Water Uptake and Acid Doping of Polybenzimidazole Electrolyte Membranes for Fuel Cells

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By means of acid doping, the polybenzimidazole (PBI) exhibits proton conductivity at temperatures up to 200°C [1]. The conductivity [2,3] and other properties of the acid-doped PBI membranes such as methanol crossover rate, thermal stability, water drag coefficient, mechanical properties, and kinetics of oxygen reduction have been studied. The membrane has been suggested to be used as the electrolyte in fuel cells with hydrogen, methanol and other types of fuels.

It is known that the conduction properties of the PBI membranes depend on the level of doping with phosphoric acid and water content. High doping levels result in high proton conductivity. The mechanical properties of the acid-doped membranes, on the other hand, become poor at high doping levels [4]. Moreover, the water content has a dramatic influence on the membrane properties [5]. In the present paper, the water uptake and acid doping of PBI membranes have been studied by gravimetry, conductometry, and IR and Raman spectroscopy.

The water uptake by PBI from the vapor phase is much higher than that for Nafion in a water activity range up to 0.9, as shown in Fig. 1. At a water activity close to one, the water uptake by PBI from the vapor phase is close to that from the liquid phase, contrary to what is seen for Nafion membranes.

When treated with phosphoric acid, the acid doping level of the PBI membranes increases with the concentration of the acid solution. The concentration of the acid inside the doped polymers is found to be much higher than in the surrounding solution (see Fig. 2). When doped with a 0.05 M acid solution, the doping acid inside the polymer has a concentration as high as 6 M. When the acid solution is in a concentration range from 3 to 11 M, the doped acid concentration inside the polymer is around 14 M, in agreement with a previous report [6].

By immersing the acid-doped membranes in methanol for a few days, a portion of the doped acid was washed away. About 2 molecules of phosphoric acid remained for each repeat unit of PBI (see Fig. 3), corresponding to the two nitrogen sites for hydrogen bonding in a PBI monomer unit. At such a doping level (i.e. 2 mol H_3PO_4/PBI), the conductivity of the membrane is about 0.018 S/cm at 180°C (see Fig. 4), which is relatively low for fuel cell applications. Higher conductivity can be achieved by the presence of so-called "free acid".

References

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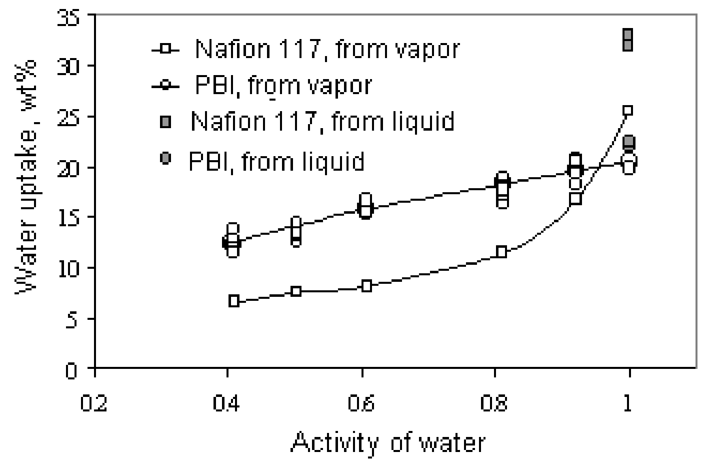

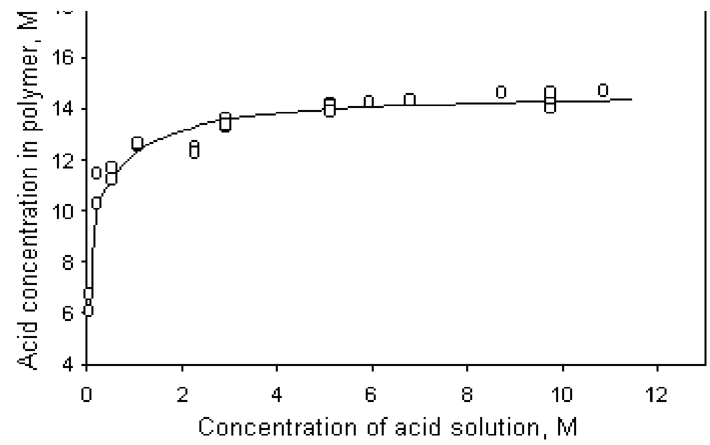

Fig.2. Acid concentration inside PBI membranes

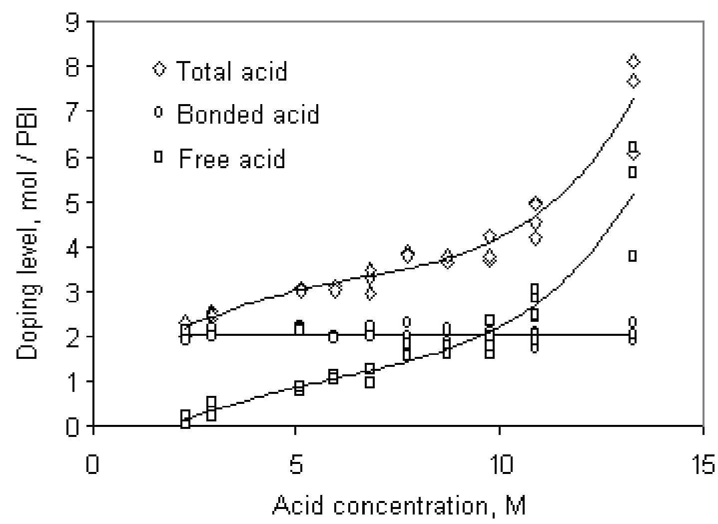

Fig.3. Bonded acid and free acid in PBI

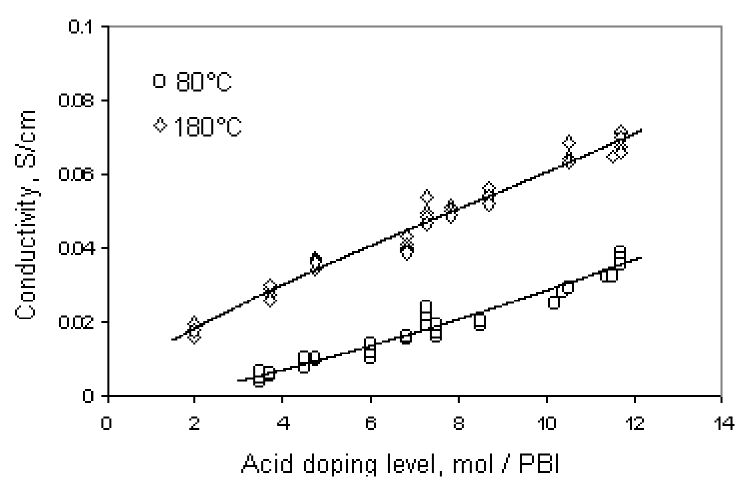

Fig.4. Conductivity as a function of acid doping level