Advanced Ionomers and Membrane Electrode Assemblies for Alkaline Membrane Fuel Cells

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Subcontractors:
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- Colorado School of Mines (CSM), Golden, CO
- 3M (in-kind), St. Paul, MN

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Project End Date: December 31, 2019

Overall Objectives

- Improve novel perfluoro (PF) anion exchange membrane (AEM) properties and stability.
- Employ high-performance PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells (AMFCs); apply models and diagnostics to AMFCs to determine and minimize losses (water management, electrocatalysis, and carbonate related).

Fiscal Year (FY) 2019 Objectives

- Quantify stability of Gen 2+ small molecule analog in comparison to Gen 2 small molecule analog.
- Demonstrate modeling of carbonate impacts on AMFC performance under dynamic operation, and validate findings with fuel cell performance.
- Demonstrate alkaline membrane fuel cell performance of 0.6 V at 600 mA/cm^2 on H2/air (maximum pressure of 1.5 atm$_a$) at T >60°C.

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 membrane electrode assemblies)
- (B) Cost (of membranes and membrane electrode assemblies)
- (C) Performance (of membranes and membrane electrode assemblies).

Technical Targets

This project will synthesize novel PF AEMs and ionomers and incorporate these into membrane electrode assemblies (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. There are four Tasks presented by Dimitrios Papageorgopoulos at the AMFC Workshop, April 1, 2016 [1].

FY 2019 Accomplishments

- Advanced PF AEM chemistry to include novel, more chemically robust head group (PF AEM Gen 2+).
- Demonstrated significant increases in power density (achieving higher than 3 W/cm^2) and durability (several examples of over 500-hour performance above 0.6 V at 600 mA/cm^2).
- Elucidated fuel cell performance through modeling efforts focused on better understanding water and carbonate transport.

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

Table 1. Technical Targets

	Task
Q2, 2017	Develop anion-exchange membranes with an area specific resistance ≤0.1 ohm cm², maintained for 500 hours during testing at 600 mA/cm² at T >60°C.
Q4, 2017	Demonstrate alkaline membrane fuel cell peak power performance >600 mW/cm² 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/cm² on H_2/air (maximum pressure of 1.5 atm_a) in MEA with 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/cm² 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/cm² under H_2/air (maximum pressure of 1.5 atm_a) in PGM-free MEA.

PGM – platinum group metal

INTRODUCTION

AMFCs are of interest primarily because they enable the use of non-Pt catalysts, the main cost/supply limitation of proton exchange membrane (PEM) fuel cells. AMFCs, therefore, offer the potential of greatly decreased polymer electrolyte fuel cell cost. Operating AMFCs under ambient conditions where carbon dioxide (CO_2) is present remains a challenge due to carbonate formation. An approach that has shown promise for CO_2 tolerance is increased operating temperature. Unfortunately, the stability of the cation side chains on the membrane polymer and water management within the membrane both become more difficult as temperature rises.

The use of perfluorinated ionomers, similar to those used in PEM systems, with tethered cation head groups that allow hydroxide conduction should help improve water transport properties and offer exceptional chemical durability of the backbone. The significant advances demonstrated in AMFC systems have been accomplished primarily through improving water management and the bonding between membrane and electrode. Both issues can be tackled much more effectively when employing PF AEMs and ionomers. The project consists of three subtasks: (1) synthesis of novel perfluorinated alkaline ionomers (NREL); (2) characterization of PF AEMs (NREL, CSM); and (3) fuel cell performance and modeling optimization (NREL, LBNL).

APPROACH

The team has focused on achieving higher-temperature, higher-power-density AMFC operation through implementation of novel alkaline PF membranes and ionomeric dispersions. PF materials are expected to enhance water transport capabilities and electrode performance/durability significantly, thereby enabling higher-temperature and higher-power-density operation. The combination of high current density and operating temperature will improve the ability of these devices to tolerate ambient CO_2 and potentially enable tolerance to these conditions. Starting with the sulfonyl fluoride form of current PF ionomers we have identified, and in several cases verified, the ability to convert commercially available precursors into anion exchange polymers and membranes. The synthesized PF ionomers have been cast into membranes, made into polymeric dispersions, and characterized in fuel cell tests. Modeling efforts have been made in parallel to better understand cell performance, loss mechanisms, and mitigation approaches.

RESULTS

Polymer synthesis has focused on Gen 2 material (shown in Figure 1). We have modified our synthesis procedure in order to achieve increased ion exchange capacity and for batches that now are synthesized at 70-g scale (a 6x increase compared to FY18). To date, we have synthesized more than 600 g of Gen 2 PF AEM and have shared this material with more than 30 collaborating institutions.

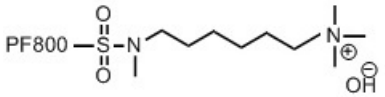

Figure 1. Chemical structures of Gen 2 PF AEMs (PF800 is 3M-supplied precursor material at 800 equivalent weight)

Our Gen 2 PF AEM materials have been tested in AMFCs under a range of conditions and have shown high performance and durability. This year we further studied the impact of water management and the influence of different electrodes on AMFC performance. Through efforts in partnering with other collaborators, University of South Carolina and Georgia Tech, we were able to elucidate the role of carbonate poisoning and CO_2 transport in operating cells [2] and demonstrate the highest AMFC performance reported to date (3.4 W/cm^2) [3].

We greatly expanded our studies of electrodes containing PF AEMs in FY 2019. Prior to this year, high performance was only achieved using ionomer materials supplied by University of Surrey [4]. In FY 2019 we established our ability to produce high-performance electrodes and cells using Gen 2 PF AEM materials in the electrodes. As shown in Figure 2, the performance and durability of cells using PF AEM in the electrodes is essentially identical to that using ethylene tetrafluoro ethylene polymer (ETFE) materials supplied by University of Surrey with identical Pt loadings (0.4 mg/cm^2).

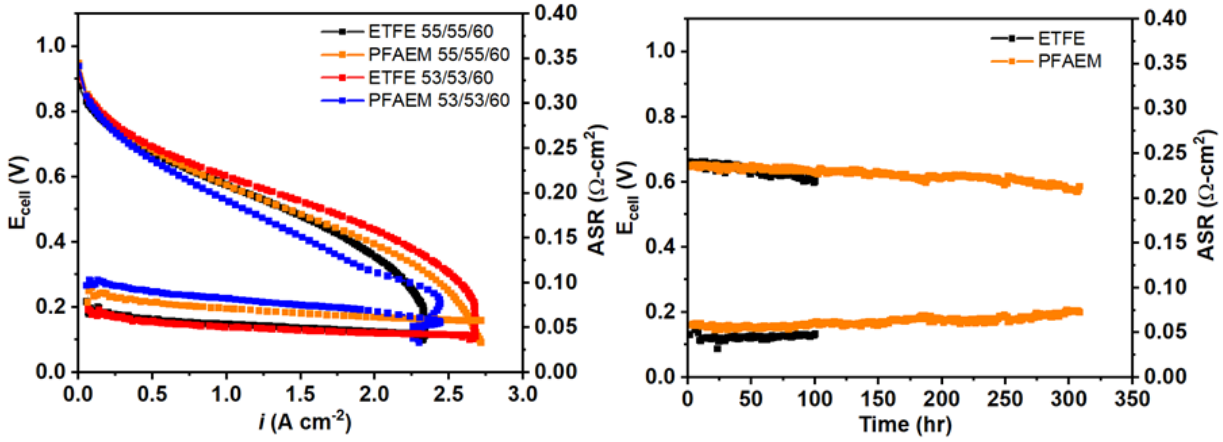

Figure 2. AMFC performance and high frequency resistance for PF AEM membranes using ETFE-based and PF AEM-based electrodes. Cell conditions given in inset left (anode/cathode/cell temperature). Durability test (right) under 600 mA/cm² hold, H_2/O_2, 60°C, 121 kPa_a, 95% relative humidity (RH).

To better understand the water management issues of AMFCs, we have extended modeling work in this area. Figure 3 shows the modeled overpotential of alkaline cells when operated in the presence of air, with and without 400 ppm of CO_2. The models were run at 60°C with H_2 and air at 50% RH, 1.2x stoich flow, 0.72 A/cm^2 average current density. The CO_2-free system predicts a much lower overpotential as observed in these systems and correlates the increased overpotential losses in the CO_2-containing system largely to anode effects. This can be explained by the current flow in the device continuously pushing carbonate anions toward the anode. These studies help confirm the need to keep CO_2 out of the fuel cell in order to enable efficient operation.

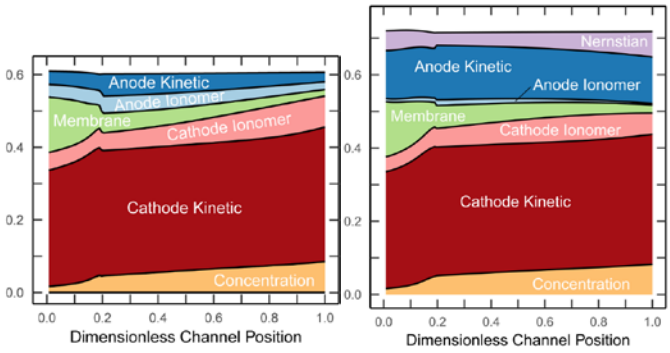

Figure 3. Modeled AMFC overpotential losses at 60°C with H_2 and air at 50% RH, 1.2x stoich flow, 0.72 A/cm² for performance without (left) and with (right) 400 ppm CO_2 in the cathode air feed

CONCLUSIONS AND UPCOMING ACTIVITIES

The project has successfully synthesized PF AEM sulfonamide-linked chemistries for highly OH- conductive AEMs. Extensive characterization has been performed on the polymer. Implementing this polymer into devices yields high AMFC power densities and reasonable durability. Modeling and diagnostic techniques are being performed to advance/optimize AMFC architecture.

Future work focuses on AMFC implementation, modeling, and diagnostics through:

- Improved performance and durability in cells
- Segmented cell studies
- Electrode optimization and diagnostic studies focused on further characterization of electrodes and elucidating performance loss and durability.
- In situ studies: limiting current, RH studies, CV, and impedance (and water management)
- Ex situ studies: microscopic, electrochemical, and spectroscopic analysis
- Integration of modeling efforts with cell testing
- Further elucidation of the impact of operating conditions (temperature, RH, current density, CO_2 concentration).

FY 2019 PUBLICATIONS/PRESENTATIONS

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9. Ami Neyerlin, Chris Antunes, Kelly Meek, Derek Strasser, Zbyslaw Oczarczyk, and Bryan Pivovar, "Advances in Alkaline Membrane Fuel Cell Performance and Durability," Polymers for Fuel Cells, Energy Storage, and Conversion Workshop, Pacific Grove, CA (2019).

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2. Y. Zheng, T.J. Omasta, X. Peng, L. Wang, J.R. John R. Varcoe, B.S. Pivovar, and W.E. Mustain, "Quantifying and elucidating the effect of CO2 on the thermodynamics, kinetics and charge transport of AEMFCs," *Energy Environ. Sci.* 12 (2019): 2806.

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