Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

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)

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NREL · Berkeley Lab · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

Project Overview

Team

Lead: Di-Jia Liu, Argonne National Laboratory

Sub: Gang Wu, U. of Buffalo,

Hui Xu, Giner Inc.

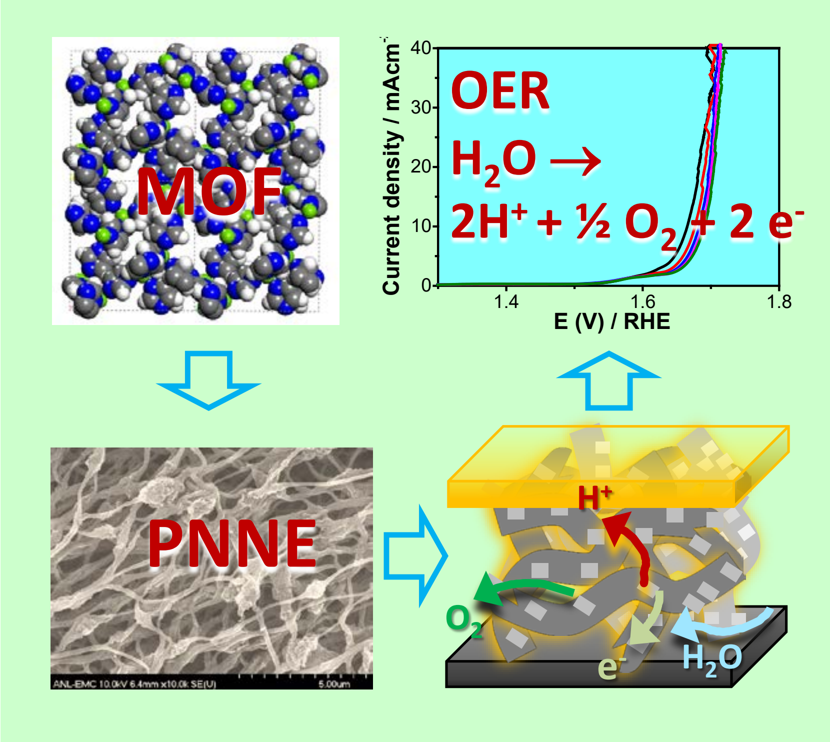
Award #	EE2.2.0.202
Start Date Year 1 End Date Project End Date	10/1/2017 09/30/2018 09/30/2020
Total DOE Share Total Cost Share Year 1 DOE Funding	$1.0M $0.1M $0.25M

Project Vision

To lower the capital cost of PEME by developing platinum group metal-free (PGM-free) OER electro-catalysts

Project Impact

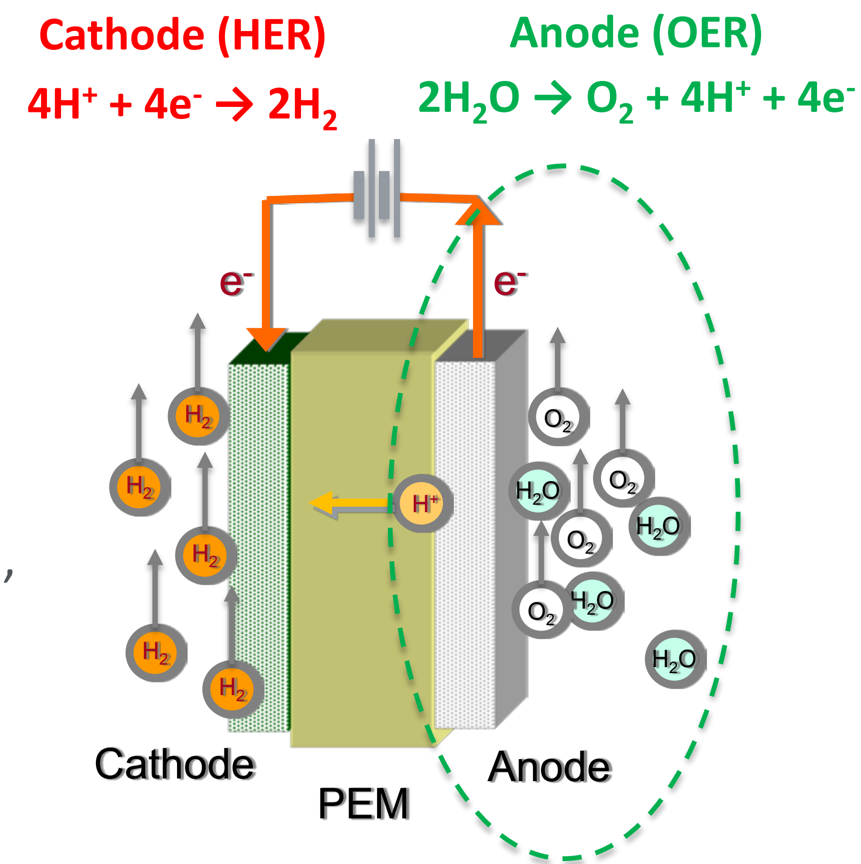
To reduce the anode catalyst cost by 20 folds by developing one or more PGM-free OER catalysts with the performance approaching to that of Ir catalyst, demonstrated at PEME level.



Relevance - Proton Exchange Membrane Electrolyzer (PEME) – Opportunities & Challenges

- **Advantages of PEME in hydrogen production**
  - High ion conductivity (x5 over alkaline system) of small footprint
  - Quick response for better integration with renewable sources (wind, solar)
  - High purity hydrogen
  - Non corrosive electrolytes
- **Challenges in PEME technology**
  - Use expensive precious metals (Pt, Ir, Ru, etc.) with high loading
  - Limited material stability under high voltage cycling
  - Limited info available for PGM-free OER catalyst in acidic media

Operating principle of PEME



We aim at next-generation, low-cost PGM-free OER catalysts

Relevance & Impact

- **Project Goal** – To produce one or more PGM-free OER catalysts with the performance approaching to the Ir catalyst but at < 1/20 of the cost, demonstrated through the operating PEM electrolyzer.
- **Project Impact** – To reducing the electrolyzer capital cost and to facilitate broad implementation of PEME for low-cost hydrogen production (<$2/kg) coupled with renewable energy sources.
- **Mission Alignment with HydroGen** – Accelerating low-cost material development to produce clean, sustainable hydrogen through advanced low-temperature electrolyzer (LTE) technologies.

Approach- Summary

Project history

Both **ANL** and **UB** teams are the pioneers in the MOF derived PGM-free catalysts for oxygen redox reactions (ORR). PGM-free catalyst for oxygen evolution reaction (OER) calls for different approach. Promising results are shown recently at both institutes. **Giner** is an industrial leader in PEMWE technology responsible for MEA/electrolyzer development.

Proposed targets

Metric	State of the Art	Proposed
Difference in overpotentials against Ir black by RDE	*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 PEME	*Non-existing for PGM-free catalyst in PEME*	*PEME/MEA with target performance of > 200 mA/cm^2 @ 1.80 V*

Barriers

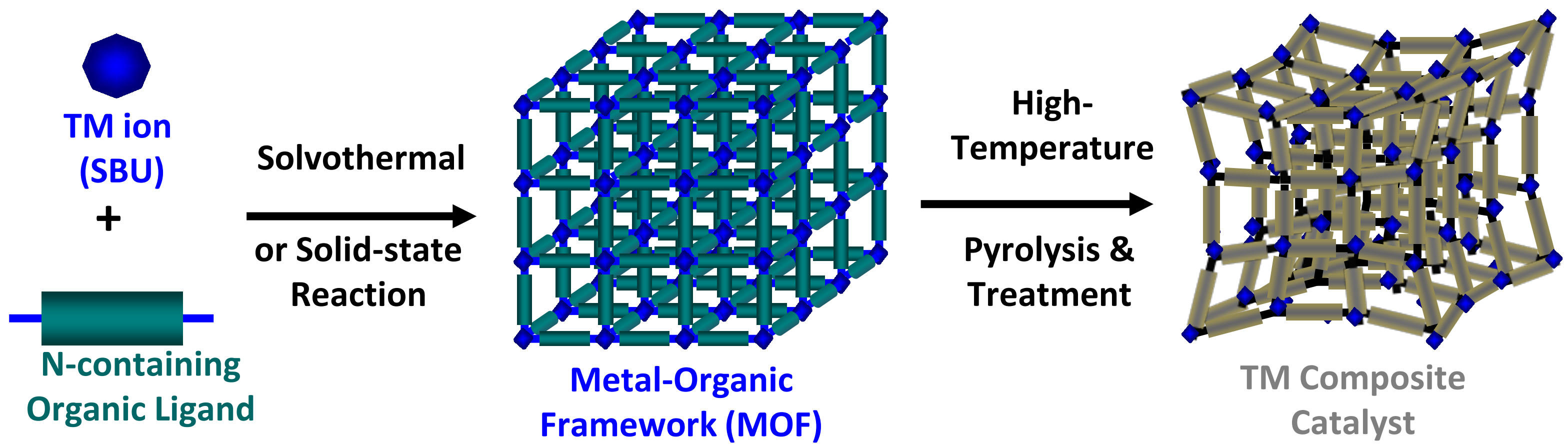
Activity: although PGM-free catalysts have shown good activity in alkaline media, few reported for acidic OER application.
Durability: instability of most conductive supports and catalytic center under high polarization potential limits the lifetime of supported catalysts.

Partnerships - HydroGen

- Computational chemistry and predictive modeling (LLNL and LBNL)
- Advanced electron microscopic imaging (SNL)
- High throughput electrode optimization support / catalyst surface characterization (NREL).

Approach – Innovation @ ANL

Metal-Organic Framework (MOF) Derived PGM-free OER Catalysts

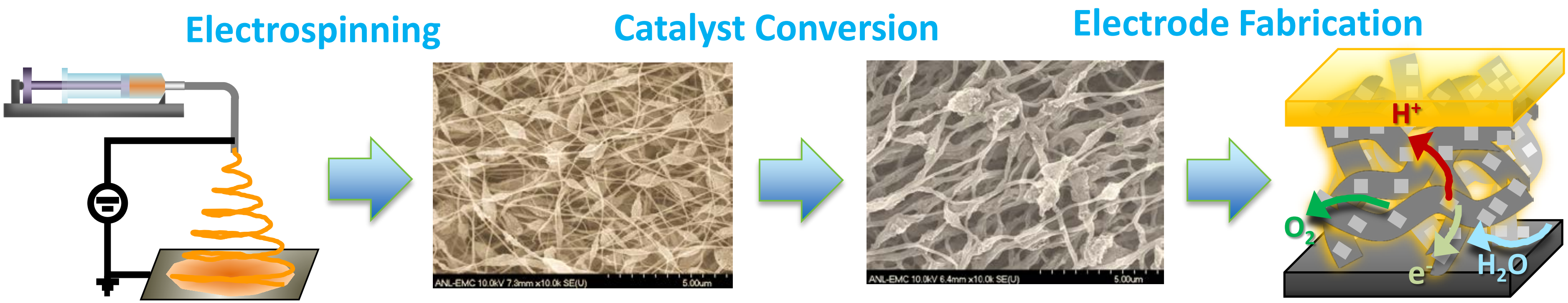


S. Ma, G. Goenaga, A. Call and D.-J. Liu, *Chem: Euro J,* **17** (**2011**) 2063
Liu, et. al. US Patent **8,835,343**

- **MOF derived catalysts can significantly reduce the cost by using inexpensive ligand and earthly abundant transition metal**
- **Framework structure offers maximal active site density and catalytic active site exposure through porous structure**

Approach – Innovation @ ANL

Porous Nano-Network Electrode (PNNE) via Electrospin at ANL



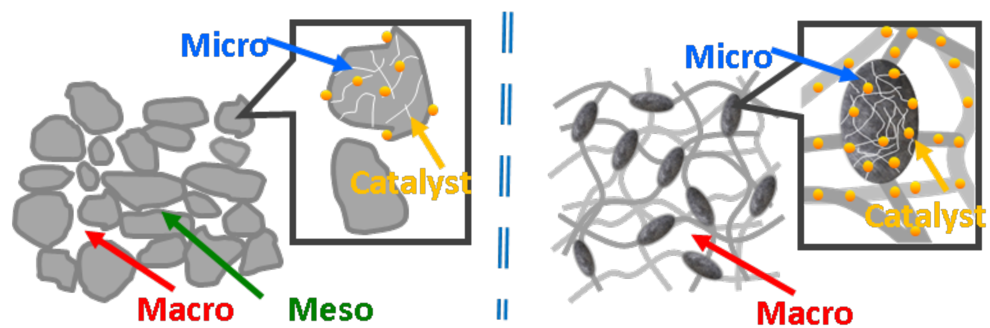
Shui, Chen, Grabstanowicz, Zhao and Liu, *PNAS*, **2015**, vol. 112, no. 34, 10629
Liu et. al. **US Patent 9,350,026**

Gas diffusion inside electrode

$D_{eff} = \varepsilon D/\tau$; ε = porosity

$\tau = (path\ l/straight\ l)^2$

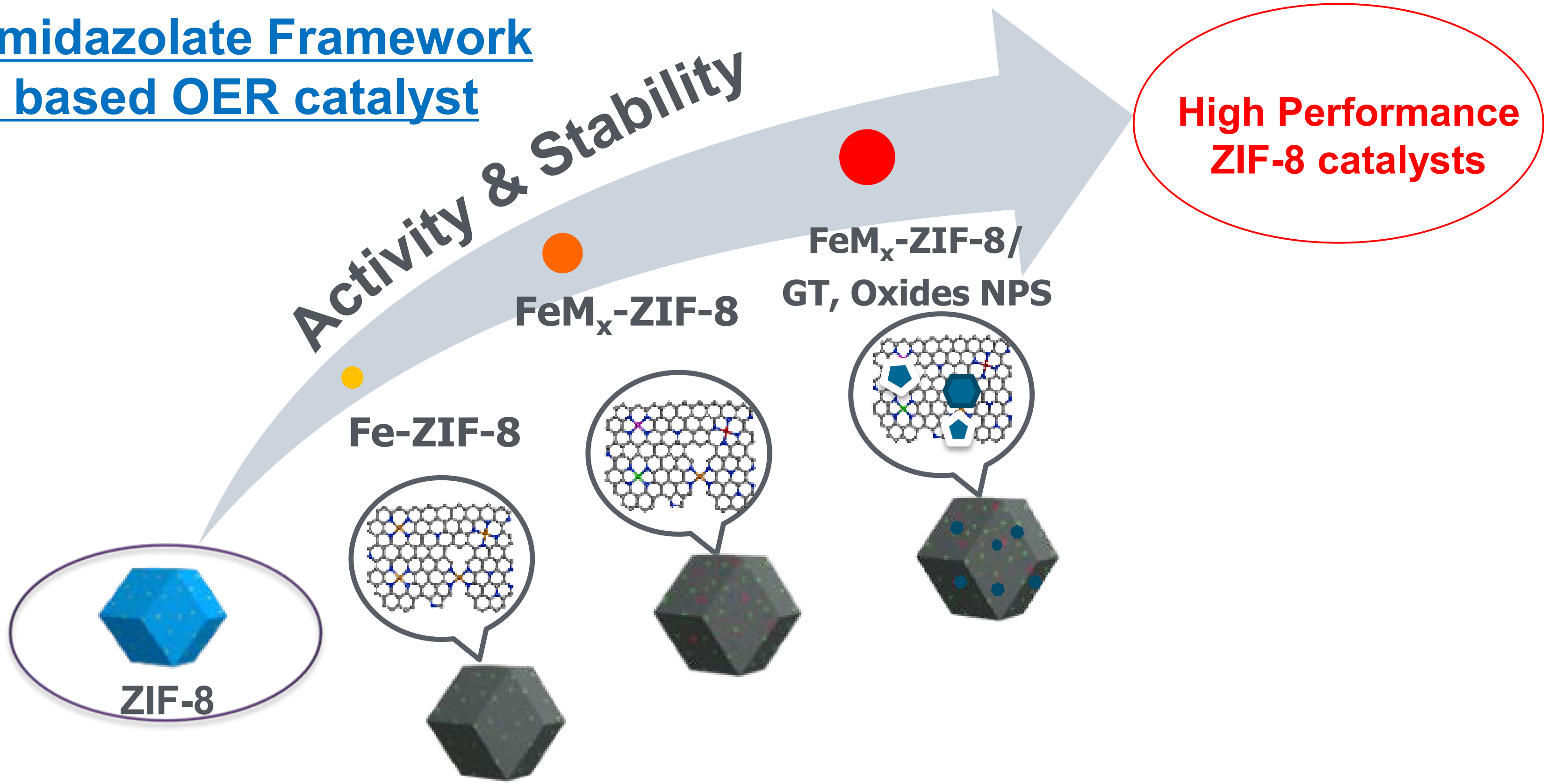
$1/D_{eff} = 1/D_{micro} + 1/D_{meso} + 1/D_{macro}$

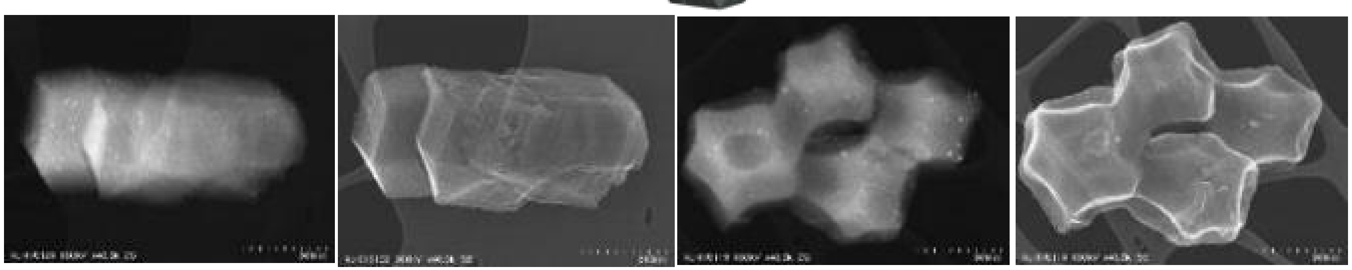


- **MOF embedded PNNE can improve OER mass/charge transfers via direct macro-to-micropore connection**
- **Continuous network offers improved connectivity between the catalytic site against deactivation by oxidative corrosion**

Approach – Innovation @ UB

Zeolitic Imidazolate Framework (ZIF-8) based OER catalyst





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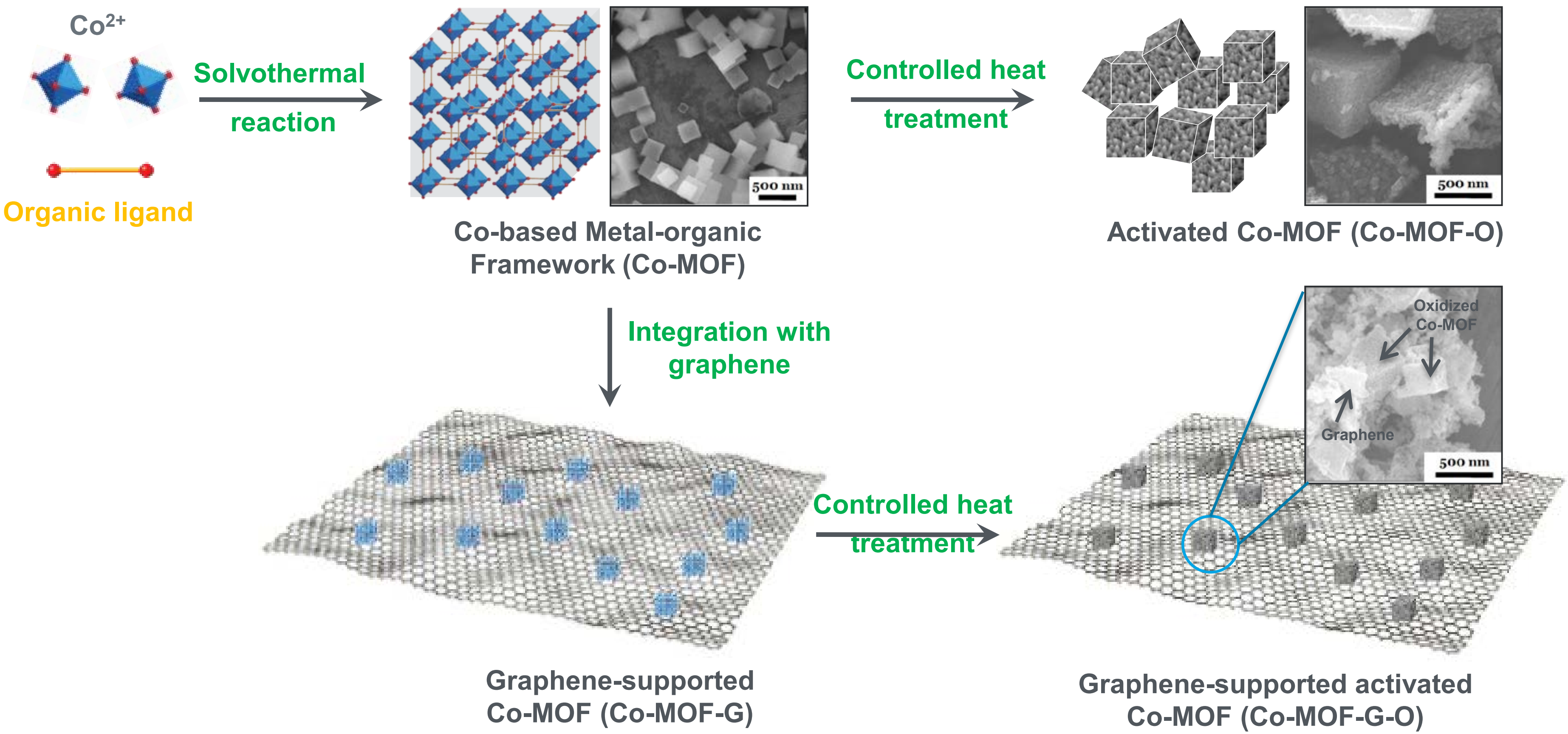
Approach – Milestones

Milestone Description	Criteria	End Date	Status
Co-ZIF based catalyst syntheses	At least 3 new Co-MOF based OER catalysts are prepared and tested. Demonstrate at least one catalyst with OER potential < 1.74 V at the current density of 10 mA/cm^2.	12/29/2017	*100% Completed*. A recent MOF-derived catalyst by ANL team showed OER potential of 1.667 V at current density of 10 mA/cm^2.
Fe-ZIF based catalyst synthesis	At least 6 new Fe-ZIF based OER catalysts are designed, synthesized, heat activated, and tested.	3/29/2018	*100% completed*: 16 TM doped ZIF-8 were synthesized and activated at UB with promising activities.
MOF templated PNNE catalyst synthesis	At least 4 MOF embedded PNNE OER catalysts with the second metal doping are prepared with at least one catalyst with SSA exceeds 200 m2/g.	6/30/2018	50% completed. Three PNNE-MOF catalysts were prepared by ANL with SSA of 90 to 150 m2/g obtained.
Catalyst Performance Evaluation by RDE	At least 14 PGM-free catalysts will be tested in acid with <30% loss of activity after 5,000 potential cycles between 1.2 and 2.0 V.	9/28/2018	In process

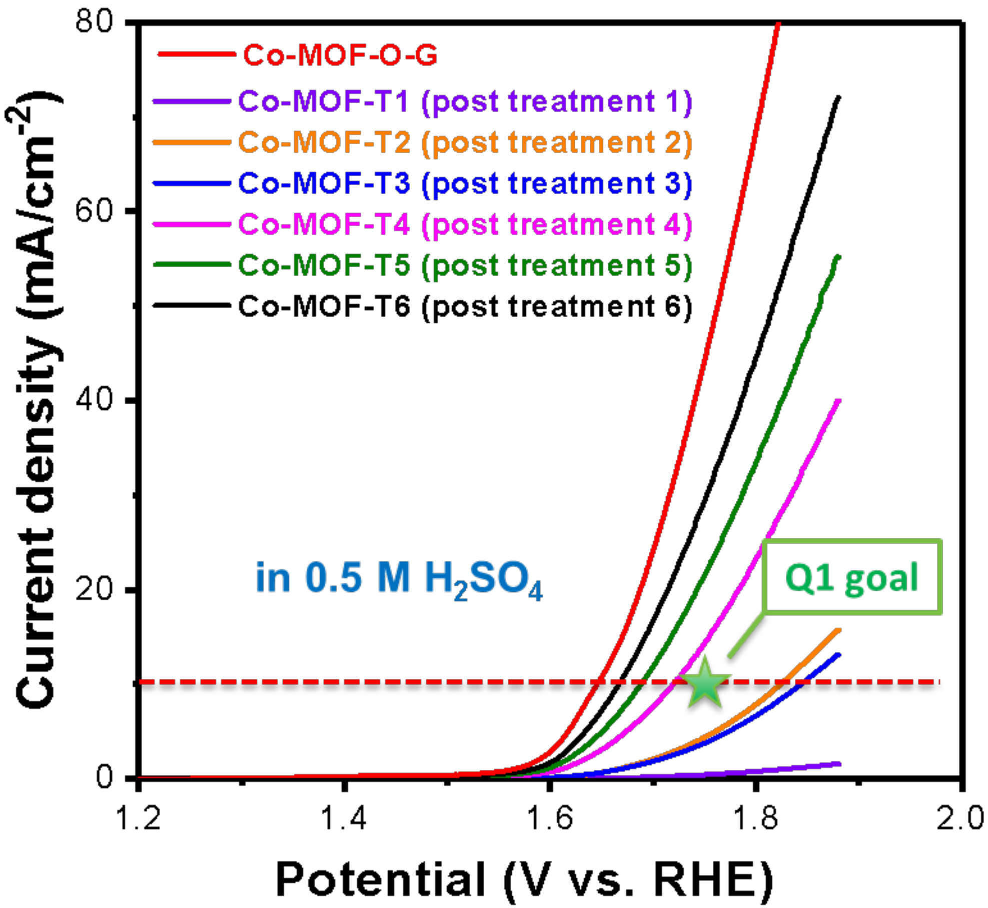
Go/NoGo: Demonstrate one or more PGM-free OER catalysts < 15 mV higher than Ir (*i* = 10 mA/cm^2 and <20 mV loss after 10000 cycles by RDE, or MEA electrolyzer at > 200 mA/cm^2 @ 1.80 V.

Accomplishments – MOF Based OER Catalyst Syntheses @ ANL



New MOF approaches are under development with potential for easier bimetallic and multi-metallic catalyst synthesis through exchange/doping

Accomplishments – Significant MOF-OER Catalyst Activity Improvement Achieved

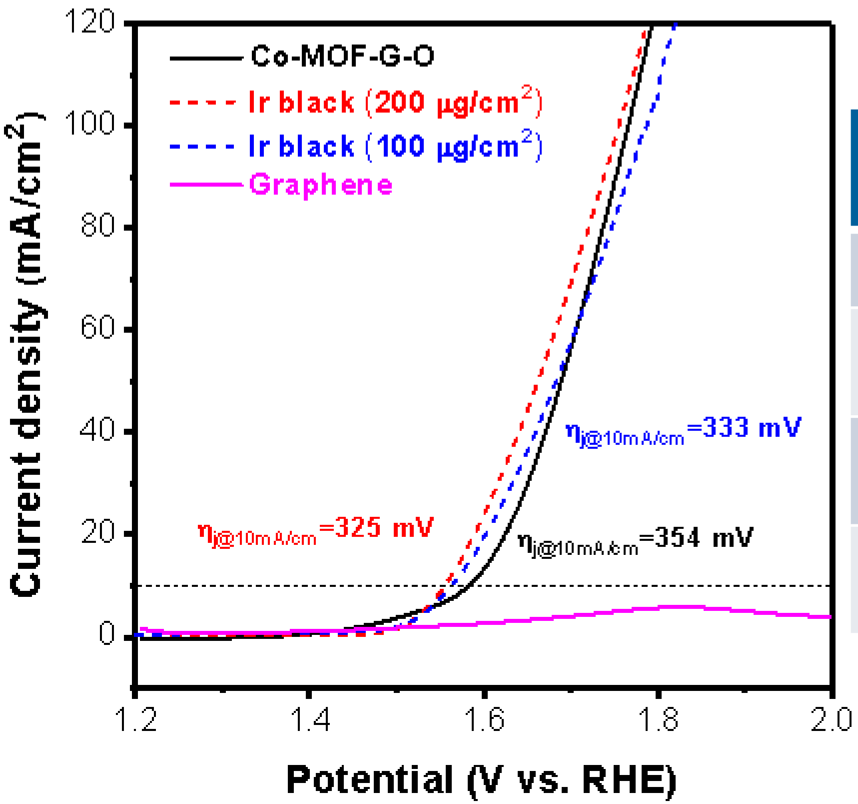


- Several new MOF-derived OER catalysts were prepared under different compositions/activations with OER activities measured by rotating disk electrode (RDE) in 0.5 M H_2SO_4.
- Progressive improvements were made with the best performing catalyst showing OER voltage of 1.644 V (vs. RHE) at 10 mA/cm^2, a benchmark for activity
- The OER activities of **four** catalysts among seven exceeded Q1 milestone goal of 1.74 V (vs. RHE) at 10 mA/cm^2.

ANL MOF-based catalyst demonstrated excellent OER activity in Acidic Electrolyte

Accomplishments – ANL MOF-OER Catalyst Outperformed PGM-free Benchmarks in Activity

ANL's new catalyst shows the activity approaching to Ir black measured over coated surface …

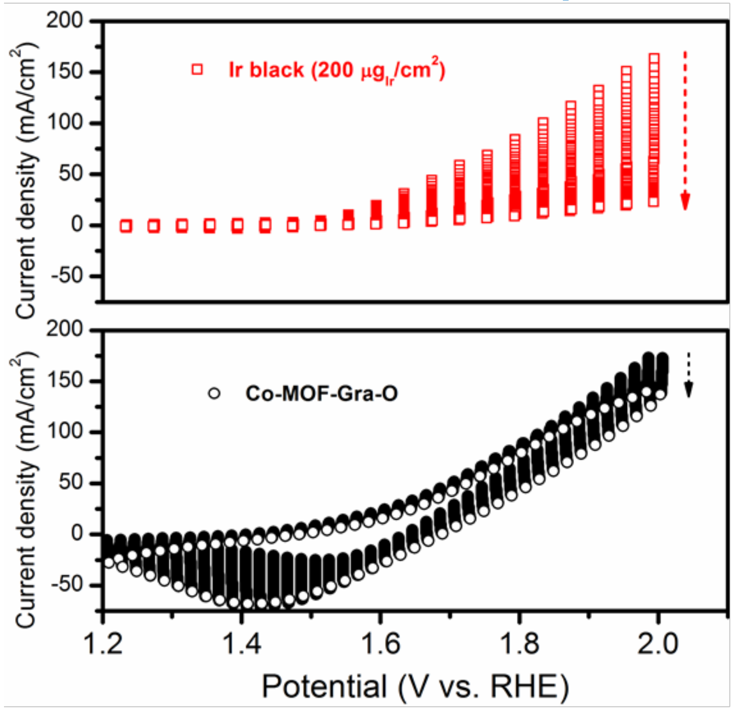


… the activity of ANL's catalyst compared favorably over several PGM-free catalysts in the literature measured under similar condition.

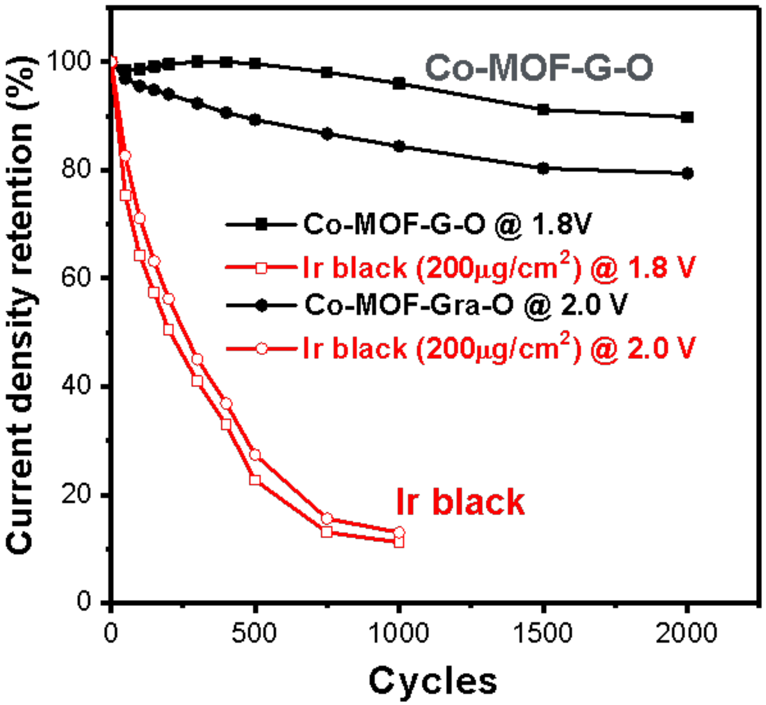
Catalysts	Overpotential @10mA/cm^2	Ref.
Co-MOF-Gra-O	**354 mV**	**This work**
Ba[Co-POM]	361 mV	Nat. Chem., 2018
Co_3O_4	570 mV	Chem. Mater., 2017
Co_3O_4@C/CP	370 mV	Nano Energy, 2016

Accomplishments – MOF-OER Catalyst Achieved Significant Durability Improvement

CVs were measured during accelerated aging through voltage cycling (1.2 to 2.0 V, scan rate = 100mV/s)…

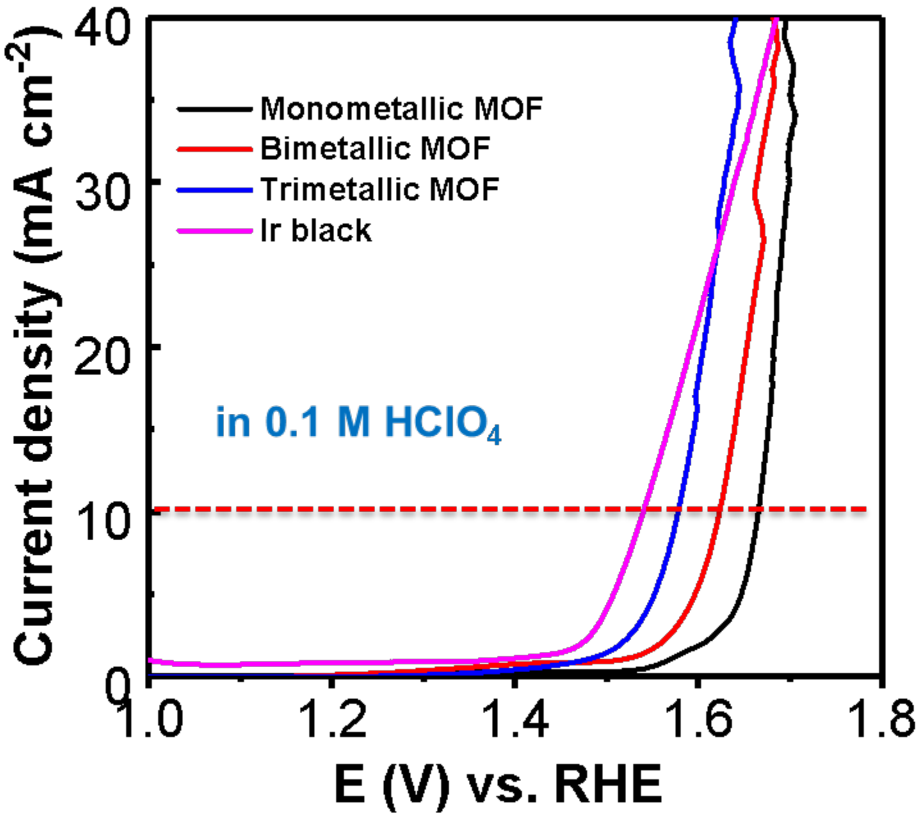


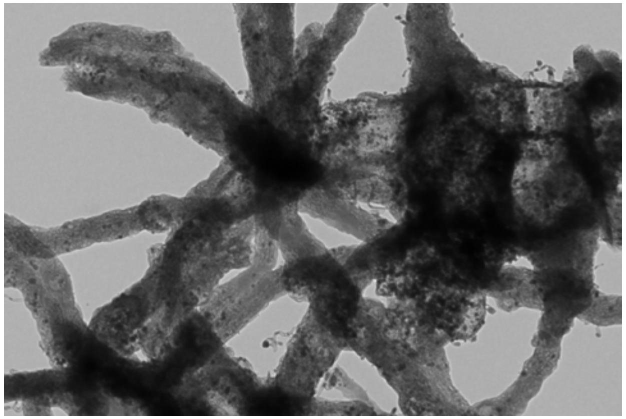
… the current density decay of Ir is significantly faster than that of ANL PGM-free catalyst



ANL's PGM-free catalyst shows excellent durability compared to Ir black when tested under voltage cycling in acidic electrolyte

Accomplishments – ANL PNNE-OER Catalyst Also Demonstrated Excellent Activity

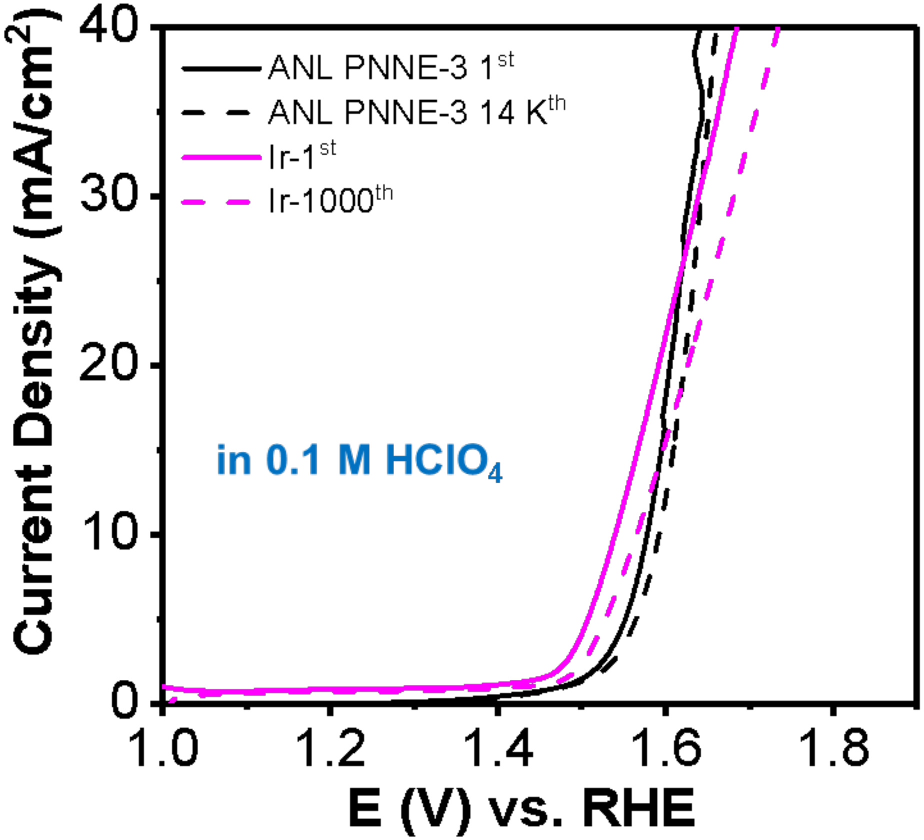




- ANL PNNE catalysts were prepared by e-spinning of MOFs in polymer slurry, followed by electrospin, forming and thermal activation
- New trimetallic MOF-based PNNE catalyst showed excellent activity of 1.58 V (RHE) at current density of 10 mA/cm^2

ANL's PNNE catalysts also outperformed PGM-free benchmarks in activity by optimizing of composition, e-spin formulation and surface property

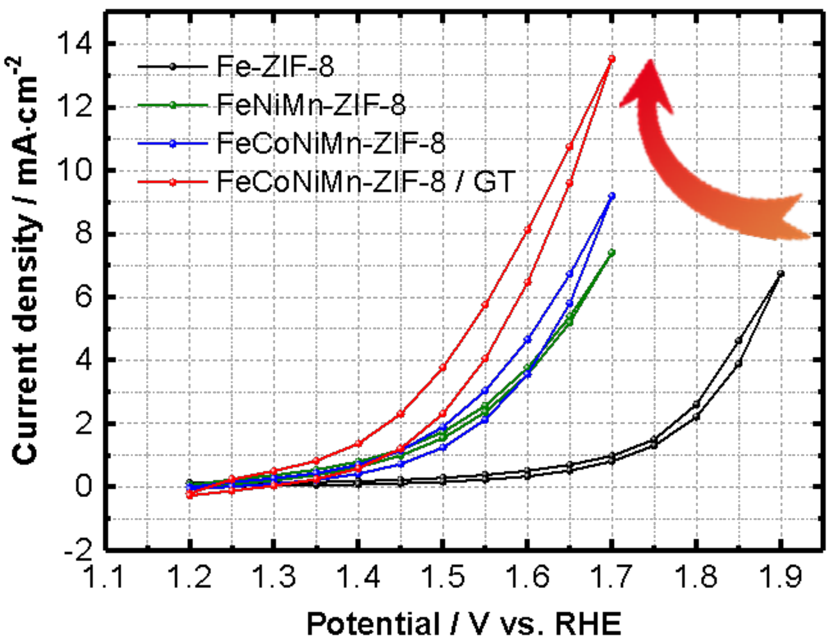
Accomplishments – PNNE Catalyst Showed Excellent Durability in Acidic Electrolyte

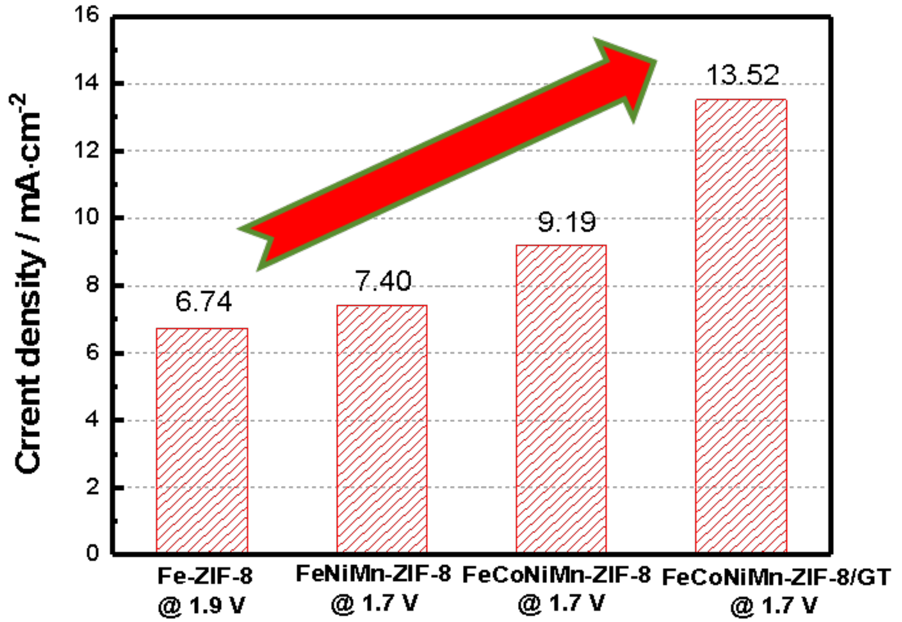


- A representative ANL PNNE catalyst (PNNE-3) showed very good durability during 14 K voltage cycling in 0.1 M $HClO_4$ electrolyte measured by RDE
- The durability outperformed Ir catalyst tested under the similar condition

Preliminary RDE investigation shows ANL's embedded PNNE catalyst with very good activity and durability; further improvement and validation at MEA level are essential.

Accomplishments – UB's FeMx ZIF-8 Catalyst Activity Made Rapid Improvement





The OER performance of FeM_x-ZIF-8 catalysts in 0.1 M H_2SO_4 solution

With metals doping, the activity is gradually improved. Ni and Co could enhanced the OER electrocatalytic activity, and Mn shows the positive effect on stability of ZIF-8 in acid media.

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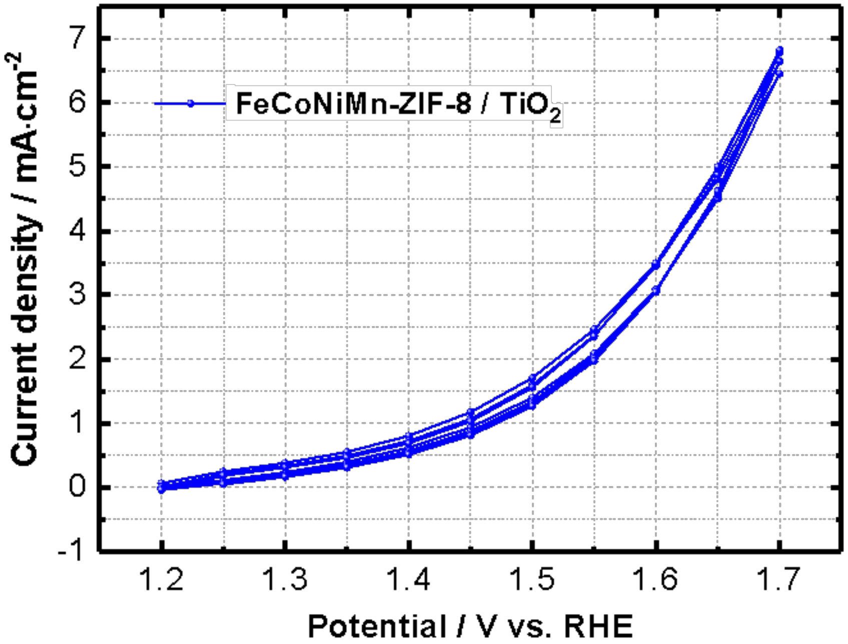
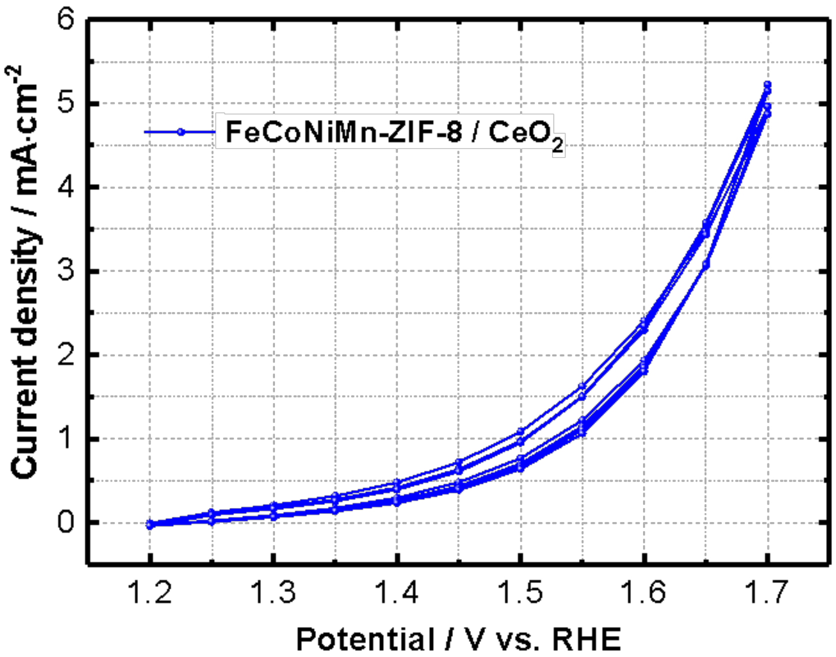
Accomplishments – UB's ZIF-8 Based Catalyst Durability Showed Promising Progress





The stability performance of ZIF-8 based catalysts promoted with TiO_2 and CeO_2 NPs

TiO_2 and CeO_2 nanoparticles are very stable in acid, showing the potential to further improve the stability of ZIF-8 based catalysts

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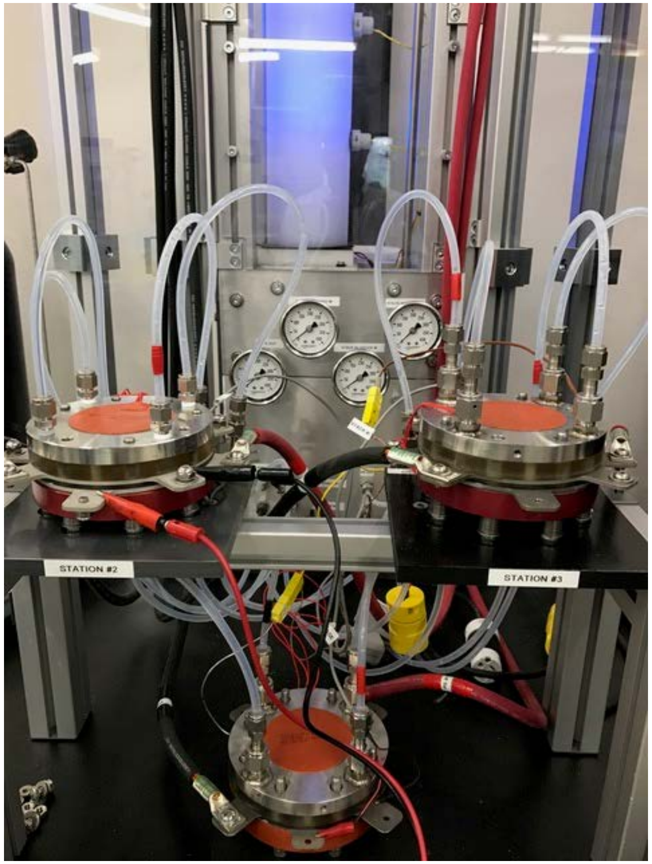
The State University of New York

Contribution – Giner

From RDE to MEA (Giner)

- Electrode design and development using a variety of aqueous and non-aqueous ionomer dispersions
- Catalyst ink processing and characterization (rheology, dynamic light scattering, zeta potential, and surface energy)
- Mitigated membranes to lower hydrogen crossover
- Dimension-stabilized membranes towards reduced membrane swelling and enhanced membrane mechanical stability
- Special anode gas diffusion media and bipolar plates for enhanced corrosion resistance

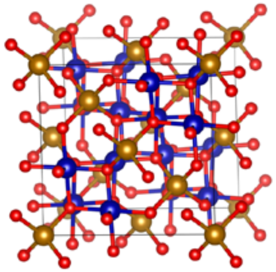


GINERLABS

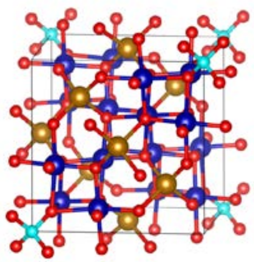
Collaboration: Computational Modeling Supports @ LLNL & LBNL

Near term: understand factors that improve electronic conductivity of C-doped oxide
Next stage: Structure-defect impact to catalyst activity and durability
Approach: Develop structural models using a combination of DFT simulations and lattice Monte Carlo simulations, to be validated by characterization.

LLNL: effect of defects on oxide conductivity (develop structural motifs for LBNL)



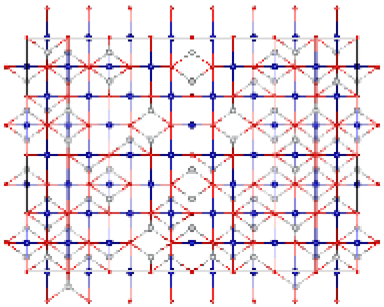
Oxide crystal

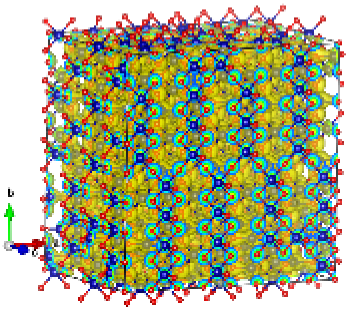


M substituted by C

Completed: modeling of O vacancies, C substitution of M/O
Ongoing: analysis of electronic structures
Next: C interstitials and N defects simulation being prepared

LBNL: construct disordered structural models using a lattice Monte Carlo & classical potential





Completed: L-MC code and potential for simple case (left)
Ongoing: analysis of the electronic structure (right)
Next: incorporate motifs developed by LLNL

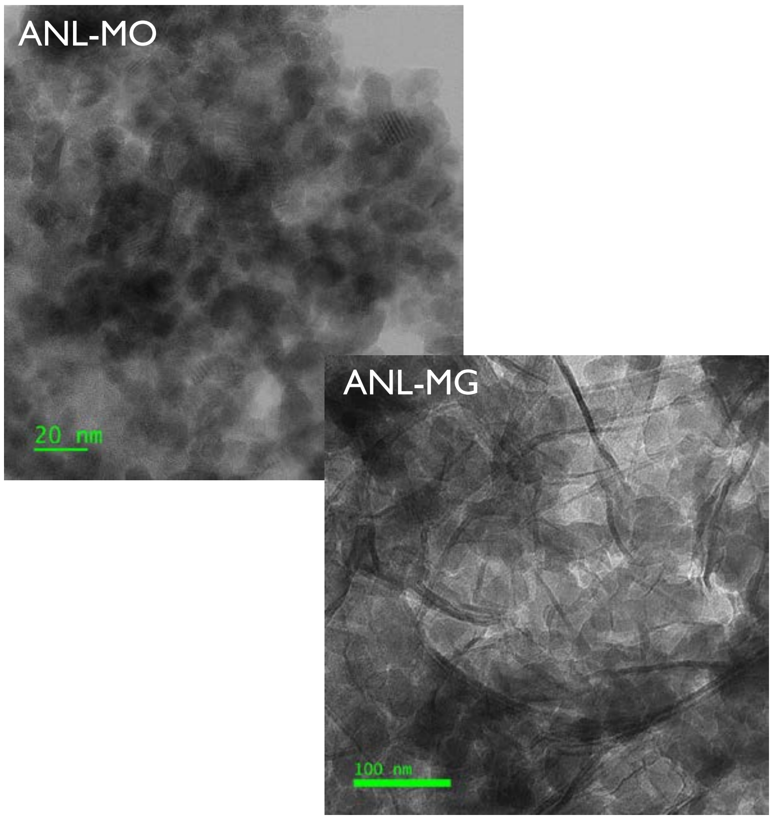
Realistic structural models are being developed at LBNL & LLNL

Lawrence Livermore National Laboratory

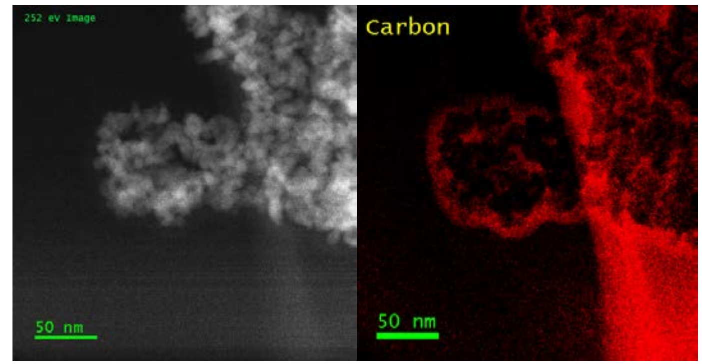
BERKELEY LAB Lawrence Berkeley National Laboratory

Collaboration: Electron Microscopic Studies @ SNL

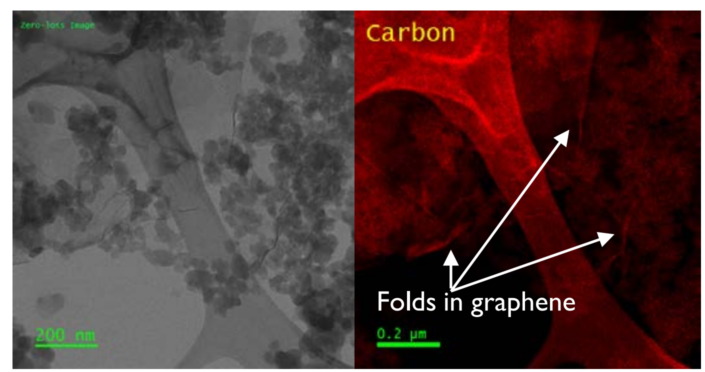
TEM reveals MOF size and graphene wrapping



Energy-Filtered TEM



Carbon coating detected on particle surface

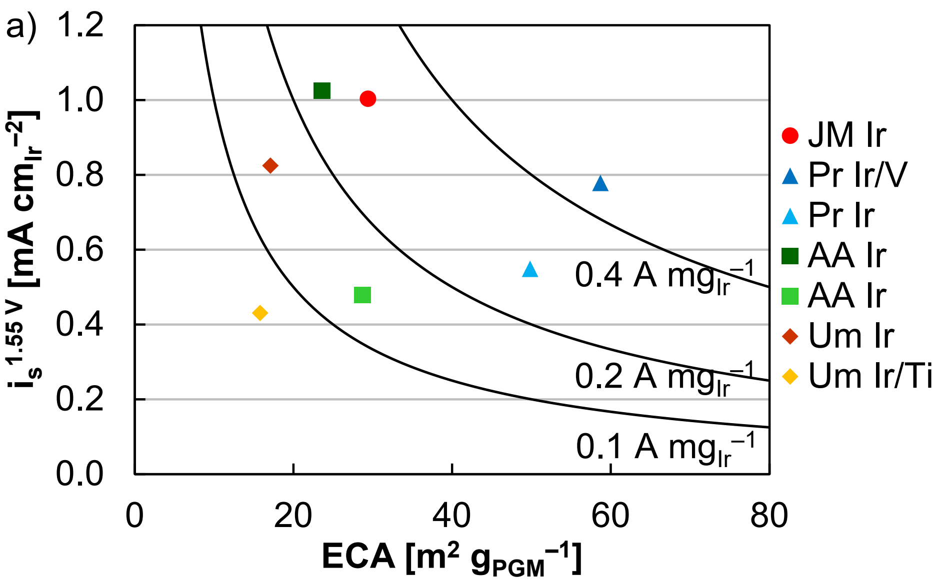


Identified particles folded by graphene

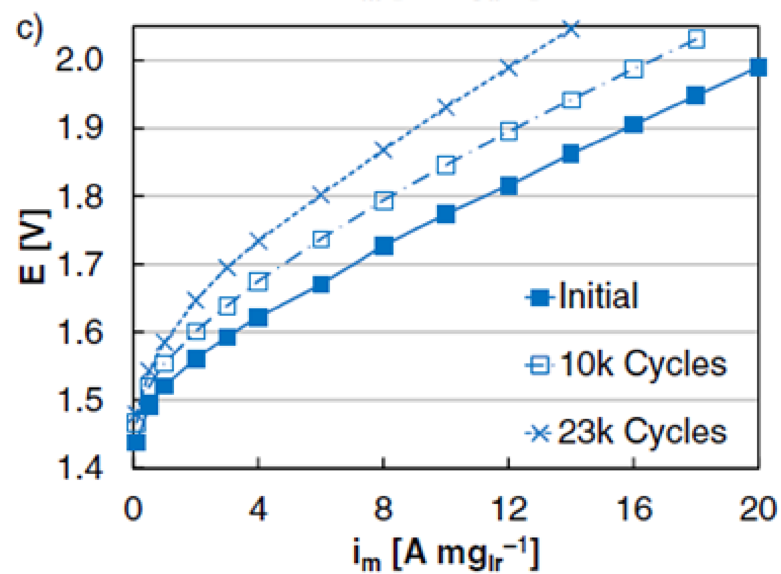
Sandia National Laboratories

Collaboration: Testing of Catalyst Activity & Durability Baselines @NREL

Catalyst performance baselines



Predict MEA durability



NREL will also support the catalyst surface characterization and high throughput electrode optimization

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Proposed Future Work

Phase I

- Continue to develop Co- and Fe-based monometallic MOF OER catalysts through elemental doping and oxide modifications to further improve activity and durability (ANL/UB)
- Continue to improve PNNE OER catalyst through e-spin and catalytic additive optimization (ANL)
- Initiate PGM-free electrode/MEA fabrication and PEME testing in meeting go/no-go criteria (ANL/Giner)

Phase II

- Explore multi-metallic MOFs through reticular synthesis and post-synthesis modification to further enhance OER catalyst activity and durability
- Explore new synthesis methods (graphene wrapping, ALD, etc.) to improve PNNE PGM-free catalyst stability
- Design, fabricate and demonstrate MEA/PEME with PGM-free OER catalyst as viable replacement for Ir, leading to 20x reduction of catalyst cost

Project Summary

- New MOF-derived PGM-free OER catalysts developed by ANL showed excellent activity and durability in acidic electrolyte compared to PGM-free benchmark catalysts in literature, with performance approaching to Ir black.
- Initial study of ANL's PNNE OER catalysts also demonstrated very promising activity and excellent durability when measured against Ir black in strong acidic electrolytes.
- UB team is making excellent progresses in activity and durability improvements for FeM_x-ZIF-8 and FeMx-ZIF-8/Oxide based catalysts.
- Collaborations with four nodes of HydroGen yielded insightful information in structural, performance and fundamental understanding of OER catalysts developed by the team.

Our initial studies have validated our project approaches demonstrated by very promising catalytic activity and durability

Acknowledgement

- Argonne National Laboratory
  - Lina Chong
  - Hao Wang
- HydrogGen 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 Shaun Alia)
- US DOE Office of Fuel Cell Technologies
  - Eric Miller – Program Manager
  - Dave Peterson – Project Manager