

V.C.7 Advanced Ionomers and MEAs for Alkaline Membrane Fuel Cells

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Project Start Date: October 1, 2015

Project End Date: September 30, 2018

- (C) Performance (of membranes and membrane electrode assemblies)

Technical Targets

This project will synthesize novel PF AEMs and ionomers and incorporate these 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. Instead, there are four milestones, given below, that are included in the Multi-Year Research, Development, and Demonstration Plan.

Milestones	
Q2, 2017	Develop anion-exchange membranes with an area specific resistance $\leq 0.1 \text{ ohm cm}^2$, maintained for 500 h 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 $\leq 0.125 \text{ mg PGM/cm}^2$.
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 h 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 hydrogen/air (maximum pressure of 1.5 atm _a) in PGM-free MEA.

PGM – Platinum group metals

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 (3.4.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) Durability (of membranes and membrane electrode assemblies)
- (B) Cost (of membranes and membrane electrode assemblies)

FY 2016 Accomplishments

- The project has successfully synthesized PF AEM sulfonamide-linked chemistries for two generations of polymer chemistry.
- Extensive characterization has been performed on synthesized PF AEMs that has demonstrated conductivity >50 mS/cm, reasonable water uptakes, and high water diffusion coefficients.
- Implementing PF AEMs into devices yielded reasonable AMFC power densities (up to 450 mW/cm² at 60°C, 121 kPa) that surpass those for commercial AEMs.
- Modeling and diagnostic techniques are being performed to advance/optimize AMFC architecture, performance, and durability.



INTRODUCTION

AMFCs are of interest primarily because they enable the use of non-Pt catalysts, the main cost and supply limitation of proton exchange membrane fuel cells. 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 proton exchange membrane 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 sub-tasks: synthesis of novel perfluorinated alkaline ionomers (NREL); characterization of PF AEMs (NREL, Oak Ridge National Laboratory/University of Tennessee, Colorado School of Mines); and 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. The PF materials proposed are expected to enhance water transport capabilities and electrode performance and durability significantly, thereby enabling higher temperature and power density operation. The combination of high current density and operating temperature will improve the ability of these devices to tolerate ambient CO₂ and potentially enabling 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

While PF chemistry improves PF sulfonic acid acidity, the strongly electron withdrawing PF backbone creates challenges for anion exchange membranes. From the readily available perfluoro sulfonyl fluoride precursor, 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 Generations (Gen) 1 and 2 PF AEMs. We have improved our processing of Gen 1 PF AEM and have demonstrated the ability to fully methylate the sulfonamide linkage resulting in non-zwitterionic polymers with conductivity as high as 55 mS/cm (liquid equilibrated at room temperature). These materials have demonstrated reasonable water uptakes and conductivity as a function of relative humidity. They have also demonstrated high water self-diffusion coefficients ($7.2 \times 10^{-6} \text{ cm}^2/\text{s}$). Unfortunately, our Gen 1 materials have shown greater than 90% loss of ion exchange capacity after two days in 2 M KOH at 80°C. We have recently demonstrated greatly (~30 X) improved stability using Gen 2 polymer, and future work is focusing on this material.

While Gen 1 PF AEM showed durability concerns, we were able to test this material as both membranes and electrode binder in fuel cell tests. Figure 2 shows the results of our Gen 1 PF AEM when used as an electrode binder compared to that of AS-4 a commercially available ionomer from Tokuyama. The PF AEM-based electrode shows slightly decreased performance relative the AS-4 in our tests. This result was surprising, as PF ionomers generally outperform hydrocarbon ionomers in proton exchange membrane systems. The Gen 1 PF AEM had limited processibility and was limited to electrode fabrication using dimethyl acetamide. Our future efforts are exploring other solvent systems that may result in improved electrode performance. When PF AEMs have been investigated as membranes in fuel cells using AS-4-based electrodes, Figure 3, performance has been slightly higher than that of commercial A201

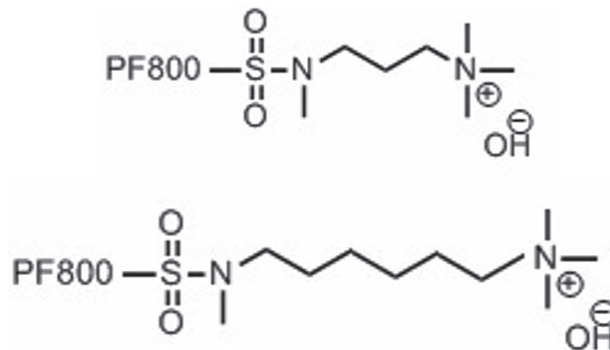


FIGURE 1. Chemical structures of Generation 1 and Generation 2 PF AEMs

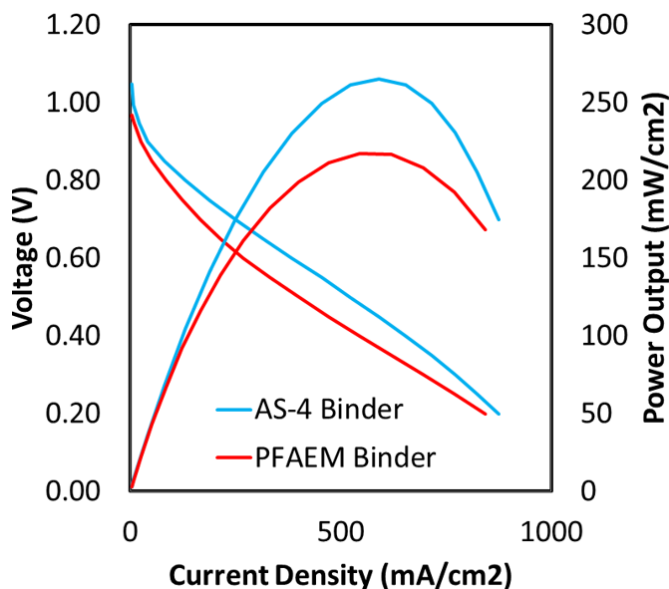


FIGURE 2. Fuel cell performance of PF AEM-based electrodes compared to AS-4-based electrodes

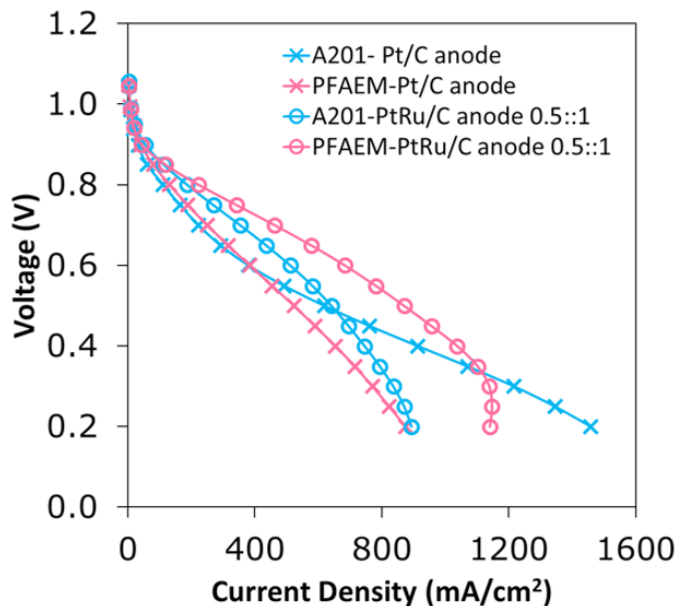


FIGURE 3. AMFC performance of PF AEM membrane compared to A201, 60°C, 121 kPa

from Tokuyama, perhaps due to improved water transport characteristics.

The areas of modeling and advanced diagnostics have both been lacking in the AMFC area, and we have been addressing them in this project. We have modeled the impact of relative humidity on performance as well as the impact of membrane thickness and water diffusivity. We have also applied CO stripping for surface area determination and

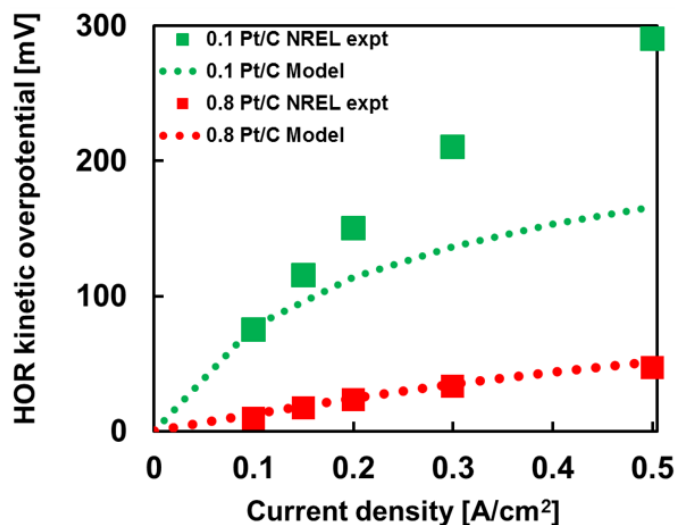


FIGURE 4. Modeling and experimental comparison of PF AEM hydrogen pump system

hydrogen pump tests to quantify anode overpotential losses. Figure 4 highlights the leveraged activities of modeling and advanced diagnostics of the project, where experimental hydrogen pump data is compared to modelling results. At high loading, the model results fit well with experimentally observed data. At lower loading, the model deviates substantially from experimentally observed performance suggesting loss mechanisms not currently captured by the model. These studies help quantify and establish mitigation approaches for performance loss.

CONCLUSIONS AND FUTURE DIRECTIONS

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 reasonable AMFC power densities that surpass those for commercial AEMs. Modeling and diagnostic techniques are being performed to advance/optimize AMFC architecture. Future work focuses on:

- Membrane Synthesis
 - Gen 3 polymer development (avoiding sulfonamide linkage)
 - Gen 2 polymer scale-up
- Characterization
 - Conductivity, stability, water transport, carbonate formation, and resulting effects
- Modeling
 - Parametric studies exploring operating conditions (temperature, relative humidity, current density, CO₂ concentration)

- Coupling oxygen reduction reaction kinetics to water transport and elucidation of water transport within the cell
- Fuel Cell Testing
 - Improved performance and durability through optimization of individual component performance

FY 2016 PUBLICATIONS/PRESENTATIONS

- 1.** Matthew R. Sturgeon, Hai Long, Andrew Park, Bryan S. Pivovar, “Advancements in Anion Exchange Membranes,” 228th ECS Meeting, Polymer Electrolyte Fuel Cells, October 14, 2015, Phoenix, AZ.
- 2.** Andrew Park, Matt Sturgeon, Ami Neyerlin, Zbyslaw Owczarczyk, Bryan Pivovar “Advances in Perfluorinated Anion Exchange Membrane Fuel Cells,” Spring 2016 MRS, March 30, 2016, Phoenix, AZ.
- 3.** Bryan Pivovar, “AMFC Workshop Overview,” 2016 AMFC Workshop, April 1, 2016, Phoenix, AZ.