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# A New Polymer Electrolyte

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## ABSTRACT

Polybenzimidazole films doped with phosphoric acid are being investigated as potential polymer electrolytes for use in hydrogen/air and direct methanol fuel cells. In this paper, we present experimental findings on the proton conductivity, water content, and methanol vapor permeability of this material, as well as preliminary fuel cell results. The low methanol vapor permeability of these electrolytes significantly reduces the adverse effects of methanol crossover typically observed in direct methanol polymer electrolyte membrane fuel cells.

## Introduction

Polybenzimidazole (PBI) is a relatively low cost ($70-100/lb), nonperfluorinated, commercially available polymer known to have excellent oxidative and thermal stability. For example, fabric woven from sulfonated PBI fibers is used in garments for firefighters. Polybenzimidazole films are also known to be good vapor barriers. The ionic conductivity of polybenzimidazole was first discussed over twenty years ago.[1,2] Aharoni and Signorelli found that polybenzimidazole salts of monoprotic acids were very poor conductors, with the conductivity inversely proportional to the anion size.[3] This suggested that the protonated benzimidazole was inert, and only the mobile anion participated in the conduction process. However, the conductivity is very different with amphoteric anions such as bisulfate and dihydrogen phosphate. Here the conductivity increases monotonically as the acid concentration increases.[4] Films of PBI that have been doped with phosphoric or sulfuric acid, form a single-phase polymer electrolyte with the acid dissolved in the polymer. Doping levels of up to 50 weight percent (w/o) can be obtained without adverse effects on the polymer properties.

One potential application for PBI membranes is in direct methanol fuel cells. The performance of these cells is limited by the lack of sufficiently active catalysts for the methanol anode. PEM methanol-air fuel cells using perfluorosulfonic acid electrolytes also suffer from excessive methanol crossover from the anode to the cathode. For example, methanol crossover rates in excess of 100 mA/cm$^2$ have been measured in PEM fuel cells employing Nafion electrolytes.[5] This results in a loss of efficiency via chemical reaction of the fuel with oxygen and depolarization of the cathode.

The operation of direct methanol fuel cells at temperatures approaching 200°C offers an opportunity to minimize the catalyst activity limitations. The higher temperatures should enhance the methanol oxidation kinetics and also should depress the poisoning effects associated with strongly adsorbed intermediates, e.g., CO. In order to take advantage of the enhanced reaction kinetics, a polymer electrolyte is required which is conductive at these temperatures, and ideally, which also has a low permeability to methanol. These qualities can be found in the acid-doped polybenzimidazole system. This paper discusses the conductivity and permeability of PBI-based polymer electrolytes. The performance of hydrogen/oxygen and methanol/oxygen PEM fuel cells using acid-doped PBI membranes is presented. Additional characterization of this system, such as studies of the conductivity mechanism, mechanical stability, and effects of the electrolyte on electrochemical kinetics, are in progress, and will be reported in a later paper.

## Experimental

Polybenzimidazole (Celanese) films were cast from a solution of the polymer in dimethylacetamide. The cast films were boiled in water for several hours to remove residual solvent, stabilizing salts, and impurities. The films were then doped by immersion in phosphoric acid for at least 16 h. Equilibration in an 11$M$ acid solution yields a doping level of roughly five phosphoric acid molecules per polymer repeat unit, i.e., 500 mole percent (m/o).

Conductivity measurements were made using the four-probe technique.[6] The apparatus was contained within a sealed stainless steel vessel, which was placed inside an oven and connected to a gas manifold system. In this manner the temperature, pressure, and composition of the gas phase in contact with the sample could be controlled.

Vapor sorption measurements were made using a two-chambered barometric sorption cell.[7] Sorption measurements were performed using both water and methanol vapors. In each case the measurements were made as a function of vapor activity by (i) holding a constant temperature (150°C) and employing varying partial pressures (10-101 kPa), and (ii) by holding a constant partial pressure (93.3 kPa) and varying the temperature (120-192°C).

## Results and Discussion

*Conductivity.*—The conductivity of a phosphoric acid-doped PBI membrane is shown in Fig. 1 as a function of water vapor activity (partial pressure of water normalized to the saturated vapor pressure), temperature, and acid-doping level. Although the conductivity is low compared to other fuel cell electrolytes, it is considerably higher than that of perfluorosulfonic acid electrolytes under similar conditions of temperature and humidity. Conductivity measurements on a series of PBI films with varying levels of doping have shown that the conductivity depends on the doping level. The conductivity at the higher doping level shown (501 m/o) is roughly twice that of the film doped to 338 m/o, under similar conditions of temperature and humidity. For both doping levels, the conductivity increases with temperature and water vapor activity. At a given temperature, an increase in water vapor activity leads to a higher water content in the electrolyte (see below), which presumably lowers the viscosity within the membrane, leading to higher mobility and conductivity. At a fixed activity, the water content in the elec-
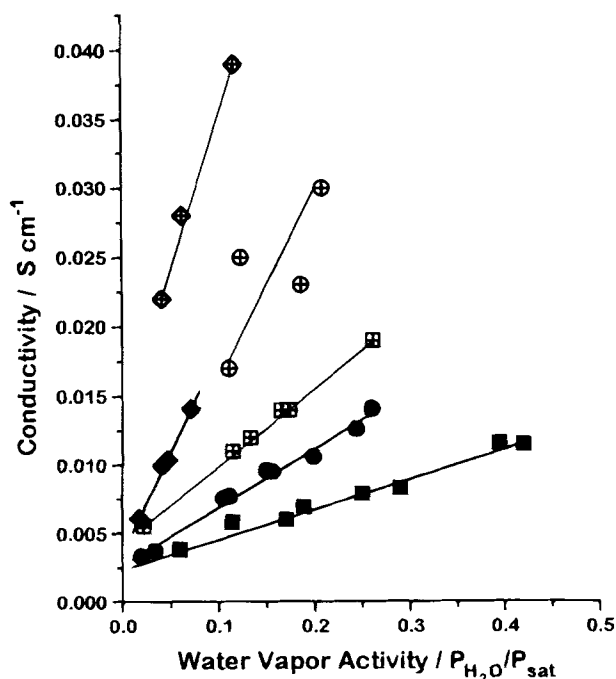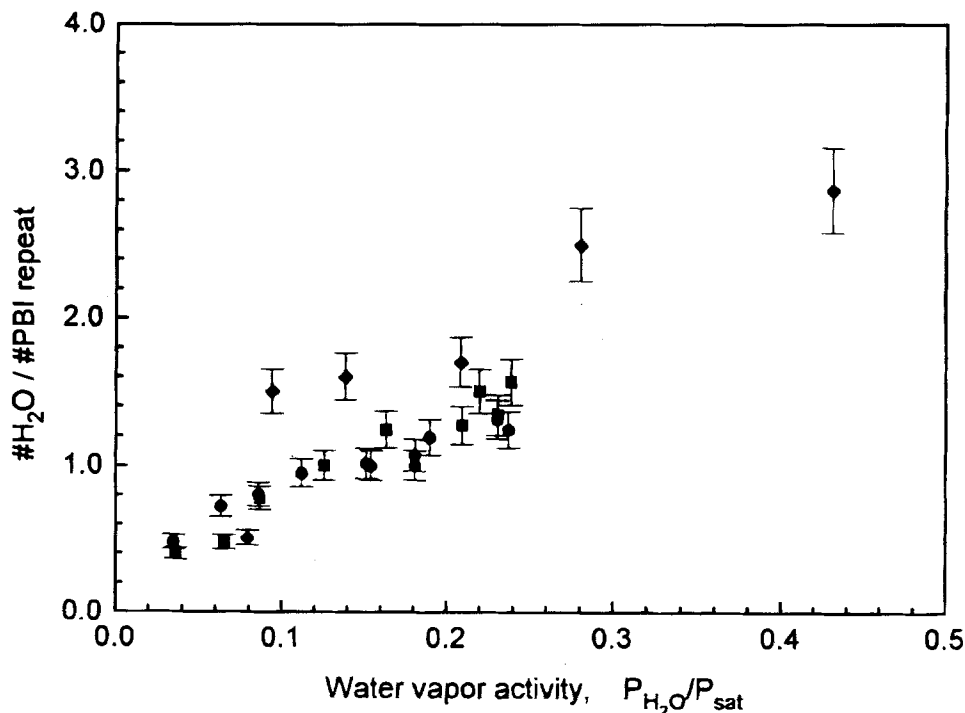


Fig. 1. Conductivity of phosphoric acid-doped polybenzimidazole. Doping level 338 m/o (filled symbols) and 501 m/o (open symbols). The lines drawn are intended only as guides for the eye. ■, □-130°C; ●, ○-150°C; ◆, ◇-190°C.

**Fig. 2. Equilibrium water sorption (water molecules per polymer repeat unit) in phosphoric acid-doped polybenzimidazole. ■, ● Constant temperature (150°C), variable water partial pressure (10-100 kPa). ◆ Constant pressure ($P_{H_2O}$ = 93.3 kPa), variable temperature (120-192°C).**

trolyte is constant, and the increase in conductivity with temperature is as expected.

*Water content.*—The equilibrium water sorption in a phosphoric acid-doped PBI membrane is shown in Fig. 2, as a function of water vapor activity. It can be seen from this figure that the solubility increases with increasing vapor activity. For a constant activity, the solubility is essentially independent of temperature. It should be noted that the water content in the system is quite low under these conditions. Given that the acid doping level of the samples was ≈500 m/o, the water content is typically one water molecule for every five phosphoric acid molecules.

*Methanol vapor permeability.*—The sorption apparatus was also used to determine the diffusivity and solubility of methanol in the phosphoric acid-doped polybenzimidazole. The sorption of methanol in the electrolyte resembles the sorption of water given above. The solubility increases with increasing vapor activity, and is essentially independent of temperature for a fixed vapor activity. Solubilities on the order of 0.5-1.5 methanol molecules per PBI repeat unit were obtained for methanol vapor activities between 0.01 and 0.1. The sorption experiments also yield the methanol diffusivity, which is ≈$10^{-8}$ cm²/s. The diffusivity of methanol and the equilibrium methanol solubility can be combined to yield the methanol permeability. Depending on the methanol activity and the temperature, the calculated permeabilities range between 1.5-15 x $10^{-16}$ m³(STP) m/m² s Pa. Increasing the methanol activity leads to higher permeability due to the higher methanol sorption. Direct measurements of the methanol permeability using a technique based on ASTM D-1434 have also yielded permeabilities on the order of 15 x $10^{-16}$ m³(STP) m/m² s Pa. [4]

From these results it can be expected that methanol crossover in a PEM fuel cell employing a doped polybenzimidazole membrane will be relatively low. Based on the calculated methanol permeability, a direct methanol fuel cell utilizing a 0.01 cm thick PBI membrane, operating at 150°C and atmospheric pressure on a 50/50 methanol/water feed, would have a methanol crossover equivalent to less than 10 mA/cm². These low methanol crossover rates have been confirmed in actual fuel cell assemblies (see below).

*Fuel cell tests.*—To demonstrate that doped PBI membranes can operate as an electrolyte at elevated temperatures, laboratory $H_2$/$O_2$ and methanol/$O_2$ fuel cell tests have been performed. In the case of $H_2/O_2$, several cells have been operated at 150°C using E-TEK Pt/C electrodes with a Pt loading of 0.5 mg/cm². The cells were operated at atmospheric pressure, with the reactant gases humidified by bubbling through distilled water. The bubblers were typically held at 48°C (hydrogen) and 28°C (oxygen). The maximum power observed in these unoptimized cells was 0.25 W/cm² at

700 mA/cm². Membrane resistances determined using the current interrupt method were found to be ≈0.4 Ω. The membrane thickness and area were 0.01 cm and 1 cm², respectively, and the doping level 500 m/o. The measured cell resistance is equivalent to a conductivity of 0.025 S/cm, in agreement with Fig. 1. The cell resistance was found to be essentially independent of the gas humidification, indicating that the water produced at the cathode is sufficient to maintain conductivity in the electrolyte. Separate measurements using similar membrane electrode assemblies and sealed anode and cathode chambers have shown that the electroosmotic drag coefficient for water in this electrolyte is essentially zero. As a result, external gas humidification is not necessary for operation of the fuel cell. A cell of this type was operated continuously at 200 mA/cm² for over 200 h with no decay in performance. A cell using both supported (cathode) and unsupported (anode) Pt catalysts has been operated without adverse effects for 600 h at 200 mA/cm² with room temperature humidification of the reactants. These long-term tests also confirm earlier thermal stability studies, which indicated that the polybenzimidazole electrolyte was stable at elevated temperatures, even in the presence of hydrogen or oxygen, and platinum. [4]

Typical cell polarization and iR free polarization curves for a direct methanol/oxygen fuel cell are shown in Fig. 3. The fuel cell electrodes were a Pt-Ru anode catalyst (Giner Inc., 4 mg/cm²) and a Pt black cathode catalyst (Johnson-Matthey, 4 mg/cm²). A 4:1 (by mole) water:methanol vapor mixture was fed to the anode. Oxygen for the cathode was humidified at room temperature. Operating at 200°C and atmospheric pressure, the cell produced over 0.1 W/cm² for current densities between 250 and 500 mA/cm². It is clear from Fig. 3 that the iR loss in this cell is significant. Given the extremely low methanol crossover observed using PBI membranes, it should be possible to use much thinner membranes without significantly lowering the cathode performance. It should also be noted that the modulus of the doped PBI films is ca. 1000 times that of Nafion. [4] Therefore the use of thin membranes should be feasible even with a significant pressure differential across the membrane. Replacing the 0.01 cm thick membrane in this direct methanol fuel cell with a membrane on the order of 0.003 cm thick would increase the power produced to ≈0.15 W/cm². Decreasing the membrane thickness would increase the methanol crossover, however the crossover rate would still be significantly lower than in conventional perfluorosulfonic acid electrolytes. [5]

Methanol crossover in actual membrane electrode assemblies has also been determined. A reversible hydrogen reference electrode was used to determine the rest potential of the oxygen cathode, (typically 0.9 V vs. RHE or greater), while hydrogen was fed to the anode. The oxygen cathode was held at this potential using a potentiostat while water:methanol vapor was introduced into the anode compartment. After a period of several hundred
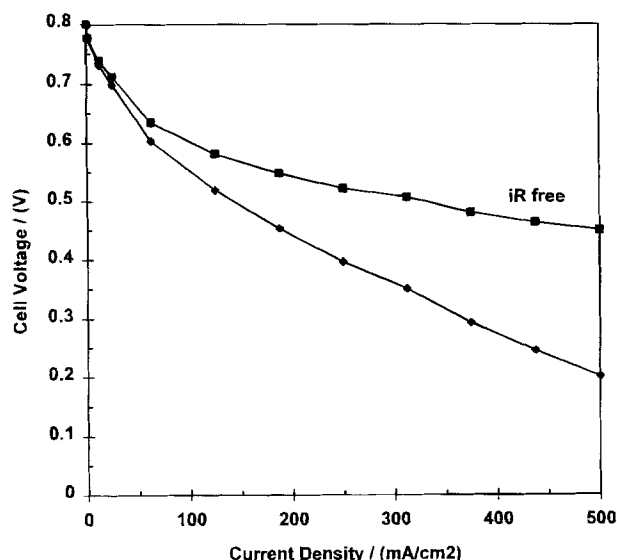
**Fig. 3.** Typical cell polarization curve and iR free polarization curve for an atmospheric pressure, direct methanol/oxygen fuel cell. Anode, 4 mg/cm$^2$ Pt-Ru, cathode 4 mg/cm$^2$ Pt, membrane PBI/H$_3$PO$_4$ (480 m/o). Anode feed 4:1 H$_2$O/CH$_3$OH (by mole), temperature 200°C. Membrane thickness 0.01 cm, area 1 cm$^2$.

seconds, a steady-state oxidation current is observed at the oxygen electrode. Given that methanol will be rapidly consumed at the potential of the oxygen electrode, this current is directly related to the rate of methanol crossover. Repeated measurements have yielded crossover currents on the order of 10 mA/cm$^2$, in excellent agreement with the methanol flux predicted from the methanol permeability measurements.

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