

V.C.4 Advanced Ionomers and MEAs for Alkaline Membrane Fuel Cells

Bryan Pivovar (Primary Contact), Matt Sturgeon,
Zbyslaw Owczarczyk, Hai Long
National Renewable Energy Laboratory (NREL)
15013 Denver West Parkway
Golden, CO 80401
Phone: (303) 275-3809
Email: Bryan.Pivovar@nrel.gov

DOE Manager

Dave Peterson
Phone: (720) 356-1747
Email: david.peterson@ee.doe.gov

Subcontractors

- Shimshon Gottesfeld (PI), Dario Dekel
CellEra, Inc., Caesarea, Israel
- Mike Yandrasits (PI), Krzysztof Lewinski, Steve Hamrock
3M, St. Paul, MN
- Andy Herring (PI), Mei-chen Kuo, Zachary Page-Belknap
Colorado School of Mines (CSM), Golden, CO

Project Start Date: April 22, 2013

Project End Date: December 31, 2015

Overall Objectives

- Synthesize novel perfluoro (PF) anion exchange membranes (AEMs) with high temperature stability and high water permeability
- Employ high performance PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells

Fiscal Year (FY) 2015 Objectives

- Produce at least two square meters of novel PF AEM membranes for systematic studies of properties including mechanical and chemical stability
- Demonstrate membrane electrode assemblies (MEA) performance $>350 \text{ mW/cm}^2$ employing novel PF AEMs in CO_2 free environments

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program's Multi-Year Research, Development, and Demonstration (MYRDD) Plan:

- (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 MEAs for fuel cell testing. The project generally supports targets outlined in the MYRDD 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 two tasks in the Technical Plan of the MYRDD Plan for alkaline membranes, this project seeks to address both.

TABLE 1. Tasks Addressed from the Technical Plan of the MYRDD Plan for Alkaline Membranes

	Task
1.4	Demonstrate an anion-exchange membrane that retains 99% of original ion exchange capacity for 1,000 hours in hydroxide form at $T > 80^\circ\text{C}$. (2Q 2013)
3.8	Demonstrate anion-exchange membrane technologies in MEA/single cells with non-PGM catalysts that maintain performance higher than 350 mW/cm^2 for 2,000 hours at $T > 80^\circ\text{C}$. (4Q, 2016)

PGM—precious group metals

FY 2015 Accomplishments

- The project has explored multiple PF AEM chemistries for amide and aryl/alkyl linkages (Grignard).
- We have improved our polymer synthesis and membrane casting.
- We have isolated zwitterionic polymers from amide linkages as a key limiting factor for polymer electrolyte performance and have developed methylation strategies to mitigate.
- We have further investigated novel Grignard chemistry, and have shown perfluoro sulfonyl fluoride precursor (PF-SFP) solubility and Grignard viability in hydrofluoro ethers (HFEs).
- We have developed and applied models to evaluate carbonate uptake/poisoning in alkaline membrane fuel cells (AMFCs).
- We have synthesized significant quantities of methylated polymers ($>100 \text{ g}$) and supplied to 3M for dispersion preparation and membrane casting.
- We have obtained initial fuel cell performances $\sim 100 \text{ mW/cm}^2$ with novel PF AEM-based fuel cells.



INTRODUCTION

AMFCs are of interest primarily because they enable the use of non-Pt catalysts, the primary cost/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 hydroxide conduction cation head groups 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: (1) synthesis of novel perfluorinated alkaline ionomers (NREL, CSM, 3M); (2) developing membranes and dispersions (3M, NREL); and (3) MEA fabrication and fuel cell testing (CellEra, 3M, NREL).

APPROACH

The team will focus 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/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 complete 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.

RESULTS

While PF chemistry improves PF sulfonic acidity, the strongly electron withdrawing PF backbone creates challenges for anion exchange membranes. From the readily available PF-SFP, different strategies can be employed to tether cations to the PF-SFP. We have focused on two, an amide linkage and an aryl/alkyl linkage employing Grignard reagents, shown in Figure 1. As of the 2014 Annual Merit Review, we had synthesized many grams of amide linked polymer, cast films and shown good water uptake and conductivity in halide salt form membranes [1]. Early polymers were difficult to dissolve and cast into high quality films, however, improved synthesis resulted in better solutions and pilot scale casting. Testing of these early membranes resulted in poor hydroxide conductivity, but reasonably high halide ion conductivity that was recoverable following ion exchange, shown in Figure 2. This behavior was unexpected due to the higher mobility of hydroxide than chloride in aqueous media. The unexpected behavior has been attributed to a weakly acidic proton on the sulfonamide

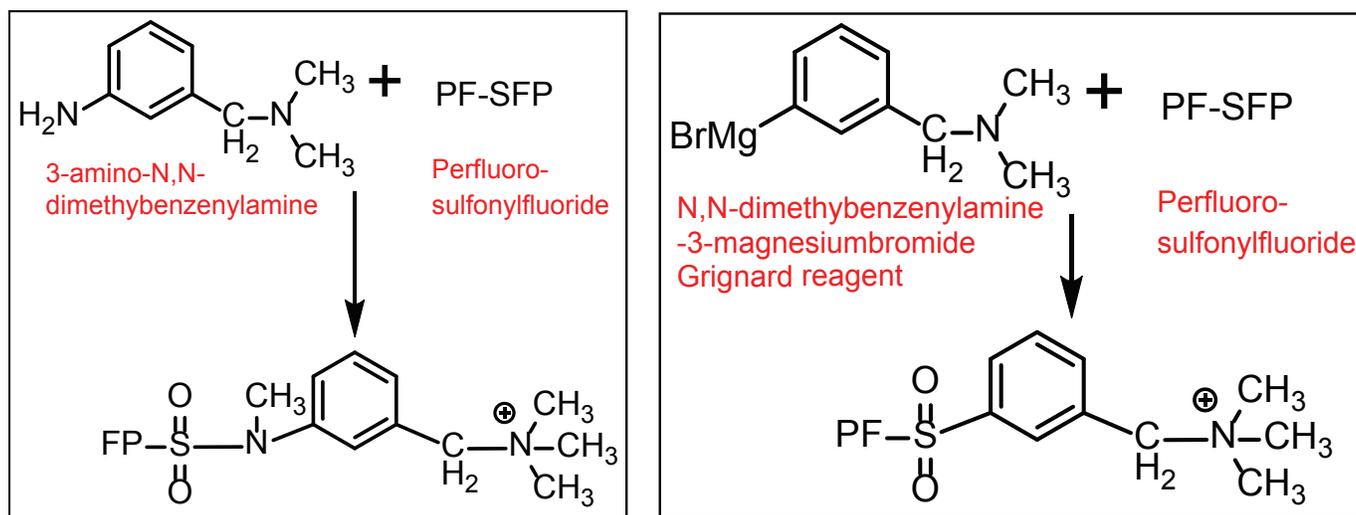


FIGURE 1. Strategies for attaching cationic groups to PF-SFP through amide (left) and Grignard chemistries

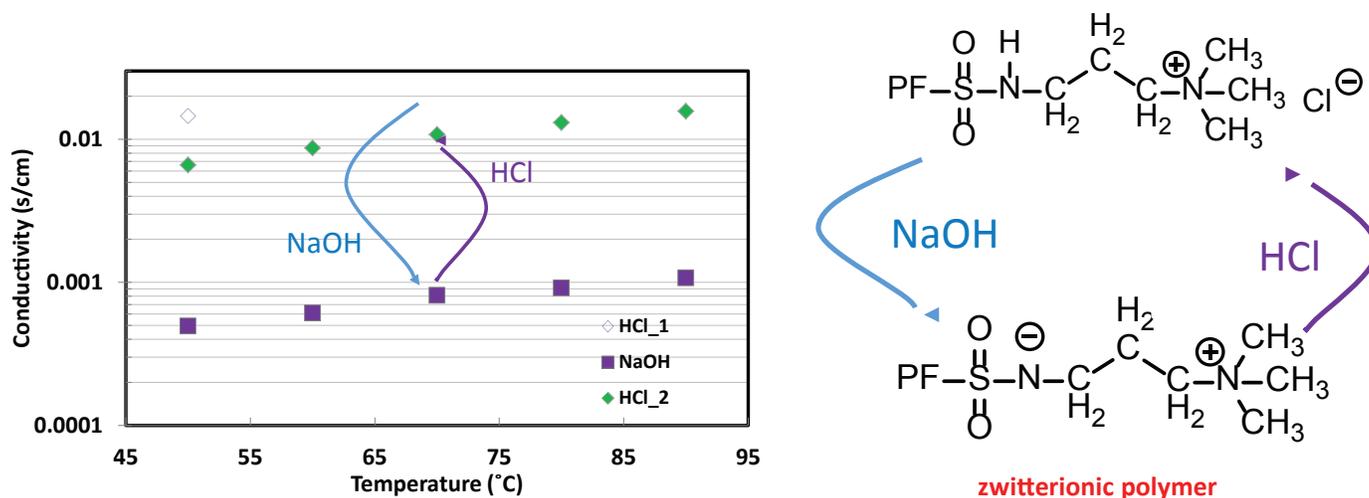


FIGURE 2. Conductivity of amide linked PF AEMs for samples in chloride form, hydroxide form, and chloride form again (left); Schematic representation of chemical structures and ion exchange that led to low conductivity zwitterionic polymers in the hydroxide form and high conductivity chloride ion form polymers (right)

linkage that forms a zwitterionic polymer upon exposure to base, also shown in Figure 2. As target polymers depend on having free hydroxide available and the zwitterionic nature of the polymer was unacceptable for required fuel cell performance, we set about modifying our chemical synthesis approaches to either replace this acidic proton through substitution or remove it entirely by exploring synthesis strategies beyond sulfonamide linkages.

While other non-amide-based synthesis routes have been explored, initial results have shown promise through methylation of the sulfonamide linkage. Through a modified chemical synthesis approach, we have confirmed methylation of the sulfonamide linkage and high hydroxide conductivities of PF AEMs. Membranes cast from these modified synthesis conditions have resulted in liquid equilibrated conductivities of ~17 mS/cm in the chloride form and ~55 mS/cm in the hydroxide form and have maintained similar conductivities when exchanged between chloride and hydroxide form at room temperature. These materials have been processed into MEAs and tested in fuel cells. Figure 3 shows a polarization curve of the methylated, amide-linked PF AEM materials at 60°C under H₂/O₂, fully humidified conditions. The sample shows good open circuit voltage but high ohmic resistance and poor high current density performance. The sample shown was prepared by applying the electrodes directly to the gas diffusion layer, but alternate fabrication routes (direct painting, decal transfer) showed similar performances. The high resistance of the cells (>0.4 ohm/cm²) and the relatively poor durability are current areas of focus. A key concern for the non-amide-based synthesis route is solubility of polymers. We have introduced HFEs and demonstrated the ability to both improve solubility and perform select target chemistries using HFEs.

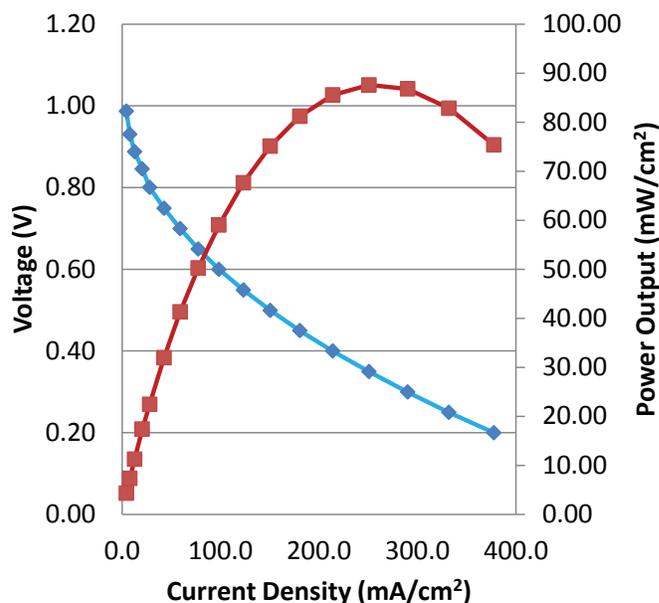


FIGURE 3. AMFC performance of methylated, amide-linked PF AEM

Carbonate formation is a known source of performance loss for hydroxide conducting fuel cells. Scrubbing CO₂ from air has been employed as a mitigation technique, but self-purge has also been promoted as a viable approach to prevent carbonate related losses. Fundamentally, the carbonate/bicarbonate/hydroxide equilibrium is poorly understood. In order to address the concern presented by carbonate poisoning and the limits of the self-purge approach, we have developed a carbonate uptake model that can be employed with a fuel cell model to determine boundary conditions that impact AMFC performance. Figure 4 shows model

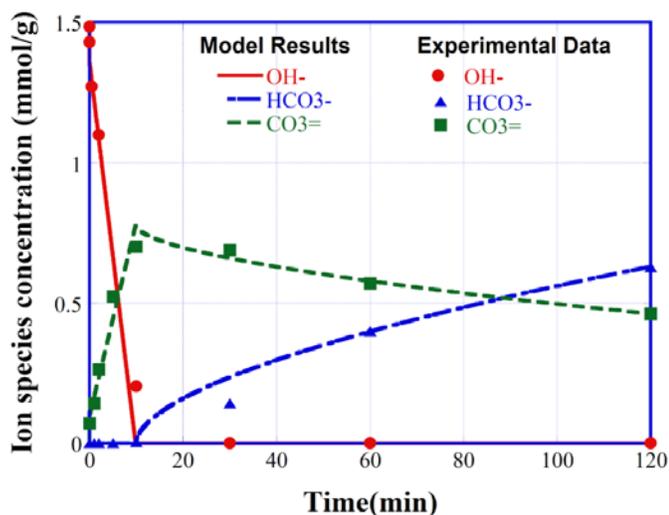


FIGURE 4. Modeling of carbonate formation and equilibrium in AEMs, experimental data from Yangai, et al. [2]

results at room temperature with experimental data for carbonate uptake from the literature [2]. The results show good agreement with experiment and can be used to explore parametric studies to determine the impact of carbonate formation in AMFC systems.

CONCLUSIONS AND FUTURE DIRECTIONS

The project has demonstrated multiple PF AEM chemistries. We have determined that initial amide linked materials were zwitterionic in nature and therefore did not possess required conductivity in the hydroxide form. We improved methylation strategies and now have polymer membranes in hand for further studies. We have determined that HFES are good solvents under specific conditions for the PF-SFP materials. This has allowed additional chemistries to be probed in a known solvent for the PF-SFP materials. Polymers/membranes have been characterized using a variety of techniques including infrared, nuclear magnetic resonance, thermal gravimetric analysis, differential scanning calorimetry, conductivity, and water uptake.

- Membrane Synthesis
 - Improved methylation/secondary amine tethering for non-protic sulfonamide linkage
 - Grignard (or related) chemistry in HFES

- Characterization
 - Continued characterization along the lines of that currently on-going
- Modeling
 - Parametric studies looking at temperature, membrane thickness, and CO₂ concentration
- Dispersion Preparation, Membrane Casting, MEA Fabrication/Fuel Cell Testing
 - Continued testing with current and next generation materials
 - Focus on improved electrode fabrication and high cell resistance

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Pivovar, B. (Nov., 2014). “Fuel Cell R&D focused on Alkaline Membranes and Advanced Catalysis at the National Renewable Energy Lab,” Presented at Wuhan University, Wuhan, China, Nov. 12, 2014.
2. Pivovar, B. (Nov., 2014). “Fuel Cell R&D focused on Alkaline Membranes and Advanced Catalysis at the National Renewable Energy Lab,” Presented at Dalian Institute of Chemical Physics, Dalian, China, Nov. 13, 2014.
3. Pivovar, B. (March, 2015). “Past, Current, and Future Research in Polymer Electrolyte Fuel Cells,” Presented at University of Colorado – Denver, Denver, CO, March 6, 2015.
4. Pivovar, B. (April, 2015). “Past, Current, and Future Research in Polymer Electrolyte Fuel Cells,” Presented at University of Wyoming, Laramie, WY, April 2, 2015.

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1. B. Pivovar, 2014 AMR, “Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells,” http://www.hydrogen.energy.gov/pdfs/review15/fc108_pivovar_2015_o.pdf.
2. Yanagi, H. and K. Fukuta, ECS Transactions, 2008. 16(2): p. 257-262.