

# Ionomer Membrane-Ionic Liquid Composites for High Temperature Proton Exchange for Fuel Cell Applications

Kenton B. Wiles and James E. McGrath

Chemistry Department and Materials Research Institute,  
Macromolecular Science and Engineering Program  
Virginia Tech, Blacksburg, VA 24061-0212

Polymer electrolyte membrane fuel cells (PEMFC) are promising candidates for vehicular transportation and stationary power. At temperatures above the boiling point of water, the traditional water-swollen membranes undergo dehumidification and performance loss. Composite membranes based on ionic containing polymers such as Nafion and directly copolymerized disulfonated poly(arylene ether sulfone) copolymers (BPSH) have recently been shown to increase high temperature conductivity by using heteropolyacid (HPA) additives.<sup>1</sup> These additives have been shown to decrease water sorption at room temperature and increase conductivity at elevated temperatures, such as 120 °C, and 40% relative humidity. However, these HPA additive composites lose almost all conductivity at relative humidities below 5% presumably due to the loss of specific water transport proton exchange mechanisms. Therefore, ionic liquids that are liquid and stable at elevated temperatures have recently been introduced as possible proton transport species without any water.<sup>2</sup>

Proton exchange membranes that derive proton conduction from water solvated fixed acid sites typically do not produce significant conductivities at temperatures in excess of the boiling point of water due to the loss of relative humidity. However, sulfonated membranes do not necessarily require water for proton transport, but they do require a dipolar solvent medium. The extreme low volatility of ionic liquids based on 1-ethyl-3-methyl imidazolium trifluoromethane sulfonate have become interesting candidates as protonically conducting additives for composite proton exchange membranes presumably due to its dipolar solvent characteristics.<sup>3</sup>

If the PEMFC protonic conductivity could be at appreciable levels at temperatures above 100 °C, many problems could be overcome. For a hydrogen fuel cell, impure hydrogen fuel containing carbon monoxide poisons the platinum catalyst thereby decreasing performance in a relatively short period of time. However, at temperatures above 110 °C, carbon monoxide desorption is faster than adsorption on the platinum surface thereby allowing less pure hydrogen gas to be employed. In addition, the reaction kinetics at both the anode and cathode increase with increasing temperature, specifically at the cathode for hydrogen/air fuel cells and at the anode for direct oxidation of organic fuels. In this work, we show that protonic conductivities can be enhanced with specific ionic liquids used as composite additives in both Nafion and BPSH membranes<sup>4</sup> at temperatures above 100 °C and relative humidities of less than 5%. Therefore, these non-volatile additives have the potential to maintain appreciable ionic conductivities over a broad temperature range with no water present.

The ionic liquids being probed are composed of 1-ethyl-3-methyl imidazolium cations and a perfluorinated anion. The three perfluorinated anions that have been used in this research are trifluoromethane sulfonate, bis(trifluoromethylsulfonyl)imide and bis(pentafluoroethylsulfonyl)imide. These unique liquids are non-volatile, thermally stable to temperatures exceeding 350 °C, non-corrosive, non-flammable and electrochemically stable. Furthermore, hydrophobicity can be tailored by using imide anions and hydrophilicity can be accomplished by using the sulfonate anions.

## Experimental:

**Ion Exchange Membranes:** Nafion 112, 1100 equivalent weight and 2 mils thick, was obtained from Electrochem Inc. and used in the proton form (Figure 1A). Disulfonated poly(arylene ether sulfone) copolymers (Figure 1B) based on biphenol and diphenyl sulfone monomers (BPSH) were synthesized, acidified and cast following the reported procedure.<sup>4</sup>

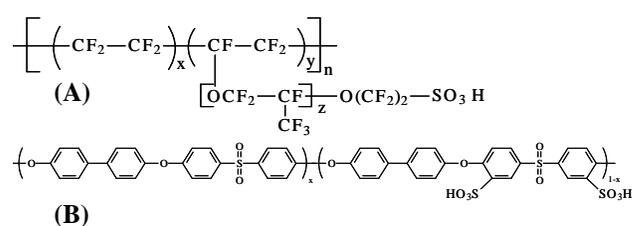


Figure 1. Chemical structures of Nafion(A) and BPSH(B)

**Ionic Liquid Imbibing:** The 1-ethyl-3-methyl imidazolium trifluoromethane sulfonate (EMITriflate) ionic liquid was added to water in a 1:1 ratio. The membrane was placed in a glass sleeve and the ionic liquid solution was added until the membrane was completely immersed in solution. The glass sleeve, membrane and liquid were then heated to 80 °C in a convection oven for 24 hours to aid in imbibing. The membranes were then blotted dry and weighed. The same procedure was performed on 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide (EMI-(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N) and 1-ethyl-3-methyl imidazolium bis(pentafluoroethylsulfonyl)imide (EMI-(CF<sub>3</sub>CF<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>N) ionic liquids, however, methanol instead of water was used to aid in imbibing.

**Conductivity:** Proton conductivity of the membranes was determined using a Solatron 1260 Impedance/Gain-Phase Analyzer over the frequency range of 10Hz- 1 MHz following the reported procedure.<sup>5</sup>

**Results and Discussion:** Ionic liquid uptake data suggested good incorporation (Table 1). Protonic conductivity of the EMITriflate composite membranes indicated enhanced conductivity as the temperature was increased to values of 180 °C from room temperature (Figure 2). The measurements were performed in a dry oven at less than 4% relative humidity.

**Conclusions:** Preliminary uptake and conductivity data suggest that the EMITriflate ionic liquid increases protonic conductivity relative to the neat copolymer membranes in the same, dehumidified environment. Further characterization data will be presented.

Table 1. Ionic liquid uptake for BPSH 45 and N112 films

	EMITriflate	EMI-(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N	EMI-(CF <sub>3</sub> CF <sub>2</sub> SO <sub>2</sub> ) <sub>2</sub> N	H <sub>2</sub> O
BPSH45	35%	74%	--	70%
N112	12%	11%	11%	25%

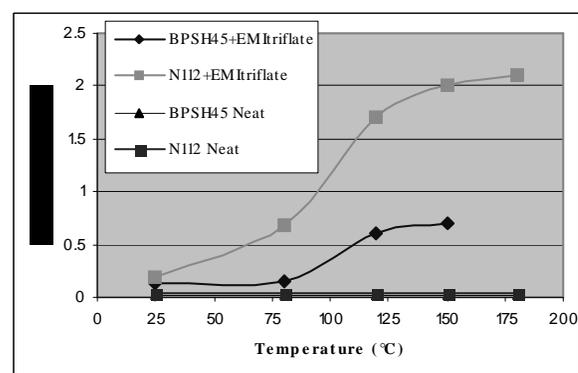


Figure 2. Temp. (°C) vs. conductivity (mS/cm) for BPSH 45+EMITriflate, N112+EMITriflate and neat films

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