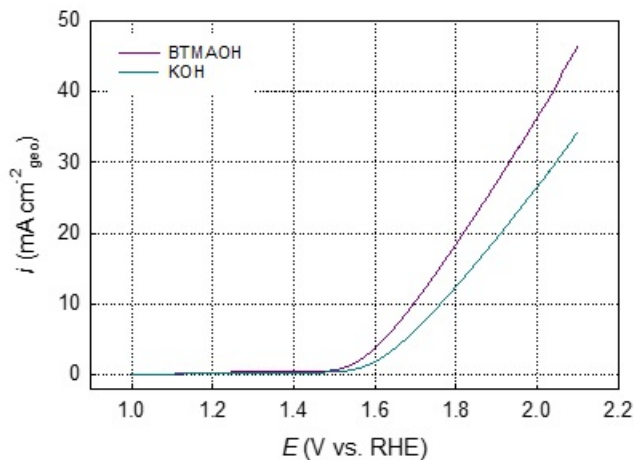




# Accomplishments

## Perovskite oxide-C in 0.1 M BTMAOH

RDE: catalyst loading:  $800 \mu\text{g cm}^{-2}$ ; 0.1 M BTMAOH; 1600 rpm; room temperature; Hg/HgO (1.0 M KOH) reference electrode; LSV 10 mV/s;  $\text{N}_2$ -saturated solution.







# Accomplishments

Current density at 1.65 V vs RHE

## OER Catalyst Go/No-Go:

- (1) 5.1 mA/cm<sup>2</sup> at 1.65 V vs RHE
- (2) the same degradation rate compared with IrO<sub>2</sub> catalyst

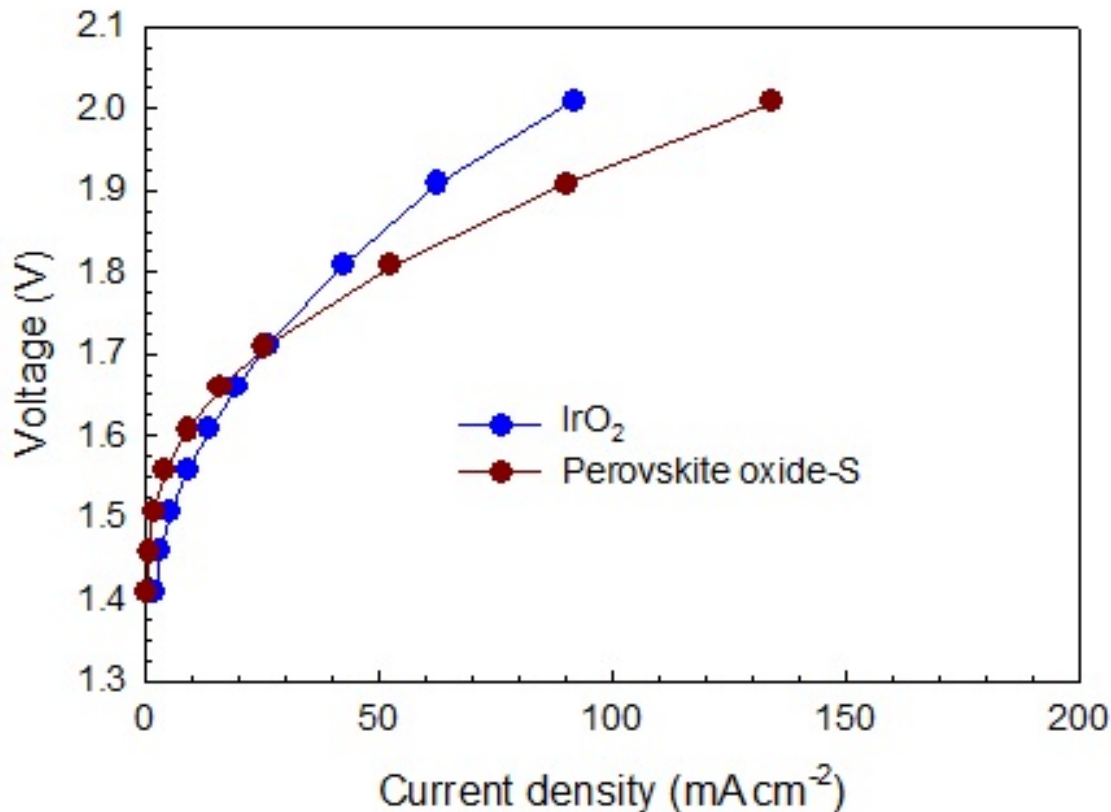
Catalyst	Current density (mA/cm <sup>2</sup> ) in 0.1 M KOH		Current density (mA/cm <sup>2</sup> ) In 0.1 M BTMAOH	
	initial	after 1000 cycles	initial	after 1000 cycles
IrO <sub>2</sub>	5.5	1.9	1.0	0.2
Perovskite oxide-S	3.1	2.0	4.1	1.8
Perovskite oxide-A	2.5	0.9	-	-
Perovskite oxide-B	4.4	2.5	5.5	3.9
Perovskite oxide-C	3.8	2.7	6.8	5.3
Perovskite oxide-D	3.9	2.7	6.2	4.8
Perovskite oxide-E	4.1	3.4	5.2	2.7





# Accomplishments

First AEM Water Electrolysis Test with IrO<sub>2</sub> and Standard Perovskite Oxide-S



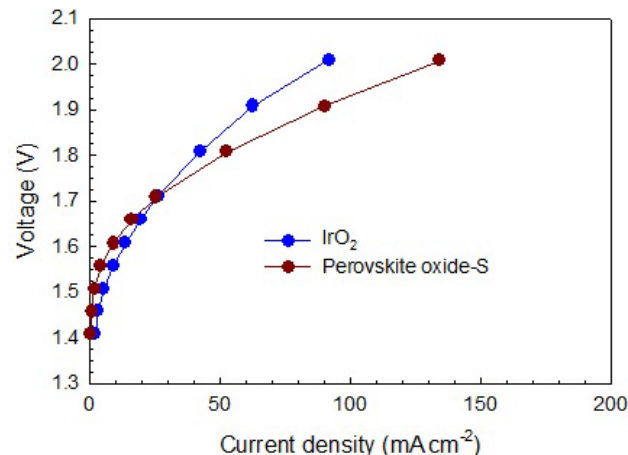
**Promising first AEM water electrolysis result obtained with the baseline OER catalyst (perovskite oxide-S) even without any optimization of electrode: Project's innovative approach has been validated.**



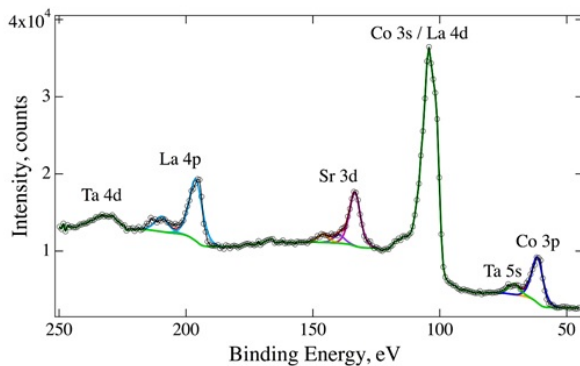
# Collaboration: Effectiveness

- Collaboration with separator for hydrogen production node (SNL) and hydrogen *in situ* test capabilities for H<sub>2</sub> production node (NREL) has enabled AEM water electrolysis measurements, resulting in significant impact on project progress

	<b>Catalyst Development</b>	
	<b>Membrane Development</b>	
	<b>MEA Fabrication &amp; Testing</b>	



- Surface analysis cluster node (NREL) has performed XPS analysis for the baseline Perovskite oxide-S (La<sub>0.85</sub>Sr<sub>0.15</sub>CoO<sub>3</sub>)

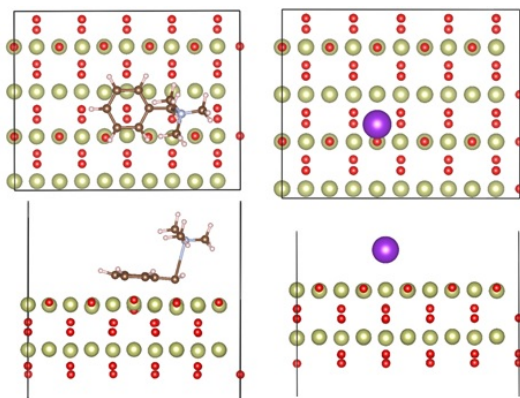


Relative elemental quantification using tabulated sensitivity factors for the La 4p, Sr 3d and Co 3p core levels produced an elemental ratio between these three elements of 50% - 18% - 32%. This indicates composition near surface of the catalyst is different from nominal bulk composition.

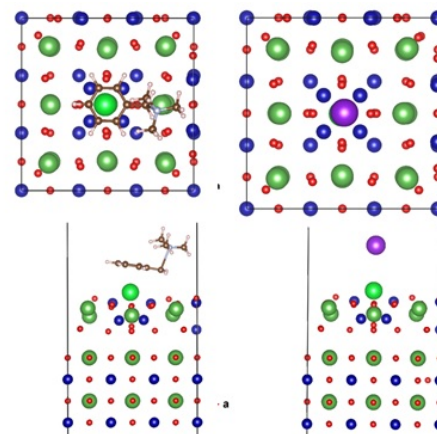


# Collaboration: Effectiveness

- **DFT and Ab initio calculations node (LBNL):** Preliminary calculations indicates that the BTMA<sup>+</sup> binding on the IrO<sub>2</sub> surface is much stronger than the La<sub>1-δ</sub>Sr<sub>δ</sub>CoO<sub>3</sub> surface. Thus, it can imply that the BTMA<sup>+</sup> binds on the IrO<sub>2</sub> surface, but not on the La<sub>1-δ</sub>Sr<sub>δ</sub>CoO<sub>3</sub> surface.



The binding configurations of the IrO-terminated surface with BTMA (left panels) and the K atom (right panels)



The binding configuration of the BTMA molecule on the La<sub>1-δ</sub>Sr<sub>δ</sub>CoO<sub>3</sub> (100) surface (left), and the K on the La<sub>1-δ</sub>Sr<sub>δ</sub>CoO<sub>3</sub> (100) surface (right).

- Interactions with the broader HydroGEN research community: (1) We will present this result at the “Oxygen or Hydrogen Evolution Catalysis for Water Electrolysis Session” at the 233<sup>rd</sup> ECS meeting; (2) We are interacting with benchmarking/protocols project team and submitted some inputs to the team; (3) We are incorporating project data in the HydroGEN data hub (<https://datahub.h2awam.org>) to exchange results and discuss research direction.



# Proposed Future Work

- **In the subsequent phases of this seeding project :**
  - ✓ Other organic alkaline electrolytes, *e. g.*, TMAOH, will be chosen for RDE OER database construction with PGM-free catalysts. The results will be used in fundamental alkaline OER/HER study, as well as for AEM water electrolyzer catalyst/ionomer design
  - ✓ Understanding phenomena at the interface between PGM-free catalyst and anion exchange ionomer using diverse analysis tools, including *in situ* x-ray absorption spectroscopy in conjunction with Surface Analysis Cluster Node and DFT and Ab Initio Calculations Node
  - ✓ AEM water electrolyzer tests will be performed in NREL, LANL, PPC with selected catalysts based on the electrochemical RDE tests
  - ✓ Pajarito Power will scale up the synthesis of PGM-free catalyst to 25 g/batch
  - ✓ The estimated budget for the subsequent phases: 0.75 M



# Project Summary

- A big progress in activity and durability of **carbon-free** perovskite OER catalysts compared to baseline perovskite oxide-S has been achieved in both KOH and BTMAOH
- **Carbon-free** perovskite oxide OER catalysts exhibit significantly higher activity and durability in BTMAOH than in KOH
- Very promising initial AEM water electrolysis results have been demonstrated with the baseline OER catalyst (perovskite oxide-S) in collaboration with SNL (membrane) and NREL (MEA fabrication and electrolyzer test)
- Patent on **carbon-free** perovskite oxides is in preparation

## Presentation

- This work will be present at the 233<sup>rd</sup> ECS Meeting: “Carbon-Free Perovskite Oxide Oxygen Evolution Reaction Catalysts for AEM Electrolyzer” on May 16<sup>th</sup>, 2018.



# Technical Back-Up Slides

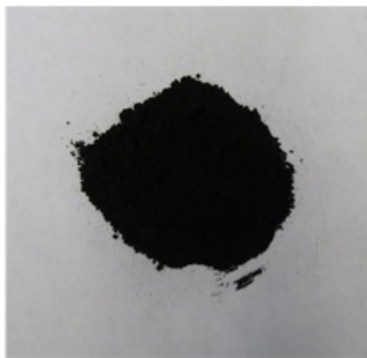


# Technical Back-Up Slides

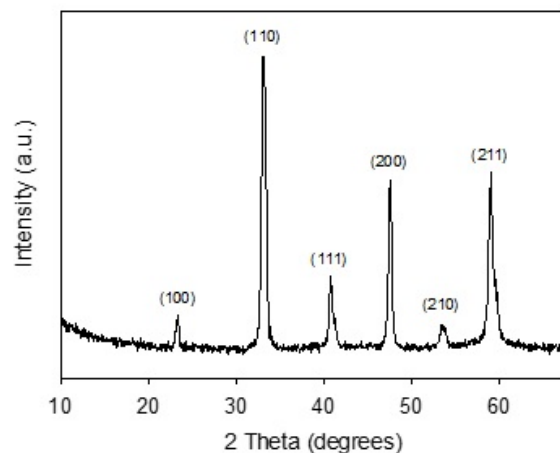
## Baseline Perovskite Oxide-S: $(\text{La}_{0.85}\text{Sr}_{0.15})\text{CoO}_{3-\delta}$

RDE: LSC  $\sim 500 \mu\text{g cm}^{-2}$ ; 0.1 M NaOH; 900 rpm; room temperature; Hg/HgO (1.0 M KOH) reference electrode; steady state potential (OCP, 20 s, 20-mV steps, 30 s/step) in  $\text{O}_2$ -saturated electrolyte

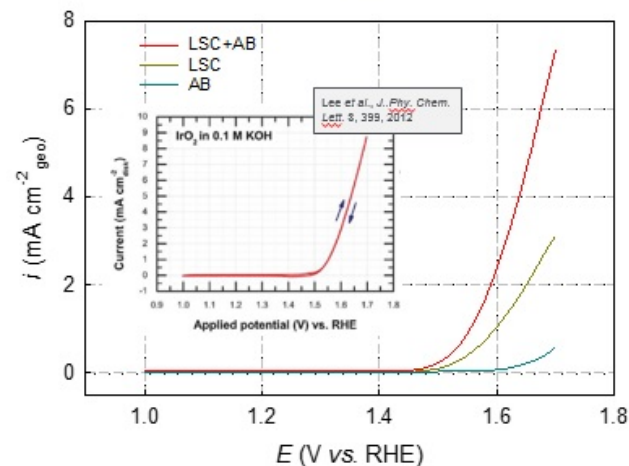
Optical Image



XRD



RDE



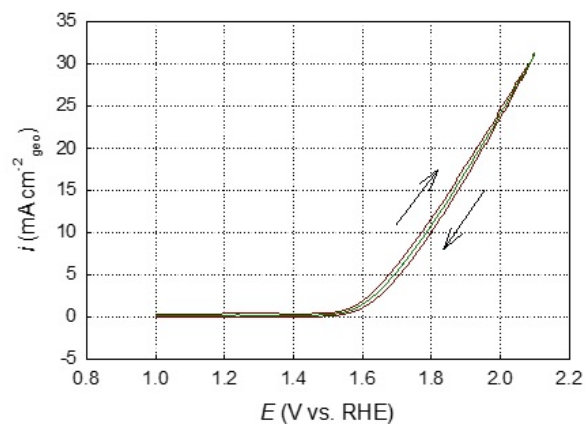
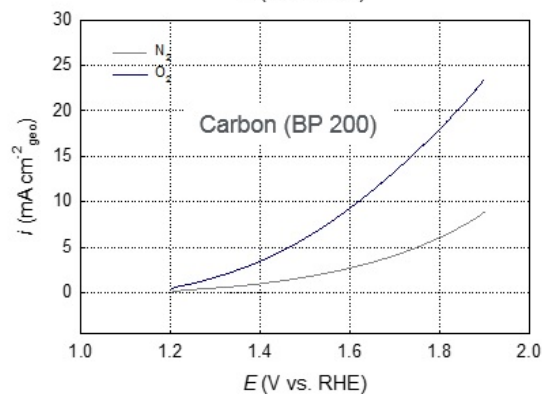
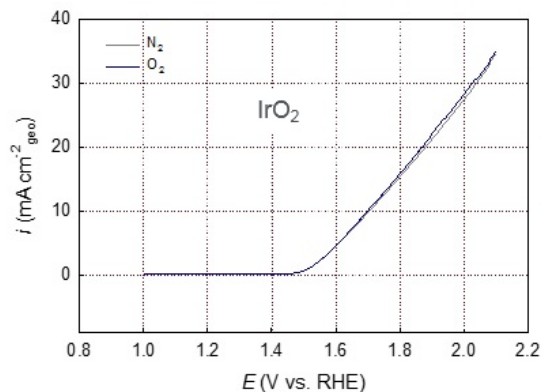
- Perovskite oxide-S showing OER activity by itself
- Addition of carbon (acetylene black, AB) results in current density enhancement, pointing to the effect higher electronic conductivity has on performance





# Technical Back-Up Slides

## OER Catalyst Test Conditions in 0.1 M KOH



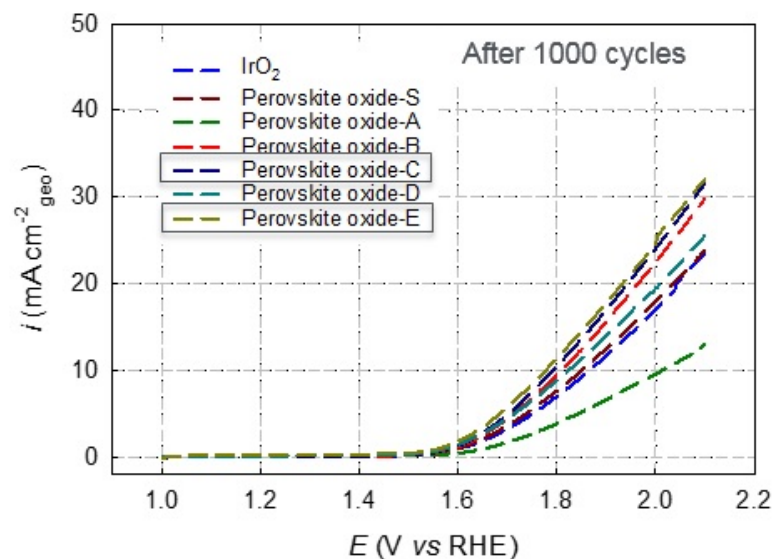
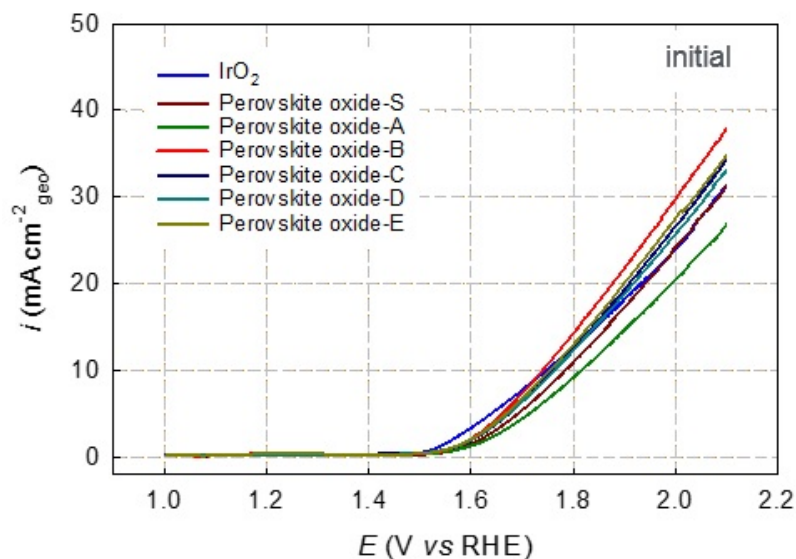
- Electrolytes saturated with N<sub>2</sub>, not O<sub>2</sub>, to correctly measure catalyst activity
- Current density values averaged over the forward and backward scans



# Technical Back-Up Slides

## OER activity and durability of carbon-free perovskite catalysts in 0.1 M KOH

RDE: catalyst loading:  $800 \mu\text{g cm}^{-2}$ ; 0.1 M KOH; 1600 rpm; room temperature; Hg/HgO (1.0 M KOH) reference electrode; LSV 10 mV/s;  $\text{N}_2$ -saturated solution;



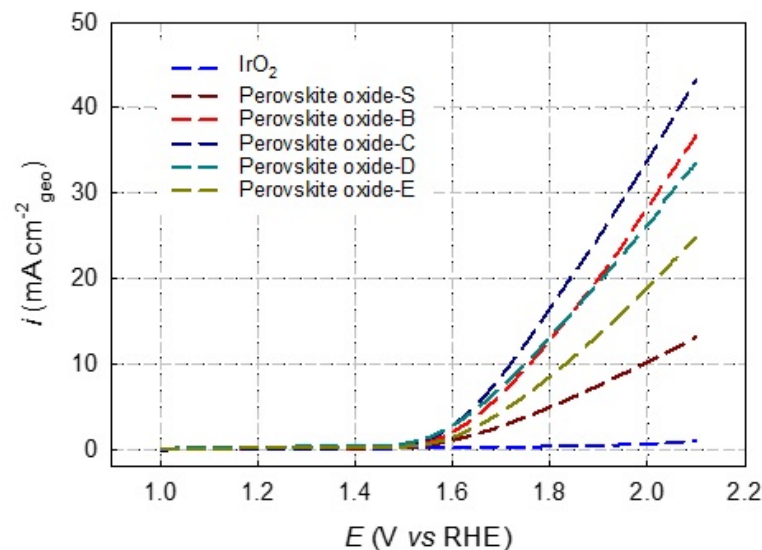
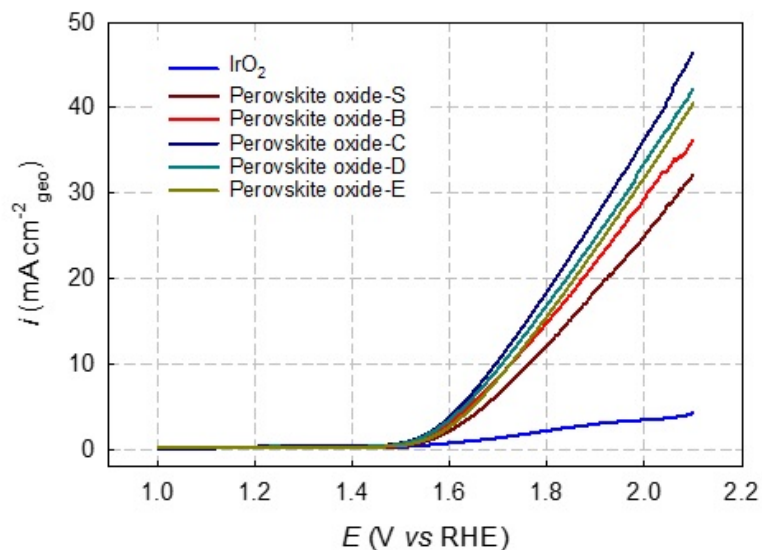
Perovskite oxide-C and -E demonstrate promising activity and durability



# Technical Back-Up Slides

## OER activity and durability of carbon-free perovskite catalysts in 0.1 M BTMAOH

RDE: catalyst loading:  $800 \mu\text{g cm}^{-2}$ ; 0.1 M BTMAOH; 1600 rpm; room temperature; Hg/HgO (1.0 M KOH) reference electrode; LSV 10 mV/s;  $\text{N}_2$ -saturated solution;



- Perovskite oxide catalysts showing higher OER activity and better durability in BTMAOH than in KOH
- $\text{IrO}_2$  exhibiting much lower OER activity in BTMAOH than in KOH