



Hawai'i Natural Energy Institute Research Highlights

Electrochemical Power Systems

PGM-Free Catalysts for PEM Fuel Cell Applications

OBJECTIVE AND SIGNIFICANCE: 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). Under this project, HNEI is developing highly active PGM-free catalysts and optimizing their incorporation into a fuel cell.

BACKGROUND: Today's PEMFC commercial energy generated systems are typically utilizing Pt-based catalysts for hydrogen oxidation and oxygen reduction reactions at anode and cathode, respectively. The substitution of oxygen reduction Pt catalysts by PGM-free materials delivers not only lower manufacturing cost (less than or equal to \$3/kW), but also ensures independence from Pt and other precious metal availability. In addition, application of PGM-free catalysts at the cathode provides tolerance to airborne contaminants (NO₂, SO₂), which typically seriously affect Pt-based PEMFC performance.

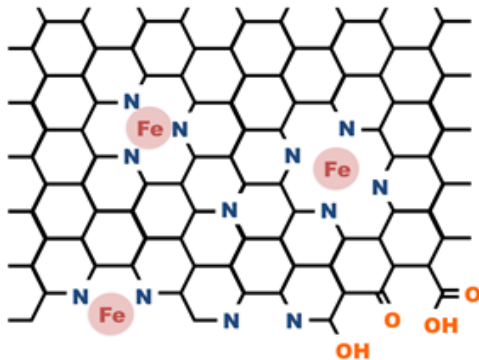


Figure 1. Schematic representation of PGM-free catalyst with Fe-N_x active sites. (2014, A. Serov, et al., *Advanced Energy Materials*, 4, 1301735).

PGM-free catalysts consist of non-precious transition metal (Fe, Co, Mn) coordinated by nitrogen inside a matrix of graphitic carbon 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) have underperformed compared to Pt based fuel cells. PGM-free fuel cell performance can be improved by designing and optimizing the cathodic catalyst layer (CL) 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). Studying the CL is complex due to the absence of well-established protocols of MEA activation and testing especially compared to Pt-containing catalysts. PGM-free fuel cell testing protocols need to optimize potentiostatic vs. galvanostatic measurements, scan rates, parameters of electrochemical impedance spectroscopy (EIS) and evaluation criteria.

Thus, the performance can be improved by synergistic efforts of materials design, fine tuning of the electrode layer and comprehensive electrochemical analysis.

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

PROJECT STATUS/RESULTS: Initiated in 2019, the project has produced several accomplishments.

Four generations of PGM-free electrocatalysts were synthesized using sacrificial support method and rationally selected precursors, conditions and treatments (Figure 2, on the following page). An application of high surface silica resulted in formation of several levels of catalysts porosity and led to 2nd catalyst generation.

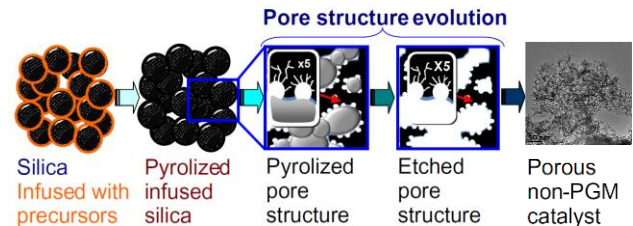


Figure 2. General schematic of used sacrificial support method for Fe-N-C catalyst synthesis.

3rd generation of the PGM-free catalysts was obtained by further catalyst treatment by NH₃ at elevated temperature. The chosen methodology led to formation of atomically dispersed Fe-N_x moieties and increase its amount due to creation of additional defects in carbon matrix (Figure 3). Raman spectroscopy demonstrated that materials maintains substantial level of graphitization.

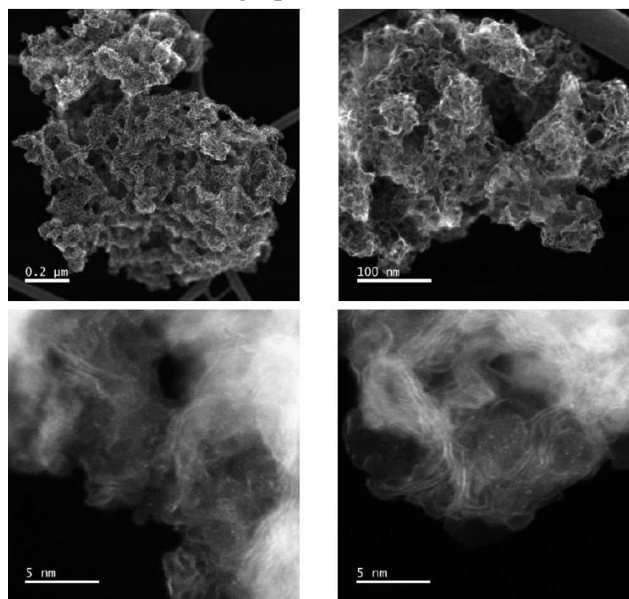


Figure 3. SEM and HRTEM images of 3rd generation of Fe-N-C catalysts (NH₃ treated).

PGM-free electrocatalysts are typically characterized by large primary catalyst particles with size higher than 1 μm, which affects where integration into the electrode structure and negatively impacted development of 3 phase boundaries and proton conductivity. In order to reduce their size additional pore-forming agents were introduced during catalyst synthesis and resulted to 4th generation of the PGM-free catalysts (Figure 4). The size of the primary catalyst particles decreased to 300-400 nm, while the catalysts surface area increased to 820 m² g⁻¹.

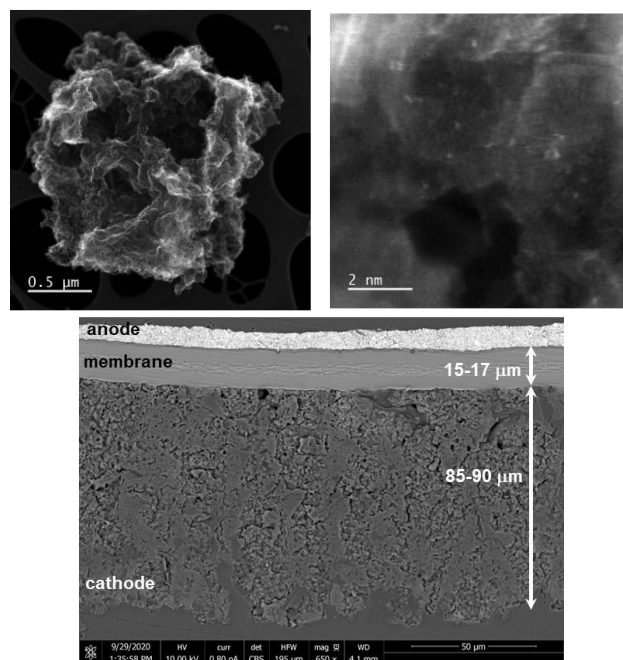


Figure 4. SEM and HRTEM images of 4th generation of Fe-N-C catalysts and MEA cross section. Atomically dispersed Fe-N_x centers are presented as bright dots at TEM images.

The electrocatalysts were successfully integrated into electrode structures. For understating effects of MEAs components on fuel cell performance, we evaluated the following parameters: membrane thickness (15-175 μm); ionomer type, ionomer equivalent weight (EW) and its loading in the cathode electrode (30-60%); PGM-free catalyst content (0.5-6.0 mg cm⁻²) and electrode structure design.

A testing protocol for PGM-free PEMFCs evaluation was established and included measurements of polarization curves from ocv to 0.6 V and from ocv to 0.2 V in forward and backward directions with simultaneous detection of HFR at 1kHz; electrochemical impedance spectroscopy (EIS) and cyclic voltammetry to obtain double layer capacitance and access MEAs integrity (lack of electrical short).

There were evaluated ~100 MEAs. The best results were obtained for membrane LYT 0009 with thickness of 18 μm, with PGM-free loading of 2-3 mg cm⁻², 40-45% ionomer loading with EW720. Figure 5 on the following page shows improvement in

performance of the different generations of PGM-free electrocatalysts in comparison with Pt based fuel cell.

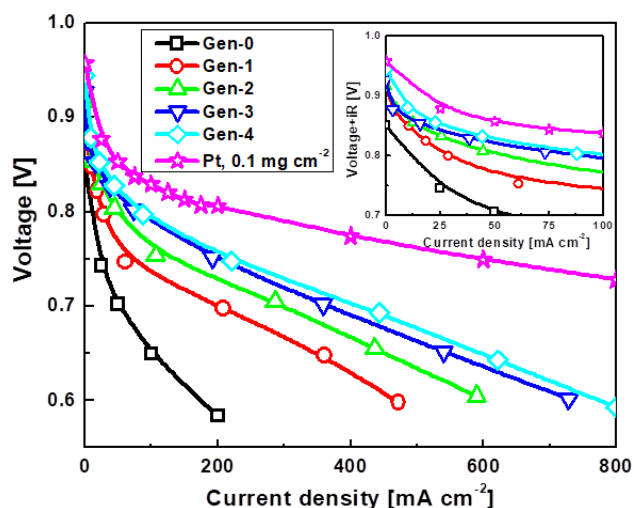


Figure 5. Polarization curves for different generation of PGM-free and Pt-based MEAs. An/Ca: H₂/O₂, 0.5 slpm, 100%RH, 150 kPa, T_{cell}=80°C.

Physic-based EIS models were adapted for fitting PGM-free impedance data and used to assess main kinetic (Tafel slope) and mass transport parameters (proton conductivity, O₂ diffusivity). New generation of the MEAs demonstrated that proton conductivity of the PGM-free cathode was improved significantly from 5-10 to 30-40 mS cm⁻¹ as well as O₂ diffusivity in the cathode structure. Moreover, the developed family of PGM-free electrocatalysts were determined to be highly selective towards 4 e⁻ oxygen reduction mechanism, which explains performance and efficiency of the catalysts. The team successfully passed intermediate milestone of 44 mA cm⁻² at 0.85 V and reached Go-no-Go target of 22-27 mA cm⁻² at 0.9 V.

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

- 2020, T. Reshетенko, 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. (Open Access: [PDF](#))
- 2020, T. Reshетенko, 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. (Open Access: [PDF](#))
- 2020, T. Reshетенko, 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. Reshетенko, 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. (Open Access: [PDF](#))
- 2019, T. Reshетенko, 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.

Funding Source: U.S. Department of Energy; Office of Naval Research; Energy Systems Development Special Fund

Contact: Tatyana Reshетенko, tatyanar@hawaii.edu

Last Updated: November 2021