Lab Call FY18 (Membrane): Spirocyclic Anion Exchange Membranes for Improved Performance and Durability

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Project Start Date: January 1, 2018
Project End Date: December 31, 2019

Overall Objectives

- Incorporate spirocyclic ammonium cations into anion exchange membranes to improve durability.
- Demonstrate improved performance and durability of alkaline membrane fuel cells (AMFCs).

Fiscal Year (FY) 2019 Objectives

- Develop ionomer solutions based on spirocyclic anion exchange membrane (AEM) polymers.
- Quantify fuel cell performance of at least three different membrane electrode assemblies (MEAs) using spirocyclic ionomers and compare to baseline AMFC performance.
- Optimize fuel cell performance based on a fully spirocyclic system where cathode and anode ionomer and membrane are spirocyclic based.

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]:

- (A) Durability (of membranes and MEAs)
- (B) Cost (of membranes and MEAs)
- (C) Performance (of membranes and MEAs).

This project will synthesize novel perfluoro (PF) AEMs and ionomers and incorporate these into MEAs for fuel cell testing. The project generally supports targets outlined in the Multi-Year Research, Development, and Demonstration Plan in application-specific areas (portable, stationary, transportation). However, as alkaline membrane fuel cells are at an earlier stage of development, specific target tables have not yet been developed. The following four tasks were presented by Dimitrios Papageorgopoulos at the AMFC Workshop, April 1, 2016 [1].

FY 2019 Accomplishments

- Synthesized spirocyclic polymers with a range of ion exchange capacity (IEC) between 1.3 and 1.7 meq/g.
- Demonstrated greater than 500 hours of durability above 0.6 V at 600 mA/cm^2 with optimized MEAs based on low IEC and thin membranes.
- Demonstrated high initial performance and durability using spirocyclic ionomer-based electrodes.

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

	Task
Q2 2017	Develop anion exchange membranes with an area-specific resistance ≤0.1 ohm cm^2, maintained for 500 hours during testing at 600 mA/cm^2 at T >60°C.
Q4 2017	Demonstrate alkaline membrane fuel cell peak power performance >600 mW/cm^2 on H_2/O_2 (maximum pressure of 1.5 atm_a) in MEA with a total loading of ≤0.125 mg_{PGM}/cm^2.
Q2 2019	Demonstrate alkaline membrane fuel cell initial performance of 0.6 V at 600 mA/cm^2 on H_2/air (maximum pressure of 1.5 atm_a) in MEA a total loading of <0.1 mg_{PGM}/cm^2, and less than 10% voltage degradation over 2,000-hour hold test at 600 mA/cm^2 at T >60°C. Cell may be reconditioned during test to remove recoverable performance losses.
Q2 2020	Develop non-PGM catalysts demonstrating alkaline membrane fuel cell peak power performance >600 mW/cm^2 under H_2/air (maximum pressure of 1.5 atm_a) in PGM-free MEA.

PGM – platinum group metal

INTRODUCTION

This project focuses on the synthesis and demonstration of novel AEMs based on spirocyclic cationic groups for greatly improved durability and performance in fuel cells. One of the most profound recent scientific advances has been the demonstration of cations and AEMs with greatly improved stability that may serve as enabling elements of AEMs in high-temperature, high-pH electrochemical devices (fuel cells and electrolyzers). Recently, it was determined that heterocyclic and spirocyclic ammonium small molecules were significantly more base tolerant compared to common tetraalkylammonium and imidazolium cations [2]. The spirocyclic small molecule 6-azonia-spiro[5.5]undecane (ASU) achieved a half-life 26 times greater compared to benzyltrimethylammonium (the most commonly applied cation in AEMs). These results have helped catalyze the development of new AEMs with exceptional base stability that serve as the focus of our efforts. Initial results with these polymers have shown promise but need to be further demonstrated and optimized [3].

APPROACH

The key technical aspects of the project are focused on synthesizing and then quantifying the obtained properties of novel spirocyclic AEMs and then using these materials effectively in MEAs and fuel cell testing. We will establish degradation rates for these materials in controlled tests that we routinely apply to similar systems with a focus on high-temperature stability in the presence of base. These studies will provide information on the ultimate stability of these polymers under well-hydrated conditions relevant to operation in devices. In the area of MEA optimization and fuel cell performance we will have significant technical challenges, where we will leverage our significant AMFC experience to explore the performance and durability of these materials as electrode ionomers and membranes.

RESULTS

Novel spirocyclic polymers were synthesized with the chemical structure and synthesis procedure presented in Figure 1. IEC of synthesized materials varied between 1.3 and 1.7 meq/g by controlling the amount of monomer provided during synthesis. These materials were characterized for properties and durability with their properties being reported in Table 2, including the peak power densities obtained when run in fuel cells. PF AEM Gen 2 results are reported for comparison purposes. Ex situ testing of membranes showed that significant chemical degradation was evident in all three samples for IEC and conductivity when tested in contact with 1 M hydroxide for 1,000 hours.

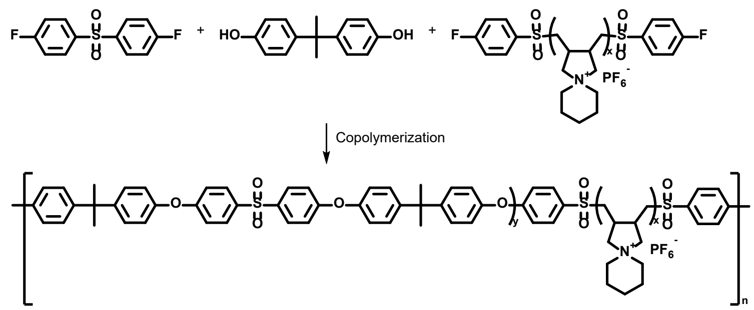

Figure 1. Chemical synthesis route and chemical structure of spirocyclic polymers

Table 2. Properties for spirocyclic polymers synthesized compared to the Gen 2 PF AEM reference polymer synthesized at the National Renewable Energy Laboratory

Polymer	IEC (measured) [mmol/g]	Cl^- Conductivity @RT in Water [mS/cm]	Water Uptake (%)	Peak Power Density (W/cm^2)
SpiroCyclic AEM	1.3	14.0	22	0.85
SpiroCyclic AEM	1.5	13.8	42	1.22
SpiroCyclic AEM	1.7	16.1	80	1.48
Gen 2 PF AEM	0.9	13.4	18	1.10

After synthesis the spirocyclic polymers were run in fuel cell operation. In order to focus on the performance of the polymers, identical electrodes were employed made by standard National Renewable Energy Laboratory synthesis approaches. These materials were based on polymers supplied by Prof. John Varcoe (University of Surrey). The highest peak power densities obtained were for high IEC samples as shown in Table 2. However, an opposite trend was found for durability, as the high IEC samples showed the lowest durability (less than 200 hours) (see Figure 2). This was assumed to be related to the high water uptake (80%) of the 1.7 meq/g polymer, whereas the low-IEC polymer (1.3 meq/g) has greatly reduced water uptake (22%) and showed greatly improved durability, reaching over 500 hours on par with baseline PF AEM materials. High frequency resistance (HFR) was mitigated by using a thin membrane for the 1.3 meq/g sample. Despite limitations in chemical stability of these membranes at 80°C, when run at 60°C long lifetimes with reasonable performances were obtained.

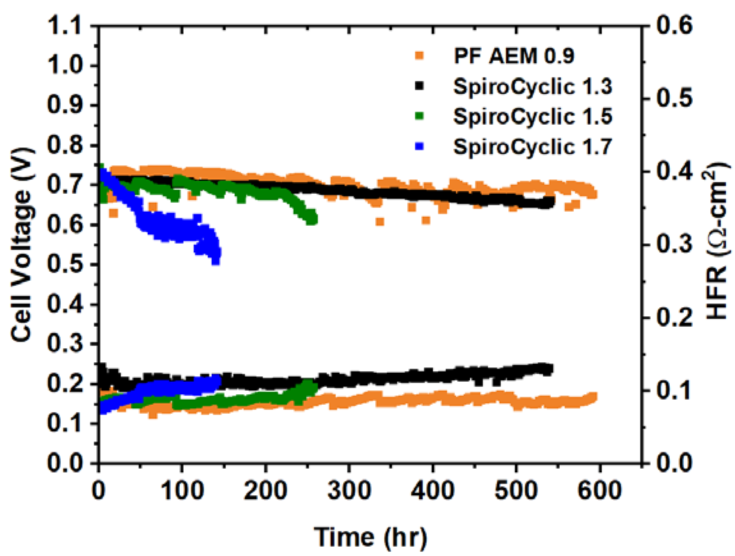

Figure 2. Fuel cell durability of three novel spirocyclic polymers compared to baseline PF AEM material for samples run at durability 600 mA/cm^2 hold, H_2/air (CO_2 free), 122 kPa_a, 60°C

CONCLUSIONS AND UPCOMING ACTIVITIES

Polymer stability remains an issue, as IEC and conductivity losses in ex situ testing were high, but fuel cell durability was reasonable when used as a membrane and in initial studies as an ionomer.

Future work includes:

- Further optimization of spirocyclic polymers as an electrode ionomer
    - Ink composition and processing
    - Specific IEC of ionomer material
- Focus on ionomer implementation of spirocyclic polymer probing cation-catalyst interactions
- Further investigation of low-PGM-loaded MEAs.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Derek Strasser, Kelly M. Meek, Ami Neyerlin, Christopher M. Antunes, and Bryan S. Pivovar, “Alkaline Exchange Fuel Cell Membrane Ionomers Containing Spirocyclic Repeat Units in an All Carbon Backbone for Enhanced Durability,” Meet. Abstr. 2019 Fall Electrochemical Society Meeting Abstract 1688

REFERENCES

1. D. Papageorgopoulos presentation, AMFC Workshop, Phoenix, AZ, April 1, 2016.
2. M.G. Marino and K.D. Kreuer, *ChemSusChem* 8, no. 3 (2015): 513-523.
3. D. Strasser et al., *J. Mater. Chem. A* 5 (2017): 9627.