

# ElectroCat: Advanced Platinum-Group-Metal-Free Cathode Engineering for High Power Density and Durability

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#### Subcontractors:

- University at Buffalo, Buffalo, NY
- Giner, Inc., Auburndale, MA
- 3M Company (3M), St. Paul, MN

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Project End Date: August 31, 2020

## Overall Objectives

- Enable high, durable power density with new cathode designs specifically for platinum group metal (PGM)-free catalysts.
- Increase PGM-free catalyst activity and stability through synthesis using a simplified, low-cost method.
- Improve PGM-free mass activity through optimization of the ionomer integration.
- Mitigate PGM-free cathode flooding for fast oxygen transport across thick electrodes.

## Fiscal Year (FY) 2018 Objectives

- Establish the synthesis of Fe-doped metal organic framework (MOF)-derived catalysts with high activity and stability.
- Establish cathode and membrane electrode assembly (MEA) fabrication processes for Fe-doped MOF-derived catalysts.

- Optimize the baseline catalyst ink preparation and deposition methods for preparing MEAs.
- Implement a computational model to guide the development of future catalysts and MEAs.

## 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<sup>1</sup>:

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

## Technical Targets

**Table 1. Progress Toward Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications**

Characteristic	Units	DOE 2025 Target	Project Status
PGM-free catalyst activity <sup>a</sup>	$V_{\text{HFR-free}}$ at 0.044 A/cm <sup>2</sup>	>0.9	0.89

<sup>a</sup> Measured in MEA at 80 °C with 1 atm O<sub>2</sub> partial pressure

## FY 2018 Accomplishments

- Synthesized high-activity Fe-doped MOF catalyst tested in rotating disk electrode (RDE), showing half-wave potentials >0.85 V. The stability of these catalysts also is promising, exhibiting a 20 mV half-wave potential loss after 30,000 cycles in RDE.
- Demonstrated an alternative precursor synthesis using water instead of methanol, providing an even lower-cost and environmentally friendly approach. Catalysts produced by this method also exhibited high activity.

<sup>1</sup> <https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Demonstrated a method to control catalyst primary particle size with a high resolution without influencing the iron content.
- Discovered the influence of primary particle size on the quality of ionomer integration with the catalyst using nanoscale resolution X-ray computed tomography.
- Optimized the ionomer integration and particle size for baseline MEA performance.
- Achieved a high MEA current density of  $28.5 \text{ mA/cm}^2$  at  $0.9 \text{ V}_{\text{HFR-free}}$  when operating on  $\text{O}_2$  at  $80^\circ\text{C}$  with 1 atm  $\text{O}_2$  partial pressure.
- Demonstrated a high PGM-free power density for  $80^\circ\text{C}$ , 1 atm air operation. A power density of  $268 \text{ mW/cm}^2$  at  $0.7 \text{ V}$  was achieved.
- Implemented a computational-MEA-model-based roadmap to higher MEA power density that accurately reflects catalyst property and cathode design parameters.

## INTRODUCTION

PGM-free cathodes have the potential to dramatically transform polymer electrolyte fuel cell (PEFC) commercialization, as their production cost could be 1/10 to 1/100 of those using costly Pt-based catalysts. Unfortunately, PGM-free catalysts and cathodes face two distinct barriers to meeting those targets: (1) PGM-free catalysts typically do not have sufficient activity and stability to replace Pt in most commercial applications; and (2) liquid water flooding and large oxygen and proton transport losses prevent PGM-free cathodes from achieving adequate power density. These losses arise because the lower volumetric cathode activity requires increased thickness of these typically hydrophilic cathode layers. Overcoming those two barriers and ultimately meeting the challenging performance targets requires a comprehensive research and development effort on new PGM-free cathodes. In this project, we are developing catalysts and MEAs for high power density and durability. With a focus on high power density, we concentrate our efforts on PGM-free catalysts that feature iron or cobalt active sites (e.g., FeN<sub>4</sub> active sites) because, to date, they have demonstrated the highest activity and provide adequate currents to facilitate the design and optimization of cathode structures for PGM-free catalysts.

## APPROACH

Overcoming those two barriers to PGM-free cathode catalysts and ultimately meeting the challenging performance targets requires a comprehensive research and development effort on new PGM-free cathodes. In this project, we combine three novel and promising approaches, described below.

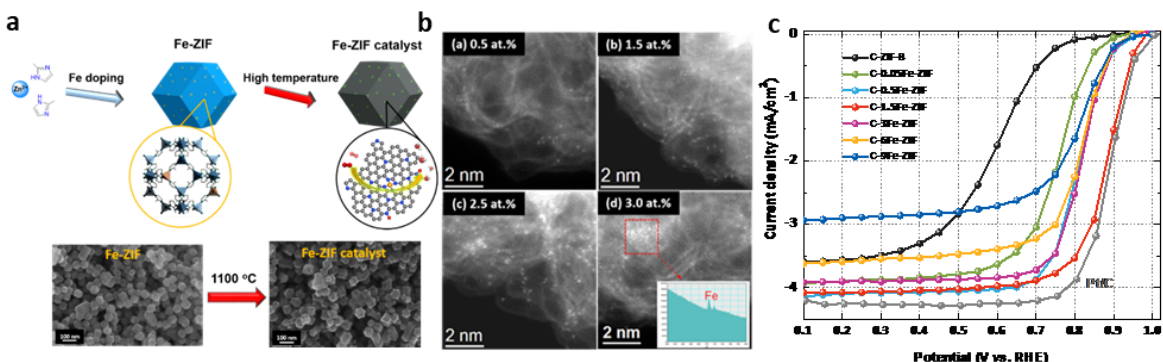
1. Advanced MOF-derived M-N-C catalysts with high activity and an impressive durability at 0.7 V in fuel cell tests. They feature a streamlined, low-cost synthesis of atomically dispersed active sites at high spatial density.
2. PGM-free specific cathode architectures that address the substantial flooding and transport resistances in thicker catalyst layers by introducing engineered hydrophobicity through additives, coatings, and support layers.
3. Advanced ionomers with high proton conductivity for low ohmic losses across the electrode and more uniform catalyst utilization for better durability. For maximum performance, the development of these strategies and materials will be combined with advanced characterization and modeling.

## RESULTS

The team members at the University at Buffalo have developed a new approach to producing highly active Fe-N-C catalysts with uniform morphology and controlled composition via chemical doping of Fe into Zn-zeolitic imidazolate framework (ZIF) precursors that require only one thermal activation step (Figure 1a). The Fe ions added during the ZIF formation were able to chemically dope into the well-defined Zn-ZIF crystals to replace Zn as metal nodes by bridging N-containing ligands, 2-methylimidazole. With only a one-step high-temperature treatment, atomically dispersed Fe catalysts that retain rhombic dodecahedron morphology of individual particles can be obtained with high oxygen reduction reaction (ORR) performance. We have discovered that the Fe content and particle sizes of the catalysts govern the ORR activity of such atomically dispersed Fe catalysts. Because the morphology and porous structure of Fe-ZIF precursors can be directly transferred into the Fe-ZIF catalysts, we are able to tune and correlate the composition and structure of Fe-ZIF precursor to tune their ORR activity.

The ORR activity of Fe-ZIF catalysts in a rotating-ring disk electrode system was investigated as a function of the precursors' Fe content, ranging from 0.05 at% to 9 at% (Figure 1c). The C-xFe-ZIF denotes the nominal Fe atomic percent in the total metal (Fe and Zn) in the synthesis of Fe-ZIF precursors. The ORR activity of these catalysts significantly improved, with an increase of Fe from 0.05 at% to 1.5 at%. The best performing Fe catalysts (C-1.5Fe-ZIF) exhibited a half-wave potential ( $E_{1/2}$ ) of 0.86 V (versus reversible hydrogen electrode), which is achieved by the abundant atomically dispersed Fe-N-C active sites seen in high-angle annular dark field-scanning transmission electron microscope images (Figure 1b). A further increase in Fe content (>1.5

at%) resulted in the gradual decrease of ORR activity. Because Fe atoms tend to aggregate starting from 2.5 at%, the drop in ORR activity for higher Fe content can be attributed to the formation of Fe metallic species.



**Figure 1.** Schematic illustration of the Fe-N-C catalyst synthesis by Fe doping into the formation of Zn-ZIF with a subsequent high temperature treatment (a, top); the scanning electron microscopy (SEM) images of the Fe-N-C catalysts (a, bottom right) derived from Fe-ZIF precursors (a, bottom left); high-angle annular dark field–scanning transmission electron microscope images of atomically dispersed Fe sites in Fe-ZIF catalysts as a function of iron (b); the RDE-measured ORR activity of Fe-ZIF catalysts as a function of iron content (c).

To further enhance the ORR performance of this catalyst, we reduce the internal transport length scales to Fe-N-C active sites by reducing the size of the primary catalyst particles. The University at Buffalo successfully obtained the different size particles—from 1  $\mu\text{m}$  to 80 nm—in catalysts by simply adjusting the reactant concentrations (Figure 2). When the catalyst particle size was submicron (e.g., 1  $\mu\text{m}$ , 200 nm), the ORR performance was insufficient, presumably due to the difficult utilization of active sites inside particles. The catalyst particle size also was carefully tuned in a smaller range (80 nm to 20 nm). For example, the individual particle size of the C-1.5Fe-ZIF catalyst was observed to be approximately 80 nm (Figure 2c). Figure 2f shows the ORR activity of catalysts as a function of their particle size, with the identical Fe content. When the size of particles in the catalyst was reduced to 50 nm, the  $E_{1/2}$  of catalysts (50 nm–C-1.5Fe-ZIF) positively shifted to 0.88 V (versus reversible hydrogen electrode) with 1.5  $\text{mA}/\text{cm}^2$  at 0.9  $V_{\text{IR-free}}$ . However, with a further reduction of particle size to 20 nm, a decrease in the  $E_{1/2}$  to 0.82 V was observed, suggesting a lower number of Fe-N-C active sites in the catalyst. This is possibly explained by the aggregation of particles in 20 nm–C-1.5Fe-ZIF (Figure 4e and inset) compared to the more isolated particles with the 50 nm catalyst (Figure 4d and inset), which may have diminished the number of accessible active sites for ORR. We further evaluated the stability of the best-performing catalysts (50 nm–C-1.5Fe-ZIF). The stability of the catalyst (Figure 2g) was tested by cycling from 0.6 V to 1.0 V in  $\text{O}_2$ -saturated  $\text{H}_2\text{SO}_4$  for 40,000 cycles at a scan rate of 50 mV/s. Half-wave voltage losses of 26 mV were observed after 30,000 cycles, revealing this catalyst exhibits good ORR stability in the rotating-ring disk electrode measurement.

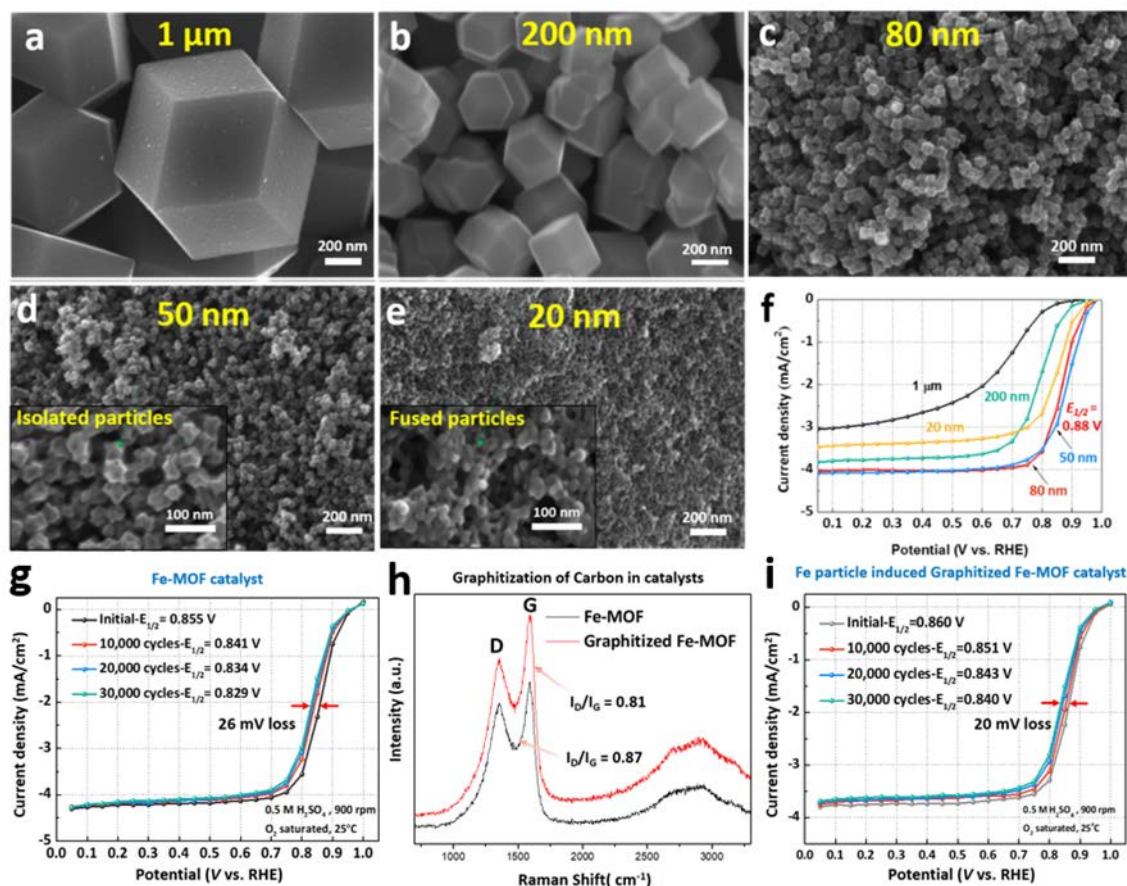
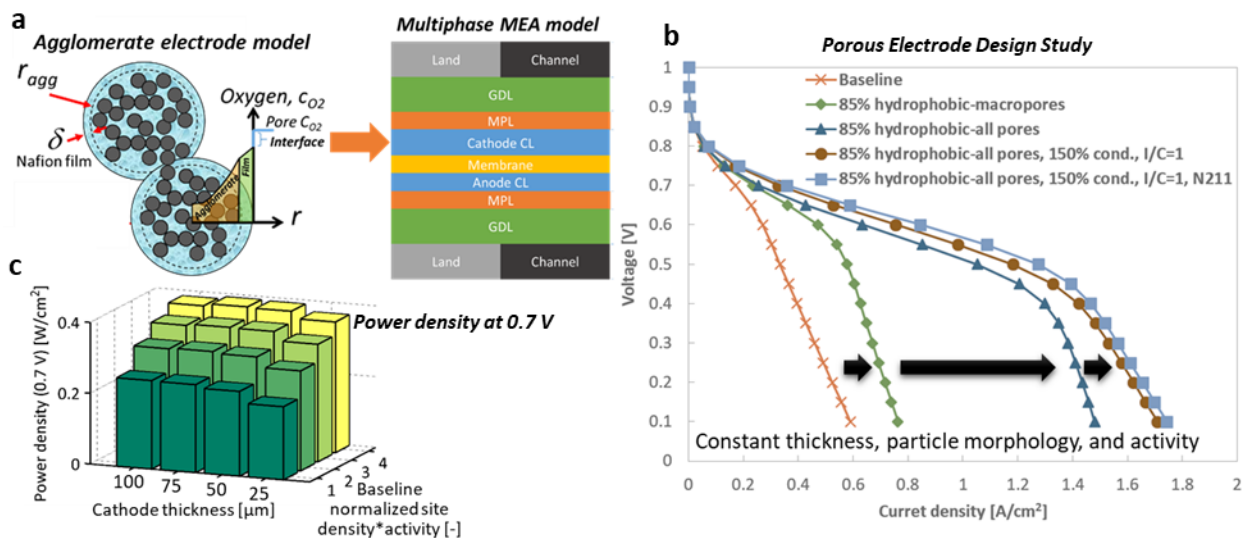


Figure 2. The SEM images of C-1.5Fe-ZIF catalysts in 1  $\mu\text{m}$  (a), 200 nm (b), 80 nm (c), 50 nm in isolated particles (d and inset), and 20 nm in fused particles (e and inset); the ORR activity of Fe-N-C catalysts derived from MOFs as a function of particle size (f); the cycling stability test of Fe-N-C catalyst (g) and graphitized Fe-N-C catalyst (i); Raman spectra of catalysts without or with improved graphitization (h).

To achieve better long-time stability of PGM-free catalysts, we increase the corrosion resistance of the carbon in Fe-N-C catalysts by increasing crystallinity/graphitization of carbon during high-temperature treatment. In the Raman spectra (Figure 2h), the increased graphitization of carbon was observed as the decreased ratio of the intensity of the D band (disordered carbon bonds) to G band (ordered carbon bonds) for the graphitized catalyst (graphitized Fe-MOF:  $I_D/I_G = 0.81$ ) compared to the one without any increased graphitization (Fe-MOF:  $I_D/I_G = 0.87$ ). The Fe-N-C catalysts with improved graphitization (graphitized-Fe-MOF) exhibited a better stability with a half-wave potential loss of only 20 mV after 30,000 cycles. The enhanced stability of the Fe-N-C catalyst is attributed to the increased regularity of carbon structure reducing the rate of oxidation of surface carbon atoms in the catalyst, which leads to the enhanced stability of Fe-N-C catalysts under long-time cycling.

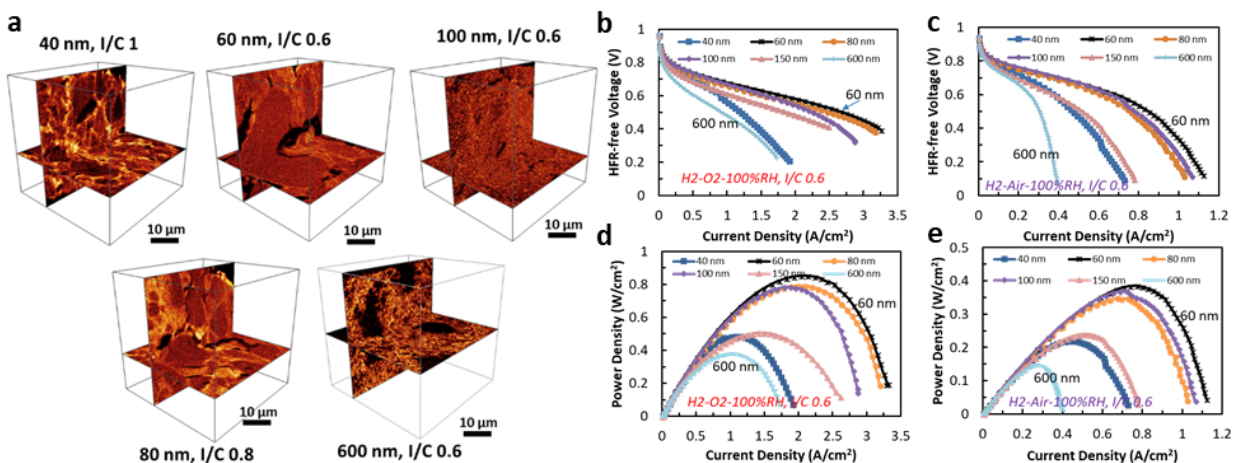
A significant focus of the project is integrating PGM-free catalysts into high-power-density PEFC cathodes. Carnegie Mellon University (CMU) uses a model-based roadmap to higher power density that translates catalyst active site density, primary particle structure, and electrode composition and morphology to the resulting MEA power density, thus giving insights into the leading voltage-loss mechanisms and areas of potential improvement. This also provides a means to generate actionable targets for the catalyst synthesis, including active site density and particle size. As Figure 3a illustrates, this approach uses a combination of a microstructurally consistent cathode model with inputs from multi-modal imaging and a multi-phase computational PEFC model. The model was implemented for the particular structure of the Fe-doped MOF-

derived catalysts, and a baseline model of the initial MEAs prepared at CMU was validated. Figure 3b shows the polarization curve predictions of the model, including the baseline case. The porous electrode design study showed that key changes leading to higher performance are to increase the ionomer effective conductivity and increase the hydrophobicity of the electrode. Both can be achieved by improved ionomer integration within the cathode. Greater conductivity also can be achieved by alternative ionomers with lower equivalent weight. Additionally, greater hydrophobicity can be achieved by using hydrophobic additives and coatings. As shown in Figure 3c, CMU used the model to evaluate the optimal loading of an optimized baseline cathode based on power density at 0.7 V as function of normalized active site density. That study showed a power density of  $>400$  mW/cm<sup>2</sup> can be achieved with a 50- $\mu$ m-thick cathode if the active site density is increased by a factor of four times.



**Figure 3.** Multi-phase PEFC model with a microstructurally consistent cathode model (a). Polarization curves from a porous electrode density study to identify methods of increasing performance over the experimentally validated baseline case (b). Predicted power density at 0.7 V as a function of normalized active site density and cathode thickness (c).

An experimental study was performed on the integration of ionomers in the cathodes by preparing and testing MEAs at CMU with varying catalyst primary particles sizes synthesized at University at Buffalo, and by varying the ionomer-to-carbon ratio. In addition to MEA testing in PEFC hardware, we performed nanoscale X-ray computed tomography (nano-CT) imaging of the cathodes in the CMU facility. This includes 3-D imaging of the ionomer distribution by absorption contrast imaging of cesium ion-exchanged ionomer. Figure 4 shows the ionomer distribution in cathodes with various particle sizes. With 40 nm catalyst, the interior of the large catalyst aggregates ( $>5$   $\mu$ m) is mostly free of ionomer, whereas the 60–100 nm catalysts show better ionomer infiltration. In the case of the 600 nm catalyst, a thick ionomer film formed around the large primary particles because of the reduced surface area available for coating.



**Figure 4.** Nano-CT imaging of the ionomer distribution in cathodes of an Fe-MOF catalyst with different primary particle sizes (a). Polarization curves (b, c) and power density curves (d, e) obtained with air and O<sub>2</sub> for MEAs prepared from Fe-doped MOF-derived catalyst with different primary particle sizes. Conditions: catalyst loading: 4 mg/cm<sup>2</sup>; cell temperature: 80 °C; flow rate H<sub>2</sub>/air or O<sub>2</sub>: 200/200 sccm, relative humidity: 100%, 1 bar H<sub>2</sub>/air or O<sub>2</sub> partial pressure, Nafion 212 membrane.

Figure 4b, 4c, and 4d show the polarization and power density curves obtained under O<sub>2</sub> and air using catalysts with different primary particle sizes with an ionomer-to-carbon ratio of 0.6. The highest activity and best mass transport were achieved using the 60 nm catalyst. With this catalyst, the current density with 1 atm O<sub>2</sub> at a fuel cell voltage of 0.9 V (high-frequency resistance corrected) was 9 mA/cm<sup>2</sup>, and the power density with 1 atm at a fuel cell voltage of 0.7 V was 228 mW/cm<sup>2</sup>. The cell performance with 80 nm and 100 nm catalysts was close to the 60 nm catalyst. A more repeatable MEA performance was achieved with 100 nm catalyst. The PEFC with the 40 nm catalyst performed badly due to the poor ionomer integration, as shown in the nano-CT images. The MEA with a 600 nm catalyst had the lowest apparent activity and lowest maximum current density, possibly due to low surface area; fewer active sites; and thicker, more hydrophilic ionomer films that led to severe flooding. The best FY 2018 performance on 1 atm O<sub>2</sub> achieved was 28.5 mA/cm<sup>2</sup> at 0.9 V<sub>HFR-free</sub> at a cell temperature of 80°C. On 1 atm air, the best current density achieved at 0.8 V was 113 mA/cm<sup>2</sup>, and the highest power density achieved at 0.7 V was 268 mW/cm<sup>2</sup> (383 mA/cm<sup>2</sup>) using 100 nm catalyst and an ionomer-to-carbon ratio of 0.8.

## CONCLUSIONS AND UPCOMING ACTIVITIES

To date, this project has shown that high activity and stability can be achieved with Fe-doped MOF-derived catalysts. Through integrated catalyst development and MEA design and testing, we discovered the tight connection between particle morphology, ionomer integration, and MEA performance. Through model and imaging guided optimization we have achieved a high power density at PEFC application-relevant voltages. Going forward, the project focus will be to further improve the stability and durability of the catalyst through improvements in the precursor synthesis and its heat treatment at University at Buffalo. This research and development will be supported by density functional theory modeling of the active sites at CMU. The MEA development will focus on increasing the hydrophobicity through additives and coatings, as well as with the use of alternative ionomers from 3M for increased conductivity and improved integration with the catalyst. Giner will support the MEA development through scale-up of the best catalysts identified at University at Buffalo and CMU.

## FY 2018 PUBLICATIONS/PRESENTATIONS

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2. Y. He, S. Hwang, D.A. Cullen, M.A. Uddin, L. Langhorst, B. Li, S. Karakalos, A.J. Kropf, E.C. Wegener, J. Sokolowski, M. Chen, D.J. Myers, D. Su, K.L. More, G. Wang, S. Litster, G. Wu, “Highly active atomically dispersed CoN<sub>4</sub> fuel cell cathode catalysts derived from surfactant-assisted MOFs: Carbon-shell confinement strategy.” *Energy and Environmental Science* (2018), doi:10.1039/C8EE02694G.
3. Hanguang Zhang and Gang Wu, “Atomic Iron-Dispersed Electrocatalysts Derived from Metal-Organic Framework for Oxygen Reduction,” AIChE Fall Meeting, Minneapolis, MN, October 29–November 3, 2017.
4. Shawn Litster, “Addressing Transport Losses in Pt-free PEM Fuel Cell Cathodes,” American Chemical Society Spring Meeting, New Orleans, LA, March 20, 2018.
5. Shawn Litster, “Advanced PGM-free Cathode Engineering for High Power Density and Durability,” Presentation at the DOE Hydrogen and Fuel Cells Program Annual Merit Review, Washington, D.C., June 2018.