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

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- University at Buffalo (UB), Buffalo, NY
- University of Pittsburgh (UP), Pittsburgh, PA
- General Motors (GM), Pontiac, MI

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Project End Date: September 30, 2020

Overall Objectives

- Develop Mn-based catalysts that achieve sufficient activity ($E_{1/2}$ >0.85 V) and stability in acidic media: potential loss of $E_{1/2}$ <10 mV after 30,000 potential (0.6 V to 1.0 V) cycling tests in rotating disk electrode (RDE) tests.
- Demonstrate fuel cell membrane electrode assemblies (MEAs) (25–50 cm^2) with a H_2/O_2 mass activity of 0.044 A/cm^2 at 0.9 $V_{iR\text{-}free}$ and H_2/air performance of 0.5 V at 1.0 A/cm^2, following DOE catalyst performance metrics.
- Limit reduction of catalyst mass activity in 25–50 cm^2 fuel cell MEAs (<30 mV after 30,000 potential cycles, 0.6–1.0 V in N_2) following DOE's catalyst support durability testing protocols or any other protocols suggested from the ElectroCatalysis Consortium (ElectroCat).
- Acquire a 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) 2018 Objectives

- Predict six planar and non-planar Mn-based active sites using computational modeling.
- In RDEs, achieve $E_{1/2}$ >0.81 V and generate 0.25 mA/cm^2 at 0.9 V. The $E_{1/2}$ drop after 30,000 potential cycles should be less than 30 mV.
- In MEAs, demonstrate H_2/O_2 performance of 0.010 A/cm^2 at >0.9 $V_{iR\text{-}free}$.

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 Plan[1]:

- Performance
- Cost
- Durability.

Technical Targets

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

FY 2018 Accomplishments

- Performed density functional theory computations to predict Mn catalysts with the best oxygen reduction reaction (ORR) activity. MnN_4 was found to be the most active among all MnN_x sites.
- Successfully synthesized Mn-based catalysts via various approaches. Strategies to increase catalytic activity have been discovered.
- In RDEs, demonstrated remarkable durability of Mn-based catalysts compared to Fe-based catalysts.

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

- In MEAs, demonstrated initial fuel cell performance using Mn catalysts and evaluated different factors to improve fuel cell performance.

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

Characteristic	Units	DOE 2020 Electrocatalyst Targets	Project Status
RDE-$E_{1/2}$	V	≥0.85	0.81
RDE-$E_{1/2}$ decrease after 30,000 cycles	mV	≤10	17
PGM-free MEA performance (H_2/O_2)	A/cm^2 @ 0.9 $V_{iR\text{-}free}$	0.044	0.016
MEA performance (H_2/air)	V @ 1 A/cm^2	0.5	0.4
MEA durability (voltage drop)	mV @ 0.044 A/cm^2	30	N/A

INTRODUCTION

Development of low-cost and high-performance cathode catalysts for the oxygen reduction reaction in polymer electrolyte 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 H_2O_2, a product of this two-electron ORR. 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 density functional theory 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 [1]. More importantly, the Mn-N-C catalysts have demonstrated enhanced stability using potential cycling (0.6–1.0 V) in O_2-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 has been formed to transform the discovery of low-cost Mn-based catalyst into fuel cell application with expertise in the following areas:

- UP conducts the catalyst modeling to find the most active Mn site for ORR reaction.
- UB synthesizes the highly active Mn-based catalyst based on the modeling predictions from UP.
- Giner designs and optimizes the MEA fabrication process and electrode structure using the Mn-based catalysts delivered from UB.
- GM further validates the system integration of PGM-catalyst-free MEAs.

RESULTS

This is the first year of the project. UP has completed modeling the activity of nine MnNx sites (x ranging from 2 to 5) for ORR using the first-principles density functional theory calculation methods. Specifically, we predicted the adsorption energy of ORR species (O_2, OOH, O, OH, and H_2O), free energy evolution following a $4e^-$ ORR pathway, and activation energy for the OOH bond breaking process on various possible active sites. UP predicts that two MnN_4 sites and one MnN_5 sites (shown in Figure 1) are able to catalyze the $4e^-$ ORR process. Moreover, we identified the MnN_4 site near a micropore (Figure 1a) to be the most active site for ORR among all the modeled ones. In contrast, the MnN_x sites with coordinated nitrogen atoms ranging from 2 to 3 are predicted to not promote the $4e^-$ ORR process. These predictions were made based on the thermodynamic analysis of the adsorption energies of ORR species and the free energy evolution of ORR processes.

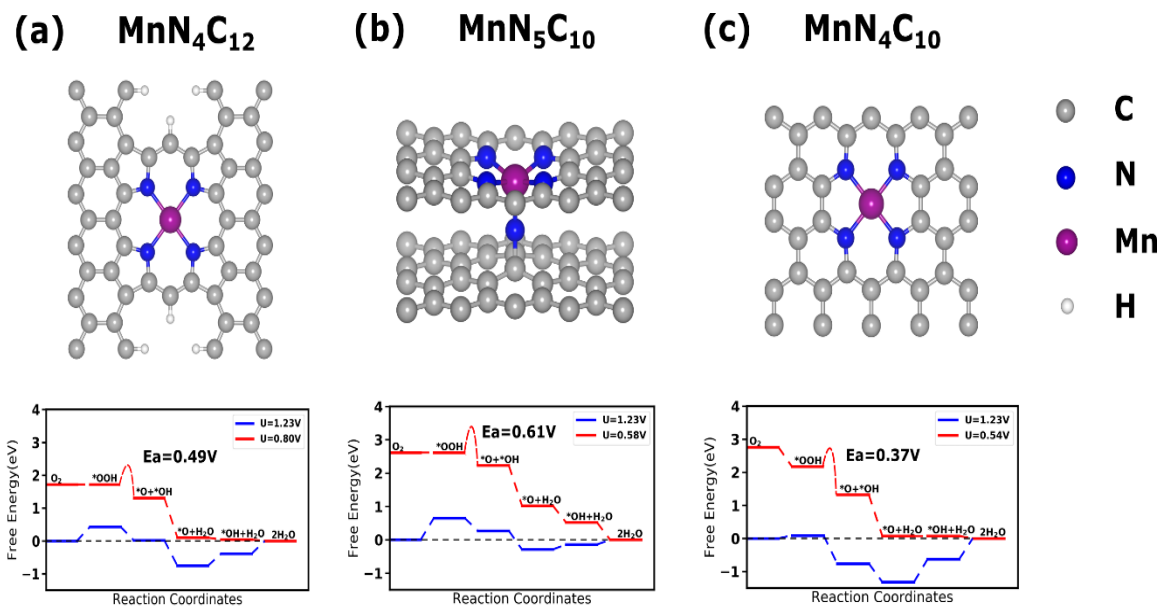

Figure 1. Modeling results of the MnN_x sites for ORR

Based on the prediction from UP, UB successfully synthesized the MnN_4-based catalyst using a two-step chemical doping and adsorption method, which is shown in Figure 2. In the first chemical doping step, Mn-doped zeolitic imidazolate framework (ZIF) precursors were synthesized in a dimethylformamide (DMF) solution. The precursors are identified as nMn-ZIF, where n is the molar ratio of Mn/(Mn+Zn) in the solution. Afterward, Mn and nitrogen co-doped carbon with a three-dimensional porous structure were obtained by pyrolyzing the Mn-containing ZIF precursor. The samples were labeled as nMn-NC. Followed by acid leaching and heat treatment, the obtained powder (labeled as nMn-NC-first) was dispersed in a solution containing Mn salt and additional nitrogen source to carry out the second adsorption step (nMn-NC-second) to introduce more Mn in the catalyst. The subsequent thermal activation can significantly improve the performance, indicating increased density of MnN_4 active sites. Electron microscopy research was conducted at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences by Dr. Cullen and Dr. More.

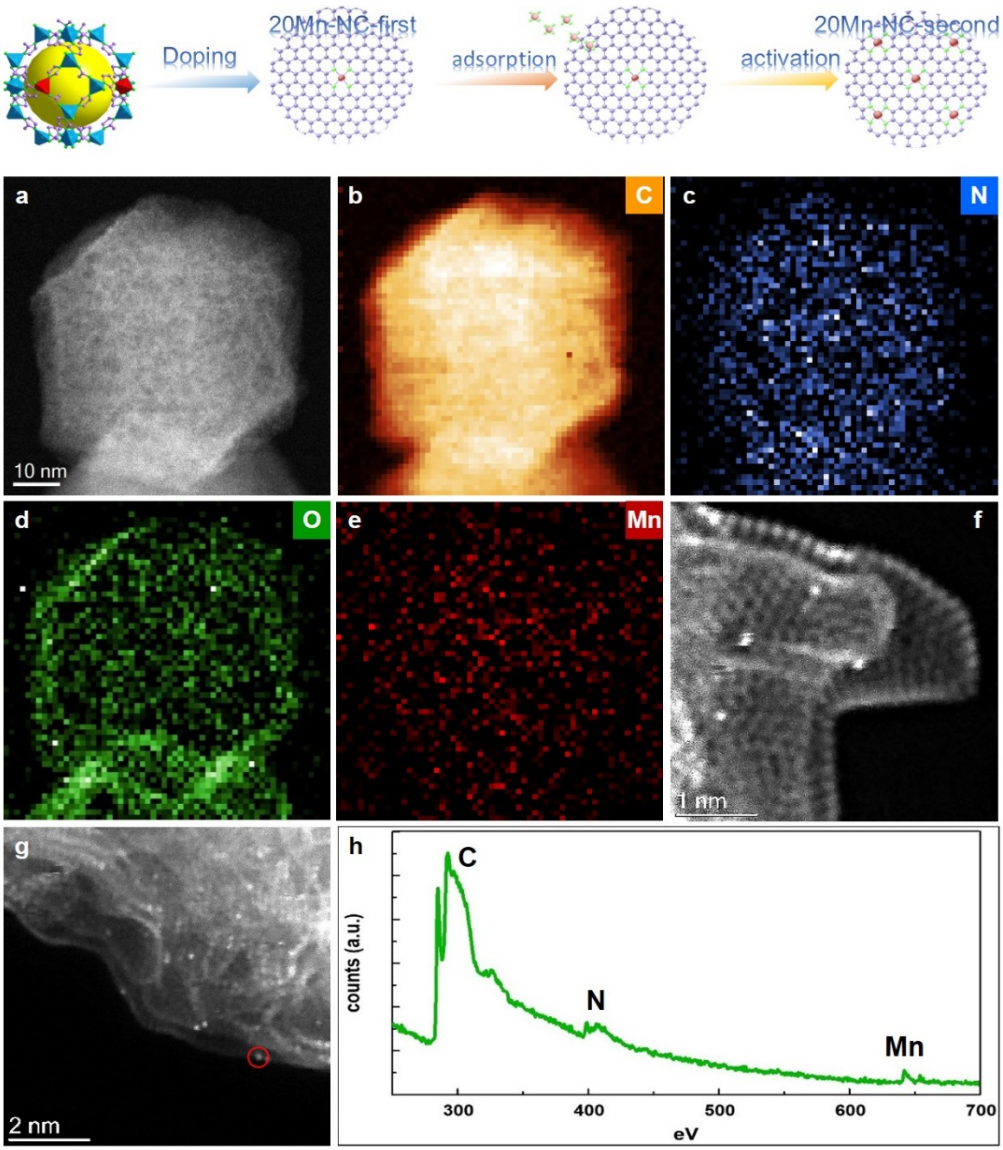

Figure 2. Schematic diagram for two-step doping/adsorbing method to gradually introduce more active sites into the three-dimensional carbon particles derived from Mn-containing ZIF precursors, and microscopy results of 20Mn-NC-second

RDE tests were carried out to compare the electrocatalytic activity of different catalysts. The RDE results are plotted in Figure 3. As can be seen in Figure 3a, the second step can help to improve the half-wave potential by 80 mV (from 0.73 V to 0.81 V). In Figure 3b, the performance of Mn-based catalyst is found to be close to that of the Fe-based catalyst produced with the same procedure. Although the initial performance of the Mn-based catalyst was slightly lower than that of the Fe-based catalyst, the durability of the Mn-based catalyst was significantly better. As can be seen in Figure 3c and 3d, the $E_{1/2}$ of the Mn-based catalyst dropped 17 mV after 30,000 potential cycles (from 0.6 V to 1.0 V), which was much smaller than that of the Fe-based catalyst (29 mV). This result indicates that an Mn-based catalyst has the potential to replace Fe catalyst as a stable PGM-free catalyst in the future with further improvement of the initial performance.

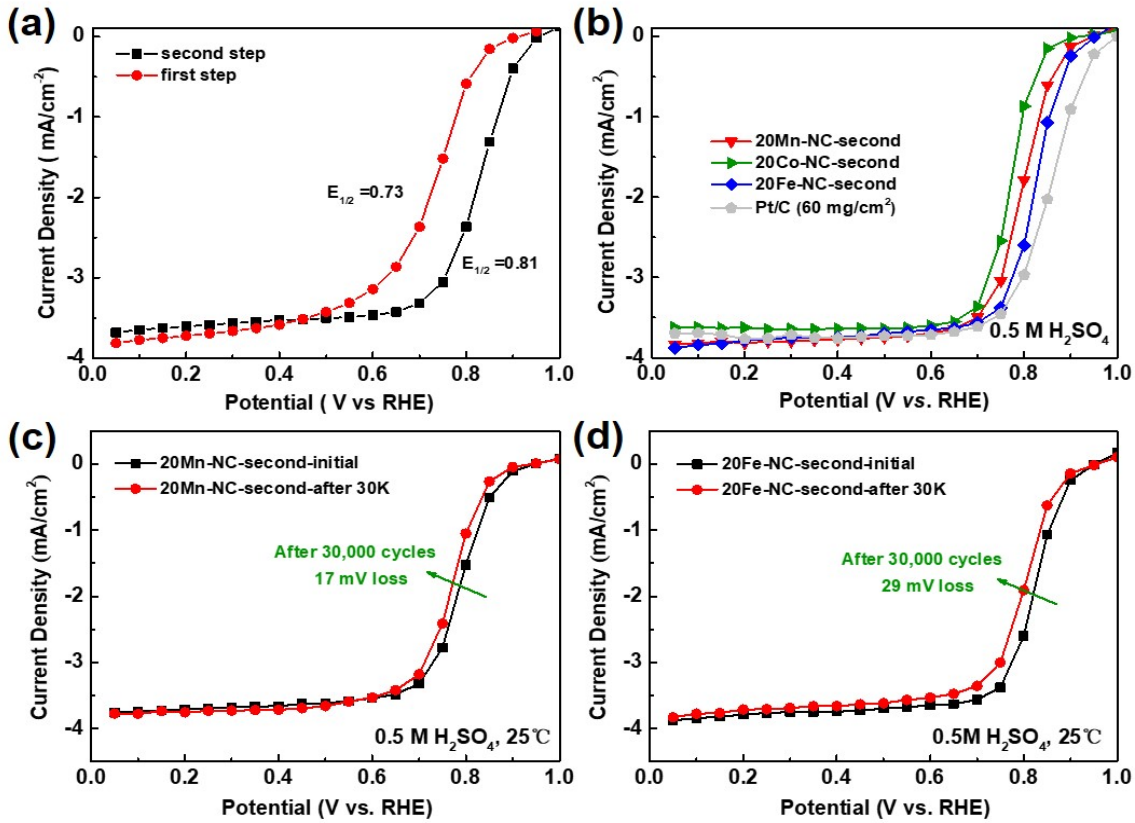

Figure 3. (a) RDE result of the Mn-based catalysts after the first step and second step synthesis; (b) RDE polarization curves of Mn-, Fe-, Co-, and Pt-based catalysts; (c, d) RDE durability tests of Mn- and Fe-based catalysts. The potential cycling is carried out between 0.6 V and 1.0 V for 30,000 cycles with a scan rate of 50 mV/s.

The MEA tests of different Mn-based non-PGM catalysts were carried out at Giner as shown in Figure 4. Figure 4a and Figure 4b show H_2/O_2 and H_2/air polarization curves of Mn-based catalysts from three different synthesis routes: metal-organic-framework (MOF)-based synthesis using DMF, water, and polyaniline hydrogel-based synthesis. Polyaniline hydrogel-based catalyst was obtained by adsorption method as mentioned above. Water-based MOF catalyst was obtained by chemical doping method. The performance rank follows this trend: two-step from DMF > one-step adsorption > one-step from water synthesis. Two-step DMF-based catalyst performed better than the one-step method (hydrogel-based and water synthesis) because the former could introduce more MnN_4 active sites. The benefits of using MOFs to produce highly active Mn-N-C catalysts for ORR are likely due to their well-defined structure, high surface area, and porous structure. From the H_2/O_2 data, the current density @ 0.9 V was about 12 mA/cm^2. We optimized the MEA fabrication process. As can be seen in Figure 4c, catalyst-coated membranes yielded better performance than gas diffusion electrodes, which likely was due to the better catalyst layer/membrane interface using catalyst-coated membranes. It can also be seen from Figure 4d that the MEA using Aquivion ionomer with a lower equivalent weight in the catalyst layer performed better than the one using Nafion 1100 equivalent weight ionomer. This might be due to the shorter polymer chain of the Aquivion ionomer that could penetrate into the smaller pores of electrodes, thus leading to increased ionomer utilization.

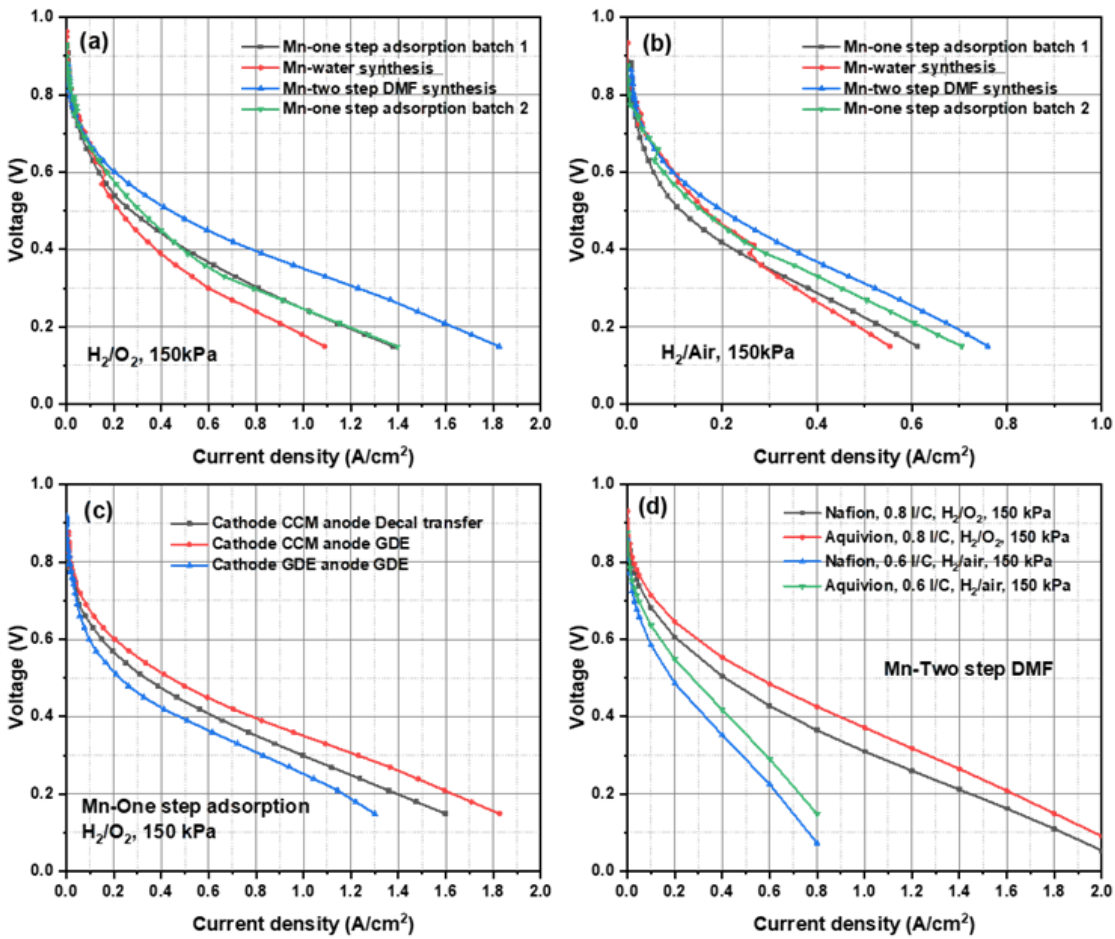

Figure 4. (a-b) IV curve of the MEAs with Mn-based catalysts synthesized via different approaches under H_2/O_2 and H_2/air testing conditions. (c) IV curves of the MEAs with different fabrication process using Mn-one-step adsorption catalyst on cathode. (d) IV curve of the MEAs using different ionomer in the catalyst layer.

CONCLUSIONS AND UPCOMING ACTIVITIES

We have successfully modeled MnN_4 sites in the $4e^-$ ORR process via density functional theory computation, using descriptors like adsorption energy and free energy. Guided by the modeling results, we synthesized Mn-based catalysts to maximize the number of MnN_4 active sites in the catalysts. In the RDE tests, they have demonstrated slightly lower initial performance than Fe catalysts but much better durability. Based on the MEA test results, the two-step DMF approach demonstrated the best performance among all synthesis routes due to increased Mn content in the ZIF structure.

Based on current progress, we have listed our upcoming plan below.

- Catalyst modeling
  - Catalyst: To achieve high activity and durability simultaneously
  - Electrode: Structure affects MEA performance
- Further improve catalyst synthesis

  - Increase effective Mn doping
  - Improve catalyst synthesis reproducibility
  - Scale up catalyst synthesis
- Optimize electrode and MEA design
  - Ink preparation
  - New electrode design (e.g., ionomer-less or -free electrode design)
  - Thick electrode transport studies (O_2 and water)
- Electrode in situ and ex situ characterizations.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. J. Li, M. Chen, Z. Wang, H. Xu, and Gang Wu, "Atomically Dispersed and Nitrogen-coordinated Manganese Catalysts for Oxygen Reduction in Proton Exchange Membrane Fuel Cells," *Nature Catalysis,* in revision (2018).
2. H. Xu, "Durable Mn-based PGM-Free Catalysts for Polymer Electrolyte Membrane Fuel Cells," DOE 2018 Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C, June 13–15, 2018.

REFERENCES

1. G. Wu et al., *Science* 332 (2011): 6028.