
Mesoporous Carbon-Based Platinum-Group-Metal-Free Catalyst Membrane Electrode Assemblies

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Subcontractors:

- University at Buffalo, SUNY, Buffalo, NY 14260
- United Technologies Research Center, East Hartford, CT 06168

Project Start Date: October 1, 2018
Project End Date: December 31, 2020

Overall Objectives

- Design and develop advanced hierarchically porous carbon sphere (HPCS)@M-N-C catalysts for platinum group metal (PGM)-free cathodes in polymer electrolyte membrane fuel cells through controllable synthesis.
- Develop PGM-free catalyst membrane electrode assemblies (MEAs) by engineering the ionomer/catalyst interfaces in cathodes for increased catalyst utilization and power density.

Fiscal Year (FY) 2019 Objectives

- Design and synthesize new types of HPCS@M-N-C catalysts and characterizations (University at Buffalo).
- Functionalize HPCS PGM-free catalysts (IUPUI).
- Develop high-performance MEA HPCS PGM-free catalysts (IUPUI).

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 Plan¹:

- Durability
- Cost
- Performance.

Technical Targets

- Achieve intrinsic high activity ($E_{1/2} > 0.85$ V) and stability (potential loss of $E_{1/2} < 20$ mV after 30,000 potential 0.6–1.0 V cycling in acidic media).
- Demonstrate fuel cell MEAs (25–50 cm²) with a mass activity of 0.044 A/cm² at 0.9 V_{IR-free} (H₂/O₂) and 0.15 A/cm² at 0.8 V (H₂/air).
- Achieve high power density of at least 0.5 W/cm² (e.g., 0.50 V at 1.0 A/cm²) following DOE catalyst performance metrics.
- Achieve sufficient durability performance of MEAs following DOE catalyst durability testing protocols or any other protocols suggested from the ElectroCat Consortium, such as voltage loss <30 mV after 30,000 potential cycles, 0.6–1.0 V in N₂.
- Obtain a fundamental understanding of the structure-property-performance relationship of the novel HPCS@M-N-C PGM-free catalysts and MEAs. The relevant measurement data and publications will be deposited into the ElectroCat database.

FY 2019 Accomplishments

- MEAs made of mesoporous Fe-N-C catalysts synthesized from chemical vapor deposition (CVD) reached 27 mA/cm² at 0.9 V_{IR-free} (H₂/O₂) and backpressure of 150 kPa_{abs} and passed the Year 1 go/no-go decision point (MEA performance: 25 mA/cm² at 0.9 V_{IR-free} using H₂/O₂ at 1.0 bar).
- Mesoporous Fe-N-C catalysts synthesized from CVD reached 0.33 mA/cm² at 0.90 V in rotating disk electrode (RDE) tests and passed

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

the Q2 milestone for catalysts ($E_{1/2} > 0.82$ V and generated 0.25 mA/cm^2 at 0.90 V in RDE tests).

- MEAs made of mesoporous Fe-N-C catalysts synthesized from CVD reached 84 mA/cm^2 at 0.80 V and 224 mW/cm^2 at 0.70 V (H_2/air) with backpressure of $150 \text{ kPa}_{\text{abs}}$ and passed the

Q6 milestone on power density for MEAs (100 mA/cm^2 at 0.80 [air] $V_{\text{IR-free}}$, 150 mW/cm^2 at 0.70 V).

Note: The project started on March 16, 2019, due to paperwork for the contract. As of October 18, 2019, the project is in the third quarter.

INTRODUCTION

The objective of this project is to design and develop a new type of mesoporous PGM-free fuel cell cathodes through innovative catalyst synthesis, MEA design and fabrication, and performance evaluation. To fully address the current problems of PGM-free cathodes and ultimately meet the challenging performance targets, a synergetic approach is proposed. This approach combines the structural design of a new type of (1) innovative HPCS PGM-free catalyst and (2) novel ionomer/catalyst interface controls within the cathode layer.

In this period, four different PGM-free catalysts have been synthesized and characterized for their performance on both RDE and MEA. The project team has functionalized these new catalysts. The formulated inks by using these catalysts were characterized in terms of the H^+ conductivity within the catalyst layer. In addition, the team has developed and tested these PGM-free catalyst MEAs. The best PGM-free catalyst MEA achieved 27 mA/cm^2 at $0.9 V_{\text{IR-free}}$ (H_2/O_2) with backpressure of $150 \text{ kPa}_{\text{abs}}$, which passed the Year 1 go/no-go decision point (MEA performance: 25 mA/cm^2 at $0.9 V_{\text{IR-free}}$ using H_2/O_2 at 1.0 bar).

APPROACH

Two major challenges for the PGM-free catalysts are (1) the low density of the active sites and (2) the dominant micropore of the catalysts, which makes most of the active sites inaccessible to O_2 . Our approaches for developing mesoporous M-N-C catalysts and MEAs include (1) designing and synthesizing new Fe-N-C catalysts via a template method and (2) utilizing the electrostatic charge attraction between ionomer particles and catalyst particles to construct the desirable catalyst/ionomer interface. The surface charges over the catalysts can be realized by covalently grafting differently charged groups (i.e., $-\text{NH}_2$ or $-\text{SO}_3\text{H}$, $-\text{PBI}$) and fine tuning the surface hydrophobicity.

Polyaniline (PANI) contains abundant nitrogen sources and is easy to convert to nitrogen-doped carbon materials through pyrolysis. The innovative PANI hydrogel method creates a 3-D network structure, which provides a high surface area and effective channel for mass transport. Therefore, the Fe-doped PANI hydrogel was identified as an ideal precursor to fabricate Fe-N-C catalysts. Subsequent thermal activation enables the formation of interconnecting carbon networks with abundant Fe- N_x active sites and tunable pore structures. The team focuses on two innovative approaches:

1. Using the hydrogel approach to make Fe-doped PANI hydrogel precursors and optimizing these precursors to (a) achieve a high enough surface area with increased density of active sites and (b) provide optimal porosity for mass transport.
2. Using the CVD method to synthesize a zinc-based zeolitic imidazolate framework (ZIF) precursor through bridging metal atoms and 2-methylimidazoles into 3-D ordered crystal frameworks with increased micropores and high surface areas.

Prepare Fe-C-N Catalysts Using PANI Hydrogel Precursors

A hydrogel loses its porous 3-D structure due to the rapid removal of the solvent. To increase the pores of the dried hydrogel, we developed following three strategies: (1) the addition of ZnCl_2 , (2) the use of ZIF to create more pores, and (3) the use of cyanamide to increase the density of active sites.

1. *Utilize $ZnCl_2$ to create Fe-C-N catalysts with more pores:* $ZnCl_2$ was incorporated into the Fe-doped PANI hydrogel during the polymerization process. The Zn species in precursors can be evaporated during the heat-treatment process, leaving a large quantity of pores. This would benefit for exposing more active sites and forming increased porosity to facilitate mass transports.
2. *Synthesize mesoporous Fe-C-N catalysts using 100-nm ZIF template:* The zinc-based ZIF-8 provides a good platform to design Fe-N-C catalysts. Here, 100-nm ZIF crystals were used as templates to form ZIF-8@PANI precursor. After polymerization of the PANI onto ZIF-8, the ZIF-8 templates can be removed with acid etching to form the hollow PANI/Fe hydrogel precursors, which yield mesoporous Fe-C-N catalysts.
3. *Increase the density of active Fe-C-N sites by using cyanamide:* To improve the catalyst activity, we increased the density of Fe-C-N active sites in the catalysts using cyanimide as the additional N source. Similar to the process mentioned above, cyanamide was incorporated into the PANI/Fe mesoporous hydrogel during the gel formation process.

Synthesize Mesoporous Fe-N-C Catalyst Using Innovative CVD

As mentioned above, the zinc-based ZIF is a good platform to design Fe-N-C catalysts. However, synthesis of mesoporous Fe-doped ZIF-8 remains a challenge because of the tedious and complex process of preparing the atomically dispersed Fe catalyst. Here, we developed a simple method by CVD growth to prepare mesoporous atomically dispersed Fe catalysts. At first, mesoporous Fe-doped ZnO nanosheets were fabricated by co-precipitation, followed by a series of heating treatments.

For the MEA work, the team focuses on:

1. Creating catalyst/ionomer interfaces through the functionalization of the PGM-free catalysts.
2. Formulating the inks for rational design of the MEAs.

Establish Catalyst/Ionomer Interface

In the conventional MEA fabrication process, the catalyst/ionomer interface is randomly formed when the solvent is evaporated and the ionomer particles are precipitated over the catalyst surface. The catalyst surface is not completely covered by ionomer particles due to the electrostatic repelling force between negatively charged $-SO_3^-$ over the ionomer surface and negatively charged oxy-contained groups (i.e., $-OH$, $-COOH$) over the carbon surface, which results in lower catalyst utilization and lower mass activity. To increase the coverage, excessive amounts of ionomer can be used, which causes a thicker ionomer film over the catalyst surface, resulting in poor high-current-density performance from the increased O_2 diffusion barrier. We propose to establish a catalyst/ionomer interface with complete coverage and an as-thin-as-possible ionomer film using the electrostatic attracting force between the negatively charged $-SO_3^-$ over the ionomer surface and the positively charged (i.e., $-NH_3^+$) groups over the catalyst surface. The positively charged group is covalently grafted onto the carbon surface via functionalization using a diazonium reaction. From our initial work, we found that the iron-based PGM-free catalysts are easily oxidized in our functionalization process. After functionalization, the performance of functionalized PGM-free catalysts significantly decreased; thus, we believe that the Fe center may be destroyed by the nitrate used during functionalization. In order to protect the active Fe center of the PGM-free catalysts, we propose to use the molecular probe to “mask” the Fe centers so that they can be protected during the functionalization process. We will functionalize the masked PGM-free catalyst to covalently bond the desired chemical groups (i.e., $-NH_2$) onto the carbon surface of the PGM-free catalyst. After functionalization with $-NH_2$ groups, the masked $-NO$ group is reduced into NH_4^+ by applying -0.2 V (vs. reversible hydrogen electrode [RHE]) in an acetic buffer solution for three cycles. In this step, the recovery process, the masked $-NO$ group is removed.

Systematically Formulate the Inks

The catalyst/ionomer interface can be formed in the catalyst ink. Additionally, the pore structure is directly associated with the simultaneous dispersion of both the catalyst particles and the ionomer particles in the inks. The project team focuses on the dispersion of catalyst and ionomer particles in different solvents using ultra-

small-angle X-ray scattering (USAXS) and cryo-transmission electron microscopy (cryo-TEM). The different ionomer/carbon ratios were also studied.

RESULTS

Mesoporous Fe-N-C Catalysts

In this budget period, four different Fe-C-N catalysts with dominant mesopores were synthesized for MEA studies. Incorporated ZnCl_2 (designated as catalyst “a”), Fe-C-N catalysts using the 100-nm ZIF template (designated as catalyst “b”), Fe-C-N catalysts utilizing cyanamide (designated as catalyst “c”), and Fe-C-N catalysts using CVD (designated as catalyst “d”) were characterized for their RDE and MEA performance (Figure 1). The results are summarized in Table 1.

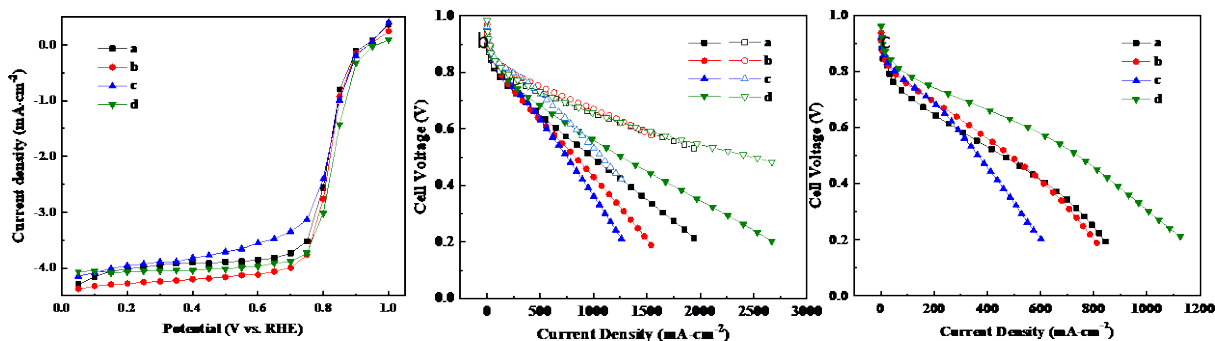


Figure 1. ORR RDE polarization curves of four catalysts in 0.5 M H_2SO_4 , 900 rpm, 25 °C (a); VIR curves of four catalyst MEAs: H_2/O_2 (b) and H_2/air (c); MEA geometric active area: 5.0 cm^2 ; catalyst loading: 0.2 mg Pt/ cm^2 :4 mg/ cm^2 (anode:cathode = 30% Pt/C:Fe-N-C-PANI catalysts); membrane: N212 (H^+); temperature: 80 °/80 °/80 °C (anode/cell/cathode); relative humidity: 100%; backpressure: 1.5 atm; flow rate: 200/400 sccm H_2/O_2 or H_2/air ; ionomer/carbon ratio: 0.8

In the catalysts with a more porous structure (catalysts a and b), increased density of active sites (catalyst c), and the use of CVD to synthesize Fe-C-N catalysts with more dominant mesoporous structure, both RDE activity (i.e., half-wave potential, current density @ 0.90 V) and MEA performance are improved, achieving 27 mA/cm^2 at 0.9 $V_{\text{IR-free}}$ (H_2/O_2) with backpressure at 150 kPa_{abs} in MEAs. Interestingly, three catalysts, a, b, and d, had very similar IR-corrected cell voltages (Figure 1b), suggesting that their kinetic performance may be the same (i.e., same active sites of Fe-C-N, all hydrogel-based catalysts), but the mass transfers were different due to the pore structures. This is also consistent with their half-wave potentials (Table 1). The different mass activity is due to the variation of density of active sites. Catalyst c shows different ohmic performance, which may result from different kinetic activity, due to the changes of N density. Catalyst d shows the best H_2/air MEA performance (Figure 1c), which may be due to the improved pore structure. Further studies on their morphology using Brunauer-Emmett-Teller (BET), Hg porosimetry, and H^+ conductivity are undergoing. These results indicate that our approaches are effective. We will further develop and optimize these methods to prepared advanced Fe-C-N catalysts with enhanced MEA performance.

Table 1. Summary of the RDE and MEA results from Figure 1

Catalyst	RDE		MEA				
	Half-Wave Potential E1/2 (V)	Current Density @ 0.90V (mA/cm^2)	OCV (V), (H_2/O_2)	Mass Activity (mA/cm^2) @ 0.9V IR-Free (H_2/O_2)	OCV (V), (H_2/Air)	Current Density (mA/cm^2) @ 0.80V (H_2/Air)	Power Density (mW/cm^2) @ 0.70V (H_2/Air)
A	0.82	0.11	0.935	6	0.91	32	110.6
B	0.82	0.17	0.935	15.5	0.91	48	132.4
C	0.81	0.2	0.963	24	0.94	68.7	128
D	0.835	0.33	0.984	27	0.94	84	218

Functionalization of PGM-Free Catalysts

To prove the “mask” approach, we used the Fe-N-C-MOF 100-nm catalyst as the model system. This catalyst was masked with $-\text{NO}$ group first, and the catalytic activity decreased from 0.542 mA/cm^2 to 0.293 mA/cm^2 at 0.8 V (vs. RHE) (red line in Figure 2a and 2b). After the removal of the masking molecules, the activity resumed to 0.542 mA/cm^2 at 0.8 V (vs. RHE), demonstrating that the masking process is reversible. Using the masking method, we functionalized the Fe-N-C-MOF 100-nm PGM-free catalyst. The performance of the catalyst recovered to some extent (red line in Figure 2c) but was much lower than its original performance (Figure 2c, black line), which may be due to the possible oxidation of the active sites by NO_2^- . We also tried SCN^- as a masking agent, which showed increased performance after functionalization (Figure 2c, blue line). Another interesting phenomenon is that the electrochemical surface area (ECSA) was affected by the masking time. There was no ECSA after 10 min of masking, but the ECSA increased as the masking time decreased. This indicates that the functionalized PGM-free catalyst particles may lose physical contact due to the complete coverage of functional groups over the surface. Thus, the electrical conduction between PGM-free catalyst particles is decreased. With less masking time, the coverage of functional groups decreased and the electric conduction improved; consequently, the ECSA increased.

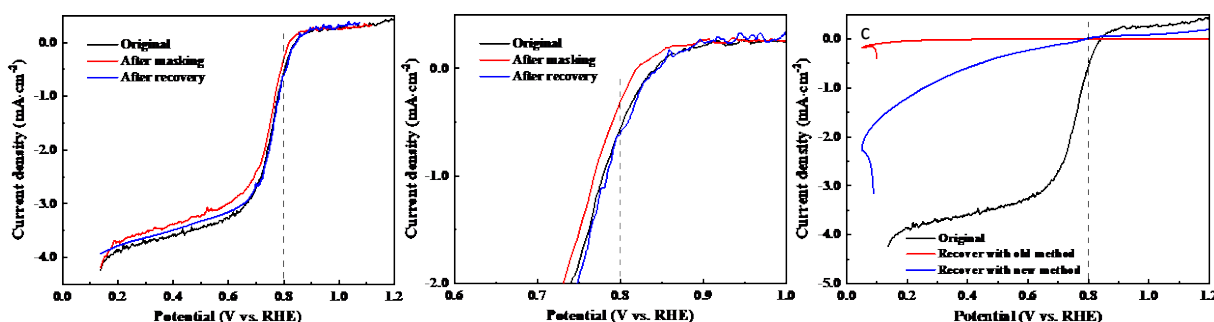


Figure 2. RDE polarization curves of (a) masking Fe-N-C-MOF 100-nm catalyst, (b) an enlargement of (a), and (c) using both NO_2^- and SCN^- as masking agents for functionalization before and after recovery process, $0.5 \text{ M H}_2\text{SO}_4$, $1,600 \text{ rpm}$

Ink Formulation

Our approach is to build the catalyst/ionomer interface in liquid utilizing the charge attraction. To do so, it is required that both ionomer and catalyst particles are dispersed well simultaneously in a catalyst ink. We systematically studied the dispersion of the ionomer and PGM-free catalyst particles in water/n-PA mixtures. The analysis of the USAXS data (Figure 3a) yields two ranges of particles, $2\text{--}4 \text{ nm}$ and $500\text{--}700 \text{ nm}$ (zone I and zone II in Figure 3a, respectively) in a spherical shape, corresponding to ionomer particles and Fe-C-N catalyst particles. When the water content increases, both the ionomer and the Fe-C-N catalyst particles become smaller (Figure 3b), suggesting that both are hydrophilic. The ionomer dispersion varies with water content: less water content ($\text{H}_2\text{O:n-PA} \leq 1:6$) results in only one distribution peak (Figure 3c), showing a spherical shape (Figure 3d). As the water content increases, two size distribution peaks appear (Figure 3d), and the ionomer particles become smaller with rod-like shapes (Figure 3e). Further increasing the water content results in the catalyst particles becoming loosely piled aggregates with ionomer rods entangled in them (Figure 3f). Different alcohols affect the dispersion of the ionomer and catalyst particles and, consequently, the MEA performance. Higher ionomer content results in a better mass activity but lower high-current-density performance, while lower ionomer content leads to lower mass activity but higher high-current-density performance (figures not shown due to space limits). Higher ionomer content leads to higher ionomer coverage over the catalyst surface but results in a thick ionomer film, which adds an excessive O_2 diffusion barrier. Lower ionomer content causes the opposite.

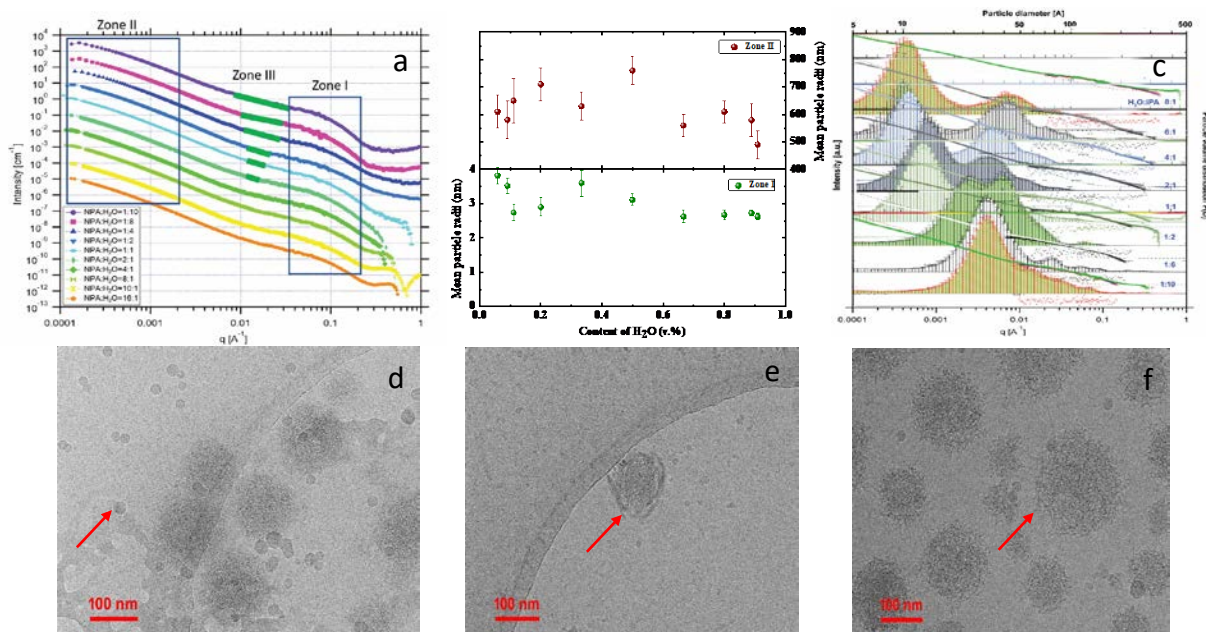


Figure 3. USAXS data of ionomer and catalyst dispersion in H₂O/n-PA mixtures (a), USAXS fitting results of ionomer and catalyst particle size (b), ionomer particle size distribution in H₂O/i-PA mixtures (c), cryo-TEM images of ionomer and catalyst particles in H₂O/n-PA = 1:4, I/C = 0.6 (d), H₂O/n-PA = 1:1, I/C = 0.6 (e), H₂O/n-PA = 4:1, I/C = 1.0 (f)

Other Activities

H⁺ conductivities within catalyst layers were measured based on the Saab et al. method [1, 2]. The effect of membrane thickness on MEA performance was also studied.

CONCLUSIONS AND UPCOMING ACTIVITIES

Improving the pore structure of the PANI hydrogel-based Fe-C-N catalysts is an effective approach to enhancing MEA performance. The concurrent dispersion of both ionomer and catalyst particles is critical for fabricating high-performance MEAs. Higher ionomer content benefits the coverage of the catalyst surface, consequently leading to higher mass activity, while the formed thicker ionomer film causes an excessive O₂ diffusion barrier, resulting in poor current density performance. Further development of the Fe-C-N catalysts with much improved pore structure and the characterization of morphology and composition (i.e., pore structure) using BET, Hg porosimetry, X-ray diffraction, TEM, and scanning electron microscopy will be carried out. Functionalization of the catalysts will be continued to establish the controlled ionomer/catalyst interface with balanced ionomer coverage and O₂ diffusion.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. X.X. Wang, M.T. Swihart, and G. Wu, *Nature Catalysis* 2, no. 7 (2019): 578.
2. M. Chen, Y. He, J.S. Spendelow, and G. Wu, *ACS Energy Letters* 4, no. 7 (2019): 1619.

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1. A.P. Saab, F.H. Garzon, and T.A. Zawodzinski, *Journal of The Electrochemical Society* 150 (2003): A214.
2. A.P. Saab, F.H. Garzon, and T.A. Zawodzinski, *Journal of the Electrochemical Society* 149 (2002): A1541.