New Approaches to Improved Proton Exchange Membrane Electrolyzer Ion Exchange Membranes

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Project Start Date: April 6, 2015 Project End Date: April 5, 2019

Overall Objectives

- Optimize electrolyzer membrane performance.
- Refine polymer/membrane and cell architecture to maximize durability.
- Down-select materials for optimization of membrane composite configuration.
- Scale up and confirm cost estimates.
- Build prototype.

Fiscal Year (FY) 2018 Objectives

- Modify cell design.
- Define ionomer specifications.
- Define membrane specifications.
- Scale up synthesis and define standard operating procedures.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹: (F) Capital Cost

- (G) System Efficiency and Electricity Cost
- (K) Manufacturing
- (L) Operations and Maintenance.

Technical Targets

- Improved performance, reduced hydrogen permeation, and lower costs compared with commercial perfluorosulfonic acid baseline.
- Membrane polarization loss after 500 hours (200 mA/cm², 400 psi, 50°C) <10 mV.
- Reduction in crossover loss at 50°C and ≥200 psi.

FY 2018 Accomplishments

- Defined cell design for prototype.
- Close to down-selection of material configuration for prototype cell stack.
- Down-selected membrane configuration for prototype cell stack.
- Demonstrated very low hydrogen crossover after 500 hours of operation at 1.8 A/cm², 50°C, 400 psi.
- Recorded >80 mV improvement in initial performance vs. Phase II baseline.
- Developed methods to reduce performance and durability hindering swell for high–ion exchange capacity (IEC) ionomers.
- A commercial coater who is keen to initiate production trials assessed continuous roll coating approaches to down-selected membrane configuration.
- Developed inverse design model for the optimal enthalpy of reduction as a function of operating conditions, including yield.
- Developed operating design model for estimating cycle efficiency.

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

INTRODUCTION

The potential to use ion exchange membrane–based electrolyzers at much higher differential pressures than fuel cells minimizes the need for additional costly mechanical compression of the hydrogen produced. However, this high pressure differential requires a robust membrane that is able to prohibit hazardous back diffusion of hydrogen to the oxygen source. A common solution to both enhance mechanical durability and reduce hydrogen diffusion is to simply increase the thickness of the membrane; however, this increases ionic resistance and can significantly reduce the efficiency of the system. Increasing the operating temperature can improve efficiency, but this usually accelerates physical and chemical membrane degradation, especially at higher pressures. Due to the limitations of current commercial membranes, new approaches are needed to enable efficient, cost-effective proton exchange membrane–based hydrogen generation.

We previously demonstrated excellent performance and low hydrogen permeation at less than half the thickness of current commercial perfluorosulfonic acid membranes. During 2018 we have further developed our ionomer chemistry, down-selected material and membrane configurations, and demonstrated reproducibility in ionomer synthesis and membrane fabrication in preparation for prototype cell stack fabrication during FY 2019.

APPROACH

Ionomers were custom synthesized and characterized at Tetramer and membranes were supplied to Proton OnSite for electrolyzer performance evaluation under conditions to emulate current commercial units. Specific ionomer and membrane variables investigated include backbone polymer architecture and molecular weight; ion exchange capacity; membrane thickness and configuration (including the incorporation of supports and additives); and membrane casting and post-cast treatment techniques. Membranes were evaluated for physical integrity, electrochemical performance, water uptake and swell, hydrogen permeability (crossover), and durability. Cell design modifications and membrane treatments also were investigated to enhance compatibility and optimize performance.

RESULTS

During this project to date, more than 70 different membranes have been produced at Tetramer and supplied to Proton OnSite for performance evaluation. During this 2018 period specifically, we have further developed our leading ionomer structures and membrane configurations and made additional down-selections based on the assessment of 30 new membranes. As a result, specification limits have been more tightly defined for ionomer backbone molecular architecture, ion exchange capacity and molecular weight, and membrane configuration. We are approaching final down-selections for prototype fabrication.

Effective methods to mitigate performance and durability issues caused by excessive swell of high-IEC ionomers have been demonstrated (Figure 1). The two most effective techniques are currently being employed as a means of further enhancing down-selected materials to extend durability.

Scale-up and reproducibility studies have been successfully carried out, incorporating process developments to improve ionomer yields and reduce waste. Our existing standard operating procedures and production cost analyses will be updated during FY 2019 based on these developments. We remain confident in the scalability of our ionomer synthesis and our previously projected membrane production cost savings (compared with commercial perfluorosulfonic acid products such as Nafion).

An initial performance improvement of >80 mV was recorded for our recent (scaled up) material downselection, compared with Phase II Tetramer baseline membrane (Figure 2).

Cell design modifications and membrane surface treatments have been investigated at Proton OnSite to enhance the compatibility of our novel membranes with existing cell hardware. These developments will be incorporated into a prototype multi-cell stack electrolyzer unit.

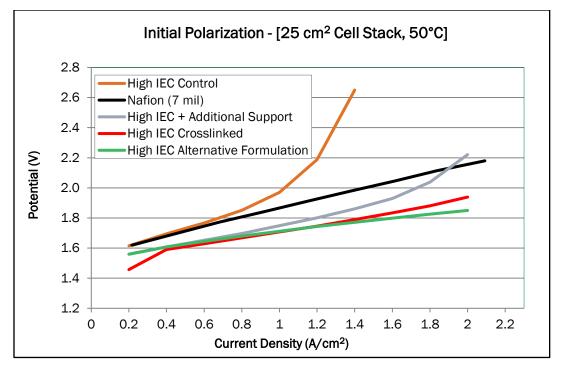
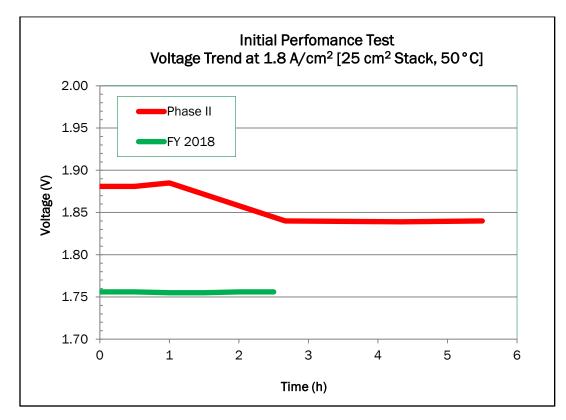
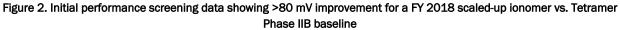


Figure 1. Performance and durability improvements of high-IEC materials by controlling swell





CONCLUSIONS AND UPCOMING ACTIVITIES

Down-selected ionomer scale-up and reproducibility studies have been successful to date and processes have been further developed to improve efficiency and reduce material costs and waste. Standard operating procedures and production cost evaluations will be updated to incorporate these developments.

Our 2018 down-selected membranes demonstrate further improved performance and reduced hydrogen permeation compared with the commercial perfluorosulfonic acid baseline (7-mil Nafion) with a potential cost reduction of >50%. The overall advantages of this new technology project to a significant reduction in hydrogen production costs.

Following the conclusion of our currently ongoing tests to demonstrate extended durability (target = 5,000 hours, 50°C, 15 bar), a multi-cell prototype electrolyzer unit will be fabricated at Proton OnSite, incorporating Proton's cell design modifications. This unit will be assessed for performance and durability under standard operating conditions to allow direct comparison with existing Nafion-based units. If funding is available, we plan to pursue commercialization with Proton OnSite.