



PGM-free OER Catalysts for PEM Electrolyzer

Di-Jia Liu (lead), Lina Chong, Hao Wang, Argonne National Laboratory
Gang Wu, University of Buffalo (Subcontractor)
Hui Xu, Giner Inc. (Subcontractor)

p157

2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and
Peer Evaluation Meeting, April 30 – May 1, 2019, Washington, D.C.

This presentation does not contain any proprietary, confidential, or otherwise restricted information



Project Overview

Team

Lead: Argonne National Laboratory

Sub: U. of Buffalo & Giner Inc.

Project Vision

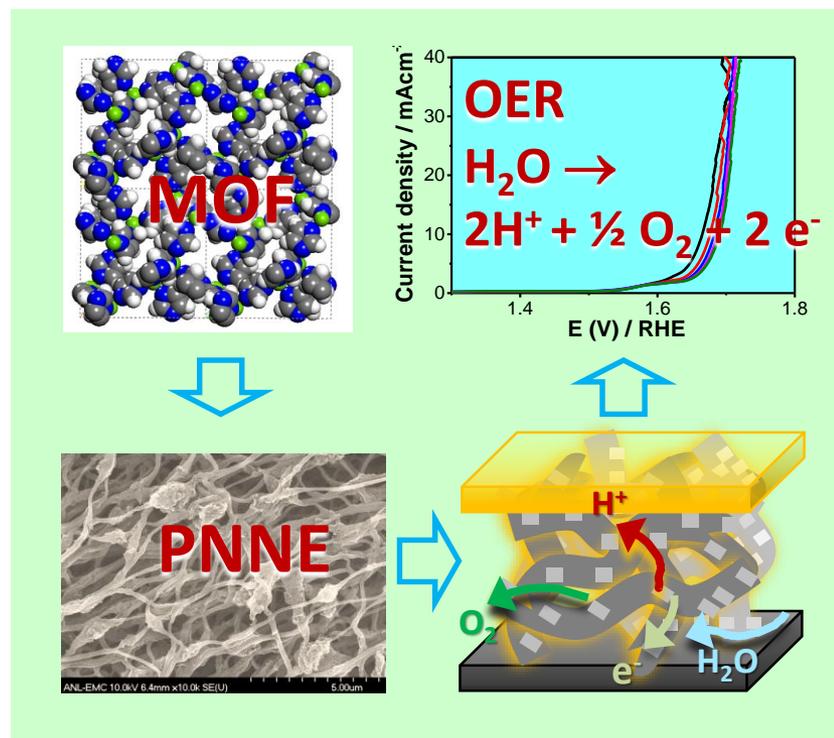
To develop platinum group metal-free (PGM-free) oxygen evolution reaction (OER) electro-catalysts as viable replacement for Ir in proton exchange membrane water electrolyzer (PEMWE)

Project Impact

To support DOE hydrogen production targets by substantially lowering the capital and operating cost of PEMWE:

- Cost: \$2 / kgH₂
- System efficiency: 43 kWh/kgH₂

Award #	EE2.2.0.202
Start Date	10/1/2017
Project End Date	09/30/2020
Year 1 Funding*	\$250k
Year 2 Funding*	\$375k



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



Approach- Summary

Project Motivation

- **ANL** is a pioneer in MOF derived electrocatalysts for ORR & OER.
- **UB** is a leader in PGM-free electrocatalyst research.
- **Giner** is an industrial leader in PEMWE system development.

The team aims at the first commercial PEMWE using PGM-free OER catalyst

Barriers

- **Cost:** Current PEMWE uses Ir as OER catalyst with high loading.
- **Activity:** PGM-free catalysts have shown promising OER activity in alkaline solution, but not in acid.
- **Durability:** Most catalyst and support materials are unstable under high polarization potential in acid.

Proposed targets

Metric	State of the Art	Expected Advance
Overpotentials against theoretical value	<i>Overpotential of ~530 mV @ 10mA/cm² for PGM-free catalyst in acid</i>	<i>Overpotential <350 mV or 15 mV higher than Ir black @ 10mA/cm² in acidic electrolyte</i>
Current density in operating PEMWE	<i>Non-existing for PGM-free catalyst in PEME</i>	<i>PEMWE with current density > 1000 mA/cm² @ 2 V & decay rate < 30 mV/1000 hours</i>

Partnerships - HydroGen

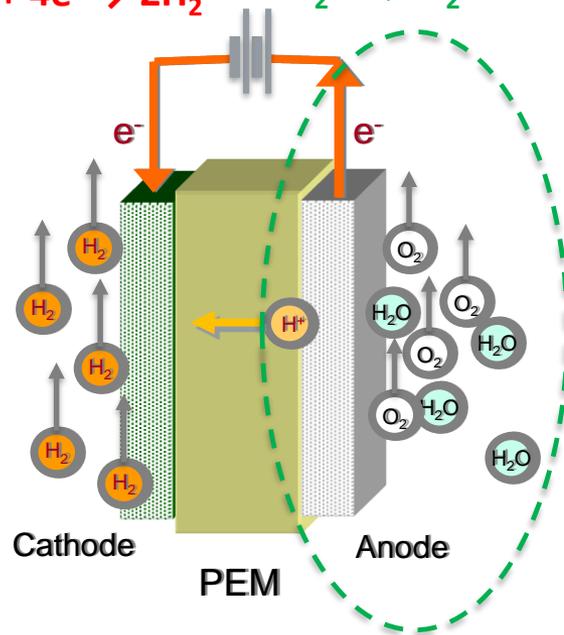
- Computational electrochemistry and predictive modeling (LLNL and LBNL)
- Advanced electron microscopic imaging (SNL)
- Electrode optimization / catalyst surface characterization (NREL)



Relevance & Impact – PGM-free OER catalyst for Low Temperature PEMWE

- ▶ **Catalyst cost reduction** – Removing the supply and price bottlenecks of precious metal (Ir, Ru, etc.) usage in LTE by replacing them with earthly abundant materials and robust, low-cost syntheses.
- ▶ **HydroGen Mission Alignment** – Accelerating low-cost PGM-free OER catalyst for H₂ production through advanced LTE.
- ▶ **HydroGen Interaction** – Collaborating with four National Labs and five nodes to improve fundamental understanding in OER catalyst development.

Operating principle of PEMWE



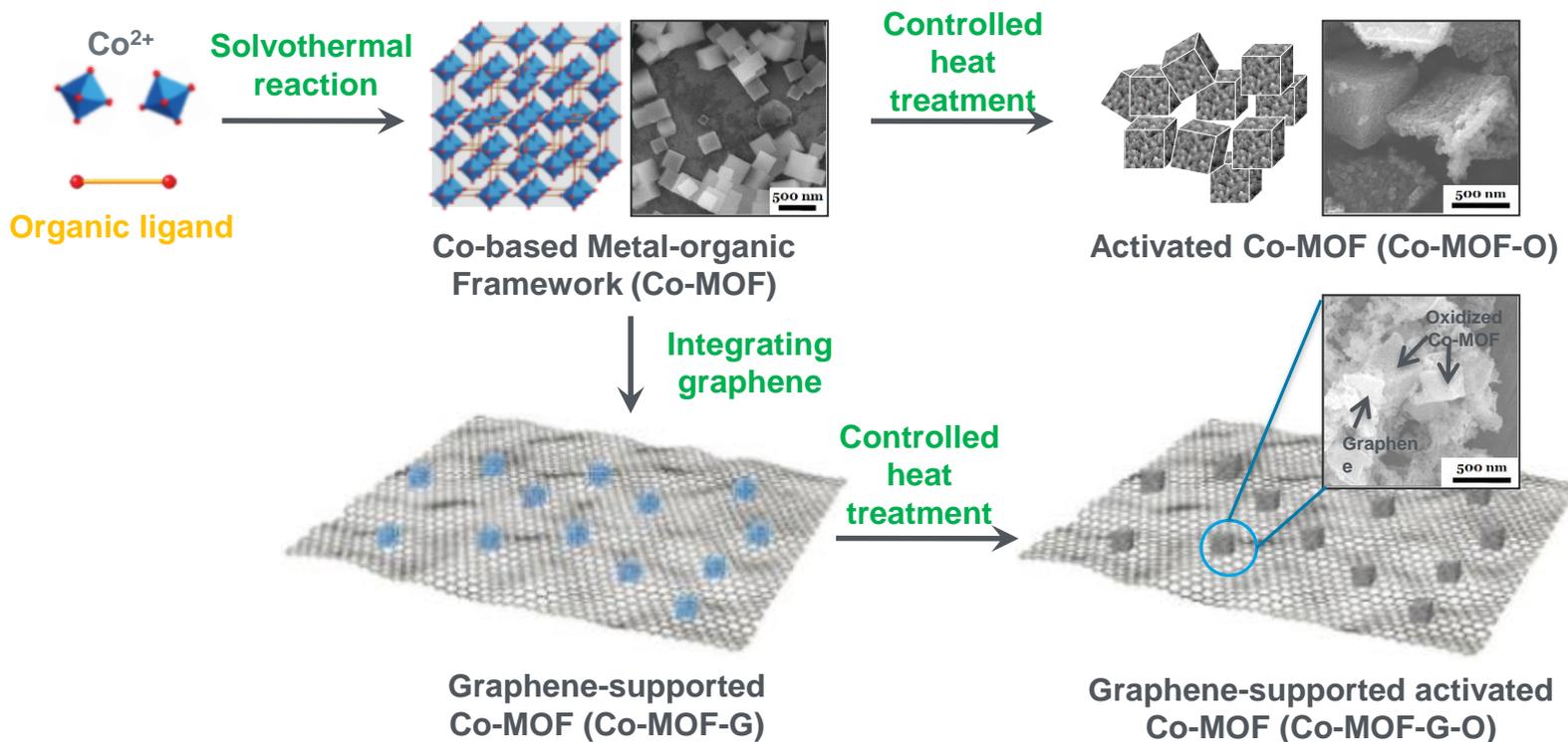
- High conductivity & smaller footprint
- Quick response for renewable sources
- High H₂ purity & non corrosive electrolyte

To demonstrate high performance, low cost PGM-free OER catalyst in operating PEMWE



Approach – Innovation @ ANL

ANL-a: Co-MOF Derived OER Catalyst



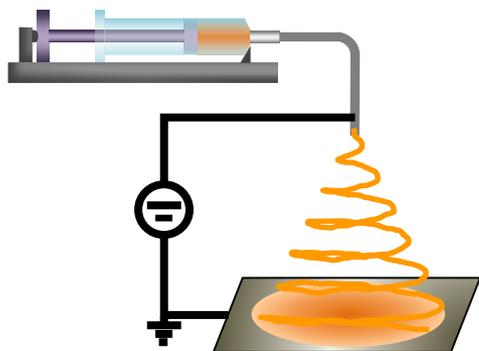
- MOF synthesis offers an inexpensive and versatile approach for multi-metallic catalyst development through low-cost metal and ligand exchange
- Framework offers maximal density and exposure of the active site through intrinsic porous structure



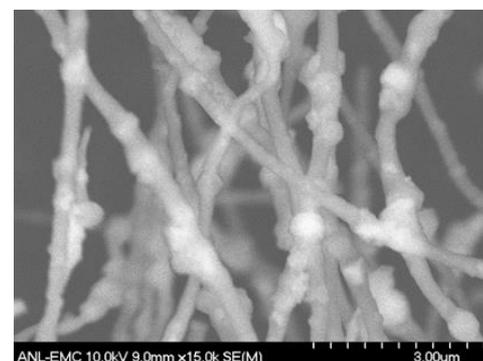
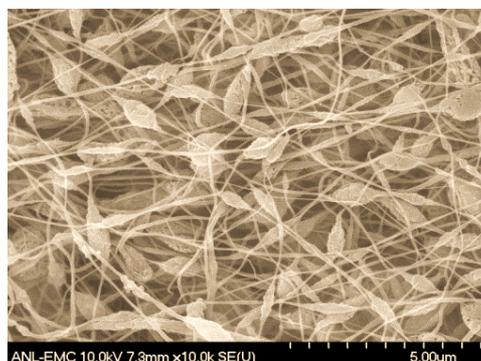
Approach – Innovation @ ANL

ANL-b: Porous Nano-Network Electrocatalyst (PNNE)

Electrospinning



Catalyst Conversion

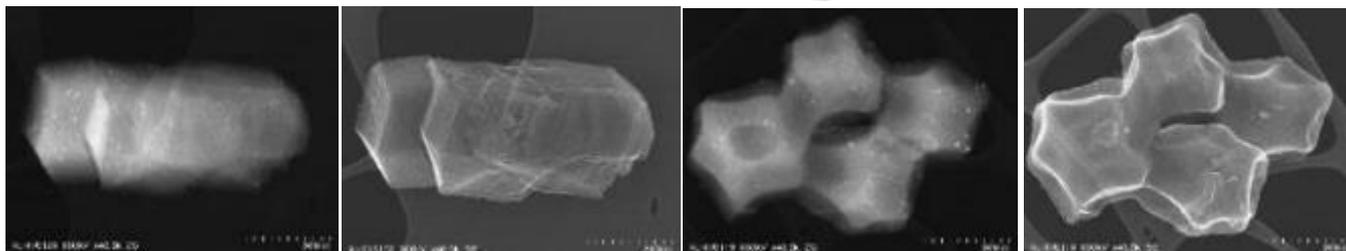
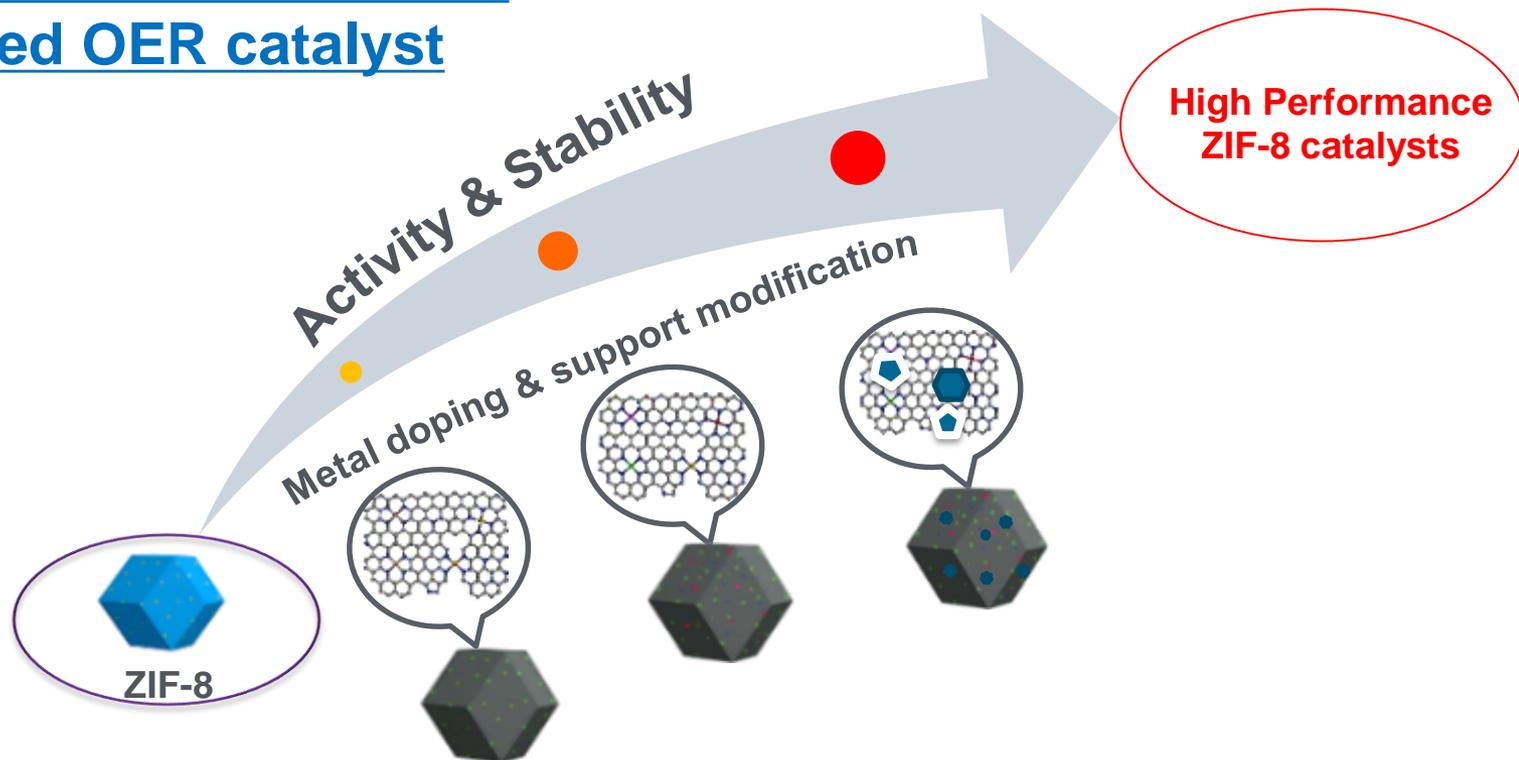


- MOF embedded PNNE can improve mass/charge transfers via direct macro-to-micropore connection
- Continuous network offers better connectivity between the catalytic site against deactivation by oxidative corrosion



Approach – Innovation @ UB

Zeolitic Imidazolate Framework (ZIF-8) based OER catalyst



University at Buffalo
The State University of New York



Approach – Budget Period 2 (BP2) Milestones

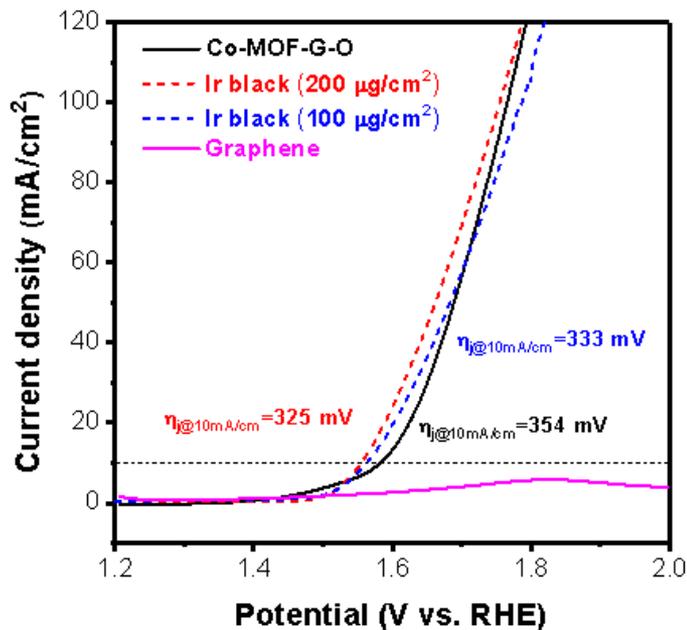
Milestone Description	Criteria	End Date	Status
MOF templated synthesis for bimetallic and multi-metallic catalysts	Prepare and test at least 4 bimetallic PGM-free OER catalysts by RDE at ANL and UB. Fabricate selected catalysts into MEA and test in PEM electrolyzer at Giner.	12/28/2018	<i>80% Completed.</i> Recent PEMWE tests of MEA containing ANL's PGM-free OER catalysts delivered a record current density of 320 mA/cm ² at 1.8 V.
Catalyst structure, morphology and active site characterizations	Complete structural studies using a variety of analytical tools to better understand catalytic activity and aging mechanism for PGM-free OER catalyst in the acidic environment resulting in mitigation strategies for decreasing degradation rates	3/31/2019	<i>70% completed:</i> Extensive studies using XRD, XAS, TEM, EDX, EELS, have been completed for two major ANL catalysts. DFT calculation shows improved understanding on catalyst conductivity
New Co-based PNNE catalyst and Fe-MOF derived catalyst and MEA fabrication and optimization	Complete the synthesis and preparation >six MEAs containing PNNE OER catalyst or Fe-MOF based OER catalyst to be delivered to Giner for PEME test with MEA performance targeting at current density > 350 mA/cm ² at 1.8 V.	6/28/2019	<i>20% completed.</i> Two new PNNE-MOF catalysts were prepared by ANL. UB sent an OER catalyst to Giner for PEME test.

- **Both ANL-a and ANL-b delivered PEM electrolyzer current density of > 200 mA/cm² @ 1.8 V, exceeding BP 1 goal.**
- **BP2 goal includes doubling current density of > 400 mA/cm² @ 1.80 V in activity, and reducing voltage loss of < 100 mV after 100 voltage cycles in durability.**



Accomplishments – ANL-a Catalysts Exceed PGM-free Benchmarks & Approach to Ir Black

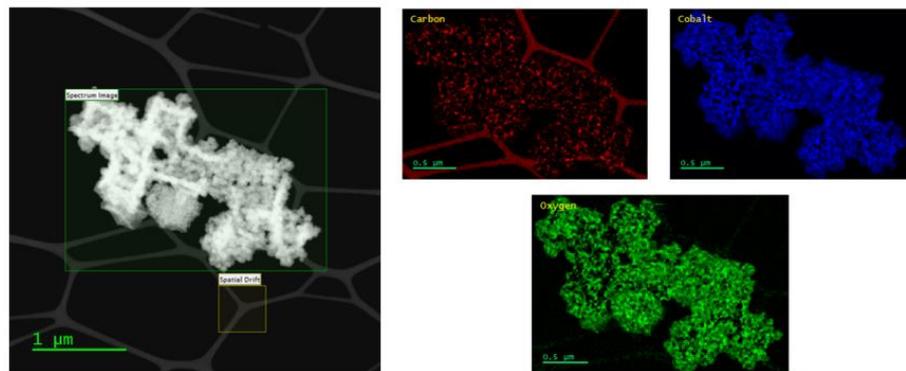
Activity of ANL-a catalyst approaches to Ir black in acidic electrolyte...



... and exceeded PGM-free benchmarks.

Catalysts	Overpotential @10mA/cm ²	Ref.
Co-MOF-Gra-O	354 mV	This work
Ba[Co-POM]	361 mV	Nat. Chem., 2018
Co ₃ O ₄	570 mV	Chem. Mater., 2017

The activated catalyst maintained the morphology of the MOF precursor

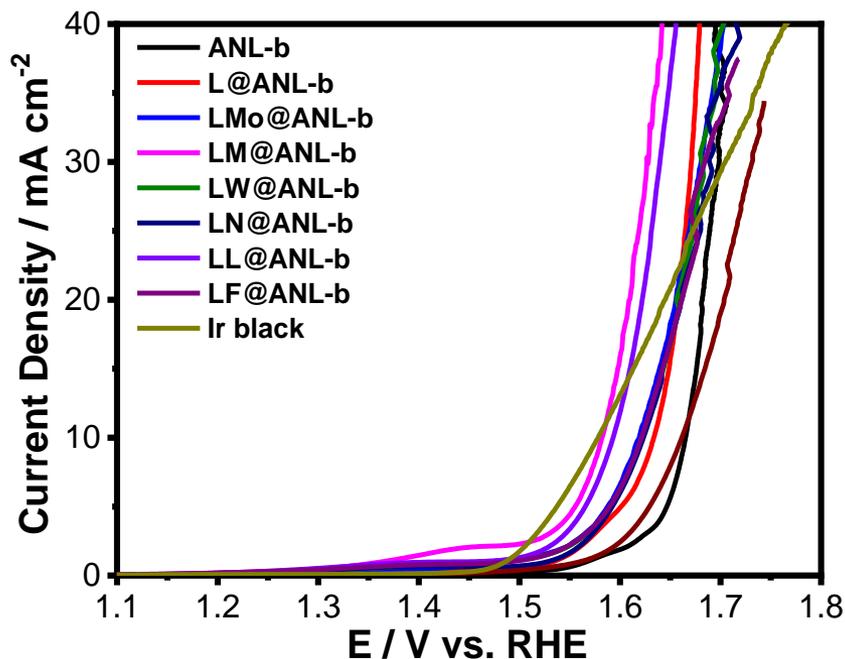


- ANL-a demonstrated lower OER overpotential than several PGM-free catalysts reported in the literature, measured by RDE/half-cell under similar condition.
- OER potential of ANL-a at 10 mA/cm² is only 20 mV to 30 mV higher than that of Ir black.

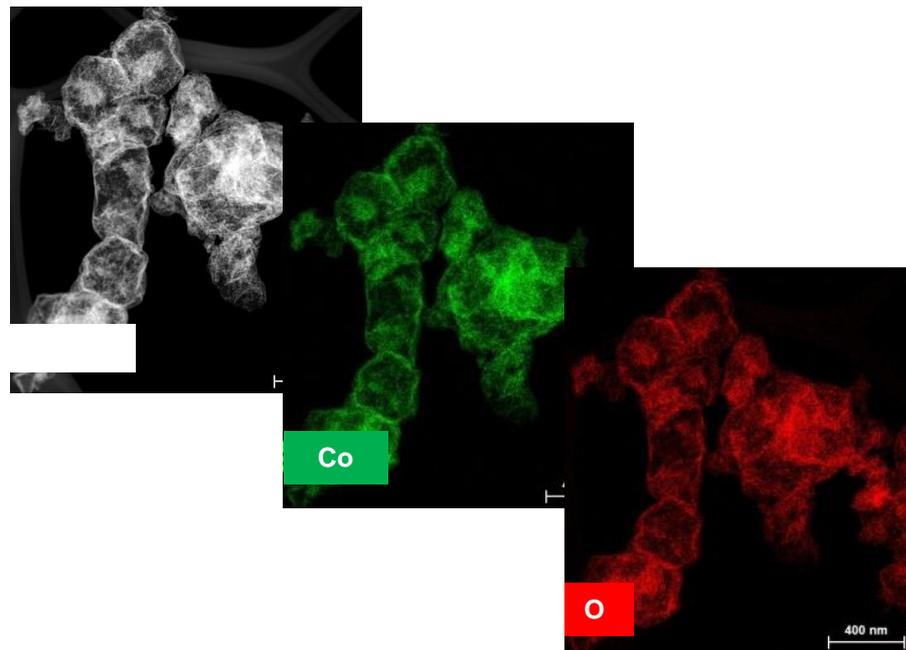


Accomplishment – ANL-b Catalysts Exceed PGM-free Benchmarks & Approach to Ir Black

Adding 2nd and 3rd metal into Co-MOF/PNNE led to consistent improvement of OER catalytic activity for ANL-b.



ANL-b catalyst showed interconnected porous framework with better active site exposure & improved transports.

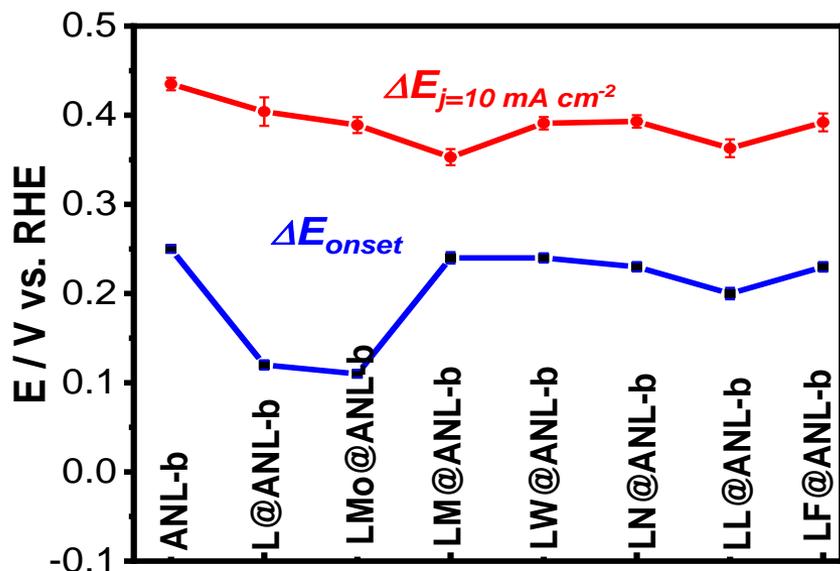


- Multiple bimetallic and trimetallic catalysts were systematically investigated for ANL-b family, which showed a progressive improvement in OER activity.
- The best ANL-b catalyst has the OER potential of only a few mVs above Ir at 10 mA/cm², measured by RDE in perchloric or sulfuric acid

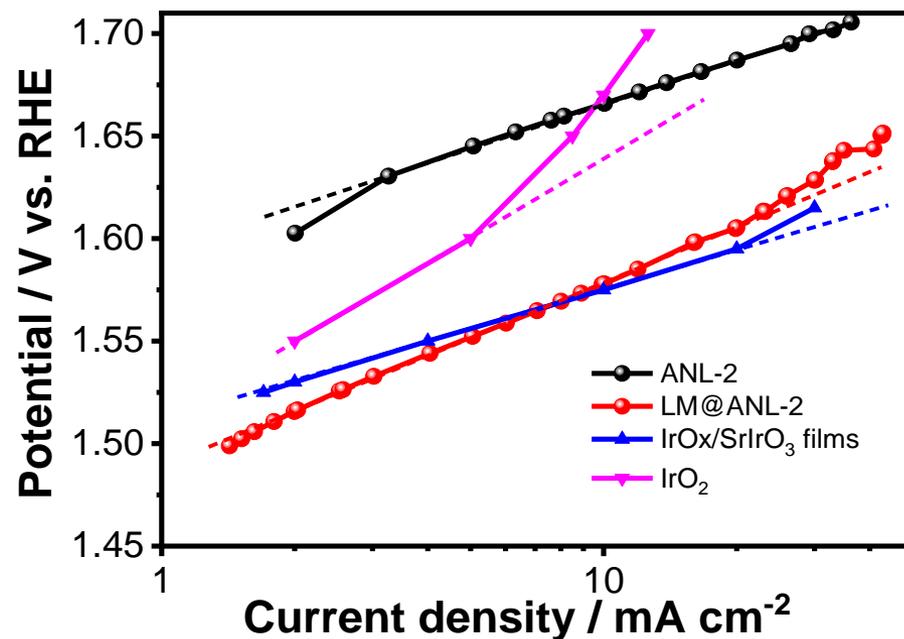


Accomplishment – OER Activity & Kinetics of Selected ANL-b Catalysts

Differences of ANL-b OER potentials over the theoretical value



Tafel plots of ANL-b catalysts versus Ir oxide and supported IrO_x film

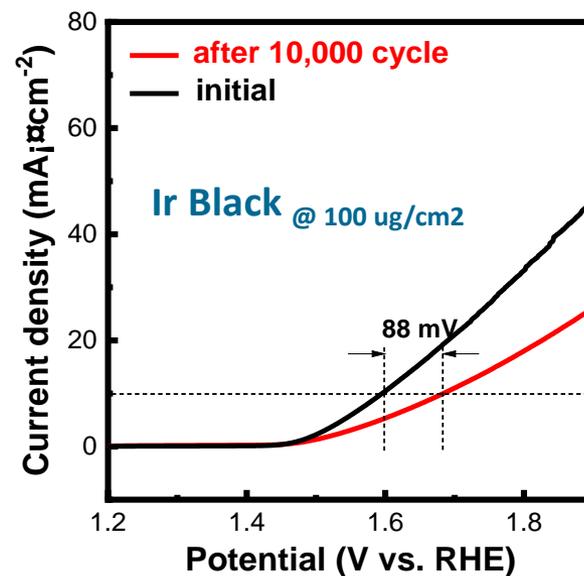
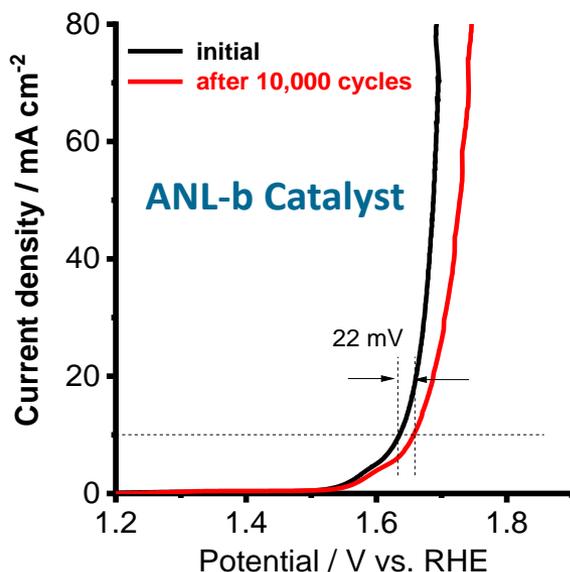
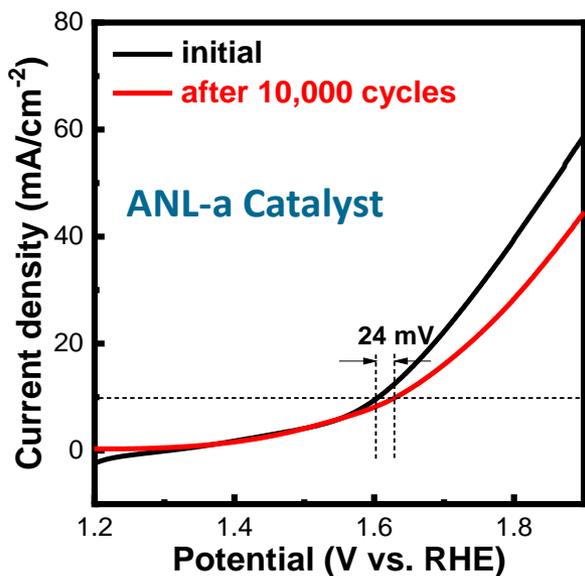


- Different metal doping in ANL-b catalyst improves surface active site structure and charge conductivity, therefore significantly enhances OER activity in strong acid
- Low Tafel slope of ANL-b catalysts shows a similar or faster kinetics compared to Ir benchmarks, which can be attributed to the nanofibrous morphology



Accomplishment – Durability of ANL PGM-free OER Catalysts

Catalyst OER polarizations before & after 10,000 voltage cycles in RDE

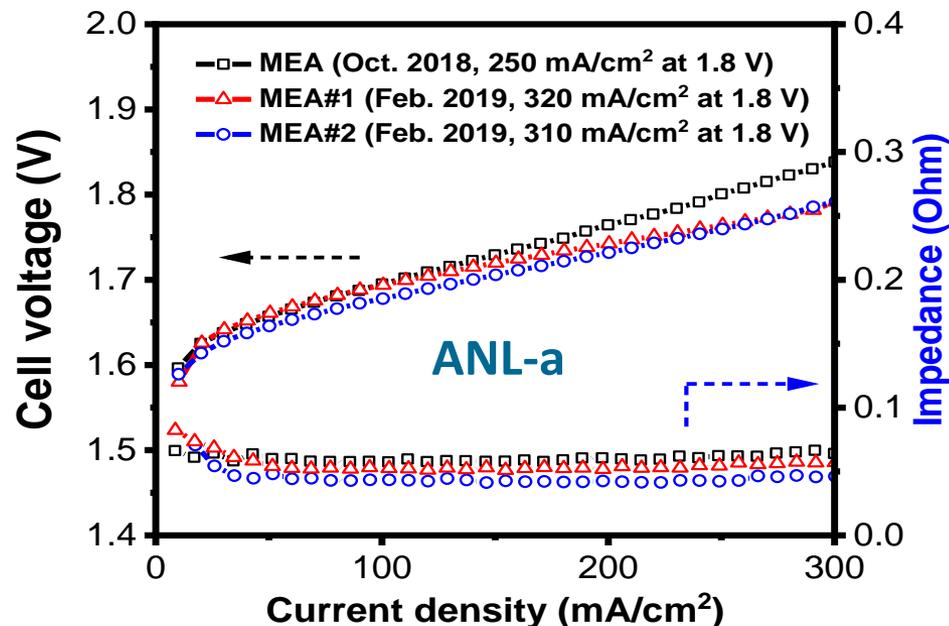


- ANL-a and ANL-b showed only small voltage lost of 24 mV and 22 mV @ 10 mA/cm^2 after 10,000 voltage cycle from 1.2 V to 2.0 V, respectively.
- Both catalysts demonstrated better stability than low-loading Ir black @ 100 $\mu\text{g}/\text{cm}^2$ (88 mV) under the same cycling condition.
- Demonstration of catalyst durability in PEMWE is planned for the next step.

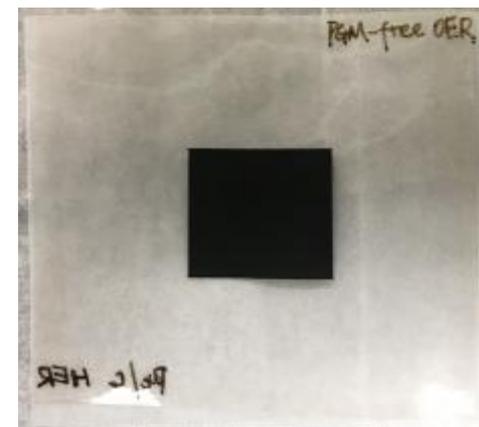


Accomplishment – Membrane Electrode Assembly (MEA) Development & Testing

- ANL-a & ANL-b catalyst MEA design & optimization were carried out at ANL.
- Over 25 MEAs were prepared and tested in PEMWE at Giner.



Anode = ANL-a PGM-free catalyst, 2mg/cm², Cathode = Pt/C, 0.35 mg/cm², Membrane = N115, 5 cm² cell, CCM, Testing condition 60 °C, 10 psi DI water at anode



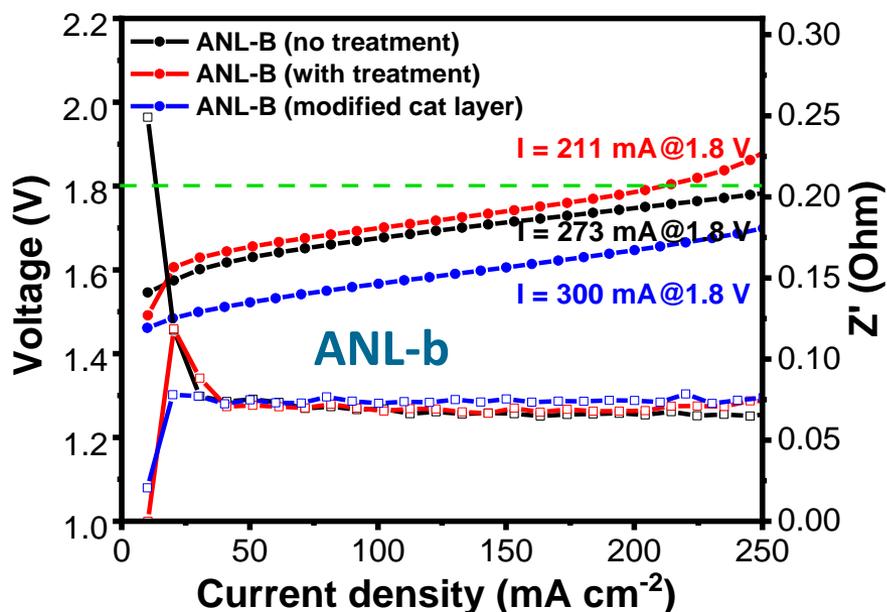
MEA coated with ANL-a PGM-free OER catalyst at anode

We demonstrated, for the first time, that an operating PEMWE with PGM-free anode catalyst delivered a current density > 300 mA/cm² @ 1.8 V, exceeding BP 1 goal!



Accomplishment – Membrane Electrode Assembly (MEA) Development & Testing

- PGM-free OER catalyst has different conductivity and surface properties from conventional FC catalyst, requiring new MEA processing conditions.
- Multiple processing parameters (catalyst loading, ionomer ratio, etc.) influence MEA performance.



Anode = ANL-a PGM-free, $\sim 1 \text{ mg/cm}^2$, Cathode = Pt/C, 0.25 mg/cm^2 , Membrane = N115, 5 cm^2 cell, CCM, 60°C , 10 psi DI water



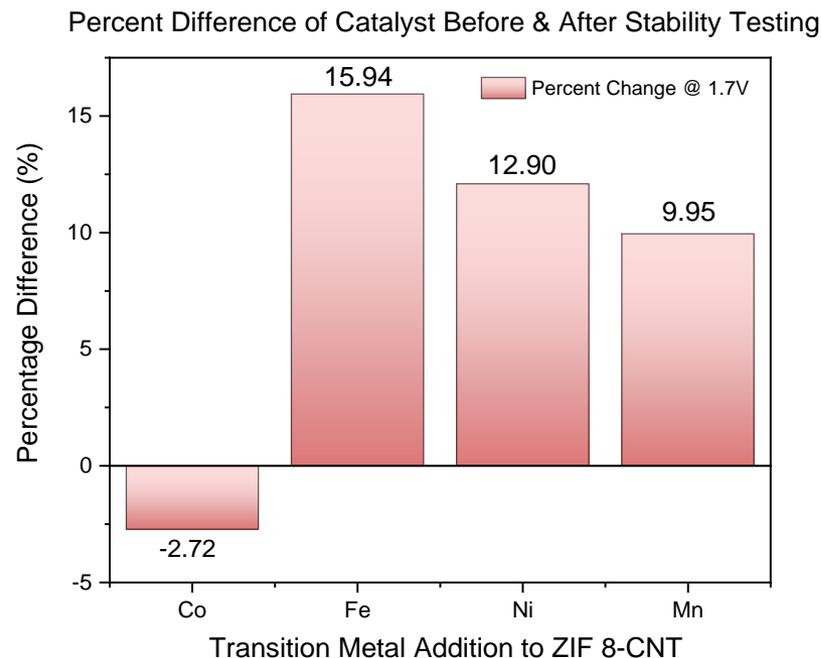
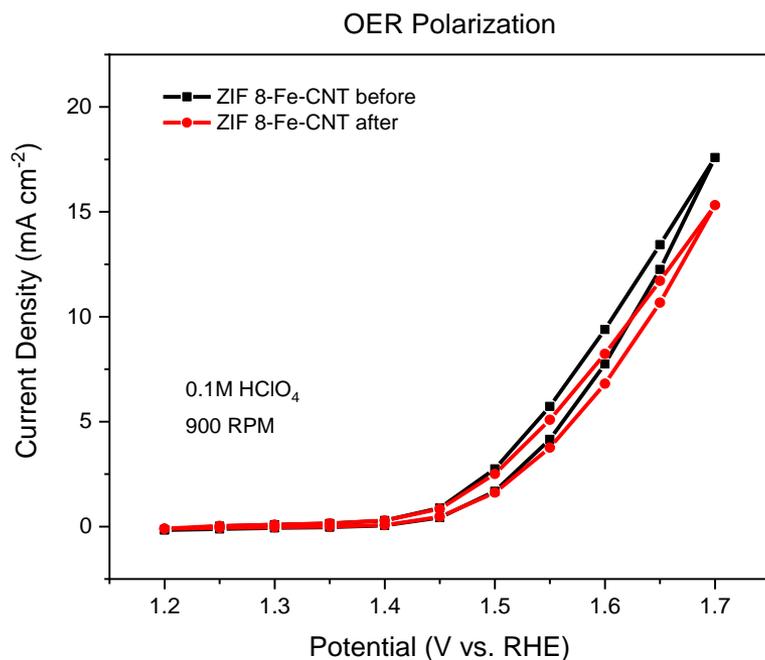
PEMWE setup at Giner

ANL-b catalyst also delivered $\sim 300 \text{ mA/cm}^2 @ 1.8 \text{ V}$ in operating PEMWE



Accomplishment – ZIF-8 Derived OER Catalysts @ UB

- Addition of TM & carbon nanotubes (CNT) in ZIF-8 increased catalyst durability and activity during 1000 polarization sweeps in 0.1M HClO₄.
- Adding urea further improved OER stability for Fe, Co, Mn, Ni doped ZIF 8

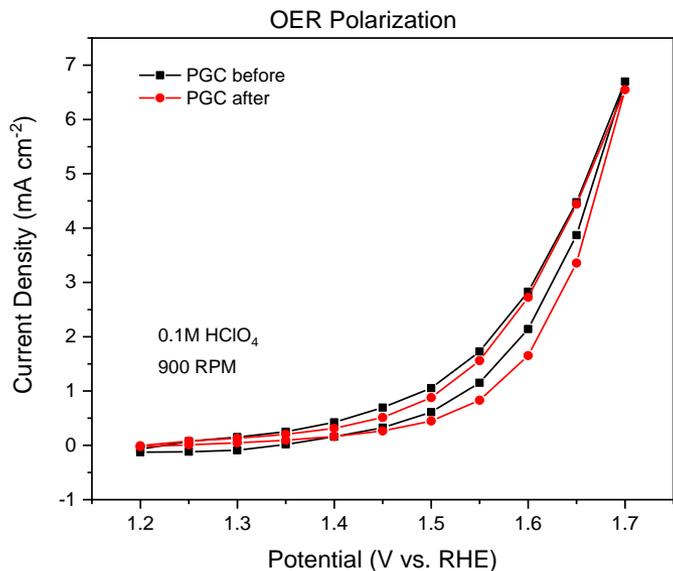


- UB's MOF catalysts show continuous improvement in OER activity and stability in acid solution
- A new catalyst has been prepared and shipped to Giner for PEMWE test

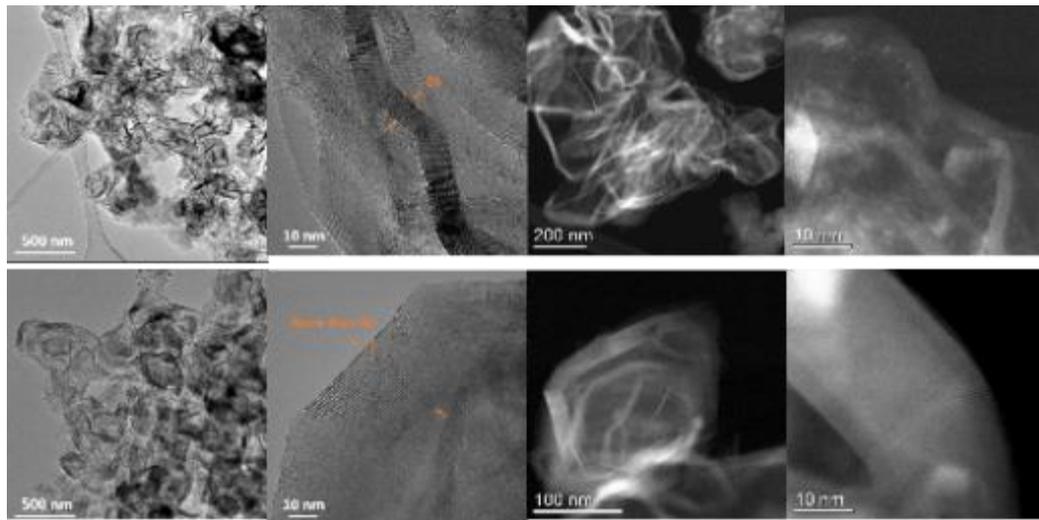
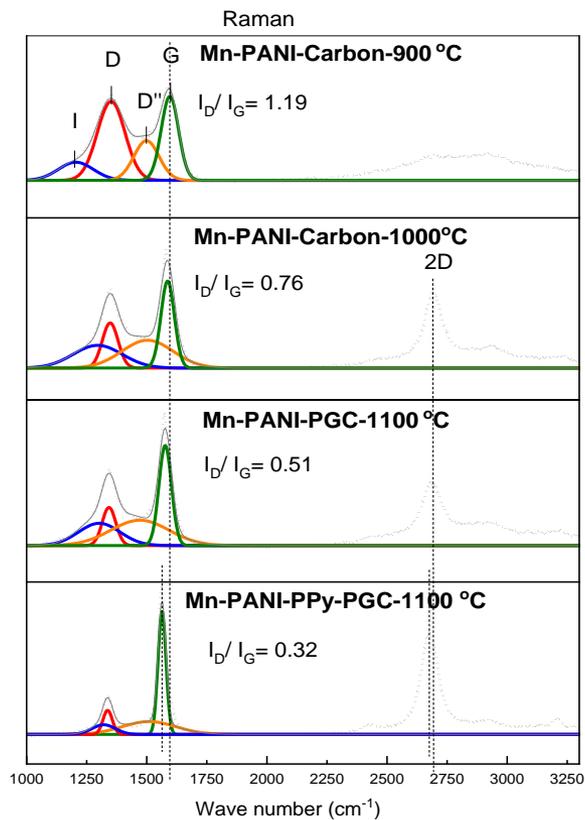




Accomplishment – New Polymer Scaffold for PGM-free Catalysts Developed @ UB



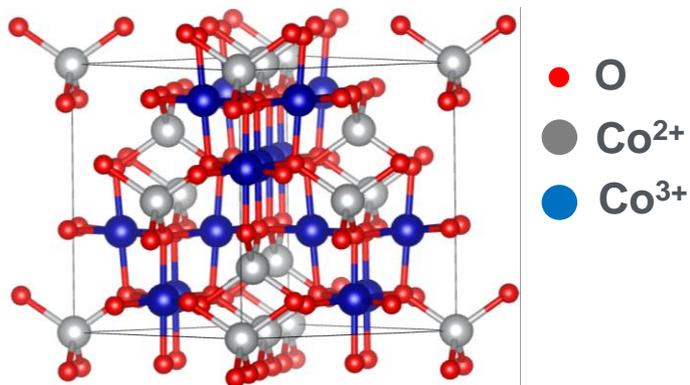
- UB's team also developed a polymer scaffold (PGC) approach showing promise in further improving activity and stability for OER in acid



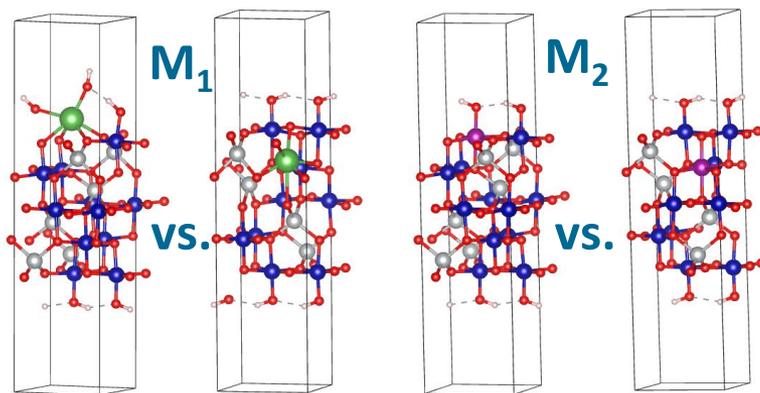


Collaboration with HydroGen @ LBNL – Modeling on Nature of Catalyst Stability & Conductivity

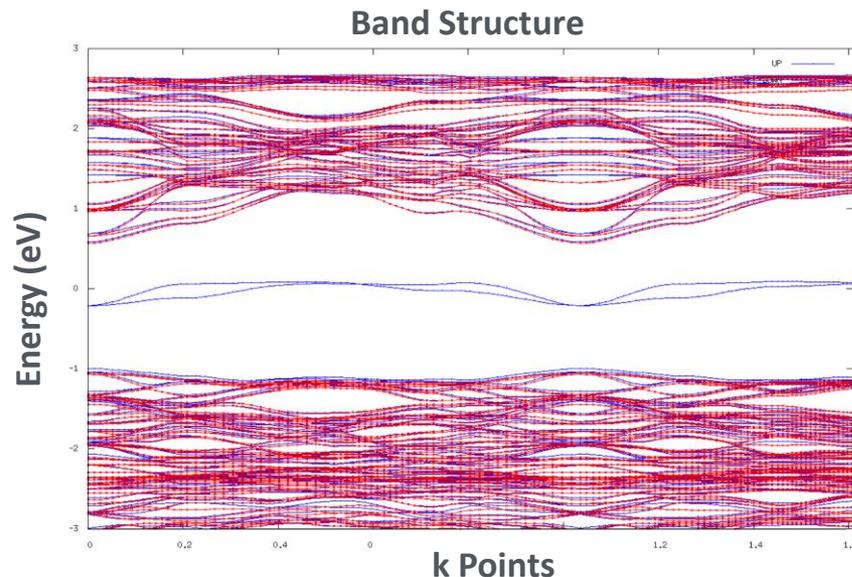
Conductivity change in catalyst by 2nd element doping



ΔE analysis on 2nd metal distribution in bulk vs. surface



In-gap valence state induced by 2nd element

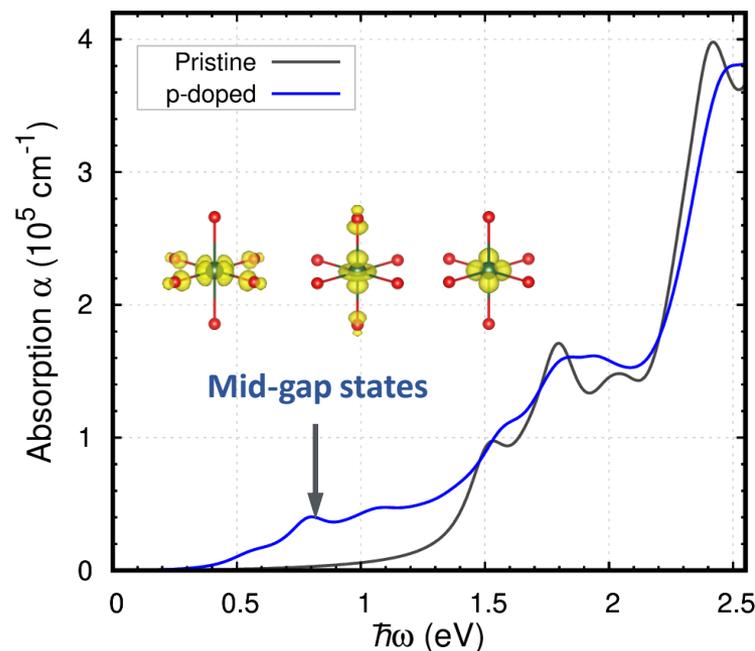
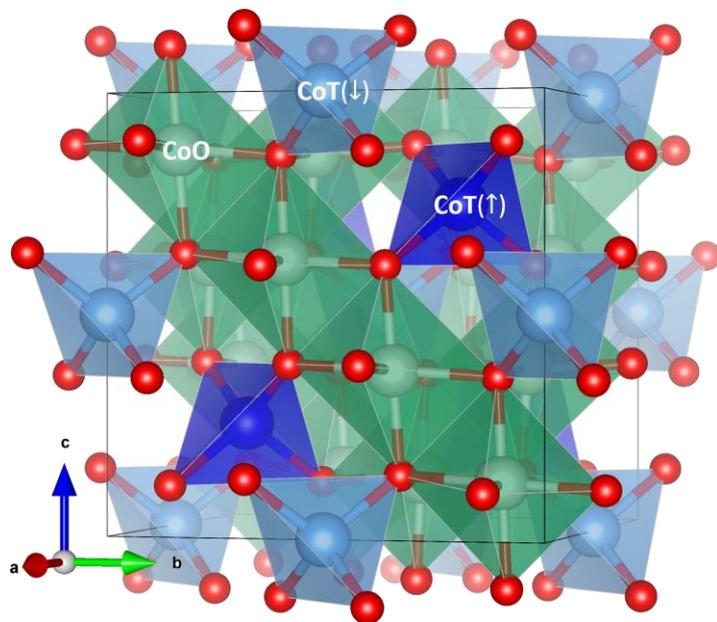


- The M₂ in oxide lattice introduce a half occupied in-gap state, enhancing electric conductivity
- Energy optimization found that 2nd ion distributes differently based on size & charge, impacting catalyst stability and consistent with the exp'l observation



Collaboration with HydroGen @LLNL – Simulation on Charge Transfer in OER Catalyst

Understanding of electronic properties on ANL OER catalyst through first-principle calculations

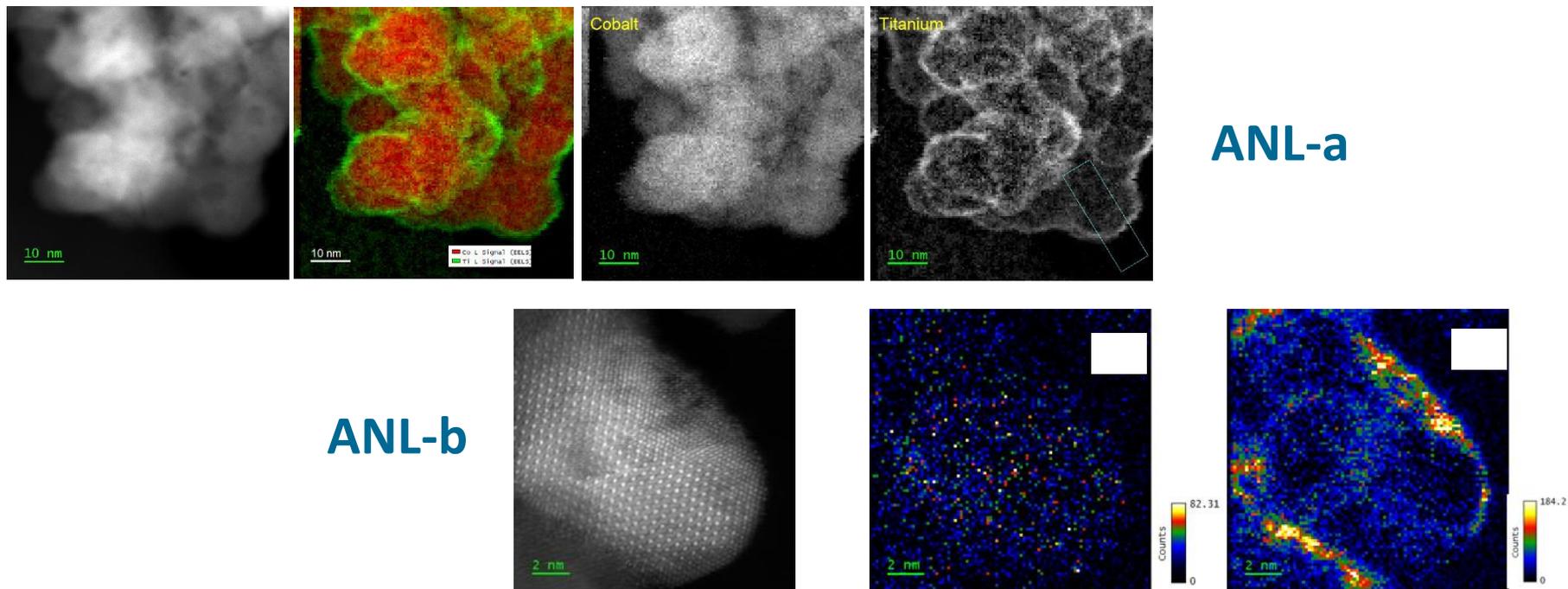


- Electronic properties for pristine and doped oxide were established, which identified the carrier conduction is governed by hole polaron hopping
- Formation of the mid-gap states is due to the hole polaron formation



Collaboration with HydroGen @ SNL – Microscopic Understanding on Morphology to Performance

High resolution STEM and TEM studies on stability/activity improvements through structural modification in ANL PGM-free OER catalysts

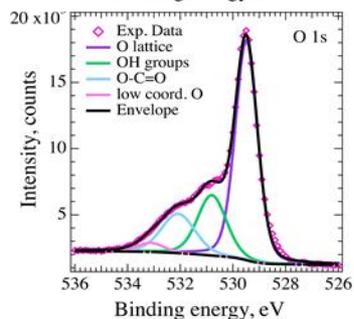
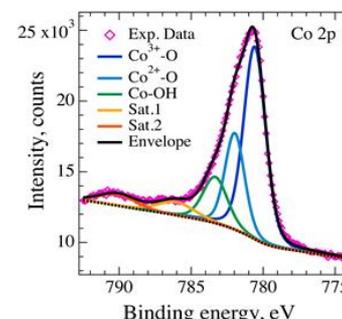
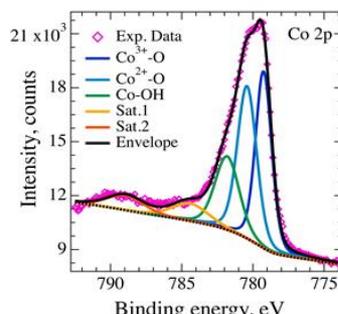
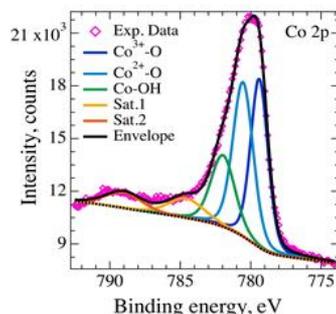
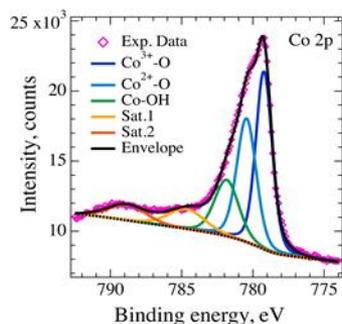


- The STEM shows a conformal TiO_2 coating of 1 to 2 nm thick surrounding ANL-a catalyst particles, serving as protective layer
- The doped metal ions distribute differently based on their sizes and charges in ANL-b, each plays its own role in promoting catalyst conductivity and stability

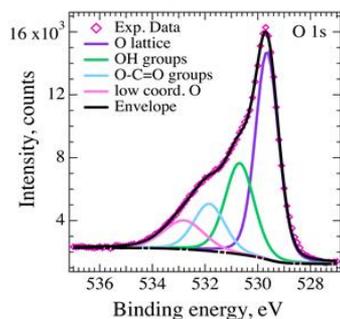


Collaboration with HydroGen @ NREL – Surface Analysis on Electronic Structure to Activity

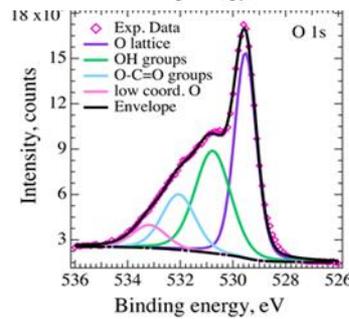
XPS analysis on elemental valance state to Co-MOF catalyst performance



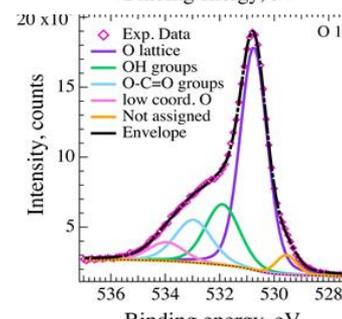
L@ANL-b



LF@ANL-b



LN@ANL-b



LW@ANL-b

- XPS revealed the dependence of Co valance state on the doping element in ANL's MOF-derived OER catalysts
- Comprehensive study also identified the electronic structural change of the critical elements before & after OER voltage cycling



Proposed Future Work

- Continue to explore multi-metallic MOFs through reticular synthesis and post-synthesis modification to further enhance OER catalyst activity and durability in RDE/PEMWE (ANL/UB)
- Continue to investigate the OER catalysts with porous nanofiber network morphology to further improve activity and durability in MEA/PEMWE (ANL)
- Explore surface metal doping (SMD) and atomic layer deposition (ALD) methods to improve PGM-free catalyst stability (ANL)
- Continue to explore metal doping in ZIF-8 and polymer scaffold (PGC) approaches with focus on catalyst activity and durability test in PEMWE (UB)
- Continue to optimize anode design and fabrication to further improve MEA performance in operating PEMWE (ANL/UB/Giner)
- Initiate the MEA/PEMWE durability study using potential cycling (ANL/Giner)
- Continue to improve fundamental understanding on the structure-function relationship of PGM-free OER catalysts using computation modeling and advanced characterization tools through collaboration with HydroGen

BP2 activities will be centered on catalyst performance in operating PEMWE



Project Summary

- Both ANL-a and ANL-b OER catalysts showed excellent activities compared to PGM-free benchmarks, with performance approaching to that of Ir black
- ANL's OER catalysts also demonstrated promising durability in acidic electrolyte through RDE/halfcell voltage cycling when measured against Ir black
- MEAs containing ANL-a and ANL-b anode delivered current density higher than 300 mA/cm², representing the first demonstration of PGM-free OER catalyst in the operating PEMWE, and exceeded BP1 goal
- UB team continued to improve activity and durability for ZIF-based OER catalysts and developed a new polymer scaffold (PGC) approach with promising potential
- Computational modeling and structural characterizations by HydroGen nodes provided insightful understanding and critical support to the OER catalyst development

The team demonstrated, for the first time, H₂ production from a PEMWE with PGM-free anodic catalyst at practical operating potential



Acknowledgement

- ▶ Argonne National Laboratory
 - Lina Chong, Hao Wang
- ▶ University of Buffalo, SUNY
 - Janel Abbott
- ▶ Giner Inc.
 - Jason Wiley
- ▶ HydroGen Consortium
 - Lawrence Livermore National Lab (led by Tadashi Ogitsu)
 - Lawrence Berkeley National Lab (led by Lin-Wang Wang)
 - Sandia National Lab (led by Josh Sugar)
 - National Renewable Energy Lab (led by Glenn Teeter & Michael Ulsh)
- ▶ US DOE Office of Fuel Cell Technologies
 - Eric Miller – Program Manager
 - Dave Peterson – Project Manager