II.B.7 New Approaches to Improved PEM Electrolyzer Ion Exchange Membranes

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Project Start Date: April 6, 2015
Project End Date: April 5, 2017

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 of polymers and confirm cost estimates.
- Build prototype.

Fiscal Year (FY) 2016 Objectives

- Optimize membrane polarization loss.
- Reduce hydrogen permeation and crossover.

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

(G) System Efficiency and Electricity Cost

(K) Manufacturing

(L) Operations and Maintenance

Technical Targets

- Membrane polarization loss after 500 h (200 mA/cm^2, 400 psi, 50°C) <10 mV
- Maintain high performance from Phase I
- Crossover loss at 50°C and 400 psi <1 mA

FY 2016 Accomplishments

- Significant reduction (~$0.60/kg H_2) in energy requirements for hydrogen production
- A 4X increase in output at 70% efficiency
- A 400 mV improvement in performance at 2 A/cm^2
- A 71% lower heating value (LHV) – exceeding the target of 68%
- A reduction in hydrogen crossover – exceeding the target by a factor of 2
- Membrane polarization loss of 9 mV after 500 h (200 mA/cm^2, 400 psi, 50°C)
- Crossover loss at 50°C and 200 psi 4 mA

INTRODUCTION

The performance needs for improved ion exchange electrolyzer membranes having the properties described under subtopic 13a Membranes and Materials for Energy Efficiency: "Membranes for Electrochemical Systems" [1] were stated as:

(a) "Electrolyzers based on ion exchange membranes are typically operated at high differential pressures, leveraging the low additional overpotential required to electrochemically compress the hydrogen to eliminate stages of mechanical compression. These membranes must therefore withstand significantly higher mechanical loads than fuel cells in order to maintain stack sealing."

(b) "The high differential pressure increases back diffusion of hydrogen, requiring additional design features to mitigate buildup of hydrogen in the oxygen stream, and resulting in efficiency losses."

(c) "Thick membranes are often used to overcome both issues leading to higher ionic resistance and therefore efficiency losses in the cell stack. Thinner membranes and higher temperatures will assist in reducing this

overpotential, but also increase polymer creep and gas permeation."

(d) "New membrane approaches are needed to enable very high efficiencies at moderate hydrogen generation pressures (e.g., 55 bar and below), and acceptable efficiencies at high hydrogen pressures (e.g., 350 bar and above)."

(e) "Membrane chemistries and reinforcement approaches are solicited that reduce hydrogen gas permeation while achieving improved LHV stack efficiencies to reach the goal of over 76% LHV stack efficiency by 2015."

Overall, the target metrics should demonstrate hydrogen permeation below that of commercial membranes while achieving improved ionic conductivity, stability up to 80°C and improved baseline efficiency, including the development of accelerated tests for electrolysis cells to prove long term durability.

APPROACH

The design of unique polymer architectures at Tetramer has been shown to be a vital part of many membrane applications. This unique approach to membrane chemistry has been employed herein to generate a membrane that meets the need for electrolyzer applications. This approach has led to a wide range of modifications to the structure of the membrane that have been explored. These modifications have been the focus of this research and have led to many advancements in technologies that have the potential to dramatically influence the current electrolyzer markets.

RESULTS

This project is well on target and no significant foreseeable problems or changes to the direction of the research have been identified. The Phase II targets shown in Figures 1 and 2 represent very aggressive goals that no commercial material has satisfied. These targets were set to dramatically influence current markets and we have chosen to compare ourselves with relevant commercial samples to ensure viability of the technology. Benefits will be seen downstream in all the technical barriers listed above. As seen by the highlighted accomplishments above, there has been a significant amount of work done to date and our progress has been very encouraging. Currently we have made a large amount of progress in the area of molecular architecture design through the use of a variety of backbone architectures that have resulted in polymers with a range of ion exchange capacities. Membranes have been designed with polymers that vary in molecular weight, contain additives, were cast from various solvents and differ in thickness to determine the effects on performance and durability. This has lead to a much more refined system being studied where the ion exchange capacities are being fine-tuned, molecular weights are being held consistent and any other potential changes are being addressed systematically since initial results have already been collected. The membrane configuration has been defined based on the testing of over 37 membranes. Many of these membranes have shown promising electrolyzer performance as seen by Figure 1, which shows preliminary electrochemical evaluations of some selected membranes. These membranes performed comparably with 2 mil Nafion® electrochemically, but with the advantage of significantly lower hydrogen crossover, which is discussed later.

Electrolyzer membrane thickness has a large influence on performance, durability and hydrogen permeation. The thinner membranes for electrolyzers are highly desired, yet still have many limitations including an increase in hydrogen crossover. This will cause the lower explosion limit to increase and is not desired. Current membranes within this project have been found to have as little as one-third the permeation of Nafion (Figure 2) for similarly thick membranes. Great progress has been made towards reaching the set target and continued research will be tailored to continue to minimize this permeation.

Increased durability has been pursued actively as well and has resulted in many modifications that have been

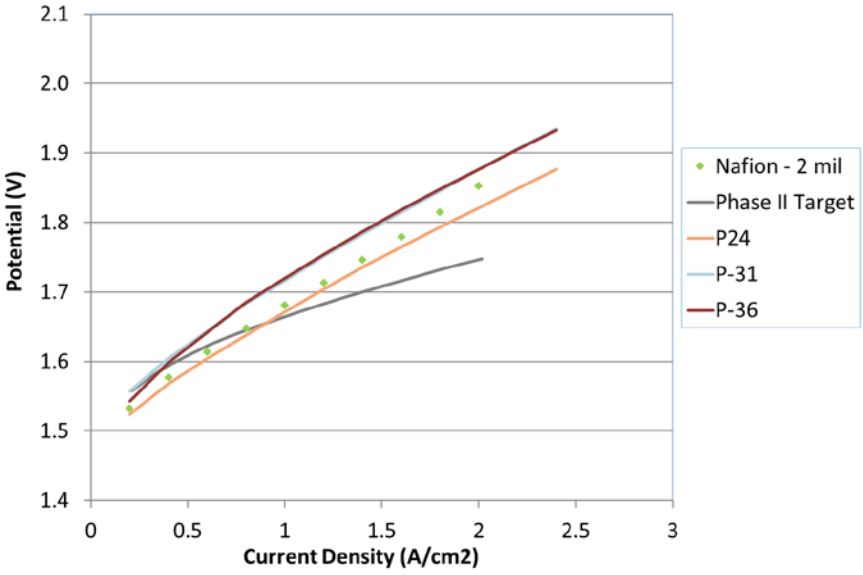

FIGURE 1. Preliminary electrochemical evaluation of several membranes with promising permeation results

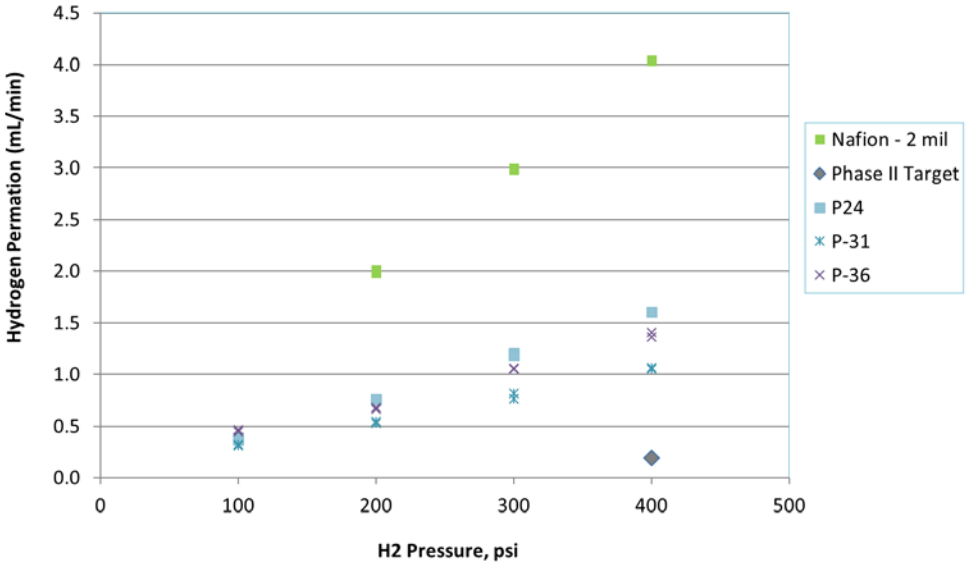

FIGURE 2. Hydrogen permeation through membranes measured electrochemically in situ on 28 cm^2 active area electrolysis cells

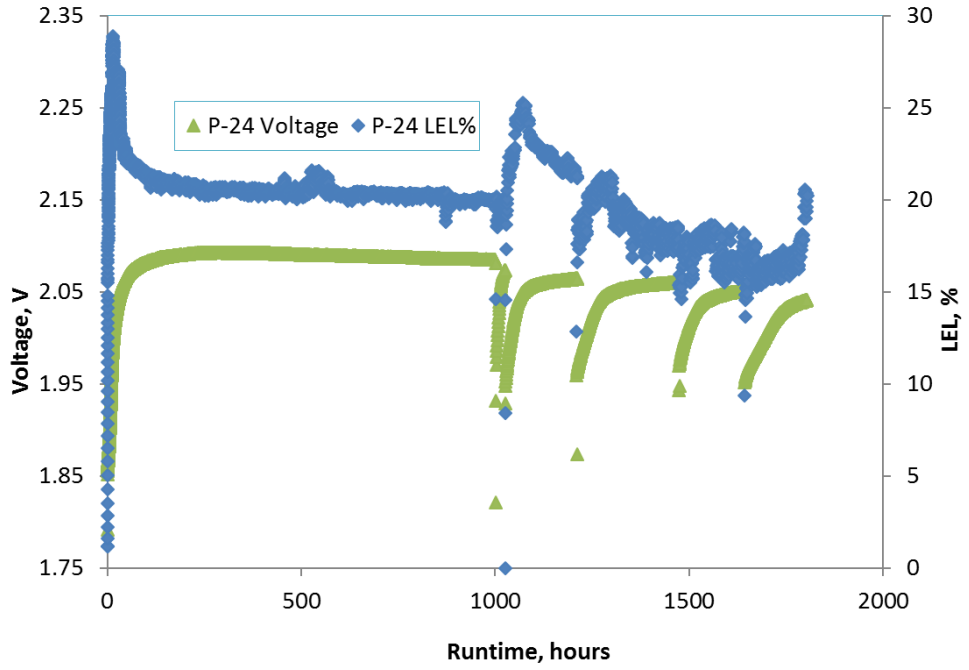

FIGURE 3. Long-term durability test on P-24 showing stable operation and acceptable percent lower explosion limit operated at 50°C, 1.8 A/cm^2 and 200 psi differential hydrogen pressure (gaps in data indicate non-stack related restarts)

explored and have shown a promise to mitigate current degradation mechanisms. This task is currently in the early stages but has already shown over 1,000 h of durability (Figure 3) and will continue to be explored.

CONCLUSIONS AND FUTURE DIRECTIONS

The current technology has currently shown to be a viable way to improve current electrolyzer membranes and will continue to be explored in the future. The need for further long-term durability measurements will be

the primary focus for the following year. The current performance improvements are very promising and if durability can be improved the material will be a dramatic improvement to current membrane materials.

REFERENCES

1. U.S. Department of Energy Topics for 2014 SBIR STTR Phase I Release I DE-FOA-0000969 Topic 13a "Membranes for Electrochemical Systems" http://science.energy.gov/~/media/sbir/pdf/docs/FY14_PIR1_Topics_07-24-13_Final_Ver_5.pdf