HydroGEN Seedling: High-Efficiency Proton Exchange Membrane Water Electrolysis Enabled by Advanced Catalysts, Membranes, and Processes

Katherine Ayers (Primary Contact), Chris Capuano
Proton OnSite
10 Technology Drive
Wallingford, CT 06492
Phone: (203) 678-2190
Email: KAyers@protononsite.com

DOE Manager: David Peterson
Phone: (720) 356-1747
Email: David.Peterson@ee.doe.gov

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Subcontractors:
• Tufts University, Boston, MA
• Oak Ridge National Laboratory, Oak Ridge, TN

Project Start Date: September 2, 2017
Project End Date: August 30, 2020

Overall Objectives

- Develop an advanced electrolysis membrane electrode assembly (MEA) that is capable of meeting the following targets:

  o Produce hydrogen at 43 kWh/kg

  o Show decay rates of less than 4 mV/1,000 h

  o Achieve costs of $2/kg hydrogen based on $0.02/kWh renewable energy input as estimated by the H2A (Hydrogen Analysis) model.

Fiscal Year (FY) 2018 Objectives

- Develop material tracking sheet and baseline current hydrogen costs.

- Demonstrate MEA performance of 1.85 V at 80°C with advanced catalyst and N117 baseline membrane.

- Quantify water distribution in operating cell with X-ray tomography.

- Complete membrane mechanical testing versus hydration condition and evaluate options for down-selection of advanced membrane.

- Demonstrate $1.8 A/cm^2$ at 1.7 V for advanced MEA.

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[1]:

(F) Capital Cost.

Technical Targets

The current program aims to meet the targets in the table below.

Metric	State of the Art	Proposed
Membrane thickness	175 microns	50 microns
Operating temperature	58°C	80°–90°C
Cell efficiency	53 kWh/kg	43 kWh/kg

FY 2018 Accomplishments

- Catalyst samples for oxygen evolution were synthesized, screened for initial performance in $25\text{-}cm^2$ electrolysis cells, and analyzed for stability through dissolution rates.

- Several anode porous transport layers were tested and evaluated through in-operando analysis using the X-ray imaging technique.

  o Increased current density at $2 A/cm^2$ was achieved in the test cell.

  o Data was provided to Lawrence Berkeley National Laboratory (LBNL) for incorporation into modeling activities.

- Oxygen evolution catalysts were deposited as electrode decals using a polytetrafluoroethylene substrate for transfer at Proton onto membrane to be formed as catalyst-coated membranes.

- Proton continued to develop the coating technique for model catalyst layers toward electrochemical and conductive imaging.

- A two-dimensional water electrolyzer model was developed; the model is able to run under differential pressure and a study was carried out to examine the effect of cathode pressure on cell performance.

- Model validation is in progress under both vapor and liquid feed conditions.

INTRODUCTION

Now that there are commercial fuel cell vehicles on the roads in the United States in regions where fueling stations are available, attention has turned to the urgent need for clean hydrogen, for fueling as well as other industrial applications. Proton exchange membrane (PEM) electrolysis is a critical near-term need that lays the groundwork for future renewable water splitting pathways. Based on cost reduction to date, PEM electrolysis systems are profitable and competitive when fielded today for hydrogen industrial gas applications and markets. However, for energy storage, hydrogen fueling, and commodity hydrogen, the price point of >$5.5 /kg hydrogen and low efficiency of >50 kWh/kg are unacceptable. The United States is also in danger of losing its competitive edge in PEM technology as European and Asian entities invest in research, development, and deployment of electrolyzer systems. However, initial feasibility work has shown that much of the materials understanding from PEM fuel cells can be applied to electrolyzers to reduce both capital and operating expense.

APPROACH

The cost and efficiency drivers for PEM electrolysis are (1) thick membranes (7–10 mm thick) to prevent excessive gas crossover and seal against 30–350 bar differential pressure, but which cause high resistive efficiency losses; (2) high catalyst loadings using conventional low-surface-area, unsupported catalysts increasing cost and decreasing efficiency; (3) manufacturing for electrode gas diffusion layers and porous transport layers (PTLs) that is not optimized for activity, durability, or cost; and (4) low-temperature operation due to membrane creep over long lifetimes at higher temperature, which again limits efficiency. This project leverages understanding of materials interactions and electrode structure to integrate thinner membranes, improved catalyst layer structures, and tailoring of catalyst-electrode interfaces to meet the targets above.

RESULTS

To increase catalyst activity, Proton synthesized high-surface-area IrOx and IrOx-RuOx blends. Because ruthenium typically dissolves at PEM electrolysis operating voltages, the approach focused on alloying the higher-activity metal in a stable matrix. Compositional ratios and synthesis techniques were evaluated through bench and performance testing. The fusion synthesis method used at Proton to fabricate catalysts was successful in increasing the surface area by >7x versus the baseline. Three candidates were focused on: 100% IrOx, 70:30 IrOx:RuOx, and 50:50 IrOx:RuOx. National Renewable Energy Laboratory (NREL) node resources were leveraged to evaluate cycling stability and demonstrated minimal metal loss in the 70:30 blend, as well as good activity in rotating disk electrode experiments. All three catalyst powders were formulated into ink suspensions and MEAs were manufactured using the deposition process used for all of Proton's commercial cell stacks to show transfer to production methods. Catalyst-coated membranes were made for the test and both polarization curves and steady-state data were collected to look for pure electrical performance and stability. Steady-state results from these tests are shown in Figure 1, confirming the rotating disk electrode evaluation.

The same catalyst compositions were incorporated into a three-cell 28-cm^2 cell stack for extended unattended operation with 30 bar differential pressure to best simulate what would be typical of a commercially fielded device. Polarization data was initially collected at current densities exceeding 4 A/cm^2, with linear response indicating no mass transfer limitations. The cell stack was allowed to run continuously under steady-state conditions in order to look for voltage decay, either indicating loss of activity through lowering of surface area or dissolution of catalyst. Under the 80°C, 30 bar differential pressure, 1.8 A/cm^2 operating condition, stable performance was observed up to 300 h for all three samples, with the 70:30 IrRu blend starting to show better electrical efficiency versus both the 50:50 Ir:Ru blend and the pure IrOx. The current density was then increased to 2 A/cm^2 and the stack was operated another 600 hours. All voltages were maintained below 1.9 V/cell, with 900 h of stable performance observed for the three high-surface-area compositions. The results from this test are shown in Figure 2, with 70:30 IrRu down-selected for integration with advanced membranes.
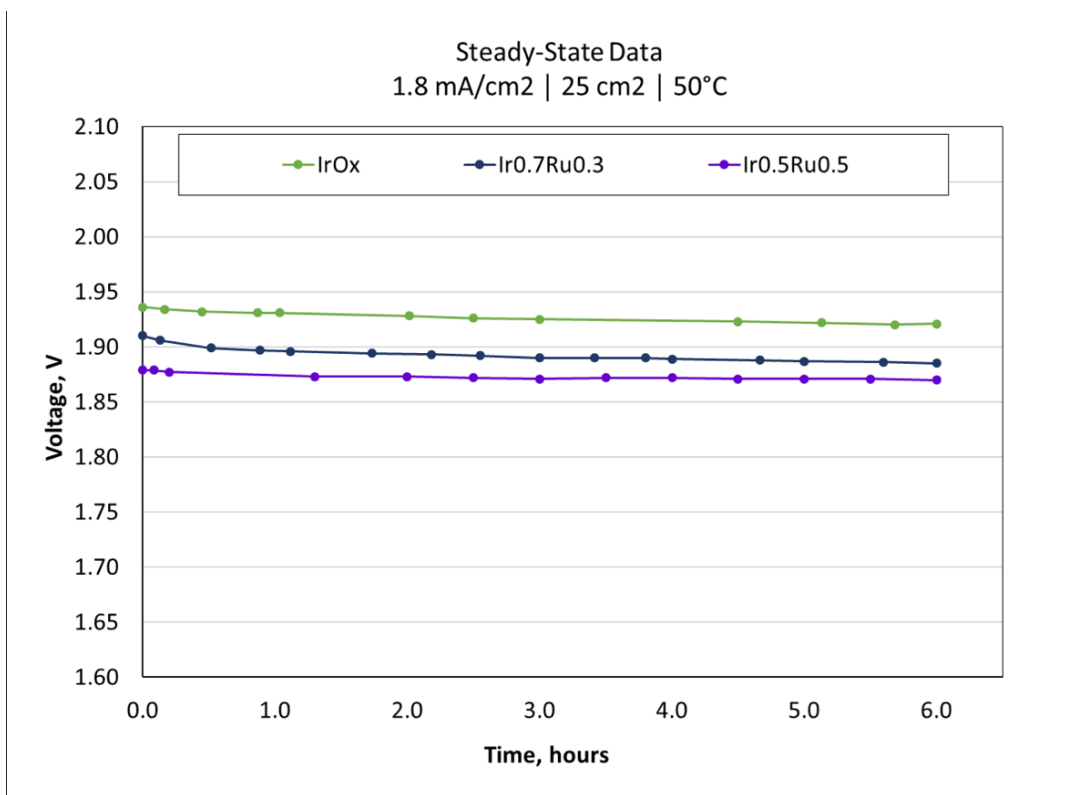
Figure 1. Short term operational data for high-surface-area IrOx, 70:30 IrRu, and 50:50 Ir:Ru
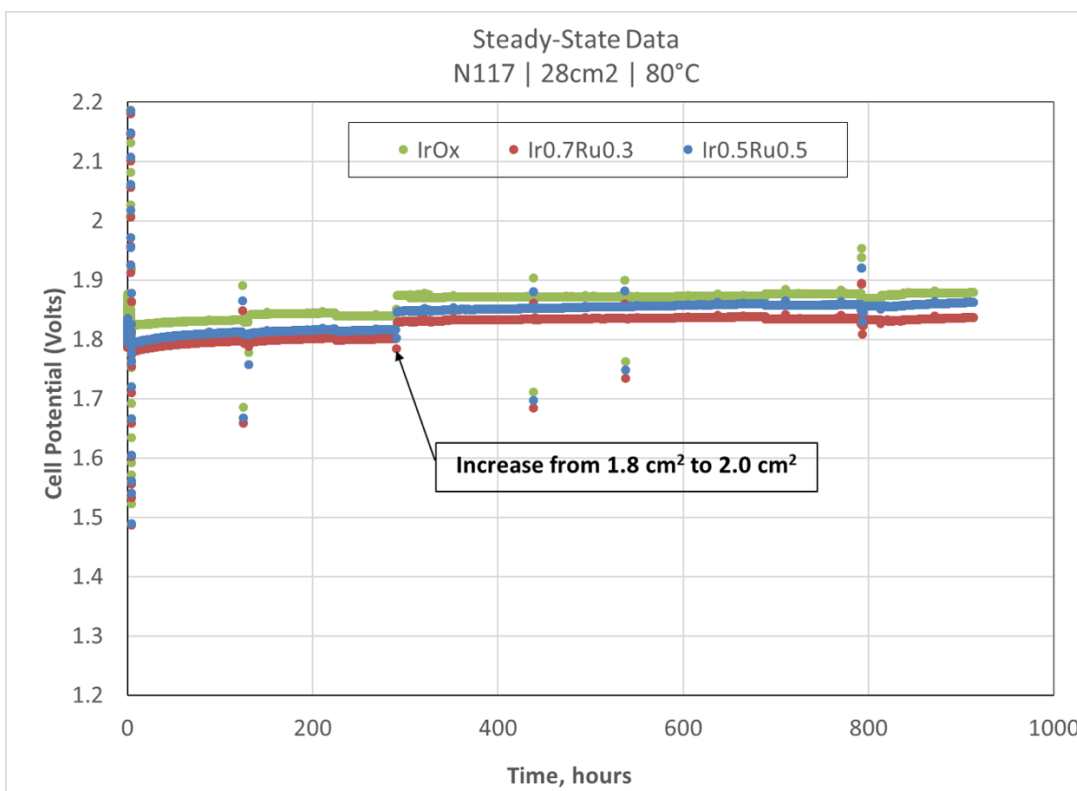

Figure 2. Steady-state operational data in Proton's 28-cm² commercial cell stack

Membrane samples were first assessed for stability and performance using Proton's baseline catalysts to isolate performance deviations to the membranes. Membranes of 50 and 90 µm were compared to baseline N117 (175 µm). Testing was initially conducted at 30 bar, 50°C, and 1.8 A/cm^2 in the same 28-cm^2 commercial cell used to evaluate the catalysts. Over a 40-h test, voltages for both alternate membranes were stable. With successful operation of the 50 µm material, this membrane was down-selected for the final milestone based on the higher efficiency and sufficient mechanical strength.

Catalyst-coated membranes were manufactured using Proton's production process with the down-selected membrane and catalyst. The milestone target was to achieve a <1.7 V operating cell potential at 1.8 A/cm^2 and 30 bar. System temperature was held at 80°C and data was collected for 7 h. As shown in Figure 3 the target of <1.7 V was achieved and held throughout the test, successfully meeting the go/no-go milestone targets. The results from this test indicate a lower-heating-value and higher-heating-value efficiency of 73% and 88%, respectively. Ongoing work is occurring through node resources at LBNL to evaluate specific creep properties as a function of hydration conditions for each membrane to predict long-term performance. Additional work was also performed with node resources at NREL to develop alternate catalyst deposition processes capable of higher loading precision and uniformity. Decals were successfully printed on polytetrafluoroethylene but transfer to membranes was incomplete. The next budget period will evaluate other deposition substrates.
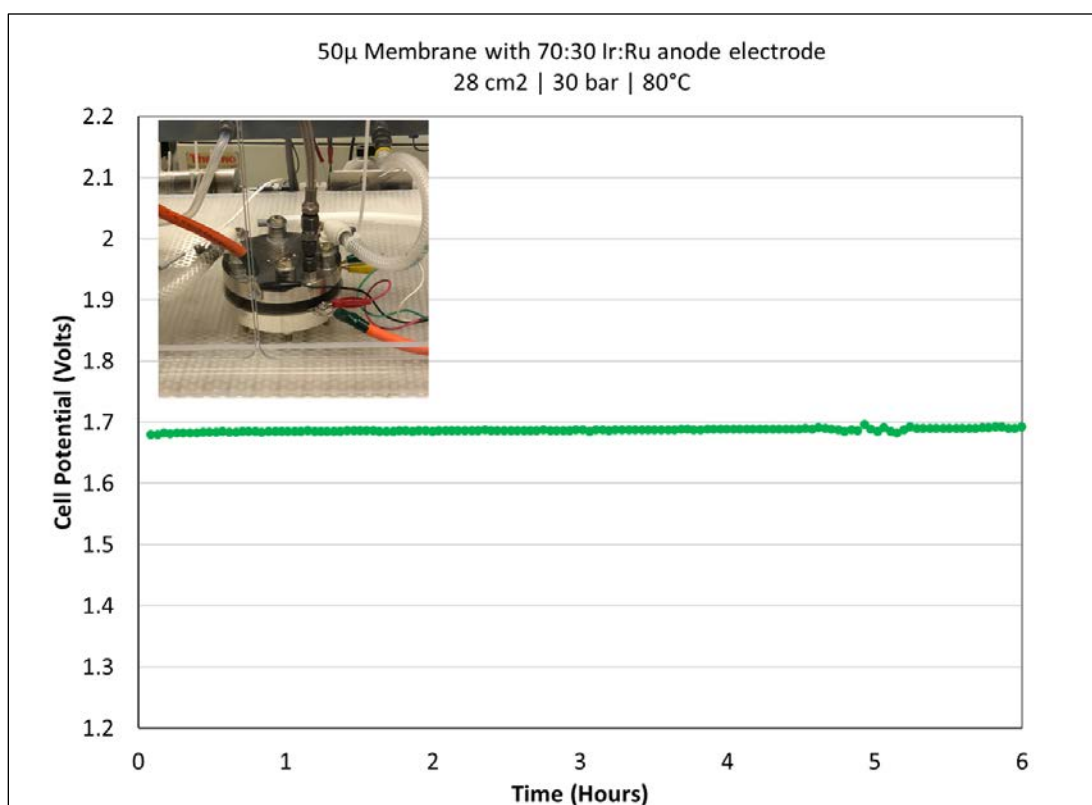

Figure 3. Steady-state data of high-efficiency MEA for go/no-go milestone

To support the next phases of development, detailed characterization of the PTL was performed. Neutron imaging of the porosity was performed, with imaging during operation at up to 2 A/cm^2 to attempt to determine water distribution as well. Tortuosity and porosity could be determined for different types of PTLs, but distinguishing water from air in the titanium matrix has proved challenging. The pore structure has been used to guide development of a cell-level model with node resources at LBNL to simulate PEM electrolyzer performance. Polarization curves are being simulated and parameters adjusted to better predict actual performance.

CONCLUSIONS AND UPCOMING ACTIVITIES

Advanced catalysts and membranes were separately evaluated to determine optimal materials and verify stability before integration. Proton successfully synthesized high-activity catalyst powders that have translated into measurable improvements in performance during operational tests. An improved membrane was identified that showed higher in-cell performance, supporting operating conditions of 1.8 A/cm^2, 80°C, and 30 bar differential pressure. The Year 1 go/no-go milestone was achieved with stable performance of the advanced integrated high-efficiency MEA at <1.7 V and 1.8 A/cm^2. Supporting efforts at NREL and LBNL to characterize the catalyst and membrane materials also contributed to the down-select and confidence in the materials selected. In-depth characterization and modeling of the PTL is ongoing to support testing under harsher conditions such as higher current and lower catalyst loading.

In the next phase of the project, Proton will continue to explore catalyst synthesis methods and alternative compositions to further enhance performance and identify other methods of manufacture of the electrodes for improved utilization. In addition, lower loading targets will be considered as a means of additional cost reductions. Longer-term testing and stress testing will be conducted on the materials described within this report, as well as testing of multiples to show repeatability. Specific next steps include:

- Complete time-dependent mechanical tests versus hydration condition for remaining membrane materials.

- Analyze PTL imaging data and try to understand whether there is a correlation between bubble formation and PTL type.

- Leverage reconstructed images to develop a micro-scale model that can be used study the effect of the micro-structure of porous layers.

- Validate the differential cell model at all operating conditions within 10% of experimental polarization data.

- Include the effect of hydrogen crossover in the two-dimensional model.

- Complete accelerated stress test cycling of MEAs fabricated with advanced catalysts and send to Oak Ridge National Laboratory for characterization of catalyst migration

FY 2018 PUBLICATIONS/PRESENTATIONS

1. K.E. Ayers, W.L. Gellett, and C.B. Capuano, "Electrochemical Generation of Fuels: Matching Research and Application for Advanced Water Splitting and Other Technologies," Electrochemical Society Meeting Spring 2018.

2. K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes," DOE Annual Merit Review and Peer Evaluation Meeting 2018.

3. K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes," Electrochemical Society Meeting Fall 2018.