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

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- University of California, Irvine, Irvine, CA
- Oak Ridge National Labs, Oak Ridge, TN

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Project End Date: August 31, 2020

Overall Objectives

- Develop an advanced proton exchange membrane water electrolysis (PEMWE) membrane electrode assembly (MEA) that meets or exceeds the Energy Materials Network (EMN) targets by addressing membrane, catalyst, catalyst layers, and their interfaces.
- Expand upon current expertise in PEMWE and previously funded DOE work, partner with experts in the field University of California, Irvine (UCI) and Oak Ridge National Laboratory (ORNL) and heavily leverage EMN resources.
- Develop a hydrogen cross-over mitigation strategy that allows for safe operation at 30 bar differential pressure.
- Develop a high technology readiness level (TRL) advanced electrolysis MEA that can meet the following targets:
 - Produce H₂ at 43 kWh/kg

- Show decay rates of less than 4 mV/1,000 h
- Achieve costs of \$2/kg H₂ based on \$0.02/kWh renewable energy input as estimated by the H2A (Hydrogen Analysis) model.

Fiscal Year (FY) 2019 Objectives

- Understand the impact of membrane hydration conditions for three membrane candidates across a temperature range of 50°C to 100°C and quantify changes in compressive strength and MEA efficiency over the temperature range.
- Define potential efficiency benefit from combined nanoparticle structure and catalyst composition and provide a strategy for catalyst powder optimization in Budget Period 2 (BP2) with a higher focus on alloys or Ir structure.
- Down-select membrane based on hydration state study of mechanical and chemical properties. Membrane selection will be determined by loss of compressive strength of no more than 20% vs. baseline membrane and hydration conditions and optimal efficiency among membranes meeting the strength metric.
- Demonstrate electrolysis cell operation, and two best of the class MEAs characterized under current densities of 500 mA/cm² and 1,000 mA/cm².

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- F. Capital Cost
- G. System Efficiency and Electricity Cost.

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

Technical Targets

This project is focused on developing standards and test protocols that result in technologies to produce hydrogen consistent with the following DOE technical targets:

- Cost: <\$2/kg of H₂.

FY 2019 Accomplishments

- Oxygen evolution reaction (OER) samples sent to National Renewable Energy Laboratory (NREL) for characterization of activity and dissolution measurements.
- Three samples from one supplier consisting of IrO_x, IrRuO_x, and IrRuNbO_x.
- Operational testing of the OER catalysts at Proton Energy Systems d/b/a Nel Hydrogen US (Proton/Nel) showed stability in performance tests and were then used to meet the BP2 go/no-go milestone.
- BP2 go/no-go milestone achieved with <4 μm/h degradation.
- Platinum group metal (PGM) loading was decreased by order of magnitude.
- Progress made on porous transport electrode fabrication with the NREL node.

- Progress made to prevent “soak through” of the ink into the porous transport layer (PTL).
- UCI completed an evaluation of the influence water flow rates and current density have on oxygen bubble formation.
- Particle and fiber PTLs were compared with fiber showing better oxygen removal due to its lower porosity.
- 4A/cm² testing was achieved.
- Mass transport became evident at 0.5 mL/min.
- Creep-related compression measurements continued at Lawrence Berkeley National Laboratory node and moved ahead with membrane characterization.
- New fixture completed, which allows for hydrated samples of the membrane to be measured while wetted.
- Also allows for temperature evaluation up to 80°C.
- Short-chain and long-chain polymers tested at room temperature and under two different compressive forces.
- Long-chain polymers showed higher resilience to creep at both forces and at both dry and wet conditions.

INTRODUCTION

Proton/Nel will develop an advanced PEMWE MEA that meets or exceeds the EMN targets by addressing membrane, catalyst, catalyst layers, and their interfaces. To accomplish this advancement, we will leverage our expertise in PEMWE and previously funded DOE work, partner with experts in the field UCI and ORNL, and heavily leverage EMN resources. The objective of this project is to develop a high TRL advanced electrolysis MEA that can meet the following targets: produce hydrogen at 43 kWh/kg, with decay rates of less than 4 mV/1000 h and at costs of <\$2/kg H₂ based on \$0.02/kWh renewable energy input as estimated by the H2A model.

APPROACH

Proton/Nel is the world leader in PEM electrolysis, having been in the industry for 20 years with the largest market share of PEM systems in the field. The core technology is derived from General Electric (GE) and United Technologies (UTC), originally used in life support applications, and historically has been highly over-engineered and under-optimized for manufacturing. 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 H₂ and low efficiency of >50 kWh/kg are unacceptable (see Table 1). The cost and efficiency drivers are (1) thick membranes (7-10 mil thick) to prevent excessive gas crossover and seal against 30–350 bar differential pressure, but causing 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 (GDL) and porous transport layers (PTL) 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. Proton/Nel has performed early feasibility work to address all four areas, but to demonstrate the improvements in cost and efficiency, additional understanding of materials interactions and electrode structure is needed. Demonstration and integration of these require a deeper understanding of the scientific and technical aspects of electrolysis-specific membranes, water distribution issues, GDL, and catalyst layer interfaces, requiring partners who are experts in the field: UCI and ORNL.

Table 1. Technical Targets of the Project

Specification	Proton State of the Art	Proton Lab Demonstrated	Specific FOA Targets
Membrane (mm)	178	50	50
Temperature (°C)	58	80	90
Total catalyst loading (mg/cm ²)	3	1.3	0.9
Durability (mV/1,000 h)	~0	7	4
Efficiency (kWh/kg)	53	44	43
Total Cost H ₂ (\$/kg H ₂)	5.41	2.25	<2
TRL	10	3/4	6

RESULTS

Year 2 Outputs

Membrane Testing

Down-selection of the membrane and processing conditions were determined based on results for two membrane chemistries and water uptake behavior vs performance under varying hydration conditions. Generally, lower membrane water content under fully flooded conditions is optimal for mechanical stability. Lower water content can also be correlated to lower protonic drag across the membrane, reducing the water management requirements on the hydrogen side of the cell. However, reduced hydration can result in lower efficiency, which is observed in stacks built with dry membranes that are hydrated in situ. In this study, membrane samples were hydrated ex-situ for two hours at the selected temperature for comparison. The water content results were higher with a higher temperature (Figure 1), but Chemistry #2 was less sensitive to temperature, as expected based on the shorter side chains and higher glass transition temperature.

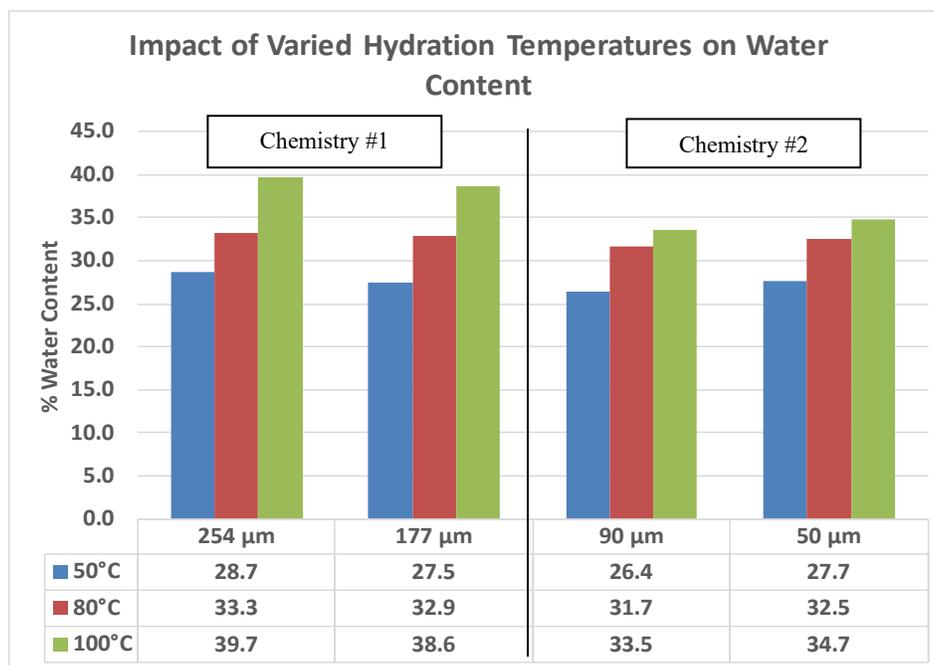


Figure 1. Water content measurements

At the same time, there were no clear trends in performance with hydration temperature, indicating that the lower hydration temperature did not have significant disadvantages.

Catalyst Characterization

Based on learnings from Proton/Nel's work in BP1 on catalyst preparation regarding the impact of catalyst properties (surface area, particle morphology, etc.) and composition (pure IrOx compounds vs. blended metal oxides), catalyst candidates were procured from two commercial companies able to produce catalyst materials in kilogram quantities. Iridium oxide with the high surface area was obtained from both companies, while the second company also provided different blends of ruthenium for activity and niobium for stability. Materials were integrated with Proton/Nel's ink formulations and deposition processes and tested for initial performance (Figure 2).

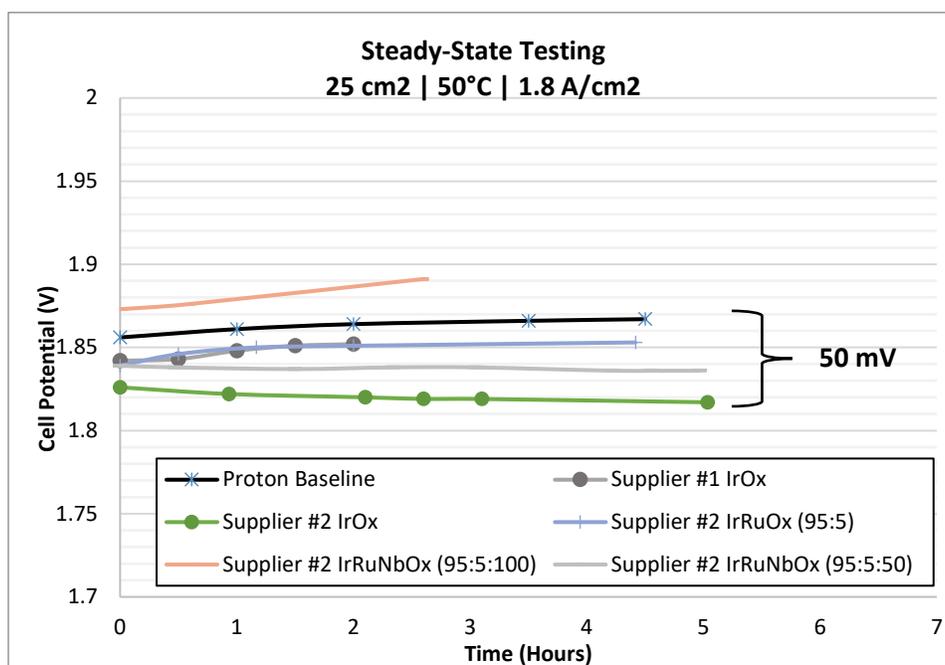


Figure 2. Catalyst screening data

Both IrOx materials performed better than the baseline on this short-term test, but Supplier #2 showed the best performance. The blended catalysts also performed relatively well, except for the catalyst with high niobium content, indicating the non-active material inhibited the catalyst properties. The three best performing candidates from Supplier #2 were incorporated into new electrodes for the longer-term milestone test.

Go/No-Go Milestone Test

Based on the membrane work and integrating these three catalyst materials, a three-cell stack was assembled for testing under standard and aggressive conditions. Of note, loadings for the original test in Figure #2 were 3.0 mg/cm² on the anode (OER) and 3.0 mg/cm² for the cathode (HER), using Pt black. For this go/no-go test, not only were these alternative OER catalysts incorporated, but the cathode was also modified with a transition from Pt black to Pt/C. This enabled our first opportunity to explore lower loadings under this program with successful processing at a loading of 0.3 mg/cm². This represented an order of magnitude reduction of PGM content on the HER side of the cell. Once assembled and placed on a test, the operation was performed at 30 bar differential pressure. Initially, the stack was operated at Proton/Nel's standard commercial conditions of 50°C and 1.8 A/cm². After the first 500 hours, the stack temperature was increased to 80°C, and after another 150 hours, the current was increased by 20%. The stack operated for over 1,400 hours before being removed for a replicate test, which is ongoing.

The metric for the milestone was to achieve less than 4 microvolts per hour and over 500 hours of operation. The decay rates for the two best-performing catalysts are shown in the trendlines in Figure 4. The last 500 hours of the test were used to calculate the decay rate because the data was relatively flat throughout, and any degradation would be expected to be worse at the most aggressive conditions. Also, if the catalyst is degrading, the decay rate often increases with operation as the number of active material decreases, and the remaining catalyst material is under higher demand. Finally, there can also be minor fluctuations in early stack operation due to break in processes, which could have skewed the data. The high surface iridium oxide material had a slightly negative apparent decay rate. Proton/Nel has observed this behavior in other stacks and hypothesized that the improvement could be due to compression and improved contact of the components under the stack load, or another break in effects. The lack of observable decay indicates that the catalyst is very stable and meets the milestone. The blended Ir-Ru catalyst also showed a low decay rate of 5 microvolts per hour, which is within the experimental error over this period of performance. It is possible that this configuration would meet the milestone as well if operated for a longer time to increase the precision of the measurement.

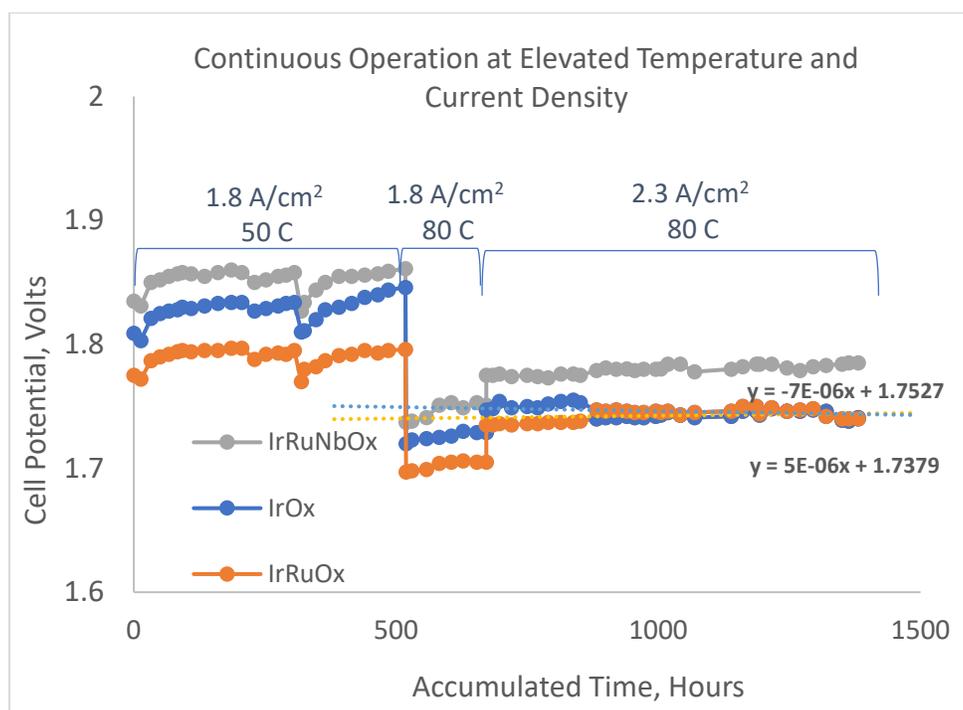


Figure 3. Steady-state data of high efficiency MEA for Go/No-Go milestone

CONCLUSIONS AND UPCOMING ACTIVITIES

This report shows:

1. The membrane hydration conditions do not make a significant difference in the electrochemical performance of the cell, but lower temperatures do result in lower water content, which should improve mechanical stability.
2. Learnings from BP1 were successfully translated to commercially ready catalyst materials and showed similar performance enhancements vs. baseline.
3. Nel has shown successful achievement of the end of Year 2 go/no-go milestone by demonstrating the stable performance of the high-efficiency MEA for over 500 hours with less than 4 microvolt/hour decay rate.

Nel will continue to verify the catalyst performance in longer-term tests and replicate lots. Mechanical studies of the membrane will be completed for varying hydration levels to quantify the differences in mechanical strength. Catalyst loadings will be explored for the OER electrode to further minimize platinum group metal usage, while the interface contact area will be quantified for different porous transport layer materials and electrode configurations. Hydrogen crossover strategies will be refined, and materials will be provided to the Nodes for performance verification.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. K. Ayers, W.L. Gellett, and C.B. Capuano, "[Electrochemical Generation of Fuels: Matching Research and Application for Advanced Water Splitting and Other Technologies](#)," Spring ECS, 2018.
2. K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes," DOE AMR, 2018.
3. K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes," Fall ECS, 2018.
4. K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes," DOE AMR, 2019.
5. K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes," Fall ECS, 2019.