

Non-PGM Cathode Catalysts using ZIF-based Precursors with Nanonetwork Architecture

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Project ID
FC113

Overview

Timeline

- Project Start: January 2013
- Project End: January 2014

Budget

- FY13 DOE Funding: \$ 140K
- Planned FY14 DOE Funding: \$ 150K
- Total Project Value: \$ 290K

Barriers

- Barriers addressed
 - A. Durability
 - B. Cost
 - C. Performance

Collaboration

- Cross-lab Catalyst Activity Evaluation
 - Los Alamos National Lab (P. Zelenay team)
- Catalyst Development
 - National University of Singapore, University of South Florida, North Illinois University



Objective - Relevance

- To design, synthesize, and evaluate highly efficient zeolitic imidazolate framework (ZIF) based non-platinum group metal (non-PGM) cathode catalysts in PEMFCs for transportation applications
- To maximize electron, heat and mass transports by incorporating the catalyst into porous nano-network structure.
- To support non-PGM catalyst development through advanced structural characterizations

Potential Advantages of ZIF-based Nano-network Non-PGM Catalysts & Their Impact on Technology Barriers

- **Cost** – ANL ZIF-based non-PGM catalysts can be scaled-up for industrial production using low-cost material through a simple “one-pot” synthesis method.
- **Performance** – ZIF-based non-PGM catalysts with nano-network structure have demonstrated the feasibility of achieving the highest active site density with improved mass/charge transfers.
- **Durability** – The highly graphitized nano-network structure offers the promise of improving the catalytic durability under fuel cell cycling conditions.



Fuel Cell Electrocatalyst Challenge



- Platinum and platinum group metals (PGMs) are current materials of choice for PEMFC catalysts
- PGM represents the highest cost component in PEMFC stack
- Various low-cost, non-PGM alternatives have been investigated for the oxygen reduction reaction; the M-N-C systems (M = Fe, Co...) are among the most promising non-PGM ORR electrocatalysts in terms of activity and durability

US DOE Performance Target for Non-PGM Electrode Catalyst Volumetric current density @ 0.8 V	2010	2017
	130 A / cm ³	300 A / cm ³



Approach - Strategy for non-PGM Catalyst Performance

New ZIF-based
Catalyst Synthesis

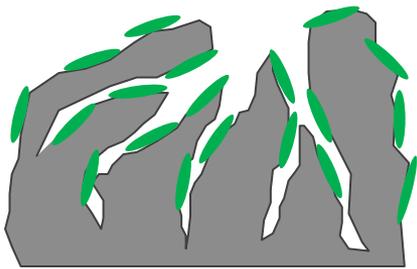
Nano-network Design
& Fabrication

Structural & Cell
Performance Studies

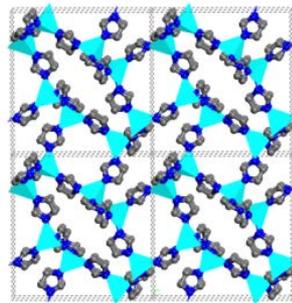
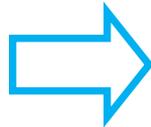
$Catalytic\ Activity \propto$
 $Turn-Over-Freq. \times Site\ Density$

- Different transition metals
- Different organic ligands
- Different metal-ligand binding energy & coordination structure

- “Support-free” and pore-former free
- Uniform distribution & high active site density
- Zeolitic imidazolate framework & porous organic polymer



Conventional

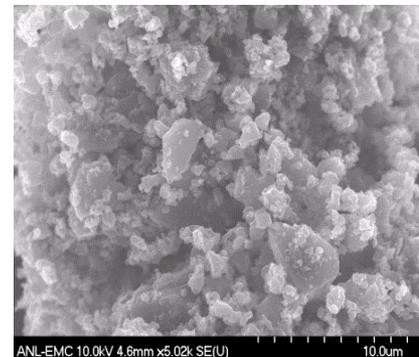


ANL's approach

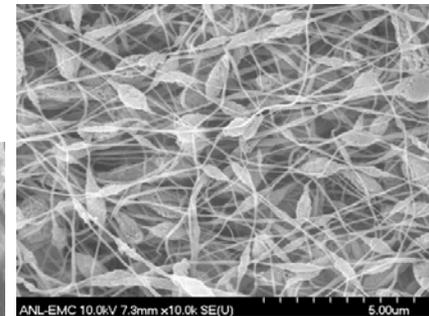
$Mass/Charge\ Transport \propto$
 $Porosity\ \&\ Network\ Connectivity$

- Higher catalyst density & activity-contributing micropore volume
- Enhanced mass/charge transfers via macropores and nano-network

Conventional

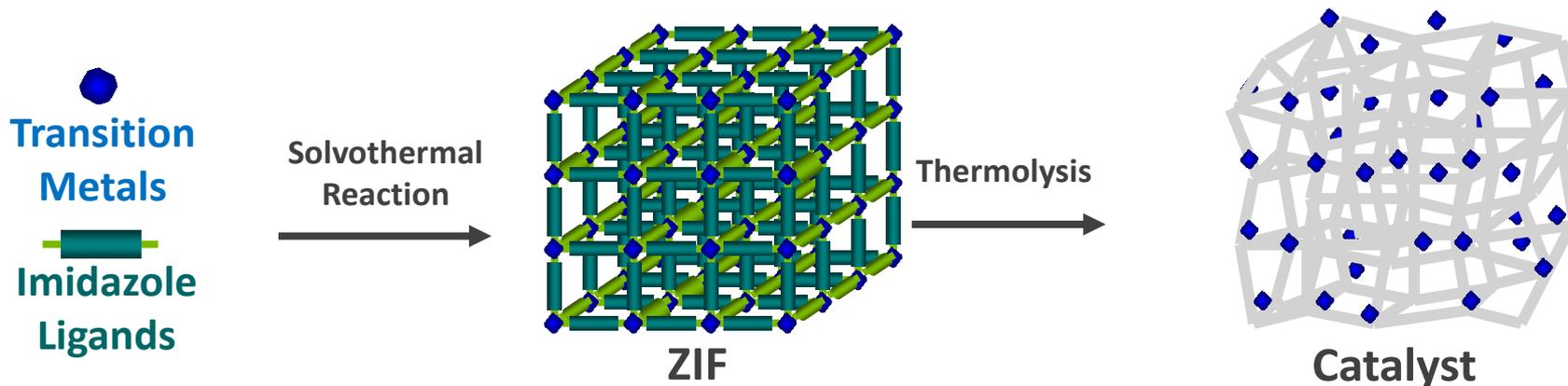


ANL's nano-network



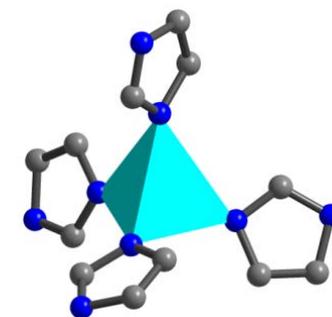
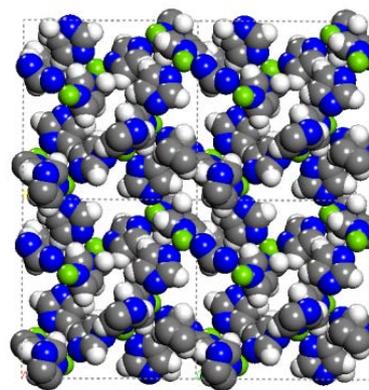
Approach: Improving Catalytic Activity with ZIFs as Precursors

Process of synthesizing ZIF/MOF-based non-PGM Catalyst



Advantages of “Support-free” ZIF-based non-PGM Catalyst Approach

- “Support-free” with the highest precursor density for active site conversion
- Porous 3-D structure with high specific surface area and uniform micropores
- Well-defined coordination between transition metal & ligand with large selection of different compositions

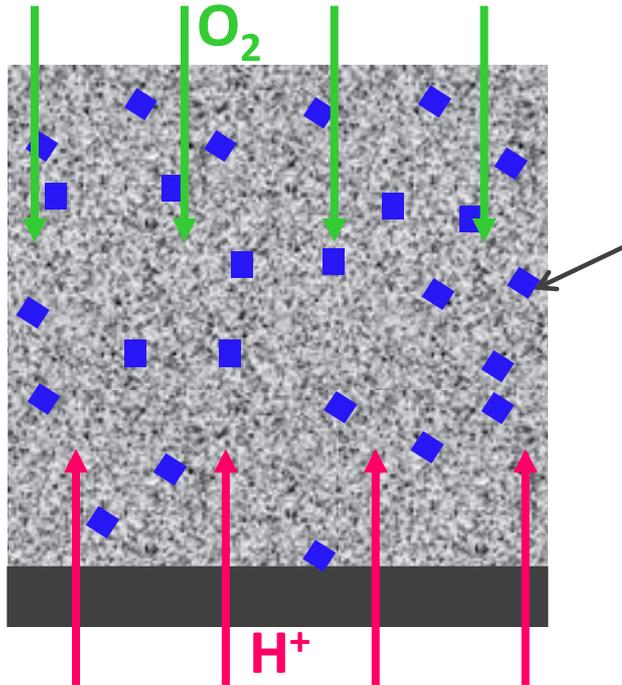


M-ligand site density =
 $3.6 \times 10^{21}/\text{cm}^3$

Ma, Goenaga, Call and Liu, *Chemistry: A European Journal*, (2011) 17 2063

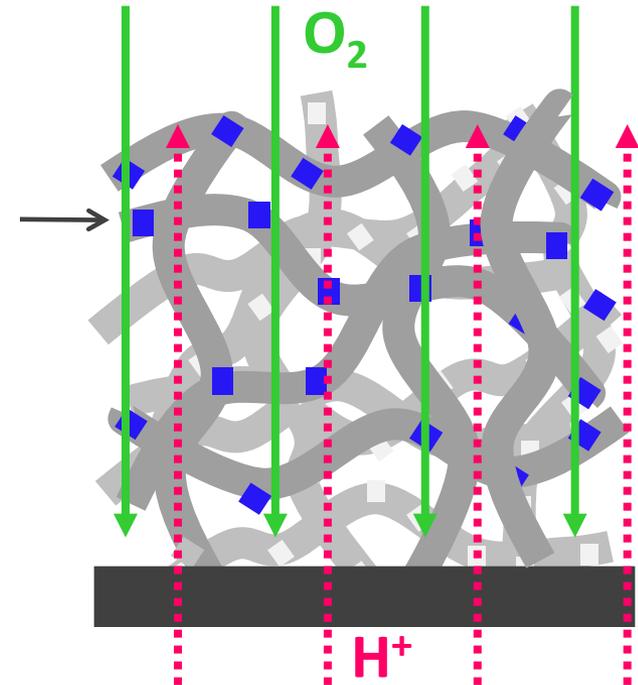
Approach: Maximizing Mass/Charge Transports via Nano-network

Conventional Support



ZIF Catalyst

Nano-network Support



- Impeded O_2 transport through porous carbon, macro \rightarrow meso \rightarrow micro
- Hindered charge/heat transfer through particle percolation
- Exposed active site at carbon surface

- Improved O_2 transport through voids between fibers, macro \rightarrow micro
- Enhanced charge/heat transfer via nano-network
- Embedded catalytic site inside nano-fibers

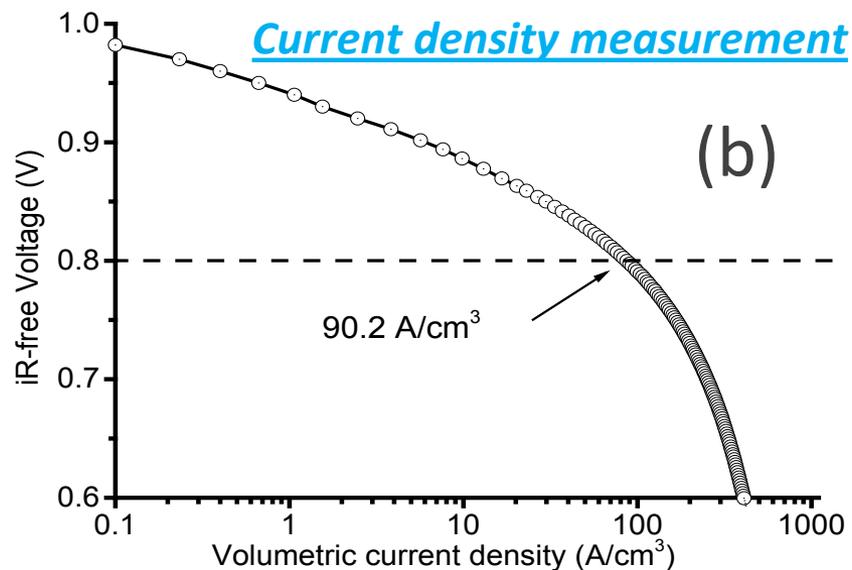
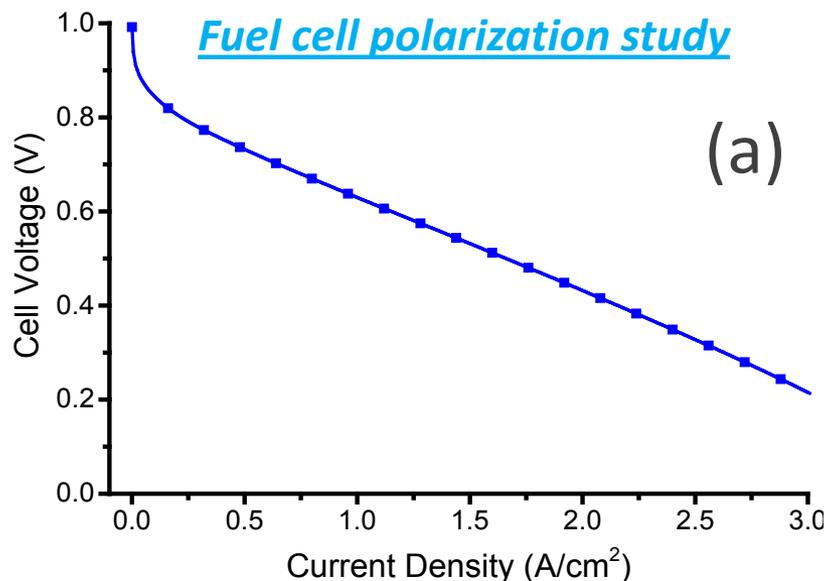
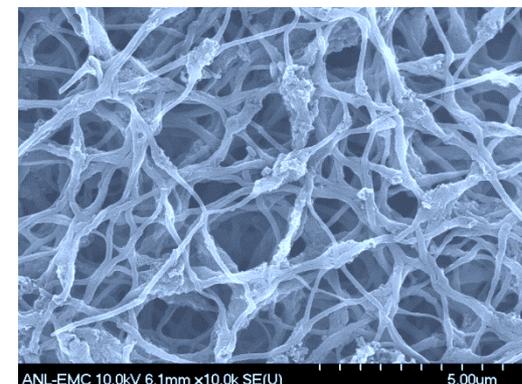
Approach - Milestones

Month/Year	Milestones	Status Update
3/13	Complete the formulation improvement of the first batch of nanofibrous catalysts and demonstrate $>90 \text{ A/cm}^3$ (@0.8V) in volumetric current density or $>3 \text{ A/cm}^2$ current density (@0.1V).	Completed. An initial reformulation of ZIF/nano-network cathode catalyst was completed. The MEA with this catalyst showed 90.2 A/cm^3 at 0.8 V and 3 A/cm^2 at 0.2 V ($P_{\text{O}_2} = P_{\text{H}_2} = 2 \text{ bar}$).
3/13	Complete the surface area, porosity and elemental analysis of representative non-PGM catalysts and establish property-function relationship.	Completed. XRD, BET, XPS and imaging methods were applied to study ANL's non-PGM catalyst structures and correlations between surface area/N-content to activity were found.
11/13	Provide Los Alamos National Lab at least two Argonne's non-PGM catalysts with potential to reach current DOE 2017 target to be evaluated under LANL's test protocols.	Completed. Two catalysts were prepared and sent to LANL and tested in fuel cells with $P_{\text{O}_2} = P_{\text{H}_2} = 1 \text{ bar}$. Cell OCV of 0.96 V and current density of 80 mA/cm^2 (@ 0.8V) were achieved.
1/14	Complete initial one-pot synthesis method development and demonstrate at least one MOF-based ORR catalyst with onset potential $> 0.9 \text{ V}$ (RHE, measured at 0.05 A/g at RDE level) using such method.	Completed & Exceeded. Four ZIF-based non-PGM catalysts were synthesized using a "one-pot" synthesis method. Three of the four have reached on-set potential $> 0.9 \text{ V}$ with half-wave potential as high as 0.81 V achieved.



Accomplishment 1: Preliminary Improvement on ANL's ZIF/Nano-network Catalyst Formulation

- A non-PGM ZIF/nano-network catalyst previously developed in our lab was reformulated under this project
- ORR activity at both RRDE and MEA levels was improved with promising performance



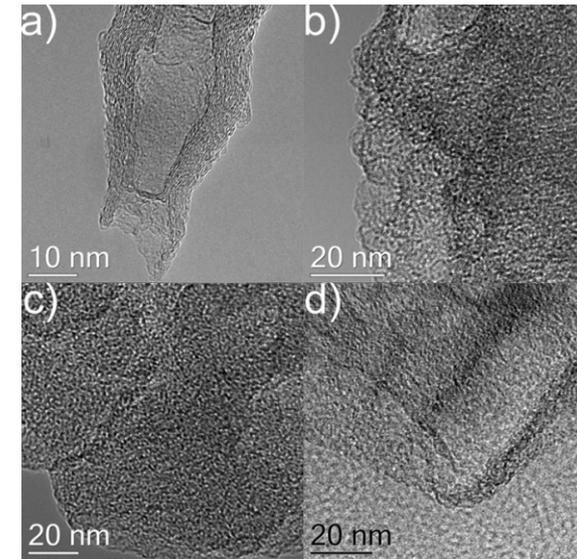
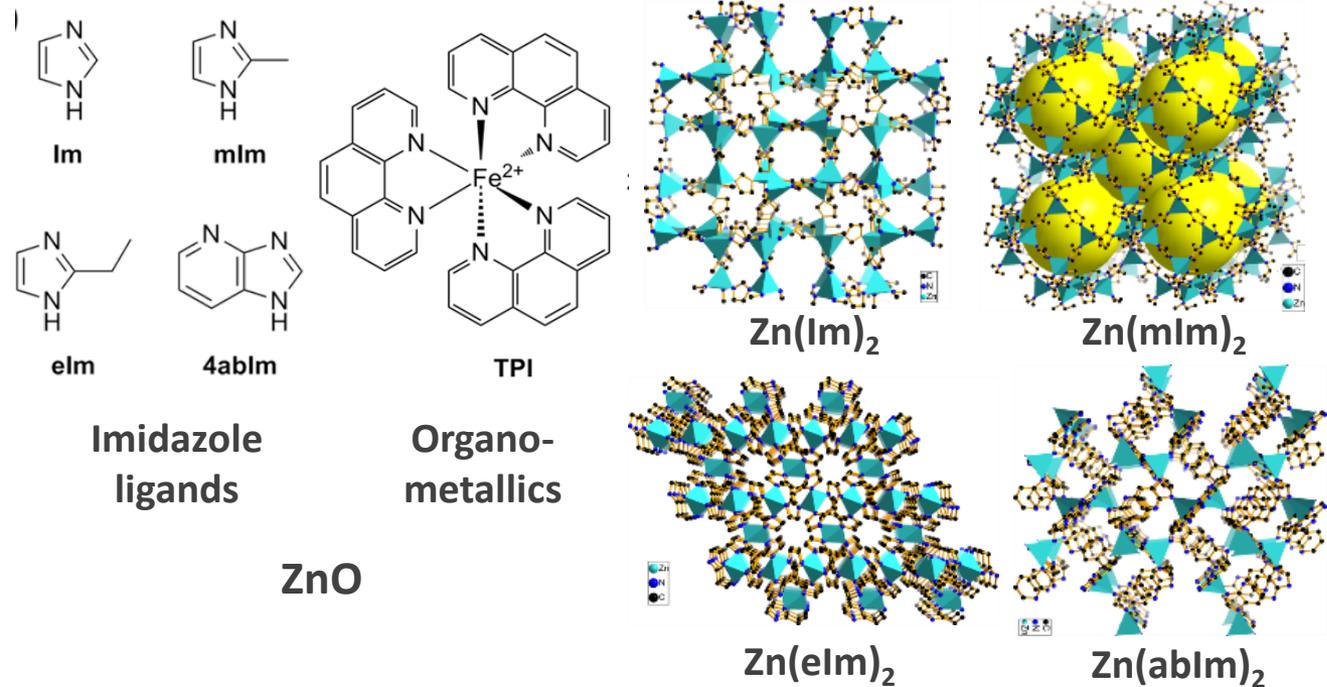
(a) Single cell with ANL's non-PGM nano-network cathode catalyst; $P_{O_2} = P_{H_2} = 2$ bar; fully humidified at $80^\circ C$, cathode loading = 3.0 mg/cm^2 , anode loading = 0.3 mg_{Pt}/cm^2 , Nafion® = 211, active area = 5 cm^2 ; (b) iR corrected volumetric current density under similar condition to (a) except cell area = 2 cm^2 , Nafion® 117, cathode catalyst loading = 2 mg/cm^2

Accomplishment 2: One-Pot Synthesis of ZIF-based non-PGM catalysts (Method)

Solid Mixing

Solid State Reaction

Thermolysis



- One-step solid-state, solvent-free synthesis without need for separation
- Use of low-cost commodity chemicals
- Robust and versatile process in screening various imidazole ligands

Accomplishment 2: One-Pot Synthesis of ZIF-based non-PGM Catalysts (Cost Reduction)

- ZIFs have been perceived as expensive materials due to elaborated synthesis/separation, and solvent waste generated
- Materials for the current approach are low-cost, bulk commodity products
- One-pot synthesis requires no solvent and separation, therefore substantially reduces the process cost and material usage

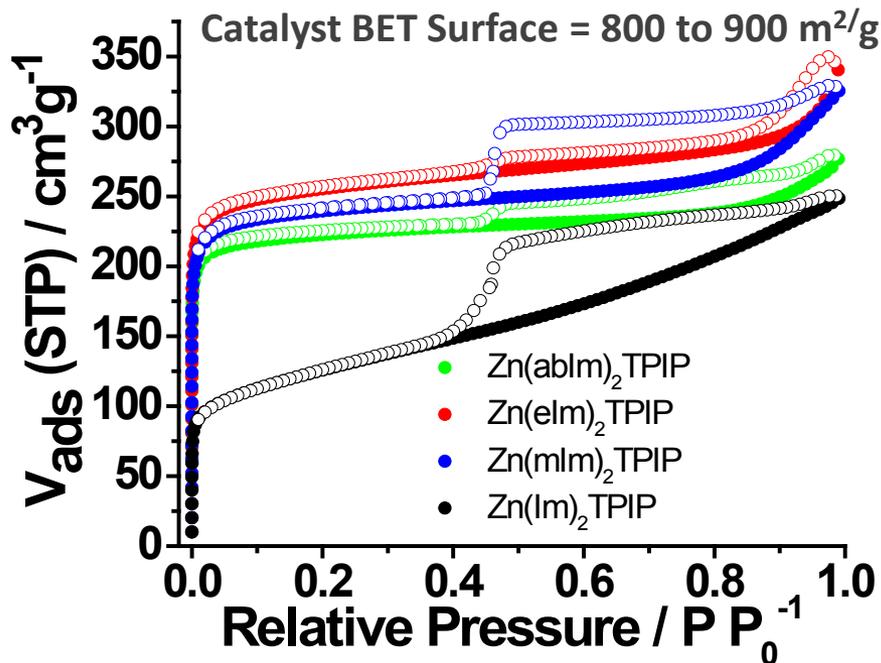
An example of raw material cost for ZIF-based non-PGM catalyst:
organic ligand = \$7/kg, metal compound = \$5/lb

D-J Liu & D. Zhao *US Patent Application* 20130273461

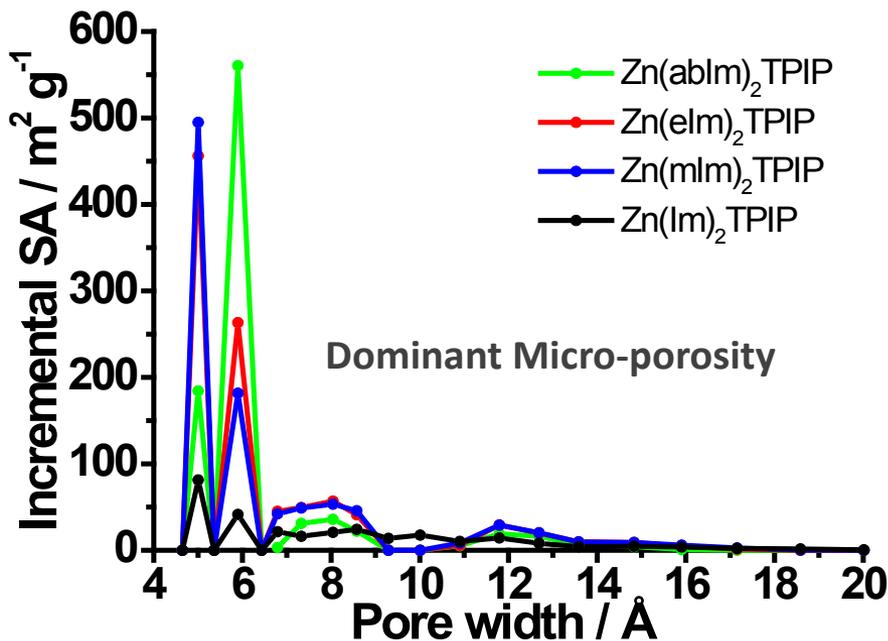


Accomplishment 2: One-Pot Synthesis of ZIF-based non-PGM Catalysts (Surface Property)

N₂ adsorption isotherm at 77 K



Pore size distribution from NLDFT



N₂-BET study shows that (a) catalyst surface areas are high after thermolysis;
(b) micropore dominates pore size distribution for heat-activated catalysts



Accomplishment 2: One-Pot Synthesis of ZIF-based non-PGM Catalysts (XPS & SEM Investigations)

N-XPS shows that pyridinic N has the highest content among various Ns in carbon

Catalyst	Pyridinic	Nitrile	Pyrrolic	Graphitic	Oxidized
Zn(Im) ₂ TPIP	34%	15%	26%	9%	16%
Zn(mlm) ₂ TPIP	43%	17%	23%	9%	8%
Zn(elm) ₂ TPIP	36%	18%	24%	8%	13%
Zn(abIm) ₂ TPIP	36%	18%	24%	7%	16%

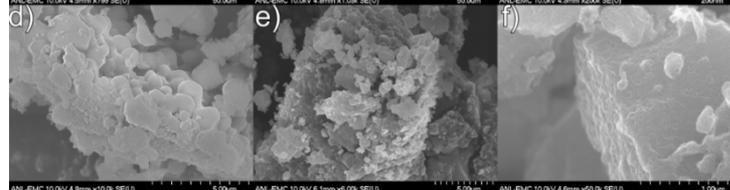
C-XPS shows that most organic carbons are converted to the graphitic form after heat-treatment

Ligand ZIFs ZIFs + TPI Catalysts

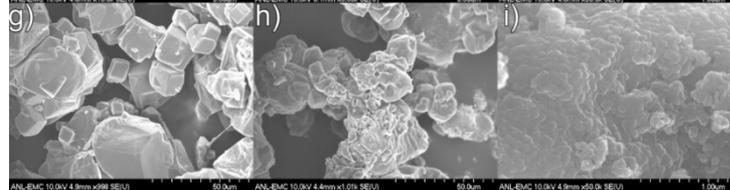
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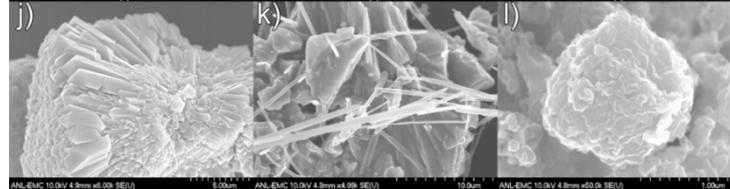
mlm



elm



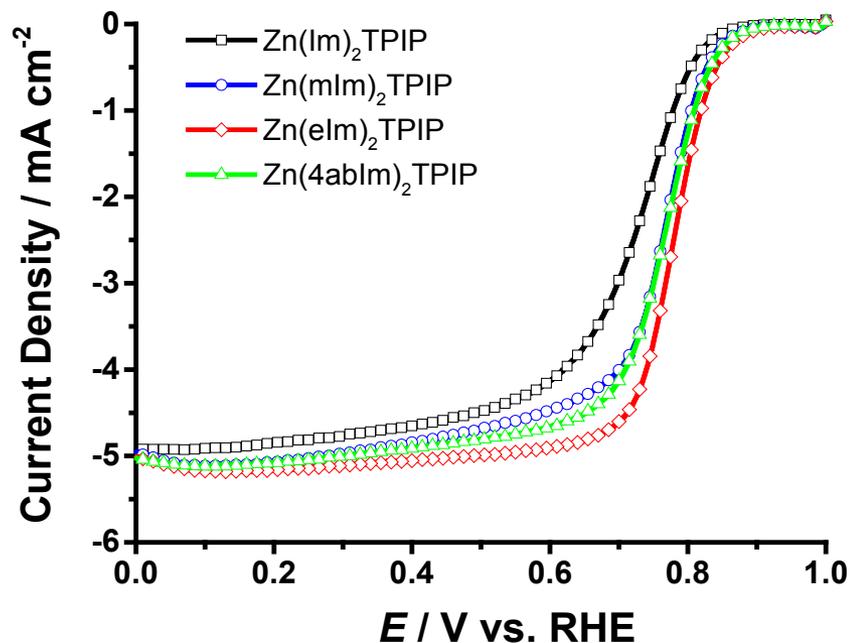
abIm



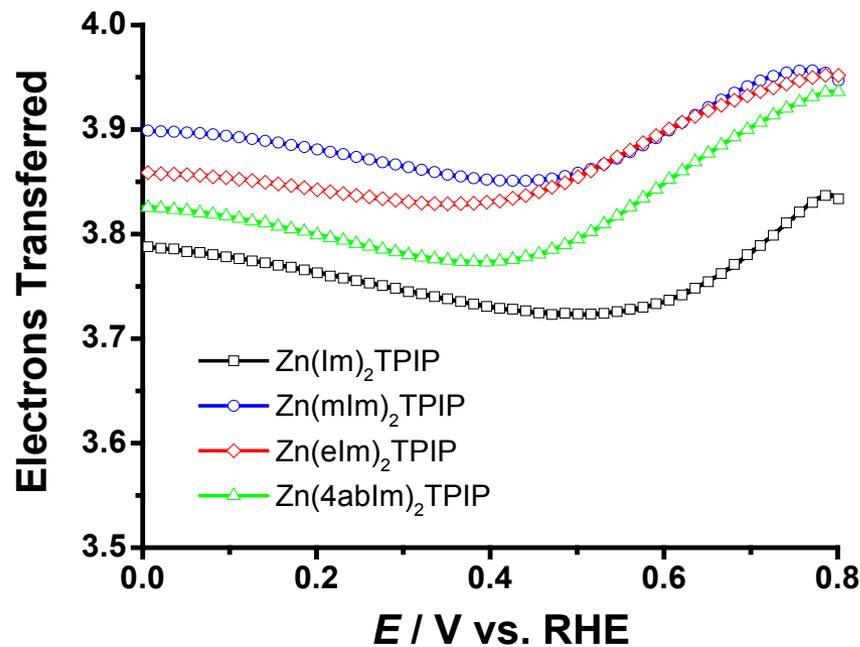
(a) Pyridinic N dominates in heat-treated ZIFs; (b) carbon is mainly graphitic though other forms also exist; (c) ZIFs have well-defined crystal structures when synthesized, and (d) they turned to amorphous after thermolysis.

Accomplishment 2: One-Pot Synthesis of ZIF-base non-PGM Catalysts (RDE Activity Study)

Linear sweep voltammograms



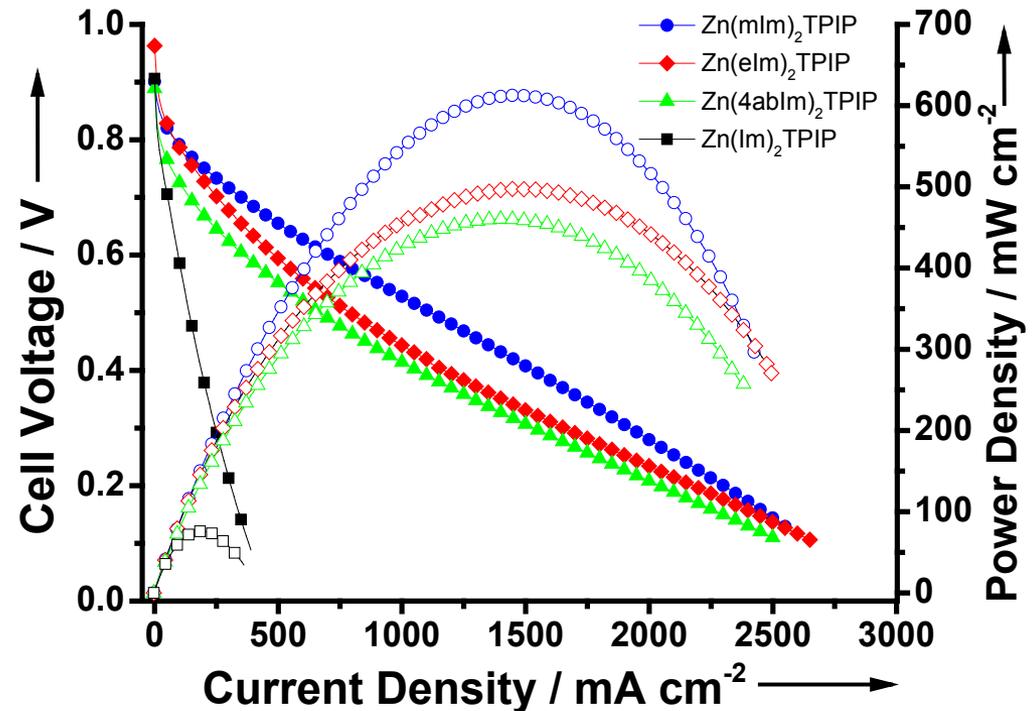
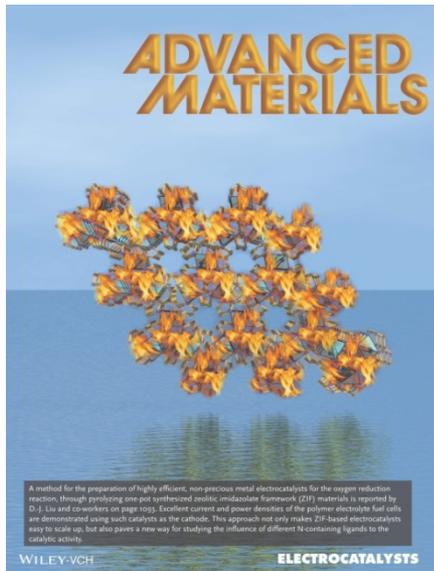
Number of e⁻ transfer measurement



Electrocatalysts	Surface Area (m ² /g)	Onset Potential E_0	Halfwave Potential $E_{1/2}$
Zn(lm) ₂ TPIP	443	0.881	0.73
Zn(mlm) ₂ TPIP	1277	0.902	0.76
Zn(elm) ₂ TPIP	920	0.914	0.78
Zn(4ablm) ₂ TPIP	976	0.904	0.76

Accomplishment 2: One-Pot Synthesis of ZIF-based non-PGM Catalysts (Single Cell Testing)

- Organic ligands in ZIFs impact the final catalytic property & activity
- Optimizing composition and process condition should lead to further activity improvements
- “One-pot” synthesis broadens the search for new N-ligand in rational design of non-PGM catalysts



80°C, fully humidified H₂ and O₂, P_{O₂} = P_{H₂} = 1.5 bar at flow rate of 300 ml/min, N-211, cathode catalyst loading = 2.2 mg/cm², anode catalyst loading = 0.3 mg Pt/cm², active area = 5 cm²

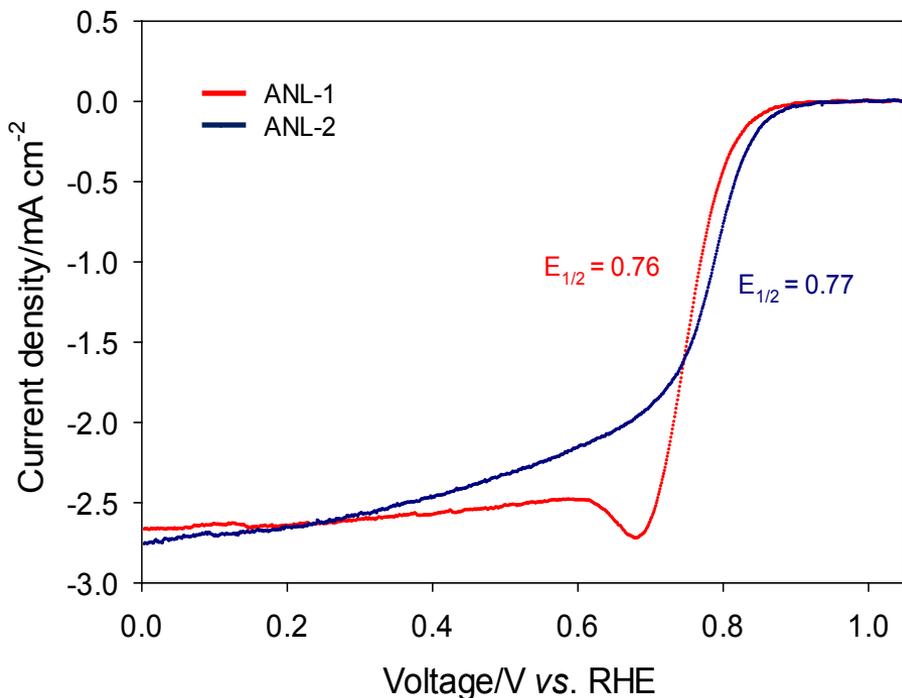
“Highly Efficient Non-Precious Metal Electrocatalysts Prepared from One-Pot Synthesized Zeolitic Imidazolate Frameworks (ZIFs)” D. Zhao, J.-L. Shui, L. R. Grabstanowicz, C. Chen, S. M. Commet, T. Xu, J. Lu, and D.-J. Liu, *Advanced Materials*, **2014**, *26*, 1093–1097 (Frontpiece)
With permission to use from *Advanced Materials*

Accomplishment 3: Catalyst Activity Test at LANL

- Over 300 mg of two ANL catalysts (ANL-1 & ANL-2) were brought to LANL
- Prior the visit, RDE experiments were performed at LANL
- An on-site visit/experiment was carried out at LANL from Nov. 17-22, 2013. 13 MEAs were tested in five days
- MEA using ANL cathode catalyst demonstrated OCV of 0.96 V at 80 °C under one bar O₂ pressure
- Cell current density with ANL catalyst reached 80 mA/cm² (direct measured) or 90 mA/cm² (*i*R corrected) at 0.8 V
- Optimization of ANL catalyst under LANL test conditions (mainly through varying ionomer/catalyst ratio) was incomplete due to limited time and samples. Work will be continued at ANL
- A joint ANL-LANL project report was submitted to DOE in January

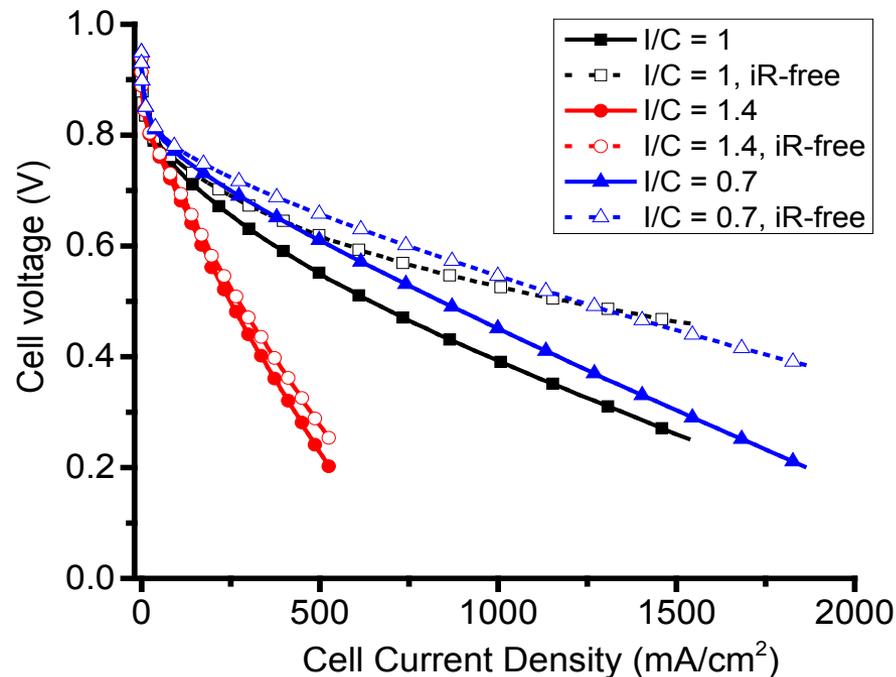
Accomplishment 3: Catalyst Activity Test at LANL (RDE & Single Cell)

RDE measurements



O₂-saturated 0.5 M H₂SO₄; scan rate = 5 mV/s;
Rotating speed = 900 rpm

Optimization of ionomer/catalyst ratio in MEA



T = 80°C; P_{H₂} = P_{O₂} = 1.0 bar; N-211; Cathode catalyst = 4 mg/cm² (ANL-1); Anode catalyst = 2 mg_{Pt}/cm²; Cell area = 5 cm²

MEA optimization showed that cell performance is sensitive to the amount ionomer over catalyst. Further optimization is continued at Argonne.

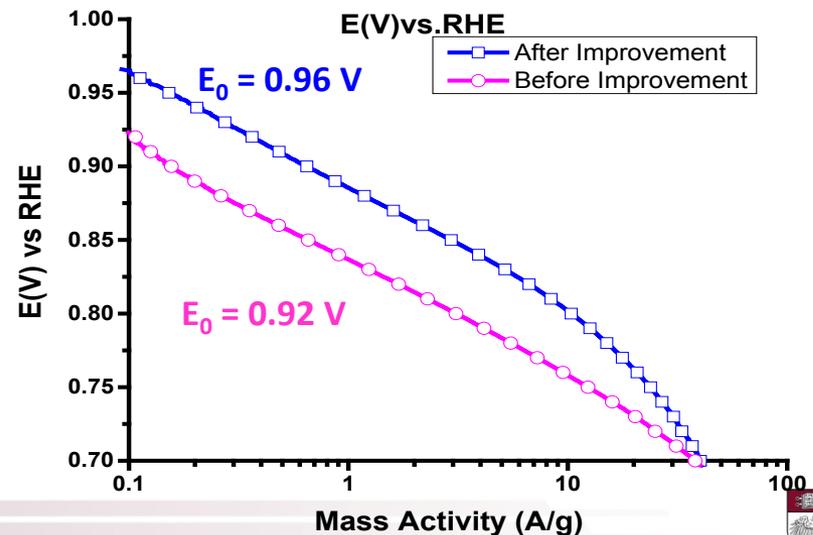
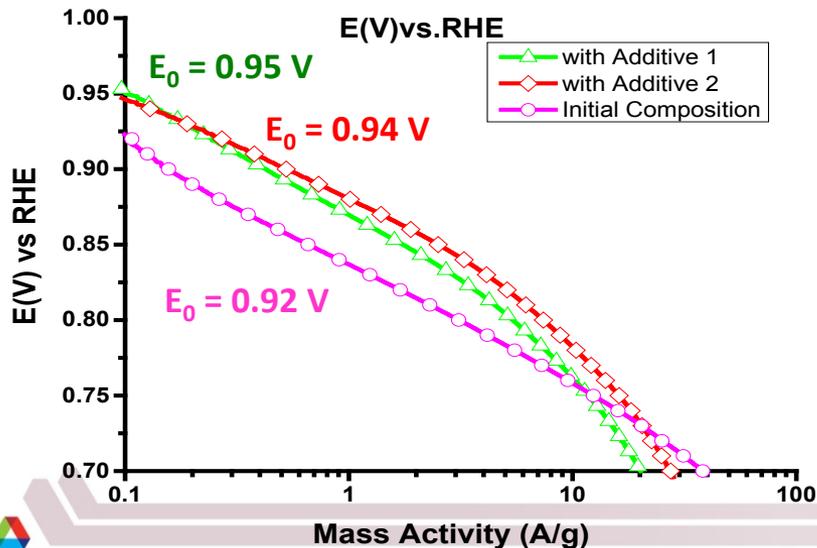
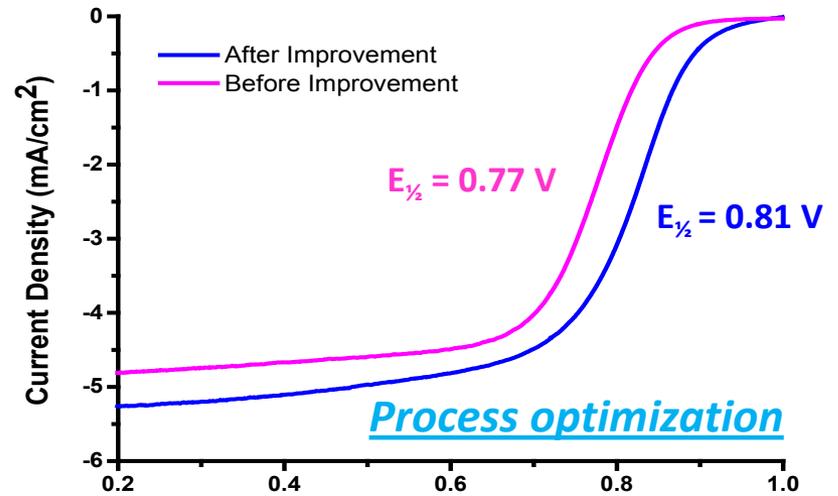
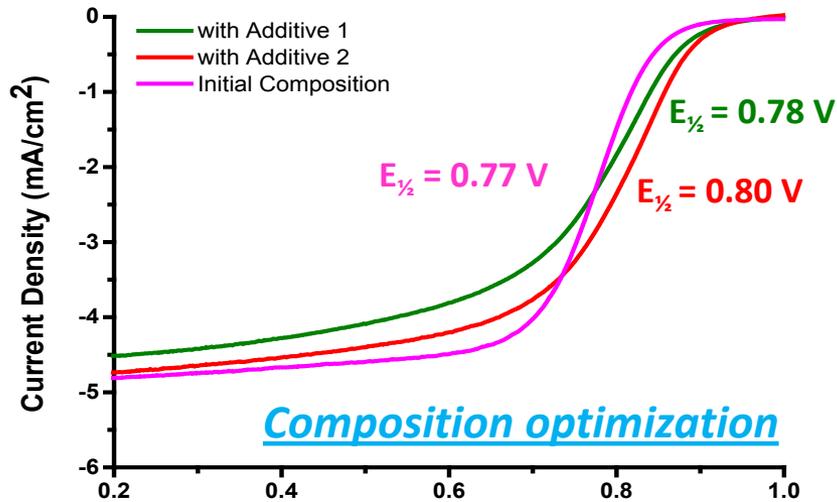
Accomplishment 4: Activity Improvement through Chemical & Process Optimizations

- The catalytic activity resulting from ZIF-based precursor is sensitive to treatment conditions. Optimization of process parameters alone could significantly improve the catalyst performance
- ZIFs/MOFs generally have high porosity and surface area, therefore could “host” additional N-containing ligands and organometallic compounds with added catalytic activity



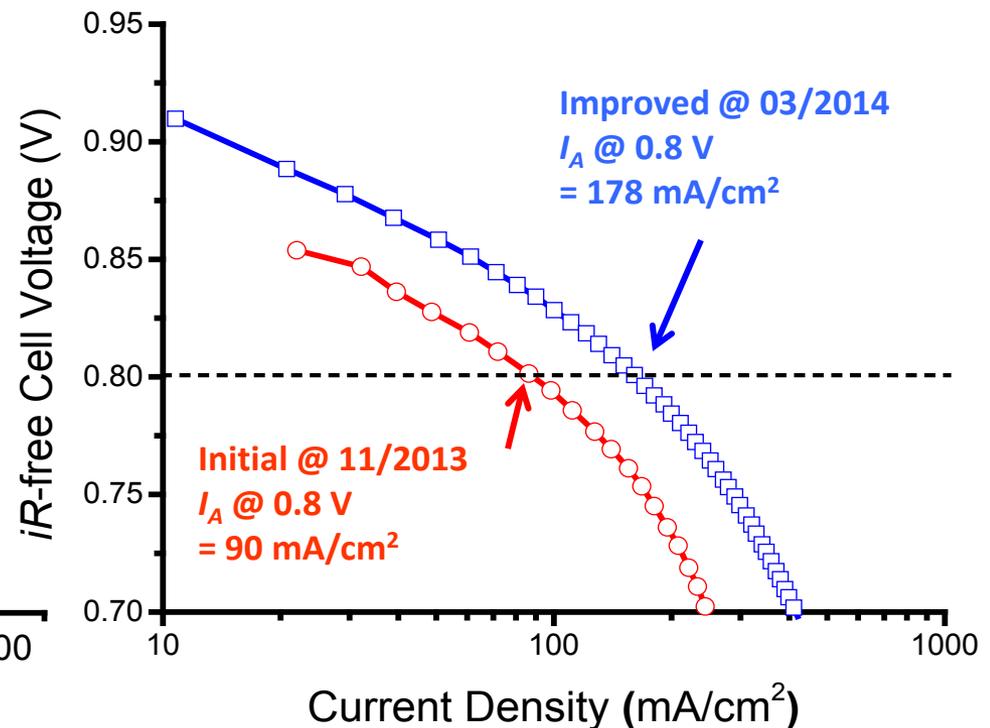
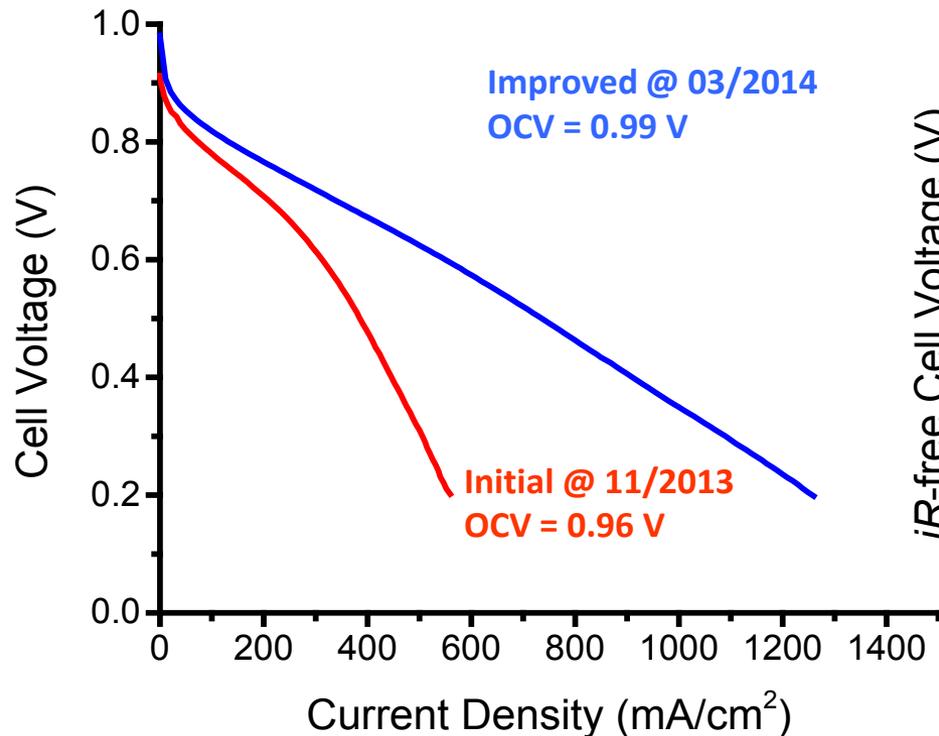
Accomplishment 4: Activity Improvement through Chemical & Process Optimizations (RDE Study)

Composition (left) and process (right) improvements led to higher onset (E_0) and halfwave ($E_{1/2}$) potentials



Accomplishment 4: Activity Improvement through Chemical & Process Optimizations (Single Cell Test)

Catalyst optimization also resulted in a significant improvement in MEA performance under the single cell test condition



Condition: $P_{O_2} = P_{H_2} = 1$ bar (back pressure = 7.3 psig) fully humidified; $T = 80$ °C; N-211 membrane; 5 cm² MEA; cathode catalyst = 4 mg/cm², anode catalyst = 0.3 mg_{Pt}/cm².

Future Works

- Activity improvement through better active site conversion and preservation under controlled process conditions
- Activity improvement through new organic and organometallic additives
- Activity improvement through new MOF/ZIF design, synthesis and conversion
- Activity improvement through morphological optimization of the nano-network
- Activity improvement through composition optimization of the nano-network

ZIF/nano-networks could serve as a novel platform for further catalyst performance improvement via new chemistries & processes



Collaborations

Partnership with Universities, National Lab and Industries

- Cross-laboratory study with Los Alamos National Laboratory (Zelenay's team) has benefited ANL's MEA preparation and catalyst testing development
- Collaborations between Argonne and several universities (National University of Singapore, Northern Illinois University, University of Southern Florida, etc.) accelerated the design/synthesis of ZIF-based non-PGM catalysts.
- In process of establishing collaborations with fuel cell OEMs and automakers in non-PGM catalyst development and evaluation

Technology Dissemination and Transfer

- Six US patent applications and granted patents of non-PGM catalysts available at Argonne for licensing
- Five major publications in non-PGM catalyst research through prominent scientific journals

This work is supported by DOE, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office - Nancy Garland (Technology Development Manager)



Summary

- Relevance:** To reduce the cost and to improve the performance of transportation fuel cells through highly efficient, ZIF-based nano-fibrous non-PGM catalysts.
- Approach:** Rational design and synthesis of high performance non-PGM catalysts made of ZIFs containing densely populated metal-imidazole ligation sites embedded in nano-network architecture with improved mass/charge transports
- Accomplishments:**
- Formulation Improvement over original ANL's ZIF/nanofiber catalyst yielded a single cell volumetric current density of 90 A/cm^3 (@0.8V, $P_{\text{O}_2} = 2 \text{ bar}$).
 - A low-cost, "one-pot" synthesis method developed at Argonne produced multiple ZIF-based catalysts with $E_0 > 0.9 \text{ V}$ and $E_{1/2}$ as high as 0.81 V.
 - A comprehensive characterization of ZIF-based electrocatalysts using various tools demonstrated the correlations between the precursor/catalyst structures and the performance.
 - Chemical and process optimizations led to an improved cell performance with current density of 178 mA/cm^2 at 0.8 V under one bar O_2 pressure.
- Collaboration:** Cross-lab collaboration with LANL improved ANL MEA fabrication process; and interactions with various universities accelerated catalyst development.
- Future Work:** ZIF/nano-networks are catalytic precursors with already high intrinsic ORR activity. They could serve as the platform for further activity enhancement via new chemistries and processes