Novel Non-PGM Catalysts from Rationally Designed 3-D Precursors

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2015 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office
Annual Merit Review and Peer Evaluation Meeting
Washington, D.C., June 8-12, 2015

Project ID
FC118

Overview

Timeline

- Project Start: July 2014
- Project End: September 2015

Barriers

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

Budget

- FY14 – FY15 DOE Funding: $ 350K
- Total DOE Fund Spent*: $172K

  * As of 3/31/2015

Collaboration

- Northern Illinois University
- National University of Singapore
- University of Illinois – Chicago
- Southern University
- SAFCell, Inc.
- DOE FCTO Catalysis Working Group

Objective - Relevance

- **To design, synthesize, and evaluate highly efficient non-platinum group metal (non-PGM) cathode catalysts using rationally designed 3-D precursors with significantly improved fuel cell performance. (Areal current density > 200 mA/cm^2 @ 0.8 $V_{iR\text{-}free}$ and > 25 mA/cm @ 0.9 $V_{iR\text{-}free}$ under 1 bar O_2)**
- **To maximize electron, heat and mass transport by incorporating the catalyst into porous nano-network structure.**
- **To support non-PGM catalyst development through structure-function relationship investigations**

Relevance of ANL Zeolitic Imidazolate Framework (ZIF)/Nano-network Non-PGM Catalyst to Technology Barriers

- **Cost** – ANL non-PGM catalysts can be scaled-up for industrial production using very low-cost material and a simple "one-pot" synthesis method.
- **Performance** – ZIF-based non-PGM catalysts 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 group metals (PGMs) are current materials of choice for PEMFC catalysts. The high price and limited reserve of PGMs add significant cost to PEMFCs.
- 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 candidates in activity and durability.

US DOE Performance Target for Non-PGM Electrode Catalyst Volumetric current density @ 0.8 V	2017	2020
	300 A / cm^3	300 A / cm^3

Current Performance Targets

Volumetric catalyst activity in MEA @ 0.8 $V_{iR\text{-}free}$ and 80 °C: **≥ 300 A/cm^3**
MEA maximum power density at 80 °C: **≥ 1000 mW/cm^2**
Performance loss @ 0.8 A/cm^2 after 30,000 cycles in N_2: **≤ 40%**

Approach – 3D "Support-free" Catalyst Design

Catalytic Activity ∝

Turn-Over-Freq. x ***Site Density***

- **Different transition metals & organic ligands**
- **Different metal-ligand coordination**

- **Carbon "Support-free"**
- **High & uniformly distributed active site density**

"Reality-check" on Non-PGM Activity

$i\ (A/cm^2) = 1.6\times10^{-19} \times TOF\ (e^-/site\cdot s) \times SD\ (cm^{-3}) \times \tau\ (cm)$*

Achievable Current Density @ 0.8 V

(Cathode loading @ 4mg·cm^{-2} / 1 bar O_2)

- **170 mA/cm²** for 1% Fe, or
- **340 mA/cm²** for 2% Fe loading

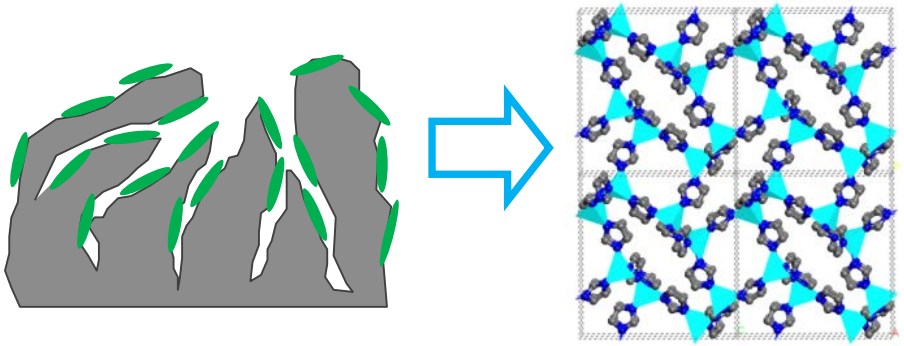
Critical assumption:

a) TM site atomically dispersed & fully utilized

b) TOF = 1/10 of Pt (**2.5** e$^-$/site.s)

* Gasteiger, *et al*. Applied Catalysis B: Environmental 56 (**2005**) 9

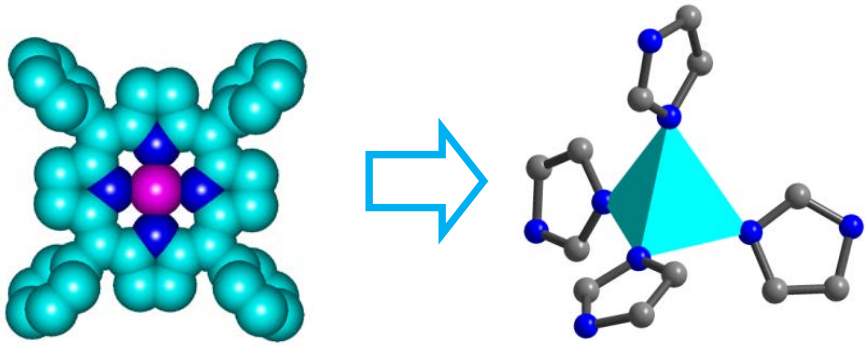
From carbon supported to "support-free" catalyst



Conventional

ANL's MOF approach

From 2D (square-planar) to 3D (tetrahedral) precursor

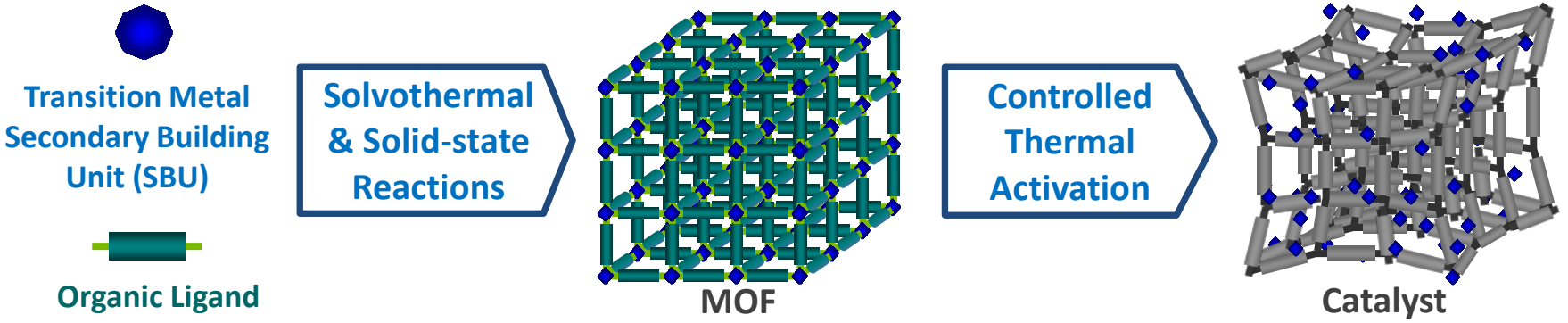


R. Jasinski, *Nature*, (**1964**)

Ma, Goenaga, Call and Liu, *Chemistry: A Euro. J* (**2011**)

Approach – MOFs as 3D Precursors

New ZIF-based Catalyst Synthesis → **Process Optimization at Catalyst/MEA Level** → **Structural & Cell Performance Studies**



"Non-Platinum Group Metal Electrocatalysts Using Metal Organic Framework Materials and Method of Preparation"
D.-J. Liu, S. Ma, G. Goenage, US Patent 8,835,343

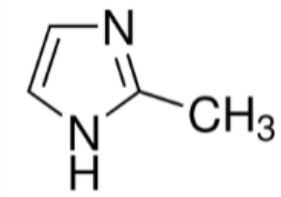
Advantages of ZIF-based non-PGM Catalyst

- Highest precursor density for active site conversion >10^{21}/cm^3
- Well-defined coordination between metal (SBU) & ligand
- Porous 3-D structure with high specific surface area (SSA) and uniform micropores after thermolysis
- Large selection of existing MOF compositions

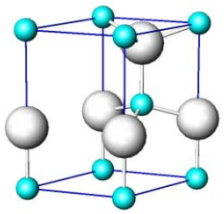
Approach – Milestones

Milestones	Month/ Year	Status Update
Complete the syntheses, optimizations and evaluations of ZIF based catalysts with selected organics as additives in precursors and achieve onset potential E_0 > 0.91 V at 0.05 A/g.	9/2014	**Completed**. The improved catalyst reached an onset potential E_0 of **0.96 V** @ 0.1 A/g and a halfwave potential $E_{½}$ of **0.82 V** when measured by RDE in O_2 saturated $HClO_4$ solution (0.1M).
Complete the synthesis, optimization, and evaluation of ZIF-based catalysts with new metal/ligand complexes in the precursors. Achieve MEA/single cell areal current density > 200 mA/cm² at $0.8V_{iR\text{-}free}$ under one bar O_2.	12/2014	**Completed and exceeded.** The average areal current density of the three best performing MEAs reached **246 mA/cm²** at $0.8V_{iR\text{-}free}$ under one bar oxygen, which exceeded the goal by **23%.**
Complete the initial ZIF/nano-network precursor and catalyst structure characterizations and improve the understanding of structure-property relationship.	3/2015	**Completed.** A clear correlation between the ZIF-based catalyst surface area and MEA/fuel cell limiting current was observed. DFT calculation on ORR pathways was completed and published.
Complete activity improvement of nano-network catalysts with alternative ZIF/slurry formulation. Achieving MEA areal current density > 25 mA/cm² at 0.9 $V_{iR\text{-}free}$ on O_2 or a volumetric current density > 95 A/cm³ @ $0.8V_{iR\text{-}free}$	7/2015	**On-going.** Catalyst optimization led to higher MEA/fuel cell current densities of **29.5 mA/cm²** at 0.9 $V_{iR\text{-}free}$ and **323 mA/cm²** at 0.8 $V_{iR\text{-}free}$ under one- bar O_2, exceeding the target. Investigation on volumetric current density is underway.

Accomplishment – A Low-Cost, "One-Pot" Preparation of ZIF-based Catalyst was Developed

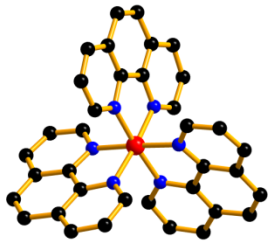


mIm

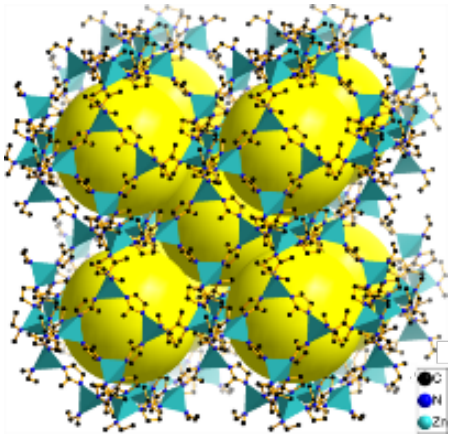


ZnO

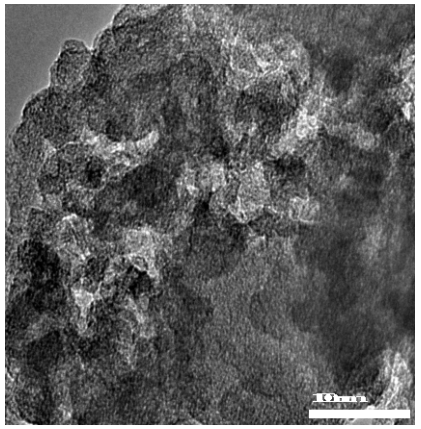
+



TPI (Fe)



$Zn(mIm)_2TPI$



$Zn(mIm)_2TPIP$ (Catalyst)

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

- Simple solid-state synthesis, solvent-free and no separation needed
- Very low-cost materials for ZIF synthesis
- Versatile process of screening various N-containing ligands

Accomplishment - Better Catalyst Synthesis & Processing Led to Excellent Activity in Fuel Cell Test under O_2

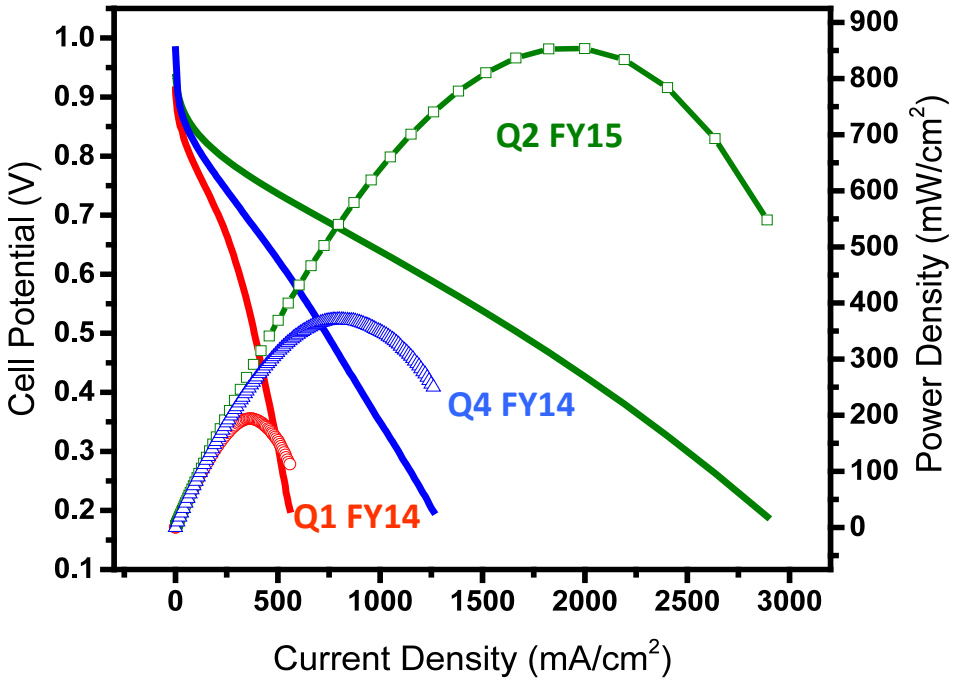
Summary of 10 Best MEA Results over 90+ MEAs Studied

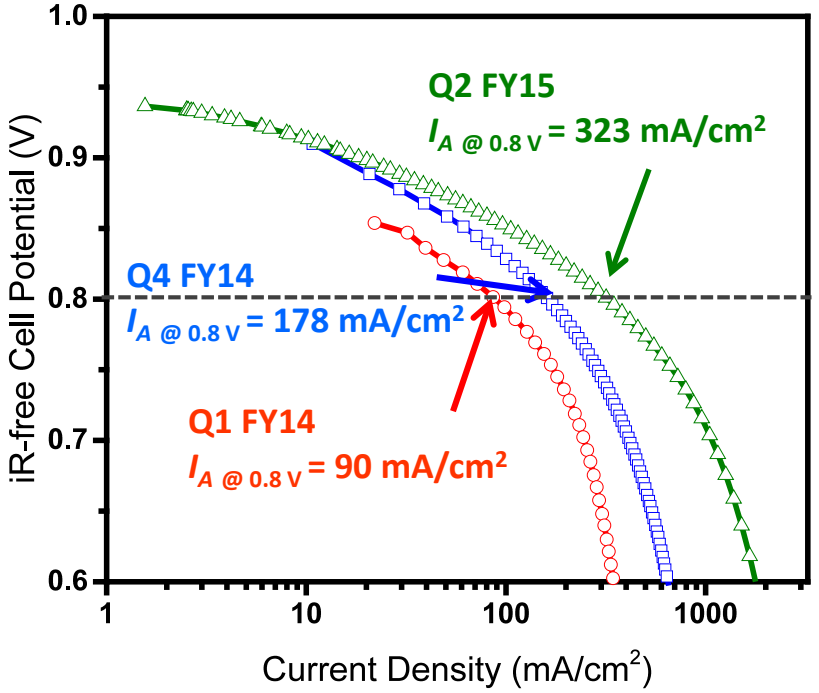
Sample Number	Cathode Catalyst Loading (mg/cm^2)	Current Density @ 0.9 $V_{iR\text{-}free}$ (mA/cm^2)	Current Density @ 0.8 $V_{iR\text{-}free}$ (mA/cm^2)	Current Density @ 0.2 V (A/cm^2)	Open Circuit Potential (V)
HMB1-81	3.5	23.0	202.6	1.88	1.011
HMB1-87	3.6	26.9	281.0	2.05	1.000
HMB1-89	3.4	25.0	281.4	2.15	0.961
HMB1-91	3.6	29.5	275.4	1.85	0.995
HMB1-94	3.8	21.2	222.8	1.64	0.946
HMB1-95	3.4	24.0	240.7	2.43	1.010
HMB1-112	4.0	26.0	234.9	1.83	0.998
HMB1-128	3.5	26.0	221.9	1.97	1.013
HMB2-71	3.4	19.2	225.1	2.42	0.980
HMB2-108	3.5	18.5	323.0	2.89	0.934
Average	**3.6**	**23.9**	**250.9**	**2.11**	**0.984**

Highlights: The fuel cell current densities reached **29.5 mA/cm²** @0.9 $V_{IR\text{-}free}$ and **323 mA/cm²** @0.8 $V_{IR\text{-}free}$ under one-bar oxygen

Accomplishment - Rational Design/Synthesis Led to Leap of Catalyst Performance in O_2

Catalyst performances were measured in MEAs/single cells with O_2 in cathode. Significant improvements were made since the beginning of the project.



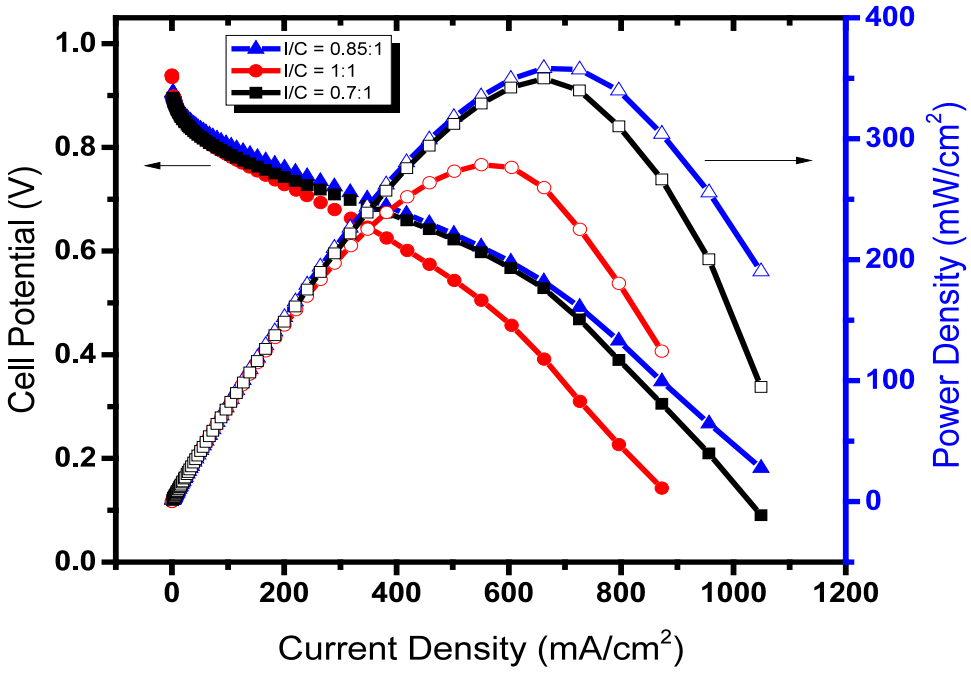


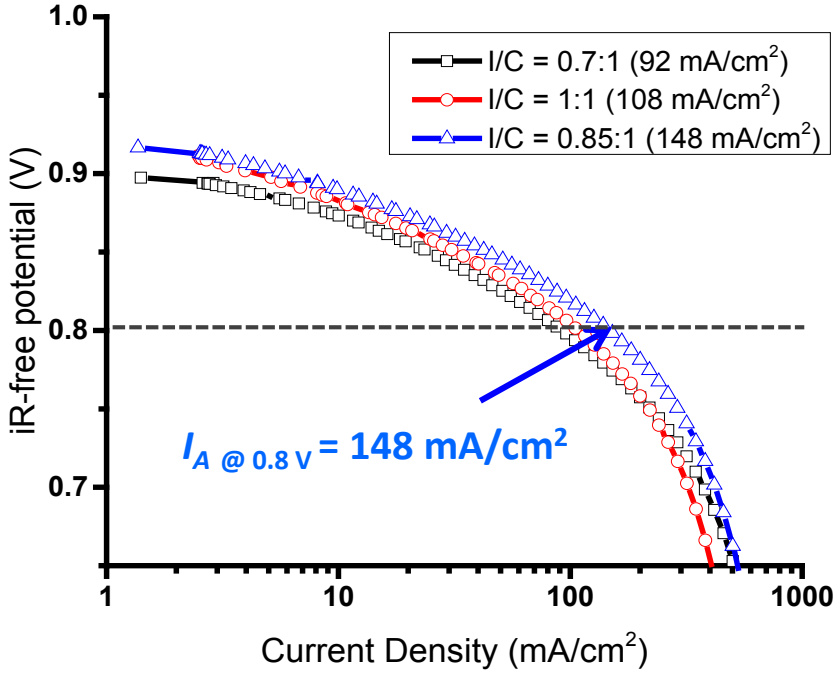
Condition: P_{O2} = P_{H2} = 1 bar (back pressure = 7.3 psig) fully humidified; T = 80 °C; N-211 membrane; 5 cm² MEA; cathode catalyst = 3.5~4 mg/cm², anode catalyst = 0.4 mg_{Pt}/cm²

Current density @ 0.8 $V_{IR\text{-}free}$ increased **80%** since the project inception at Q4 FY2014 or **260%** over one-year ago

Accomplishment - Process Improvement also Produced Excellent Fuel Cell Performance under Air

Excellent current and power densities were observed in MEA under one-bar air at cathode after ionomer-to-catalyst ratio (I/C) was optimized



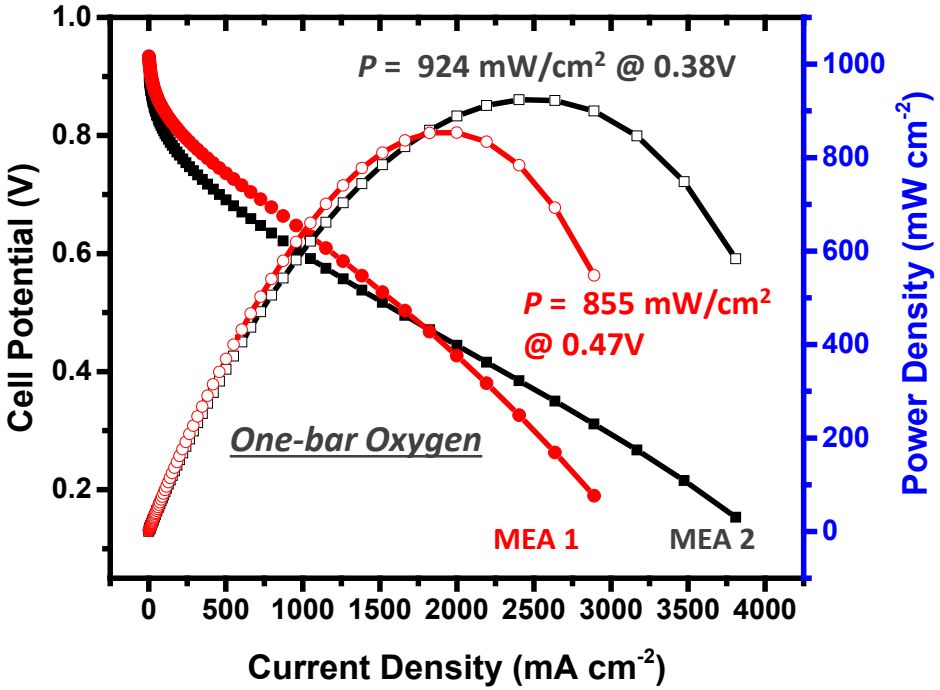


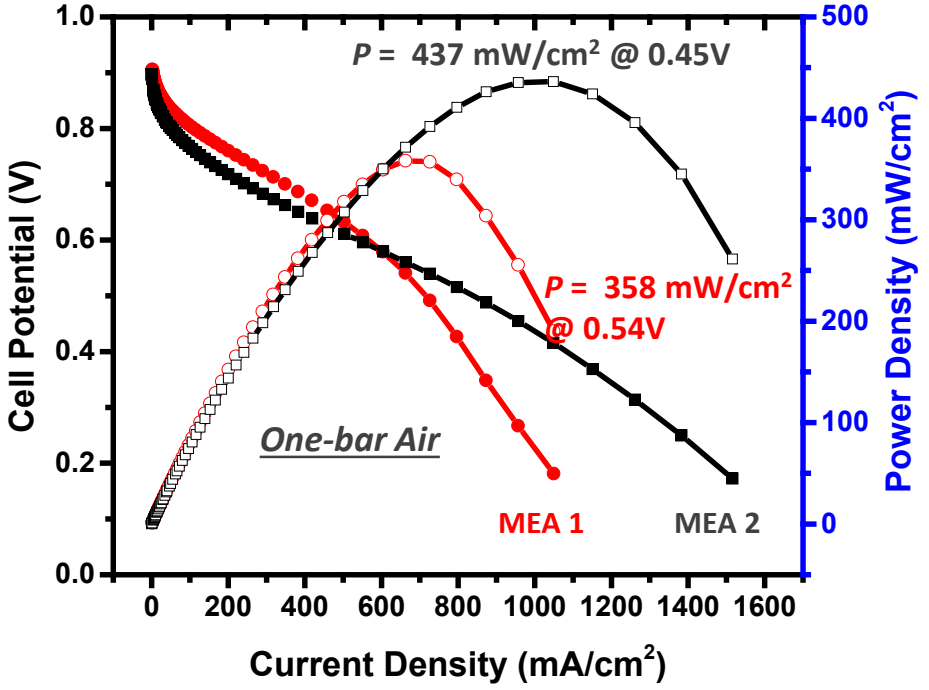
Condition: P_{air} = P_{H2} = 1 bar (back pressure = 7.3 psig) fully humidified; T = 80 °C; N-211 membrane; 5 cm² MEA; cathode catalyst = 3.5 mg/cm², anode catalyst = 0.4 mg_{Pt}/cm².

Highlights: The fuel cell specific activities reached to **7 mA/cm²** @ 0.9 $V_{IR\text{-}free}$ and **148 mA/cm²** @ 0.8 $V_{IR\text{-}free}$ under one-bar air

Accomplishment - Record Fuel Cell Power Densities were Achieved under both Oxygen & Air

Engineering catalyst morphology and MEA architecture can alter fuel cell performances between kinetic and mass-transport limited regions



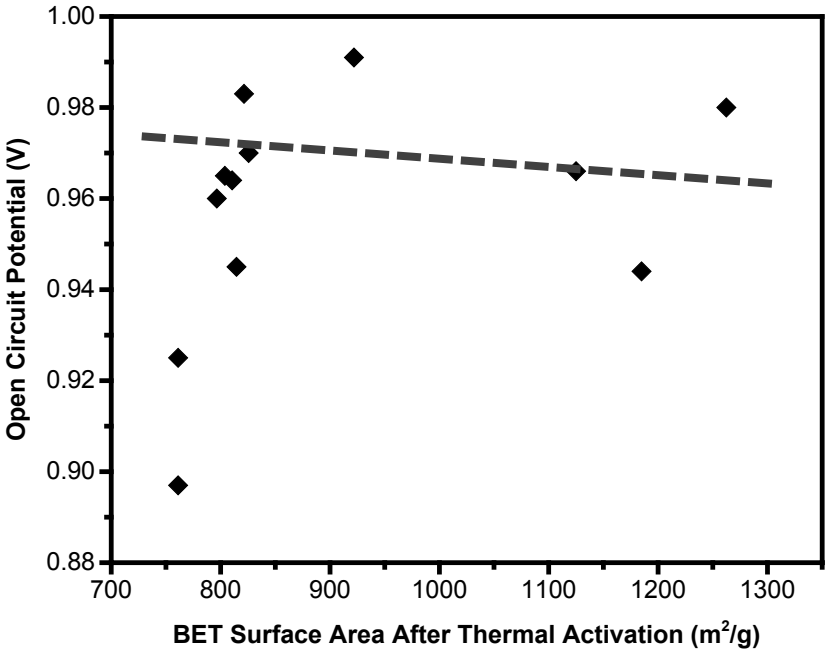


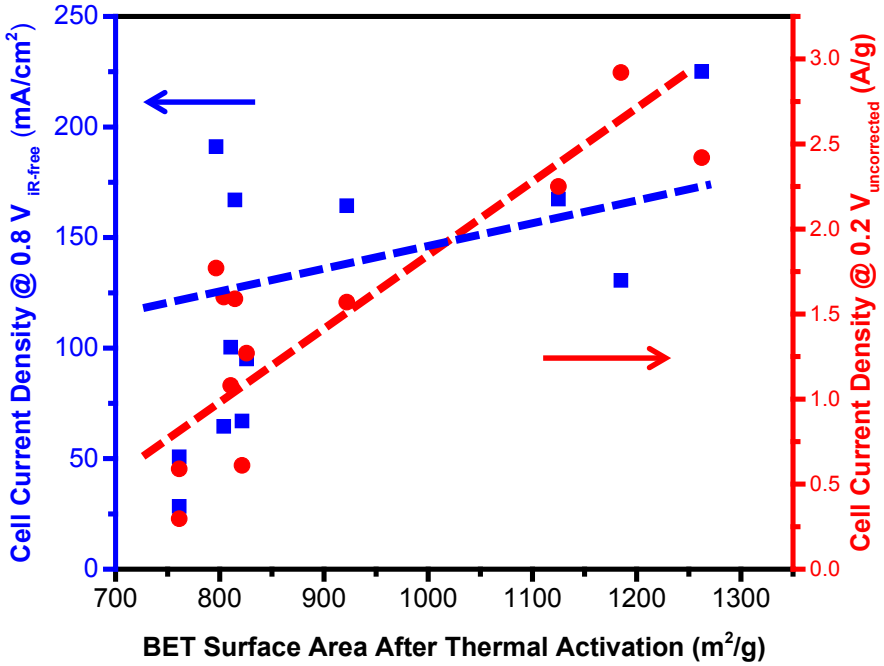
Condition: P_{air} or P_{O2}= P_{H2} = 1 bar (back pressure = 7.3 psig) fully humidified; T = 80 °C; N-211 membrane; 5 cm^2 MEA; cathode catalyst = 3.5 mg/cm^2, anode catalyst = 0.4 mg_{Pt}/cm^2.

Highlights: The fuel cell power densities reached **924 mW/cm²** under one-bar oxygen and **437 mW/cm²** under one-bar air.

Accomplishment - Correlation between Surface Property & Catalyst Performance was Identified

A systematic study on ZIF-based catalysts with different specific surface areas (SSAs) showed that, although SSA does not correlate with OCV (Left), it is proportional to MEA/fuel cell current in the mass transport region (Right).

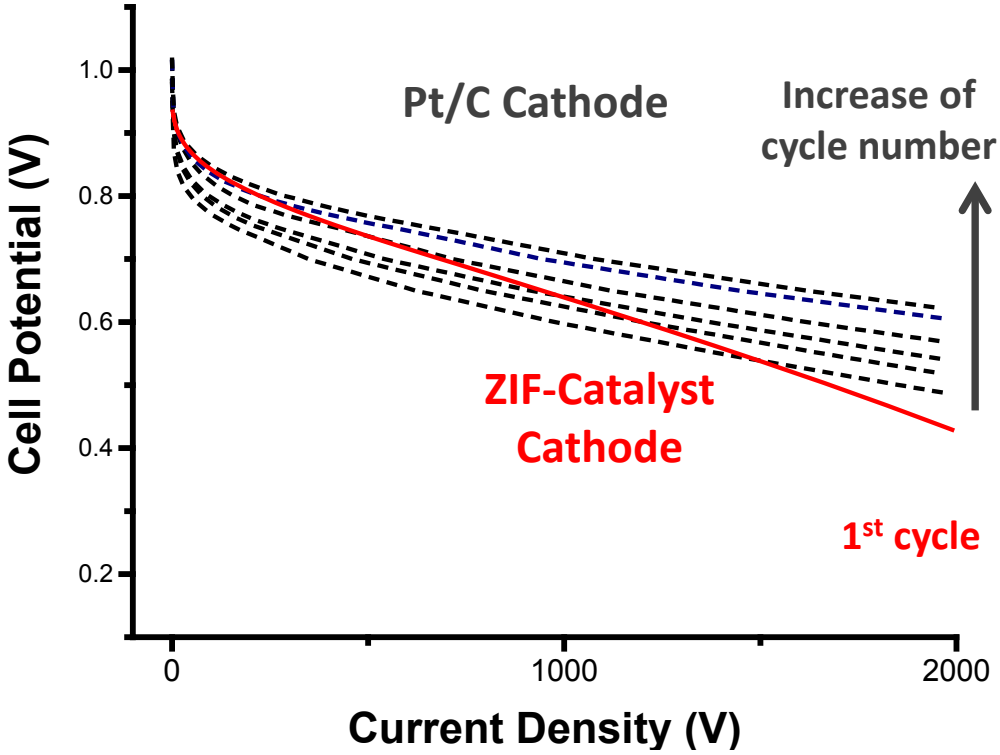




A strong correlation between cell current and catalyst specific surface area supports the hypothesis that active sites are uniformly decorated in the micropore surface of ZIF-derived catalyst, which is different from Pt catalysts

Accomplishment - Comparative Study between ZIF-derived Non-PGM Catalyst & Commercial Pt/C was Performed

A Side-by-Side MEA/Fuel Cell Study under Identical Test Conditions

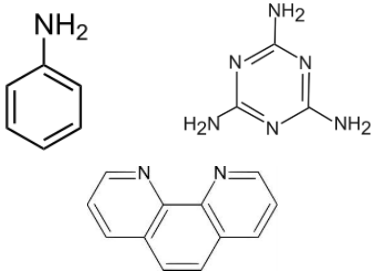


Condition: $P_{O2} = P_{H2}$ = 1 bar (back pressure = 7.3 psig) fully humidified; T = 80 °C; N-211 membrane; 5 cm^2 MEA; anode catalyst = 0.4 mg_{Pt}/cm^2, ZIF-catalyst cathode loading = 4 mg/cm^2, Pt/C cathode loading = 0.5 mg_{Pt}/cm^2

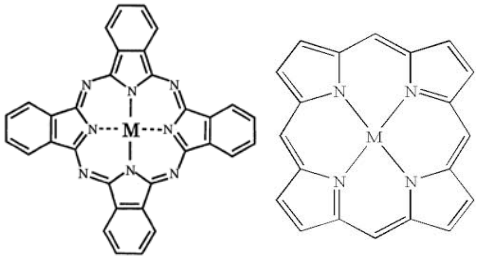
- ZIF-derived non-PGM catalyst showed fast break-in and comparable performance at kinetic region
- At high current region, ZIF-based catalyst showed lower performance, indicating the need for better accessible catalytic sites and higher turn-over frequency
- Durability of ZIF-based non-PGM catalyst still needs to be significantly improved

Accomplishment – New Strategy to Improve Catalytic Activity through Additive Infiltration was Developed

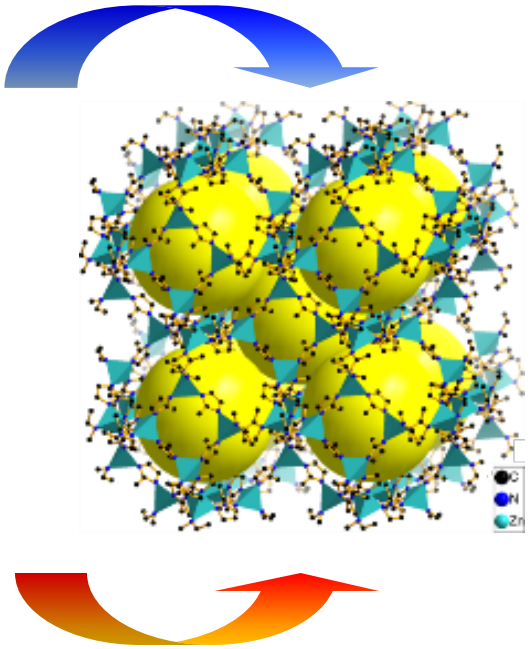
N-containing organic ligands and/or organo-metallic complexes can be readily infiltrated into porous ZIF for composition/activity refinement

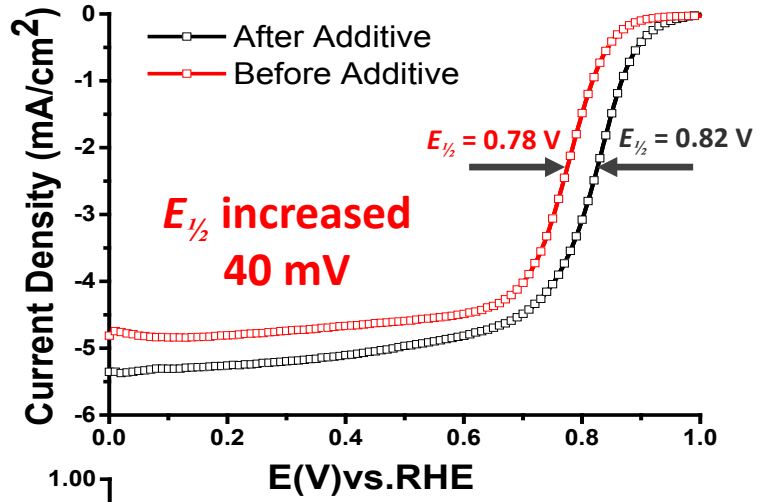


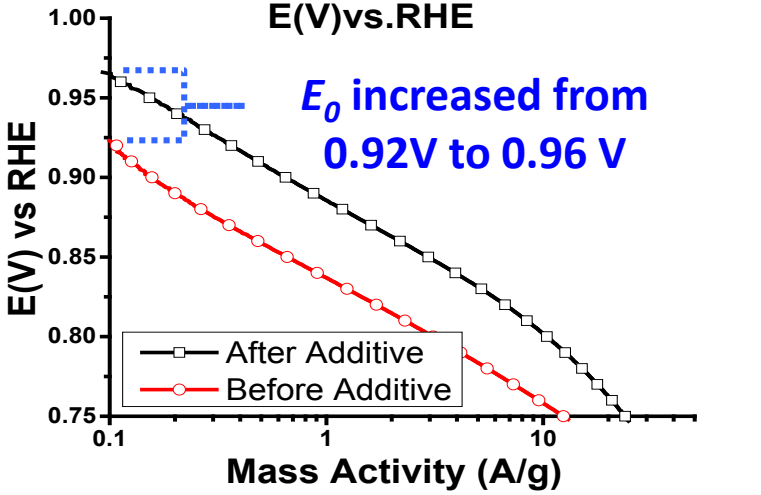
N-ligand examples



TM-complex examples





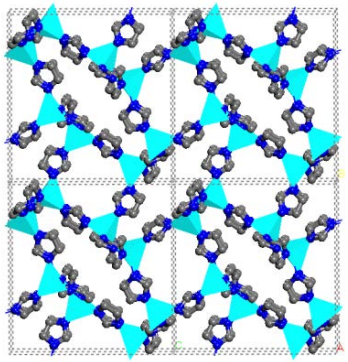


Well-defined crystal structure and inner porosity render MOFs as ideal hosts for adding N-containing ligands and/or organometallics for surface functionalization

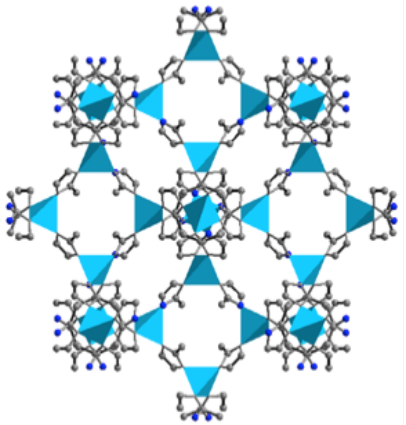
Accomplishment – Study on Co-ZIFs as Precursors for Fe-free Non-PGM Catalysts was Initiated

- Mitigation of MEA degradation by Fe induced Fenton reaction requires alternative transition metals
- In Co-ZIF, Co is also coordinated by N from four imidazole with unit volume packing density as high as $3.6 \times 10^{21}/cm^3$!
- High BET surface area ~ 1500 m^2/g was achieved in our lab recently

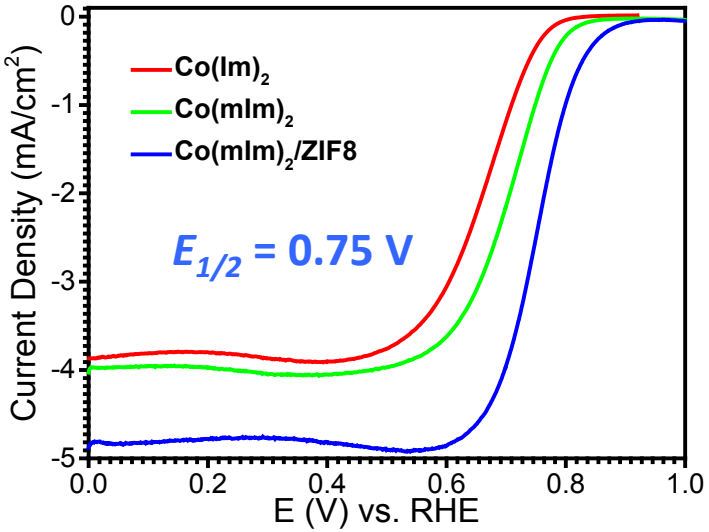
Co/N_4 Coordination Chemistry

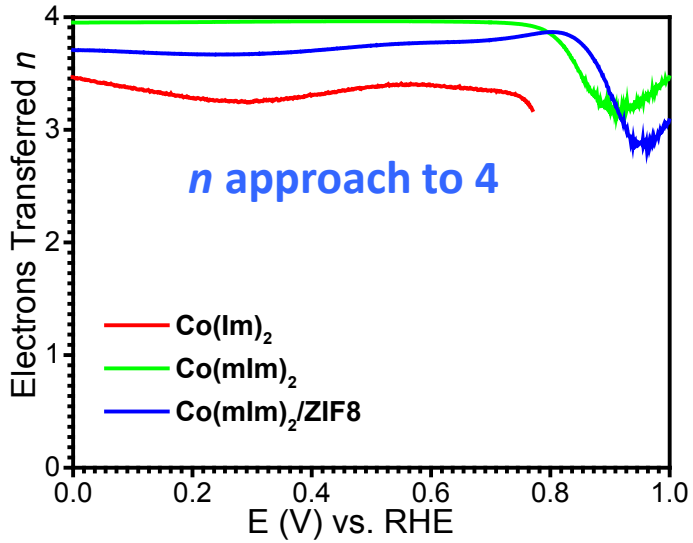


$Co(Im)_2$



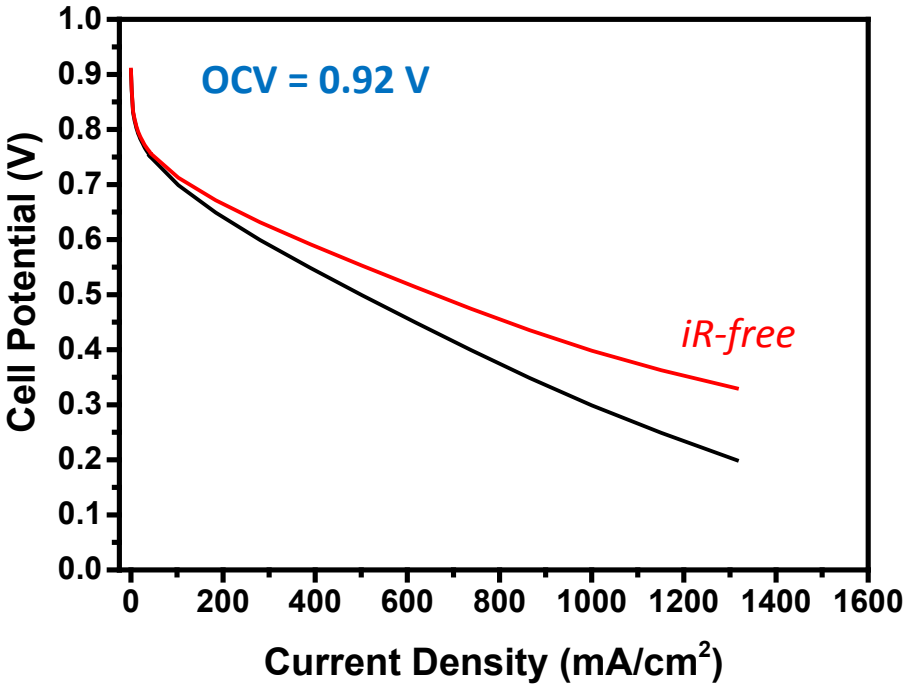
$Co(mIm)_2$

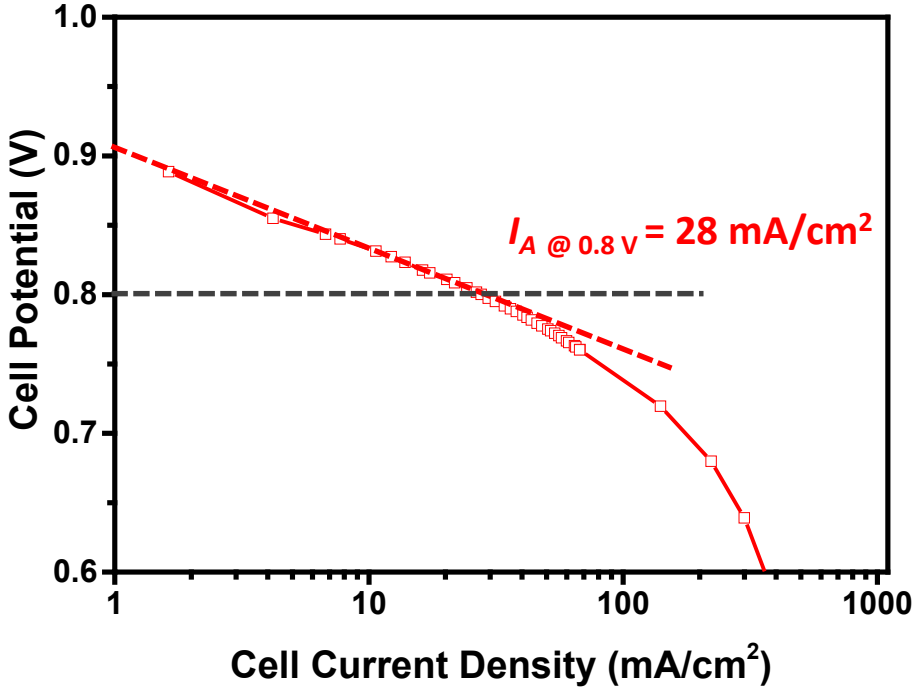




Accomplishment - Promising Activity of Co-ZIF Derived Catalyst was achieved at MEA/Fuel Cell Level

Initial MEA/single fuel cell tests of the catalyst from heat-treated binary $Co(mIm)_2/Zn(mIm)_2$ showed a promising performance





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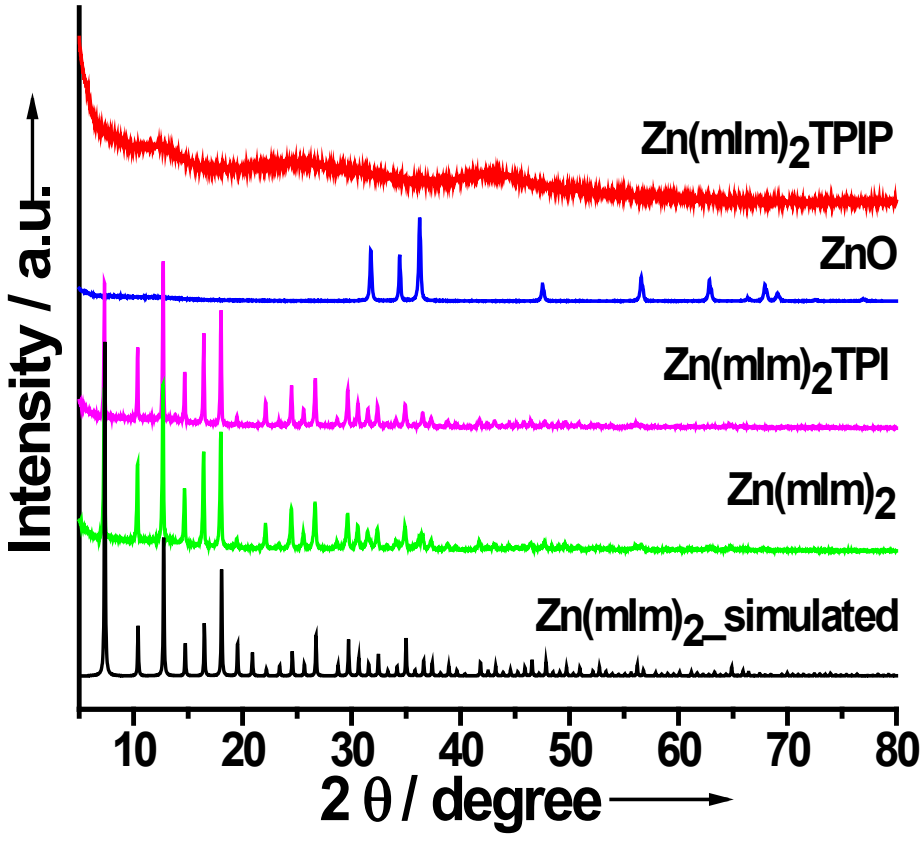
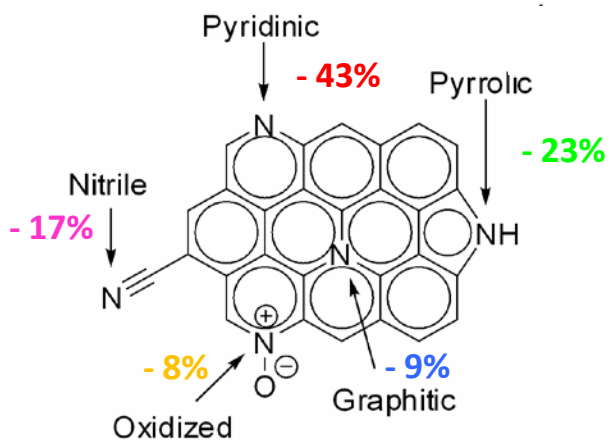
The Co-only catalyst showed respectable performance in a single fuel cell study. Significant improvement is still necessary

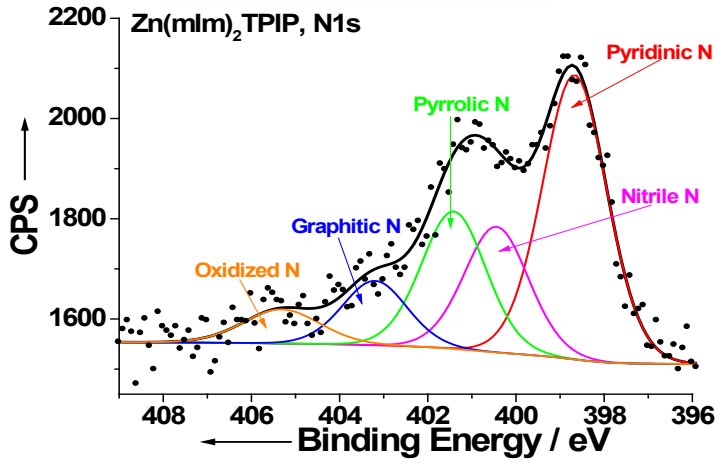
Accomplishment - XRD and XPS Characterizations of Precursors & Catalyst

XRD study on catalyst prepared at different stages



XPS study on different Ns in catalyst

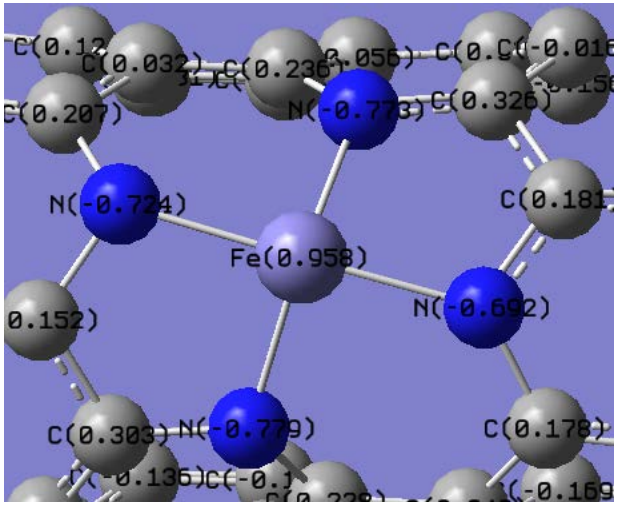


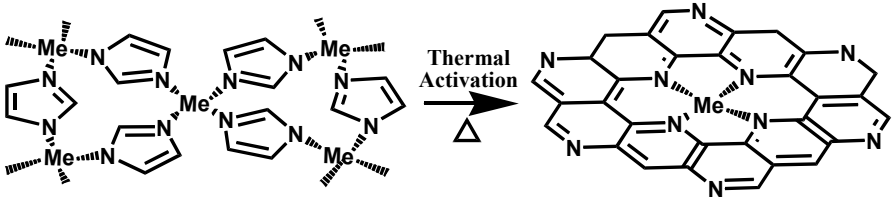


- XRD shows the complete conversion from ligand to ZIF after "one-pot" synthesis
- XPS shows pyridinic/pyrrolic nitrogens dominate in the heat-treated ZIF

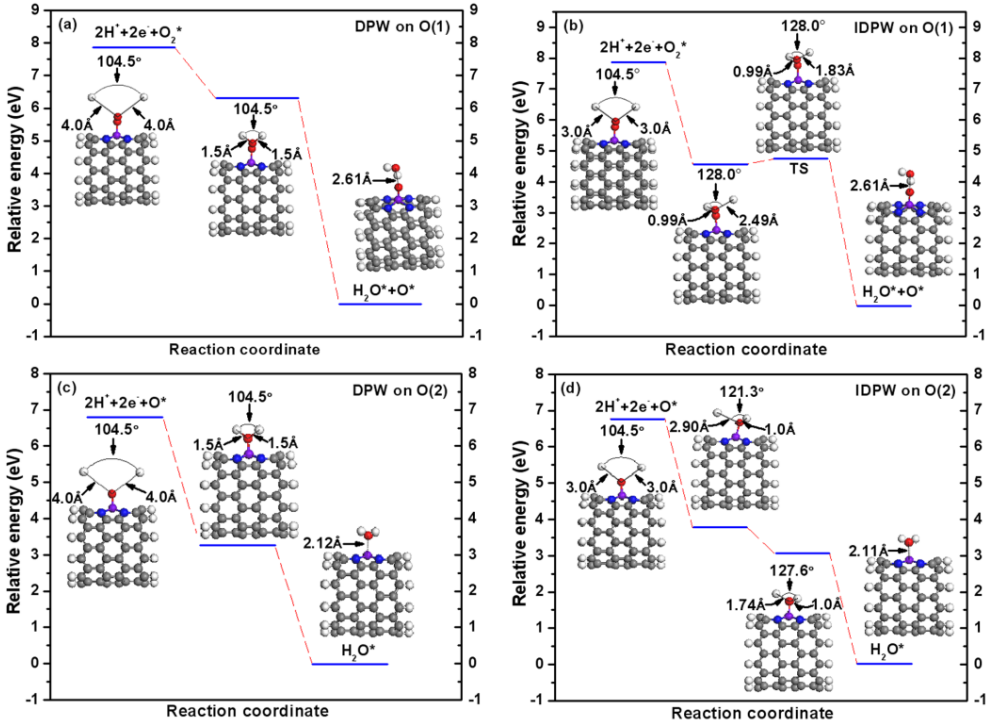
Accomplishment -Computational Modeling of TM/N_x/C Site Structure & ORR Pathways

"Stability and charge distribution of Fe/N_4/C site was confirmed by DFT calculation"
- Collaboration with University of Illinois



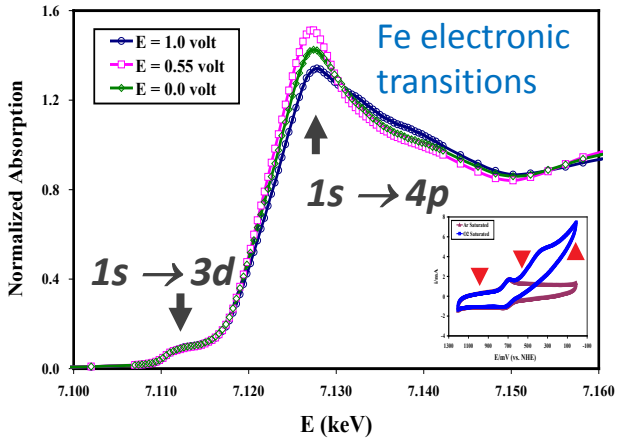


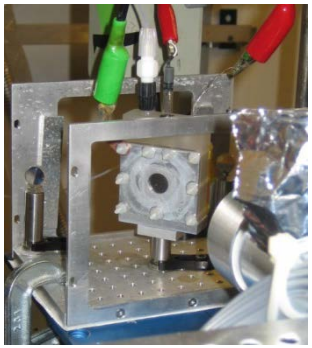
"Two potential ORR reaction pathways over Fe/N_4/C active site were identified"
- Collaboration with Southern University

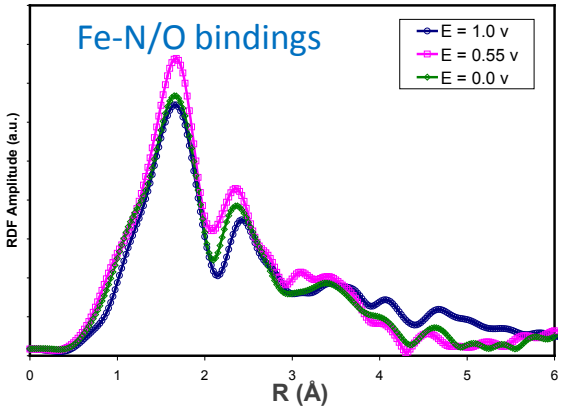


F. Gao, G.-L. Zhao, Z. Wang, D. Bagayoko , D.-J. Liu, *Catalysis Comm*. 62 (**2015**) 79–82

Accomplishment - *In Situ* X-ray Absorption Spectroscopic Study on Active Site Redox Mechanism







Iron oxidation state and coordination structure under different polarization potentials shed lights on O_2-TM binding and ORR rate

Collaborations

- Northern Illinois University – Guest graduate student researcher (Heather Barkholtz)
- Shanghai Jiaotong University – Guest graduate student researcher (Lina Chong)
- National University of Singapore – “One-pot” ZIF synthesis development (Prof. D. Zhao)
- Southern University – DFT calculation on ORR reaction pathways (Prof. G. Zhao)
- University of Illinois Chicago – DFT calculation on $Fe/N_4/C$ active site structure and stability (Dr. P. Zapol & Prof. P. Kral)
- University of South Florida/University of Tennessee – Co-ZIF catalyst studies (Prof. S. Ma & Dr. G. Goenaga)
- SAFCell, Inc. – Evaluation of ANL’s non-PGM catalyst in high temperature solid acid electrolyte fuel cell (Dr. C. Chisholm)
- DOE FCTO Catalysis Working Group – Catalyst development information exchange

Proposed Future Work

Reminder of FY 2015

- Complete volumetric activity measurement and improvement over ZIF-derived catalysts
- Complete catalyst and MEA durability study under potential cycling using DOE AST protocol
- Complete the structure-function relationship study and process optimization to achieve higher catalyst property & performance

Future Catalyst Development

- Activity and durability improvements through rapid interrogation and screening of new series of MOF/ZIF design, synthesis and conversion
- Activity and durability improvements through high-throughput screening of new organic and organometallic additives supported by statistical optimization methodology
- Activity and durability improvements through rational design and high-throughput optimization of new nano-network electrode architecture

"One-pot" synthesis & ZIF/nano-network could serve as a new development platform for next-generation, high performance non-PGM materials

Technology Transfer Activities

- We established non-disclosure agreements (NDAs) with one major automaker and one small company on Argonne's non-PGM catalysts for potential licensing. Other NDAs are currently under evaluation.
- We provided catalyst samples for technical evaluation by industrial partner.
- We participated in a university led, multi-companies and national labs proposal team in response to recent ARPA-e call, aiming at commercialization of non-PGM catalyst.
- We currently have a portfolio of **10** US patents/patent applications in non-PGM catalysts ready for licensing, ranging from functionalized carbon nanotubes, metal-organic framework and porous organic polymer derived materials, and nano-network catalyst/electrode architecture.
- Two new patent applications filed since the inception of this project
  - "Electrocatalysts using porous polymers and method of preparation" **US Patent Application filed on March 16, 2015**
  - "Non-platinum group metal electrocatalysts using metal organic framework materials and method of preparation" **US Patent Application filed on February 27, 2015**

Summary on Accomplishments

- A versatile, low cost "one-pot" synthesis method was developed that enabled rapid syntheses and tests of over 90 MEAs containing ZIF-based non-PGM catalysts.
- The best fuel cell specific activity of **323 mA/cm^2** @0.8 $V_{IR\text{-}free}$ was achieved under one-bar oxygen, exceeding project target (200 mA/cm^2) by 62%. An average over 10 best performing MEAs yielded specific activity of **250 mA/cm^2** @0.8 $V_{IR\text{-}free}$.
- A record fuel cell specific activity of **29.5 mA/cm^2** @0.9 $V_{IR\text{-}free}$ was achieved under one-bar oxygen, exceeding project target (25 mA/cm^2) by 18%.
- A record fuel cell specific activity of **148 mA/cm^2** @0.8 $V_{IR\text{-}free}$ was achieved under one-bar air.
- The highest fuel cell power densities of **924 mW/cm^2** under one-bar oxygen and **437 mW/cm^2** under one-bar air were achieved.
- Infiltration of N-containing organics and transition metal precursors to ZIFs improved the halfwave potential from 0.76 V to **0.82 V**.
- Three Co-ZIF derived catalysts were prepared as an effort towards Fe-free non-PGM materials, fuel cell specific activity reached **28mA/cm^2** @0.8 $V_{IR\text{-}free}$.
- Computational DFT calculations demonstrated active site stability and revealed two ORR pathways over $Fe/N_x/C$ catalysts.

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