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Recent Progress in Preparation and Characterization of
PBI Membranes for PEMFC

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As a solid electrolyte membrane for high temperature proton exchange membrane fuel cells (PEMFCs), phosphoric acid doped polybenzimidazole (PBI) [1] has received much attention recently [2-4]. The membrane possesses good mechanical properties [5], high proton conductivity at low water activities [6,7], and excellent thermal stability at temperatures up to 200°C. Low methanol crossover rate and nearly zero water drag coefficient have also been reported.

Polybenzimidazoles (PBI) of different molecular weights have been synthesized in lab scale through different routes, both with and without catalysts. The polymers are characterized with respect to molecular weight and its distribution, solubility, thermal stability, etc. Membranes are prepared by solution casting and doped with acids.

When doped with phosphoric acid the membranes exhibit proton conductivity. The acid doping, however, results in high volume swelling. At an acid doping level of above 5 mole phosphoric acid per mole repeat unit of the polymer, a level necessary to obtain high enough proton conductivity for fuel cell applications, a volume swelling by about 120% was observed. The volume swelling means separation of the polymer backbones, which, in turn, reduces the mechanical strength and increases the H₂ and O₂ permeability of the membranes.[8] By synthesizing high molecular weight polymers, the mechanical strength of the acid doped membranes can be significantly improved, as shown in Fig.1. Cross-linking by acid-base blends and introducing inorganic fillers have also been proved to be effective means to reduce the swelling and strengthen the membranes.

Fig.1. Engineering stress at break of acid doped PBI membranes as a function of molecular weight at 180°C. The acid doping level is indicated in the figure.

Long tern durability has been a main concern in the development. Over 5000 hours of continuous operation has been demonstrated at 150°C with ambient hydrogen

and oxygen. A daily startup-shutdown test operating with hydrogen and air has been cycled more than 600 times between room temperature and 150°C within a period of over 20,000 hours. 30% of the performance loss is observed, major part of which occurred during the first 50 cycles.

Fig.2. Lifetime test of a PBI cell with hydrogen and air under ambient pressure. The cell operates for about 7 hours every working day at 150°C and close down the rest of time during the overall time frame shown in the figure. The membrane was PBI doped with 5.6 mol H₃PO₄. Platinum loading of each electrode was 0.61 mg Pt/cm².

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