V.A.12 Non-PGM Cathode Catalysts using ZIF-Based Precursors with Nanonetwork Architecture

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Overall Objectives

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

Fiscal Year (FY) 2014 Objectives

- Develop and improve a one-pot method for ZIF-based non-PGM catalyst synthesis and demonstrate at least one oxygen reduction reaction (ORR) catalyst with onset potential >0.9 V.
- Characterize the surface property and chemical composition of ZIF-derived non-PGM catalysts and establish property-function relationships.
- Complete initial design and synthesis of nano-network catalysts and demonstrate significantly improved volumetric and areal current densities at the membrane electrode assembly (MEA)/single cell level.

Technical Barriers

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

(A) Durability
(B) Cost
(C) Performance

Technical Targets

This project aims at developing non-PGM high-efficiency 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 2014 Status
Non-Pt catalyst activity per volume of supported catalyst	A/cm^3 @ 800 $mV_{iR\text{-}free}$ (iR – internal resistance)	300/300[a]	90.2[b]

[a] T = 80°C, fully humidified H_2/O_2, P = 150 KPa
[b] Measured in single fuel cell: $P_{O2} = P_{H2}$ = 2 bar; fully humidified at 80ºC, cathode loading = 2.0 mg/cm^2, anode loading = 0.3 mg_{Pt}/cm^2, Nafion® = 117.

FY 2014 Accomplishments

- A one-pot synthesis method for non-PGM catalyst was developed and four ZIF-derived catalysts with different organic ligands were produced. Three of the catalysts showed onset potential >0.9 V with half-wave potential as high as 0.81 V achieved.
- A process improvement of a ZIF-based catalyst yielded a high fuel cell areal current density of 178 mA/cm^2 @ 0.8 V under one bar oxygen pressure.
- An initial optimization of ZIF/nano-network catalyst was completed. The MEA with this catalyst at the cathode reached a volumetric current density of 90.2 A/cm^3 at 0.8 V and areal current density of 3 A/cm^2 at 0.2 V ($P_{O2} = P_{H2}$ = 2 bar).

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INTRODUCTION

Finding inexpensive, earth-abundant materials to substitute the PGMs has been the ultimate goal for PEMFC catalyst research. Since the electrode/catalyst materials contribute to nearly half of a fuel cell stack cost, there is an urgent need to reduce or replace PGM usage in order to meet the DOE 2017/2020 cost target of $\$30/kW_e$ for automotive applications. Among all the non-PGM candidates explored so far, transition metal-doped nitrogen-carbon (TM-N-C) composites appear to be the most promising ones. Generally, these catalysts are prepared by applying TM-N_x molecular complexes over amorphous carbon support, followed by thermal activation. Since non-PGM catalysts are known to have lower turn-over frequency *per catalytic site* than platinum, their active site densities have to be substantially higher in order to deliver a comparable performance. Using carbon support dilutes the active site density and limits the potential of reaching higher performance. New approaches to circumvent such dilution include the uses of catalyst precursors such as metal-organic frameworks (MOFs) [1-3] and porous organic polymers (POPs) [4]. These precursors are intrinsically porous or porous after thermal activation. Since the potential active sites, TM-N_4, are adjacent to each other and uniformly distributed in MOFs and POPs, these rationally designed precursors have the promises to produce the highest catalytic site density therefore the most active catalysts.

At Argonne National Laboratory, we pioneered the approaches of using MOFs and POPs as precursors for preparing highly efficient non-PGM ORR catalysts [1,3,4]. MOF/POP syntheses were perceived as tedious and costly, due to multiple reaction steps and the use of chemicals for crystallization and separation. To address such concern, we recently developed a novel "one-pot" solid-state synthesis method for preparing ZIF-derived (a subclass of MOF) catalysts [5]. The new approach not only greatly simplifies the preparation of ZIF-based non-PGM electrocatalysts, rending it suitable for large-scale production at very low cost, but also paves the way of exploring a variety of ZIFs in searching for better catalysts.

APPROACH

The project includes two parallel approaches. The first approach focuses on optimizing the newly developed "one-pot" synthesis method for ZIF-derived non-PGM catalysts. This solid-state reaction uses imidazole as the ligand and zinc oxide as the secondary building unit, both are inexpensive commodity chemicals at the price range of \$3/lb to \$5/lb. The method is robust and applicable to a variety of imidazoles, therefore feasible for exploring ZIFs with different organic group substitution. Study on such substitutions could lead to better understanding on the impact of ligand structure to the final catalyst activity. The ZIF-precursors are converted to non-PGM catalyst through thermolysis. The heat-activation is crucial to the catalyst performance and needs also to be optimized.

The second approach is to improve mass and charge transfers of ZIF-derived catalysts through new electrode architecture. To compensate lower turn-over frequency of non-PGM catalysts by simply increasing the usage will cause higher mass and charge transfer resistances from the thicker electrode layer. To circumvent such a barrier, we developed a novel network electrode structure in which the catalytic sites are embedded in the micropores of the nanofibers. The charge transfer is accomplished by carbonaceous network whereas the mass transport is facilitated by the voids between the fibers. Such network nearly eliminates the presence of mesopores without affecting microporous surface area and the active sites density.

RESULTS

Four ZIF-based precursors containing ligands of 2-methylimidazole (HmIm), imidazole (HIm), 2-ethylimidazole (HeIm), as well as 4-azabenzimidazole (H4abIm) were prepared through solid-state reaction with zinc oxide in the presence of 5 wt% phenanthroline iron(II) perchlorate (TPI). The corresponding iron-doped ZIFs are named as $Zn(mIm)_2TPI$, $Zn(Im)_2TPI$, $Zn(eIm)_2TPI$ and $Zn(abIm)_2TPI$, respectively. The molecular structures of the imidazole ligands, the organometallic iron complex and the lattice structures of the four ZIF precursors are given in Figure 1. Upon thermal activation at elevated temperature, the organic ligands are converted to carbonaceous composite with much improved electro-conductivity and the catalytic activity. We also carried out extensive structural characterizations for these precursors before and after the activation using techniques such as powder X-ray diffraction, nitrogen sorption isotherms, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy (TEM), and surface Raman spectroscopy. Figure 1 also shows the TEM images of the four catalysts after thermal conversion. We found, for example, nearly all the ZIFs, other than $Zn(eIm)_2TPI$, have no initial surface areas. The corresponding catalysts produced after the thermolysis, however, showed very high specific surface areas in the range of 800 to 1,200 m^2/g. Furthermore, they all possessed high fractions of micropores within the total pore volume. Both are important factors in controlling the overall catalytic activity.

The catalytic activity was tested at both rotating disk electrode (RDE) and MEA levels. Cathodic linear sweep voltammograms of all four catalysts were collected in an oxygen saturated $HClO_4$ (0.1 M) solution. All four samples exhibited prominent ORR activities with excellent onset (E_0) and half-wave potentials ($E_{½}$) potentials. We also found that the catalytic activity was sensitive to the processing condition. For example, by optimizing the processing parameters, we were able to improve onset potential from 0.91 to 0.96 V and half-wave potential from 0.75 to 0.81 V, respectively. Excellent catalytic activity was also demonstrated by the MEA/single cell measurement. Figure 2 shows (a) current-voltage polarization and (b) Tafel plot of iR-free potential as the function of areal current density

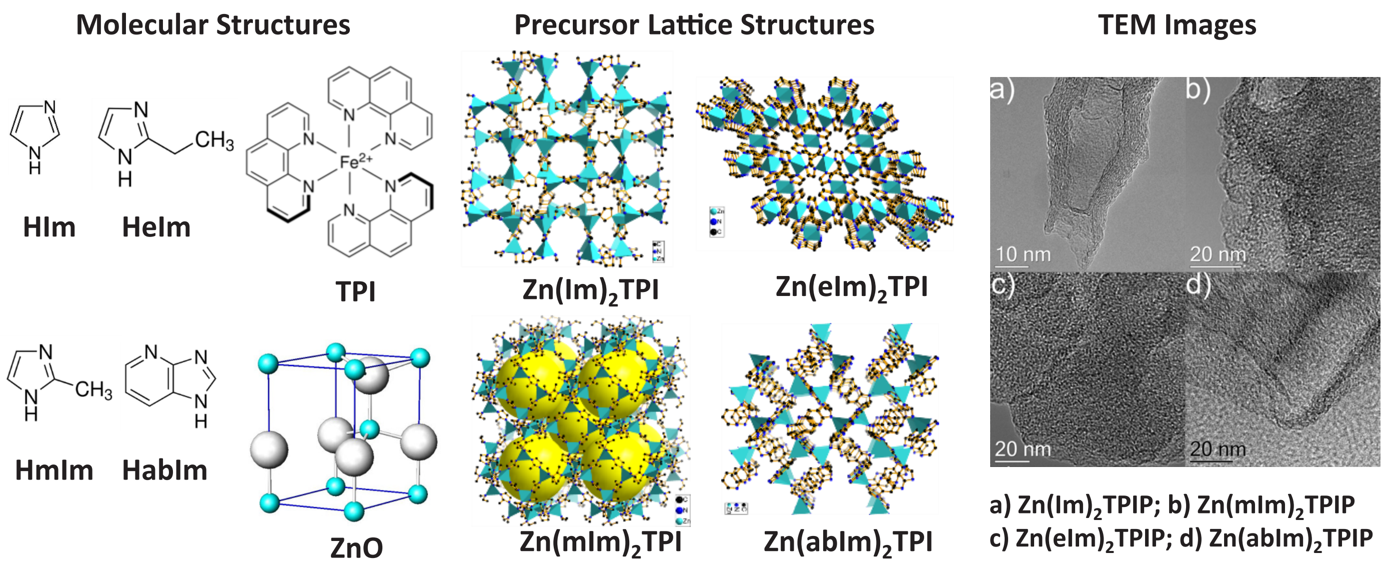

FIGURE 1. Left – molecular structure of four imidazole ligands, ZnO and iron organometallic complex; Center – lattice structures of four corresponding ZIF precursor containing iron complex (not shown); Right – TEM images of thermally activated ZIF catalysts.

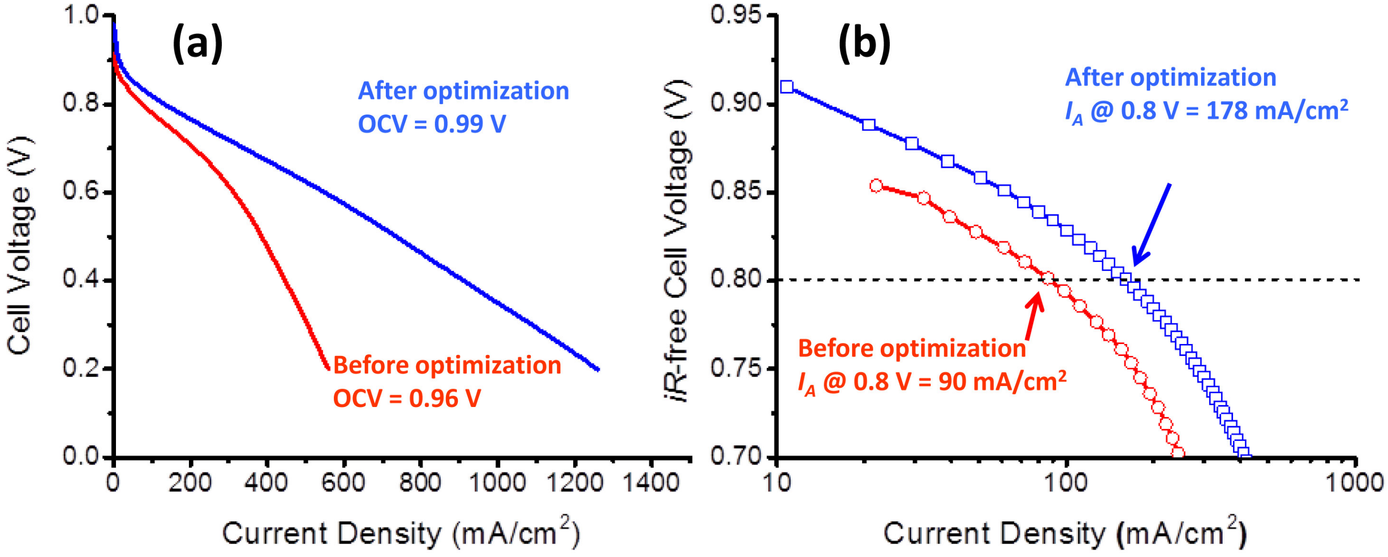

FIGURE 2. (a) Current-voltage polarizations and (b) Tafel plots of iR-free cell potential versus areal current density of MEAs/single fuel cells containing a ZIF-based non-PGM catalyst before and after post-treatment optimization. Condition: $P_{O2} = P_{H2}$ = 1 bar (back pressure = 7.3 psig) fully 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.

of a single fuel cell containing a $Zn(mIm)_2TPI$ catalyst before and after the post-treatment optimization. Significant improvement in fuel cell performance was observed, with open-circuit potential increased from 0.96 V to 0.99 V and current density (@ 0.8 V) increased from 90 mA/cm^2 to 178 mA/cm^2, all under one bar oxygen pressure. These values are among the highest reported in the literature.

We also successfully improved formulation and parameters in processing the nanofibrous network electrode. The nano-network was prepared from a polymeric mixture containing catalyst precursor and fiber-forming reagents. Optimizing these ingredients is essential for the overall catalytic activity while maintaining good electronic conductivity and oxygen/water mass transports. We formulated multiple mixtures and obtained several catalysts

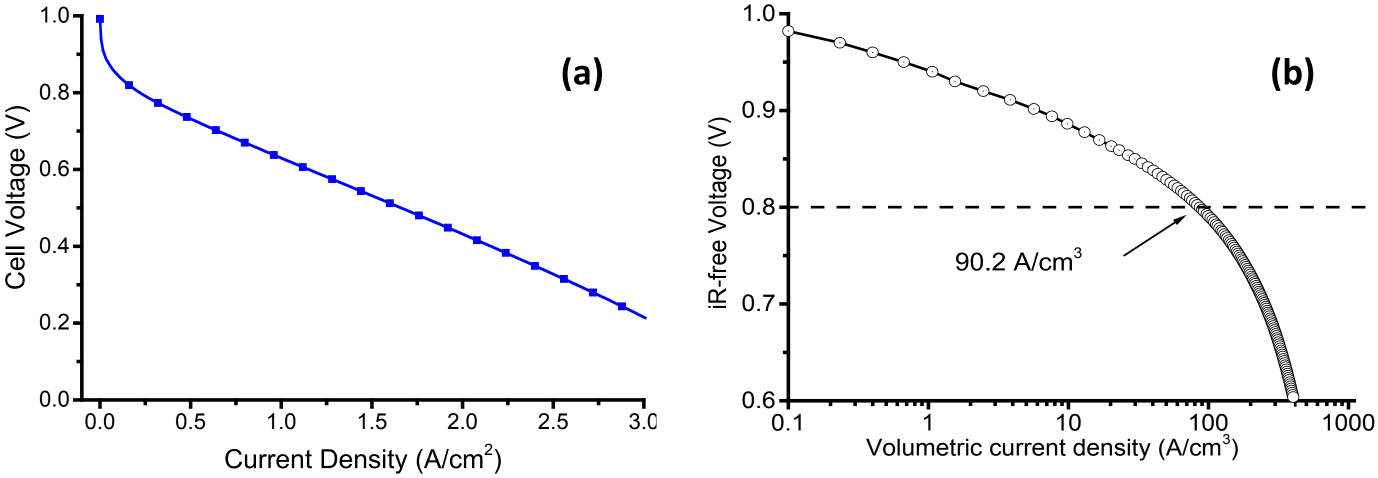

FIGURE 3. (a) Current-voltage polarization and (b) Tafel plot of iR-free cell potential versus volumetric current density of a MEA prepared with non-PGM nano-network cathode. Condition: $P_{O2} = P_{H2} = 2$ bar; fully humidified at 80ºC, cathode loading = 3.0 mg/cm^2, anode loading = 0.3 mg$_{Pt}$/cm^2, Nafion® = 211, active area = 5 cm^2; (b) iR-corrected volumetric current density under similar condition as (a) except Nafion® = 117, cathode catalyst loading = 2 mg/cm^2.

with excellent activity. These nanostructured catalysts were also integrated into the cathode layer of MEAs and tested by single fuel cells. Figure 3a shows an optimized current-voltage polarization obtained from a fuel cell test. Very high current density up to 3 A/cm^2 at 0.2 V was achieved where no flooding was observed. Figure 3b shows a Tafel plot of iR-corrected cell potential as the function of the volumetric current density in a separate MEA test under 2 bar oxygen pressure. A value of 90.2 A/cm^3 was obtained at 0.8 V.

CONCLUSIONS AND FUTURE DIRECTIONS

This one-year project is concluded with the following major accomplishments:

- A low-cost, "one-pot" synthesis method produced multiple ZIF-based catalysts with $E_0 > 0.9$ V and $E_{1/2}$ as high as 0.81 V, measured by RDE in O_2-saturated acidic electrolyte.
- A comprehensive characterization of the ZIF-derived catalysts demonstrated the good correlations between the precursor/catalyst surface structures and the performance.
- Process optimizations led to an improved non-PGM cathode performance achieving areal current density of 178 mA/cm^2 at 0.8 V under one bar O_2 pressure.
- Formulation improvement over the original ANL's ZIF/nano-network catalyst yielded a cathode volumetric current density of 90 A/cm^3 (@ 0.8 V, $P_{O2} = 2$ bar).

The approach of ZIF-derived nano-network electrode opens up new directions for further non-PGM fuel cell performance improvement, including:

- Better active site conversion and preservation through controlled process conditions.
- Higher catalytic activity through new organic ligand and organometallic additive designs.
- Higher overall electrode performance through nano-network morphological and composition optimization.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. "Highly Efficient Non-Precious Metal Electrocatalysts Prepared from One-Pot Synthesized Zeolitic Imidazolate Frameworks (ZIFs)" Dan Zhao, Jiang-Lan Shui, Lauren R. Grabstanowicz, Chen Chen, Sean M. Commet, Tao Xu, Jun Lu, and Di-Jia Liu, *Advanced Materials*, 2014, *26*, 1093–1097 DOI: 10.1002/adma.201304238. (Frontpiece article)

2. "Highly-Active and "Support-free" Oxygen Reduction Catalyst Prepared from Ultrahigh Surface Area Porous Polyporphyrin" Shengwen Yuan, Jiang-Lan Shui, Lauren Grabstanowicz, Chen Chen, Sean Commet, Briana Reprogle, Tao Xu, Luping Yu and Di-Jia Liu, *Angew. Chem. Int. Ed.,* 2013, 52(32), 8349–8353 DOI: 10.1002/anie.201302924.

3. "New Approach to High-Efficiency Non-PGM Catalysts Using Rationally Designed Porous Organic Polymers" S. Yuan, G. Goenaga, L. Grabstanowicz, J. Shui, C. Chen, S. Commet, B. Reprogle and D.-J. Liu, ECS Transaction, 2013 58(1): 1671-1680.

4. "Non-PGM Cathode Catalysts using ZIF-based Precursors with Nanonetwork Architecture", Di-Jia Liu, Dan Zhao, Jianglan Shui, Lauren Grabstanowicz, Sean Commet, Poster presentation at 2014 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 16–20, 2014.

5. "New Approach to High-Efficiency Non-PGM Catalysts Using Rationally Designed Porous Organic Polymers", Shengwen Yuan, Jianglan Shui, Lauren Grabstanowicz, Chen Chen, Sean Commet, Briana Reprogle and Di-Jia Liu, Oral Presentation at 224nd Electrochemical Society Meeting, San Francisco, Oct 27 – Nov. 1, 2013.

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