Hawai'i Natural Energy Institute Research Highlights

Electrochemical Power Systems

PGM-Free Catalysts for PEM Fuel Cell Applications

OBJECTIVE AND SIGNIFICANCE: This project's purpose was the development of platinum group metal free (PGM-free) catalyst for electrochemical oxygen reduction offers a potential to reduce the production cost of proton exchange membrane fuel cells (PEMFC) and expand application opportunities for fuel cell powered systems. HNEI developed highly active PGM-free catalysts to optimize their incorporation into an electrode structure and fuel cell.

BACKGROUND: Commercial fuel cells are typically utilizing Pt-based catalysts for hydrogen oxidation and oxygen reduction at anode and cathode, respectively. The substitution of oxygen reduction Pt catalysts by PGM-free materials lowers manufacturing cost (less than or equal to $3/kW) and ensures independence from Pt and other precious metal availability. In addition, PGM-free cathode catalysts provide tolerance to the main air-polutants like NO_2 and SO_2, which compromises Pt-based PEMFC operation. Therefore, application of PGM-free electrocatalysts opens pathways to production of low-cost and contaminat tolerant PEMFCs.

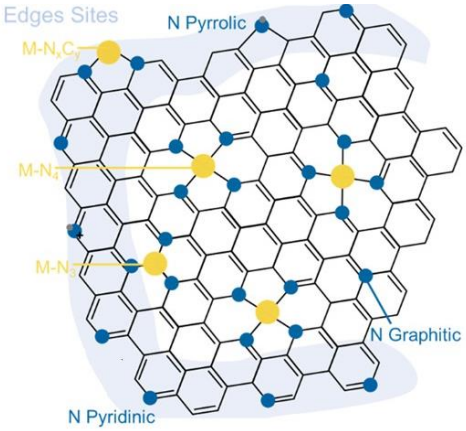

Figure 1. Schematic representation of PGM-free catalyst with M-N_x active sites[1].

PGM-free catalysts consist of non-precious transition metal (M=Fe, Co, Mn) coordinated by nitrogen inside a matrix of graphitic carbon (M-N-C) and can be inexpensively manufactured at scale (Figure 1). These catalysts possess high intrinsic activity for oxygen reduction measured in electrochemical half-cell configuration. However, PGM-free electrocatalysts integrated in membrane electrode assembly (MEA) demonstrated lower performance compared to Pt-based fuel cells. Their performance can be improved by designing and optimizing the cathodic catalyst layer (CCL) and MEA construction such that: 1) it efficiently provides oxygen access to Fe-N_x active sites through catalyst morphology control; 2) it removes water from the CL by tuning the hydrophobicity of the PGM-free catalysts and the catalyst layer structure; and 3) it increases proton conductivity by homogeneous mixing of catalysts and ionomer. The performance can be improved by synergistic efforts of materials design, fine tuning of the electrode layer and comprehensive electrochemical analysis.

This project was a joint collaboration between industry (Pajarito Powder LLC, IRD Fuel Cell) and academia (HNEI) and was primarily funded under U.S. Department of Energy project "Active and durable PGM-free cathodic electrocatalysts for fuel cell application" (DE-EE0008419). HNEI's role was to conduct electrochemical evaluation of the PGM-free PEMFCs using advanced and proven electrochemical techniques.

PROJECT STATUS/RESULTS: The project was initiated in January 2019 and completed in December 2021. During the project, several generations of PGM-free electrocatalysts were synthesized using sacrificial support method, rationally selected precursors, conditions and treatments to expolore various approacheds in development of active center (Figure 2).

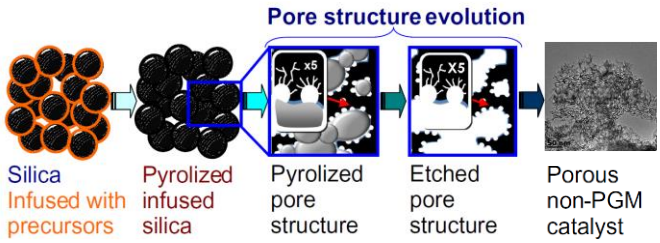

Figure 2. General schematic of used sacrificial support method for Fe-N-C catalyst synthesis.

The chosen catalyst synthesis led to formation of atomically dispersed M-N_x moieties and increased its

[1] Adapted from Asset, T., et al. (2019). Investigating the nature of the active sites for the CO_2 reduction reaction on carbon-based electrocatalysts. ACS Catalysis, 9(9), 7668-7678. https://doi.org/10.1021/acscatal.9b01513

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amount due to creation of additional defects in carbon matrix. The electrocatalysts had advanced textural properties: high surface area and large pore volume. Raman spectroscopy demonstrated that carbon matrix maintained substantial level of graphitization.

It should be noted that the PGM-free catalysts loading in MEAs is in the range of 2-4 mg_{cat} cm^{-2} – which forms CCL with thickness up to 100 μm – whereas Pt-containing electrodes have catalyst content of 0.1-0.4 mg_{Pt} cm^{-2} with maximum thickness of 10-12 μm. In addition, PGM-free electrocatalysts are typically characterized by large primary catalyst particles with size higher than 1 μm. So, all these particularities of the PGM-free electrocatalysts affect their successful integration into the electrode structure and impact development of advanced three-phase boundaries and proton conductivity.

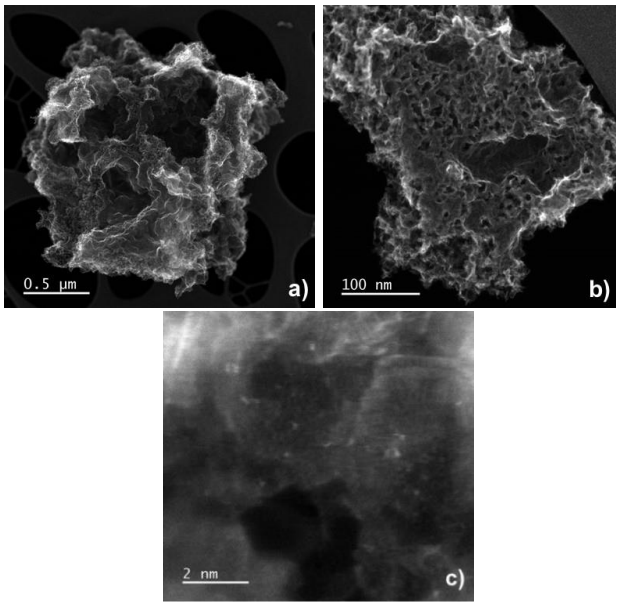

Figure 3. SEM (a, b) and HRTEM (c) images of Fe-N-C catalysts after addition of pore-forming agents. Atommically dispersed Fe-N_x canters are presented as bright dots at HRTEM image (c).

In order to improve intrinistic catalytic activity and reduce primary catalyst particles, we evaluated the impacts of additional heat treatment of the catalysts in different atmospheres (inert gas, NH_3) and introduced pore-forming agents and metal (Zn, Mn) additives on the Fe-N-C morphology and performance. It was determined that heat treatment in NH_3 led to an increase of atomically dispersed Fe-N_x moiteis, while the pore-forming agents reduced the size of catalyst particles to 0.5 μm while keeping high surface area (> 800 m^2 g^{-1}) and porosity (Figure 3).

The introduction of Mn in combination with variation of synthesis parameters led to formation of surface area of 1400 m^2g^{-1} with pore volume of 1.0 cm^3g^{-1} and 300-400 nm primary particles. Integration of the Fe-Mn-N-C catalysts into the electrode structure showed that CCL consisted of grains with size from several to 20 μm, which were bounded together with ionomer and developed porous network penetrating the thick cathode catalyst layer (Figure 4).

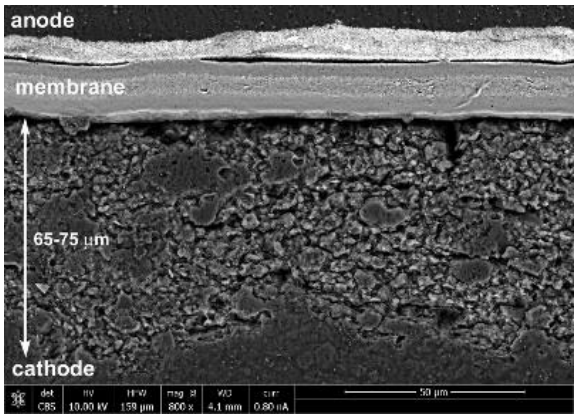

Figure 4. SEM image of MEA cross section.

Using Focus Ion Beam SEM method, it was determined that Fe-Mn-N-C catalyst layer were characterized by the highest porosity (19%) (Figure 5), which together with high hydrophobicity of the electrode improved water management and prevented flooding.

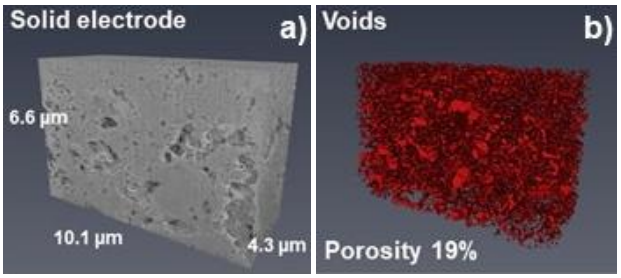

Figure 5. 3D reconstruction of solid electrode (a) and voids (b) for Fe-Mn-N-C.

Electrochemical evaluation of the membrane electrode assemblies showed exceptional proton conductivity and oxygen permeability of the Fe-Mn-N-C catalysts, which improved overall performance

of PGM-free fuel cells even with highly loaded and thick cathodes.

In order to understand the performance, we evaluated: 1) more than 150 MEAs and studied impacts of membrane types, membrane thickness, ionomer equvalent weight, and its loading in the cathode electrode (30-60%), 2) PGM-free catalyst content (0.5-6.0 mg cm^{-2}), and 3) electrode structure design. We developed testing protocols and procedures to obtaine full set of electrochemcial diagnistics of the MEAs.

The gained expertise and knowledge allowed us to improve the electrocatalyst and CCL design further and developed 5th generation of the material with performance approaching Pt-based MEAs (Figure 6). However, mass transport and durability of the PGM-free fuel cells still require further improvement and these are tasks for the future projects.

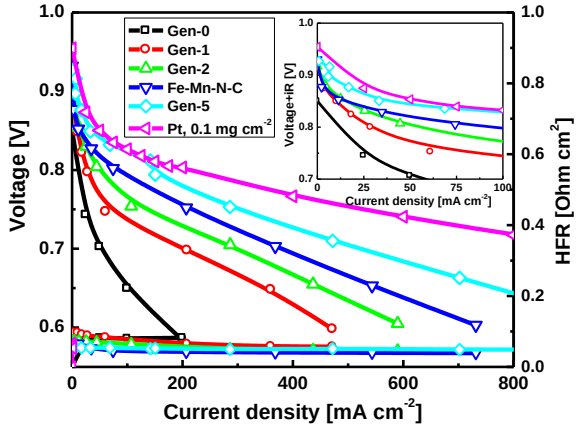

Figure 6. Polarization curves for different generation of PGM-free and Pt-based MEAs. An/Ca: H_2/O_2, 0.5 slpm, 100%RH, 150 kPa, T_{cell}=80°C.

This project produced a number of works, including the ones listed below:

- 2022, T. Reshetenko, et al., **Design of PGM-free cathodic catalyst layers for advanced PEM fuel cells**, Applied Catalysis B: Environmental, Vol. 312, Paper 121424.
- 2022, S. Akula, et al., **Mesoporous textured Fe-N-C electrocatalysts as highly efficient cathodes for proton exchange membrane fuel cells**, Journal of Power Sources, Vol. 520, Paper 230819.
- 2020, T. Reshetenko, et al., **Electron and proton conductivity of Fe-N-C cathodes for PEM fuel cells: A model-based electrochemical impedance spectroscopy measurement**, Electrochemistry Communications, Vol. 118, Paper 106795.
- 2020, T. Reshetenko, et al., **The Effect of Proton Conductivity of Fe–N–C–Based Cathode on PEM Fuel cell Performance**, Journal of the Electrochemical Society, Vol. 167, Issue 8, Paper 084501.
- 2020, T. Reshetenko, et al., **Effects of cathode proton conductivity on PGM-free PEM fuel cell performance**, Presented at the ECS 2020-02 Meeting, Honolulu, Hawai‘i, October 4-9, Abstract 2686.
- 2019, T. Reshetenko, et al., **Impedance Spectroscopy Characterization of PEM Fuel Cells with Fe-N-C-Based Cathodes**, Journal of the Electrochemical Society, Vol. 166, Issue 10, pp. F653-660.
- 2019, T. Reshetenko, et al., **Comprehensive Characterization of PGM-Free PEM Fuel Cells Using AC and DC Methods**, Presented at the ECS 2019-02 Meeting, Atlanta, Georgia, October 13-17, Abstract 1617.
- 2019, A. Serov, et al., **PGM-Free Oxygen Reduction Reaction Electrocatalyst: From the Design to Manufacturing**, Presented at the ECS 2019-01 Meeting, Dallas, Texas, May 26-30, Abstract 1487.

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