

V.L.1 Advanced Ionomers and MEAs for Alkaline Membrane Fuel Cells

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Project Start Date: April 22, 2013
Project End Date: April 22, 2015

Overall Objectives

- Synthesize novel perfluoro (PF) anion exchange membranes (AEMs) with high-temperature stability and high water permeability.
- Employ novel PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells.
- Demonstrate high performance, durability, and tolerance to ambient carbon dioxide.

Fiscal Year (FY) 2014 Objectives

- Evaluate applicability of Grignard chemistry in linking hydroxide conducting head group (e.g. benzyltrimethylammonium, BTMA) to PF sulfonyl fluoride precursor polymer.
- Supply at least three novel PF AEMs to CellEra for fuel cell testing and characterization.
- Report alkaline membrane fuel cell (AMFC) performance of three novel membrane electrode assemblies (MEAs) using PF AEM materials.

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)
- (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 Multi-Year Research, Development, and Demonstration Plan in application specific areas (portable, stationary, transportation). However, as AMFCs 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 Multi-Year Research, Development, and Demonstration Plan for alkaline membranes, this project seeks to address both (Table 1).

TABLE 1. Alkaline Membrane Tasks

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 $350 \text{ mW}/\text{cm}^2$ for 2,000 hours at $T > 80^{\circ}\text{C}$. (4Q, 2016)

PGM – precious metal group

FY 2014 Accomplishments

- Demonstrated multiple PF AEM chemistries that have spacer groups separating cation from PF backbone.
- Synthesized significant quantities of polymers (>150 g).
- Delivered novel membranes for fuel cell testing.
- Developed and demonstrated novel Grignard chemistry to allow more facile functionalization.
- Polymers/membranes have been characterized using a variety of techniques including infrared (IR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), differential scanning calorimetry (DFT), conductivity, and water uptake.



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 carbon dioxide conditions 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 cations and water management 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: synthesis of novel perfluorinated alkaline ionomers (NREL, CSM, 3M); developing membranes and dispersions (3M, NREL); and 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 CO_2 , potentially enabling complete tolerance to ambient CO_2 . 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 will be cast into membranes, made into polymeric dispersions, and characterized. The procedures will draw on existing membrane-making know-how and likely will be similar to that reported in the literature for Tosflex dispersion preparation. Most of the characterization performed on these materials is anticipated to be routine.

RESULTS

Due to the highly electron withdrawing polymer backbone, BTMA was chosen as a model cation as the benzyl group will act as a spacer unit, mitigating concerns regarding stability. Two linking strategies were explored in order to synthesize the PF AEMs, sulfonyl amide linkage and direct sulfonyl aryl linkage through a Grignard precursor (Figure 1). It was determined, through small molecule analogs (perfluoro-1-butanefluoride) and IR analysis of the resultant perfluoro polymer, that the proposed Grignard reaction (Figure 1) successfully links the desired head group (N,N-dimethylbenzylamine) with the PF sulfonyl fluoride precursor (PF-SFP) through a direct sulfonyl-aryl bond. Grignard chemistry was investigated due to its high degree of control and the ability to avoid sulfonamide linkages. However, DFT calculations (Figure 2) suggest enhanced stability of sulfonamide linkage (23.4 vs. 22.1 kcal/mol), and based on the ease of synthesis and membrane fabrication considerations; we have focused our efforts primarily on the aryl-amide linkage chemistry shown in both Figures 1 and 2.

Our initial attempts at membrane fabrication produced materials with less than optimum physical properties. Subsequent improvements in synthesis and casting have

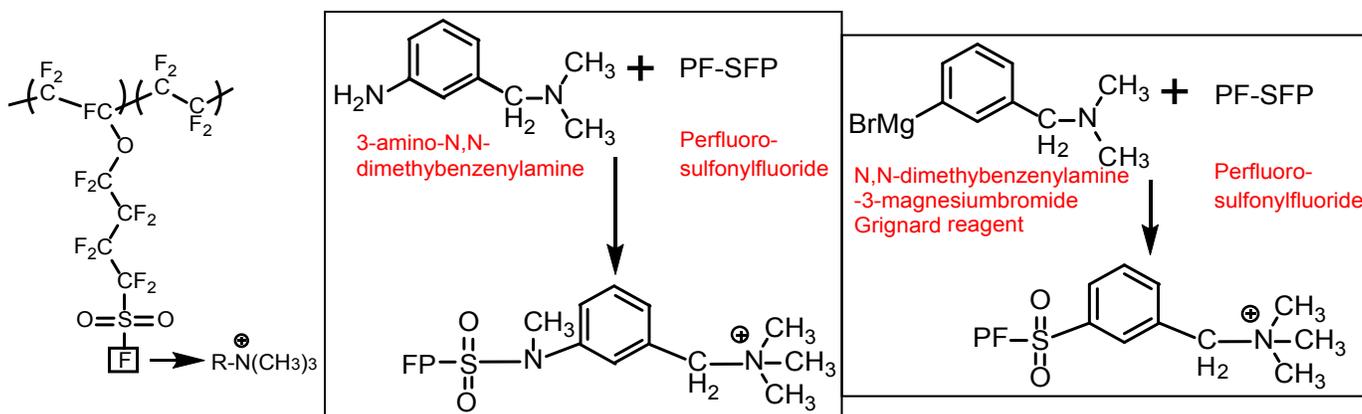


FIGURE 1. Strategies linking hydroxide conducting BTMA head group to PF-SFP (left) through amide (middle) and Grignard chemistries.

R	Linkage	DFT Hydroxide Stability (kcal/mol)		
		Benzyl CH ₂	Ammonium CH ₃	β elimination
	Amide	NA	24.7	19.7
	Amide	23.4	24.5	NA
	Aryl	22.1	24.1	NA

FIGURE 2. DFT studies of hydroxide stability of three initial target synthesis routes.

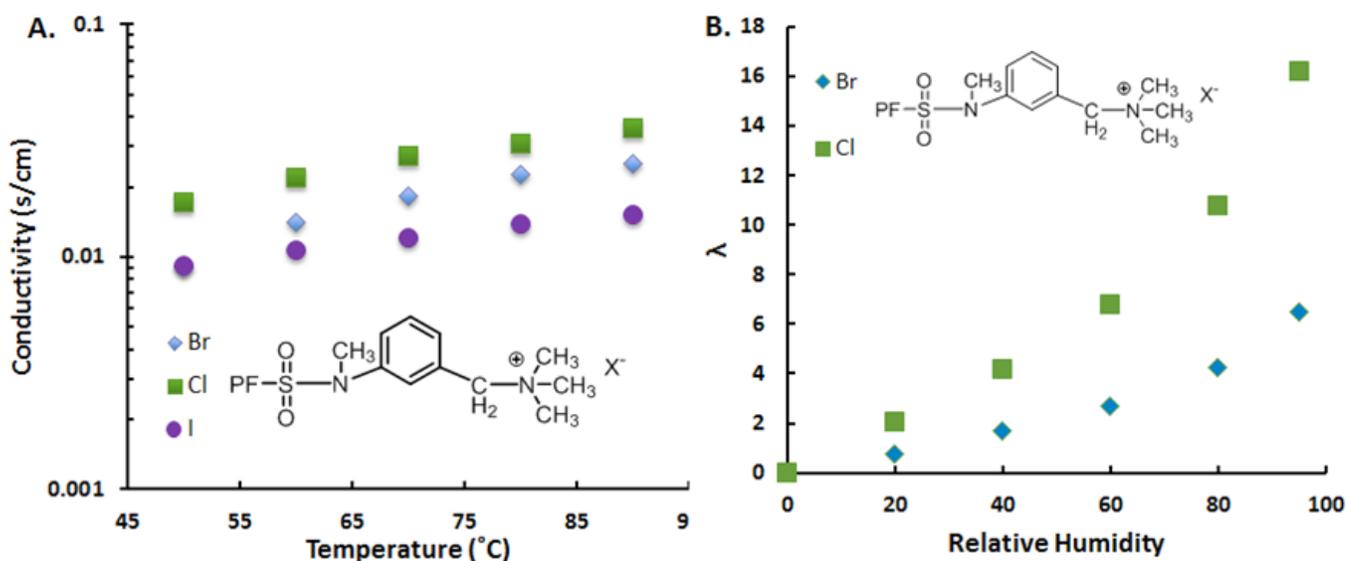


FIGURE 3. Conductivity (A) and water uptake data (B) of PF-AEM films consisting of a perfluoro sulfonyl polymer backbone and a BTMA cationic head group, X represents various counter-anions synthesized through anion exchange techniques.

more recently been achieved and we anticipate future work in this area to be accomplished with greatly improved materials properties. We have focused our efforts on scaled up synthesis (we have synthesized more than 150 g of polymer) and improved reactant purity. NREL has focused primarily on scale up and increased reactant purity. Colorado School of Mines has focused on scale up, membrane casting conditions, and characterization of membrane properties. 3M has focused on membrane casting and is targeting membranes 4 inches wide in sheets up to 2 m long for initial membrane fabrication. The availability of this material to the research community will allow the advancement of PF AEM technology to be greatly accelerated. CellEra has begun AMFC testing using materials from the project.

Figure 3 shows the conductivity and water uptake of three different films. It is expected that the hydroxide forms of the materials (avoided to date to minimize complications of carbonate formation and remove degradation concerns)

will exhibit even greater conductivities. The materials properties for both conductivity and water uptake presented in Figure 3 and measured elsewhere in the project are reasonably consistent with expectation of a PF AEM. The amide-linked PF AEM was sent to CellEra for AMFC testing. Initial AMFC results showed poor performance when PF AEMs were employed as membranes, probably due to the relatively poor mechanical properties of the initial samples. When used as electrode ionomers, fuel cell performance was equivalent or slightly improved compared to state-of-the-art hydrocarbon ionomers. However, mass transport issues occurred within these initial tests, possibly due to unoptimized electrode structures.

CONCLUSIONS AND FUTURE DIRECTIONS

The project has demonstrated multiple PF AEM chemistries that have spacer groups separating cation

from PF backbone. We have synthesized significant quantities of polymers (>150 g). We have developed and demonstrated novel Grignard chemistry to allow more facile functionalization of the PF-SFP. Polymers/membranes have been characterized using a variety of techniques including IR, NMR, TGA, DSC, conductivity, and water uptake.

- Membrane Synthesis:
 - Scaling up of established chemistry, focus on aryl amide linkage.
- Characterization:
 - Expand membrane characterization to include OH⁻ form and more complete data set including titration to evaluate ion exchange capacity. Durability testing of membranes.
- Dispersion/Solution Preparation:
 - Ability to form or optimize solution/dispersions for electrodes and membrane fabrication. Higher temperature processing. Increase number of solvents investigated.
- Fuel Cell Testing

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Pivovar, B. “Past, Current, and Future Research in Polymer Electrolyte Fuel Cells.” Presented at Purdue University, West Lafayette, IN, April 3, 2014.
2. Pivovar, B. “Past, Current, and Future Research in Polymer Electrolyte Fuel Cells.” Presented at Iowa State University, Department of Chemical and Biological Engineering, Ames, IA, September 19, 2013.
3. Pivovar, B. “Fuel Cell R&D at NREL.” Presented at Los Alamos National Laboratory, August 16, 2013.
4. Pivovar, B. “Alkaline Membrane Fuel Cells, Current R&D and Future Potential.” Presented at Transport Processes in Energy Systems, Cornell University, Ithaca, NY, August 7, 2013.
5. Pivovar, B. “Alkaline Membrane Work at NREL.” Presented at University of Surrey, Guildford, England, May 16, 2013.