

## II.B.3 High Performance Platinum Group Metal Free Membrane Electrode Assemblies through Control of Interfacial Processes

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### Subcontractors:

- The Pennsylvania State University, College Park, PA
- University of New Mexico, Albuquerque, NM
- Northeastern University, Boston, MA

Project Start Date: May 1, 2015

Project End Date: April 30, 2017

### Overall Objectives

- Evaluate non-platinum group metal (PGM) catalysts as gas diffusion electrodes (GDEs) in half cells.
- Evaluate most promising non-PGM GDEs in full-cell anion exchange membrane (AEM) water electrolysis configuration against PGM counter electrode.
- Further the fundamental understanding of non-PGM active sites and reaction mechanisms.
- Demonstrate translation from solution testing to solid electrolyte interface.
- Conduct assessment of ex situ and in situ stability comparisons to connect ex situ lab evaluation and in situ device results.
- Improve membrane and ionomer durability vs. current commercial options.
- Optimize water management through improved flow field and gas diffusion layer design.
- Fabricate full-scale membranes and ionomer solution for electrolyzer testing.
- Identify most promising non-PGM GDEs for full-cell operation and test PGM-free membrane electrode assembly (MEA) for durability (500 mA/cm<sup>2</sup> for up to 500 h).

### Fiscal Year (FY) 2017 Objectives

- Show durability of down-selected, scale-up batch of non-PGM catalysts for >500 h.
- Further the fundamental understanding of non-PGM active sites and reaction mechanisms using synchrotron based in situ spectroscopy.
- Perform in situ operational testing of new reinforced membranes with increased chemical and mechanical degradation resilience.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(F) Capital Cost

### Technical Targets

This project is working to establish a new cost curve for water electrolysis through elimination of the highest cost materials in the cell stack, such as platinum group metals (PGMs) and valve metals such as titanium. While electrolysis still has significant needs in manufacturing in order to reach 2020 targets and beyond, the end cost will be largely dependent on raw material costs. In the long term, non-PGM catalysts for the hydrogen and oxygen evolution reactions are needed. The current program aims at meeting the following targets.

- PGM content: none
- Cell voltage: <2 V
- Cell current: 500 mA/cm<sup>2</sup>
- Durability: 500 h of stable operation

### FY 2017 Accomplishments

- Completed an evaluation of best method for supplying feed water to the stack during electrolysis operation.
- Integrated catalysts from program partners with AEM materials for a full non-PGM MEA.
- Scaled up batches of non-PGM catalysts to 15 g quantities and delivered to Proton.
- Successfully operated a full non-PGM stack at <2 V and 500 mA/cm<sup>2</sup>.

- Initiated interfacial studies to elucidate the effects of catalyst, ionomer, and carbonate interactions.



## INTRODUCTION

Water electrolysis powered by wind or solar can provide a renewable source of hydrogen fuel for fuel cell vehicles. The DOE cost goals for the production of renewable hydrogen are aggressively set to compete with existing fossil fuel-based infrastructure. Fuel cells and electrolyzers based on proton exchange membranes are well-known and continue to realize reductions in cost and improvements in performance. To meet DOE goals for hydrogen production, and for growing energy markets, reductions in capital and operating costs are needed in order to justify electrolysis as a solution.

To date, the only pathway with promise to achieve platinum group metal (PGM)-free electrode formulations in membrane-based electrolysis cells is utilization of AEMs. The basic local environment of the membrane allows a range of stable transition metals and metal oxides to be utilized at high potential for catalysis. AEMs also enable the use of much less expensive flow field materials other than the titanium often used in polymer exchange membrane systems. At the same time, the solid-state electrolyte eliminates the need for corrosive liquid electrolytes such as concentrated potassium hydroxide and allows leveraging of high-performance MEA technology. Proton and team members Northeastern University and Penn State University have been exploring this technology since 2010 through an Advanced Research Projects Agency - Energy project in the GRIDS program and have made significant progress in understanding the limitations and potential of this AEM chemistry.

## APPROACH

In the first year, project focus will be on catalyst synthesis and activity screening. Hydrogen evolution reaction catalysts will be based on Ni-Mo nanoparticles and other mixed oxides, while oxygen evolution reaction catalysts will focus on ternary catalysts based on Ni, Fe, Co, and Mo. A sacrificial support method will be used to synthesize novel catalyst materials in high surface area format. Electrochemical characterization will be used to down-select materials with appropriate physical parameters for in cell testing. In parallel, polymers based on polyphenylene oxide will be synthesized for use in ionomer solutions and membrane materials to look for higher membrane and ionomer stability than incumbent polymer materials. Gas diffusion layer (GDL) materials and flow field designs will be optimized for AEM electrolysis performance and incorporated into the cell stack. Materials selection, as well

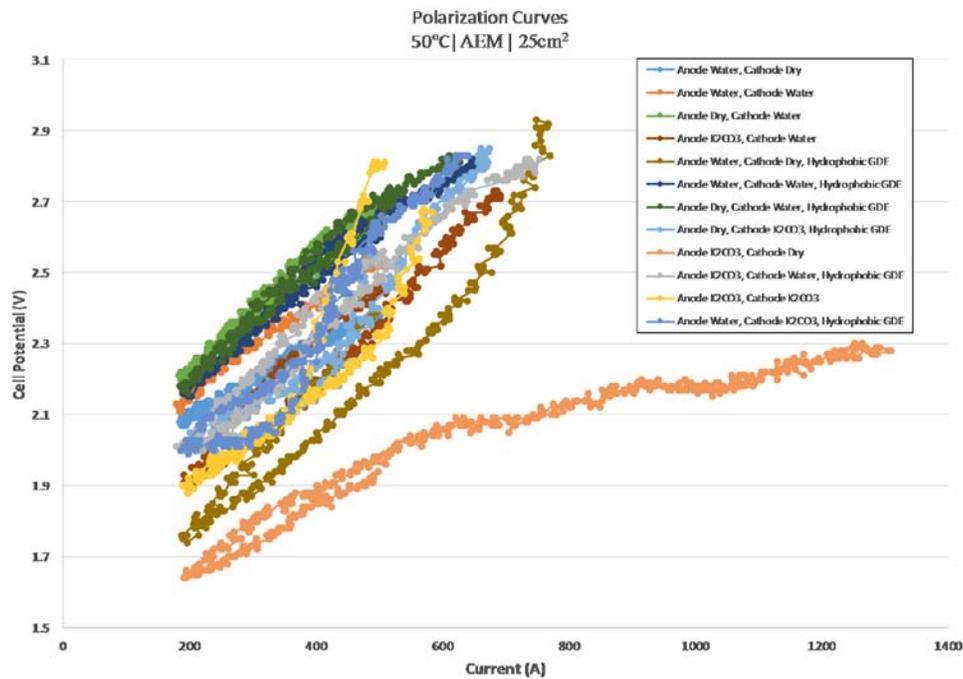
as application methods for coatings, will be examined for controlling the hydrophobicity and hydrophilicity of the GDL materials.

In Year 2, results from the first year will be leveraged to optimize the GDE interface, including treatments for improved water management. Additional characterization methods will be used to study the structure activity relationships of the non-PGM catalysts, to understand catalyst-ionomer interactions. The best performing catalysts based on the sacrificial support method approach will be scaled up to 10–25 g batches. On the membrane task, cation spacer polymers will be explored based on 5–10 times greater hydroxide stability vs. the side chain benzyl-linked cation materials. System architectures will be determined for optimum performance, and a test system will be built with capability for anode water feed, cathode water feed, or both. A water transport cell will also be fabricated to help understand flow characteristics as a function of membrane type, GDL, and operating conditions. Focus in cell testing will be on longer term durability testing, once initial performance targets have been met.

## RESULTS

The newly commissioned AEM test stand was used to evaluate numerous operational modes to identify the system configuration that would support the most stable operation and electrical efficiency. Fixed inputs were the A201 Tokuyama membrane used, AS-4 ionomer, and baseline PGM catalysts. The cells were rebuilt for each test using new components all cut from the same sheet stock to minimize variations due to the material and manufacturing variability. Inputs that were flexed during the test focused on supplying water to either the cathode, anode, or both simultaneously. We also looked at the use of hydrophobic and hydrophilic GDEs to evaluate the water management at the electrode and membrane interface, as well as introducing carbonate into the water feed to improve conduction with the membrane and electrode structure. Polarization data from this test is included in Figure 1.

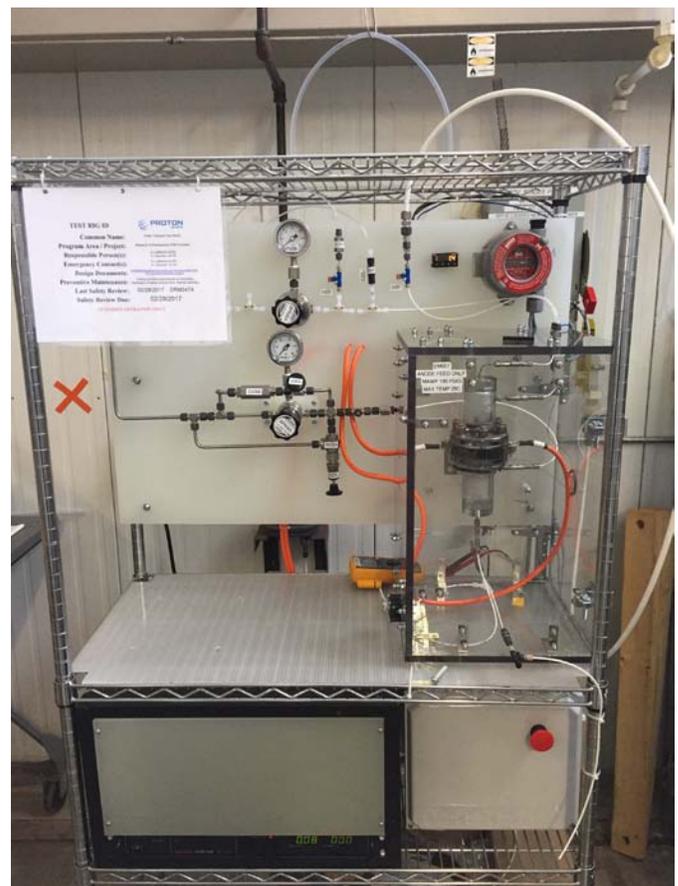
Since the alkaline water electrolysis cell consumes water at the cathode, prior to testing it was expected that the cathode fed configurations would produce the greatest stability and highest performance. Interestingly, this was not the case. Most of the configurations showed very poor performance when water was directly fed to the cathode, both with carbonate and without. Similarly, the inclusion of hydrophobic GDEs did not improve cell efficiency. The configuration that showed the lowest cell potential, while enabling operational current densities up to 1,300 mA/cm<sup>2</sup>, was the anode fed, carbonate water feed. This mode of operation had been the predominant configuration during AEM testing under this program and will be the selected configuration for the program final durability test.



**FIGURE 1.** Operational mode evaluation polarization data collected at 50°C

The mechanical and electrical sections of the water transport fixture were completed and the system passed Proton’s internal safety review. All components for the vessel were received and were assembled to verify against the model. All parts were made of clear polycarbonate to visualize the water flux and transport across the membrane surface during the various planned tests with alternative membrane samples and GDLs, as work continues to improve upon cell design, stability, and performance. The manufactured parts were machined, annealed, and vapor polished to produce endcaps capable of an operating pressure of 200 psi. Hydrostatic testing is conducted at 1.5x the operating point to meet industry standards for electrolysis. Hydrostatic testing was completed successfully and the vessel was installed into the system and operational verification was performed. An image of the fully built system is shown in Figure 2.

To increase membrane robustness, supported membranes were fabricated at Penn State for testing at Proton OnSite. Most samples were produced with Nylon, but polyether ether ketone and poly-tetrafluoroethylene meshes were also trialed. The addition of the mesh was intended to increase the mechanical properties of BTMA40 baseline membranes that have been tested extensively to measure degradation. In initial tests, the mechanical properties of the membranes were markedly improved with the addition of a support. Preliminary cell testing has demonstrated less cracking and mechanical degradation in the supported samples. In addition, overall life was improved under steady-state operation. Earlier non-reinforced samples tested from Penn



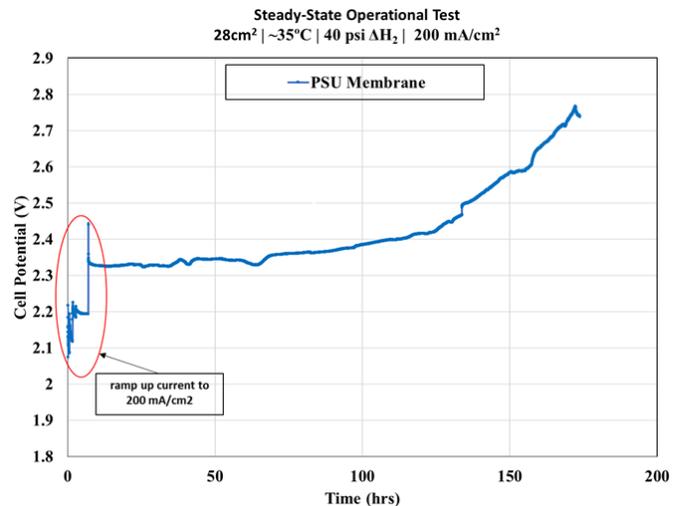
**FIGURE 2.** Image of water transport system and installed vessel

State had only demonstrated several hours of life before mechanical failure. Procedurally, one test was operated in deionized water and then removed for analysis and then similarly, a following test was prepared with an identical piece of the reinforced membrane and operated with the carbonate electrolyte. The samples were operated with PGM catalysts in both the cathode and anode electrodes. Both samples achieved 17 h of operation with no obvious signs of failure. The tests were halted at this point, membranes were visually inspected, and were returned to Penn State for instrumental analysis. A follow-up test was assembled and placed on test for steady-state operational testing to assess the length of time the sample would operate under in carbonate before failure. As shown in Figure 3, the cell operated for >150 h before the voltage had increased to the point where the upper shutdown limit of 2.8 V was reached. It should be noted that the cell did not fail mechanically. Upon test completion, the cell was disassembled and returned to Penn State for post operational analysis. This test represents the longest operational test at Proton of the membrane developed by Penn State demonstrating the significant improvements realized over the course of the program.

The final durability test stack was assembled as a three-cell 28 cm<sup>2</sup> stack; a manufacturing issue identified early in the test required removal of one of the cells and the stack was operated as a two-cell stack. The configuration leveraged improvements in cell design to manage the thinner AEM materials available. The test was operated at 50°C, 50 psi hydrogen generation pressure, 500 mA/cm<sup>2</sup>, and with carbonate added to the anode water feed. Proton's traditional test stand was used since it provided continuous data acquisition of all operating parameters, including gas cross-over measurements to sense for membrane failure. Electrodes were fully non-PGM based. This stack uses Proton's commercial production stack to represent the most realistic operating conditions possible. The test exceeded the final milestone target of 500 h, achieving 1,000 h, doubling the program requirement. The full data set from this test is included in Figure 4.

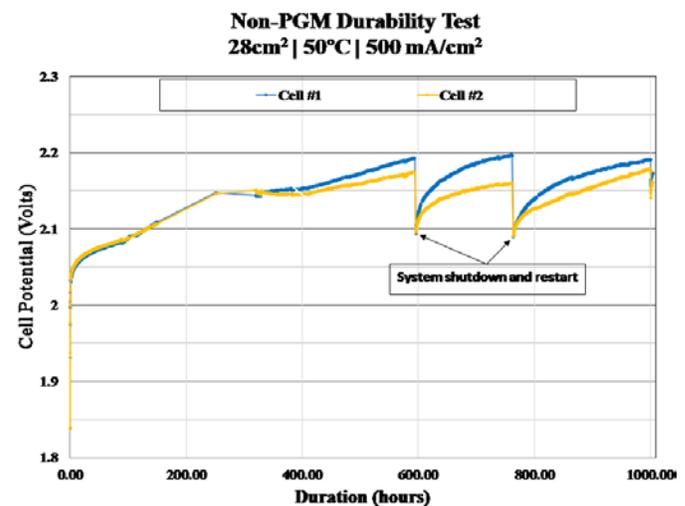
## CONCLUSIONS AND UPCOMING ACTIVITIES

Non-PGM catalysts have been successfully incorporated into a full MEA and verified through in-cell operational testing. Test stand modifications helped to advance understanding of operational modes and support the final durability test. Work conducted at Penn State has continued to make improvements in membrane durability, leveraging one of Proton's commercial suppliers through the procurement and inclusion of reinforcements during casting. The final test deliverable met the final program milestone by operating for over 500 h with a full non-PGM cell.



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**FIGURE 3.** Supported BTMA40 membrane with Nylon mesh operational data



**FIGURE 4.** Results from final non-PGM durability test showing 1,000 h of operation

## FY 2017 PUBLICATIONS/PRESENTATIONS

1. "High Performance Platinum Group Metal Free Membrane Electrode Assemblies through Control of Interfacial Processes," Poster, DOE Merit Review, June 2017, Christopher Capuano, Proton OnSite.
2. "Catalytic and Mass Transport Effects of Carbonate Ions at an Anion Exchange Membrane Interface (PGM vs. non-PGM) for a Practical and Efficient Water Splitting Cell," ECS Conference, May 2017, Huong Doan, Northeastern University.
3. "PGM-Free OER and HER Electrocatalysts for Alkaline Electrolyzers in Alkaline Media," ECS Conference, May 2017, Alexey Serov, University of New Mexico.