

II.B.4 High Temperature, High Pressure Electrolysis

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Contract Number: DE-SC0011310

Subcontractor:
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State University (Virginia Tech), Blacksburg, VA

Project Start Date: November 18, 2014
Project End Date: November 17, 2016

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) 2016 Objectives

- Optimize formulation of non-perfluorinated membranes for conductivity/permeability ratio and lifetime.
- Demonstrate increased lifetime with medium pressure (70 bar) operation.
- Demonstrate high lifetime and efficiency at 350 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.

(F) Capital Cost

(G) System Efficiency and Electricity Cost

(L) Operations and Maintenance

Technical Targets

Progress has been made in achieving the DOE targets listed in the Multi-Year Research, Development and Demonstration Plan. 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	0.57 1,000
System Energy Efficiency	% (LHV) kWh/kg	72 46	75 44	67 50
Stack Energy Efficiency	% (LHV) kWh/kg	76 44	77 43	75 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. These goals would contribute significantly to reaching the 2020 DOE hydrogen production targets of:

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

FY 2016 Accomplishments

- Optimized crossover mitigation with the Virginia Tech non-perfluorinated membranes.
- Evaluated 15 different membrane variations at 70 bar and 95°C (when possible) for membrane degradation and performance.
- Manufactured hardware and MEA for 350 bar testing.



INTRODUCTION

Electrolysis of water is an important tool for energy storage in wind and solar applications. The DOE has identified a need for electrolyzer efficiencies to reach 77% LHV by 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 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 (C/P) and operate at as high a temperature as possible without compromising the membrane. The overall objective for this DOE Small Business Innovation Research 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 2 with reference to Nafion, and this goal has been achieved. These membranes were then tested for degradation and performance at 70 bar.

APPROACH

The general approach for this project is to test the C/P 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 to which additives have been added to increase durability and to decrease gas crossover. The best performing of these membranes will be scaled up into a short stack build which 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 initial goal in Phase I of this project was to fabricate, test and select membranes that possess 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 2. Only one of these membranes was included in the Phase II testing – HQS-22 – due to the difficulty in consistently fabricating the other two ionomers. One PFSA membrane tested 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 the Solvay ionomer was included in the durability testing.

Durability and performance testing is almost complete for all the membranes configurations in the matrix. The main marker for chemical degradation of PFSA ionomers is fluoride release rate. Giner measures fluoride in the cell exit water as a measure of membrane degradation. Figure 2 shows the typical durability test. Fluoride numbers for the test shown in the figure were below the detectable limit (~20 ppb) for the entire test, and voltage was stable at the various temperatures. This suggests that chemical degradation was not an issue for this membrane with the degradation modification. Table 2 shows the results of the degradation testing for all the membranes in the matrix.

Notable is the large jump in estimated lifetimes for PFSA with degradation mitigation. The Solvay ionomer shows improvement in estimated lifetime with degradation mitigation, but this improvement is not nearly as large as for

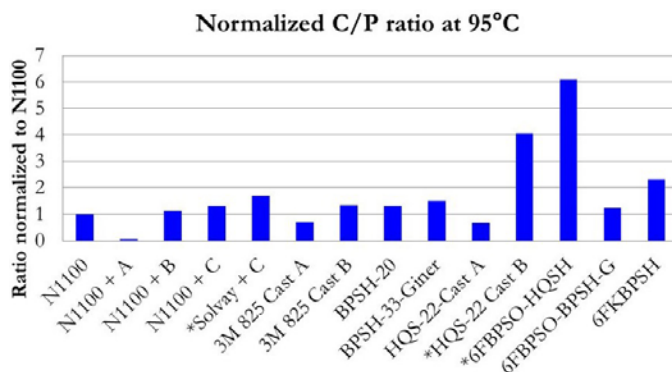


FIGURE 1. Conductivity, permeability and the C/P ratio for the membranes tested under the Phase I program. The go/no-go ratio is 2, and membranes above this ratio were moved on to the durability stage.

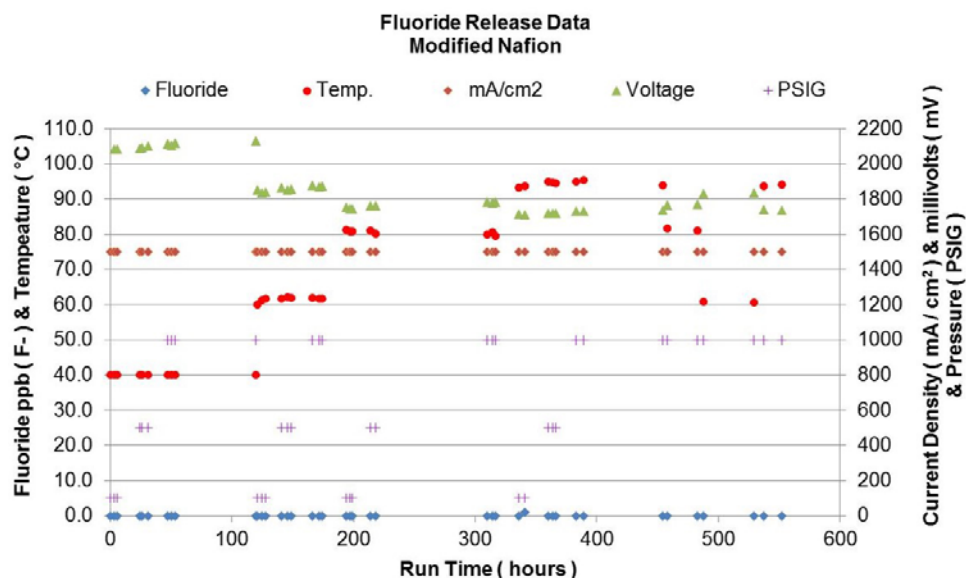


FIGURE 2. Various parameters measured during the durability test of a Nafion membrane treated with a degradation mitigant

TABLE 2. Results for Degradation Testing (40–95°C, 7–70 bar)

Test #	Membrane	Type	XM*	DM (%)**	Test length (h)	Failure	Est. Life (h) [†]
1	N115	PFSA	yes	0	518	no	7,000
2	N115	PFSA	yes	0.25	456	no	>100,000
3	N115	PFSA	yes	0.5	411	no	>100,000
4	N115	PFSA	yes	1	552	no	>100,000
5	N115	PFSA	yes	2.5	1017	no	>100,000
6	Solvay E79	PFSA	yes	0	697	no	4,000
7	Solvay E79	PFSA/DSM	yes	0.5	488	no	15,000
8	Solvay E79	PFSA	yes	0.5	356	yes	-
9	HQS-22	HC/DSM	no	0	25	no	-
10	HQS-22	HC/DSM	yes	0	41	yes	-
12	HQS-22	HC	yes	0	74	yes	-
13	HQS-22	HC/DSM	yes	0.5	20	yes	-
14	HQS-22	HC/DSM	yes	0.5	2	yes	-

* XM – Crossover mitigation added. ** DM – Degradation mitigation level as multiple of baseline amount.

[†] Estimated lifetimes are for MEAs operated at 95°C and 70 bar.

DSM - Dimensionally Stable Membrane; HC - Hydrocarbon

Nafion. Unfortunately, the HQS-22 MEAs degraded very quickly under test conditions in all configurations. Virginia Tech has just provided the project with two direct-fluorinated hydrocarbon membranes that show promise, but have not been tested at the time of this publication. Giner will also test one more PFSA under the degradation test protocol. This will be a 3M ionomer of low equivalent weight.

Testing at 350 bar is ready to commence at Giner, and will begin after the last degradation test is completed. This test will be biased to hydrogen pressure, with the cathode operating at 350 bar and the anode at <5 bar. The first MEA on test will be a Solvay E79 incorporated with Giner's DSM technology, which strengthens the membrane via a polymer matrix. Figure 3 shows an image of the 350 bar hardware.



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

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions at this time:

- Giner's degradation mitigation can improve expected lifetimes of PFSA ionomers significantly, affecting capital cost.
- This degradation mitigation transfers well to other PFSA ionomers.

Future work includes:

- High pressure (350 bar) testing of membranes for performance and degradation.
- Testing short-stack configuration of the best MEAs under high-pressure conditions.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. C. Mittelsteadt. "The Next Generation of PEM Electrolysis" (paper presented at BIT's 6th Annual New Energy Forum 2016, Goyang City, South Korea, June 30 – July 2, 2016).