Active and Durable Platinum-Group-Metal-Free Cathodic Electrocatalysts for Fuel Cell Application

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Subcontractors:
- IRD Fuel Cells, Albuquerque, NM
- Hawaii Natural Energy Institute (HNEI), Honolulu, HI

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Project End Date: December 31, 2021

Overall Objectives

- Develop platinum group metal (PGM)-free electrocatalysts for oxygen reduction reaction (ORR).
- Scale up the catalysts to 50 g batches (Pajarito Powder).
- Integrate PGM-free catalysts into the industrial state-of-the-art membrane electrode assemblies (MEAs) (IRD) and comprehensively evaluate by electrochemical methods (HNEI).
- Demonstrate fuel cell performance of 44 mA/cm^2 at 0.9 V (Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration [MYRDD] Plan conditions).

Fiscal Year (FY) 2019 Objectives

- Develop an activation protocol for testing Fe-N-C catalysts.
- Synthesize, characterize, and evaluate performance of two generations of Fe-N-C catalysts.
- Perform the integration of these catalysts into industrial quality MEAs.
- Accomplish two performance-based milestones (Milestone 1: 25 mA/cm^2 at 0.83 V and Milestone 2: 25 mA/cm^2 at 0.85 V) and the first go/no-go design point (25 mA/cm^2 at 0.9 V).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office MYRDD Plan[1]:

- Increase activity of PGM-free ORR catalysts
- Decrease cost of PGM-free catalyst manufacturing
- Increase the durability PGM-free catalysts.

Technical Targets

This project is devoted to synthesis of novel Fe-N-C catalysts with increased density of active sites, integration of these materials into industrial quality MEAs, and comprehensive electrochemical evaluation under DOE Electrocatalysis Consortium (ElectroCat) recommended protocols in order to achieve or exceed the following technical targets:

- Demonstrate 44 mA/cm^2 at 0.9 V (iR-free, H_2/O_2 configuration, 1 bar O_2, 80°C, 100% relative humidity [RH])
- Demonstrate performance in H_2/air at 0.8 V (the value is under discussion by the ElectroCat consortium).

FY 2019 Accomplishments

- The team synthesized 25 different catalysts on a batch level of 25 g.
- IRD manufactured more than 150 industrial quality MEAs on a 25-cm^2 form-factor.
- HNEI and Pajarito Powder established an activation protocol with minimal initial performance degradation.
- IRD initiated optimization of MEA fabrication with Gen-2 catalysts (ionomer/membrane type,

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

ionomer loading, catalyst coated membrane vs. CCS, hot pressing conditions, etc.)

- HNEI initiated comprehensive electrochemical analysis of Gen-2 MEAs manufactured by IRD.
- The team successfully exceeded a second milestone (Q2) of 25 mA/cm^2 at 0.85 V (MYRDD Plan recommended conditions). Actual I_d demonstrated is 32 mA/cm^2 at 0.85 V.

INTRODUCTION

PGM-free ORR electrocatalysts possess high intrinsic activity measured by a rotating disk electrode method [1]. However, under fuel cell operating conditions, PGM-free ORR electrocatalysts have underperformed compared to platinum catalysts. PGM-free ORR electrocatalysts' fuel cell performance can be improved by designing and optimizing the cathodic catalyst layer and MEA construction such that (1) it efficiently provides oxygen access to ORR active sites (through catalyst morphology control); (2) it removes water from the catalyst layer (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) [2–4].

Studying the catalyst layer is complex due to the absence of well-established protocols of MEA activation, especially compared to platinum-containing catalysts. PGM-free fuel cell testing protocols would need to optimize potentiostatic vs. galvanostatic measurements, scan rates, parameters of electrochemical impedance spectroscopy, and beginning of experiment criteria. To make the PGM-free catalyst's fuel cell performance comparable to platinum, the synergistic effort of materials design, fine tuning of the catalyst layer, and comprehensive electrochemical analysis is required.

APPROACH

This project aims to provide commercially viable PGM-free electrocatalysts as well as the world's first commercial supply of MEAs with PGM-free cathodes through multidisciplinary R&D efforts led by Pajarito Powder, LLC. Pajarito Power will synthesize M-N-C catalysts using a powerful manufacturing platform, VariPore. This method is based on controllable formation of catalytically active materials with interconnected pores using particle and pore formers, followed by their selective removal. Being industrially used for production of commercial PGM-free ORR catalysts, VariPore will produce electrocatalysts at 10–20 g scales with reproducible controllable physicochemical properties (surface area, level of graphitization, internal porosity, etc.).

For the first time, catalysts in this project will be supplied beyond bench scale, using a commercial manufacturing process qualified for producing quality and effective PGM-free ORR catalysts. With equal importance, a world-class MEA manufacturer, IRD, will perform the catalyst layer design and MEA manufacturing using its commercial fabrication technology and previously gained know-how on integration of PGM-free ORR catalysts into high-performing electrodes. The experienced comprehensive analysis of PGM-free catalysts performance performed by HNEI will be a guideline for Pajarito Powder and IRD on improving materials and electrode structures. Finally, by successful development of PGM-free ORR materials and optimized MEA structure, the team will achieve the fuel cell target performance and meet go/no-go requirements.

RESULTS

The first generation of Fe-N-C (with atomically dispersed Fe-N_x active sites) was integrated into a small area (5-cm^2) MEA using Pajarito's in-house robotic ultrasonic sprayer. The variable parameters were ionomer content: 45, 50, and 55 wt % of Nafion (equivalent weight = 1,100). The catalyst loading was selected according to the preliminary data obtained at Pajarito Power as 3 mg/cm^2, which provides measurable activity at high potentials (from open circuit voltage [OCV] to 0.8 V). The first series of MEAs with Nafion content of 50 wt % was evaluated in fuel cell tests at Pajarito Powder using different activation protocols. The activation protocols used were:

a. Fully humidified (100% RH) hydrogen and oxygen were supplied to the anode and cathode of the MEA during the cell warm-up from 25°C to 80°C, the backpressure was increased to the DOE recommended value (1 bar of O_2 partial pressure), and polarization curves were recorded under potentiostatic control from OCV down to 0.6 V (protocol was discussed during ElectroCat Workshop January 2019, Santa Fe, NM).

b. Fully humidified (100% RH) hydrogen and oxygen were supplied to the anode and cathode of the MEA during the cell warm-up from 25°C to 80°C, the cell was held at OCV for 12 h followed by increase of backpressure to 1 bar of O_2 partial pressure, and polarization curves were recorded under potentiostatic control from OCV down to 0.6 V.

c. The electrochemical cell was shorted to prevent OCV running during the warm-up procedure from 25°C to 80°C followed by backpressure adjustment and polarization curve recording as described in (a) and (b).

It was found that electrochemical performance and short-term durability are different under the above described activation protocols (data analyzed for activation (b) and (c); analysis of (a) will be done next reporting period). Figure 1 demonstrates fuel cell performance of 12 h OCV hold activation protocol in seven consecutive runs (as well as zoom-in kinetics part of polarization curve). The performances at milestone design points (voltage at 25 mA/cm^2 and 44 mA/cm^2) are reported in Table 1.

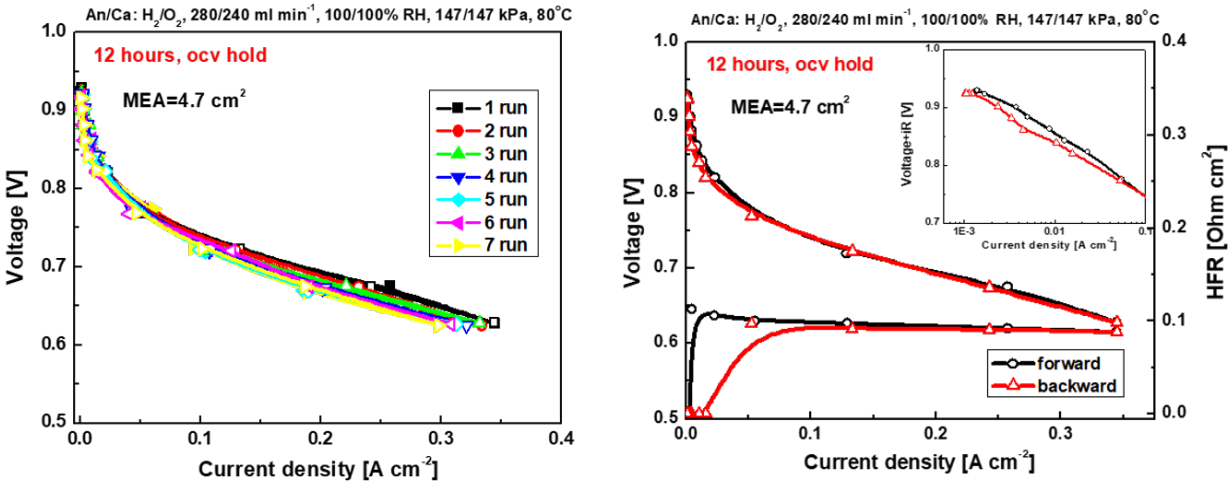

Figure 1. Performance of MEA activated by 12 hours OCV hold

Table 1. Performance Analysis of MEAs Activated by 12 h OCV Hold

Performance	1 IV run	2 IV run	3 IV run	4 IV run	5 IV run	6 IV run	7 IV run
U at 25 mA/cm^2 [V]	0.821	0.82	0.816	0.811	0.808	0.813	0.816
U at 44 mA/cm^2 [V]	0.794	0.796	0.793	0.783	0.782	0.791	0.795
I at 0.85 V [A/cm^2]	0.0115	0.0102	0.0094	0.0107	0.0087	0.0107	0.0109

It can be clearly seen that the voltage oscillates at 25 and 44 mA/cm^2 on level of measurement error bar. And despite the Milestone 1.3 performance (25 mA/cm^2 at 0.83 V) not being achieved, the performance degradation from the first to the seventh run was not observed, in contrast to previously reported experimental data. This activation protocol can be considered as promising if initial performance of catalyst will be improved (Task 2).

The results of the activation protocol based on the shorted cell are presented in Figure 2. The numerical analysis of performance is presented in Table 2.

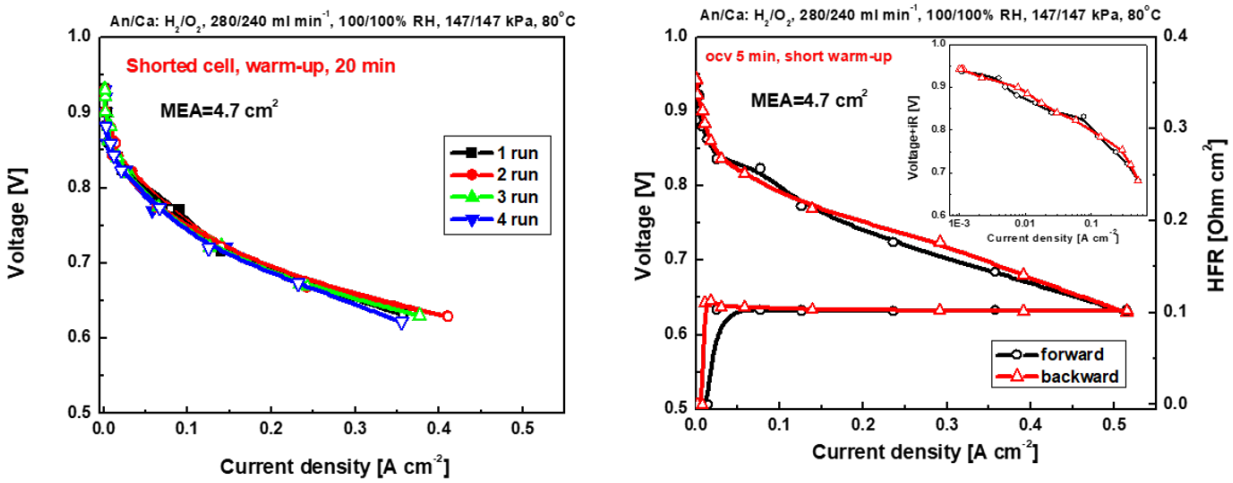

Figure 2. Performance of MEA activated by shorting the electrochemical cell

Table 2. Performance Analysis of MEAs Activated by Shorting the Electrochemical Cell

	1 IV run	2 IV run	3 IV run	4 IV run
U at 25 mA/cm² [V]	0.829	0.836	0.83	0.825
U at 44 mA/cm² [V]	0.813	0.815	0.805	0.8
I at 0.85 V [A/cm²]	0.014	0.0162	0.0129	0.0085

The team successfully accomplished Milestone 1, achieving 25 mA/cm^2 at 0.83 V. Further analysis is ongoing.

Pajarito Powder provided to IRD six PGM-free Fe-N-C based catalysts synthesized by VariPore method using different pore-forming agents. Silica particles with different surface area, particle size, aggregate size, and agglomeration size were used to improve accessibility of active sites. Surface area of materials was varied in the wide range from 450 to 750 m^2/g due to fine control of silica particles and ratio of silica to organic precursor. The precursor was pipemidic acid, which was previously identified as a promising agent for creation of porous carbon matrix with Fe-N_x centers.

Pajarito Powder and HNEI studied and compared the performance of six PGM-free MEA samples produced by IRD using an industrial mass-production digital printing method (using the six catalysts described above). IRD manufactured catalyst coated membranes with active area of 24 cm^2, anode Pt loading of 0.2 mg/cm^2, and PGM-free cathode loading of 3.0 mg/cm^2. Anode thickness was estimated to be ~8 μm, membrane thickness was 16 μm, and cathode thickness was found to be 95 μm.

To provide sufficient compression ratio of ~20%–25%, anode gasket thickness was chosen to be 0.006-in. (150–160 μm) while the cathode was 0.10-in. (250 μm). Pajarito Powder used gas diffusion layer H23C8 from Freudenberg and HNEI employed 25BC from Sigracet. MEAs were obtained by hot-pressing of gaskets, gas diffusion layers, and catalyst coated membranes at 140°C, 1,500–2,000 lb force for 3–5 min.

Activation protocol includes warming up the cell without gas flow to 80°C followed by anode and cathode purge by fully humidified H_2 and O_2 at 150 kPa backpressure and OCV conditions. Polarization curves were measured right after 10 min of H_2/O_2 purge. IVs were performed under voltage control mode from OCV to 0.6 V (five curves) and from OCV to 0.2 V (three curves). High-frequency resistance was measured simultaneously with polarization curves using a multichannel impedance spectroscopy tool at a frequency of 1 kHz.

Figure 3 shows IV curves recorded at HNEI and Pajarito Powder. HNEI testing results showed that the performance of the samples followed the order N2EZF > N2EWG > N2EYP > N2ETU > N2EXE = N2EXI. Pajarito Powder data demonstrated the following order: N2EZF > N2EWG = N2ETU > N2EYP > N2EXE > N2EXI. There is a negligible discrepancy between the HNEI and Pajarito Powder results, which could be explained by different gas diffusion layers and some variation in operating conditions. However, the data revealed the close trend in the performance.

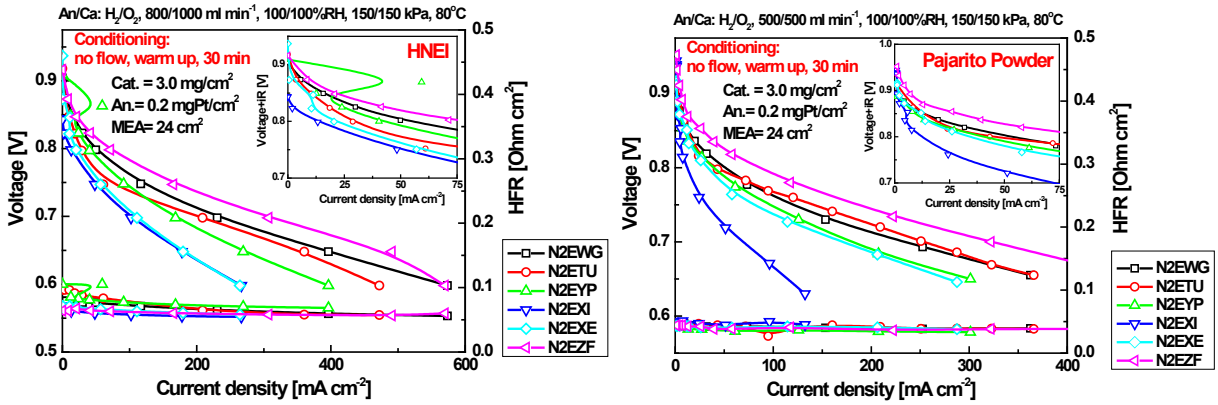

Figure 3. Polarization curves obtained at HNEI (left) and Pajarito Power (right)

HNEI also studied the effects of hot-pressing on the performance of the N2EZF and N2EYP samples (Figure 4). Interestingly, that performance of N2EZF-1 and N2EYP-1 (hot-pressed, HNEI) is very close to the Pajarito Power results. It should be noted that we observed a "bump" on the IV curve at low current density for the N2EYP-1 sample, the nature of which is unknown for us at this moment (Figure 4, right). N2EZF-2 and N2EYP-2 were assembled in the cell hardware without any hot-pressing of the components. It was found that the lack of a hot-pressing step in MEA assembling did not seriously affect N2EYP-2 performance, but we did not detect the "bump" on IV (Figure 4, right). In the case of N2EZF-2, we observed a decrease in the performance compared to the previous samples (Figure 4, left). The effect of hot-pressing is still not clear to us, and for the sake of consistency we intend to keep the hot-pressing step.

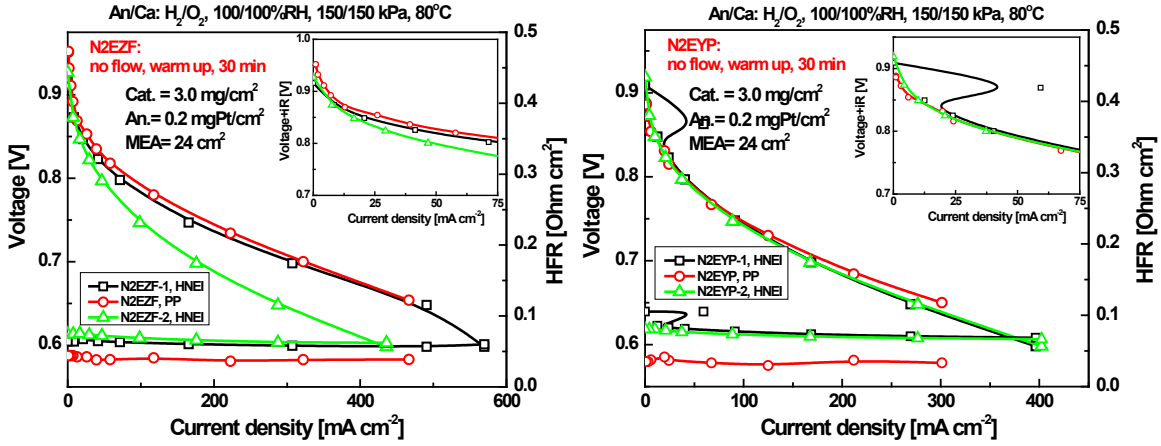

Figure 4. A comparison of the effects of MEA hot pressing on N2EZF and N2EYP samples

Such an excellent similarity in the performance trends independently measured at Pajarito and HNEI allows the team to avoid duplicating each other's effort and double the throughput of catalyst evaluation.

Pajarito Powder synthesized an additional six electrocatalysts using the method described above with a different organic precursor, nicarbazin, which has a high decomposition temperature. These catalysts are being

characterized at Pajarito. Simultaneously, IRD manufactured a series of MEAs with these catalysts, which were delivered on July 25, 2019 to HNEI and Pajarito. MEAs are under evaluation.

CONCLUSIONS AND UPCOMING ACTIVITIES

The team successfully synthesized 25 different catalysts on a batch level of 25 g. These catalysts were integrated into more than 150 industrial quality MEAs by IRD on 25-cm^2 form-factor. The team successfully exceeded the project's first and second milestones (Q1 and Q2) of 25 mA/cm^2 at 0.83 V and 0.85 V, respectively (MYRDD recommended conditions). Actual I_d demonstrated for the second milestone is 32 mA/cm^2 at 0.85 V. A set of industrial Gen-2 MEAs will be electrochemically evaluated at IRD, Pajarito Powder, and HNEI. Pajarito Powder is optimizing synthesis conditions on the best-performing Fe-N-C catalysts. A non-disclosure agreement with ElectroCat is being reviewed and will be signed by mid-August. Pajarito Powder initiated contacts on evaluation of the best-performing catalysts by high-resolution transmission electron microscopy (Oak Ridge National Laboratory), catalyst layer (National Renewable Energy Laboratory), and molecular probing (Los Alamos National Laboratory) experiments.

FY 2019 PUBLICATIONS/PRESENTATIONS

Publications

1. C.L. Vecchio, A. Serov, H. Romero, A. Lubers, B. Zulevi, A.S. Aricò, and V. Baglio, "Commercial Platinum Group Metal-Free Cathodic Electrocatalysts for Highly Performed Direct Methanol Fuel Cell Applications," *J. Power Sources* 437 (2019): 226948.
2. T. Reshetenko, A. Serov, A. Kulikovsky, and P. Atanassov, "Impedance Spectroscopy Characterization of PEM Fuel Cells with Fe-NC-Based Cathodes," *J. Electrochemical Society* 166 (2019): F653–F660.

Presentations

1. A. **Serov**, G. McCool, H. Romero, S. McKinney, A. Lubers, M. Odgaard, T.V. Reshetenko, and B. Zulevi, "PGM-Free Oxygen Reduction Reaction Electrocatalyst: From the Design to Manufacturing," ECS Meeting 235, Dallas, TX, 2019.
2. A. Serov, G. McCool, H. Romero, S. McKinney, A. Lubers, M. Odgaard, T.V. Reshetenko, and B. Zulevi, "Are PGM-free Catalysts Ready for the Prime Time?" Invited: EFCD 2019, La Grande Motte, France, 2019.
3. A. Serov, G. McCool, H. Romero, S. McKinney, A. Lubers, M. Odgaard, T.V. Reshetenko, and B. Zulevi, "VariPore: A Powerful Manufacturing Platform for Fuel Cell and Electrolyzer Applications," ECS Meeting 236, Atlanta, GA, 2019.
4. T. Reshetenko, A. Serov, A. Kulikovsky, and P. Atanassov, "Comprehensive Characterization of PGM-Free PEM Fuel Cells Using AC and DC Methods," ECS Meeting 236, Atlanta, GA, 2019.

REFERENCES

1. 2020 technical performance and durability targets listed in Table 3.4.5 of the Fuel Cells MYRDD:
2. http://energy.gov/sites/prod/files/2016/06/f32/fcto_myrdd_fuel_cells_0.pdf.
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4. S.T. Thompson, A.R. Wilson, P. Zelenay, D.J. Myers, K.L. More, K.C. Neyerlin, and D. Papageorgopoulos, "ElectroCat: DOE's Approach to PGM-Free Catalyst and Electrode R&D," *Solid State Ionics* 319 (2018): 68–76.
5. A. Serov, A.D. Shum, X. Xiao, V. De Andrade, K. Artyushkova, I.V. Zenyuk, and P. Atanassov, "Nano-Structured Platinum Group Metal-Free Catalysts and Their Integration in Fuel Cell Electrode Architectures," *Applied Catalysis B: Environmental* (2017), https://doi.org/j.apcatb.2017.08.067.