

V.N.11 New Proton-Conducting Fluoropolymer Electrolytes for PEM Fuel Cells

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Objectives

The overall objective of the research is to provide new electrolyte membranes and electrode materials consisting of integrated catalysts and fluorinated electrolytes for use in PEFC power sources. The research will be pursued in two thrusts, one focused on new proton-conducting fluoropolymer electrolyte membranes for use under high-temperature ($\geq 120^\circ\text{C}$) and low-humidity ($\leq 25\%$ RH) conditions, and another focused on electrolyte integration into fuel-cell electrodes by covalent attachment of electrolytes onto carbon supports. The objectives of work in the first thrust area are the discovery, synthesis, characterization, and evaluation of new polymeric proton-conducting electrolyte membranes. We utilize and build upon synthetic methods which were developed at Clemson and used in the recent past to synthesize related materials, and also develop new synthetic methods to prepare the target polymer electrolytes. The objectives of work in the second thrust area are to develop methods for accomplishing robust attachment of proton-conducting polymer electrolytes onto carbon supports, and to characterize the resulting materials with special attention to their mixed electronic and ionic conduction and electrochemical properties.

Technical Barriers

This research seeks to overcome technical barriers to implementation of PEMFC technology associated with low protonic conductivity in polyelectrolyte membranes at high temperatures (above 120°C) and low water activities (RH below 25%). It seeks to develop polymer electrolyte membranes that will overcome this conductivity barrier while also retaining dimensional stability (little to no swelling on contact with liquid water) and durability (lifetimes up to 5,000 hours are

desired). Project-specific technical barriers include limitations from undesired chemical reactivity of trifluorovinyl ether monomers with strong acids which constitutes a barrier to the preparation of polymer electrolytes having high molecular weight, capabilities for crosslinking, and good dimensional stability.

Abstract, Progress Report and Future Directions

Part 1. Fluorosulfonimide Ionomers

Figure 1 presents a representative structure of a fluorosulfonimide ionomer prepared by co-polymerization of a suitably substituted fluorosulfonimide trifluorovinyl ether monomer with tetrafluoroethylene (TFE). Methods for accomplishing this are described in published works [1].

Copolymers of variable equivalent weight have been prepared by adjustment of monomer feed ratios and other polymerization conditions. Studies of ionic conductivity of pure copolymers (meaning, not blended) reveal that polymers with higher equivalent weight have lower conductivity but better mechanical properties, whereas polymers with lower equivalent weight have higher conductivity but poor mechanical properties.

We have recently explored the blending of ionomers, typically combining one having a lower equivalent weight with one having a higher equivalent weight, to give a blended ionomer that has the best attributes of ionic conductivity and mechanical properties from its constituent components. Figure 3 presents representative results. In one instance the ionic conductivity of the blend was found to be higher than that of either component alone, and also higher than that of Nafion[®] of a much lower EW than either component of the blend. These findings are especially promising insofar as they suggest the blends of low and high EW fluorosulfonimide ionomers may have a different and possibly superior internal morphology/phase structure relative to pure ionomers, which could help promote better proton transport.

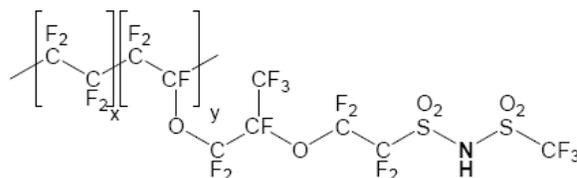


FIGURE 1. Structure of a Fluorosulfonimide Ionomer

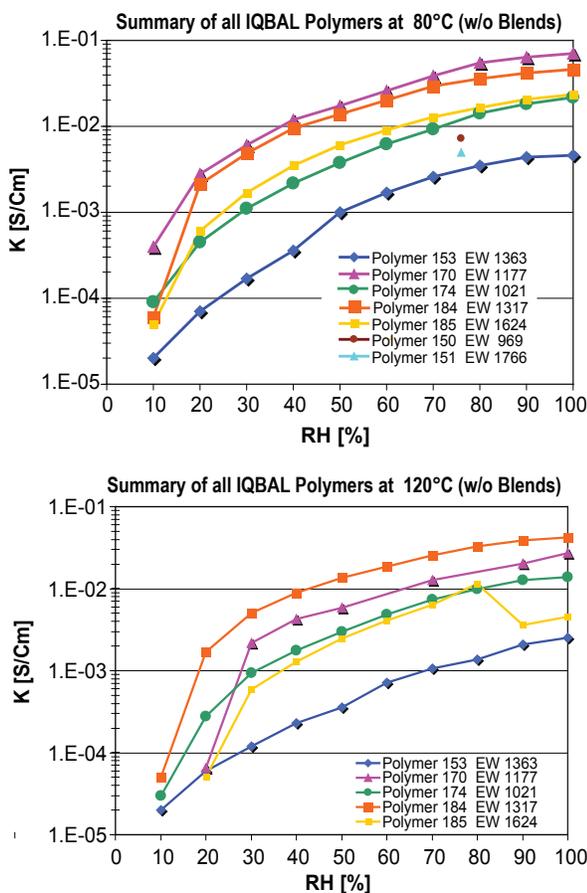


FIGURE 2. Ionic conductivity of a series of pure (not blended) fluorosulfonimide ionomers at variable temperature (80°C, top; and 120°C, bottom) and relative humidity. Legend provides equivalent weights and identifies samples by number.

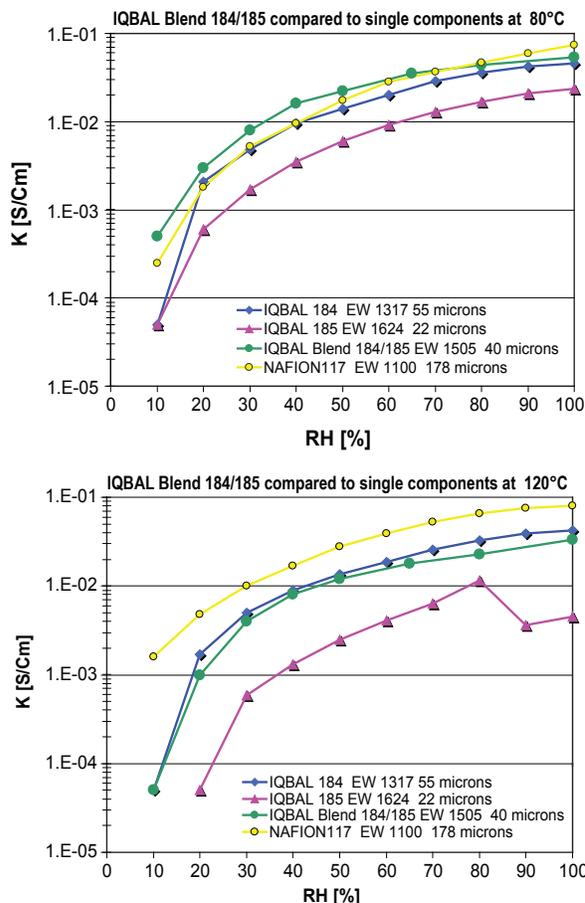


FIGURE 3. Ionic conductivity of selected fluorosulfonimide ionomer blends prepared by mixing pure copolymers of differing equivalent weight. In one case (80°C, top) the ionic conductivity of the blend is higher than that of either constituent by itself.

Part II. Ionomers via polycondensation of partially fluorinated bisphenols and sulfonated dichlorophenylsulfones.

Sulfonated poly(arylene ether sulfone) (PAES) containing the perfluorocyclobutyl (PFCB) unit have been prepared by the polycondensation of a unique bis-phenol (Bisphenol -T) with two dichlorodiphenylsulfones (DCDPS) under nucleophilic substitution conditions. The degree of sulfonation of these copolymers can be controlled by changing the feed ratio of the monomers as depicted in Figure 4. Also, the introduction of the PFCB functionality into the backbone of sulfonated PAES improves processability and mechanical properties of the copolymers.

Sulfonated BPVE polymer, represented in Figure 5, has been investigated as a potentially viable choice for making proton exchange membranes. BPVE polymers (Mn ~40K) were directly sulfonated by treatment with

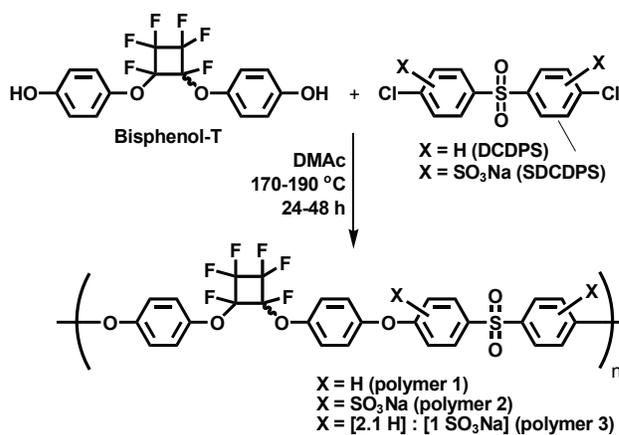


FIGURE 4. Synthesis of sulfonated Perfluorocyclobutyl (PFCB) Containing Aryl Ether Sulfone Polymers. Conditions: (i) K_2CO_3 , DMAC, 170°C, 24 h.

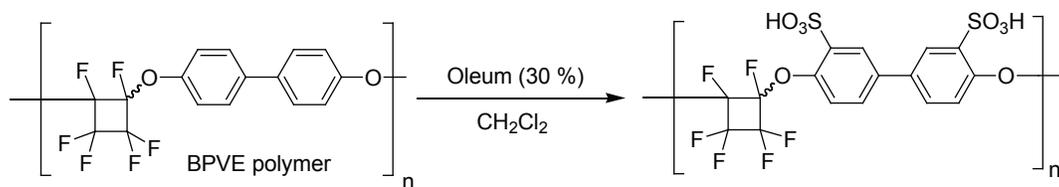


FIGURE 5. Scheme for Direct Sulfonation of BPVE Polymer

fuming sulfuric acid (oleum). The degree of sulfonation can be controlled precisely by varying the amount of oleum added per gram of the polymer. Both of these polymers exhibit excellent processability and good thermal stability and are of potential interest for high temperature, automotive fuel cell applications.

Part III. Electrolytes Grafted onto Carbon

Progress was made with grafting aryl fluorosulfonimide groups onto polished glassy carbon electrodes. Electrochemical and XPS analysis confirmed the presence of fluorosulfonimide groups on the surface following a grafting step involving electroreduction of an aryl fluorosulfonimide diazonium zwitterion. The work was recently published. Ongoing work seeks to graft diazonium salts onto carbon so as to expose phenol and/or aryl chloride or fluoride groups. These chemically modified carbons will be subjected to polymerization reactions involving bisphenols and sulfonated dihalophenylsulfones to grow sulfonated polyaryl ether electrolytes off of the carbon surface. The resulting materials will be used to fabricate thin-film electrodes

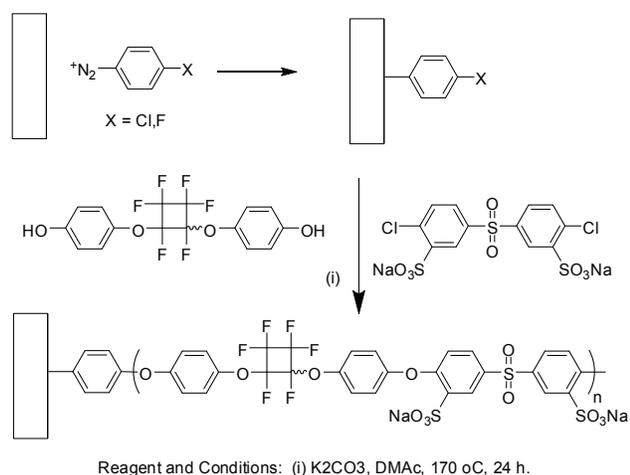


FIGURE 6. Illustration of one of our proposed approaches to modifying carbon surfaces with polymer electrolytes. An anchoring group is attached to carbon using aryl diazonium chemistry then this group is functionalized using known step-growth condensation polymerization methods. A wide range of bisphenol and bis(chlorophenyl)sulfone monomers are possible and will be tested in work in progress.

for which both electronic and ionic conductivity will be independently measured. The goal of this portion of the work will be to demonstrate independent control over both electronic and ionic conduction in fuel-cell electrodes. This capability, once achieved, will allow for greater flexibility in optimizing overall fuel-cell electrode performance.

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