

V.F.12 Novel Non-PGM Catalysts from Rationally Designed 3-D Precursors

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Overall Objectives

- To design, synthesize and evaluate highly efficient nonplatinum group metal (non-PGM) cathode catalysts using rationally designed three dimensional (3-D) precursors with significantly improved fuel cell performance
- To support non-PGM catalyst development through improved understanding on the structure–function relationship

Fiscal Year (FY) 2015 Objectives

- Complete the synthesis and optimization of zeolitic imidazolate framework (ZIF)-based catalysts with new precursor chemistries
 - Achieve membrane electrode assembly (MEA)/single cell areal current density $>200 \text{ mA/cm}^2$ at $0.8 \text{ V}_{iR-free}$ and $>25 \text{ mA/cm}^2$ at $0.9 \text{ V}_{iR-free}$ under 1 bar O_2
- Complete the characterizations on precursors and catalysts and improve the understanding of structure–property relationship
- Complete catalyst activity improvement through synthesis and engineering process refinements
 - Achieve volumetric current density $>95 \text{ A/cm}^3$ at $0.8 \text{ V}_{iR-free}$ in MEA/fuel cell test under 1 bar O_2

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration Plan:

- (A) Durability (of catalyst and fuel cell)
- (B) Cost (replacement of Pt usage at cathode)
- (C) Performance (improvement of non-PGM catalyst systems)

Technical Targets

This project aims at developing high efficiency, non-PGM materials as the low cost cathode catalyst replacements for platinum. Technical targets for this project are presented in Table 1.

TABLE 1. Current Status towards Meeting Technical Targets for non-PGM Electrocatalysts for Transportation Applications

Characteristic	Unit	2017/2020 Targets	ANL 2015 Status
Non-Pt catalyst activity per volume of supported catalyst	A/cm^3 at $800 \text{ mV}_{iR-free}$	300/300	108.7 ^a

^a Measured in single fuel cell: 5 cm^2 cell, $P_{\text{O}_2} = P_{\text{H}_2} = 1 \text{ bar}$ at 100% relative humidity (gauge pressure = 7.3 psig); flowrate = 200 ml/min, $T = 80^\circ\text{C}$, cathode loading = 2.5 mg/cm^2 , anode loading = 0.3 mg-Pt/cm^2 , Nafion[®] membrane = 211.

FY 2015 Accomplishments

- We completed the synthesis and optimization of Fe-doped, ZIF-based non-PGM catalysts. The average areal current density of ten best performing fuel cells reached to 250 mA/cm^2 at $0.8 \text{ V}_{iR-free}$ under 1 bar oxygen, exceeding the goal by 25%. The best performing MEA achieved fuel cell current density of 29.5 mA/cm^2 at $0.9 \text{ V}_{iR-free}$ under 1 bar O_2 , exceeding the goal by 18%.
- We completed the ZIF-based precursor and catalyst structure characterizations. A clear correlation between the catalyst surface area and the fuel cell limiting areal current density was observed.
- We completed catalytic activity improvement through alternative ZIF synthesis and engineering process optimization. A volumetric current density of 108 A/cm^3 was also achieved at $0.8 \text{ V}_{iR-free}$, surpassing the project goal.



INTRODUCTION

Since Pt-based electrode catalyst contribute to nearly half of a fuel cell stack cost, finding inexpensive, earth-abundant materials as replacement of PGMs has been identified as a long-term goal by DOE FCTO for proton exchange membrane fuel cell research. For automotive

applications, DOE's 2017/2020 volumetric activity target for non-PGM catalyst is 300 A/cm^3 and the cost target is less than $\$30/\text{kW}_e$. Recently, transition metal doped nitrogen-carbon (TM-N-C) composites received a great deal of attention due to their more promising catalytic activity over other non-PGM materials. Generally, TM-N-C composites are prepared by applying TM-N_x molecular complexes or polymers over amorphous carbon support, followed by thermal activation. Using the catalytically inert carbon support dilutes the active site density therefore limits the catalyst potential to reach the highest possible performance. At Argonne National Laboratory, we developed several new approaches in recent years to circumvent the dilution issue by using "self-supported" transition metal-organic compounds such as metal-organic frameworks (MOFs) or porous organic polymers (POPs) [1-4]. Since MOFs and POPs are intrinsically porous with potential active sites, TM-N_x uniformly distributed and interconnected by organic linker, they have the potentials to produce the highest catalytic site density therefore the most active catalysts [5].

This project focuses on MOF-based non-PGM catalyst development. Although the concept of MOF-based electrocatalyst has been demonstrated, the catalyst preparations have yet to be optimized to reach their full potentials. Under this project, new synthesis and process methods and their operating parameters will be investigated to improve the catalyst performance. The catalysts prepared using the zeolitic imidazolate framework (ZIF, a subclass of MOF) are the focus of the investigation. We will enhance the catalyst activity over our own previous records and the benchmark materials by the others and demonstrate the improvement at the catalyst as well as MEA/fuel cell levels. The goal is to achieve fuel cell areal and volumetric current densities that meet or exceed the project's targets.

APPROACH

This project consists of three main approaches. They are (1) new composition chemistry, exploring new catalyst precursor by applying different organometallic complexes, organic additives and synthetic chemistry; (2) physical property investigation, understanding the structure-performance relationship through precursor and catalyst characterizations; and (3) process optimization, improving catalytic activity by optimizing of ZIF synthesis and posttreatment parameters.

The new composition chemistry focuses on exploring different transition metal complexes and/or nitrogen containing organic compounds as additives to ZIF precursor by infiltration or during direct synthesis. The impact of these additives to the catalyst performance will be evaluated through rotating disk electrode (RDE) and MEA measurements. The physical property study aims at correlating surface-electronic property and morphology between precursor and the catalyst using different characterization tools. The results will serve as guidance for new catalyst design and improvement. The processing optimization targets the controls of precursor and catalyst synthesis conditions to maximize catalyst activity and fuel cell performance.

RESULTS

Our ZIF-based catalyst preparation applies a low cost, "one-pot" solid state synthesis to incorporate transition metal precursor inside of ZIFs with well-defined crystal structure, followed by high temperature pyrolysis. Figure 1 shows an example of preparing Fe-doped non-PGM catalyst via Zn-based ZIF, Zn(mIm)₂. Zn(mIm)₂ has high porosity and

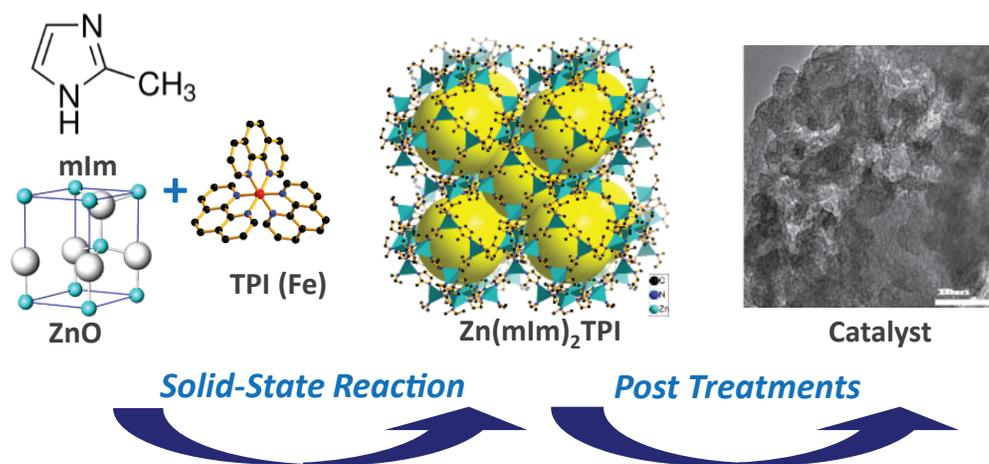


FIGURE 1. Schematics of one-pot synthesis of ANL's ZIF-based non-PGM catalyst by reacting methylimidazole (mIm), zinc oxide (ZnO), tris-1,10-phenanthroline iron(II) perchlorate (TPI) in solid state to form ZIF precursor, Zn(mIm)₂TPI, before pyrolyzed to catalyst.

internal surface area, which could serve as host to various TM organometallics or N-containing organic ligands. By incorporating such compounds into ZIF before thermal conversion, one could add additional active sites to further enhance the overall catalytic activity. Under this project, we have investigated several N-containing organic additives such as phenanthroline and polyaniline to $\text{Zn}(\text{mIm})_2$. They were incorporated during the “one-pot” synthesis and were uniformly mixed inside or nearby ZIF’s cavity. We found that these ligands could indeed enhance the catalyst activity when embedded to $\text{Zn}(\text{mIm})_2$ prior to thermal activation, leading to higher oxygen reduction reaction (ORR) onset and halfwave potentials. For example, the addition of phenanthroline increased the catalytic ORR onset potential (E_0) from 0.91 V to 0.96 V and the halfwave potential ($E_{1/2}$) from 0.76 V to 0.82 V, respectively, measured by the RDE experiments.

The performance of non-PGM catalysts derived from ZIF-based precursors could also be influenced by the processing parameters from ZIF crystallization to pyrolysis. We devoted a significant amount of effort in the process optimization under this project. Since the improvement can only be properly gauged by fuel cell performance, we evaluated more than 100 MEAs to evaluate the catalyst activity. Our process optimization has led to substantial improvement in the catalyst and fuel cell performance. For example, Figure 2a shows the current-voltage polarization and power density distribution of a representative MEA prepared during the second quarter of FY 2015. The measurements were conducted under 1 bar oxygen at 80°C. For comparison, we also plotted the polarization and power density curves for the catalyst sample prepared at the project beginning. A major improvement has been achieved. In fact,

the average areal current density measured over 10 selected MEAs has reached to 250 mA/cm^2 at $0.8 \text{ V}_{iR\text{-free}}$, compared to 178 mA/cm^2 observed at the project inception. This value represents a 40% improvement and exceeds our project target (200 mA/cm^2). We also measured the areal specific activity at $0.9 \text{ V}_{iR\text{-free}}$ and obtained the best value of 29.5 mA/cm^2 , surpassing the project goal of 25 mA/cm^2 . We also measured the volumetric activity of our best performing catalyst in fuel cell and achieved the specific current density of 108 A/cm^3 at $0.8 \text{ V}_{iR\text{-free}}$ (Figure 2b). This is by far the best value for a non-PGM catalyst to our knowledge. In addition to oxygen, we investigated the catalyst performance in air. Figure 3 shows examples of current-voltage polarization and power density distribution of two MEAs prepared with two of our ZIF-based catalysts identical in composition but different in morphology. The fuel cell measurements were conducted under 1 bar air with 100% relative humidity (RH) at 80°C. The result clearly shows that the morphology has significant impact to fuel cell current and power densities even though good performances were observed in both cases. The best areal current activities were 148 mA/cm^2 at $0.8 \text{ V}_{iR\text{-free}}$ and 110 mA/cm^2 at $0.8 \text{ V}_{\text{uncorrected}}$, respectively.

We also carried out an extensive investigation on the structure–performance relationship of the ZIF-derived catalysts. Specifically, we prepared a series of ZIF-based non-PGM catalysts of different specific surface areas (SSAs) and tested their activities under fuel cell operating condition. Figure 4 shows the areal current densities at both $0.8 \text{ V}_{iR\text{-free}}$ and $0.2 \text{ V}_{\text{uncorrected}}$ as the functions of catalyst SSA. Positive correlations were found between the current densities and the SSA, particularly at the mass–transport limiting region (0.2 V). Such observation supports the hypothesis that

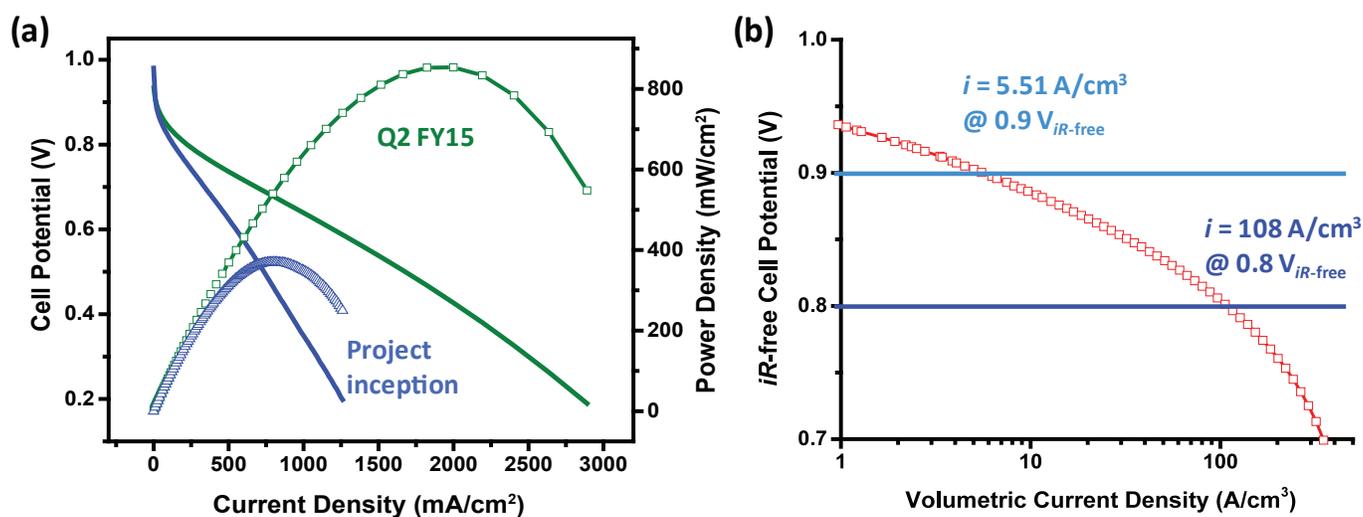


FIGURE 2. (a) Comparison of the current-voltage polarizations and power densities of the fuel cells tested at the project start and at the end of Q2 FY 2015.

(b) Volumetric current density of a representative ANL non-PGM catalyst measured in a MEA/fuel cell test. Conditions: $P_{\text{O}_2} = P_{\text{H}_2} = 1 \text{ bar}$ (back pressure = 7.3 psig) fully humidified; Flowrate $\text{O}_2 = \text{Flowrate}_{\text{H}_2} = 200 \text{ ml/min}$; $T = 80^\circ\text{C}$; N-211 membrane; 5 cm^2 MEA; cathode catalyst = $3.5\text{--}4 \text{ mg/cm}^2$, anode catalyst = $0.4 \text{ mg}_p/\text{cm}^2$.

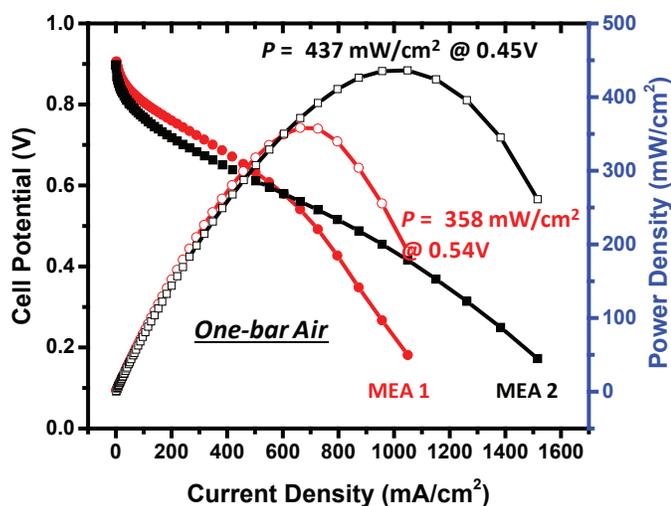


FIGURE 3. The current-voltage polarizations and power densities of two representative MEAs with ZIF-derived cathode catalyst tested in fuel cells. Conditions: $P_{\text{air}} = P_{\text{H}_2} = 1$ bar (back pressure = 7.3 psig) 100 RH; $T = 80^\circ\text{C}$; N-211 membrane; 5 cm^2 MEA; cathode catalyst = 3.5 mg/cm^2 , anode catalyst = $0.4\text{ mg}_{\text{Pt}}/\text{cm}^2$.

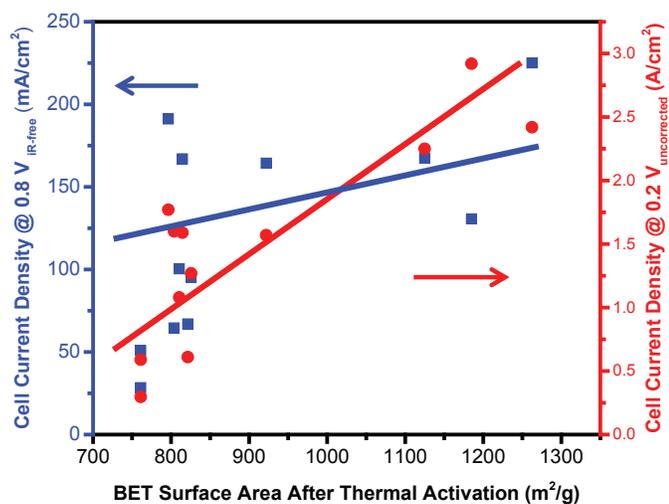


FIGURE 4. Fuel cell areal current densities measured at 0.8 V and 0.2 V as the functions of Brunauer-Emmett-Teller surface area of non-PGM cathode catalysts.

the active sites in the ZIF-derived catalyst are uniformly decorated on the micropore surface with their numbers proportional to the total SSA. This is in contrast to that of Pt-based catalysts.

CONCLUSIONS AND FUTURE DIRECTIONS

- The team has met and exceeded all the project milestones.

- ANL's ZIF-derived non-PGM catalyst achieved areal specific activity of 250 mA/cm^2 at $0.8\text{ V}_{iR\text{-free}}$, 29.5 mA/cm^2 at $0.9\text{ V}_{iR\text{-free}}$ and volumetric activity of 108 A/cm^3 at $0.8\text{ V}_{iR\text{-free}}$ when tested in fuel cell at 80°C under fully humidified 1 bar O_2 , all exceeded the project goals.
- Tested under fully humidified 1 bar air at 80°C , ANL's ZIF-derived non-PGM catalyst achieved areal current density of 148 mA/cm^2 at $0.8\text{ V}_{iR\text{-free}}$ or 110 mA/cm^2 at $0.8\text{ V}_{\text{uncorrected}}$.
- A structure–property characterization study identified the correlation between the catalyst specific surface area and the fuel cell current density, revealing a key difference in active site distribution between non-PGM and PGM catalysts.
- During the project, ANL team filed three United States patent applications, received two granted United States patents and published three peer-reviewed journal articles.

ANL's ZIF-based non-PGM catalysts open up the following research directions:

- Improving catalytic activity and durability through new organic ligand and organometallics choices including nonferrous metals
- Improving catalyst activity/durability through new MOF/ZIF design, synthesis and conversion
- Better mass/charge transport and water management through new morphology and electrode architecture such as interconnected nano-network

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

- “Non-platinum group metal electrocatalysts using metal organic framework materials and method of preparation,” Di-Jia Liu, Shengqian Ma, Gabriel Goenaga, **US Patent 8,835,343**.
- “Electrocatalysts using porous polymers and method of preparation,” Di-Jia Liu, Shengwen Yuan, Gabriel Goenaga, **US Patent 9,012,344**.
- “Nanofibrous Electrocatalysts,” Di-Jia Liu, Jianglan Shui, Chen Chen, **US Patent Application 20140093790**.
- “Non-Platinum Group Metal Electrocatalysts Using Metal Organic Framework Materials and Method of Preparation,” Di-Jia Liu, Shengqian Ma, Gabriel Goenaga, **US Patent Application 20150056536**.
- “Non-Platinum Group Metal Electrocatalysts Using Metal Organic Framework Materials and Method of Preparation,” Di-Jia Liu, Shengqian Ma, Gabriel Goenaga, Dan Zhao, **US Patent Application 20150180045**.

6. “Electrocatalysts Using Porous Polymers and Method of Preparation,” Di-Jia Liu, Shengwen Yuan, Gabriel Goenaga, **US Patent Application 20150194681**.

7. Student Poster Award First Place - Solid State Science and Technology to Heather Barkholtz for her research on “Highly Active Non-PGM Catalysts Prepared from Metal-Organic Frameworks,” under Di-Jia Liu at Argonne National Laboratory, 227th ECS Spring Meeting, Chicago, IL, May 24–28, 2015

FY 2015 PUBLICATIONS/PRESENTATIONS

1. “High-efficiency non-precious metal catalyst containing metal-organic framework precursor inside of carbon nano-network,” Jianglan Shui, Chen Chen, Lauren R. Grabstanowicz, Dan Zhao and Di-Jia Liu, *Proceedings of National Academy of Sciences, USA* (2015), vol. 112, no. 34, 10629–10634.

2. “Highly Active Non-PGM Catalysts Prepared from Metal-Organic Frameworks,” Heather M. Barkholtz, Lina Chong, Zachary B. Kaiser, Tao Xu, and Di-Jia Liu, Invited Contribution to Special issue on Polymer Electrolyte Membrane Fuel Cell in *Catalysis* 5, 955-965, (2015) doi:10.3390/catal5020955.

3. “Catalytic Reaction on FeN₄/C Site of Nitrogen Functionalized Carbon Nanotubes as Cathode Catalyst for Hydrogen Fuel Cells,” Feng Gao, Guang-Lin Zhao, Zhou Wang, Diola Bagayoko, Di-Jia Liu, *Catalysis Communications* 62, 79–82, (2015) doi:10.1016/j.catcom.2015.01.015.

4. “Non-Precious Metal Fuel Cell Catalysts Prepared By Rationally Designed Porous Materials,” Heather Barkholtz, Lina Chong, Dan Zhao, Di-Jia Liu, Conference paper at 5th European Fuel Cell Forum, 2015.

5. “MOFs and POPs – Two new classes of porous precursors for highly efficient non-PGM catalyst design and synthesis,” Di-Jia Liu, Invited presentation at *Electrocatalysis and Fuel Cell Discussion*, La Grande Motte, France, September 13–16, 2015.

6. “Novel Non-PGM Catalysts from Rationally Designed 3-D Precursors,” Di-Jia Liu, Poster presentation at 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.

7. “Highly Active Non-PGM Catalysts Prepared from Metal-Organic Frameworks,” Heather M. Barkholtz, Zachary Kaiser, Di-Jia Liu, Poster at 227th Electrochemical Society Meeting, Chicago, IL May 24-28, 2015.

8. “New Material Chemistries and Structural Investigations for Next-Generation Energy Storage and Conversion Applications,” Di-Jia Liu, Department of Chemistry Seminar, University of Illinois at Chicago, February 26, 2015.

9. “Oxygen Reduction Reactions in Fuel Cell & Li-Air Battery: Insights of New Catalyst Design & Catalytic Mechanism,” Di-Jia Liu, College of Engineering Seminar, Peking University, Beijing, China, Sept. 23, 2014.

10. “Recent Developments in New Materials and Characterization Techniques for Energy Storage and Conversion,” Di-Jia Liu, Department of Chemistry Seminar, University of Nebraska - Lincoln, Oct. 20, 2014.

11. “Recent advancements in non-precious metal fuel cell catalysts prepared by rationally designed porous materials,” Di-Jia Liu, Plenary talk at *XIV International Congress of the Mexican Hydrogen Society*, Cancun, Mexico, October 2, 2014.

REFERENCES

1. S. Ma, G. Goenaga, A. Call and D.-J. Liu, *Chemistry: A European Journal* 17, 2063 (2011).

2. D. Zhao, J.-L. Shui, C. Chen, X. Chen, B.M. Repragle, D. Wang and D.-J. Liu, *Chem. Sci.*, 3 (11), 3200 (2012).

3. D. Zhao, J.-L. Shui, L.R. Grabstanowicz, C. Chen, S.M. Commet, T. Xu, J. Lu, and D.-J. Liu, *Advanced Materials*, 26 1093 (2014).

4. S. Yuan, J.-L. Shui, L. Grabstanowicz, C. Chen, S. Commet, B. Repragle, T. Xu, L. Yu and D.-J. Liu, *Angew. Chem. Int. Ed.*, 52(32), 8349 (2013).

5. E. Proietti, F. Jaouen, M. Lefèvre, N. Larouche, J. Tian, J. Herranz and J.-P. Dodelet, *Nature Comm.* 2, 416 (2011).