# PGM-free OER Catalysts for PEM Electrolyzer

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**p157**

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# Project Overview

## Team

**<u>Lead</u>:** Argonne National Laboratory

**<u>Sub</u>**: U. of Buffalo & Giner Inc.

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

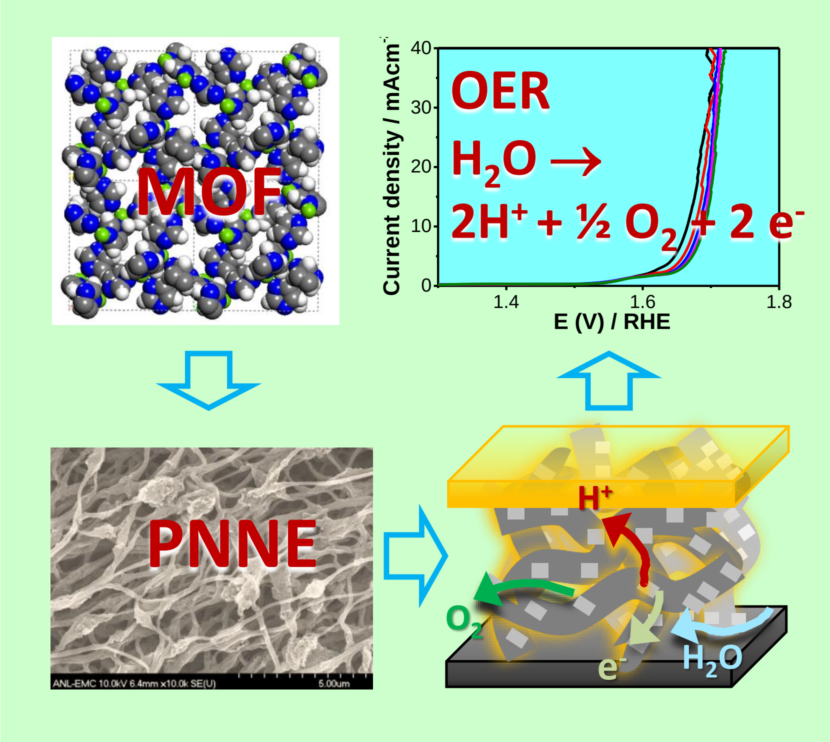
## Project Vision

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 / $kgH_2$
- System efficiency: 43 $kWh/kgH_2$




*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**

## Proposed targets

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

## 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.

## 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 $H_2$ production through advanced LTE.
- **HydroGen Interaction** – Collaborating with four National Labs and five nodes to improve fundamental understanding in OER catalyst development.

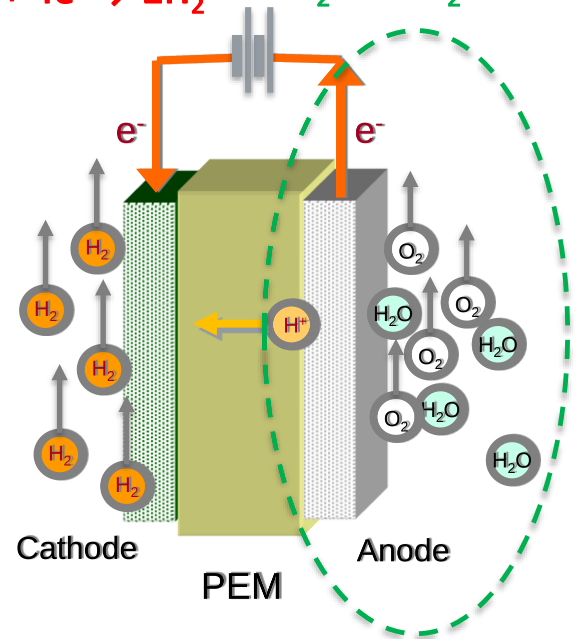
***Operating principle of PEMWE***

Cathode (HER)

$4H^+ + 4e^- \rightarrow 2H_2$

Anode (OER)

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

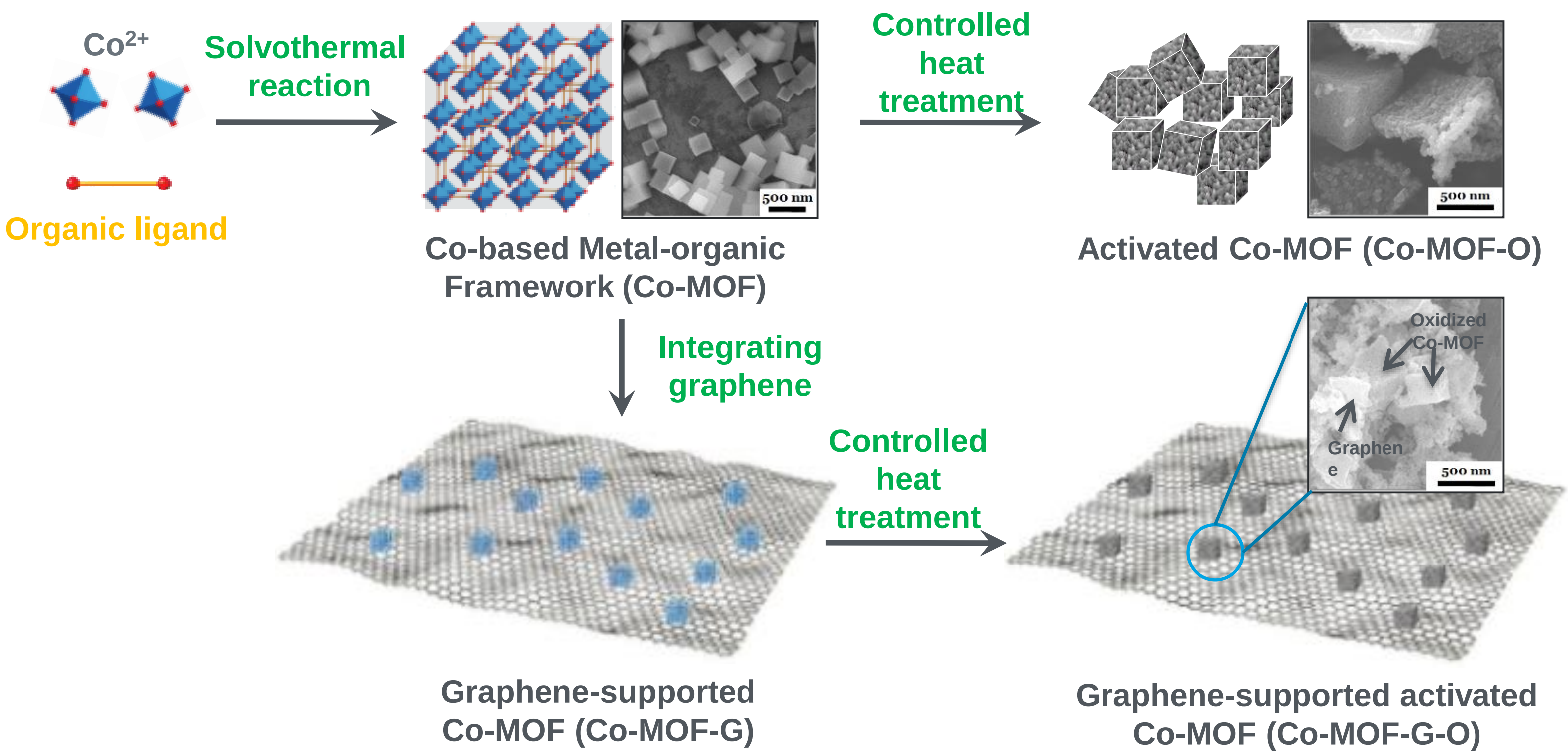



- High conductivity & smaller footprint
- Quick response for renewable sources
- High $H_2$ purity & non corrosive electrolyte

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

# Approach – Innovation @ ANL

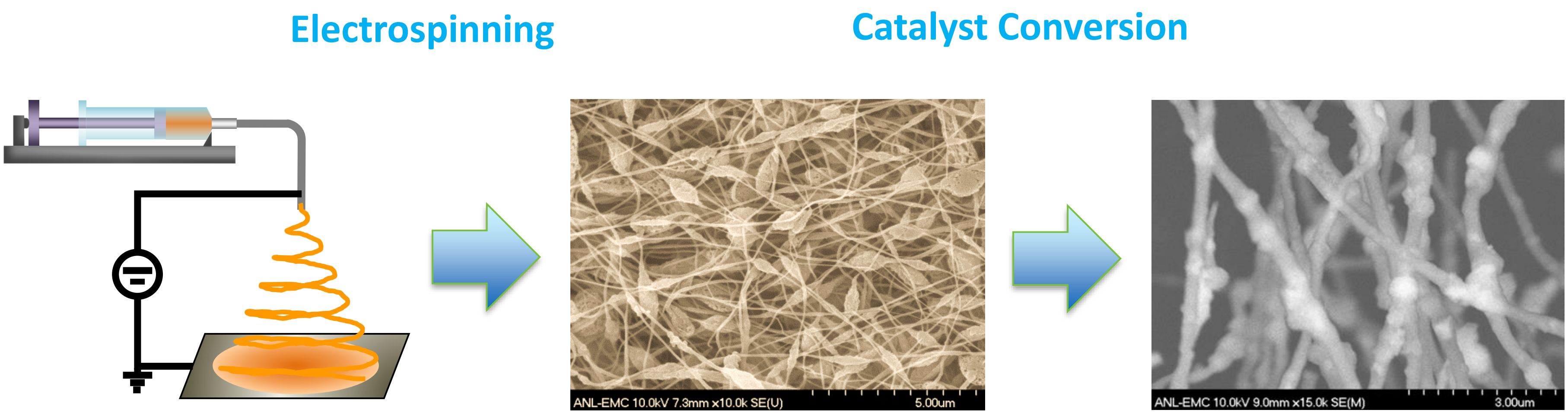
## ANL-a: Co-MOF Derived OER Catalyst




- **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

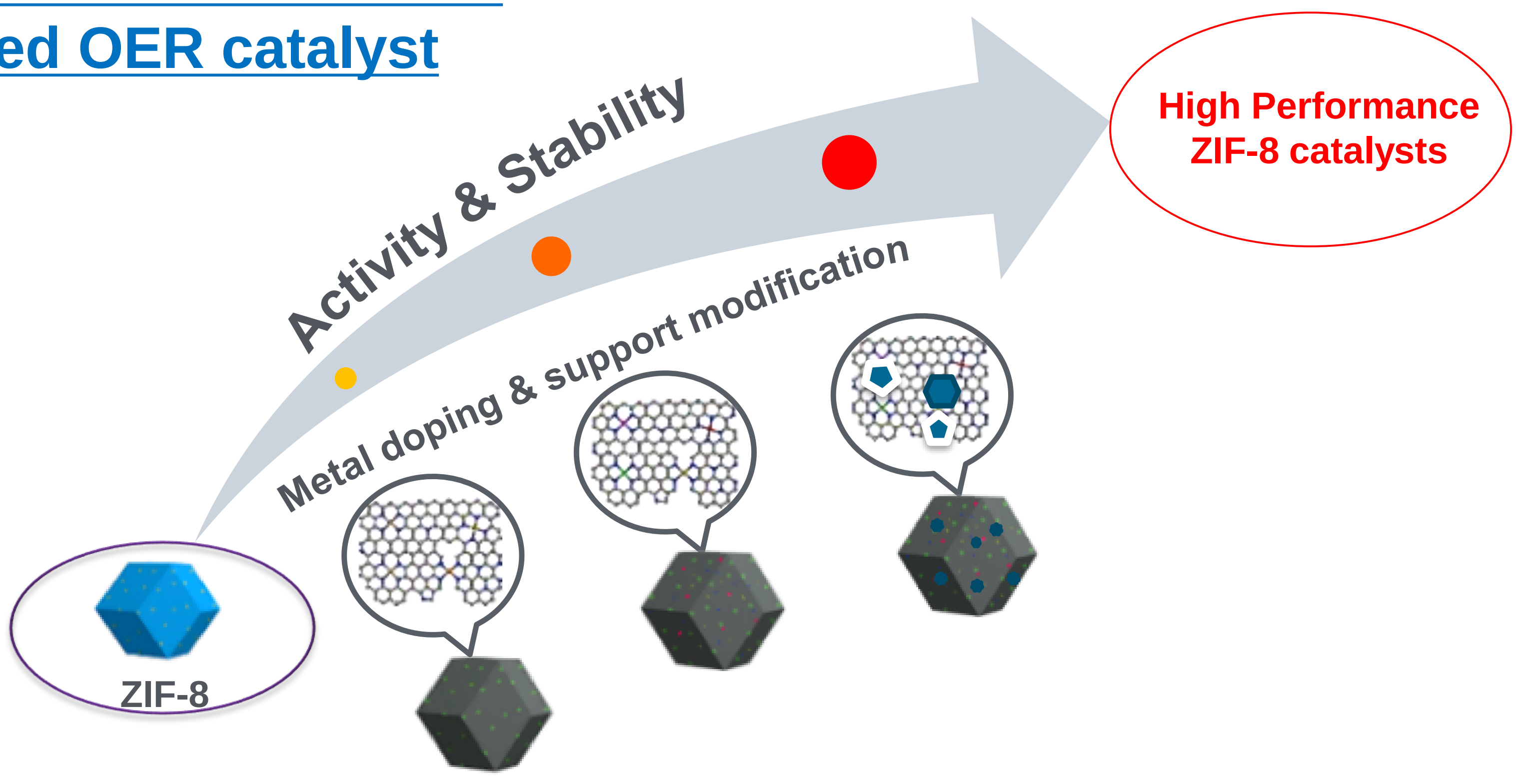
## ANL-b: Porous Nano-Network Electrocatalyst (PNNE)

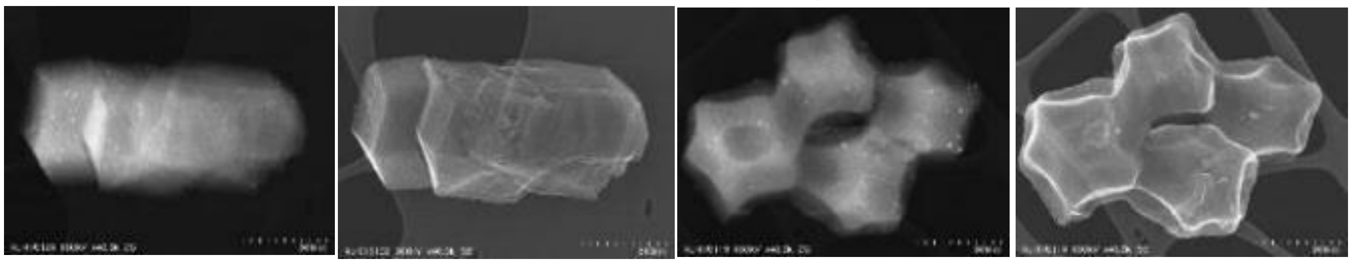



- **MOF embedded PNNE can improve mass/charge transfers via direct macro-to-micropore connection**
- **Continuous network offers better connectivity between the catalytic site against deactivation by oxidative corrosion**

# Approach – Innovation @ UB

## Zeolitic Imidazolate Framework (ZIF-8) based OER catalyst



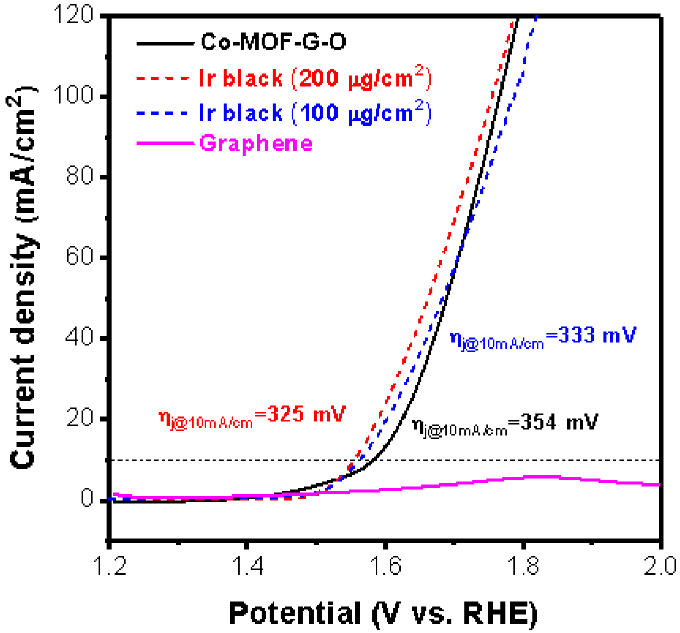
# Approach – Budget Period 2 (BP2) Milestones

| 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 | *80% Completed*. 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 | *70% completed*: 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 | *20% completed*. 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/cm$^2$ @ 1.8 V, exceeding BP 1 goal.**
- **BP2 goal includes doubling current density of > 400 mA/cm$^2$ @ 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

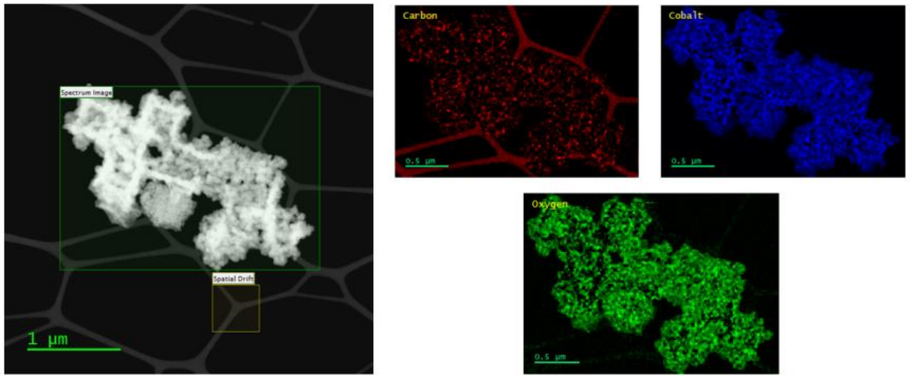
***Activity of ANL-a catalyst approaches to Ir black in acidic electrolyte…***




***… and exceeded PGM-free benchmarks.***

| Catalysts | Overpotential @10mA/cm² | Ref. |
|---|---|---|
| **Co-MOF-Gra-O** | **354 mV** | **This work** |
| Ba[Co-POM] | 361 mV | Nat. Chem., 2018 |
| $Co_3O_4$ | 570 mV | Chem. Mater., 2017 |

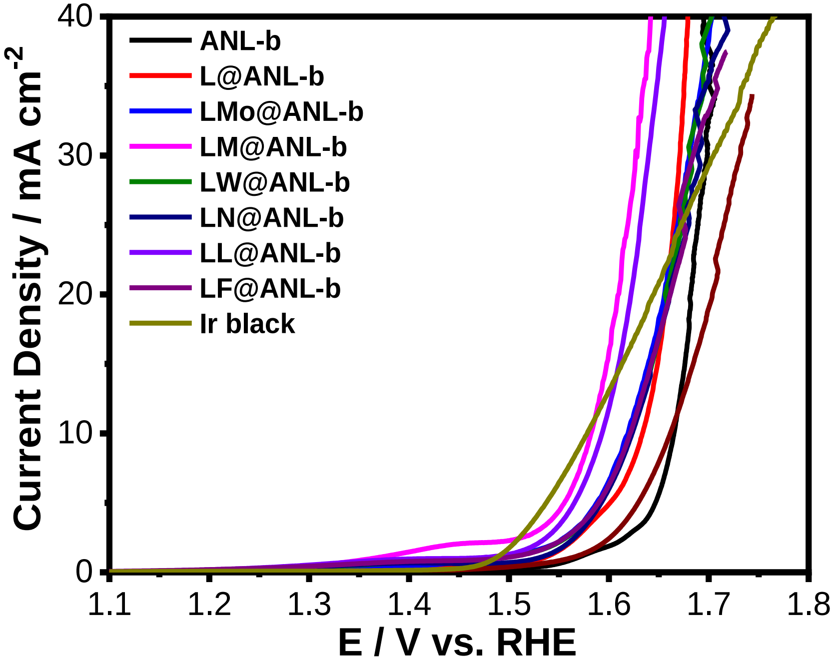
***The activated catalyst maintained the morphology of the MOF precursor***



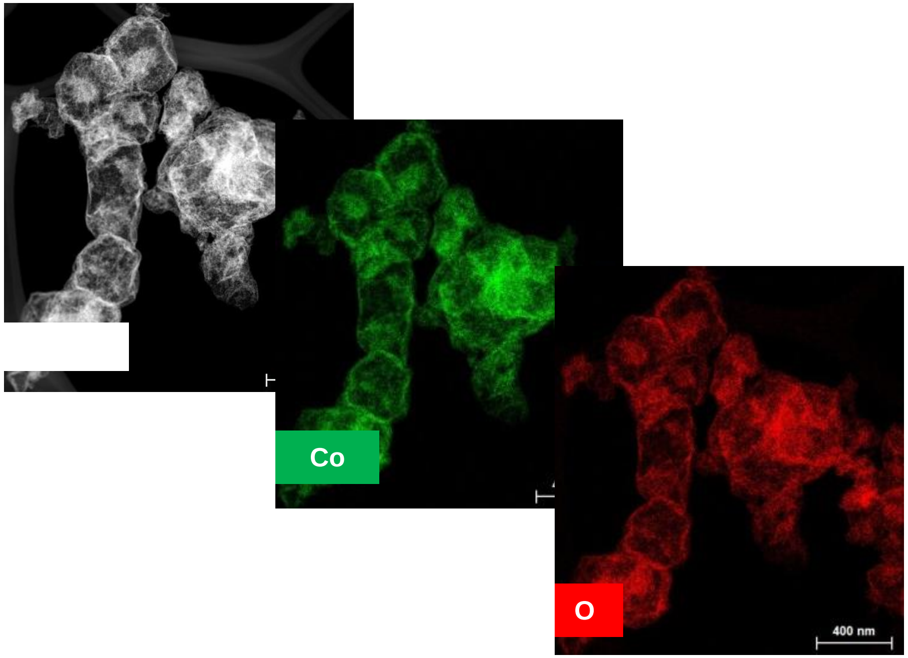

- ANL-a demonstrated lower OER overpotential than several PGM-free catalysts reported in the literature, measured by RDE/half-cell under similar condition.
- OER potential of ANL-a at 10 mA/cm² is only 20 mV to 30 mV higher than that of Ir black.

# 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.***



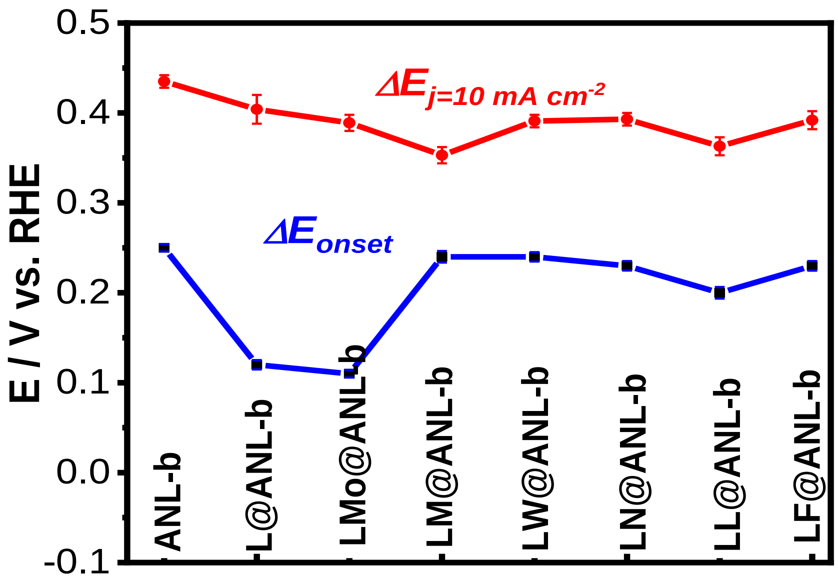

***ANL-b catalyst showed interconnected porous framework with better active site exposure & improved transports.***



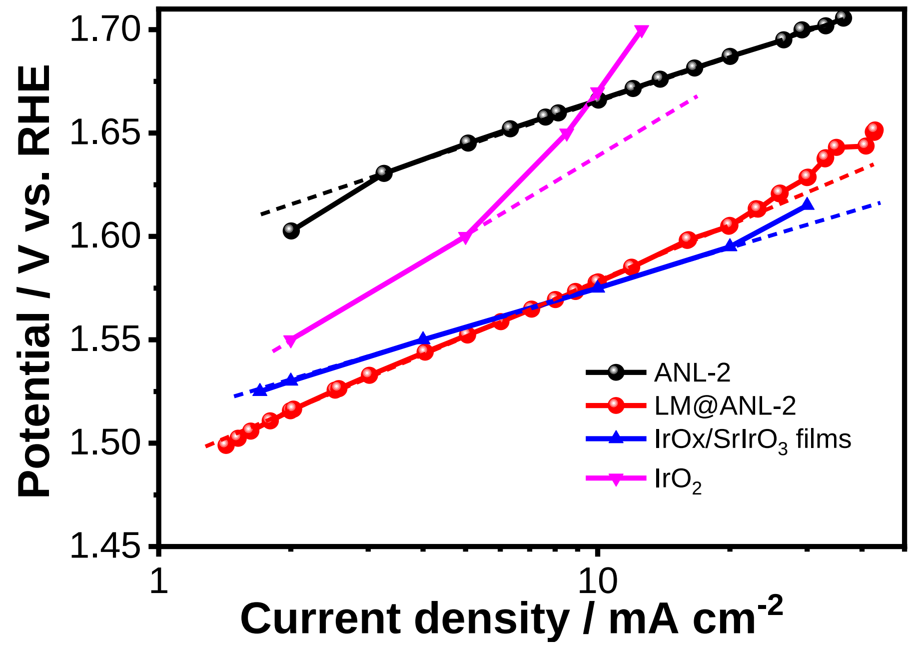

- Multiple bimetallic and trimetallic catalysts were systematically investigated for ANL-b family, which showed a progressive improvement in OER activity.
- The best ANL-b catalyst has the OER potential of only a few mVs above Ir at 10 $mA/cm^2$, measured by RDE in perchloric or sulfuric acid

# 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



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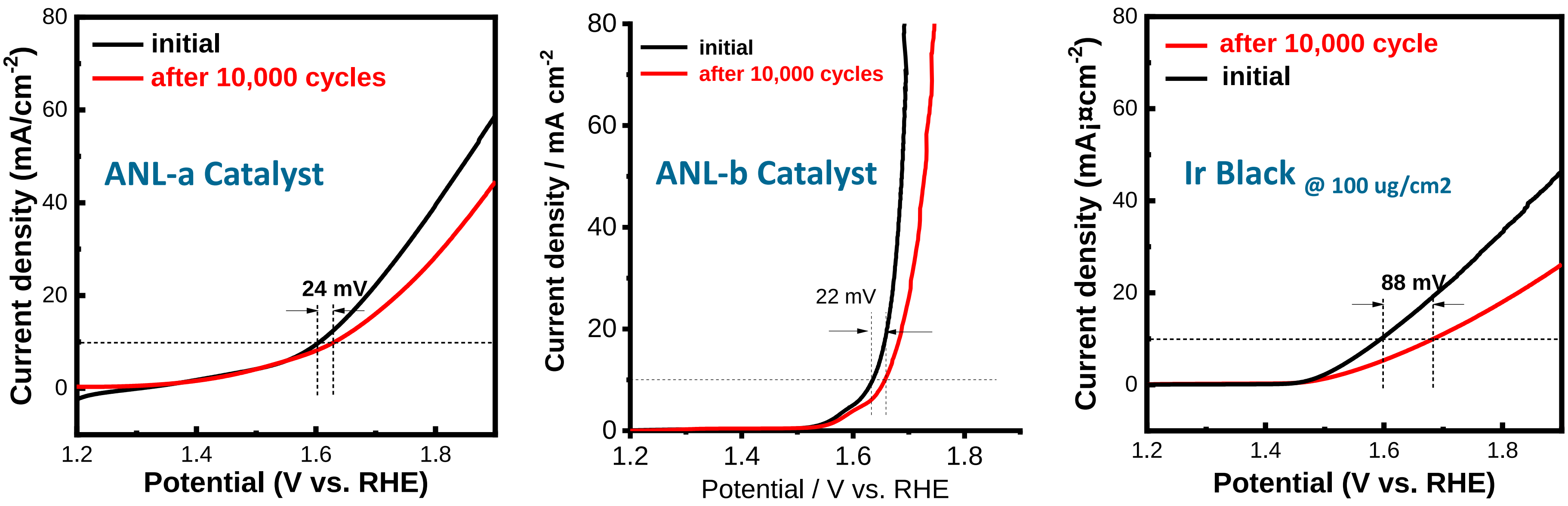
# Accomplishment – Durability of ANL PGM-free OER Catalysts

## *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 @ 100µg/$cm^2$ (88 mV) under the same cycling condition.
- Demonstration of catalyst durability in PEMWE is planned for the next step.



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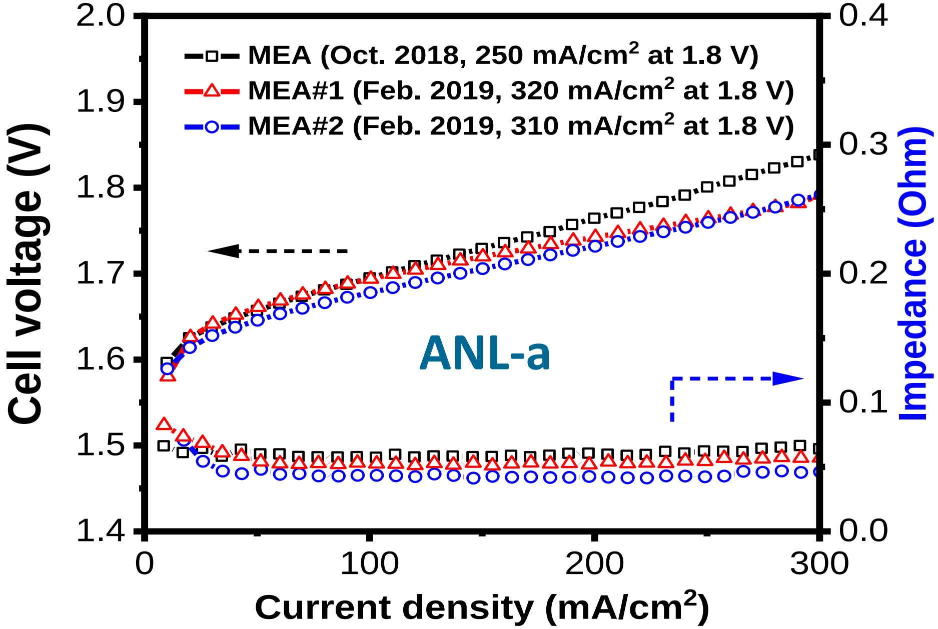
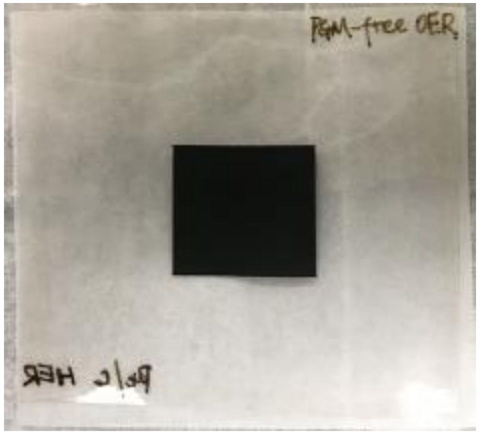
# Accomplishment – Membrane Electrode Assembly (MEA) Development & Testing

- 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

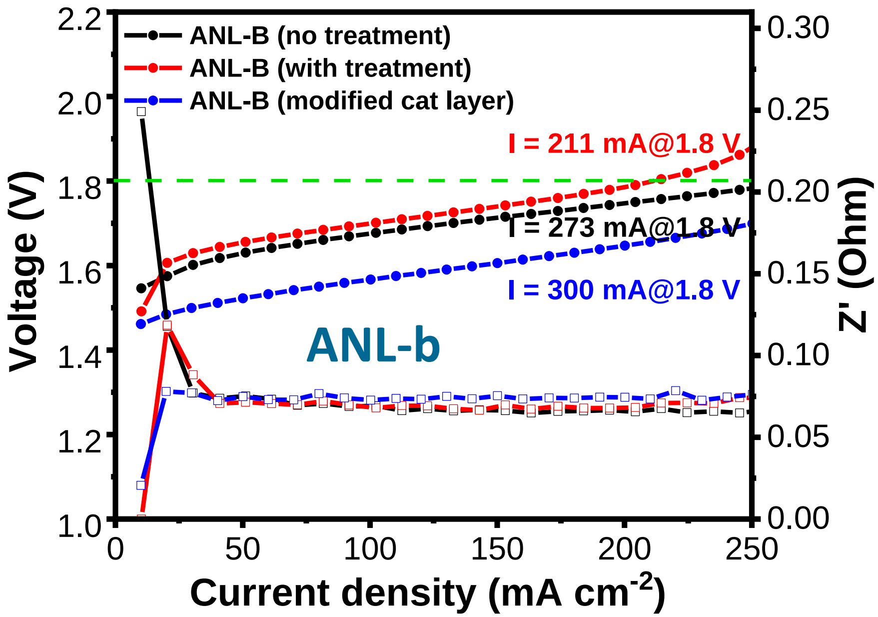



**MEA coated with ANL-a PGM-free OER catalyst at anode**

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.



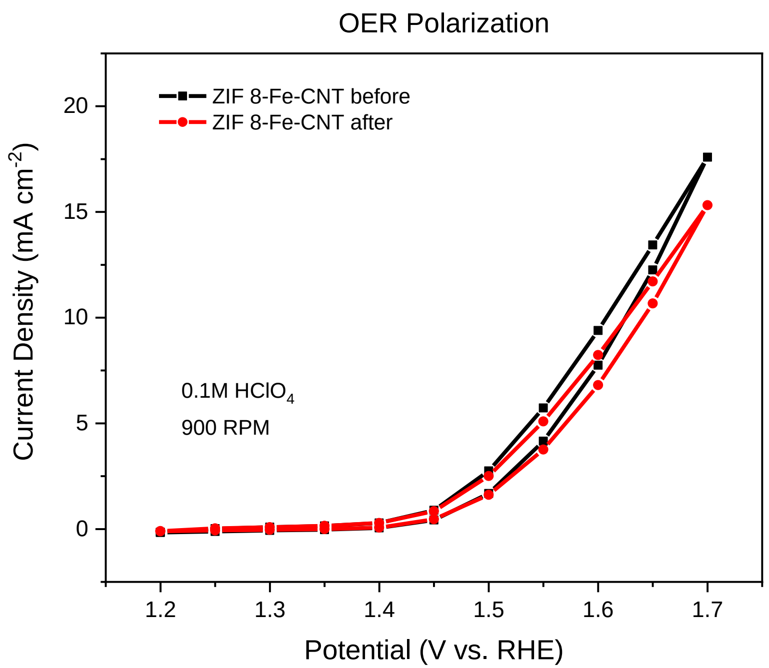

Anode = ANL-a PGM-free, ~1mg/cm$^2$, Cathode = Pt/C, 0.25 mg/cm$^2$, Membrane = N115, 5 cm$^2$ cell, CCM, 60 ˚C, 10 psi DI water

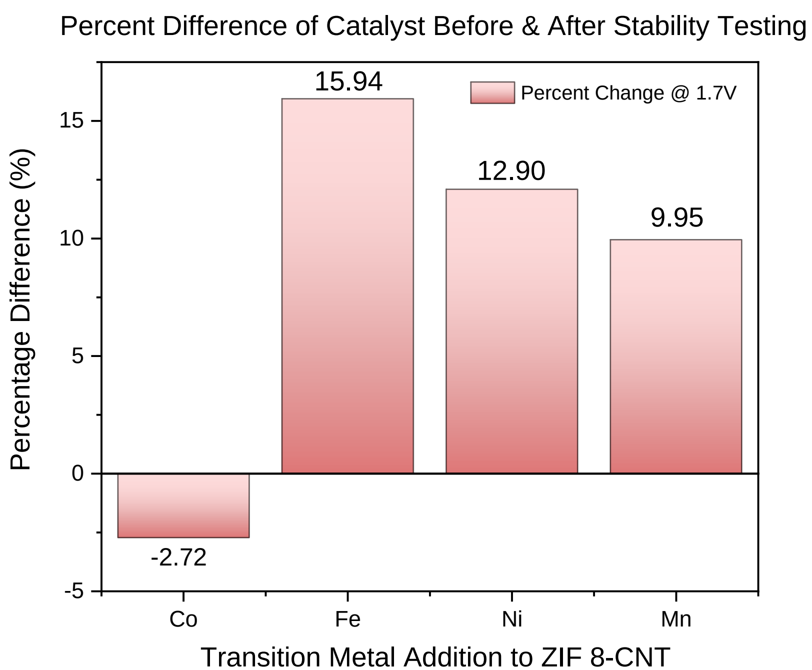

**PEMWE setup at Giner**

**ANL-b catalyst also delivered ~ 300 mA/cm$^2$ @ 1.8 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 $HClO_4$.
- Adding urea further improved OER stability for Fe, Co, Mn, Ni doped ZIF 8

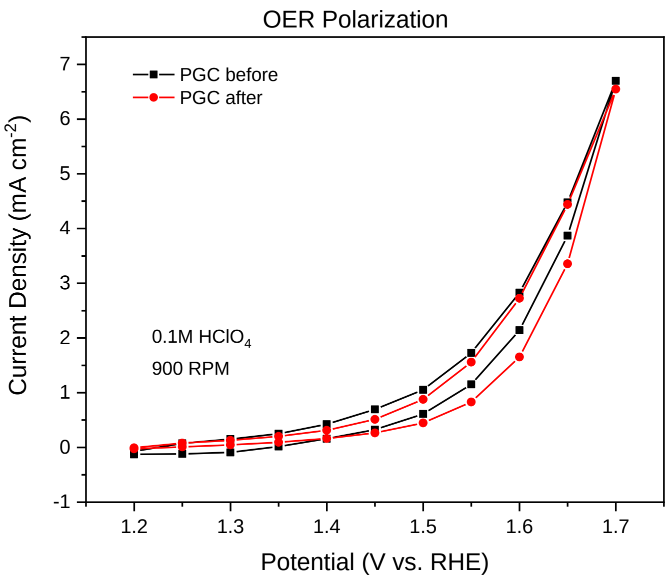


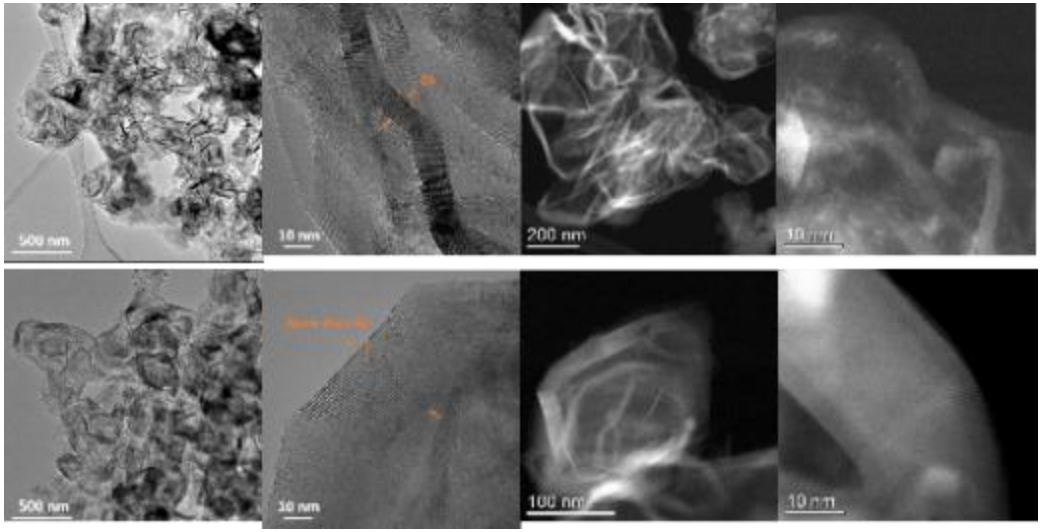

- **UB's MOF catalysts show continuous improvement in OER activity and stability in acid solution**
- **A new catalyst has been prepared and shipped to Giner for PEMWE test**

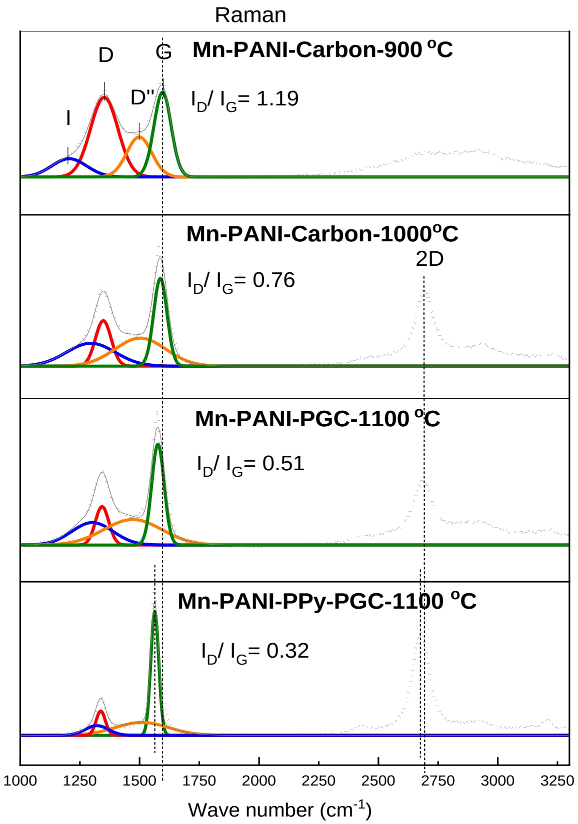
University at Buffalo
The State University of New York

# 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

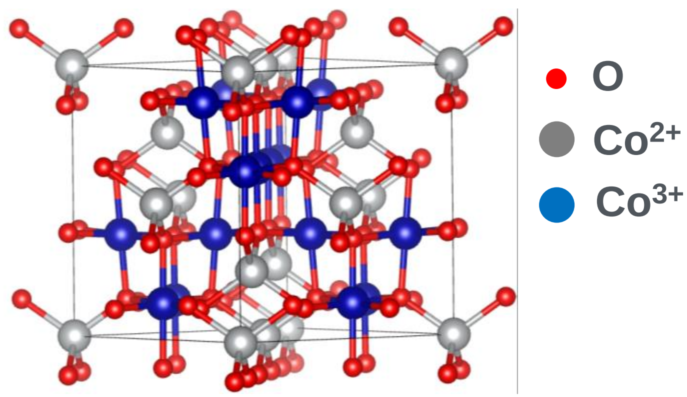


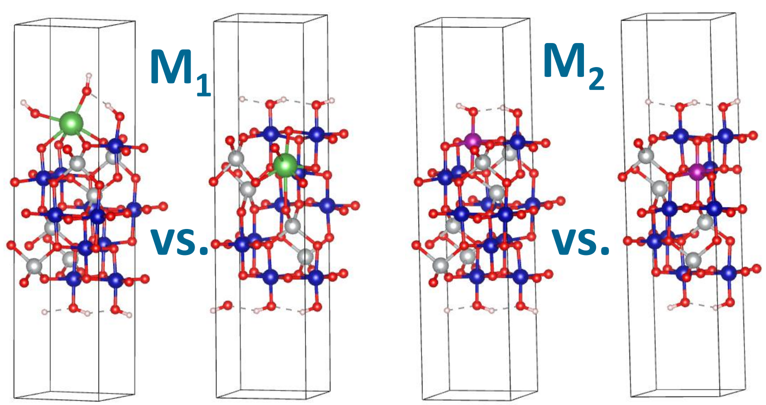

University at Buffalo
The State University of New York

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

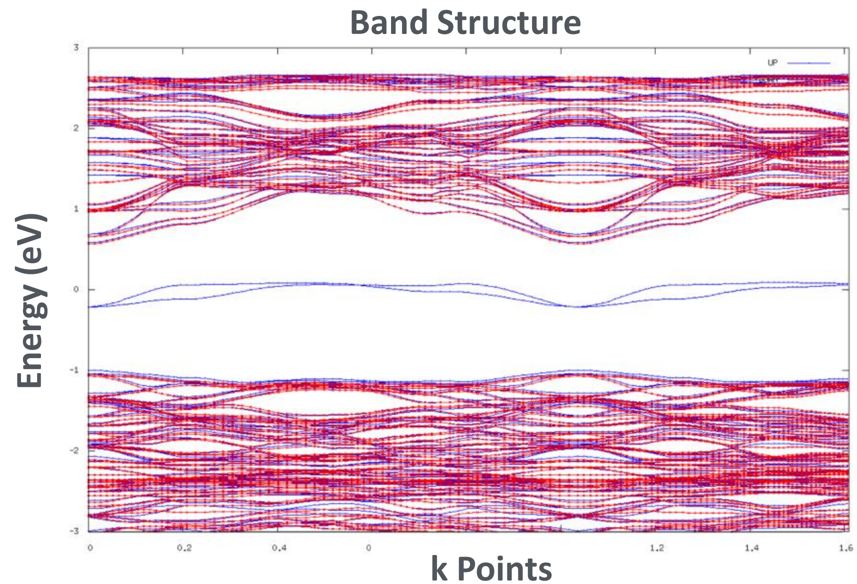
## *Conductivity change in catalyst by 2nd element doping*




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



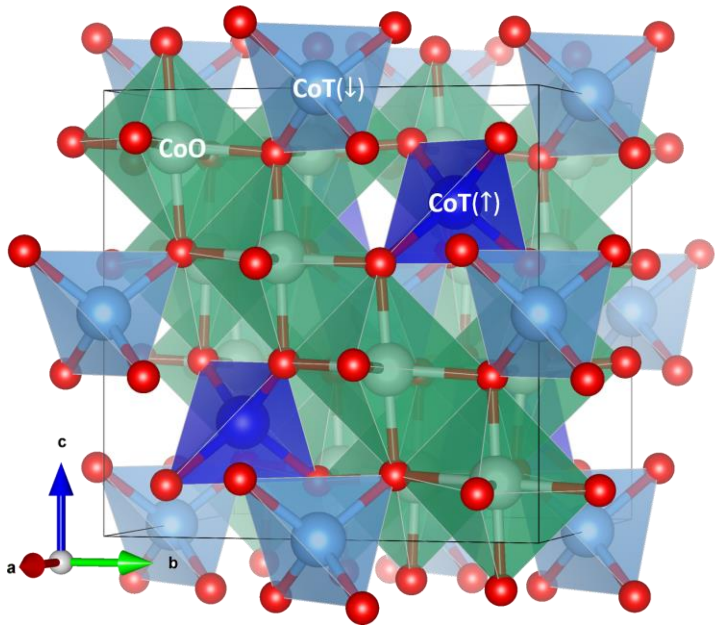

## *In-gap valence state induced by 2nd element*

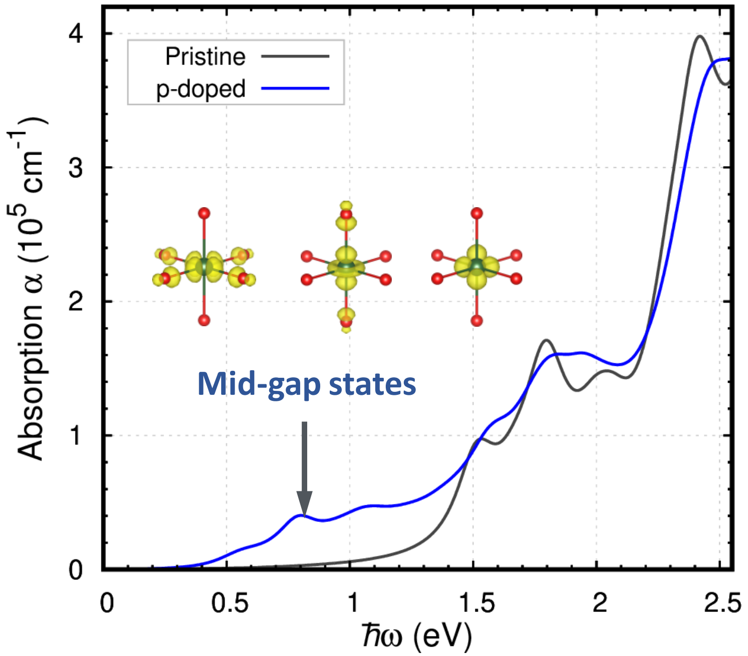



- The $M_2$ in oxide lattice introduce a half occupied in-gap state, enhancing electric conductivity
- Energy optimization found that 2nd ion distributes differently based on size & charge, impacting catalyst stability and consistent with the expt'l observation

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

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



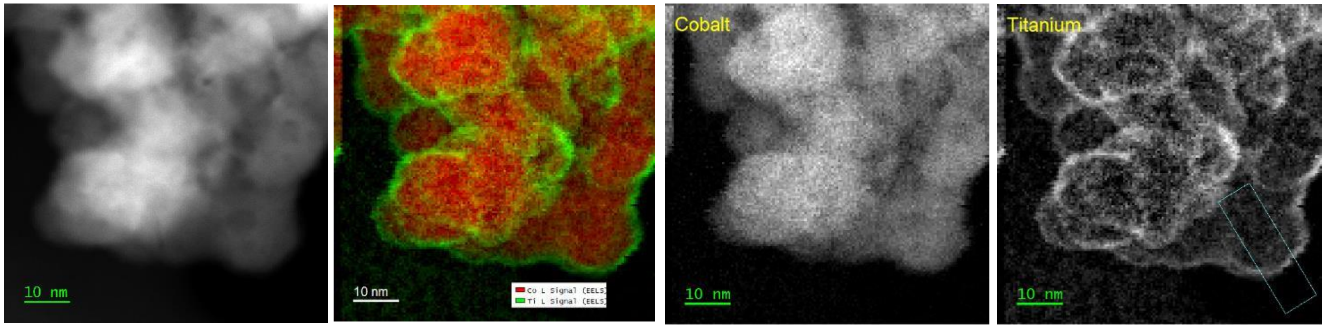




- Electronic properties for pristine and doped oxide were established, which identified the carrier conduction is governed by hole polaron hopping
- Formation of the mid-gap states is due to the hole polaron formation

Lawrence Livermore National Laboratory

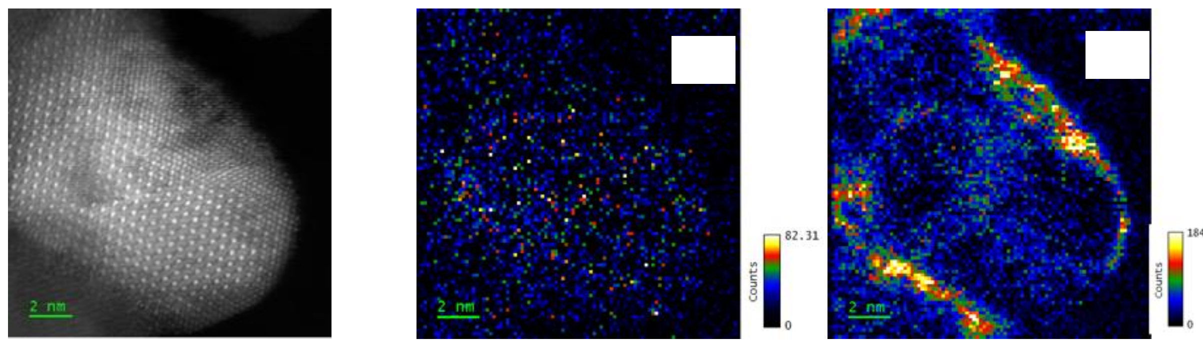
# Collaboration with HydroGen @ SNL – Microscopic Understanding on Morphology to Performance

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




**ANL-a**

**ANL-b**

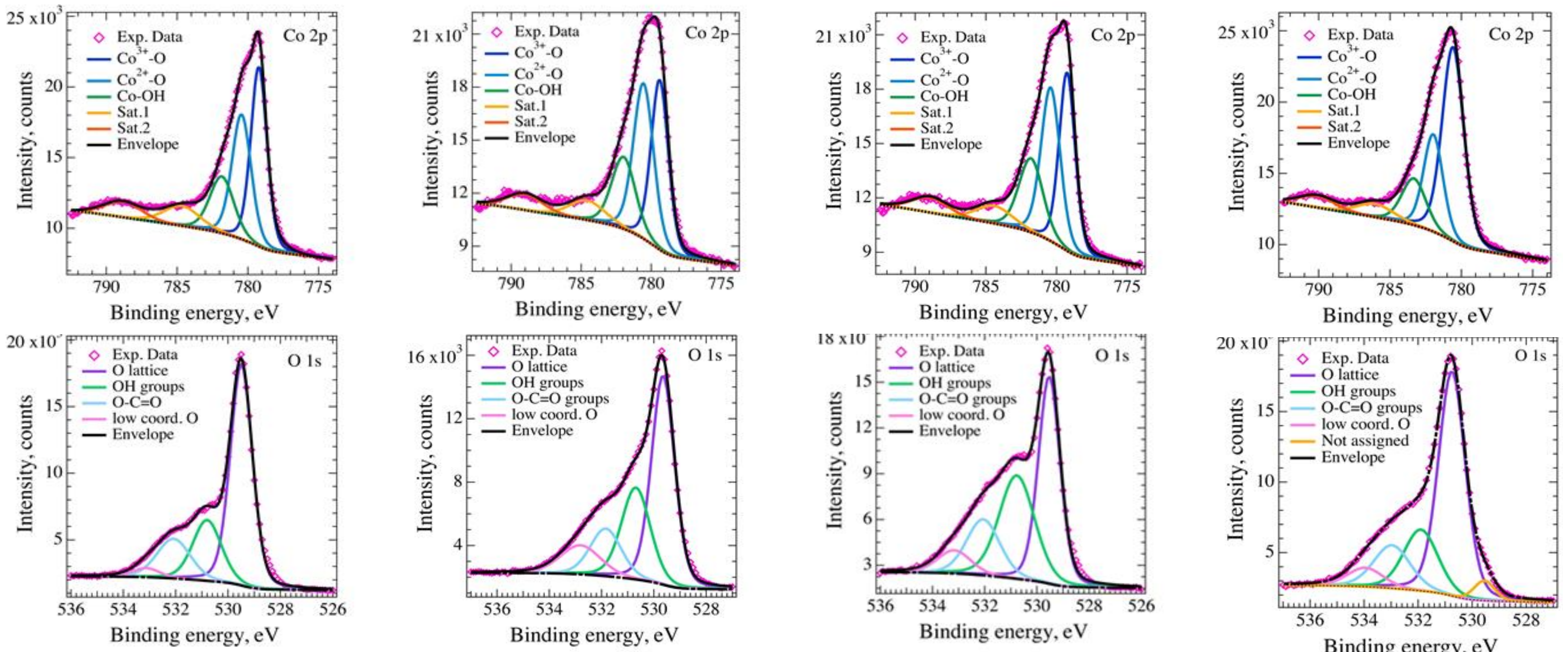



- The STEM shows a conformal $TiO_2$ coating of 1 to 2 nm thick surrounding ANL-a catalyst particles, serving as protective layer
- The doped metal ions distribute differently based on their sizes and charges in ANL-b, each plays its own role in promoting catalyst conductivity and stability

Sandia National Laboratories

# 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/cm$^2$, 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, $H_2$ production from a PEMWE with PGM-free anodic catalyst at practical operating potential**

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  - Sandia National Lab (led by Josh Sugar)
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  - Eric Miller – Program Manager
  - Dave Peterson – Project Manager