

II.B.6 Economical Production of Hydrogen through Development of Novel, High Efficiency Electrocatalysts for Alkaline Membrane Electrolysis

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Subcontractors:

- Washington University, St. Louis, MO
- Georgia Institute of Technology, Atlanta, GA
- Pajarito Powder, Albuquerque, NM

Project Start Date: April 11, 2016
Project End Date: April 10, 2018

Overall Objectives

- Refine the pyrochlore synthesis technique for electrocatalysis of oxygen evolution reaction (OER).
- Replicate catalyst synthesis in the manufacturing environment and scale up.
- Compare commercial and optimized ionomers and refine formulations based on the results.
- Scale up down-selected ionomers for demonstration in electrolyzers.
- Integrate optimized catalyst, membrane, and ionomer materials into the cell stack and verify performance through durability testing.
- Develop and implement accelerated stress tests for the anionic chemistry.
- Verify a 12–14 cell stack configuration for laboratory scale hydrogen generation.
- Complete the design and build of a 12–14 cell prototype system.

Fiscal Year (FY) 2017 Objectives

- Reproduce the Washington University synthesis process at Pajarito Powder and confirm the results through physical and electrochemical characterization.

- Down-select an ionomer(s) based on stability nuclear magnetic resonance (NMR) to elevated temperature in KOH.
- Hold a concept system design review.
- Synthesize a 50-gram batch of OER catalyst at Pajarito.
- Verify sealing for a 12–14 cell 28 cm² cell stack.
- Complete fabrication of the prototype system.

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

The only metrics for hydrogen production at the system level are \$/kW and \$/kg. These high-level metrics cause difficulties in highlighting even major changes at the component level. However, the final cost will be largely dependent on raw material costs. Developing and scaling stable alkaline membrane technology is also important in establishing feasibility of the technology. The current program aims to meet the following targets.

- Scale up of catalyst synthesis to 50 g batches and show a pathway to kilogram scale
- Verify cell stack scale-up to 12–14 cells
- Durability: 500 h of stable operation

FY 2017 Accomplishments

- Operational testing of the candidate ionomers was initiated at Georgia Tech.
- Pre- and post-operated samples were shipped to Washington University where a methodology using NMR was applied to look for evidence of degradation.
- Synthesis procedure for scale-up of the high surface area pyrochlore catalysts was provided to Pajarito, as part of the tech transfer effort (milestone).
- The 14-cell stack design was completed, and a single 14-cell stack was assembled, bench-tested, and verified against Proton acceptance testing procedures.

- Operational testing of the prototype system was initiated.



INTRODUCTION

As the need for renewable energy capture grows, the balance between electricity feedstock cost and capital cost shifts, due to the ability to obtain low cost electrons but at lower capacity factors. Since the electrolyzer is on for a lower percentage of the time, the capital cost has a larger impact on the overall lifecycle cost. Anion exchange membrane (AEM)-based electrolyzers offer a pathway to significantly reduce the cost of the cell stack, by enabling low cost oxygen flow fields such as nickel or stainless steel, as well as reduction or elimination of platinum group metals in the catalyst layer. The team has demonstrated the exceptional activity and stability of lead ruthenate pyrochlore electrocatalysts for the oxygen evolution reaction. While these catalysts still contain some noble metal, eliminating the titanium from the cell has a greater impact on cost and provides an initial stepping stone for product cost reduction.

In theory, AEM-based electrodes should represent a drop-in replacement to Proton's existing cell stack designs. However, the supply chain for AEMs is still developing, and membrane formats are smaller than the typical Nafion rolls produced for fuel cell and electrolyzer applications. Introduction of new materials into the cell stack that are unproven in the field also represents a large capital risk at megawatt scale. Proton's laboratory product provides an opportunity to introduce these materials to market at a lower risk entry point and gain field experience on the pathway to eventually applying AEM technology for larger energy related applications.

APPROACH

Proton will continue to work with the Ramani group at Washington University to scale up catalyst synthesis and transition to Pajarito Powder, a commercial company. Proton will also continue to incorporate the most promising membrane and ionomer combinations in order to optimize performance and stability. As one option, Proton will evaluate ionomers developed in Kohl's group at Georgia Tech, which have been used in systems at Acta.

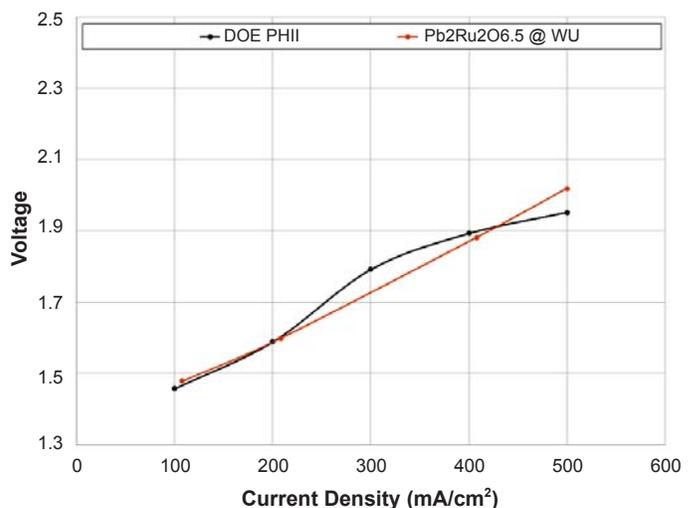
In parallel, Proton will work to scale the stack to an appropriate capacity for the laboratory product portfolio. The planned capacity will supplement existing options rather than supplanting an existing product, to provide more value for the same investment. Proton will leverage work previously done for the U.S. Air Force on a higher capacity hydrogen generator with similar footprint to our lab line. Approaches for electrolyte management (pure water or supporting

electrolyte) will be finalized and the resulting system design completed.

RESULTS

Washington University synthesized $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ OER catalysts and provided them to Proton for operational testing. Materials provided were assembled into a single 25 cm^2 stack; results were collected and compared to the values obtained at the end of the Phase II program. This was done to show translation of the process after the Ramani group moved from their previous location at Illinois Institute of Technology. Polarization data (Figure 1) indicated comparable performance to the previous DOE Phase II target through a maximum current density of 500 mA/cm^2 at 50°C . The method for the synthesis of $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ OER catalysts was then transmitted to Pajarito Powder to initiate technology transfer and proceed with synthesis scale up. The selection of the material for scale up was based on OER activity and stability during electrolyzer experiments. Washington University is assuring that common synthesis protocol by opening several ways of communication (on-site visit, emails, phone calls, samples sent for analysis, and detailed reports). Washington University verified at its labs that the shared protocol produced 3.1 g of $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ with a percentage of crystalline pyrochlore in the range of 40–60%, a Brunauer-Emmett-Teller surface area of approximately $100\text{ m}^2/\text{g}$, an electronic conductivity of at least 100 S/cm , and an OER activity (measured at a potential of 1.5 V vs. reference hydrogen electrode) of 200 A/g .

The stability of the AEM binders synthesized at Georgia Tech was investigated by using NMR spectroscopy. The binders were extracted from the gas diffusion electrodes after



PHII – Phase II

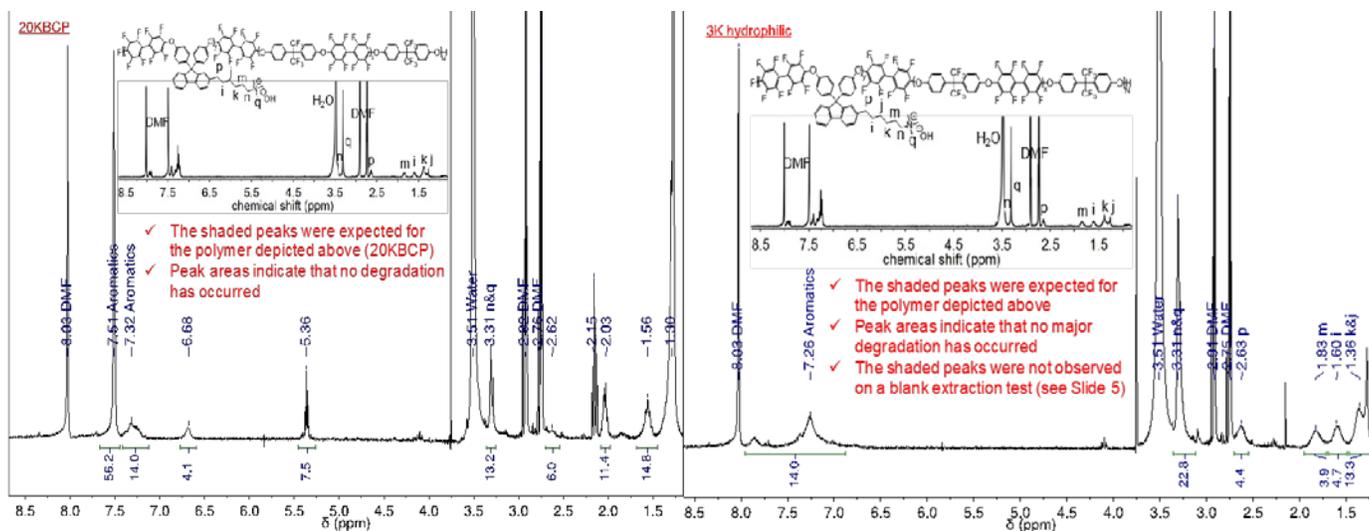
FIGURE 1. Polarization curve comparison between Phase II end of program results and the process re-established at Washington University (WU)

several hours of operation at Georgia Tech. The intent of these experiments was to identify any signs of degradation in the binders occurring during operational testing in the AEM water electrolyzer stack. Figure 2 shows the ^1H NMR spectra for two of the binders tested. Evaluation of both the pristine and operated ionomer spectra revealed peaks characteristic for both ionomers, with no new peaks commonly encountered in degraded ionomers. Moreover, the peak areas were close to the expected values. All these findings suggest the binders tested do not suffer chemical degradation during electrolyzer operation. Longer term operation of the electrolyzer and postmortem analysis of the binders are required to confirm these preliminary findings. The experiments are ongoing.

Work at Proton has been conducted in parallel on the stack and system design and development. Building upon Proton's 28 cm^2 commercial cell stack, a 14-cell stack assembly drawing was created and modeled to support the build and test of the new article. After confirming the stack up configuration and procuring the components required for fabrication, build success was achieved as verified by Proton's standard acceptance test procedure, which is comprised of four assessment elements: (1) a high frequency resistance measurement conducted at ambient and full pressure conditions to ensure minimal resistive losses in each cell, (2) an electrical isolation measurement to verify the absence of potential shorting in or between cells, (3) a pressurized leak test at up to 1.5 times normal operating pressure to confirm no evidence of a cross-cell or overboard leak, and (4) an operational test at full current and pressure to confirm acceptable overall performance.

Additional efforts were focused on the design and development of the prototype system for operation of the 14-cell stack. Instrumentation has been identified for mass flow rate and dew point measurements to verify actual versus the target values for hydrogen generation and purity. The 14-cell stack was installed and operated within the system. Initial temperature profiles within the system enclosure have been collected and will be used to further understand the impact to system and stack components (instrumented stack and system shown in Figure 3). Further work has been planned to conduct a more thorough analysis, where an environmental enclosure has been developed to subject the system to elevated atmospheric temperature. As part of this, a pressure swing adsorption dryer will be tested and tuned to improve hydrogen gas purity through this range of conditions.

Proton also placed a single cell 28 cm^2 AEM water electrolysis stack on test to evaluate steady-state durability of the integrated project elements. The purpose was to combine inputs from partners at Georgia Tech, Pajarito Powder, and Washington University. Georgia Tech provided ionomer which was used at Proton in the fabrication of OER electrodes. Washington University, assisted Pajarito Powder with the synthesis details required to produce lead ruthenate powders for use as an OER catalyst. Pajarito Powder refined the synthesis steps to increase throughput and quantity. Materials were provided to Proton and processed into electrodes for the durability test. The cell stack and system used were based on the designs shown in Figure 3. Steady-state current densities were held constant at 500 mA/cm^2 and achieved $>900\text{ h}$ of operation, showing the successful collaboration of all partners to provide robust materials



DMF – n, n-di-methyl formamide

FIGURE 2. (Left) ^1H -NMR of "20KBPC" AEM binder after operational testing in a water electrolyzer. The insert figure shows the spectrum of the pristine material. (Right) ^1H -NMR of "3K hydrophilic" AEM binder after operational testing in a water electrolyzer. The insert figure shows the spectrum of the pristine material.

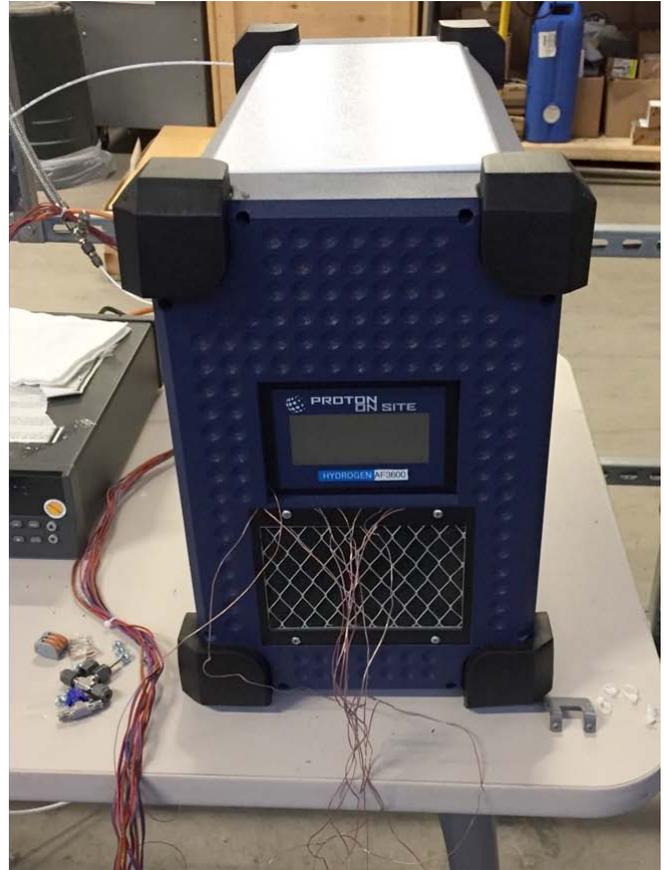
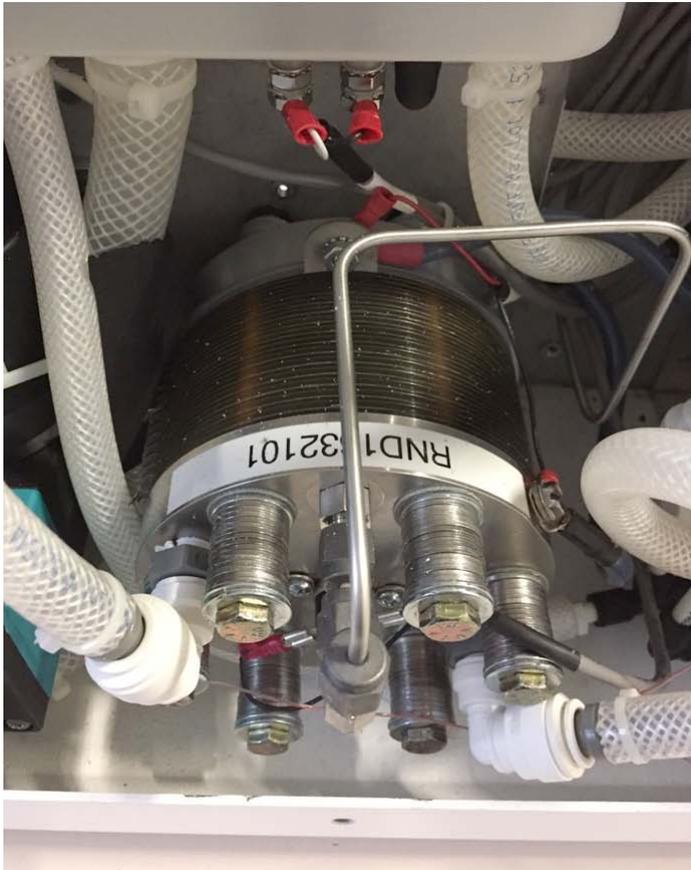


FIGURE 3. Cell stack and system instrumented for thermal measurements

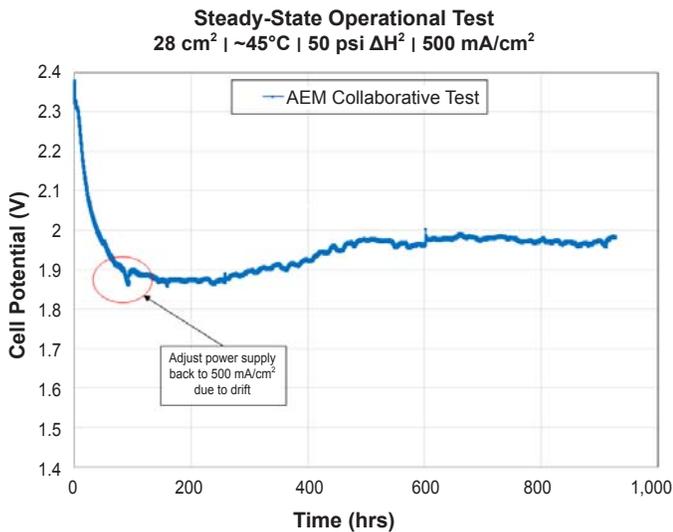


FIGURE 4. One-cell, steady-state test results collected from the durability assessment

capable of achieving stable extended operation. The results from this test are shown in Figure 4.

CONCLUSIONS AND UPCOMING ACTIVITIES

Several ionomer dispersions developed at Georgia Tech have been synthesized and show early promise in degradation studies. Longer duration tests will be used to down-select the final configuration and understand degradation effects, supported by accelerated degradation studies at Washington University. Synthesis of the lead ruthenate catalyst was recreated at the new Washington University labs and then successfully transferred to Pajarito Powder, where catalysts are in the early stages of scale-up. A 14-cell stack was assembled and functionally verified in the full-scale prototype system designed for the larger cell stack and associated hydrogen generation rates. A long-term steady-state test was conducted with inputs from all partners showing the collaborative effort and technical capability to execute the plan for scale-up and improved durability AEM water electrolysis membrane electrode assembly components.

Next steps include evaluation of advanced materials, and work to define the eventual system design, as follows:

- Compare catalysts synthesized at Washington University and Pajarito Powder.

- Scale-up to 50-gram batch size of the pyrochlore catalyst at Pajarito.
- Characterize degradation mechanisms for Georgia Tech ionomers based on post operational analysis.
- Down-select the best ionomer identified through operational and instrumental analysis.
- Hold a concept review for the proposed system.
- Create a system product requirements document, detailing the prototype system input/output criteria.
- Fix design points, procure components and fabricate a prototype system based on the on-going thermal, hydrogen flow rate, and hydrogen purity assessment.
- Integrate and test a multi-cell stack with the scaled-up catalysts and down-selected ionomers from program partners.