PGM-free OER Catalysts for PEM Electrolyzer

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2020 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting

Project Overview

Team

Lead: Argonne National Laboratory

Sub: U. of Buffalo & Giner Inc.

Award #	EE2.2.0.202
Start Date Project End Date	10/1/2017 09/30/2020
Year 1 Funding* Year 2 Funding* Year 3 Funding*	$250k $375k $375k

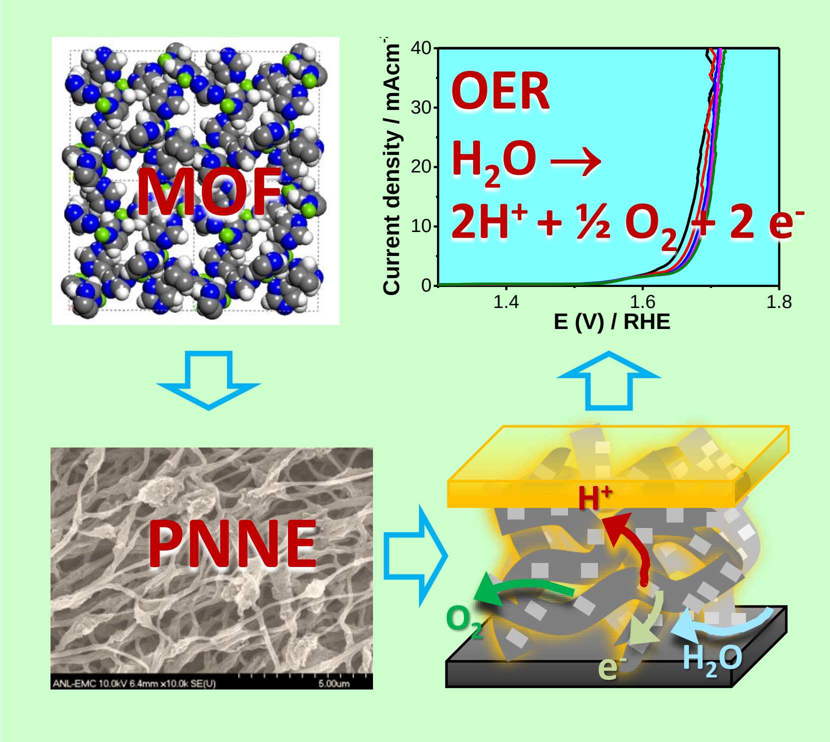
Project Vision

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)

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.

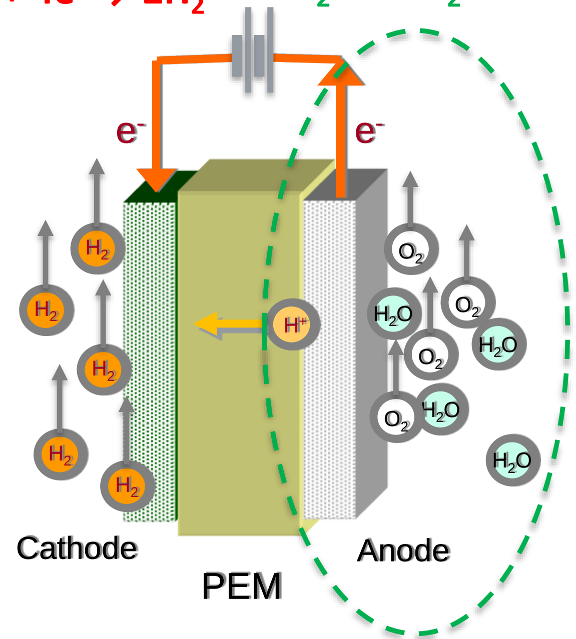
Operating principle of PEMWE

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- 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 > 500 mA/cm^2 @ 1.75 V & decay rate < 2 mV/h for 100 hours*

Barriers

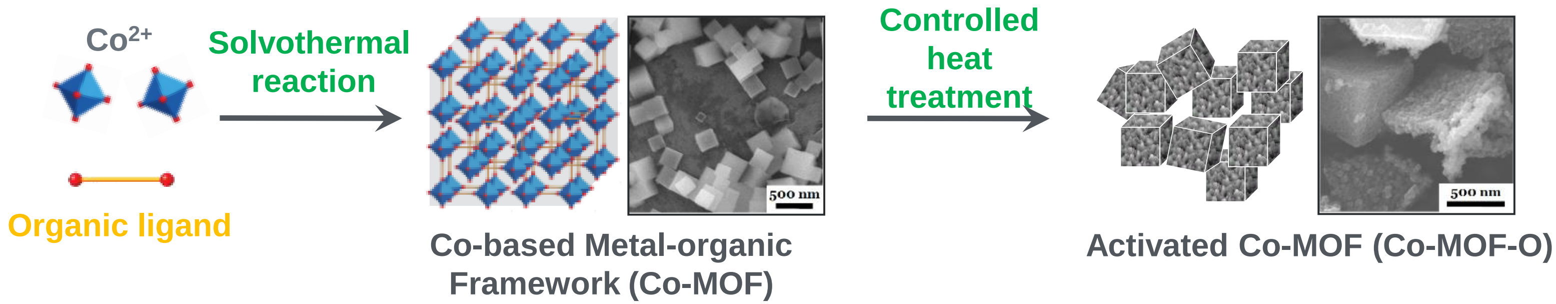
- **Cost:** Current PEMWE uses Ir as OER catalyst with high loading
- **Activity**: PGM-free catalysts have shown promising OER activity in alkaline solution, but not in acid
- **Durability**: Most catalyst and support materials are unstable under high polarization potential in acid

Partnerships - HydroGen

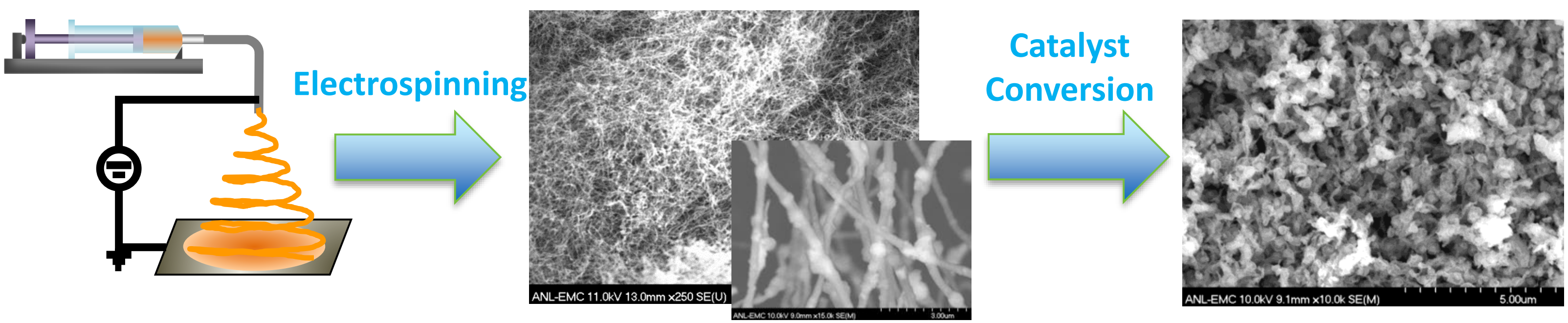
- Computational electrochemistry and predictive modeling (LLNL and LBNL)
- Advanced electron microscopic imaging (SNL)
- Electrode optimization / catalyst surface characterization (NREL)
- Mass transport modeling (LBNL)

Approach – Catalyst Innovations @ ANL

ANL-a: Co-MOF Derived OER Catalyst



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

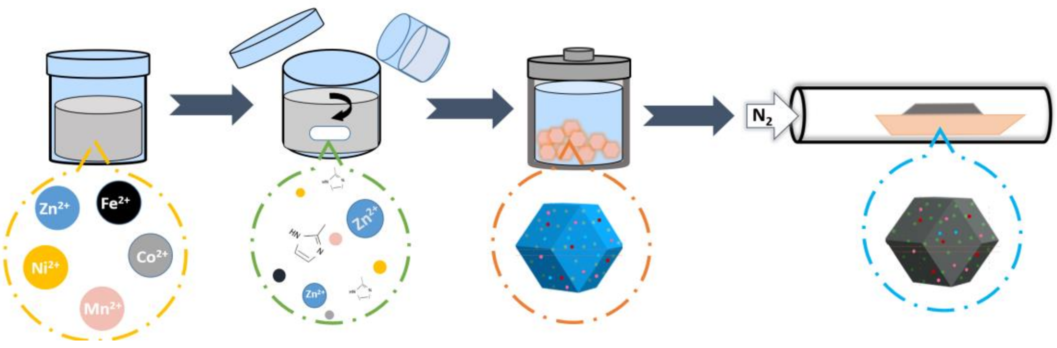


Liu & coworkers, *Proceedings of National Academy of Sciences*, **2015**, vol. 112, no. 34, 10629

- **MOF synthesis offers an inexpensive and versatile approach for multi-metallic catalyst development through metal and ligand exchanges**
- **MOF derived catalyst offers maximal density and exposure of the active site through intrinsic porous structure.**
- **PNNE improves mass/charge transfers via direct macro-to-micropore connection and offers better connectivity between the catalytic site against deactivation by oxidative corrosion**

Approach – Catalyst Innovation @ UB

MOF & Other Porous Precursor based OER catalysts



Metal salt methanol solution Organic Frameworks

Addition of linker solution

Formation of large ZIF 8 in 60ºC solution

Heat Treatment in N_2 atmosphere forming N-C (or M-N-C)

Amorphous Phosphide based PGM-free catalyst

- **UB team will explore the doping of W and Ta into Co-Fe-P systems and to replace carbon by metal carbinde to improve catalytic activity and stability**

University at Buffalo
The State University of New York

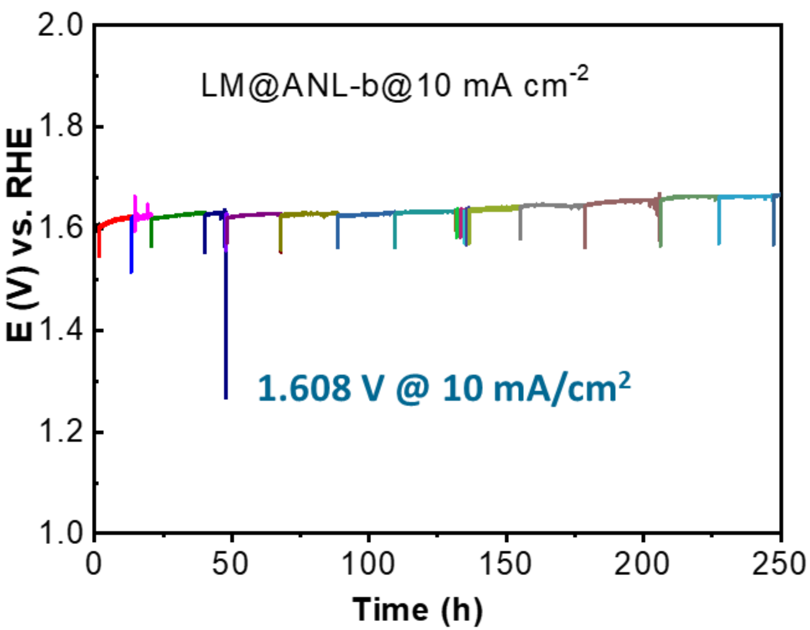
Approach – Budget Period 3 (BP3) Milestones

Milestone Description	Criteria	End Date	Status
Understanding of structure-function relationship through advanced structural characterization	Complete high resolution imaging and spectroscopic studies on cobalt based bimetallic OER catalyst developed at ANL, generate a fundamental understanding of the PGM-free catalyst activity and stability under acidic operating condition	12/31/2019	*100% Completed*. Extensive studies on electron microscopy, combined with X-ray absorption and computational modeling revealed fundamental OER mechanism of ANL's catalyst
Exploration amorphous phosphide based PGM-free catalyst	Complete design and syntheses at least 4 binary metal phosphide-based and multiple heteroatom doped catalysts. Demonstrate at least one catalyst of > 50 mA/cm2 @1.7 V measured by RDE with activity loss < 50 mV @ current density of 10 mA/cm2 after 1000 cycles at UB.	3/31/2020	*50% completed*: UB team demonstrated progress in new catalyst and constructed an in-house electrolyzer for accelerated study
Preparation of MEAs with improved activity and durability	Complete MEAs preparation using PGM-free catalysts downselected at ANL and UB for the testing at Giner	6/30/2020	*20% completed*. Two new PGM-free catalysts developed by UB showed promising initial activity.

- **An ANL-b delivered PEM electrolyzer current density of > 400 mA/cm^2 @ 1.8 V and < 100 mV drop at i = 200 mA/cm^2 after 10,000 cycles, far exceeding BP 2 goal**
- **BP3 goal includes current density of > 500 mA/cm^2 @ 1.75 V in activity, and less than voltage loss of 2 mV/hr over 100 hour test at current density of 100 mA/cm^2**

Accomplishment – ANL-b Outperformed Benchmark Catalysts in Durability during Chronopotentiometric Test in Acid

- ANL-b catalyst durability was tested by RDE in acid (pH = 1) over 250-hour under constant current @ 10 mA/cm^2
- The catalyst shows better combined durability and activity than some published results from the premier labs worldwide



	Nocera [a]	Lewis [b]	Blasco-Ahicart [c]	ANL-b
E_0 (V)	1.810	1.900	1.610	**1.608**
I_0 (mA/cm^2)	1	10	10	**10**
η_0 (mV)	580	670	380	**378**
t (hour)	50	168	0.5	**250**
ΔE (mV)	20	65	100	**58**
pH	2	0	0	**1**

a. D. Nocera & coworkers, Chem. Sci., 2017, 8, 4779
b. N. Lewis & coworkers, *Energy Environ. Sci*., 2017, 10, 2103
c. Blasco-Ahicart, et. al. *Nat Chem* 2018, 10, 24

E_0: potential at beginning of test

I_0: current density used in test

η_0: overpotential at beginning

t: test time

ΔE: potential increase at end of test

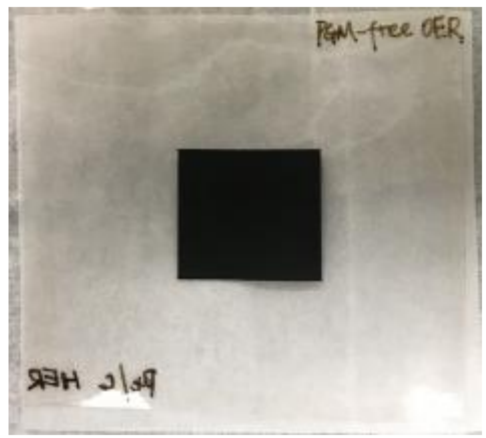
Accomplishment – Developing Membrane Electrode Assembly (MEA) for PEMWE

Challenges in MEA development

- Little or no information is available for PGM-free OER catalyst in PEMWE
- Different conductivity and surface properties from conventional fuel cell catalyst requires new MEA processing conditions
- Multiple processing conditions (catalyst loading, ionomer ratio, etc.) can significantly influence MEA performance

Key processing parameters optimized at ANL & tested by Giner

- Catalyst:ionomer ratio
- Catalyst loading
- Application methods (spray vs. painting, etc.)
- Hot pressing temperature & pressure
- Pre-treatment (acid wash, etc.)



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

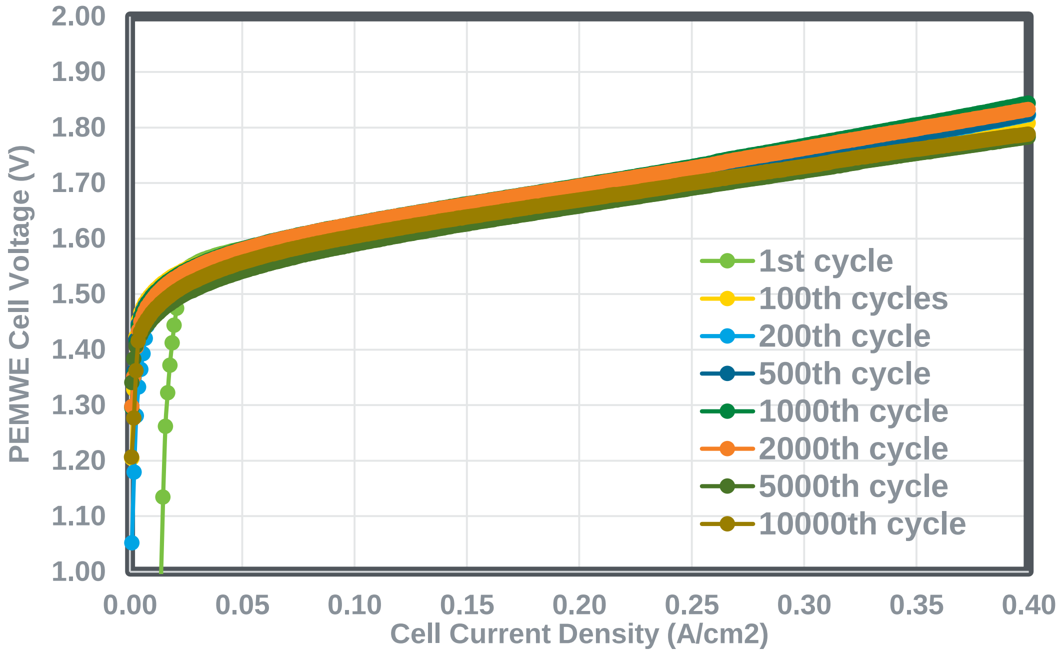
PEMWE setup at Giner

Argonne NATIONAL LABORATORY

GINER LABS

Accomplishment – Durability Study of ANL Catalyst in MEA/PEMWE by Potential Cycling

- Over 15 MEAs containing ANL-b OER catalyst at anode were prepared and brought to Giner in August for evaluation under PEMWE operating condition
- In addition to PEMWE polarization, the MEA was also subject up to 10,000 voltage cycles from 1.4 V to 1.7 V in an accelerated stress test (AST)



1st cycle
Cell voltage$_{@ 0.4A/cm2}$ = 1.78 V

100th cycle
Cell voltage$_{@ 0.4A/cm2}$ = 1.80 V

2000th cycle
Cell voltage$_{@ 0.4 A/cm2}$ = 1.84 V

5000th cycle
Cell voltage$_{@ 0.4 A/cm2}$ = 1.78 V

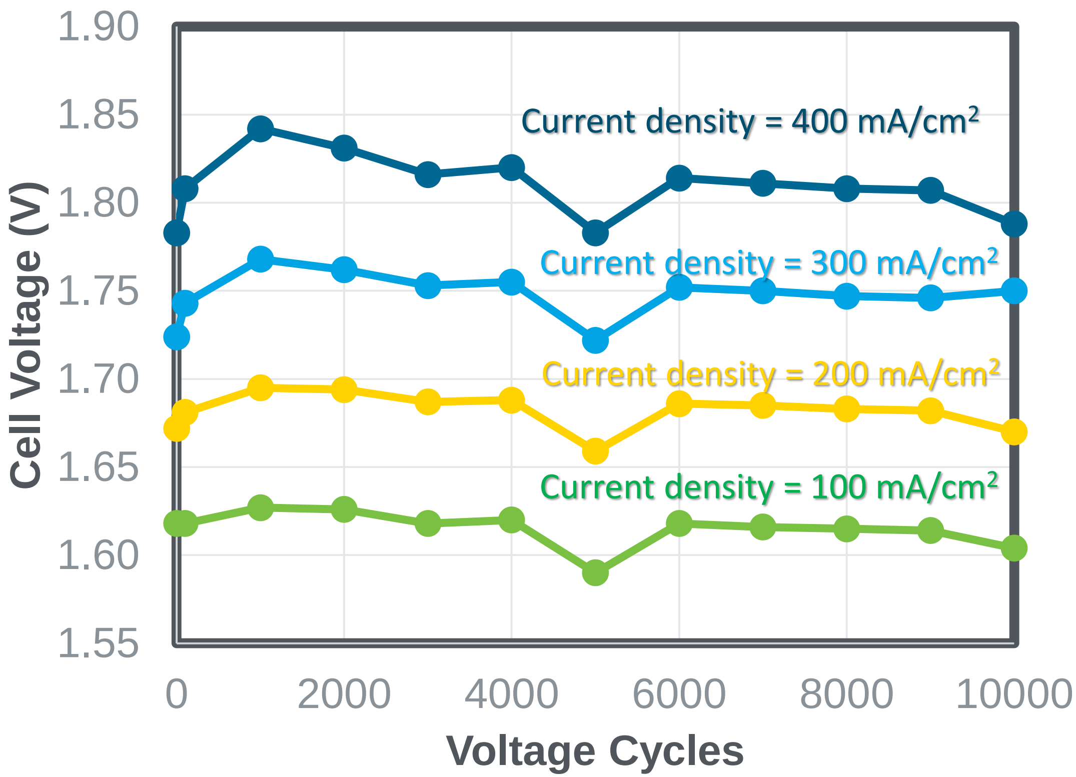
10000th cycle
Cell voltage$_{@ 0.4 A/cm2}$ = 1.79 V

Anode = ANL-b PGM-free, 2 mg/cm^2, Cathode = Pt/C, 0.5 mg/cm^2, Membrane = N115, 5 cm^2 cell, CCM, 60 ˚C, 10 psi DI

ANL-b catalyst delivered 400 mA/cm^2 @ 1.78 V in PEMWE, a 100% increase over FY18 goal and exceeded BP2 activity performance target!

Accomplishment – Durability Study of ANL Catalyst in MEA/PEMWE by Potential Cycling

The MEA showed relatively stable cell voltages at different current densities during the voltage cycling AST



1st cycle

Cell voltage$_{@200\ mA/cm2}$ = 1.670 V

Δ Cell voltage = 0 mV

100th cycle

Cell voltage$_{@200\ mA/cm2}$ = 1.681 V

Δ Cell voltage = 11 mV

2000th cycle

Cell voltage$_{@200\ mA/cm2}$ = 1.695 V

Δ Cell voltage = 25 mV

5000th cycle

Cell voltage$_{@200\ mA/cm2}$ = 1.659 V

Δ Cell voltage = - 11 mV

10000th cycle

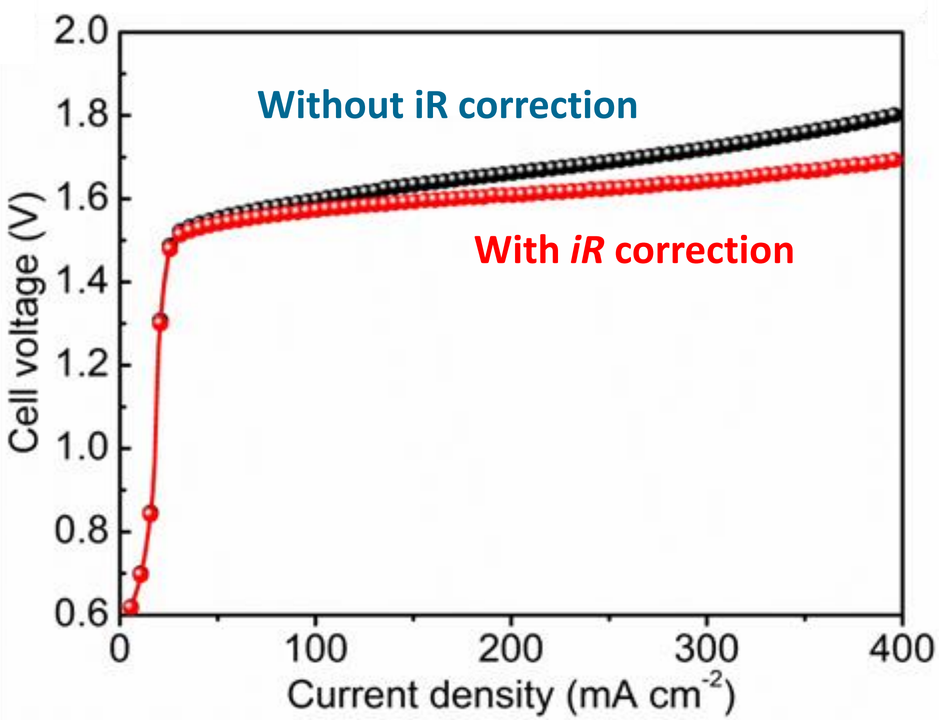
Cell voltage$_{@200\ mA/cm2}$ = 1.670 V

Δ Cell voltage = 0 mV

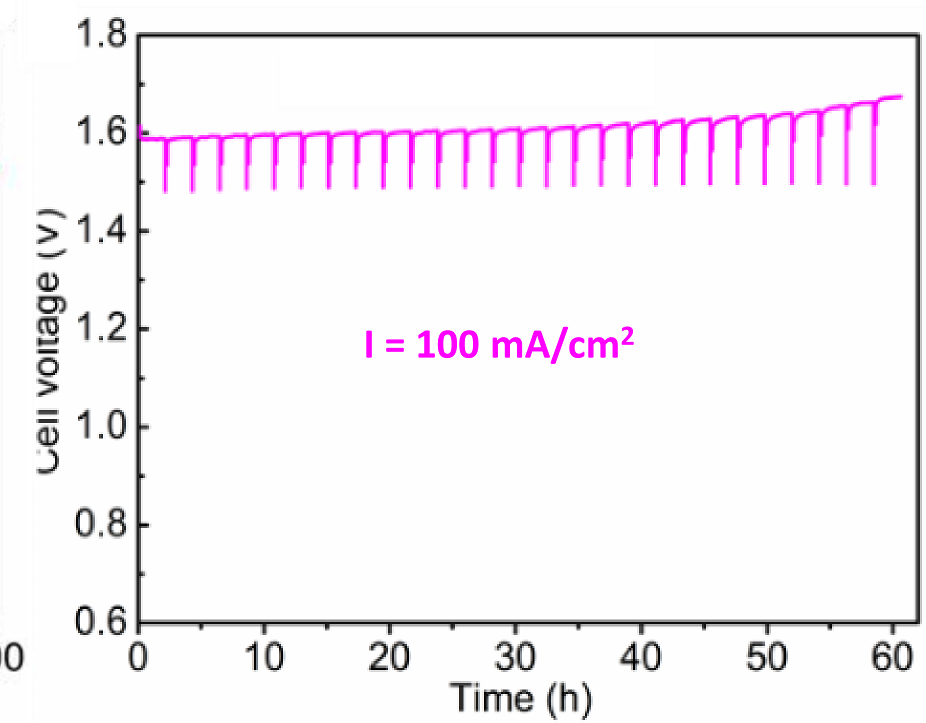
ANL-b MEA also demonstrated < 25 mV loss @ 200 mA/cm^2 after 10000 voltage cycles, exceeded GNG for durability target of < 100 mV!

Accomplishment – ANL PGM-free Catalyst also Outperformed Literature Report in PEMWE Testing

ANL's PGM-free OER catalyst demonstrated a SOA i-V polarization in PEMWE …



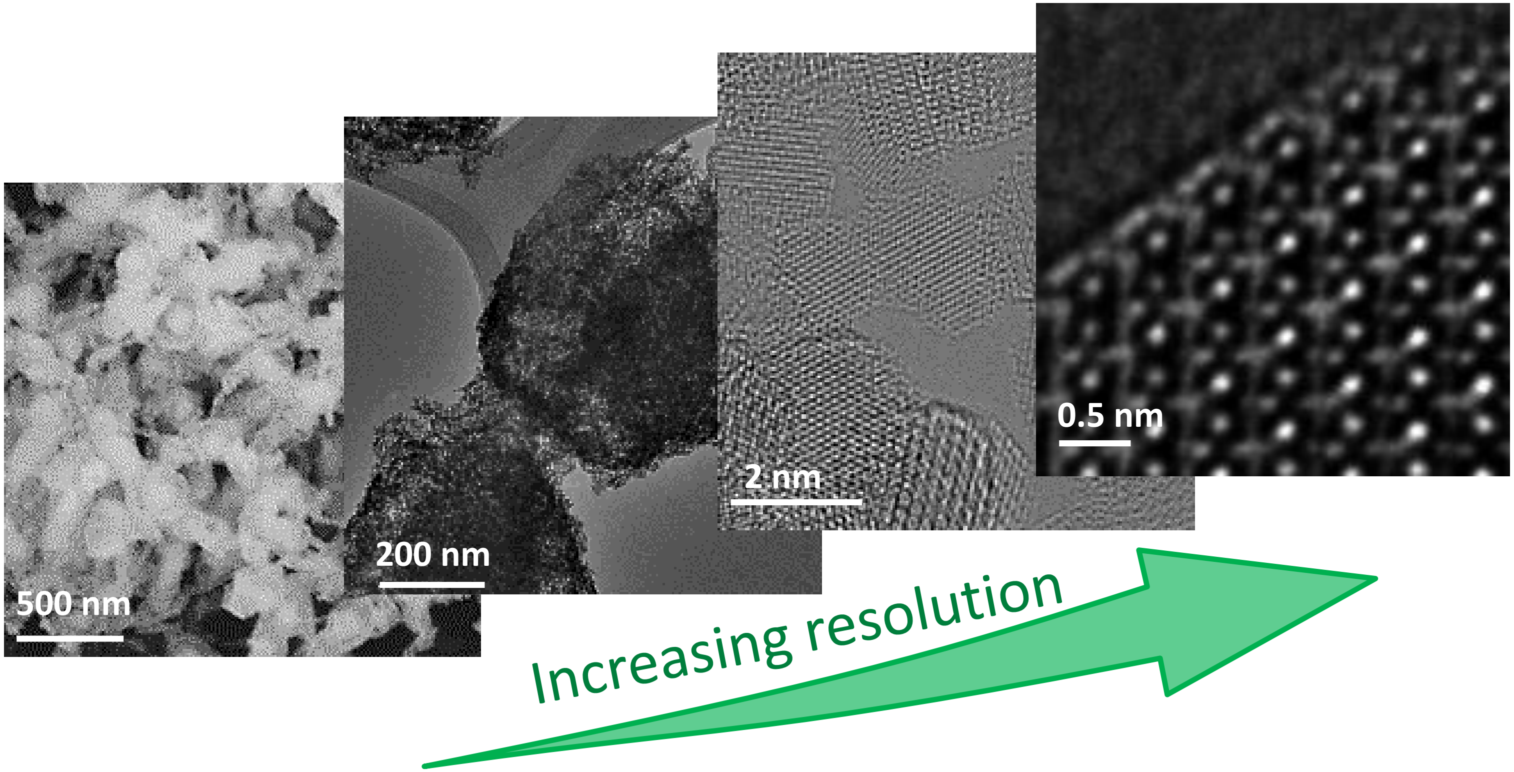
… it also showed a promising stability with cell voltage increase at 1.5 mV/hr over 60-hr span at 100 mA/cm^2



Anode = ANL-a PGM-free, 1 mg/cm^2, Cathode = Pt/C, 0.5 mg/cm^2, Membrane = N115, 5 cm^2 cell, CCM, 60 ˚C, 10 psi DI

Accomplishment – Understanding on catalyst's structure through high resolution electronic imaging

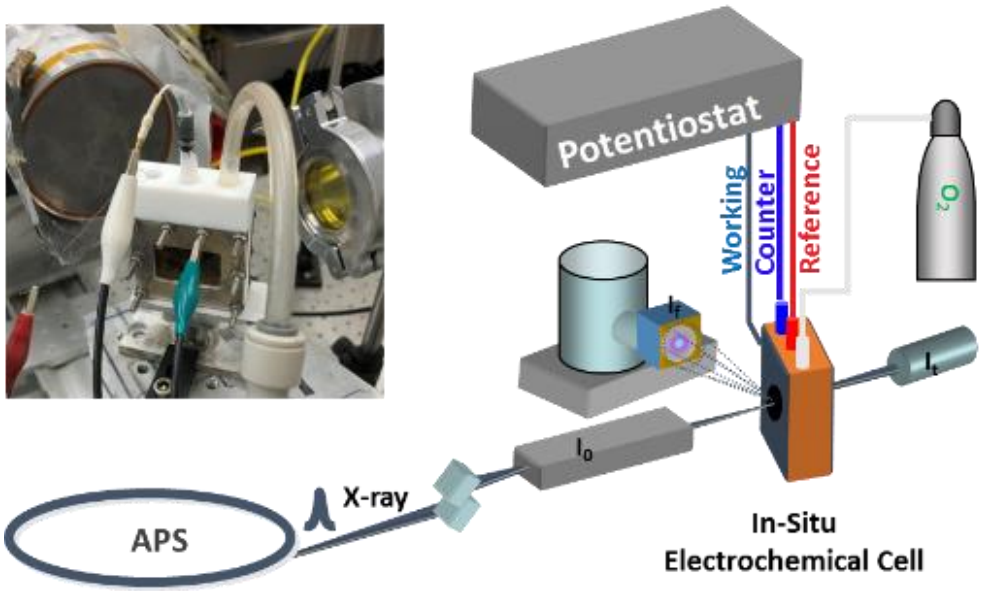
Various characterization tools are applied, including SEM/TEM, XRD, XPS, Raman, BET, etc., to decipher the catalyst structure – function relationship



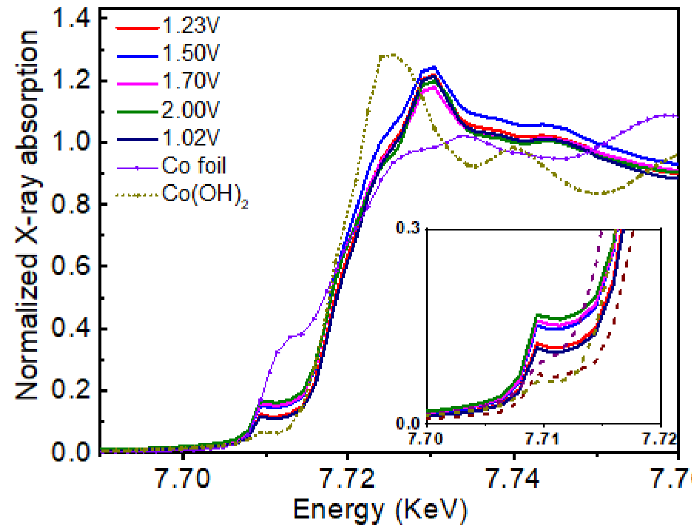
SEM, TEM, HAADF-TEM and EELS revealed ANL's OER catalyst morphology, phase/element distributions and provided critical insight on the catalyst performance

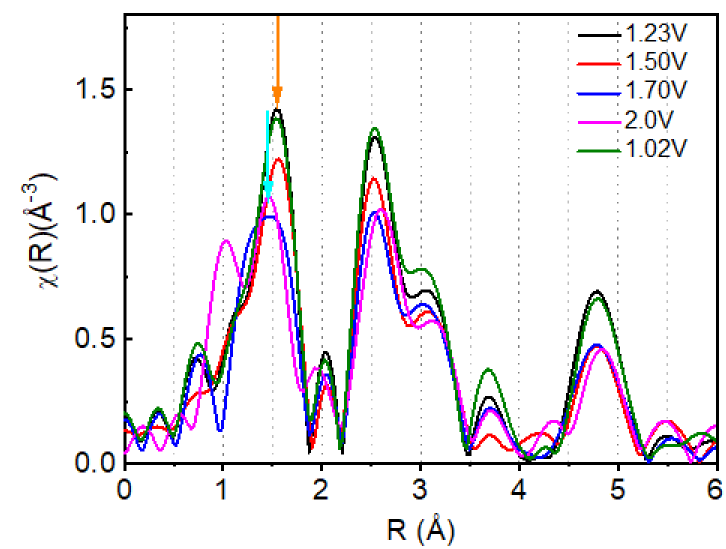
Accomplishment – Understanding on catalyst's electronic & coordination structure through X-ray absorption spectroscopy

operando x-ray absorption spectroscopy (EXAFS/XANES) revealed a reversible change in active site oxidation and coordination under reaction condition



***In situ* XAS experiment at ANL for OER catalyst investigation under electrolysis condition**





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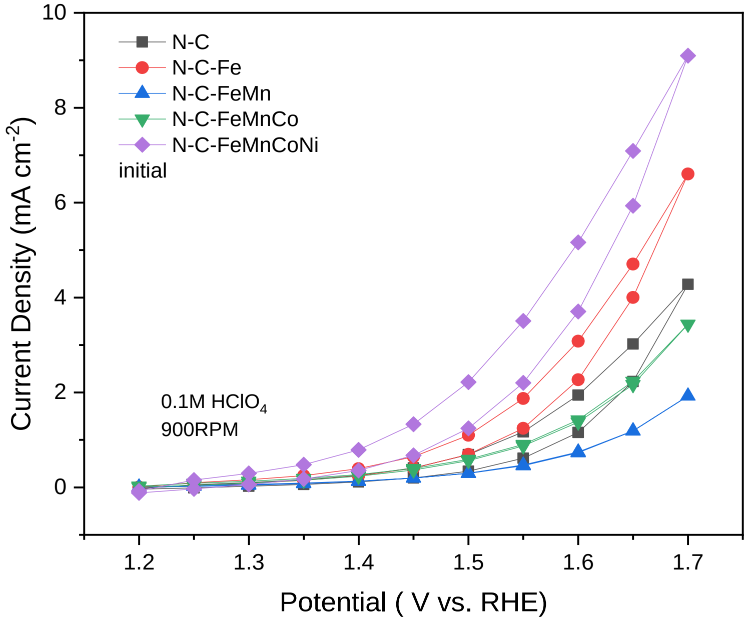
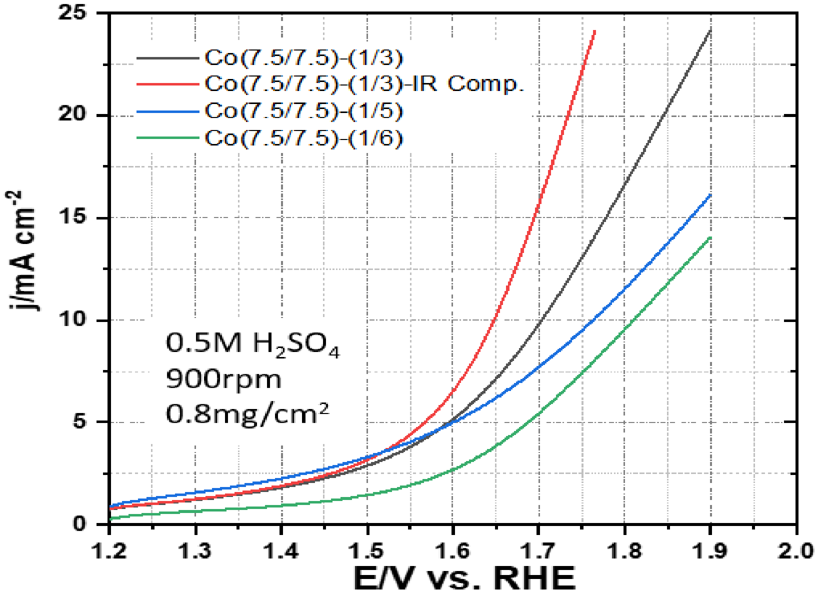
Accomplishment – Multiple Metal Doped & Metal Phosphide Mixed M-N-C Catalysts Showed Promising OER Activities

Improving OER activity through different metal doping



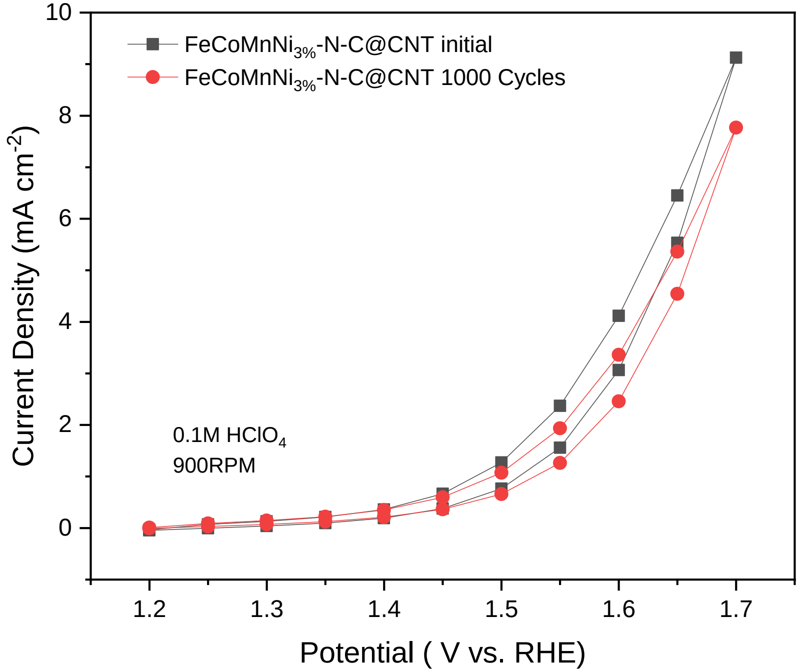
Metal phosphide represents another promising approach

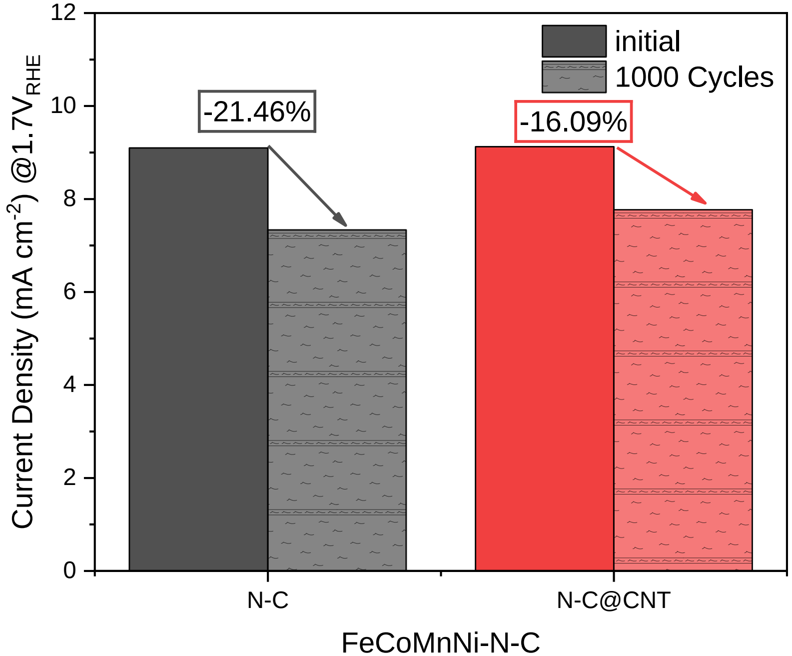


- **The synergic effect between different metals increased the OER performance and stability (9.09 mA cm^{-2} @ 1.7VRHE) in 0.1 M $HClO_4$**
- **Initial performance of the CoP@Co-N-C with different ratios between CoNPs@Co-N-C and NaH_2PO_2 showed trend of improvement**

University at Buffalo
The State University of New York

Accomplishment – Addition of CNT to N-C Catalyst Can Improve Conductivity therefore OER Activities



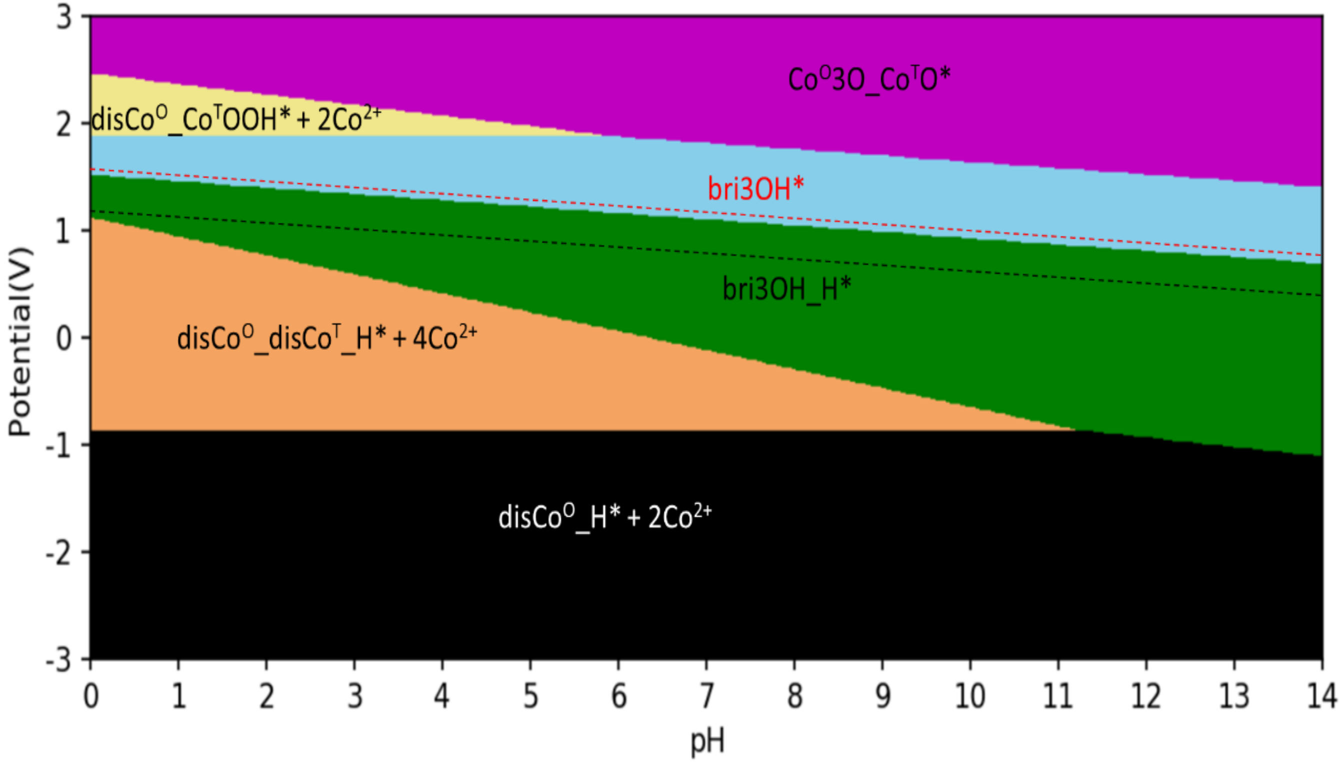


- **CNT addition to FeCoMnNi-N-C leads to a 5% lower degradation between initial and 1000 polarization curves**

University at Buffalo
The State University of New York

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

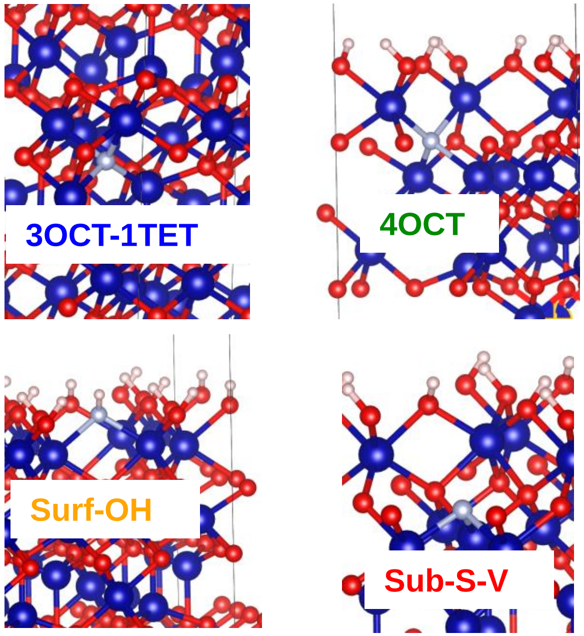
Surface Pourbaix diagram at different pH

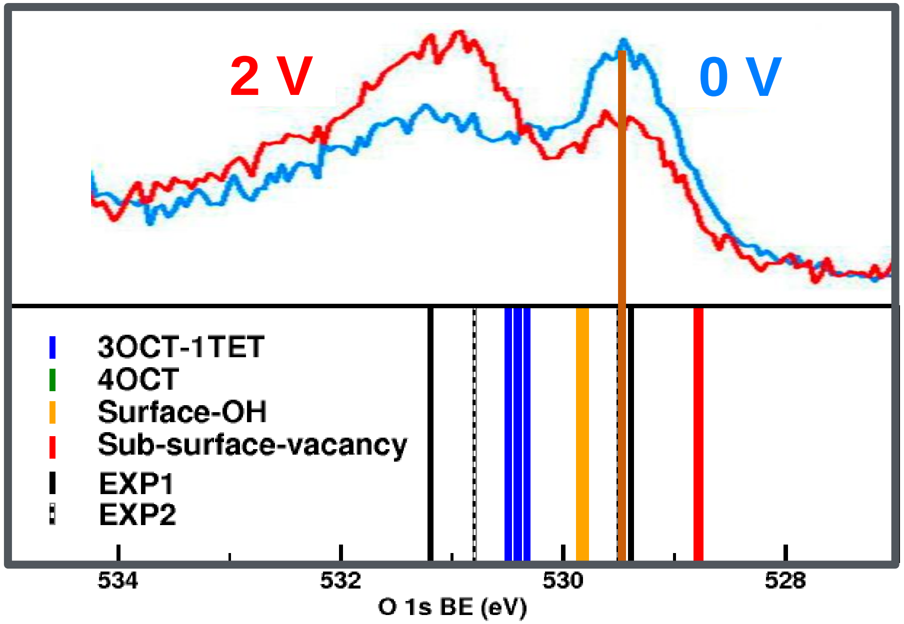


- Surface Pourbaix diagram shows certain lattices in ANL's PGM-free catalyst maintain low solubility under low pH, illustrating the root-cause of improved durability in acid

Lawrence Berkeley National Laboratory

Collaboration with HydroGen – *ab initio* XPS Calculations of Surface Structural Model @ LLNL





Local structure of 1s core excited O atoms. 3OCT-1TET O is shared by 3 octahedra, 4OCT O is shared by 4 octahedra, Surface-OH is O at the surface forming OH, Sub-S-V O is O beneath of surface vacancy

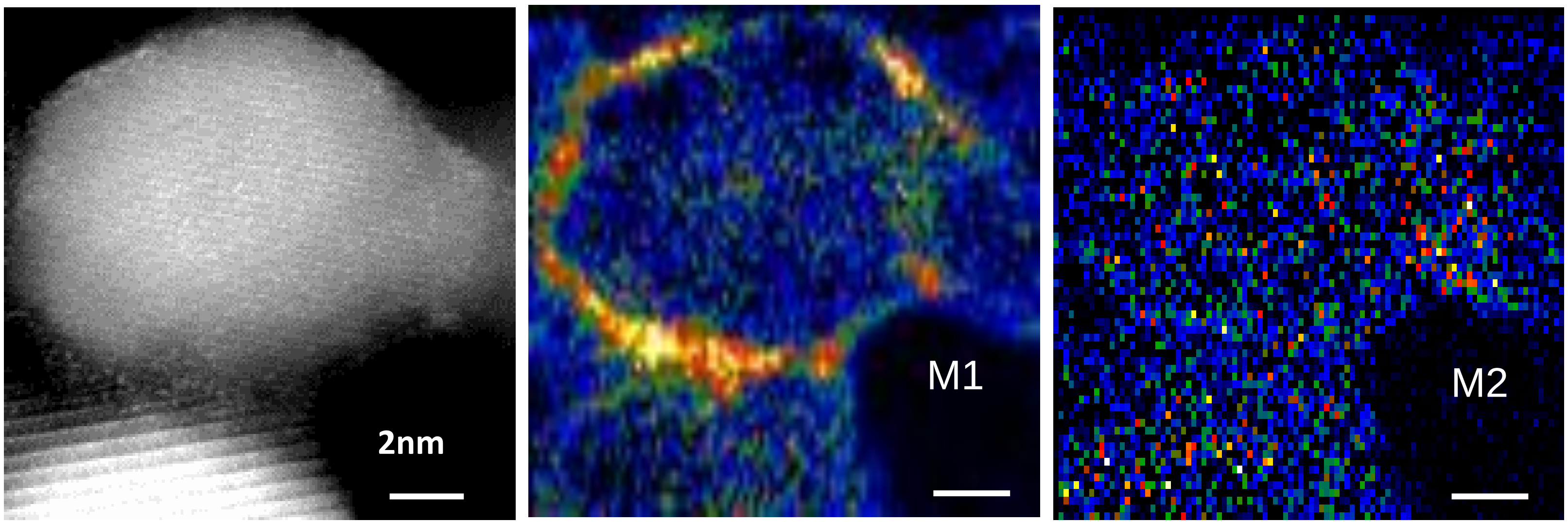
Top: In-operando O 1s XPS of Co_3O_4 from JPCC **122**, 13894 (2018) measured with (2 V)/without (0 V) anodic potential. **Bottom**: our DFT XPS peak positions compared to EXP1 [J. Vac. Sci. Tech. A **14**, 1637 (1996)] and EXP2 [Surf. Sci. 59, 413 (1976)]. Theoretical 4OCT peak as well as JPCC 2018 main peak position is aligned to EXP1's main peak position.

- LLNL team is focusing on computational simulation of catalytic electronic state through operando XPS

Lawrence Livermore National Laboratory

Collaboration with HydroGen – Understanding on Metal Doping to Catalyst Performance @ SNL

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



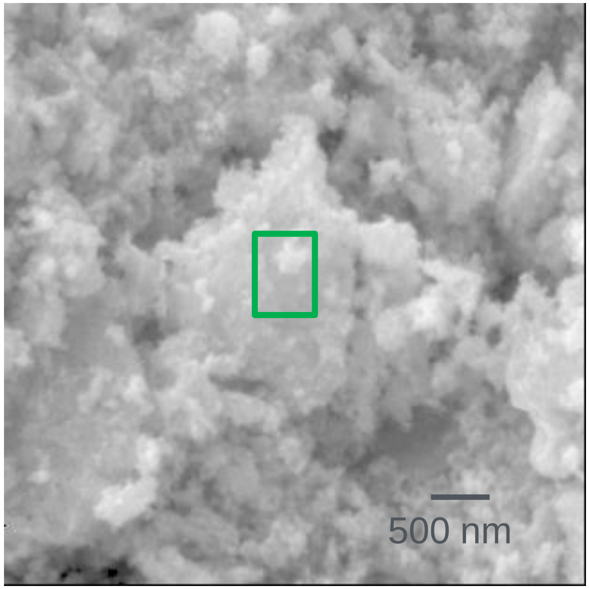
- **STEM investigation shows the distributions of different metals depending on their atomic radii and charges, consistent with the computational modeling results**
- **The doped metals played important roles in promoting catalyst conductivity and activity**

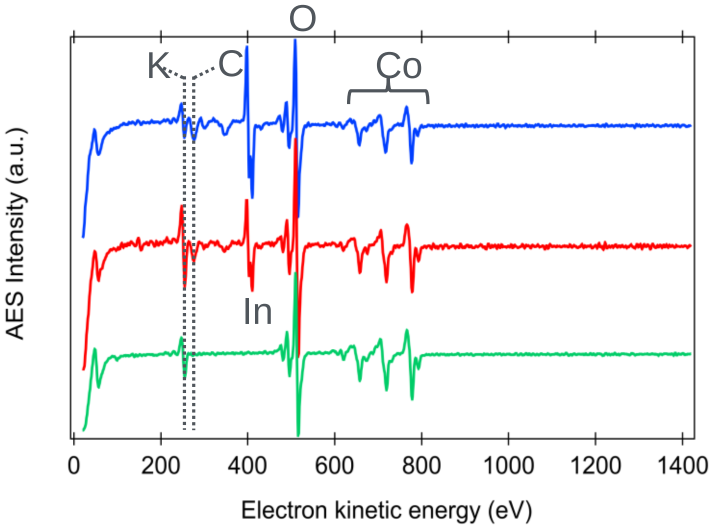
Sandia National Laboratories

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

Auger Electron Spectroscopy analysis on catalyst surface elemental valance state

SEM of one AES region (green trace)





Atomic Concentration (%)

C	O	S	K	Co	In
15	44	0.32	9.1	13	18
12	46	0.83	19	13	9.4
0.0	58	0.20	16	23	0.0

- XPS reveals the dependence of Co valance state on the doping element in ANL's MOF-derived OER catalysts
- AES provides microfocused, location-sensitive surface electronic structural analysis

Proposed Future Work

- Continue to enhance PGM-free OER catalyst activity and durability by exploring multi-element doping through reticular MOF synthesis, surface modification and post-synthesis treatment (ANL)
- Continue to explore C-free, phosphide based PGM-free catalyst with focus on activity and durability test in PEMWE (UB)
- Continue to optimize anode design and cell fabrication to improve MEA/PEMWE cell voltage-current polarization and durability in meeting BP-3 performance target (ANL/UB/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

BP3 tasks will focus on meeting the combined catalyst activity and durability targets, demonstrated in the operating PEMWE

Project Summary

- Both ANL-a and ANL-b OER catalysts showed significantly improved activities and durability in the acidic electrolyte when measured against Ir black as benchmark
- A PEMWE cell containing ANL-b anode catalyst delivered a current density higher than 400 mA/cm^2 at 1.8 V, representing the-state-of-the-art (SOA) performance for a PGM-free OER catalyst, and exceeded BP2 goal
- The same MEA demonstrated excellent durability with less than 25 mV cell voltage increase at 200 mA/cm^2 after 10,000 voltage-cycles, representing SOA PGM-free OER catalyst stability in the operating PEMWE and exceeded BP2 goal
- The catalyst also showed promising stability under the constant current aging test in PEMWE, surpassing the SOA reported in the literature
- Computational modeling and structural characterizations by HydroGen nodes, together with ANL's *in situ* XAS work, provided insightful understanding on the PGM-free OER catalysis mechanism

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  - Jason Wiley, Zach Green
- HydrogGEN Consortium
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  - Lawrence Berkeley National Lab (led by Lin-Wang Wang)
  - Sandia National Lab (led by Josh Sugar)
  - National Renewable Energy Lab (led by Craig Perkins)
  - Laurence Berkeley National Lab (led by Adam Webb)
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