V.A.3 Innovative Non-PGM Catalysts for High-Temperature PEMFCs

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- Dr. Barr Halevi, Pajarito Powder, LLC, Albuquerque, NM

Other Partners:
- Dr. Emory De Castro, Advent Technologies Inc., Cambridge, MA, Industry, Special Materials Supplier
- Dr. Ludwig Lipp, eT2M, Danbury, CT, Industry, T2M Research Vendor

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Project End Date: December 31, 2017

Overall Objectives

This objective of this project is to revolutionize high-temperature proton exchange membrane fuel cell (PEMFC) technology based on polymer membranes imbibed with phosphoric acid through development of stable, high-performance non-precious cathode catalysts. High-temperature PEMFCs operate in a range of 150–220°C, making them ideal candidates for combined heat and power applications. This incubator effort is however exclusively focused on catalyst development for H_3PO_4-imbibed PEMFCs.

The principle objectives of this effort are:

- Develop non-platinum group metal (PGM) catalysts based on a metal-organic framework (MOF) with unique iron–nitrogen–carbon active sites that are immune to anion poisoning. Elimination of Pt from the cathode would lower total Pt loading from the current state of the art of 3 mg/cm^2 to less than 1.5 mg/cm^2, thereby halving the cost of the catalyst in the membrane electrode assembly (MEA). These catalysts will be scaled up from the ~1 g laboratory level to 100 g batch size.
- Develop unique corrosion resistant support structures for enhanced corrosion resistance as compared to conventional carbon-based supports.
- Provide enhanced mass transport within the reaction layer and gas diffusion layer using a combination of modeling and experiments for obtaining mass transport parameters designed to enable systematic formulation of the gas diffusion and reaction layers.
- Prepare MEAs and perform fuel cell testing using test conditions designed to experimentally obtain mass transport parameters. Perform durability testing relevant to stationary fuel cells. This project aims to meet and exceed the current PGM-based high temperature polymer electrolyte membrane MEA metrics of 200 mA/cm^2 in H_2/air, 0.65 V with 2.5 bar total pressure at 180°C.
- Perform economic analysis of the fuel cell system to determine market segments for deployment.

Technical Barriers

Cost is the primary barrier preventing membrane imbibed phosphoric acid (PA) fuel cells and similar systems from reaching commercial reality, with noble metal loading representing a significant cost component. Cost of noble metals in current state-of-the-art membrane-based PA systems is approximately $800–1,000/kW. Our goal is to bring this cost to below $500/kW. Durability limitations due to carbon corrosion also represent a major barrier to commercialization. This project will address both of these issues, thereby enabling commercialization of membrane imbibed PA fuel cells on an accelerated schedule.

Technical Targets

The technical targets for the second year of this project are listed in Table 1 with status towards these milestones given below.

- Fifth quarter (Q5) target: demonstration of chronopotentiometric durability testing @ 650mV (air, 2.5 bar) showing less than 5% losses in activity for 24–48 h.
  - Target Achieved at NEU using both NEU MOF and Pajarito PMF-2010 catalyst. PMF-2010 data shown later in this report.
- Sixth quarter (Q6) target: demonstration of corrosion resistance durability at OCP (air, 2.5 bar), showing less than 3% losses in activity for 3 h.

TABLE 1. Milestone Summary Table

Task Title	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process	Anticipated Quarter
Durability Studies	Durability testing on scaled up samples based on reactive ball milling (30–50 g batch). The sequence will include reactive ball-milled materials.	MEA performance of 200 mA/cm^2 at 0.6 V, H_2/air, 180°C, 2.5 bar total pressure. Chronoamperometric testing at 0.8 V (H_2/air) 2.5 bar total pressure (180°C) with 5% loss in activity for 24 h and 48 h.	Q5
Durability Studies	Corrosion testing of SSM-based materials.	Open circuit test on SSM-based materials at 180°C, H_2/air	Q6
Final Down Select	Down select of scaled up integrated material containing FE-MOF-based active site, SSM-based microporous layer incorporated on GDL structures.	Achieving H_2/air performance target of 200 mA/cm^2 at 0.65 V, 180°C, 2.5 bar pressure.	Q7
Fuel Cell Test Validation	Fuel cell test validation with 100 cm^2 MEA using PA-imbibed membrane and non-PGM cathode catalyst.	Achieving H_2/air performance target of 200 mA/cm^2 at 0.65 V, 180°C, 2.5 bar total pressure	Q8

SSM – sacrificial support method

  - Target Achieved at NEU using both NEU MOF and Pajarito PMF-2010 catalyst. PMF-2010 data shown later in this report.
- Seventh quarter (Q7) target: (July–September 2017): catalyst downselect, showing performance of 200 mA/cm^2 at 650 mV (air, 2 bar).
  - Currently 25 mV shy of target (data shown in this report). However, PMF-2010 material is currently being sieved for particle size uniformity, which should allow for enhanced transport and higher subsequent performance.
- Eighth quarter (Q8) target: (October–December 2017): scale-up to larger MEAs, tested at NEU (45 cm^2) while maintaining Q7 performance. Preliminary testing (shown in this report) demonstrates no performance losses as electrodes are increased from 5 cm^2 to 45 cm^2.
  - Currently 25 mV shy of target (data shown in this report).

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INTRODUCTION

New materials tested at NEU have demonstrated higher performance than acquired during the first year of the project leading up to a successful go/no-go decision point. Additionally, these materials have shown themselves to be very stable under multiple durability protocols. This includes both chronopotentiometric measurements as well as a protocol designed to facilitate carbon corrosion. Subsequently, the catalyst in question (described later) has been chosen to be the material of choice going forward (catalyst downselect), and variants on it will be the focus of the remaining portion of the project.

APPROACH

All of the data in this report focuses on a new catalyst from Pajarito Powder, hereon referred to as PMF-2010 (referred to in previous reports as NPC-2010). It demonstrated higher single-cell performance than the MOF-based materials (both the NEU solution reaction as well as the Pajarito Powder solid state reaction) and the other UNM materials tested throughout this project, and therefore has been chosen as the material going forward, as was directed in the Q7 target metric (catalyst downselect).

In general, it is a catalyst based off of the technology that was used for the development of an earlier catalyst. More specifically, the PMF-2010 is a precious metal free oxidiation reduction reaction catalyst designed for stability and is made using Pajarito's VariPore process. The VariPore process is based on a combination of licensed (UNM) and internally developed intellectual property and allows for intrinsic control of pore size, a critical catalyst characteristic for improved performance. The catalyst was developed out of a UNM/automotive original equipment manufacturer project, using know-how evolved over four years of PGM-free development, and further developed by Pajarito for high-temperature polymer electrolye membrane operations in consultation with Advent Technologies.

RESULTS

At the time of the last annual report, NEU testing on the MOF catalyst was roughly 50 mV shy of the air performance metric (200 mA/cm^2 at 650 mV in air, 2.5 bar). Additionally, a UNM IMID catalyst had been tested offsite at the University of South Carolina and had achieved the necessary performance metrics. Since then, Pajarito Powder has a newly developed catalyst prepared through their silica support method that has far outperformed the other materials in this project to date. Single-cell 5 cm^2 MEA performance in oxygen is shown below in Figure 1a (associated Tafel plot in

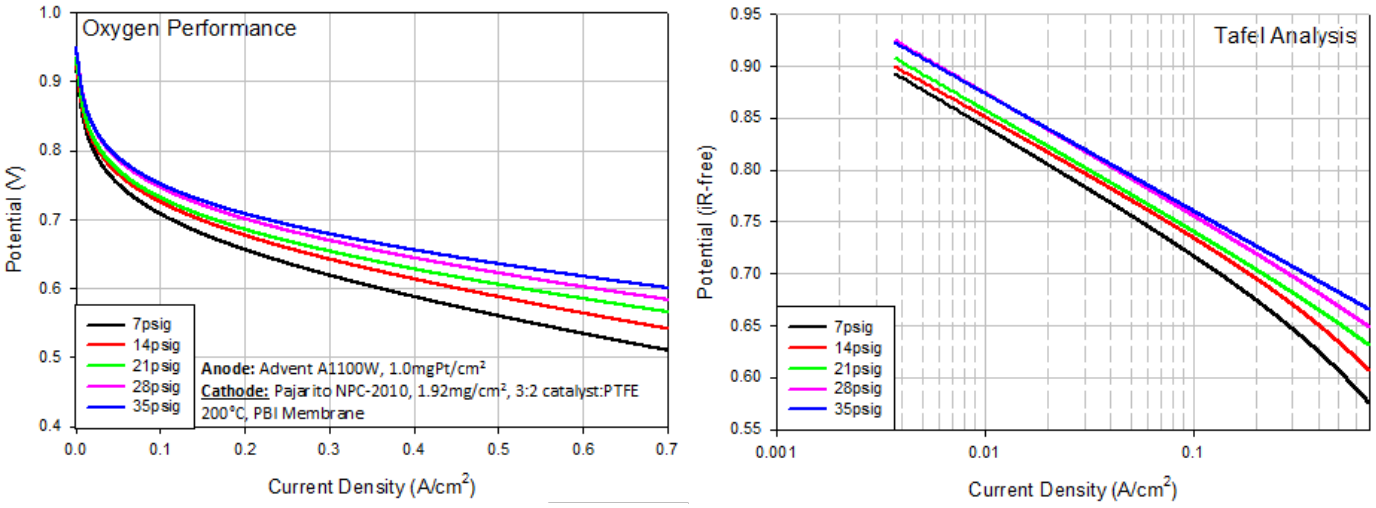

FIGURE 1. (a) Oxygen performance of Pajarito PMF-2010 as a function of applied backpressure, 5 cm^2, (b) oxygen performance of Pajarito PMF-2010 as a function of applied backpressure, 5 cm^2, Tafel analysis

Figure 1b), while performance in air is shown in Figure 2, all figures as a function of applied backpressure.

As can be seen in Figure 1a, the oxygen performance reached 710 mV at 100 mA/cm^2 at 7 psig (1.5 bara), well exceeding the target of 100 mA/cm^2 at 700mV. In addition, in air, the performance achieves 200 mA/cm^2 at 625 mV at 21 psig (2.5 bara), far elapsing the established target of 200 mA/cm^2 at 600 mV. This represents the best single-cell performance to date of any material tested over the course of this project. While this initial performance is very good, it is also key to demonstrate stability over the numerous metrics established for this work. The first of two methods that were previously established was chronopotentiometric measurements in air at 2.5 bar, where less than 5% losses in activity need to be observed over the course of 24–48 h. The second metric is to show less than 3% losses during a protocol meant to accelerate the effects of carbon corrosion. Therefore, the cell is held at its open circuit potential for 3 h in air at 2.5 bar. Figures 3 and 4 demonstrate the results of these experiments.

As is evident in Figures 3 and 4, regardless of which of the testing protocols was implemented, the catalyst performance was not altered, demonstrating that the PMF-2010 catalyst was incredibly stable. Additional durability protocols will be used in future experiments, including a temperature cycling procedure that would simulate a startup/shutdown protocol typical of a stationary power generation unit. Also, experiments are in progress to more intricately study the performance of this particular catalyst as a function of operating temperature, which could potentially allow for the operating temperature to be reduced from the current 200°C. It is expected that the higher temperature would generally correspond to a higher performance. However, the higher temperature should theoretically result in less long-

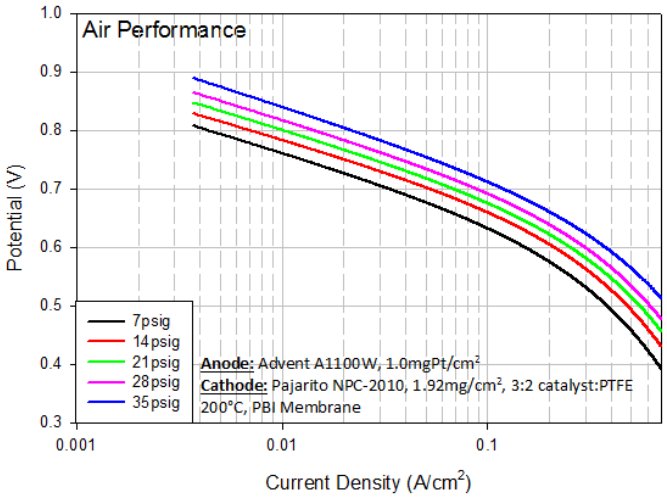

FIGURE 2. Air performance of Pajarito PMF-2010 as a function of applied backpressure, 5 cm^2, Tafel analysis

term stability, as the operating temperature of 200°C is close (<10°C) from a temperature at which the PBI membrane will start to degrade. Additionally, the higher temperature should further increase the carbon corrosion. This was largely the reasoning behind the initial target cell temperature of 160°C. Given that the catalyst is not showing any signs of degradation during the implemented protocol, it is reasonable to run the cell at a higher temperature in order to take advantage of the higher cell performance.

Often, scaling up in the electrode will cause a small drop in performance. Therefore, in an effort to predict the losses that might occur while achieving the Q8 metric (200 mA/cm^2 at 650 mV), preliminary studies were done to scale the electrode size from the above-used 5 cm^2 single-cells to

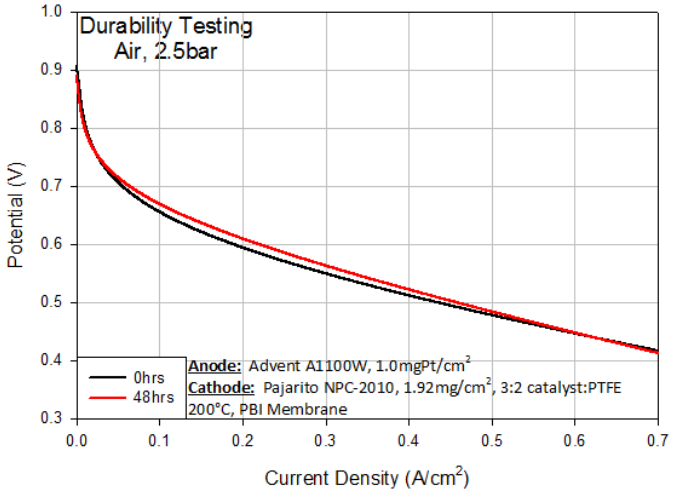

FIGURE 3. Chronopotentiometric durability in air at 2.5 bar, 48 h, 5 cm^2

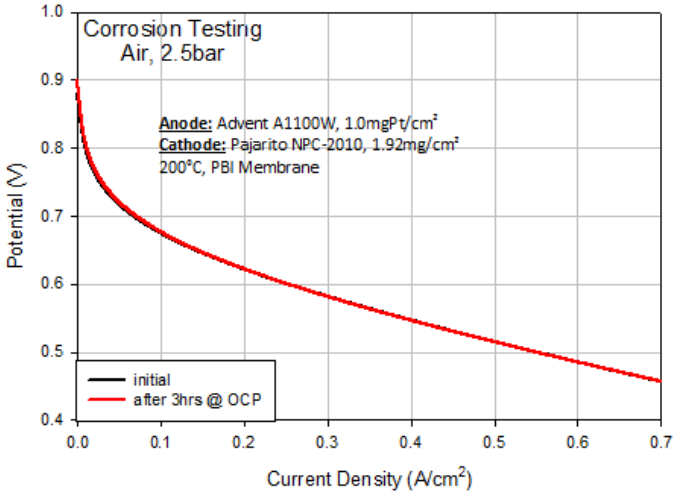

FIGURE 4. Corrosion Resistance durability in air at 2.5 bar, 3 h, 5 cm^2

45 cm^2 single-cells. Figure 5 demonstrates the results of these experiments.

From Figure 5, it is clear that the 5 cm^2 and 45 cm^2 MEAs performed at the same level. This is encouraging in that it is no longer anticipated that there will be performance losses when trying to reach the Q8 target from the Q7 metric. Therefore, in addition to the single-cell 5 cm^2 performance only being 25 mV from the Q7 target, the single-cell 45cm^2 performance is also only 25 mV from the Q8 target.

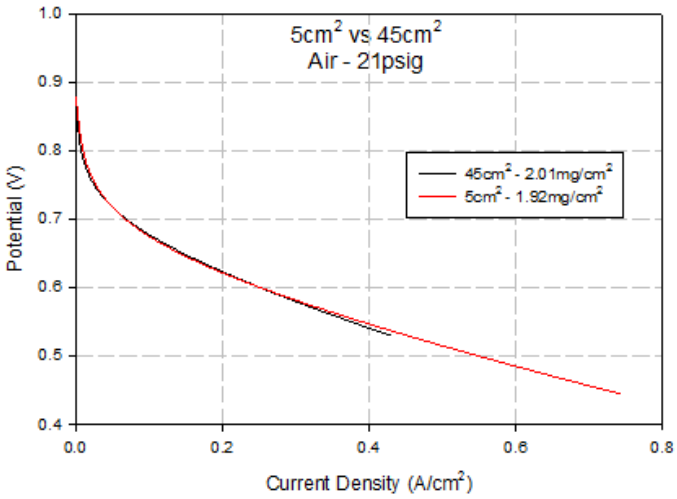

FIGURE 5. Comparison of 5 cm^2 and 45 cm^2 single-cell performance, air, 2.5 bar

CONCLUSIONS AND UPCOMING ACTIVITIES

The data shown demonstrates that the PMF-2010 catalyst from Pajarito Powder has achieved all single-cell performance metrics that were established for the first year of the project, including surpassing the go/no-go target. Additionally, it satisfies both durability metrics set forth as the Q5 and Q6 targets. It stands 25 mV shy of achieving both the Q7 target (end of September, catalyst downselect) as well as the Q8 target (end of December, 45 cm^2 scale-up).

At this time, the pathway by which the remaining 25 mV can be gained is through electrode modifications in order to optimize the gas transport through the gas diffusion electrode. Along these lines, two processes are currently being investigated. First, sieving of the catalyst is being done. Previously, Advent Technologies determined on its platinum-based systems that catalyst powders should be sieved in order to achieve particular particle size distributions, which allows for optimal gas and mass transport. All of the work shown above was done with an unsieved catalyst material. Therefore, Pajarito Powder is currently sieving an identical material, and this material will be tested at NEU. The second method that is being undertaken is to alter the particle size distribution of the initial catalyst itself. Pajarito has already prepared a variant on the PMF-2010 that incorporates a smaller particle size, which will be tested at NEU once provided. They are also working on a larger particle size material, which will also subsequently be tested at NEU. It is anticipated that between particle size optimization of the catalyst and optimization of the particle size distribution through sieving, that the final 25 mV could be gained to successfully meet the Q7 and subsequently the Q8 final metrics.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Use of Hybrid Cathodes to Reduce Platinum Content in High Temperature PEMFCs (Ryan Pavlicek, Kara Strickland, Sanjeev Mukerjee), presentation at the 229th Meeting of the Electrochemical Society (June 1, 2016; San Diego, CA).

2. Evaluation of the Durability of a Metal-Organic Framework Catalyst in High-Temperature Proton Exchange Membrane Fuel Cells (HT-PEMFCs) (Todd Miller, Ryan Pavlicek, Sanjeev Mukerjee), presentation at the 231st Meeting of the Electrochemical Society (May 31, 2017; New Orleans, LA).