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

Barriers

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

Budget

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

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

***Oxygen Reduction Reaction*: $O_2 + 4\,H^+ + 4\,e^- \rightarrow 2H_2O$**

- 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	2010	2017
Volumetric current density @ 0.8 V	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**

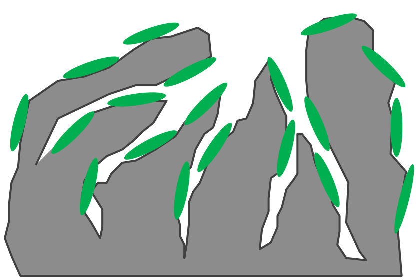
Catalytic Activity ∝
Turn-Over-Freq. x *Site Density*

Turn-Over-Freq.:

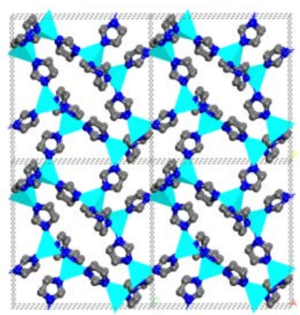
- Different transition metals
- Different organic ligands
- Different metal-ligand binding energy & coordination structure

Site Density:

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



Conventional

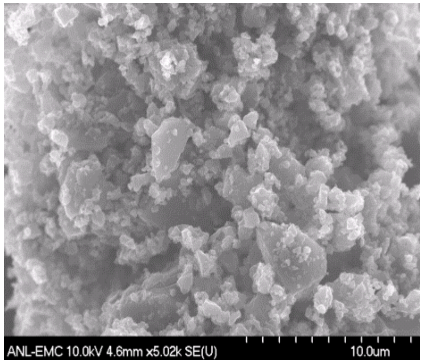


ANL's approach

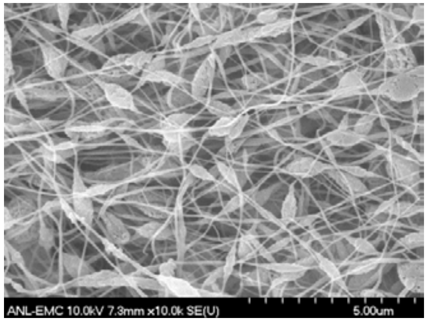
Mass/Charge Transport ∝
Porosity & Network Connectivity

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

Conventional

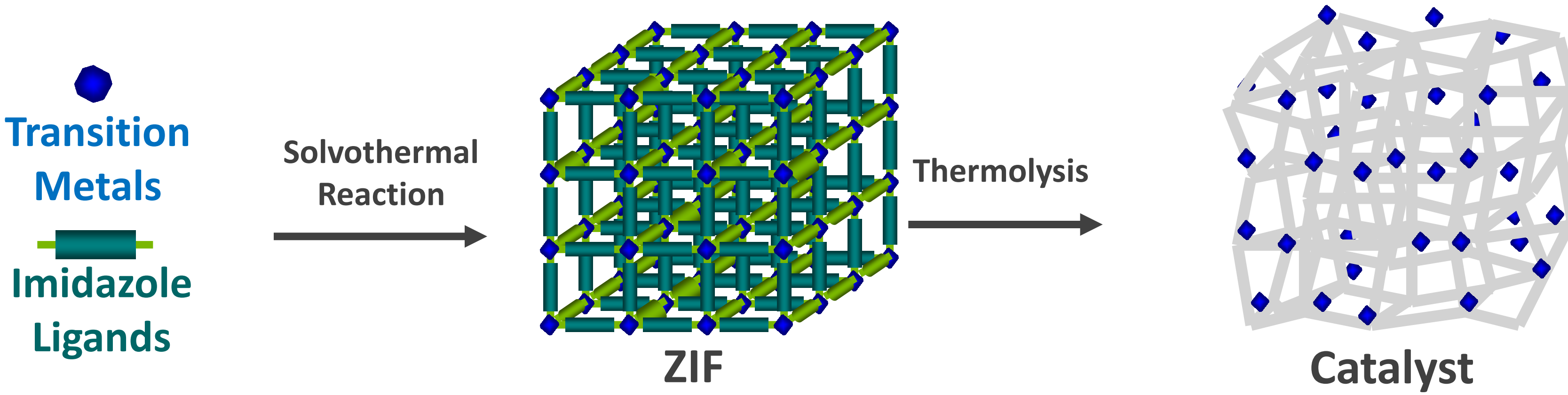


ANL's nano-network



Approach: Improving Catalytic Activity with ZIFs as Precursors

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

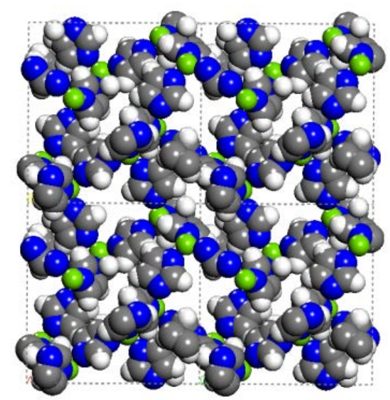


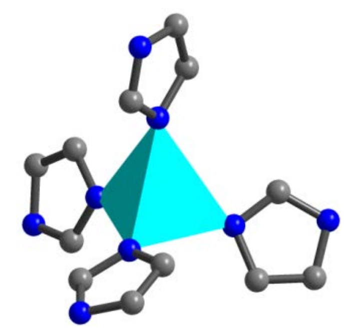
Advantages of "Support-free" ZIF-based non-PGM Catalyst Approach

– "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

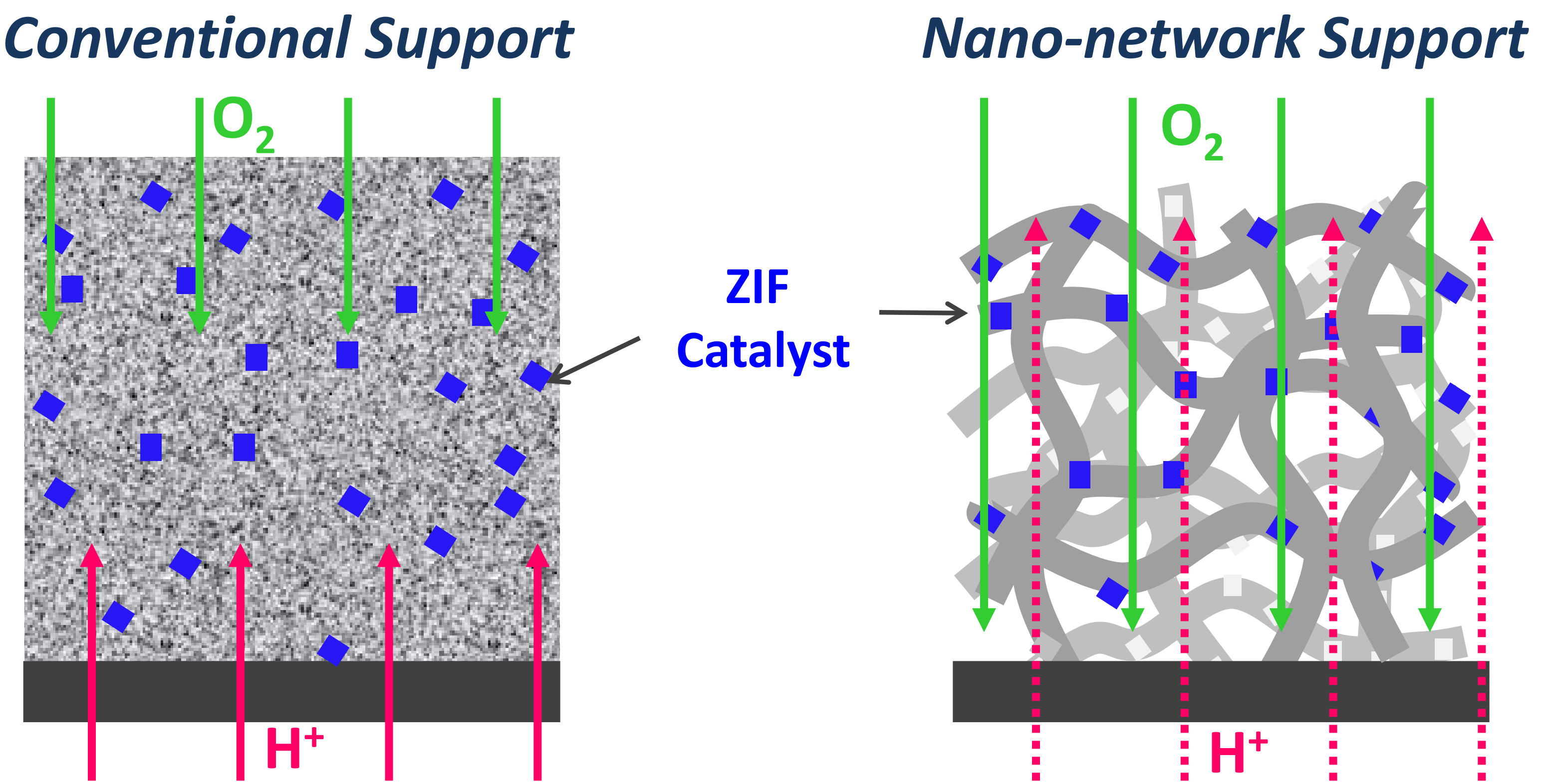




M-ligand site density = $3.6 \times 10^{21}/cm^3$

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

Approach: Maximizing Mass/Charge Transports via Nano-network



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

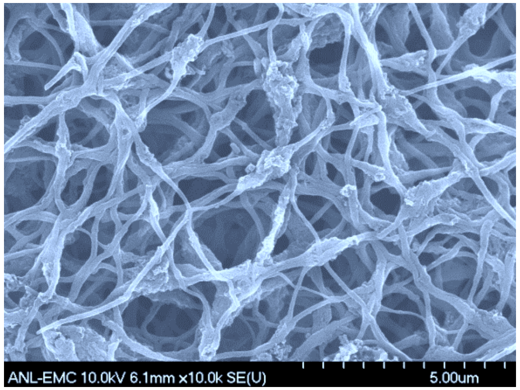
- Improved O_2 transport through voids between fibers, macro → micro
- Enhanced charge/heat transfer via nano-network
- Embedded catalytic site inside nano-fibers

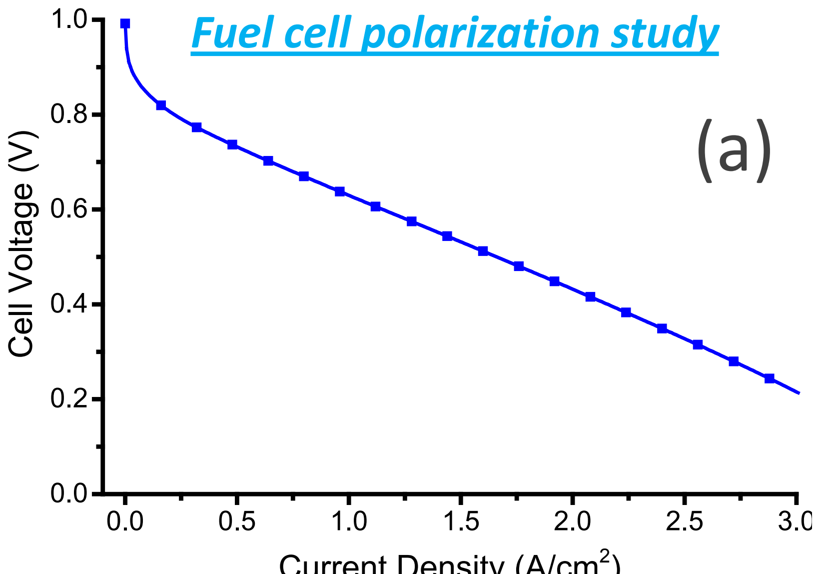
Approach - Milestones

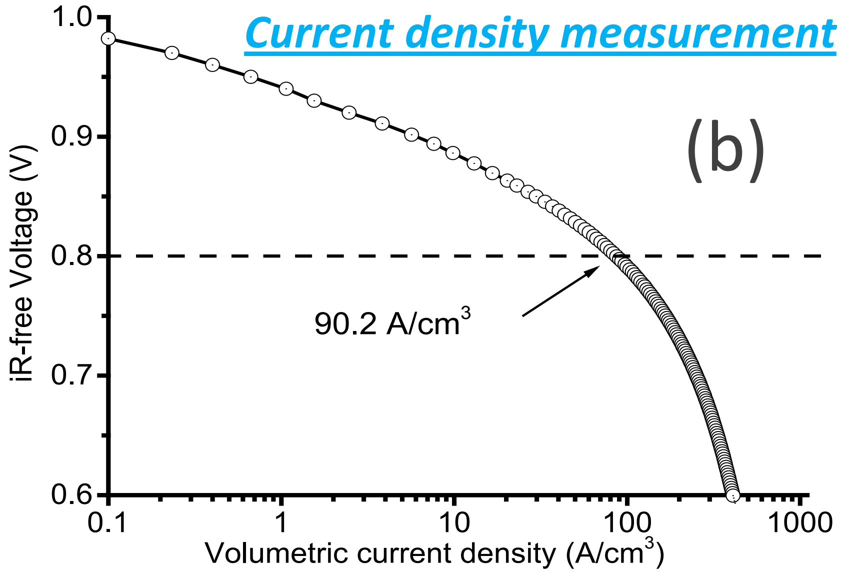
Month/ Year	Milestones	Status Update
3/13	Complete the formulation improvement of the first batch of nanofibrous catalysts and demonstrate >90 A/cm^3 (@0.8V) in volumetric current density or >3 A/cm^2 current density (@0.1V).	**Completed**. An initial reformulation of ZIF/nano-network cathode catalyst 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_{O2} = P_{H2} = 2 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_{O2} = P_{H2} = 1 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 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 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**



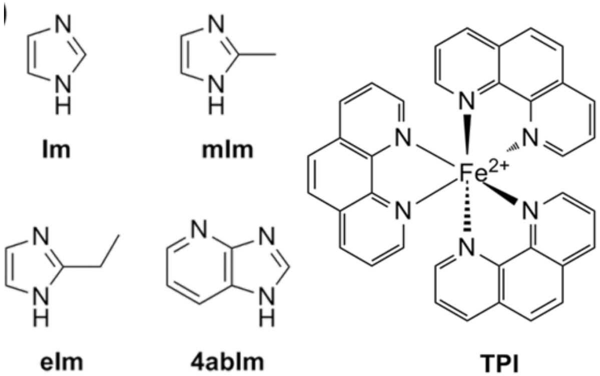




(a) Single cell with ANL's non-PGM nano-network cathode catalyst; P_{O2} = P_{H2} = 2 bar; fully humidified at 80ºC, cathode loading = 3.0 mg/cm², anode loading = 0.3 mg_{Pt}/cm², Nafion® = 211, active area = 5 cm² ; (b) iR corrected volumetric current density under similar condition to (a) except cell area = 2 cm², Nafion ® 117, cathode catalyst loading = 2 mg/cm²

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

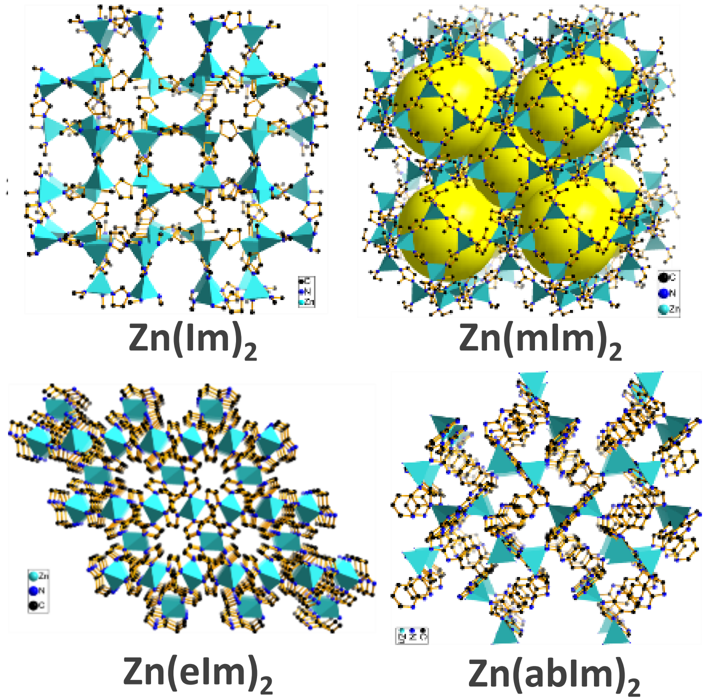
Solid Mixing → **Solid State Reaction** → **Thermolysis**

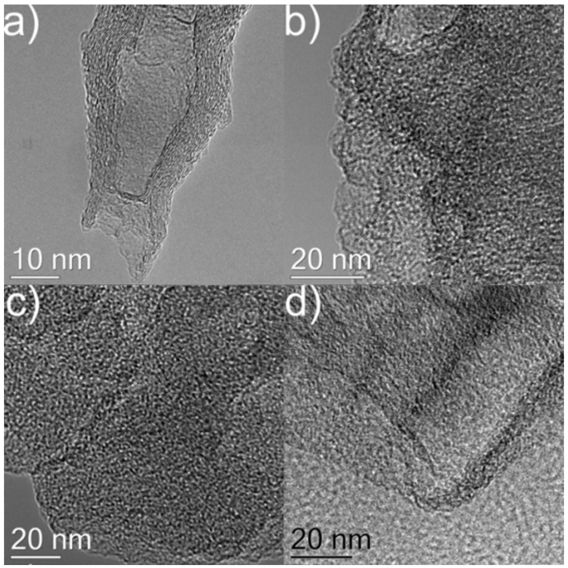


Imidazole ligands

Organo-metallics

ZnO





a) $Zn(Im)_2$TPIP; b) $Zn(mIm)_2$TPIP
c) $Zn(eIm)_2$TPIP; d) $Zn(abIm)_2$TPIP

- 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)

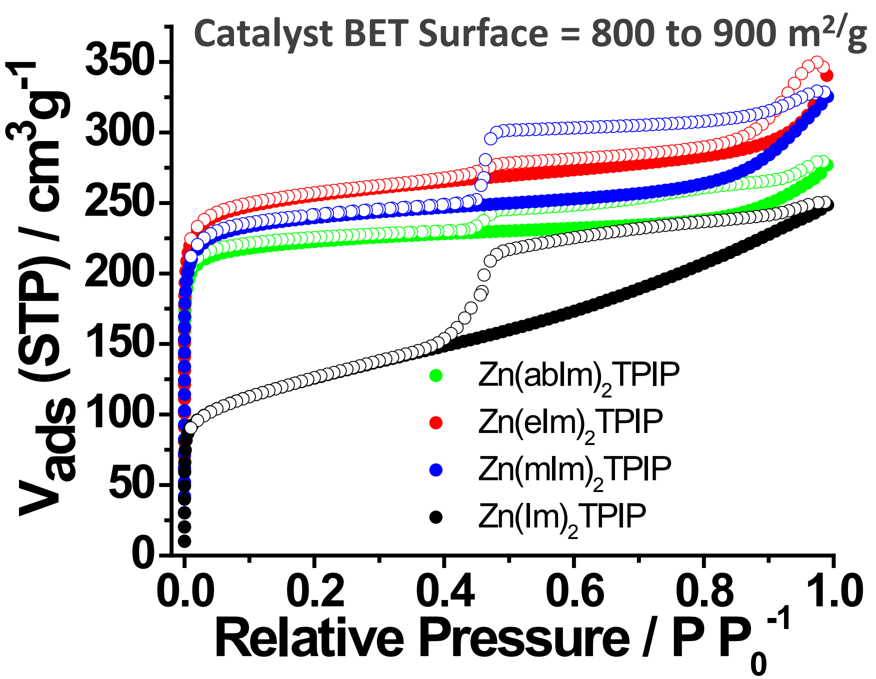
- ZIFs have been perceived as expensive materials due to elaborated synthesis/separation, and solvent waste generated
- Materials for the current approach are low-cost, bulk commodity products
- One-pot synthesis requires no solvent and separation, therefore substantially reduces the process cost and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

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

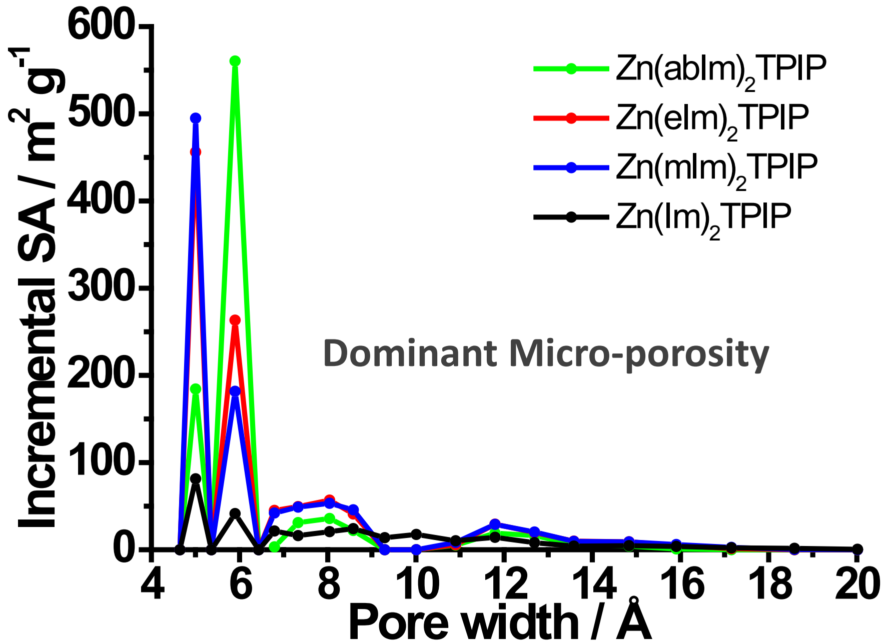
D-J Liu & D. Zhao ***US Patent Application*** 20130273461

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

N_2 adsorption isotherm at 77 K



Pore size distribution from NLDFT



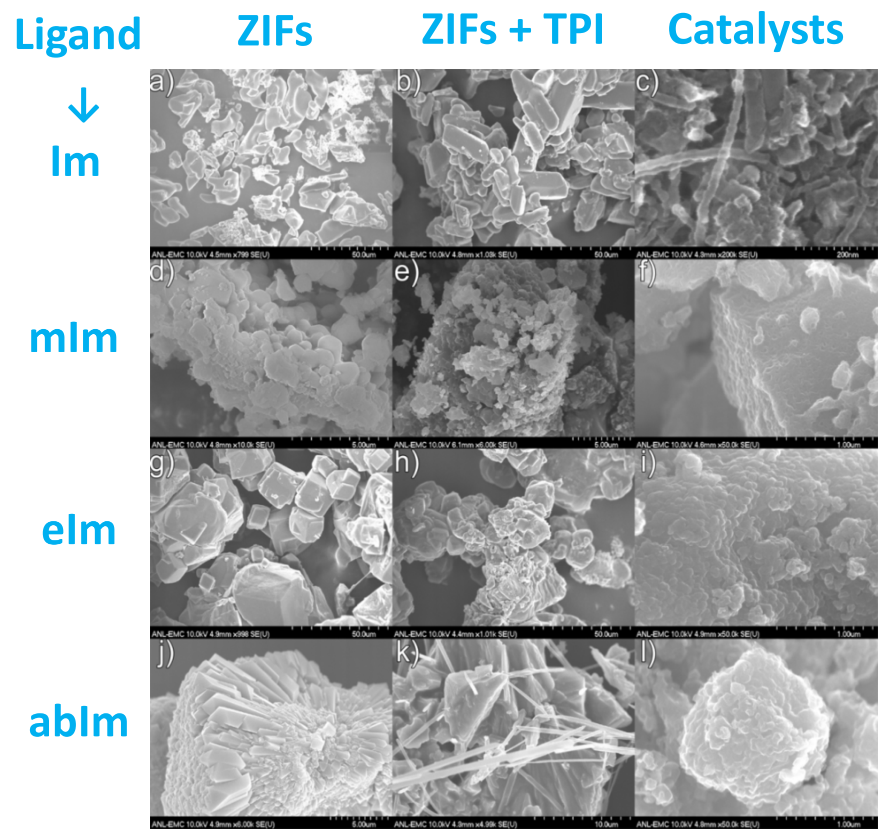
N2-BET study shows that (a) catalyst surface areas are high after thermolysis; (b) micropore dominates pore size distribution for heat-activated catalysts

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
$Zn(Im)_2TPIP$	34%	15%	26%	9%	16%
$Zn(mIm)_2TPIP$	43%	17%	23%	9%	8%
$Zn(eIm)_2TPIP$	36%	18%	24%	8%	13%
$Zn(abIm)_2TPIP$	36%	18%	24%	7%	16%

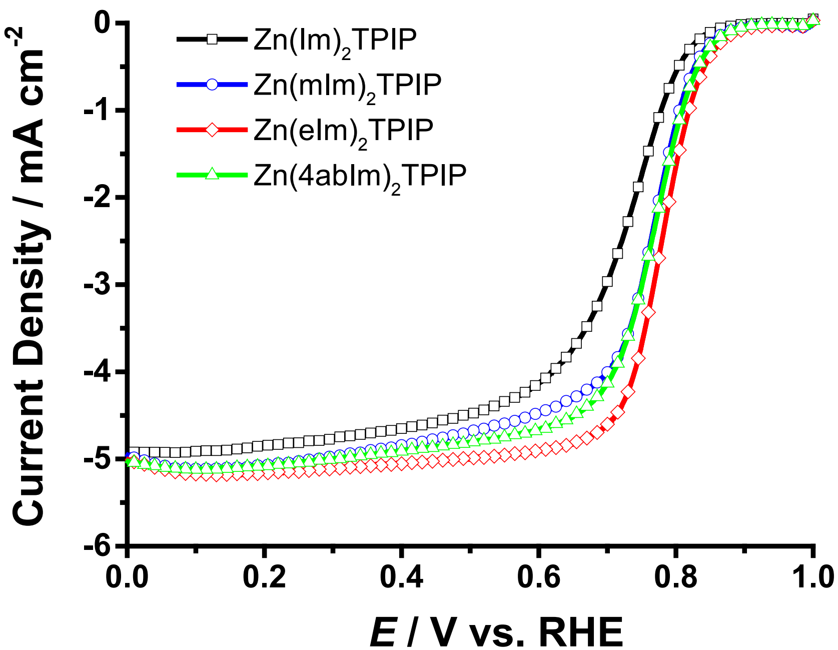
C-XPS shows that most organic carbons are converted to the graphitic form after heat-treatment



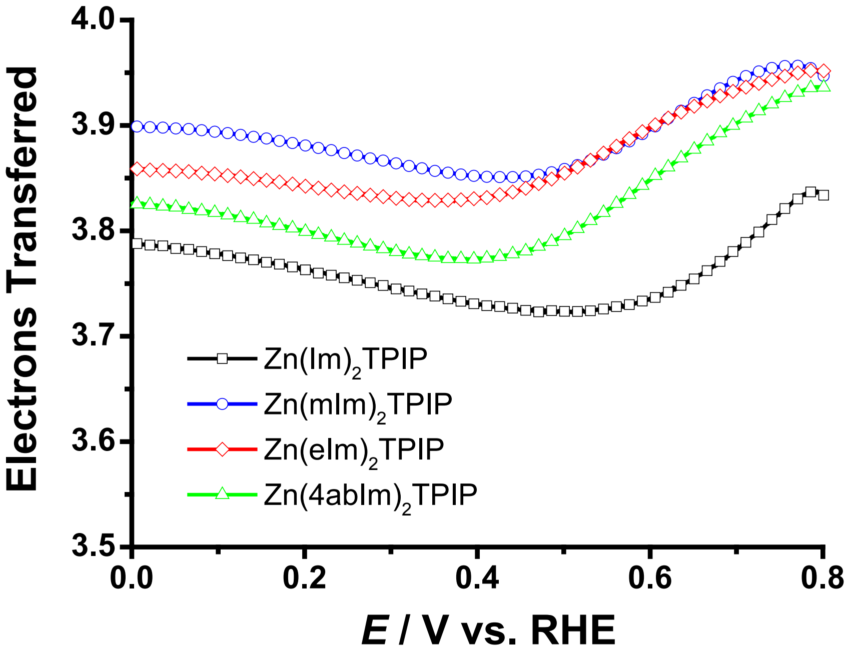
(a) Pyridinic N dominates in heat-treated ZIFs; (b) carbon is mainly graphitic though other forms also exist; (c) ZIFs have well-defined crystal structures when synthesized, and (d) they turned to amorphous after thermolysis.

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

Linear sweep voltammograms



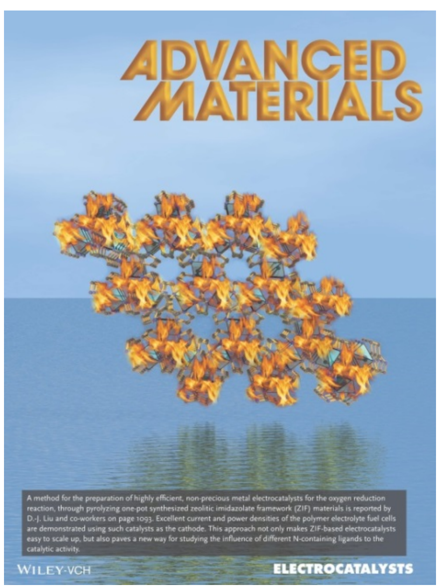
Number of e$^-$ transfer measurement

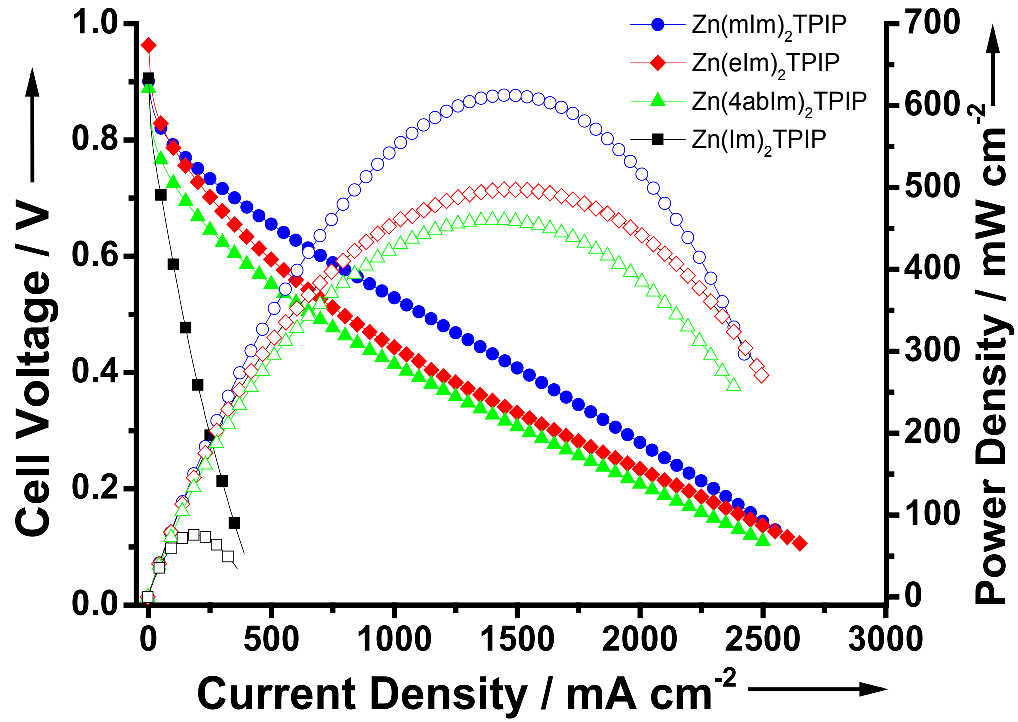


Electrocatalysts	Surface Area (m^2/g)	Onset Potential E_0	Halfwave Potential $E_{½}$
Zn(Im)$_2$TPIP	443	0.881	0.73
Zn(mIm)$_2$TPIP	1277	0.902	0.76
Zn(eIm)$_2$TPIP	920	0.914	0.78
Zn(4abIm)$_2$TPIP	976	0.904	0.76

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 H_2 and O_2, $P_{O2} = P_{H2}$ = 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

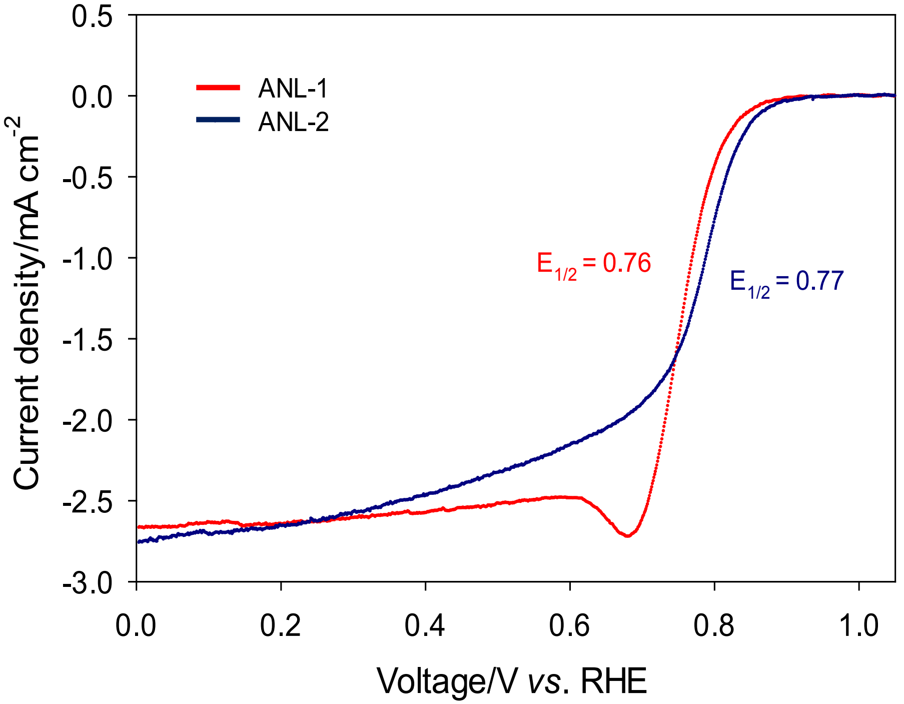
"Highly Efficient Non-Precious Metal Electrocatalysts Prepared from One-Pot Synthesized Zeolitic Imidazolate Frameworks (ZIFs)" D. Zhao, J.-L. Shui, L. R. Grabstanowicz, C. Chen, S. M. Commet, T. Xu, J. Lu, and D.-J. Liu, *Advanced Materials*, **2014**, *26*, 1093–1097 (Frontpiece)
With permission to 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 O_2 pressure
- Cell current density with ANL catalyst reached 80 mA/cm^2 (direct measured) or 90 mA/cm^2 (*iR* 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

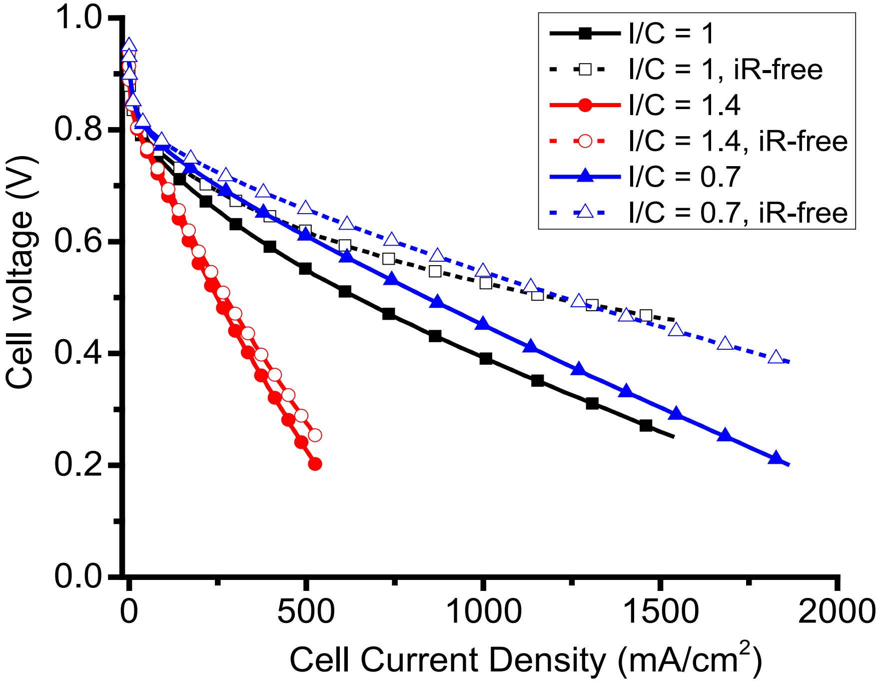
Accomplishment 3: Catalyst Activity Test at LANL (RDE & Single Cell)

RDE measurements



O_2-saturated 0.5 M H_2SO_4; scan rate = 5 mV/s; Rotating speed = 900 rpm

Optimization of ionomer/catalyst ratio in MEA



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

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

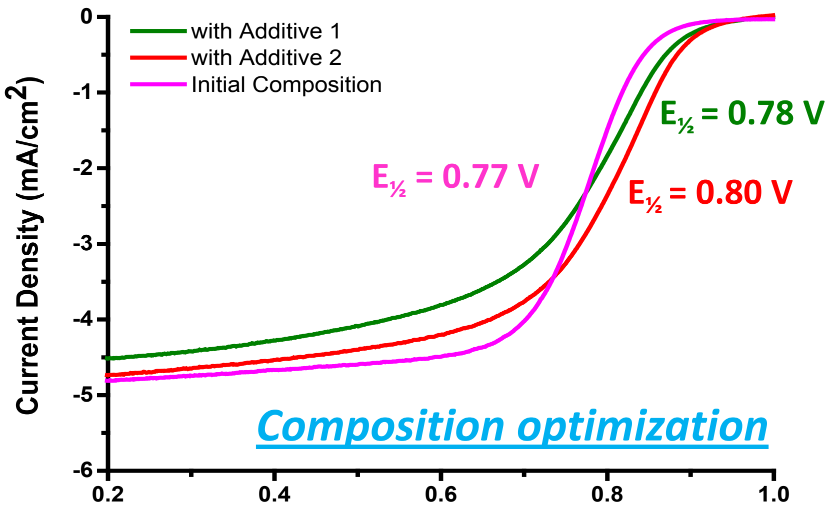
Accomplishment 4: Activity Improvement through Chemical & Process Optimizations

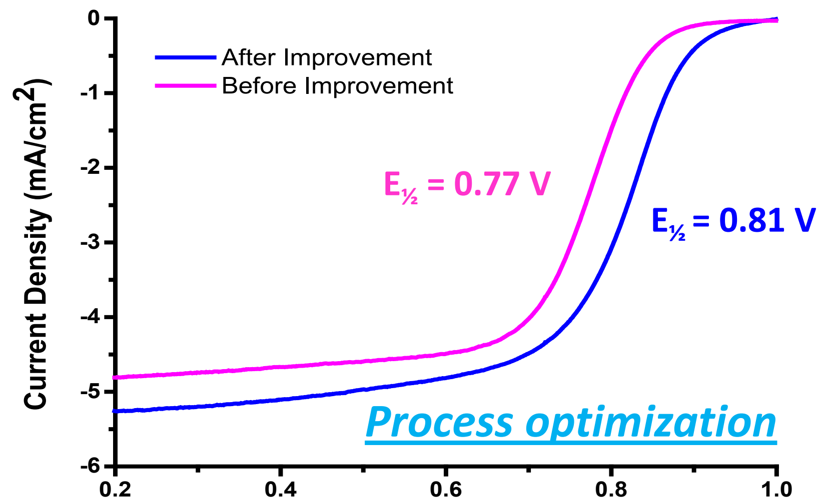
- The catalytic activity resulting from ZIF-based precursor is sensitive to treatment conditions. Optimization of process parameters alone could significantly improve the catalyst performance

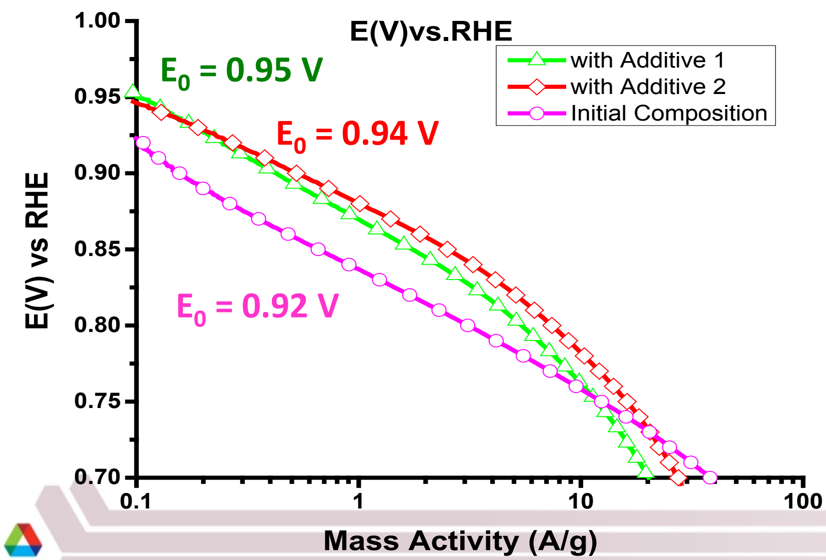
- ZIFs/MOFs generally have high porosity and surface area, therefore could "host" additional N-containing ligands and organometallic compounds with added catalytic activity

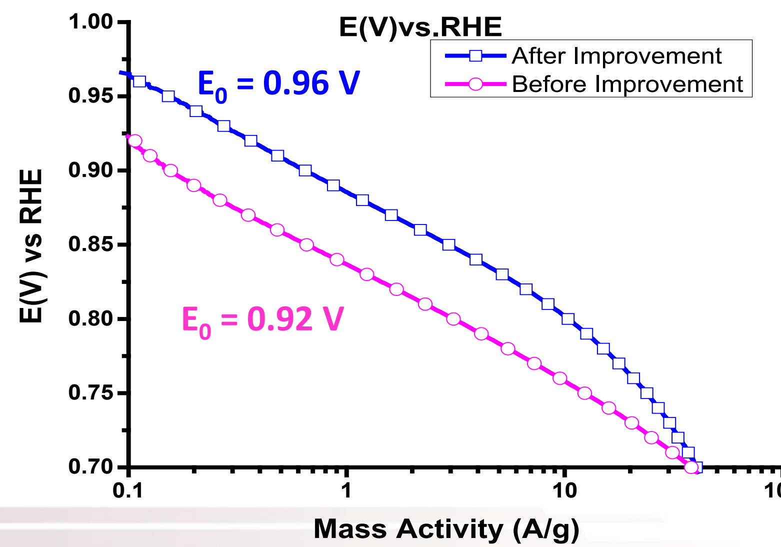
Accomplishment 4: Activity Improvement through Chemical & Process Optimizations (RDE Study)

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



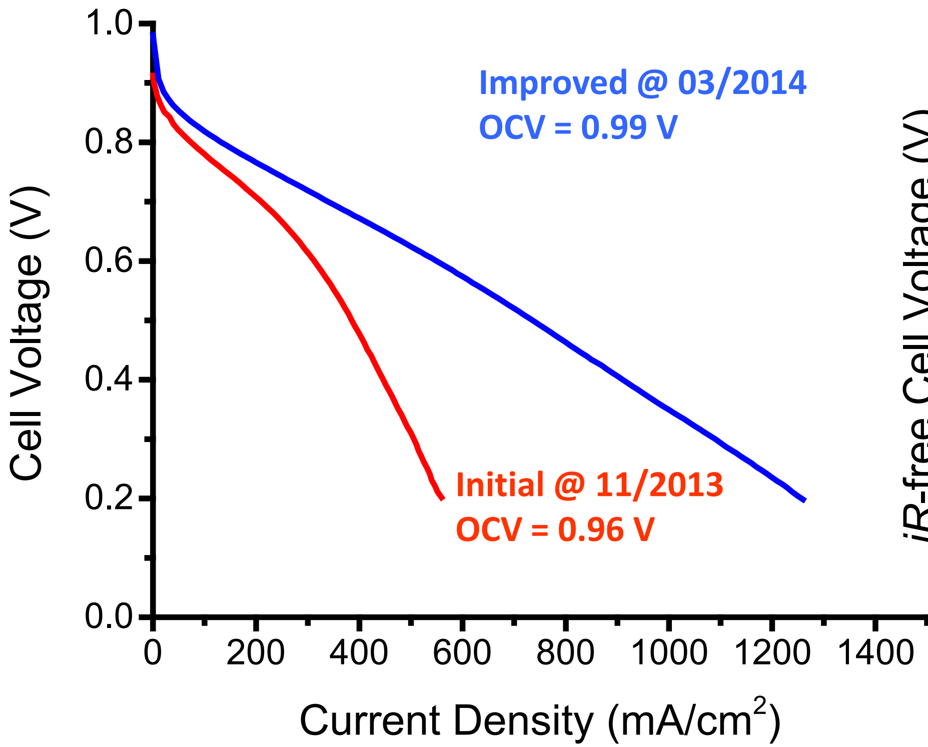


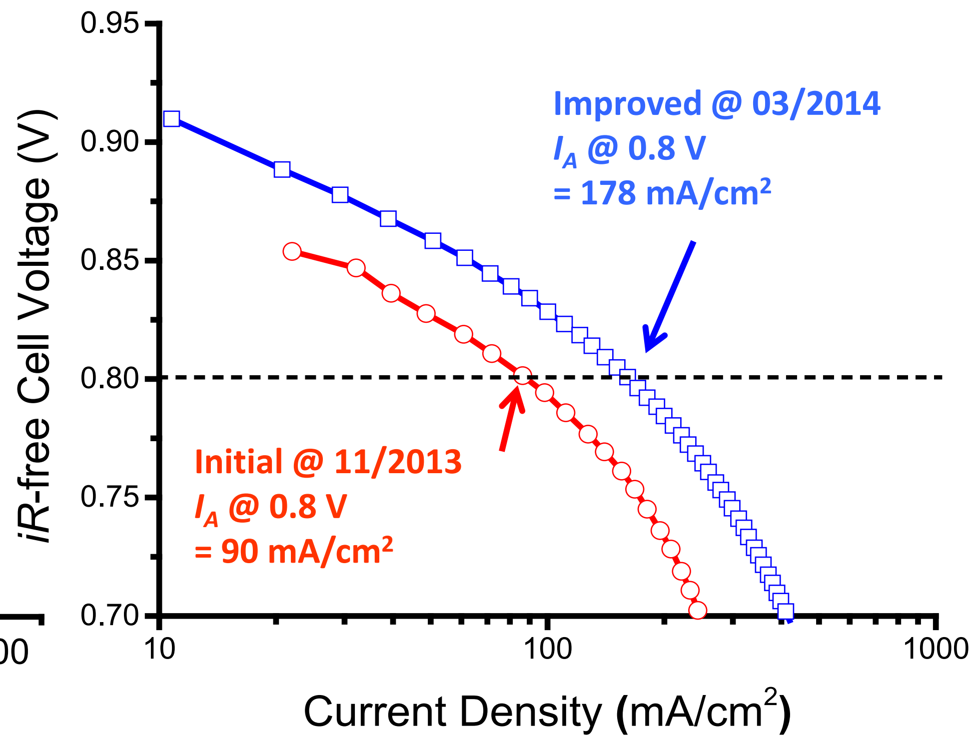




Accomplishment 4: Activity Improvement through Chemical & Process Optimizations (Single Cell Test)

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





Condition: $P_{O2} = P_{H2}$ = 1 bar (back pressure = 7.3 psig) fully humidified; T = 80 °C; N-211 membrane; 5 cm^2 MEA; cathode catalyst = 4 mg/cm^2, anode catalyst = 0.3 mg_{Pt}/cm^2.

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_{O2} = 2 bar).
- A low-cost, "one-pot" synthesis method developed at Argonne produced multiple ZIF-based catalysts with $E_0 > 0.9$ 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