

## V.C.8 Dimensionally Stable High Performance Membranes

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Chulsung Bae, Rensselaer Polytechnic Institute (RPI)  
Troy, NY

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Project End Date: November 21, 2016

### Overall Objectives

- Develop novel hydrocarbon membranes with high performance at low relative humidity (RH) and high temperature for use in transportation fuel cells.
- Quantitatively characterize these membranes at various RH and temperatures for the following.
  - Gas permeability
  - Water uptake
  - Proton conductivity
  - Mechanical stability

### Fiscal Year (FY) 2016 Objectives

- Initialize development and characterization of the above membranes.

### 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.

- (A) Durability
- (B) Cost
- (C) Performance (cell issues)

### Technical Targets

The main objective of this Phase I project is to fully characterize the fundamental properties of truly novel hydrocarbon membranes for use in fuel cell membrane electrode assemblies. Future projects will assess actual performance and lifetimes in a fuel cell environment with the goal of meeting the following DOE fuel cell targets.

- Area specific proton resistance at maximum operating temperature and water partial pressures from 40–80 kPa: 0.02 ohm cm<sup>2</sup>
- Area specific proton resistance at 80°C and water partial pressures from 25–45 kPa: 0.02 ohm cm<sup>2</sup>
- Area specific proton resistance at 30°C and water partial pressures up to 4 kPa: 0.03 ohm cm<sup>2</sup>
- Cost: \$20/m<sup>2</sup>
- Durability: 20,000 cycles until >15 mA/cm<sup>2</sup> crossover or >20% loss in open circuit voltage

### FY 2016 Accomplishments

- Synthesized two polysulfone ionomers with fluoroalkylsulfonic acid side chains for testing.
- Designed the synthesis of a graft copolymer based on poly(biphenyl alkylene).



### INTRODUCTION

The development of perfluorosulfonic acid membranes, such as Nafion<sup>®</sup>, has greatly contributed to fuel cell technologies and these materials are still widely used as the benchmark membrane in fuel cells. Due to its perfluorinated structure and superacidic pendant side chain, Nafion<sup>®</sup> possesses high proton conductivity as well as good chemical stability. Although higher charge density and proton conductivity could be achieved by shortening the length of side chains bearing the sulfonic acid group (i.e., lowering equivalent weight), such as Hyflon Ion<sup>®</sup> of Solvay and 3M ionomer, their improvements have been incremental. Thus, perfluorosulfonic acids are still not an ideal fuel cell membrane material and their drawbacks (e.g., high cost and low mechanical strength at high temperature) require development of alternative polymer electrolyte membranes (PEMs) for successful adoption of fuel cells as reliable and inexpensive energy conversion devices. Using novel hydrocarbon-perfluorinated hybrid ionomers with high hydrophilic–hydrophobic phase separation, Rensselaer Polytechnic Institute will develop an improved

fuel cell membrane with high conductivity at low RH and high temperature. Giner will use its dimensionally stable membrane technology to improve the strength and dimensional stability of these membranes, as well as their world class membrane characterization facility to screen the PEMs. The goal of this proposed project is the development of ionomeric membranes with high conductivity and mechanical strength for use in low RH, high temperature transportation fuel cell applications.

## APPROACH

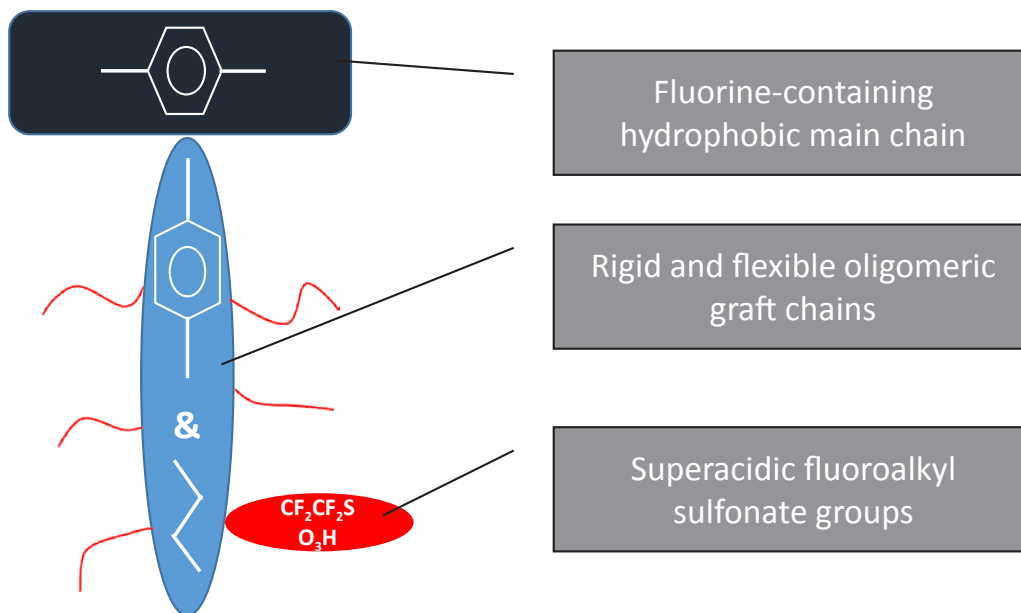
Over the past decades, extensive efforts have been devoted to the development of hydrocarbon-based PEMs, and many aryl and alkyl sulfonated polymers have been described. In general, these sulfonated aromatic polymer PEMs with high ion exchange capacity and high conductivity swell excessively under high hydration conditions and give much lower proton conductivity than Nafion when RH or water content of the membrane is reduced. To achieve highly conductive materials under low hydration conditions, creation of well-connected hydrophilic channels within the membrane through architectural controls of polymer morphology has been pursued over the past decade. The low proton conductivity of these aromatic PEMs under reduced RH conditions is generally believed to be due to (i) the lack of a nanostructured domain morphology with sufficient domain size and connectivity through which protons and water molecules can transport rapidly, and (ii) the less acidic pendant side chain compared to that of Nafion. Concerns about ionic domain size and connectivity have prompted research efforts focused on PEM morphology. Morphology control can be manipulated by many factors, such as

concentration and length of sulfonic acid group, structures of polymer backbones, and pendant chains and their distribution sequences. The general consensus is that ionic nanostructure achieved by phase separation of hydrophilic ionic groups and hydrophobic polymer backbone is critical for enhanced proton transport at low RH. Accordingly, multiblock copolymer PEMs with well defined ionic domains have been prepared by polycondensation of sulfonated hydrophilic oligomers and non-sulfonated hydrophobic oligomers and they achieved more enhanced proton conductivities than the corresponding randomly sulfonated counterparts. The goal of this program will be to take these findings and generate a polymer with large segregated domains, with the highest possible localized charge density using acid functionalities of the highest possible strength. The general structure of these polymers is shown in Figure 1.

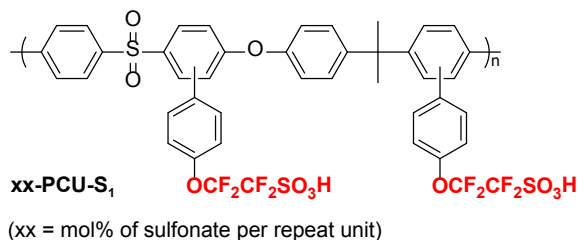
## RESULTS

Two sulfonated poly(arylene ether sulfone) (PSU) ionomers with fluoroalkylsulfonic acid (200-PSU(22K)-S1 and 200-PSU(60K)-S1) were synthesized for this project at RPI and sent to Giner for characterization. These samples are similar in structure to Figure 2, but with different molecular weights (22 and 60 kg/mol). Previous work by the RPI group [1] has shown that these superacid-functionalized membranes have large segregated domains with high localized charge density.

Unfortunately, these ionomers formed very brittle films that could not withstand testing. Different solvent structures and casting methods were tried, but the poor mechanical properties persisted.

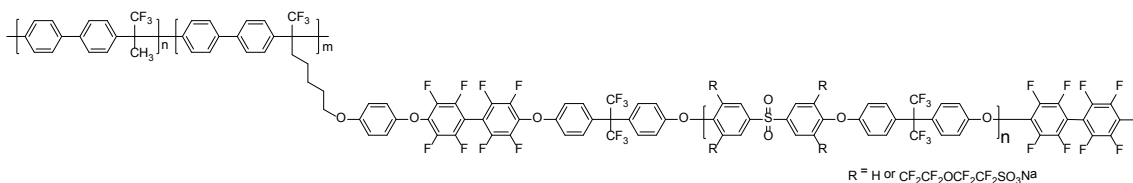


**FIGURE 1.** The general structure of the target ionomeric polymers for this project



**FIGURE 2.** The molecular structure of sulfonated PSU ionomers

Currently, the RPI group is working on the synthesis of graft copolymers based on poly(biphenyl alkylene), shown in Figure 3. The main polymer backbone was prepared using acid-catalyzed polycondensation method, which affords high molecular weight, aryl-ether free, chemically and mechanically stable backbone. The copolymer composed of the hydrophobic main chain and the graft chain with pendant perfluoroalkylsulfonic acid group is expected to show the formation of ionic aggregates thus larger segregated ionic domains. The unexpected leaving of a post doc at RPI has pushed back the timing of this synthesis, but Giner should be receiving samples soon.



**FIGURE 3.** The molecular structure of perfluoroalkylsulfonated graft copolymers

## FUTURE DIRECTIONS

- Optimize casting procedure for polysulfone with fluoroalkylsulfonic acid to improve mechanical properties.
- Synthesize the graft copolymers based on poly(biphenyl alkylene).
- Optimize casting for the graft copolymers.
- Incorporate the dimensionally stable membrane substrate with the ionomers to increase mechanical strength.
- Characterize the membranes at various RH and temperatures with respect to the following.
  - Proton conductivity
  - Water uptake
  - Gas permeability
  - Mechanical strength

## REFERENCES

1. *Polym. Chem.* **2013**, *3*, 272–281.