
ElectroCat: Durable Mn-Based Platinum-Group-Metal-Free Catalysts for Polymer Electrolyte Membrane Fuel Cells

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Subcontractor(s):

- University at Buffalo, Buffalo, NY
- University of Pittsburgh, Pittsburgh, PA
- General Motors, Pontiac, MI

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Project End Date: September 30, 2020

Overall Objectives

- Achieve sufficient activity ($E_{1/2} > 0.85$) and stability in acidic media: potential loss of $E_{1/2} < 10$ mV after 30,000 potential (0.6 to 1.0 V) cycling tests in rotating disk electrode (RDE) tests.
- Demonstrate fuel cell membrane electrode assemblies (MEAs) ($25\text{--}50\text{ cm}^2$) with a mass activity of 0.044 A/cm^2 at $0.9\text{ V}_{\text{Ir-free}}$ and H_2/air performance of 0.5 V at 1.0 A/cm^2 , following DOE catalyst performance metrics.
- Limit the loss of catalyst mass activity in $25\text{--}50\text{ cm}^2$ fuel cell MEAs, < 30 mV after 3,000 potential cycles, $0.6\text{--}1.0\text{ V}$ in N_2 , following DOE's catalyst support durability testing protocols or any other protocols suggested from the Electrocatalysis (ElectroCat) Consortium.
- Acquire fundamental understanding of the structure-property-performance relationship of the novel Mn-N-C platinum group metal (PGM)-free catalysts. The relevant

computational data, measurement data, and publications will be deposited into the database of ElectroCat.

Fiscal Year (FY) 2019 Objectives

- Predict active sites with highest stability and $4e^-$ oxygen reduction reaction (ORR).
- In RDEs, achieve $E_{1/2} > 0.82\text{ V}$ and generate 0.50 mA/cm^2 at 0.9 V . The $E_{1/2}$ drop after 30,000 potential cycles should be less than 10 mV .
- In MEAs, demonstrate H_2/O_2 performance: 0.020 A/cm^2 at $> 0.9\text{ V}_{\text{Ir-free}}$.

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:

- Performance
- Cost
- Durability.

Technical Targets

The DOE 2020 technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Constructed density functional theory (DFT) modeling to predict that MnN_4 active site has better stability than FeN_4 site due to reduced central metal leaching, nitrogen corrosion, and carbon corrosion.
- Precisely controlled the particle size and morphology of Mn-N-C catalysts in aqueous phase to improve their ORR activity and performance.
- Synthesized sulfur-doped Mn via a one-step method, which further increased the MEA performance and durability.

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

- Designed MEAs using optimized Mn catalysts that met the Year 2 go/no-go milestone (20 mA/cm² @ 0.9 V iR-free for H₂/O₂) and achieved 423 mW/cm² maximum power density for H₂/air.
- Demonstrated good durability of the MEA using voltage cycling protocol.

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

Characteristic	Units	DOE 2020 Targets	Project Status
RDE-E _{1/2}	V	≥0.85	0.81
RDE-E _{1/2} decrease after 30,000 cycles	mV	≤10	14
MEA performance (H ₂ /O ₂)	A/cm ² @ 0.9 V _{iR-free}	0.044	0.0206
MEA performance (H ₂ /air)	V @ 1 A/cm ²	0.5	0.4
MEA performance (H ₂ /air)	A/cm ² @ 0.8 V	150	82
MEA durability (voltage drop)	mV @ 0.044 A/cm ²	30	47

INTRODUCTION

Development of low-cost and high-performance cathode catalysts for the ORR in proton exchange membrane fuel cells (PEMFCs) remains a grand challenge for large-scale transportation applications. The primary goal of this project is to significantly reduce the cost of PEMFCs by replacing expensive and rare PGM catalysts with PGM-free catalysts. Among studied PGM-free catalyst formulations, nitrogen and transition metal (M: Fe, Co, or Mn) co-doped carbon (M-N-C) catalysts prepared by high-temperature pyrolysis have demonstrated great promise to replace Pt [1]. Compared to other metals, Fe-N-C catalysts have exhibited the best activity for the ORR in acidic media but suffer from insufficient stability. Furthermore, a major issue associated with Fe-containing catalysts is the production of corrosive OH[•] radicals when in contact with H₂O₂, a product of the two-electron reduction reaction. To address these ionomer/membrane degradation issues due to the intrinsic nature of iron, PGM-free and Fe-free catalysts are highly demanded for low-cost PEMFC technologies.

Motivated by predictions from the first principles DFT calculations at the University of Pittsburgh (UP), the team at the University at Buffalo (UB) has successfully prepared active and stable Mn-N-C catalysts. The activity of the Mn-N-C catalysts measured using RDEs in acidic electrolytes is approaching the state-of-the-art Fe-N-C catalysts. More importantly, the Mn-N-C catalysts have demonstrated enhanced stability using potential cycling (0.6–1.0 V) in O₂-saturated acidic electrolytes. Therefore, in this project, the UP and UB team will collaborate with Giner, Inc. (Giner) and General Motors (GM) to further develop novel Mn-based catalysts and implement them into PEMFCs. Our cohesive efforts will completely address the Fenton reagent issue stemming from currently studied Fe-N-C catalysts and make PGM-free cathode catalysts feasible for PEMFCs.

APPROACH

A strong team was formed to transform the discovery of low-cost Mn-based catalysts into fuel cell application with expertise in the following areas:

- UP conducted the catalyst modeling to understand and predict the degradation mechanisms of Mn sites for ORR reaction.
- UB synthesized the highly active Mn-based catalysts with tunable particle size and sulfur-doping.
- Giner optimized the MEA fabrication process and electrode structure using the Mn-based catalysts delivered from UB. Meanwhile the MEA durability study is also performed.
- GM will further validate the system integration.

RESULTS

This is the second year of the project. UP has finished modeling the stability of the MnN_4 sites during ORR using the first-principles DFT calculation methods [2]. These predictions were made based on the thermodynamic analysis of the possible degradation reactions on MnN_4 sites during ORR. The computational results are shown in Figure 1. The computation predicts that MnN_4 sites have better stability than FeN_4 sites due to reduced central metal leaching and higher resistance to nitrogen corrosion and carbon corrosion than both FeN_4 and CoN_4 sites. Moreover, O_2 adsorption on the active sites would facilitate the metal leaching process.

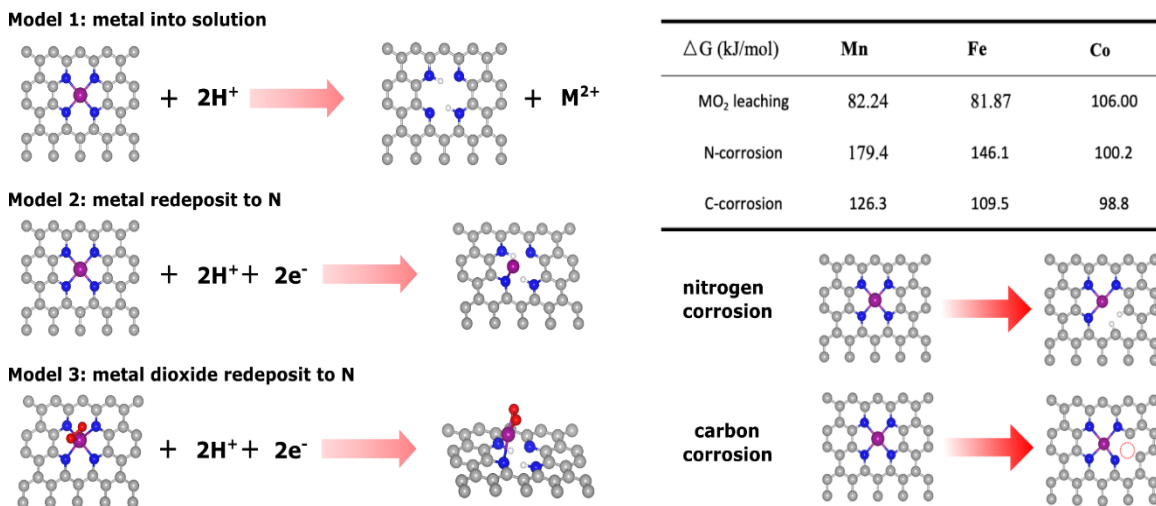


Figure 1. Modeling results of the degradation of MnN_4 sites

UB successfully synthesized the MnN_x based catalyst with a precisely controlled particle size as shown in Figure 2a. The Mn and nitrogen co-doped carbon with a 3-D porous structure was obtained by carbonizing the Mn-doped zeolitic imidazolate framework (ZIF) precursor. The polyhedral morphology of Mn-doped ZIF-8 is retained even after pyrolysis, and the particle size can be accurately controlled from 40 to 200 nm by adjusting the reactant concentration during the synthesis of Mn-doped ZIF-8 nanocrystal precursors. This highly controllable synthesis, with precise tuning of catalyst morphology and structure, has provided an excellent opportunity to establish the relationship between MEA structure and fuel cell performance. It was further found that the 40-nm Mn catalysts aggregate together to generate secondary particles, which undermines the distribution of ionomer and blocks the Mn active sites. On the other hand, when the particle size is increased to the optimal 80 nm, the Mn-based catalysts can disperse well to generate a smooth surface and porous structure that facilitate mass transport and ionomer distribution and dispersion.

In addition, the two-step synthetic strategy was replaced by a facile one-step approach, boosting the fuel cell performance through modification of the catalyst composition. As shown in Figure 2b, ZIF-8 precursors were initially synthesized (the particle size is around 80 nm, which is optimal for MEA performance) and then subjected to high-temperature treatment to build porous nitrogen-doped carbon. The obtained ZIF-derived porous nitrogen-doped carbon (N-C) was used as a host to adsorb Mn and S sources, followed by thermal activation to obtain Mn-N-C-S catalyst. For comparison, the Mn-N-C catalyst was prepared under the same procedure except for the S-doping. RDE tests were performed to compare the electrocatalytic activity of these catalysts (Figure 2c). The half-wave potential of Mn-N-C-S catalyst is ca. 0.81 V, which is much higher than that of Mn-N-C catalyst. The MEA performance was also tested under H_2 - O_2 conditions. The current density at 0.9 V is about 20 mA/cm^2 , which meets the milestone for Year 2. The current density of the Mn-N-C-S catalysts was well maintained at the high-voltage region, suggesting that the Mn-N-C-S catalysts were stable (Figure 2d and Figure 2e).

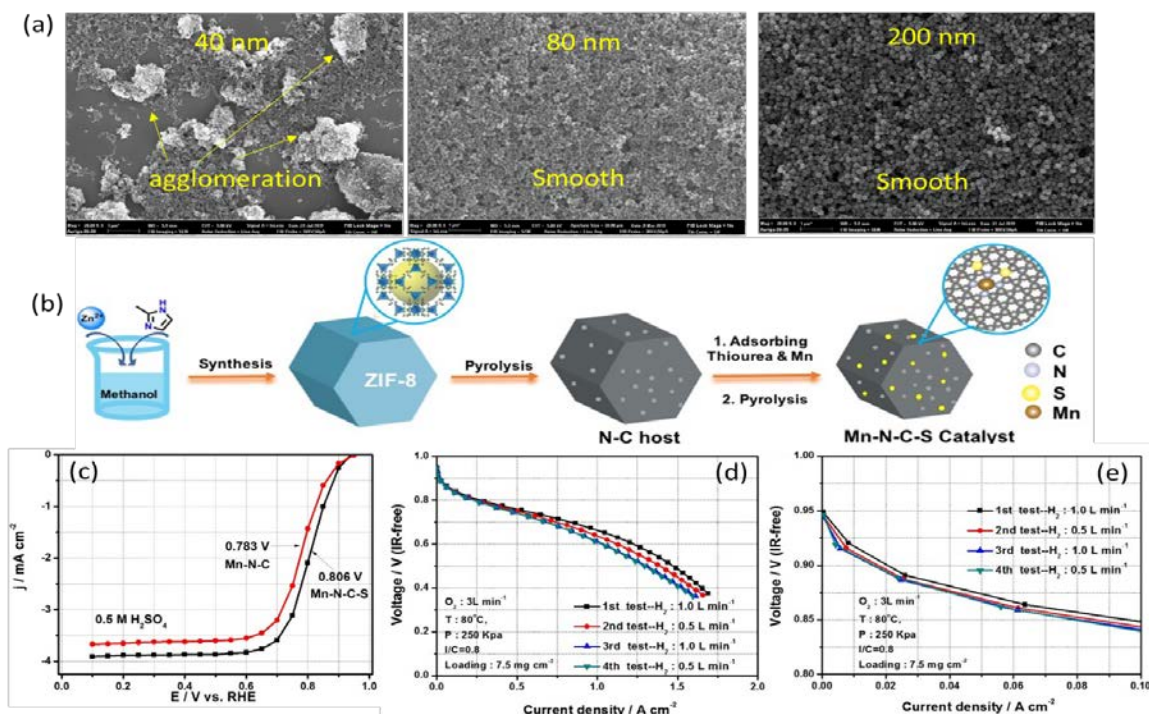


Figure 2. (a) Particle size control of Mn-N-C catalysts ranging from 40 nm to 200 nm. (b) Schematic diagram for the one-step method to introduce Mn and S into the 3-D carbon host derived from ZIF precursors. (c) ORR polarization curves of Mn-N-C and Mn-N-C-S catalysts. (d) MEA performance of Mn-N-C-S catalysts under $\text{H}_2\text{-O}_2$ conditions. (e) Polarization curves of Mn-N-C-S catalysts at the high-voltage region under $\text{H}_2\text{-O}_2$ conditions.

The MEAs of different Mn-based PGM-free catalysts were designed and tested at Giner. It was previously discovered that Mn catalysts from two-step water synthesis had better performance compared to one-step synthesis. Therefore, we decided to optimize the MEA performance using the two-step water-synthesized catalyst. We first studied particle size impact and found that 80-nm catalyst had the best MEA performance (Figure 3a). The poor performance of the catalyst with smaller particle size (50 nm) is due to the agglomeration. The catalyst with larger particle size (200 nm) has less exposed active sites thus reducing the catalytic activity.

The ionomer-to-carbon (I/C) ratio also influences the MEA performance. We have optimized I/C ratio for the 80-nm catalyst. It can be seen from the polarization curves (Figure 3b) that the I/C ratio of 0.8 results in the best H_2 /air power density. For electrode structure optimization, we have also developed a freeze-drying approach for MEA fabrication. It is well known that the dense electrode structure for a PGM-free catalyst layer hinders the ionomer and O_2 access, causing huge transport losses. We thus utilize the volume expansion of water during liquid-solid transformation to expand the pore size in the catalyst layer. Figure 3c shows the H_2 /air performance of a baseline MEA and one made by the freeze-drying approach. It can be seen that freeze-drying does help to improve the transport region in the polarization curve.

After UB demonstrated that the S-doped Mn catalyst had better performance than the Mn-only catalyst, we evaluated this catalyst and compared it with the previous catalysts. The MEA activity, in terms of current density at 0.9 V (H_2/O_2) iR-corrected voltage, has improved from 10.6 mA/cm^2 at the end of year 2018 to 20.6 mA/cm^2 in this year. The H_2 /air performance of S-doped catalyst and the original two-step water-synthesized catalyst are compared in Figure 3d and significant improvement is observed. The current density at 0.7 V improved from 220 mA/cm^2 to 341 mA/cm^2 and the current density at 0.8 V improved from 42 mA/cm^2 to 82 mA/cm^2 . The latter is close to that of state-of-the-art Fe catalyst.

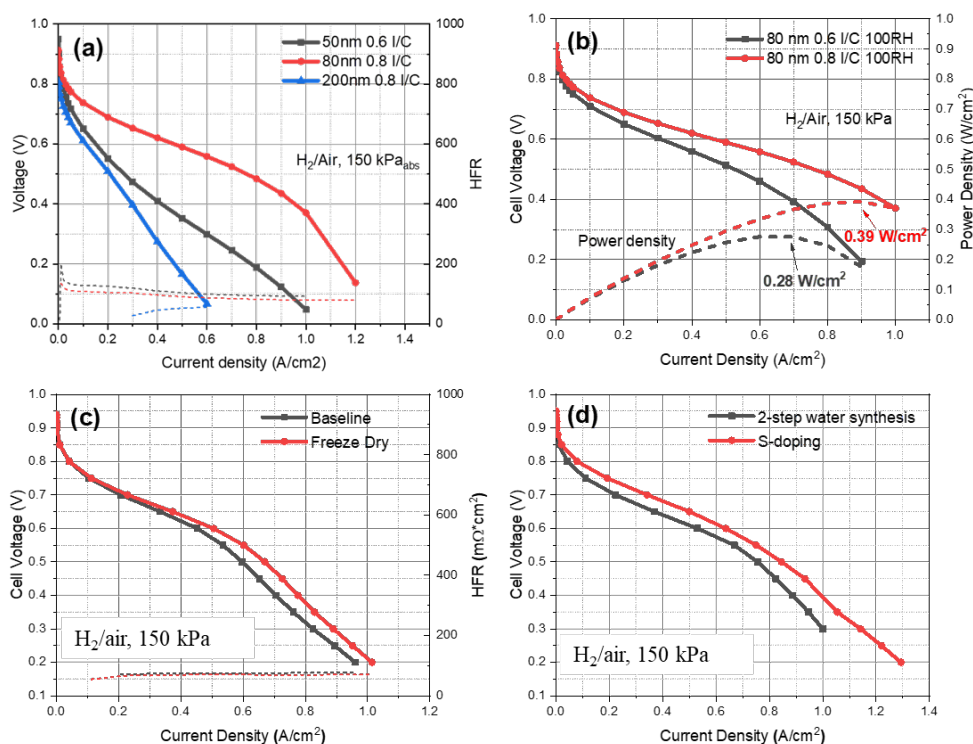


Figure 3. (a) H₂/air performance for catalysts with different particle sizes; (b) I/C optimization for 80-nm catalyst; (c) H₂/air performance of baseline and freeze-drying-fabricated MEAs; and (d) MEA performance comparison of two-step water-synthesized and S-doped catalysts.

In FY 2019, we also started to carry out the MEA durability testing systematically. We encountered the poor durability of two-step water-synthesized Mn catalysts, which decayed significantly after a quick polarization scan. The S-doped catalyst shows much better durability with little decay after three polarization scans. The MEA durability of two types of Mn catalyst was evaluated by holding the cell voltage at 0.65 V. The testing result is shown in Figure 4a. Better performance and current density retention have been observed for S-doped Mn catalyst. Giner also made Mn catalyst in house. The durability of the MEA using Giner catalyst was studied by cyclic voltammetry cycling. Only 37 mA/cm² current density loss at 0.6 V under H₂/air was observed after 30,000 cycles (Figure 4b), which meets the end milestone of our project.

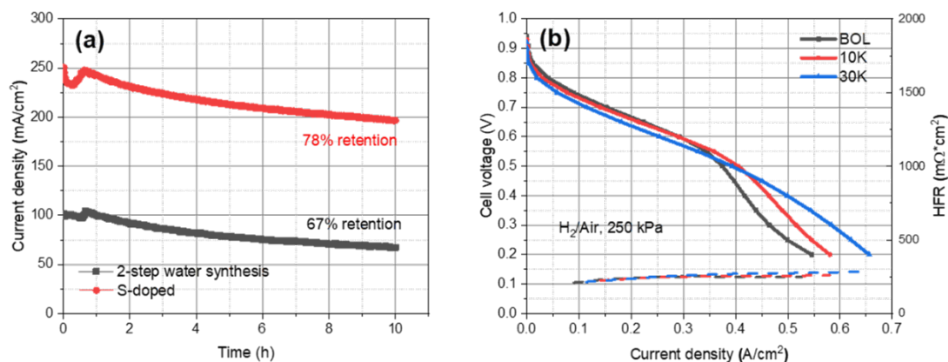


Figure 4. (a) Durability tests under 0.65 V constant voltage condition of both the S-doped Mn catalyst and the two-step water-synthesized Mn catalyst. (b) Polarization curves of the S-doped Mn catalyst at BOL, after 10,000 cyclic voltammetry cycles, and after 30,000 cyclic voltammetry cycles.

CONCLUSIONS AND UPCOMING ACTIVITIES

We have successfully predicted high stability of MnN_4 sites using DFT computation. A variety of Mn-based catalysts were synthesized by tuning particle size, and S-doped Mn catalysts demonstrate the best activity in the RDE studies. Catalyst ink formulation and electrode optimization were conducted to improve the MEA performance and showed that the electrode freeze-drying approach can improve the mass transport in the catalyst layer. MEAs made with S-doped Mn catalyst show great potential in both activity and durability.

Based on current progress, we have listed our upcoming plans below:

- Computation will be used to predictively examine how doping of sulfur could increase the density and the intrinsic activity of MnN_4 active sites in the ORR catalysts.
- The sulfur doping content will be optimized and the catalyst with the optimal ratio of Mn/S will be systematically studied.
- Morphology and pore size control of the catalyst will be investigated, including template-assisted hollow structure, mesopore/macropore control, and concave shape.
- Further optimization of the MEA fabrication process using S-doped Mn catalyst will be conducted using ionomers with different gas permeability and hydrophobicity.
- Thick electrode studies will be carried out to study local oxygen resistance and water transport.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Fan Yang, Magali Spinetta, Sichen Zhong, Mengjie Chen, Gang Wu, and Hui Xu, “Durable Mn-Based PGM-Free Electrodes for Polymer Electrolyte Membrane Fuel Cells,” 236th ECS meeting, Atlanta, GA, 2019.
2. Thomas S. Stracensky, Shuo Ding, Judith Lattimer, Sanjeev Mukerjee, and Hui Xu, “One-Step Synthesis of Manganese Doped Single Atom Catalysts for Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells,” 236th ECS meeting, Atlanta, GA, 2019.

REFERENCES

1. G. Wu, K.L. More, C.M. Johnston, and P. Zelenay, “High-Performance Electrocatalysts for Oxygen Reduction Derived from Polyaniline, Iron, and Cobalt,” *Science* 332 (2011): 6028.
2. K. Liu, Z. Qiao, S. Hwang, Z. Liu, H. Zhang, D. Su, H. Xu, G. Wu, and G.F. Wang, “Mn- and N-doped Carbon as Promising Catalysts for Oxygen Reduction Reaction: Theoretical Prediction and Experimental Validation,” *Appl. Catal. B-Environ.* 243 (2018): 195–203.