

II.B.4 High Temperature, High Pressure Electrolysis

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(L) Operations and Maintenance

Technical Targets

Progress has been made in achieving the DOE targets listed in the MYRDDP. Table 1 lists the DOE's technical targets and where our research and development efforts stand to date.

TABLE 1. DOE Technical Targets and Giner, Inc. Status

Characteristic	Unit	2015 Target	2020 Target	Giner, Inc. Status
Electrolyzer System Capital Cost	\$/kg \$/kW	0.50 300	0.50 300	- 1,000
System Energy Efficiency	% (LHV) kWh/kg	72 46	75 44	- 45.5
Stack Energy Efficiency	% (LHV) kWh/kg	76 44	77 43	- 44.5

LHV - lower heating value

The goal of this project is to increase the efficiency of the PEM (electrolyzer stack and to improve durability of the membrane electrode assemblies [MEAs]), while providing hydrogen at a pressure of 350 bar. This project is still in the early stages. These goals would contribute significantly to reaching the 2020 DOE hydrogen production targets of:

- Hydrogen Levelized Cost: \$4/kg H₂ (Dispensed)
- Stack Energy Efficiency: 43 kWh/kg H₂
- Electrolyzer System Capital Cost: \$300/kW

FY 2015 Accomplishments

- Discovered, with Virginia Tech, novel, non-perfluorinated ionomer membranes that demonstrate conductivity to permeability ratios above two times that of Nafion®
- Designed and fabricated new hardware that will withstand the 350 bar differential operating pressure of the electrolyzer stack
- Demonstrated 1,000 h of stable electrolyzer performance at 1,000 psi and 95°C



INTRODUCTION

Electrolysis of water is an important tool for energy storage in wind and solar applications. DOE has identified a need for electrolyzer efficiencies to reach 77% LHV by

Overall Objectives

- Develop a polymer electrolyte membrane (PEM) with a high ratio of conductivity to permeability, which leads to an increase in efficiency
- Optimize lifetime of developed PEM using various methods
- Demonstrate improved lifetime and efficiency under high pressure (350 bar) operation

Fiscal Year (FY) 2015 Objectives

- Optimize crossover mitigation in nonperfluorinated membranes
- Optimize formulation of nonperfluorinated membranes for conductivity/permeability ratio and lifetime
- Demonstrate increased lifetime with medium pressure (70 bar) operation

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 (MYRDDP):

(F) Capital Cost

(G) System Efficiency and Electricity Cost

2020. High pressure direct electrolysis is a desirable method for hydrogen generation and energy storage due to the reduced need for high pressure pumps and compressors. Direct electrolysis at elevated pressure permits hydrogen and/or oxygen tanks to be refilled directly, and reduces the overall mass, complexity, and cost of the electrolysis system. Efficiency can be increased by operation at a higher temperature, which increases both conductivity and oxygen evolution kinetics. However, this efficiency comes at the expense of higher permeability. Gas crossover (permeability) plays an increasingly significant role in performance as pressure rises, decreasing efficiency and accelerating membrane degradation while leading to potentially dangerous levels of hydrogen in oxygen and vice versa. Increasing membrane thickness or lowering cell operating temperature can decrease crossover, but also decreases efficiency. Given the permeability and conductivity at a given temperature, it is straightforward to optimize membrane thickness for efficiency. The key to making efficiency gains then is to increase the ratio of conductivity/permeability and operate at as high a temperature as possible without compromising the membrane. The overall objective for this DOE Small Business Innovation Research (SBIR) program is the development of a PEM with maximum conductivity/permeability ratio while simultaneously greatly reducing membrane degradation rates (2x and 10x improvement over Nafion[®], respectively). Perfluorinated sulfonic acid- (PFSA) and hydrocarbon-based membranes generated with various additives, ionomer compositions and support structures were prepared and evaluated for conductivity and permeability as a function of temperature and water activity. The initial goal was to produce membranes with conductivity/permeability ratios greater than two with reference to Nafion[®], and this goal has been achieved.

The optimized membranes developed under this work are currently being tested for durability and performance in Giner, Inc.'s high-pressure cell hardware at pressures up to 5,000 psi. Combinations of various additives are used to increase durability and reduce gas crossover in the MEA.

APPROACH

The general approach for this project is to test the conductivity/permeability ratio for both commercial and experimental membranes. Those membranes showing conductivity/permeability ratios more than twice that of Nafion[®] are tested for durability. The durability is then tested with unadulterated membrane, and with membrane that has additives to increase durability and to decrease gas crossover. The best performing of these membranes will be scaled up into a short stack build that will then be tested at high pressure and high temperature for performance and durability.

The initial stage of the project has been completed with several non-PFSA membranes showing promise. Testing is now focused on medium pressure testing for durability and performance.

RESULTS

The overall goal of the first phase of this project was to fabricate, test and select membranes that possess conductivity to permeability (C/P) ratios higher than that of Nafion[®], to achieve the DOE goal of 76% LHV electrolyzer efficiency. A secondary goal was to ready a test station for testing membranes early in Phase II. Both of these goals were realized.

In total, 15 different ionomers were procured or fabricated and tested for conductivity and hydrogen permeability in Phase I. Excluding unmodified Nafion[®], six were PFSA ionomers – three modified N1100 membranes and three low equivalent weight membranes. The remaining eight were hydrocarbon-based membranes made by Virginia Tech, our Phase I partner and Rensselaer Polytechnic Institute. Figure 1 shows the results of testing for the 15 membranes.

As can be seen in the figure, three hydrocarbon membranes exceed the Phase I goal of a ratio of two. These membranes will be included in the Phase II testing. One PFSA membrane tests close to the goal – the Solvay Aquivion 790 equivalent weight membrane with a C/P of 1.7. In the interests of keeping a PFSA membrane in the study, and with the hope that novel treatments can increase the C/P ratio significantly, the Solvay ionomer will be included in the durability testing.

Baseline durability testing has been completed on Nafion[®] and is moving to the hydrocarbon ionomers. The main marker for chemical degradation of Nafion[®] is fluoride. Giner measures fluoride in the cell exit water as a measure of membrane degradation. Figure 2 shows the typical durability test. Fluoride numbers for this test were below the detectable

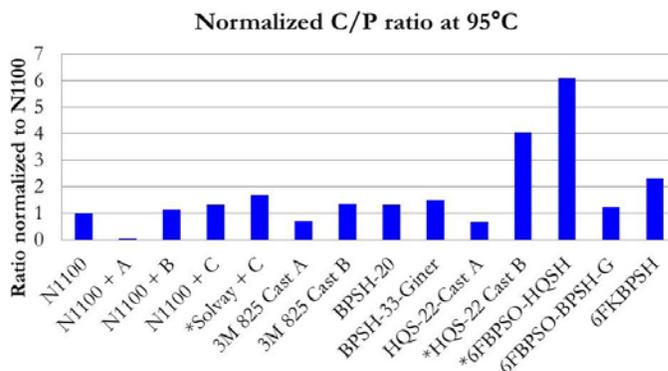


FIGURE 1. Conductivity, permeability and the C/P ratio for the membranes tested under the Phase I program. The go/no-go ratio is 2, and membranes above this ratio were moved on to the durability stage.

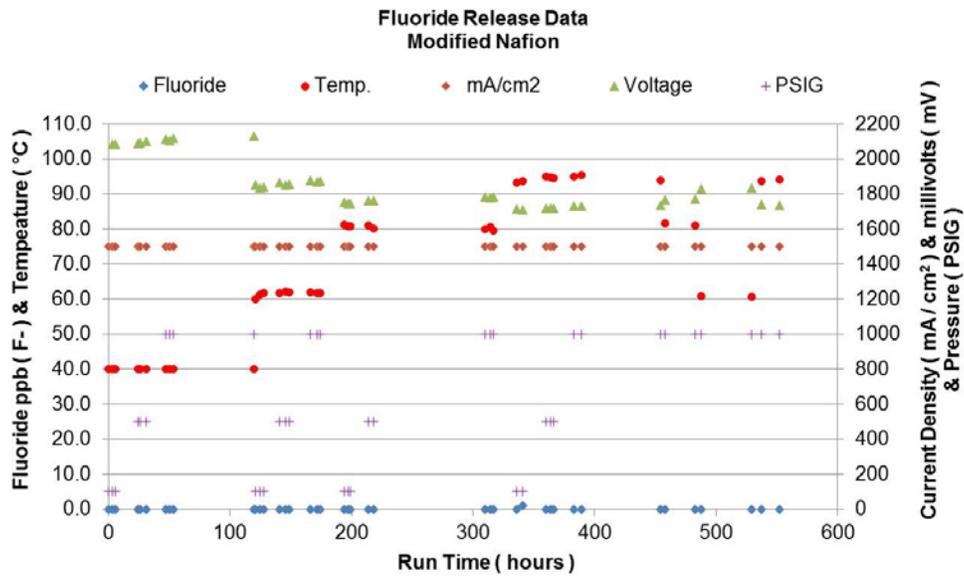


FIGURE 2. Various parameters measured during the durability test of a Nafion® membrane treated with a degradation mitigant

limit (~20 ppb) for the entire test, and voltage was stable at the various temperatures. These results suggest that chemical degradation was not an issue for this membrane with the degradation modification. Table 2 compares unmodified Nafion® N117 with Giner’s modified N115, showing marked improvement in chemical durability with a thinner membrane at higher temperature and pressure.

TABLE 2. Comparison of Modified and As-Received Nafion®

Membrane	Pressure	Temperature	Stabilized	Estimated Lifetime (h)
N117	100 psi	80°C	None	10,000
N115	1,000 psi	95°C	Yes	>30,000

A new bipolar plate design was fabricated under this project capable of 350 psi operation without additional support. This design consists of two valve metal plates laser-welded together to provide a well-sealed flow path with low pressure drop for both the anode and cathode flows. The plates have been received and tested at pressures up to 70 bar with no overboard or cross-cell sealing issues. Testing up to 350 bar will be performed. Figure 3 shows an image of the 350 bar hardware.

CONCLUSIONS AND FUTURE DIRECTIONS

Although the project is still in early stages several conclusions can be drawn.



FIGURE 3. Fuel cell stack hardware designed to withstand 350 bar operational pressure

- Novel membranes have been discovered in this project with conductivity to permeability ratios much higher than that of Nafion®.
- Nafion® with Giner's degradation mitigant has shown no chemical degradation during operation up to 1,000 hours at 1,000 psi and 95°C.
- New high pressure bipolar plates have been designed and manufactured for operation in the high pressure test station.

Future work includes the following.

- Testing the novel membranes for performance and durability with and without Giner's additives for degradation and gas-crossover mitigation
- High pressure testing of membranes for performance and degradation
- Testing short-stack configuration of the best MEAs under high pressure conditions

FY 2015 PUBLICATIONS/PRESENTATIONS

1. C. Mittelsteadt. "PEM Electrolysis: Ready for Impact," *ECS Transactions*. Accepted.
2. C. Mittelsteadt. "PEM Electrolysis: Ready for Impact," 2015 ECS Fall Meeting, Invited.
3. C. Mittelsteadt, J Riffle, J.Willey, J. Rowlett, A. Daraei, J. McGrath, "Aromatic Block Copolymers for High Pressure Electrolysis," 2015 North American Membrane Society Meeting. Boston, June 2015.