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

Shawn Litster (Primary Contact), Bahareh Tavakoli, Aman Uddin, Lisa Dunsmore, Diana Beltrán, Leiming Hu, Reeja Jayan, Laisuo Su, Venkat Viswanathan, Hasnain Hafiz
Carnegie Mellon University (CMU)
5000 Forbes Avenue
Pittsburgh, PA 15213
Phone: 412-268-3050
Email: litster@andrew.cmu.edu

DOE Manager: David Peterson
Phone: 240-562-1747
Email: David.Peterson@ee.doe.gov

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- University at Buffalo (UB), Buffalo, NY
- 3M Company (3M), St. Paul, MN

Project Start Date: September 1, 2017
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) 2019 Objectives

- Improve synthesis of Fe-doped metal organic framework (MOF)-derived catalysts for improved stability and durability.
- Evaluate the impact of ionomer on PGM-free membrane electrode assembly (MEA) performance.

- Develop new PGM-free MEA structures with improved water management.
- Establish scaled-up synthesis of the Fe-doped MOF-derived catalyst.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

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

Technical Targets

The DOE technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Synthesized a new, high activity Fe-doped MOF catalyst showing half-wave potentials >0.88 V when tested by rotating disk electrode (RDE).
- Demonstrated greatly improved stability with graphitized and highly graphitized Fe-MOF catalyst. After a 50-hour 0.85-V hold in RDE with O₂, the highly graphitized catalyst only loses 5 mV of half-wave voltage versus 50 mV with the baseline 2018 Fe-MOF catalyst.
- Demonstrated a 0.7 V current density of 430 mA/cm² and power density of 302 mW/cm² at 80°C with 1 atm air partial pressure. The same MEA yielded a high limiting current density of 1.8 A/cm² and a maximum power density of 0.57 W/cm².
- Demonstrated a high maximum power density of 0.61 W/cm² and 0.7 V power density of 0.41 W/cm² at an automotive-relevant

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

- operating point of 94°C with 1.7 atm O₂ partial pressure.
- Demonstrated a 20% increase in limiting current density by microstructuring the cathode catalyst layer with a perforated microporous layer (MPL).
- Identified the importance of ionomer coating hydrophobicity on PGM-free MEA performance.
- Performed density functional theory studies of Fe-N-C active sites and oxygen reduction reaction (ORR) to generate a Pourbaix diagram of active site adsorbate state that is combined with activity calculations.
- Evaluated the impact of including cerium oxide radical scavenger in the Fe-MOF cathode on the durability of MEAs.

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 ^a	V _{HFR-free} at 0.044 A/cm ²	>0.9	0.89

^aMeasured in MEA at 80°C with 1 atm O₂ partial pressure

INTRODUCTION

PGM-free cathodes have the potential to dramatically transform polymer electrolyte fuel cell 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) the 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., FeN₄ active sites) because, as 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:

- Advanced MOF-derived M-N-C catalysts with high activity and 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.
- 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.
- 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 UB 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 ORR performance.

In FY 2019, the UB team made several advancements in the activity and stability of the Fe-MOF catalyst. In terms of activity, the synthesis was adjusted to achieve a high activity with RDE half-wave voltages >0.88 V as shown in Figure 1b (O_2 saturated in 0.5 H_2SO_4 at 900 RPM). In the same year, UB developed a new approach to synthesizing a Fe-MOF based on pre-pyrolysis of ZIF-8 precursor without iron and then adsorbing Fe at nitrogen moieties in the carbon particles. This process had led to a new understanding of the active site's formation temperature dependence, and the active sites can be formed in thermal processes after the prior removal of the zinc. In addition, this approach has led to dramatic increases in ORR activity. As Figure 1c shows, UB's MEA measurements with these catalysts have demonstrated a current density of 30 mA/cm^2 at 0.9 V (no IR correction) at $1\text{ atm } O_2$ partial pressure, 80°C . This activity was achieved using a thinner Nafion 212 membrane and loading of 4 mg/cm^2 , which is notably lower than that typically used to demonstrate MEA activity and evidences the high mass activity of this catalyst.

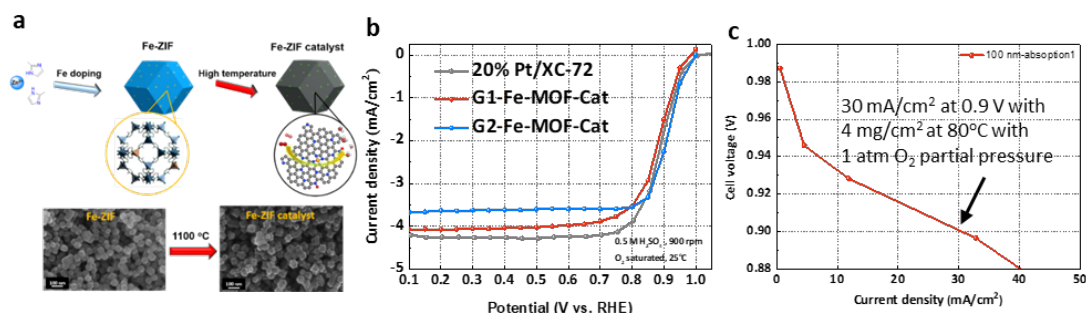


Figure 1. (a) Schematic illustration of the Fe-N-C catalyst synthesis by Fe doping into the formation of Zn-ZIF with a subsequent high temperature treatment (top); the scanning electron microscopy (SEM) images of the Fe-N-C catalysts (bottom right) derived from Fe-MOF precursors (bottom left). (b) The measured ORR RDE activity of two generations of Fe-MOF catalysts and comparison to Pt/C catalyst. (c) Fe-MOF catalyst activity evaluated by MEA polarization curve at 80°C with $1\text{ atm } O_2$ partial pressure.

In terms of catalyst stability, the UB team has established a method to produce a highly graphitized Fe-MOF. Using this catalyst, the RDE half-voltage loss after 50 hours of 0.85 V was reduced to 5 mV versus 20 mV with the first-generation graphitized catalyst in FY 2018. A further, more aggressive test for carbon corrosion stability was performed by cycling the RDE potential between 1 and 1.5 V in nitrogen-saturated electrolyte. The highly graphitized Fe-MOF catalyst exhibited zero half-wave voltage loss while the FY 2018 baseline catalyst exhibited a 70 mV half-wave voltage loss during this test (see Figure 2).

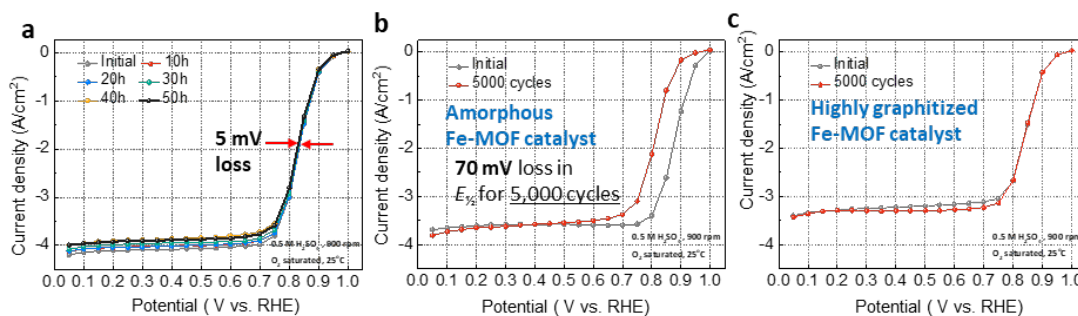


Figure 2. (a) The RDE-measured ORR activity of highly graphitized Fe-MOF catalyst as a function of voltage hold time at 0.85 V in O_2 saturated electrolyte. (b, c) Comparison of RDE activity loss between FY2018 baseline amorphous catalyst and highly graphitized catalyst after 5,000 cycles between 1.0 and 1.5 V in nitrogen-saturated electrolyte (b,c).

The team at CMU has continued to advance MEA performance through a wide range of studies in FY 2019. These studies include an evaluation of ionomer equivalent weight (EW) and type, oxygen resistance analysis by experiment and modeling, and cathode microstructuring. Based on power density, the best performing MEA to date at 80°C with 1 atm air partial pressure exhibited a 0.8 V current density of 110 mA/cm², a 0.7 V power density of 0.30 W/cm², a maximum power density of 0.57 W/cm², and a high limiting current density of 1.8 A/cm². By increasing the operating temperature and air partial pressure to 94°C and 1.7 atm, the 0.7 V and maximum power density increased to 0.41 W/cm² and 0.60 W/cm², respectively (see Figure 3a).

Working with 3M, the CMU group performed combined RDE and MEA studies evaluating the effect of ionomer on PGM-free cathode performance by evaluating performance over a range of ionomer equivalent weights (EW 725–1,200) and ionomer types (3M PFSA vs. Nafion). A key motivation of varying the ionomer is to increase the proton conductivity of the cathode to improve the catalyst effectiveness across its thickness. A key finding from this work was the sensitivity of the cathode performance to the hydrophilicity of the ionomer films. In general, as Figure 3b shows, higher 80°C air MEA performance at 100% RH was achieved using more hydrophobic ionomers with higher EW with a greater proportion of hydrophobic fluoropolymer backbone.

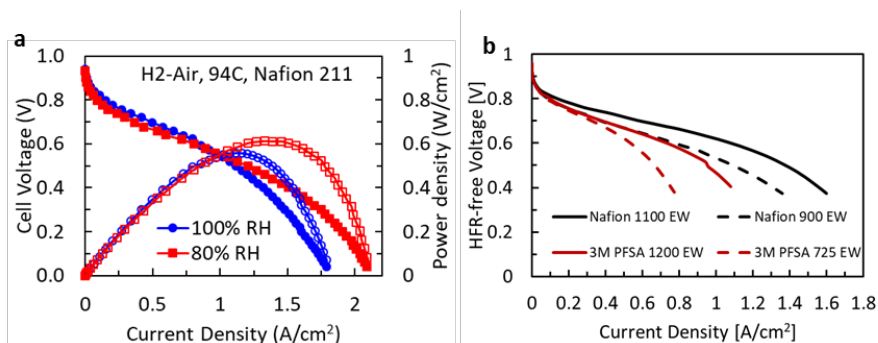


Figure 3. (a) Fuel cell polarization curves for operation on air at 94 °C with 1.7 atm air partial pressure for 80% and 100% gas relative humidity. (b) Fuel cell polarization curves for operation on air at 80 °C with 1.0 atm air partial pressure and 100% gas relative humidity for variations in ionomer EW and type.

To improve water management, the CMU team developed a method to prepare gas diffusion electrodes (GDEs) with 3D microstructured catalyst layers by coating the PGM-free catalyst slurry onto laser-perforated MPLs. As Figure 4a shows, the intrusion of the catalyst layer through the MPL provides a low capillary pressure barrier to reject water from the catalyst layer while still maintaining continuous contact between the catalyst layer and the MPL. Using this approach, a 20% increase in limiting current density was achieved for air operation (see Figure 4b), with a continuous trend of increased maximum power density with closer spacing of the 150-μm diameter perforations.

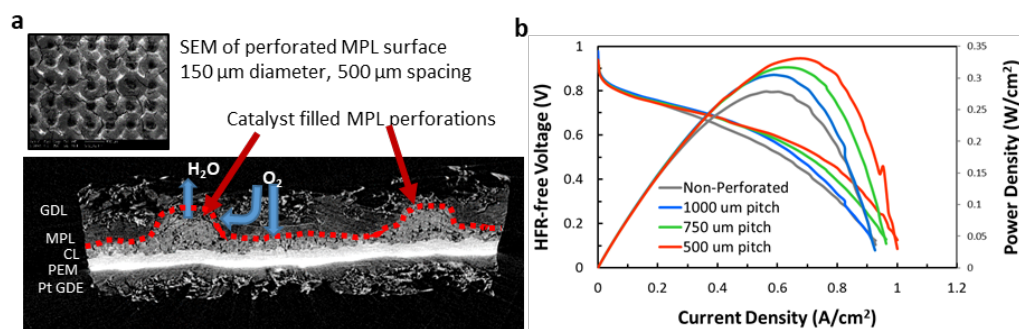


Figure 4. (a) SEM image of the laser perforated MPL before catalyst layer application (top left) and micro-computed tomography virtual slice showing the intrusion of the catalyst layer into the perforated MPL (bottom). (b) Fuel cell polarization and power density curves for operation on air at 80 °C with 1.0 atm air partial pressure and 100% gas relative humidity for variations in the pitch distance between perforations.

MEA durability tests have been performed at CMU using the FY 2018 baseline catalyst with and without the addition of cerium oxide radical scavenger. A key finding is the durability of the MEA performance can be separated into reversible and irreversible components (see Figure 5a), where it is suggested that the fast time-scale reversible component is an active site poisoning and the long time-scale loss of activity is attributed to carbon corrosion. Through 0.7 V holds in 1 atm partial pressure air with cathodes of varying loading, we identified that the long time-scale degradation rate scaled as 0.3 mA/mg/h with the FY 2018 baseline catalyst. In the experiments with cerium oxide added, no significant change in durability was observed at cell voltages above 0.6 V. However, the addition of cerium oxide significantly reduced the degradation of the high-current-density performance (see Figure 5b and 5c).

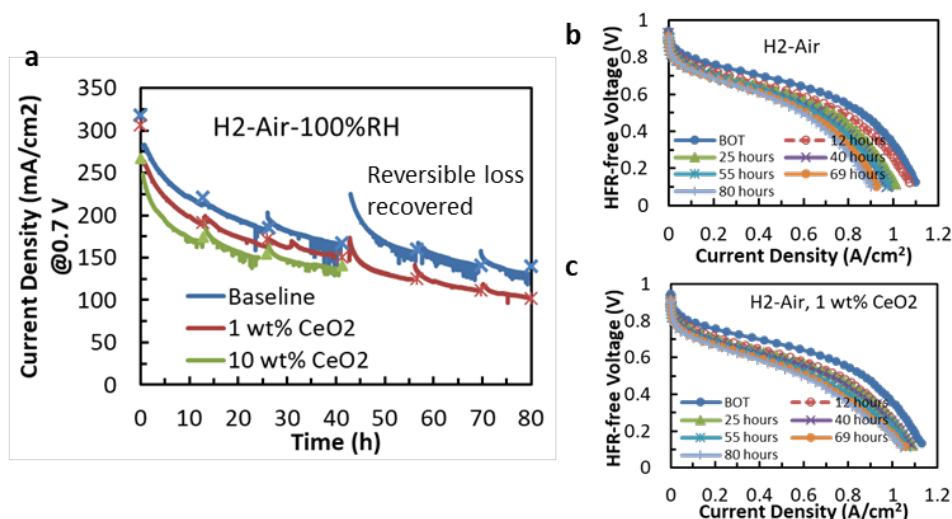


Figure 5. (a) Current density time series during 0.7 V holds at 80°C with 1.0 atm air partial pressure and 100% gas relative humidity for baseline cathode without cerium oxide and two levels of cerium oxide loading. A large recovery was obtained at 40 hours with the baseline electrode following an 8 day disconnection from the test stand. (b, c) Comparison of polarization curves taken at points in time during the 80-hour voltage holds for no cerium oxide and 1 wt % cerium oxide added to the cathode.

The Giner team has adopted UB's catalyst synthesis method and developed the ability to synthesize significantly larger batches of catalyst to support MEA development activities that require large amounts of catalyst. Key to this activity was scaling from the 1-L reactor vessel for precursor synthesis to a 20-L vessel at Giner. With this reactor, 10 g of precursor, or 2 g of catalyst, can be synthesized in one batch. Giner's activities included modifying several of the precursor synthesis procedures for MOF production in the larger vessel. Testing at Giner and CMU has shown the best scaled-up Giner catalyst is approaching the UB baseline catalyst's FY 2018 performance (320 mA/cm² vs. 380 mA/cm² at 0.7 V at 80°C with 1 atm air partial pressure).

CONCLUSIONS AND UPCOMING ACTIVITIES

To date this project has shown that high activity and stability can be achieved with Fe-doped MOF-derived catalysts. The new advancements in catalyst activity and stability are encouraging to addressing the challenges of PGM-free polymer electrolyte fuel cell cathodes in the future. Catalyst studies have shown that control of the catalyst carbon structure can greatly enhance stability. MEA performance studies have shown how the modification of the cathode structure and the wettability of the cathode can greatly influence the power density and the severity of liquid water flooding in thick electrodes. Likewise, MEA durability studies have shown the significant degradation rate of the baseline catalyst, but they also show that some of that loss is reversible and some of the irreversible loss can be mitigated with additives like cerium oxide. Going forward into FY 2020, the project activities will continue to focus on increasing catalyst activity and stability and improving MEA performance and durability. A key aspect of the MEA work will be to control and modify the wettability of the cathode for greater hydrophobicity when using high-conductivity, low-EW ionomers. These activities will be supported by the scaled-up synthesis of high-performance Fe-MOF catalyst.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. 2019 Annual Merit Review Award for Fuel Cell Research and Development, Shawn Litster.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. D. Beltrán and S. Litster, “Half-Wave Potential or Mass Activity? Characterizing Platinum Group Metal-Free Fuel Cell Catalysts by Rotating Disk Electrodes,” *ACS Energy Letters* 4 (2019): 1158–1161.
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. Myers, D. Su, K.L. More, G. Wang, S. Litster, and G. Wu, “Highly Active Atomically Dispersed CoN₄ Fuel Cell Cathode Catalysts Derived from Surfactant-Assisted MOFs: Carbon-Shell Confinement Strategy,” *Energy and Environmental Science* 12 (2019): 250–260.
3. X.X. Wang, V. Prabhakaran, Y. He, Y. Shao, and G. Wu, “Iron-Free Cathode Catalysts for Proton Exchange Membrane Fuel Cells: Cobalt Catalysts and Peroxide Mitigation Approach,” *Advanced Materials* 31, no. 31 (2019): 1805126
4. H. Zhang, H.T. Chung, D.A. Cullen, S. Wagner, U.I. Kramm, K.L. More, P. Zelenay, and G. Wu, “High-Performance Fuel Cell Cathodes Exclusively Containing Atomically Dispersed Iron Active Sites,” *Energy and Environmental Science* 12, no. 8 (2019): 2548–2558.
5. X.X. Wang, M.T. Swihart, and G. Wu, “Achievements, Challenges and Perspectives on Cathode Catalysts in Proton Exchange Membrane Fuel Cells for Transportation,” *Nature Catalysis* 2 (2019) 578–589.
6. M. Chen, Y. He, J.S. Spendelow, and G. Wu, “Atomically Dispersed Metal Catalysts for Oxygen Reduction,” *ACS Energy Letters* 4 (2019): 1619–1633.
7. S. Litster, “Advances in Electrode Diagnostics and Design for Low-Cost Pt-Free Fuel Cells and Safer, High Energy Density Li-ion Batteries,” Chemical and Petroleum Engineering Department Seminar, University of Pittsburgh, Pittsburgh, PA (Oct. 19, 2018).
8. M.A. Uddin, L. Langhorst, Y. Guo, H. Zhang, M. Chen, D. Cullen, K. More, H. Xu, G. Wu, and S. Litster, “Development of PEFC Membrane Electrode Assemblies for Iron-doped Metal Organic Framework Catalysts,” Fall Meeting of the Electrochemical Society, Cancun, Mexico (Oct. 1, 2018).
9. S. Litster, “Development of High Power Density Fuel Cells Using Platinum Group Metal-Free Oxygen Reduction Electrocatalysts,” (Keynote) 68th Canadian Chemical Engineering Conference, Toronto, Canada (Oct. 30, 2018).
10. S. Litster, “Addressing Transport Losses in Low-Pt and Pt-Free PEM Fuel Cell Cathodes,” (Invited) 2018 AIChE Annual Meeting, Pittsburgh, PA (Oct. 31, 2018).
11. S. Litster, “Advances in Electrode Diagnostics and Design for Low-Cost Pt-Free Fuel Cells and Safer, High Energy Density Li-ion Batteries,” Chemical and Biological Engineering Department Seminar, Drexel University, Philadelphia, PA (Nov. 30, 2018).
12. S. 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. (May 2019).
13. H. Hafiz and V. Viswanathan, “Characterization of Platinum Group Metal-Free Catalysts Using X-Ray Absorption Spectroscopy,” NAM 26, North American Catalysis Society Meeting, Chicago, IL (June 2019).