

# ZIRCONIUM PHENYLPHOSPHONATE/ POLY(ARYLENE ETHER SULFONE) COMPOSITE MEMBRANES FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

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## Introduction

Proton exchange membrane fuel cells (PEMFCs) using methanol or hydrogen as fuel are attractive prospects for alternative energy sources. High temperature operation of these fuel cells is desirable due to faster reaction kinetics, higher tolerance to impurities in the fuel stream, and better water management. The current state-of-the-art perfluorinated membranes exhibit decreased performance at high temperatures due to a loss in proton conductivity at temperatures greater than 80 °C. The high cost of such membranes also makes them relatively unattractive.

Poly(arylene ether sulfone)s are good candidates for PEMFCs because they exhibit good proton conductivity as well as lower methanol permeability and cost than Nafion<sup>®</sup>.<sup>1</sup> The introduction of certain inorganic components into PEMs has been found to increase the fuel cell performance, especially at high temperatures.<sup>2</sup>

## Experimental

The synthesis of the disulfonated poly(arylene ether sulfone)s with 35 mole % disulfonated moiety (BPSH-35) used for this work has been previously reported.<sup>3</sup> The random copolymer structure is shown in Figure 1. Zirconyl chloride (30% solution in hydrochloric acid) and phenylphosphonic acid were obtained from Aldrich as used as received. HPLC-grade methanol was obtained from EMD Chemicals and used without further purification. Platinum-ruthenium and platinum black were used as received from Johnson-Matthey, and 5 wt. % Nafion dispersion with an equivalent weight of 1100 was obtained from Solution Technologies.

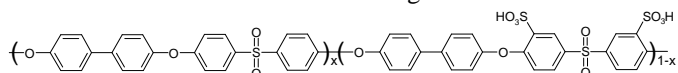


Figure 1. Structure of BPSH-35.

Copolymer membranes in the acid form were boiled in deionized water for one hour before use. The membranes were then immersed in zirconyl chloride solution at 80 °C (the concentration and soaking time were varied). Upon removal from the zirconyl chloride solution, the membranes were rinsed with deionized water and immersed in 0.2 M phenylphosphonic acid for 24 hours at room temperature. Finally, the membranes were thoroughly rinsed and dried in a vacuum oven at 110 °C.

The amount of zirconium phenylphosphonate (ZrPP) in the membranes was determined by weight difference after drying as follows:  $(W_c - W_p)/W_c \times 100$  where  $W_c$  and  $W_p$  refer to the dry weights of the composite membrane and the pure copolymer membrane, respectively. The water uptakes of membranes are reported in weight percent as follows:  $\text{water uptake} = (W_{\text{wet}} - W_{\text{dry}}) / (W_{\text{dry}}) \times 100$  where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weight of the wet and dry membranes, respectively. Thermogravimetric analysis (TGA) of dried samples (10-15 mg) was performed on a

TA Instruments TGA Q500 in air with a heating rate of 10 °C/min. Membrane-electrode assemblies (MEAs) were prepared by painting using a 5 wt. % Nafion dispersion, water, and catalyst (platinum-ruthenium on the anode and platinum black on the cathode). The catalyst loadings were approximately 10 mg/cm<sup>2</sup> on the anode and 6 mg/cm<sup>2</sup> on the cathode. Direct methanol fuel cell (DMFC) performance was measured using a Fuel Cell Technologies fuel cell test stand using a standard 5 cm<sup>2</sup> test cell with 0.5 M methanol and a cell temperature of 80 °C. The thickness of all membranes was 3-4 mil.

## Results and Discussion

The amount of ZrPP within the membrane can be controlled by varying the soaking time in the zirconyl chloride solution. The preparation and incorporation of different amounts of ZrPP in the composite membranes will be presented separately.<sup>4</sup> Membranes containing varied amounts of ZrPP from 3 to 12 wt% were prepared. The water uptake of the membranes decreased as more ZrPP was added; however, the proton conductivity decreased as well.

TGA experiments in air showed that the decomposition temperature increased from 304 °C for the virgin copolymer to 348 °C for a composite membrane containing 8 wt% of ZrPP.

The DMFC performance of these composite membranes was significantly dependent upon the amount of ZrPP in the membrane. While membranes with large amounts of ZrPP did not have sufficient proton conductivity, those with lower amounts (~ 3-4 wt%) of ZrPP had sufficiently high proton conductivity, and lower water uptake and methanol permeability. Therefore, the membranes with small amounts of ZrPP exhibited improved DMFC performance over BPSH-35 and Nafion 1135 (Figure 2). The open circuit voltage of the ZrPP composite was the highest of the three membranes tested, indicating that the inclusion of ZrPP lowers the methanol permeability of the MEA.

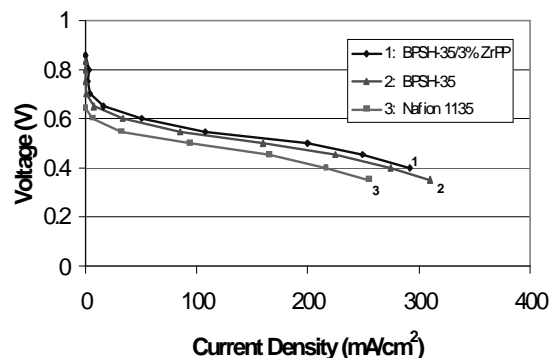


Figure 2. DMFC performance of Nafion, virgin BPSH-35, and BPSH-35/ZrPP composite membranes.

**Acknowledgement.** The authors would like to thank the National Science Foundation "Partnership for Innovation" Program (HER-0090556) and the Department of Energy (DE-FC36-01G01086) for their support of this research effort.

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