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# Advanced Ionomers and Membrane Electrode Assemblies for Alkaline Membrane Fuel Cells

Bryan Pivovar (Primary Contact), Derek Strasser, Kelly Meek, Chris Antunes, Ami Neyerlin, Andrew Park, K.C. Neyerlin, Shaun Alia, Hai Long, and Zbyslaw Owczarczyk  
National Renewable Energy Laboratory  
15013 Denver West Parkway  
Golden, CO 80401  
Phone: (303) 275-3809  
Email: [Bryan.Pivovar@nrel.gov](mailto:Bryan.Pivovar@nrel.gov)

DOE Manager: David Peterson  
Phone: (720) 356-1747  
Email: [David.Peterson@ee.doe.gov](mailto:David.Peterson@ee.doe.gov)

#### Subcontractors:

- Lawrence Berkeley National Laboratory, Berkeley, CA
- Colorado School of Mines, Golden, CO
- 3M Company, St. Paul, MN

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## 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).

## 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<sup>1</sup>:

- (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). As alkaline membrane fuel cells are at an earlier stage of development, however, specific target tables have not yet been developed. There are four tasks presented by Dimitrios Papageorgopoulos at the AMFC Workshop, April 1, 2016 [1].

- Q2, 2017: Develop anion-exchange membranes with an area-specific resistance  $\leq 0.1$  ohm cm<sup>2</sup>, maintained for 500 hours during testing at 600 mA/cm<sup>2</sup> at T >60°C.
- Q4, 2017: Demonstrate AMFC peak power performance >600 mW/cm<sup>2</sup> on H<sub>2</sub>/O<sub>2</sub> (maximum pressure of 1.5 atm<sub>a</sub>) in MEA with a total loading of  $\leq 0.125$  mg-PGM/cm<sup>2</sup>.
- Q2, 2019: Demonstrate AMFC initial performance of 0.6 V at 600 mA/cm<sup>2</sup> on H<sub>2</sub>/air (maximum pressure of 1.5 atm<sub>a</sub>) in MEA, a total loading of <0.1 mgPGM/cm<sup>2</sup>, and less than 10% voltage degradation over 2,000-hour hold test at 600 mA/cm<sup>2</sup> 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<sup>2</sup> under hydrogen/air (maximum pressure of 1.5 atm<sub>a</sub>) in platinum group metal (PGM)-free MEA.

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<sup>1</sup> <https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

## FY 2018 Accomplishments

- The project has repeatedly demonstrated fuel cell performance greater than 1 W/cm<sup>2</sup> and durability greater than 500 hours during testing at 600 mA/cm<sup>2</sup>.
- The project has developed novel perfluoro polymers based on sulfonamide linkage chemistry (Generation [Gen] 2), including improving ion exchange capacity and tethering of novel cations (Gen 2+ chemistries).
- PF AEM Gen 3 chemistry was determined to be a no-go due to difficulties in achieving extent of reaction required for viable membrane performance.
- Building on the high performance of ethylene tetrafluoro ethylene polymer (ETFE)-based electrodes, PF AEM electrodes and full PF AEM cells now also have demonstrated performance of greater than 1 W/cm<sup>2</sup>.
- Model development is providing insight into the role of water and carbon dioxide in these systems, allowing the performance potential and limitations of AMFCs to be better understood.

## INTRODUCTION

AMFCs are of interest primarily because they enable the use of non-Pt catalysts, the main cost/supply limitation of polymer electrolyte membrane fuel cells (PEMFCs). AMFCs, therefore, offer the potential of greatly decreased polymer electrolyte fuel cell cost. Operating AMFCs under ambient conditions where carbon dioxide is present remains a challenge due to carbonate formation. An approach that has shown promise for carbon dioxide 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 PEMFC 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 (National Renewable Energy Laboratory [NREL])
2. Characterization of PF AEMs (NREL, Oak Ridge National Laboratory/University of Tennessee Knoxville, Colorado School of Mines)
3. Fuel cell performance and modeling optimization (NREL, Lawrence Berkeley National Laboratory).

## 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 power density operation. The combination of high current density and high operating temperature will improve the ability of these devices to tolerate ambient CO<sub>2</sub> and potentially enable tolerance to these conditions. Starting with the sulfonyl fluoride form of current perfluoro 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

Although PF chemistry improves PF sulfonic acid (PFSA) acidity, the strongly electron withdrawing PF backbone creates challenges for anion exchange membranes. From the readily available perfluoro sulfonyl fluoride precursor (PF-SFP), different strategies can be employed to tether cations to the polymer backbone. We have focused on an amide linkage as shown in Figure 1 for our Gen 1 and Gen 2 PF AEMs and an aryl linkage for Gen 3. Although small molecule studies of Gen 3 chemistry showed good chemical stability, we abandoned the approach due to the extent of the reaction difficulties occurring while performing modification to the base polymer, and instead focused on tethering cations with increased stability onto our Gen 2 platform. The advanced cation tethering is in progress, but we have shown the ability to achieve reasonable ion exchange capacity and conductivity with advanced imidazolium-based cations. To date, we have synthesized more than 300 g of Gen 2 PF AEM and have shared this material with more than 20 collaborating institutions.

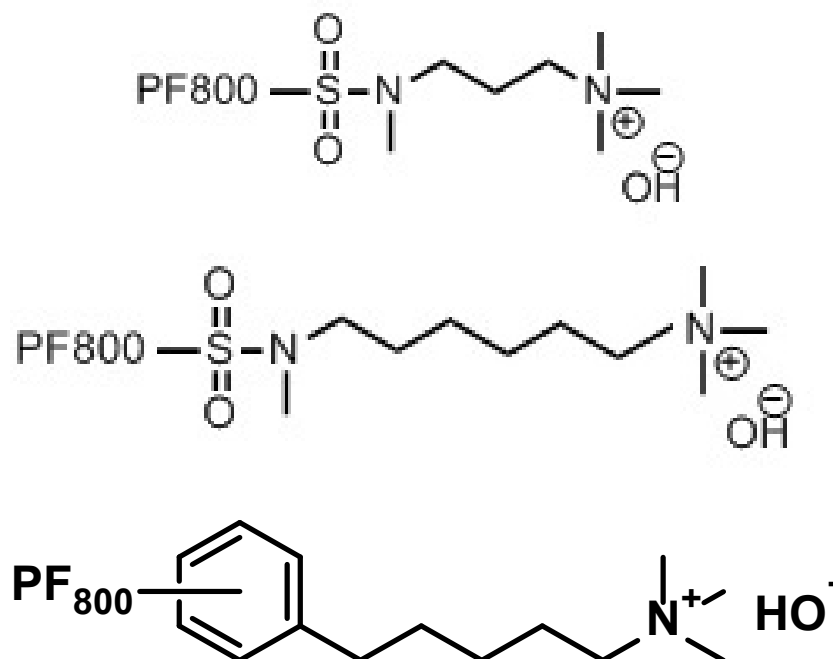


Figure 1. Chemical structures of Gen 1 (top), Gen 2 (middle), and Gen 3 (bottom) PF AEMs

Our Gen 2 PF AEM materials have been tested in AMFCs under a range of conditions and have shown high performance and durability as presented in last year's report. This year we further studied the impact of water management and the influence of different electrodes on AMFC performance. We had two primary electrodes studied, those developed by collaborators Professor Bill Mustain (University of South Carolina) based on ETFE ionomer supplied by Professor John Varcoe (University of Surrey). These electrodes have demonstrated performance above 1.9 W/cm<sup>2</sup> and are based on a hand-milling technique for mixing, followed by air-brush spraying onto gas diffusion layers to obtain gas diffusion electrodes (GDEs) [2]. The AMFC performance and high frequency resistance (HFR) of these MEAs is shown in Figure 2 as a function of reactant gas feed relative humidity (RH). In the tests presented, RH was kept constant in anode and cathode feed for each subsequent test. The results highlight the propensity of these cells to flood and dry out within narrow RH windows. The HFR values obtained allow relative hydration levels to also be probed.

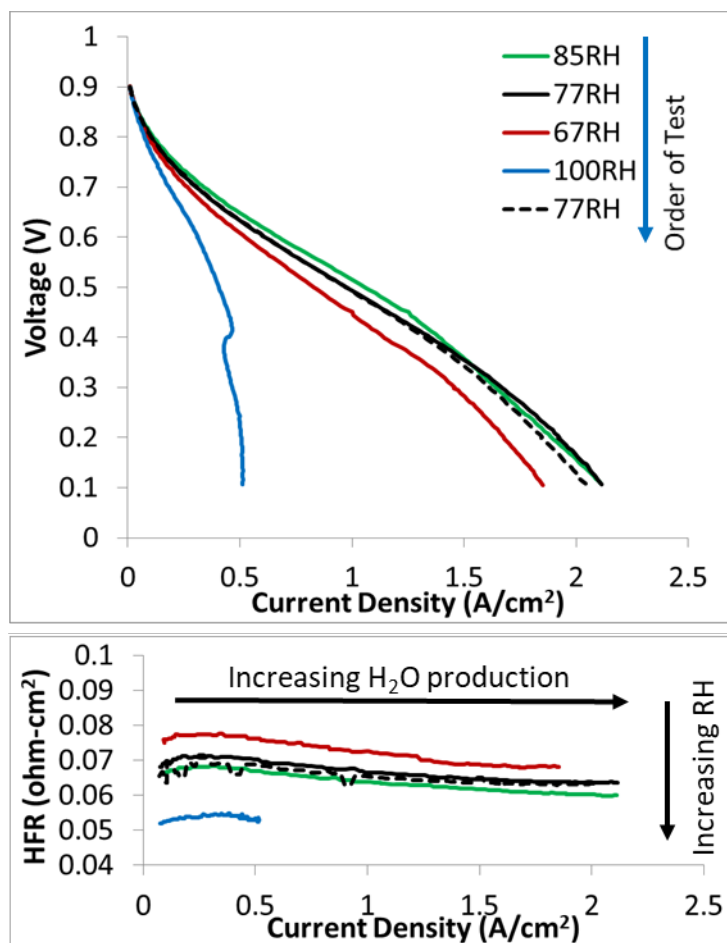


Figure 2. AMFC performance and HFR for PF AEM membranes using ETFE-based GDEs

We greatly expanded our studies of electrodes containing PF AEMs this past year. Figure 3 compares the performance and HFR obtained for different electrodes at optimized RH conditions. The PF AEM electrodes studied were prepared using standard catalyst preparation techniques and a PF AEM Gen 2 dispersion. The performance differences observed for ETFE-based electrodes and PF AEM-based electrodes are quite significant and obvious. For the samples prepared, ETFE greatly outperformed PF AEM samples, with performance being most significant for ETFE at the anode. Durability difference, not shown, was greater for ETFE at the cathode, but in both cases ETFE electrodes were found to be superior. Through modification of fabrication route, we subsequently have improved PF AEM performance significantly. A key observed property in these experiments has been HFR and trends with increasing current density, where flooding and dehydration can be observed.

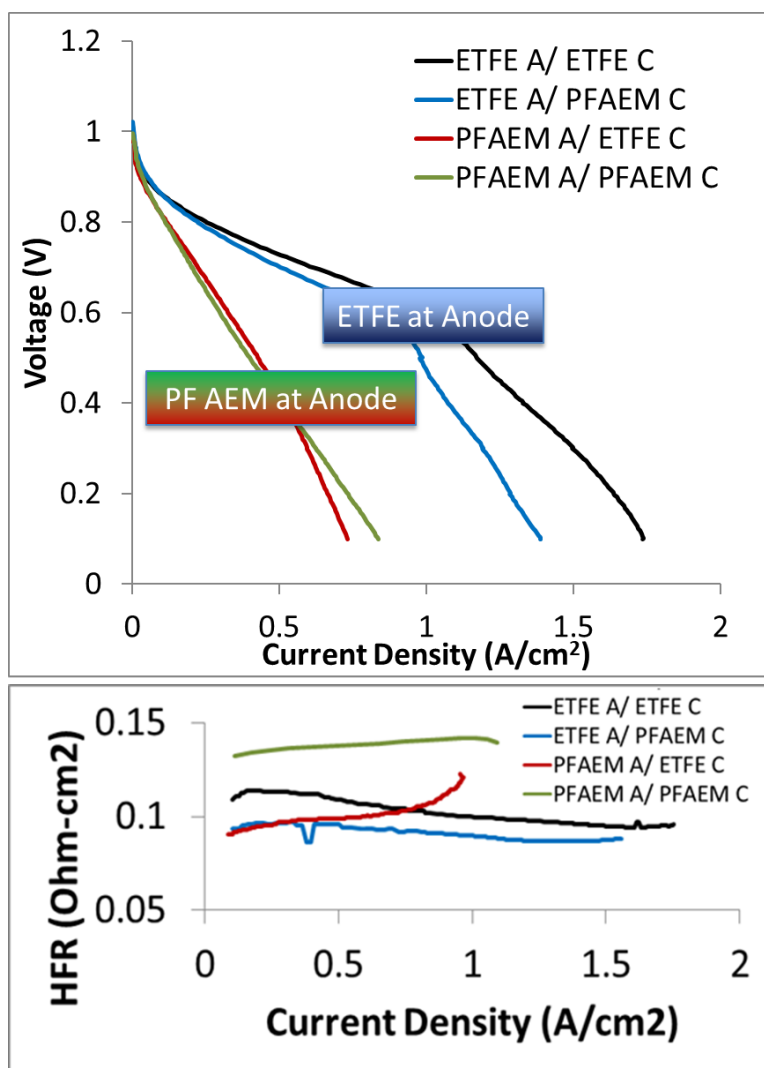


Figure 3. AMFC performance and HFR for PF AEM membranes using ETFE-based GDEs and PF AEM Gen 2 catalyst-coated membranes

To better understand the water-management issues of AMFCs we have focused modeling development in this area. Figure 4 shows the change of water content across an MEA and into the gas diffusion layers and flow channels for small changes in RH (1°C and 2°C changes in dewpoint). The model shows that even with these modest changes in dew point, the accumulation of water in the gas diffusion layer and the anode catalyst layer can be significant. These results are consistent with our observed performance, Figure 2, and in neutron studies performed on these and related AMFCs [2].

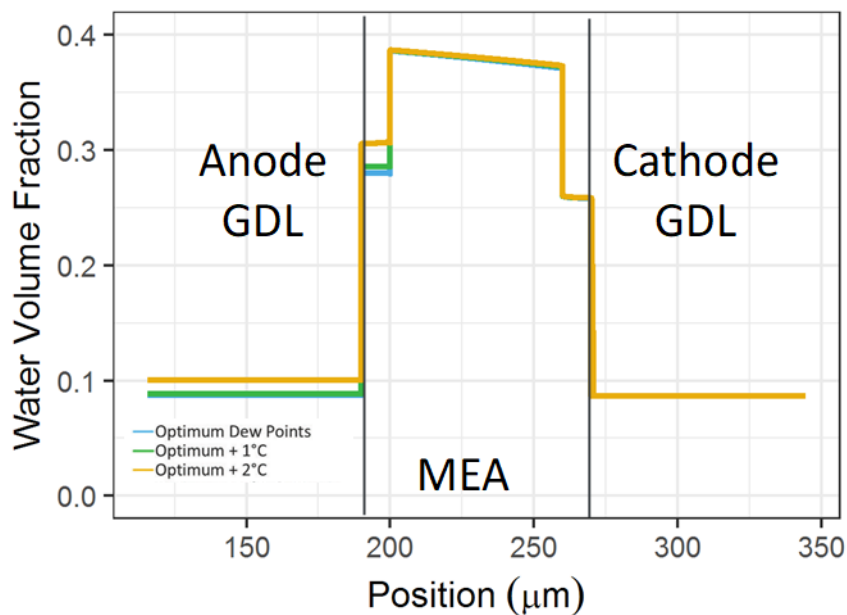


Figure 4. Water-management modeling of AMFC performance with slight variations in RH

## CONCLUSIONS AND UPCOMING ACTIVITIES

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

- Polymer synthesis: Gen 2+ polymer development.
- Characterization:
  - Obtaining information about membrane properties (including stability).
  - Continuing studies on stability, conductivity, water transport, and carbonate.
- AMFC implementation, modeling, and diagnostics:
  - Improved performance and durability in cells, closing the gap between experimental and modeling efforts.
  - Segmented cell studies.
  - Electrode optimization and diagnostic studies focused on further characterization of electrodes and elucidating performance loss and durability.
  - In situ: limiting current, RH studies, cyclic voltammetry, and impedance (and water management).
  - Ex situ: 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<sub>2</sub> concentration).

## FY 2018 PUBLICATIONS/PRESENTATIONS

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2. T.J. Omasta et al. *Energy Environ. Sci.* 11 (2018): 551–558.