

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

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 Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan in application to 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 Multi-Year Research, Development, and Demonstration Plan for alkaline membranes; this project seeks to address both.

	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°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°C. (4Q, 2016)

PGM – precious-grade metal

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) 2013 Objectives

Synthesize three unique PF anion-exchange polymer chemistries from the sulfonyl fluoride form precursor

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, MEAs)
- (B) Cost (of membranes and MEAs)
- (C) Performance (of membranes and MEAs)

FY 2013 Accomplishments

None to date



INTRODUCTION

Alkaline membrane fuel cells (AMFCs) are of interest primarily because they enable use of non-Pt catalysts, the primary cost/supply limitation of proton exchange membrane fuel cells PEMFCs. AMFCs, therefore, offer the potential of greatly decreased PEMFC 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 PEM systems, with tethered cations 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. This project consists of three sub-tasks: (I) synthesis of novel perfluorinated alkaline ionomers

(NREL, CSM, 3M); (2) 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, potentially enabling complete tolerance to ambient CO₂.

Most AEMs are based on hydrocarbon polymer chemistry. From significant work in the area of PEMs, water transport has been shown to be significantly higher in PF polymers, particularly at lower hydration levels [1].

Starting with the sulfonyl fluoride form of current PF ionomers (see Figure 1) we have identified and in several cases verified the ability to convert commercially available precursors into anion-exchange polymers and membranes. Synthesis work will focus on linkage chemistry with spacer groups to better mate the highly electron withdrawing backbone with the highly electropositive cation. This linkage and mating of dissimilar materials has been shown to be a major limitation for chemical stability in these systems. A handful of cations and linkage chemistries have already been identified for initial study. The synthesis of novel ionomers is the first critical task and will represent the majority of our initial efforts. This effort will focus on investigating different tethering chemistry/strategies, investigating different spacer groups, and different covalently tetherable cations.

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.

We will implement novel PF AEMs and dispersions into MEAs. Due to the experience of our team members with similar perfluorinated sulfonic acid materials, this implementation should be relatively straightforward when both ionomer and membrane are in PF form. While the use of non-precious catalysts are the primary driving force for AMFC study, in order to maximize efficiency most testing will involve Pt electrodes as a baseline material, as there is ample experimental justification that these results can be translated to non-precious catalyst systems once demonstrated with Pt.

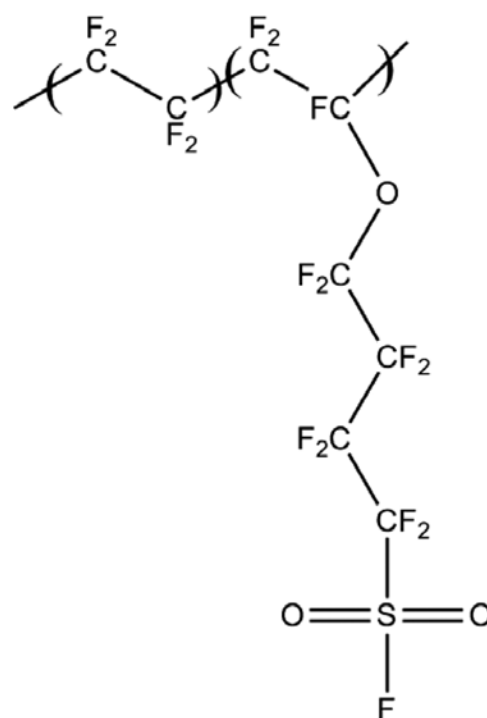


FIGURE 1. Sulfonyl Fluoride Precursor Form of PF Ionomers

RESULTS

The project started in April 2013. Subcontracting has been initiated with all of the subcontractors and the sub-contract with CSM is in place and has active work occurring. Initial efforts on the project have focused on evaluating promising synthesis routes, obtaining materials, and characterizing reactions.

CONCLUSIONS AND FUTURE DIRECTIONS

As the project is just at its inception, we have little in terms of conclusions, and instead have a focus on future directions:

- PF Ionomer Synthesis (NREL/CSM, 3M)
 - Cation tethering to sulfonyl fluoride precursor form through sulfur-nitrogen linkage (NREL/CSM, 3M)
 - Development and application of alternative chemistries (NREL/CSM, 3M)
- PF AEMs and Ionomeric Dispersions (3M, NREL/CSM)
 - Membrane casting (3M, NREL/CSM)
 - Polymer dispersion preparation (3M, NREL/CSM)
 - Membrane characterization (NREL/CSM, 3M)
- MEA Fabrication/Fuel Cell Testing (CellEra, NREL, 3M)

- Water management and CO₂ tolerance studies (CellEra)
- PF AEM and ionomeric dispersions in MEA fabrication and fuel cell testing (CellEra, NREL, 3M)
- Detailed Assessment of Cost and Manufacturability (CellEra, 3M, NREL)

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Principal Investigator, Bryan Pivovar, has been awarded the 2012 Charles Tobias Young Investigator Award (Electrochemical Society).

REFERENCES

1. Kreuer, K.D., et al., Chemical Reviews, 2004. **104**(10): p. 4637-4678.