Advanced Anion Exchange Membranes with Tunable Water Transport for Platinum-Group-Metal-Free Anion Exchange Membrane Fuel Cells

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- University of South Carolina (USC), Columbia, SC
- 3M Company (3M), Maplewood, MN
- National Renewable Energy Laboratory (NREL), Golden, CO

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Project End Date: November 30, 2020

Overall Objectives

This project will enable high-performance, long-lifetime, low platinum group metal (PGM) (PGM loading ≤ 0.125 mg/cm^2) anion exchange membrane fuel cells (AEMFCs) through:

- Synthesis and fabrication of novel, thin, mechanically supported anion exchange membranes (AEMs) and electrode ionomers with validated, outstanding water transport properties and stability.
- Integration of these new polymers with high-performing low-PGM and PGM-free catalysts and electrodes to achieve target power and durability metrics for state-of-the-art AEMFCs.
- Demonstration of precise control over the distribution of water in operating cells.

Fiscal Year (FY) 2019 Objectives

The objectives in FY 2019 are to:

- Fabricate new AEMs and ionomers with tunable water transport and robust durability.
- Demonstrate AEMFC operation for 500 hours at 600 mA/cm^2 and >0.6 V with H_2/O_2 at ≥60°C, pressure ≤1.5 atm_a, and 5 cm^2 active area.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.[1] The overall fuel cell themes are shown below, but our focus is on emerging AEMFC technology.

- Durability—focused on demonstrating moderate durability of AEMFCs based on understanding of water transport.
- Cost—enabling AEMFCs will lower the cost of the catalysts and the membranes.
- Performance—understanding water transport is key to high performance AEMFCs.

Technical Targets

This project is conducting work to accelerate the development of AEMFCs. Insights gained from these studies will be applied to the construction of single cells and ultimately fuel cell stacks that meet the following DOE fuel cell performance targets:

- Durability of 5,000 hours (equivalent to approximately 150,000 miles of driving) with less than 10% loss of performance.
- Cost: $20/$kW_{net}$.
- Performance @ 0.8 V of 300 mA/cm^2 (and 600 mA/cm^2 steady-state @ 0.6 V for alkaline).

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

FY 2019 Accomplishments

- Synthesized and delivered more than 25 membrane samples (four different compositions) to project partners for testing, including supported samples.
- Demonstrated a 5 cm^2 AEMFC with peak power density ≥1 W/cm^2 and 600 mA/cm^2 steady-state operation with V ≥0.6 V; H_2, O_2 reacting gases; T ≥60°C; and pressure ≤150 kPa.
- Demonstrated more than 500 hours of operation at 600 mA/cm^2 with V >0.6 V; H_2, O_2 reacting gases; T ≥60°C; and pressure ≤150 kPa.

INTRODUCTION

This project is focused on synthesizing, characterizing, and testing a series of AEMS with varying water transport properties to determine the effect of water transport on the performance and durability of AEMFCs. New membranes based on polyolefin chemistry with a range of water transport characteristics will be tested in an operating AEMFC to study how the water transport of the membrane impacts the water balance of the cell and ultimately the cell performance and durability. Reasonable durability has been obtained for new generations of membranes in AEMFCs, but the details of how the water transport of the membrane influences the water transport and performance in the cell have not been elucidated. Thus, our project is designed to codify the role that water balance plays in AEMFC performance and to disseminate this information to the community for advanced AEMFC development.

AEMFC performance has progressed to a point where more in-depth device performance and durability studies must be performed. Now that cell power densities are cresting at 1 W/cm^2 for 100s or 1,000s of hours, more detailed cell dynamics studies are needed to determine the key factors that limit the performance and durability of AEMFC technology. We have hypothesized that water transport can significantly influence the performance of the cell. Coupled with low-resistance membranes and high-performance electrodes, we have preliminary data showing that sufficient water transport in the cell is required to achieve high power densities. Currently, it is unknown how water transport impacts operating durability of the cell. We are targeting water transport rates in AEMs that match those of perfluoro sulfonic acids, which we know have reasonable water transport properties. In this project, Penn State will synthesize a range of AEMs with different crosslinking chemistries and measure the water transport in these polymers. Membrane samples will be provided to cell testing partners at USC and NREL for characterization of the performance and durability of the samples as a function of water transport properties. 3M will examine larger-scale membrane casting using high-performance supports and will also examine AEMFC durability.

APPROACH

Our approach is based on a new polyolefin AEM chemistry [1, 2]. The general formulation of the membranes is shown in Figure 1 and has been previously reported as detailed in references 1 and 2.

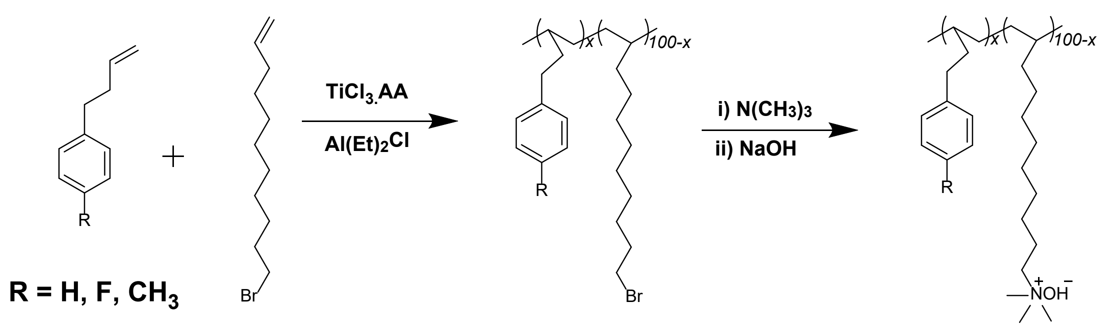


Figure 1. Baseline Ziegler-Natta (Z-N) polyolefin AEM chemistry

These ionomers can be incorporated into supported membranes and tested in fuel cells. Once supported membranes are fabricated, they will be characterized for their conductivity and water transport properties and selections will be made for fuel cell device testing.

AEMFCs with advanced electrodes will be operated under steady-state conditions to achieve the performance and durability metrics of the project. Namely, we aim to demonstrate, with the above membrane chemistry, 2,000 h cell operation at 600 mA/cm^2 with V >0.6 V and less than 10% voltage fade under conditions of H_2/O_2; T ≥60°C; P ≤1.5 atm$_a$; total membrane electrode assembly (MEA) PGM loading ≤0.125 mg/cm^2. These membranes and cells will be studied for their water transport using membrane diffusion measurements and neutron radiography to connect the water transport characteristics of the membrane, to the water balance in the cell, to the cell's performance and durability. This project will break new ground in understanding the importance of water transport on AEMFC performance and durability.

RESULTS

A large range of membranes were fabricated and delivered to project partners for testing. Table 1 details the individual membrane samples and some of their characteristics. Repeats of all sample compositions were fabricated to ensure repeatability of the testing, and repeats were also retained for detailed characterization studies. The "Feed % of 11-bromoundecene" column determines the ion exchange capacity (IEC) of the final membrane. This Feed % is what is charged to the reactor during polymerization and must be confirmed by proton (^{1}H) nuclear magnetic resonance (^{1}H NMR) on the synthesized polymer. With the experimental percentage of 11-bromoundecene in the copolymer determined by ^{1}H NMR, the IEC of the samples can be calculated and reported.

Table 1. Samples Sent from Penn State to Project Partners for Testing

Sample name	Feed % of 11-bromoundecene	% of 11-bromoundecene by NMR	^{1}H NMR IEC (meq/g)	Thickness (µm)
Ph3A	25	32	2.01	218
Ph5A	25	36	2.22	222
Ph5B	25	36	2.22	233
Ph5C	25	36	2.22	219
Ph6A	30	31	1.96	160
Ph6B	30	31	1.96	192
Ph6C	30	31	1.96	180
PH5E2	25	36	2.22	37
PH5E1	25	36	2.22	39
Ph5F1	25	36	2.22	84
Ph5F2	25	36	2.22	94
Ph5F3	25	36	2.22	61
FPH2A	25	32	1.89	59
FPH2B	25	32	1.89	68
PH5G	25	36	2.22	82
PH5H	25	36	2.22	71
PH5I	25	36	2.22	131
PH5O	25	36	2.22	97
PH5P	25	36	2.22	137
PH5Q	25	36	2.22	152
PH6M	30	31	1.96	120
PH6N	30	31	1.96	92
PH6O	30	31	1.96	135
FPH2K	25	32	1.89	77
FPH2L	25	32	1.89	69
FPH2M	25	32	1.89	47

The samples had varying thickness, which can impact the area specific resistance (ASR) in the cell with thicker membranes having higher ASR and lowering the cell power output, but we can currently produce membrane samples and achieve thicknesses between 50 and 70 microns.

These membrane samples were all mechanically supported using expanded poly(tetrafluroethylene) supports (provided by 3M) and had the appearance shown in Figure 2. Samples on the order of 5-in. x 5-in. in area can routinely be produced to meet the goals of the project. We are currently developing the expertise to make larger quantities of polymer to machine cast membranes as the project moves into Year 2.

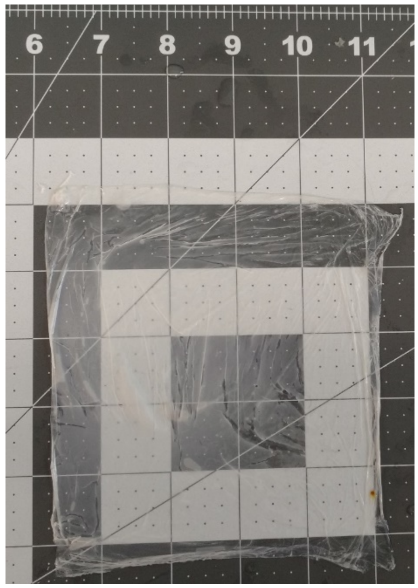


Figure 2. Supported Z-N polyolefin-based AEM

The membranes have been characterized for their physical properties to determine their potential for high-performance operation in a cell. Figure 3 shows the conductivity of the membranes as a function of temperature and the measured IEC of the samples. While the conductivity is reasonable, the IECs are lower than suggested from NMR measurements on the base polymers. This is likely due to incomplete quaternization of the membranes. Thus, our casting and quaternization procedures will be refined in the coming work.

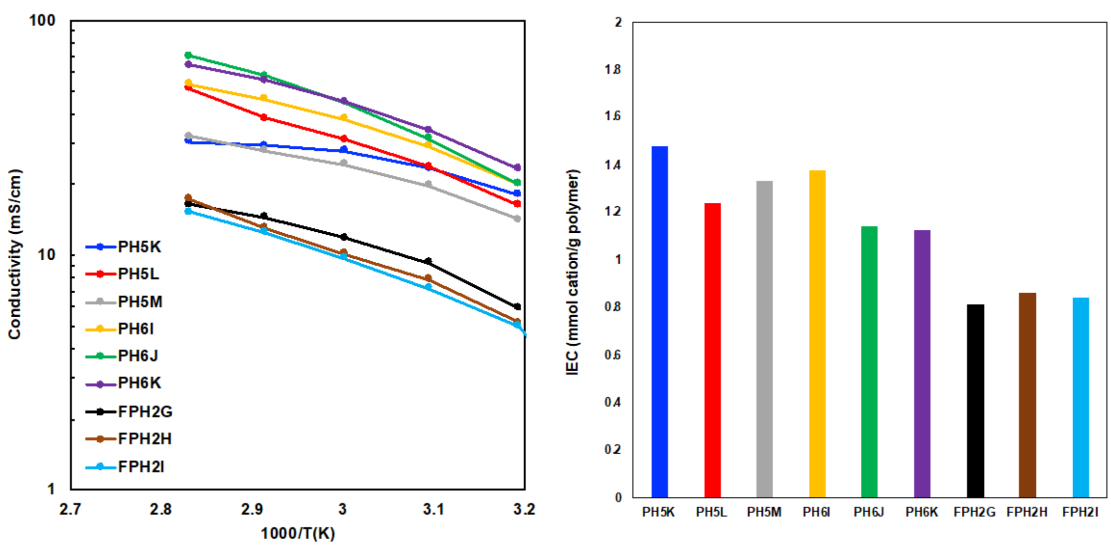
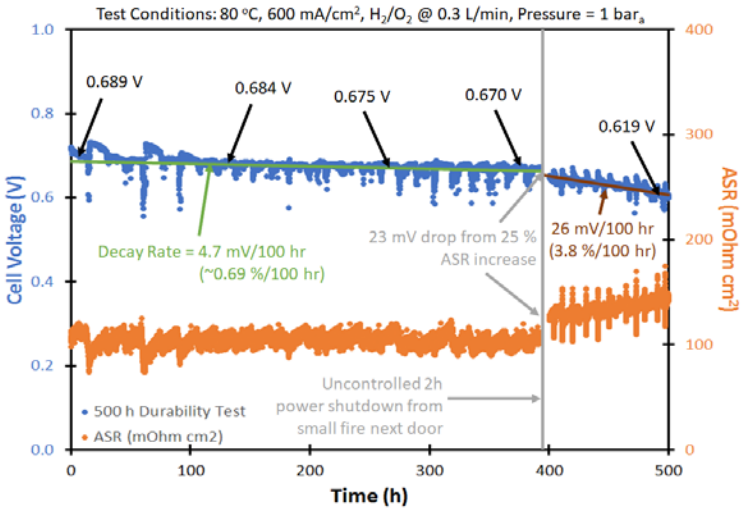


Figure 3. Conductivity (left) as a function of inverse temperature and IEC (right) for polyolefin membranes for various samples

The annotated durability plot to meet the Year 1 go/no-go decision point is shown in Figure 4. Even with an unanticipated shutdown, as noted in the figure, the cell still met the entire 500 h lifetime test of 600 mA/cm^2

above 0.6 V. In the first part of the test before the shutdown, the degradation rate was very low. Thus, we anticipate that 2,000 h lifetime is achievable.



- Generation 3 electrodes
- Cell temperature: 80 °C
- Anode
  - Loading : 0.66 $mg_{PtRu}cm^{-2}$
  - Dew Point: 75-77 °C
- Cathode
  - Loading: 0.61 $mg_{Pt}cm^{-2}$
  - Dew Point: 78-79 °C
- A/C Flowrate: 0.3/0.3 L min^{-1}
- A/C Back Pressurization: 0/0 kPa

Figure 4. Lifetime testing of an AEMFC with Penn State membrane and USC electrodes

Overall, the membrane synthesis and cell testing is on track. We need to further characterize the membranes' water transport and cell water balance while achieving the durability and performance metrics laid out for Year 2.

CONCLUSIONS AND UPCOMING ACTIVITIES

Year 2 of this project will be focused on demonstrating 2,000 hours of cell lifetime with cell V >0.6 V at 600 mA/cm^2 with less than 10 % voltage fade. This is a stretch goal and improvements in membranes and electrodes are needed to achieve this level of performance and durability.

In concert with the cell performance goal, we aim to collect more fundamental information on the water transport characteristics of the fabricated membranes and relate these membrane transport measurements to the observed water balance in the cell. Membranes with known water transport parameters will be imaged in operating AEMFCs using neutron radiography. Through this work, we hope to elucidate connections between the materials, cell water transport, and device performance and durability.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. "Advanced AEMs with Tunable Water Transport for PGM-Free AEMFCs," poster FC308, DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluation Meeting, Arlington, VA, April 29–May 1, 2019.

REFERENCES

1. L. Zhu, X. Peng, S.L. Shang, M.T. Kwasny, T.J. Zimudzi, X. Yu, N. Saikia, J. Pan, Z.-K. Liu, G.N. Tew, W.E. Mustain, M. Yandrasits, and M.A. Hickner, "High Performance Anion Exchange Membrane Fuel Cells Enabled by Fluoropoly (olefin) Membranes," *Advanced Functional Materials* 29, no. 26 (2019): 1902059.
2. L. Zhu, X. Yu, X. Peng, T.J. Zimudzi, N. Saikia, M.T. Kwasny, S. Song, D.I. Kushner, Z. Fu, G.N. Tew, W.E. Mustain, M.A. Yandrasits, and M.A Hickner, "Poly (olefin)-Based Anion Exchange Membranes Prepared Using Ziegler–Natta Polymerization," *Macromolecules* 52, no. 11 (2019): 4030–4041.