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Polybenzimidazole based nanocomposite membranes with enhanced proton conductivity for high temperature PEM fuel cells

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ABSTRACT

In this study, phosphoric acid doped PBI nanocomposite membranes were prepared by dispersion of various amounts of inorganic nanoparticles in PBI polymer followed by phosphoric acid (H_3PO_4) doping for high temperature proton exchange membrane fuel cells (HT-PEMFC). All of the PBI composite membranes were cast from the same PBI polymer with the same molecular weight. Titanium dioxide (TiO_2), silicon dioxide (SiO_2) and inorganic proton conductor zirconium phosphate (ZrP) were used as inorganic fillers. The PBI based composite membranes were characterized in terms of their acid uptake and acid leaching properties, mechanical properties, chemical stabilities in N–N Dimethylacetamide (DMAc) and impedance analyses. Thermal gravimetric analysis confirmed the improved thermal stability of the PBI composite membranes. The existence of inorganic fillers was improved the acid retention capability. Electrochemical Impedance Spectroscopy (EIS) showed that the introduction of 5 wt. % SiO_2 or 5 wt. % ZrP helps to increase proton conductivity. The composite membrane with TiO_2 retained low conductivity values than pristine PBI and this is a result of its non-uniform membrane structure. The highest proton conductivity of 0.200 S/cm was obtained for PBI/ZrP composite membrane with the highest value of H_3PO_4 doping level. Nyquist plots are drawn for all the membranes at different temperatures and the plots showed good fit with Randle's circuit. As a result the experimental results suggested that the PBI based composite membranes may be a promising electrolyte used in HT-PEMFC.

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Introduction

Fuel cells offer a highly efficient and environmentally friendly technology for energy conversion avoiding the limitations of Carnot cycle. Polymer electrolyte membrane fuel cells (PEMFC)

are considered as one of the most promising options to power transportation vehicles [1].

PEMFC are operating using polymer proton conducting polymers as electrolyte and platinum (Pt)-based materials as catalyst. Their significance is mainly due to the low operating temperature compared to other types of fuel cells, high power density, and easy scale-up. These properties make PEMFCs a

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promising candidate for transportation, stationary, and portable applications [2].

Nafion membranes are the most common membrane type for PEMFCs. They have high proton conductivity, high chemical and thermal stability and high mechanical stability. However, their conductivity is highly dependent on humidification which limits operating temperature at 100 °C which is not favorable because high temperature PEMFC (HT-PEMFC) has significant advantages over low temperature PEMFC (LT-PEMFC). The ability to operate at higher temperatures enables CO tolerance at Pt catalyst layer. Under 150 °C, Pt catalyst used in the cell is poisoned by CO in H₂ so using ultra-pristine hydrogen which is expensive and hard to find becomes necessary. Above 160 °C, poisoning of catalyst becomes less important [3]. Thus, increasing temperature makes addition of a reformer to the system possible, which facilitates a cheaper hydrogen resource for fuel cell. Also, water management and cooling systems are an issue for Nafion based PEMFC. Hydrogen and Oxygen should be carefully hydrated and at the same time, flooding from the electrodes should be prevented. In HT-PEMFCs, humidification is no longer an issue [4]. Also better electrode kinetics which results in faster electrode reactions can be obtained at higher temperatures [3]. Many non-fluorinated membranes were researched as an alternative to Nafion[®]. Most of them are thermally stable sulfonated polymers, which also need fully humid environment to keep high proton conductivity values. Recently, acid doped PBI membranes have been studied widely since it does not require humidification to give high conductivity values and has excellent thermal stability [5–7].

PBI is an amorphous polymer with a fairly high glass transition temperature approximately 425–436 °C. It has good thermal and chemical resistance [8]. However, it has low conductivity values compared to the Nafion. Wainright et al. were the first one suggesting the application of acid-doped PBI based membranes for fuel cell applications [9]. Different types of acids have since been investigated and phosphoric acid (H₃PO₄) and sulfuric acid have been found to be more appropriate for HT-PEMFC usage. Particularly phosphoric acid has high thermal stability, which makes it a preferable candidate for acid doping of PBI. H₃PO₄ doping of PBI increases the membrane performance in terms of conductivity up to several magnitudes. However, phosphoric acid doped PBI membranes also have technological limitations due to: (1) low mechanical properties caused by high doping levels, (2) catalyst particle agglomeration, (3) leaching of acid from the membrane especially at high temperatures and humidity levels [10]. In the literature, developing composite membranes as a solution to the first and third problems has been studied widely. In order to overcome the above mentioned disadvantages, many types of filler were investigated in literature such as clay [11], graphene [12,13], and silica particles [14].

To improve the high temperature performance of HT-PEMFC, the PBI based composite membranes were prepared in this study. It is pointed out that there is not any literature covering the comparison of electrochemical performance of PBI/SiO₂, PBI/TiO₂, and PBI/ZrP composite membranes for HT-PEMFC applications. In the present study, PBI based nanocomposite membranes with different inorganic nanoparticles and phosphoric acid doping levels were prepared and

characterized for HT-PEMFC application. The main goal of this work is to develop PBI based nanocomposite membranes with different filler and compares the impedance and proton conductive properties. Three types of inorganic fillers, TiO₂, SiO₂ and ZrP were used as a conductive material additive to enhance the properties of PBI membrane. Their influences on the thermal, morphological and mechanical properties were studied using thermogravimetric analysis (TGA), SEM and stress–strain measurements. The effects of different inorganic particle, phosphoric acid doping level, and temperature on the proton conductivities were investigated. Special attention was paid to measure the acid leaching percentages for temperatures between 95 °C–110 °C. The proton conductivity of phosphoric acid doped PBI and its composites were measured at 140 °C, 165 °C and 180 °C.

Experimental methods

Materials

Diaminobenzidine tetrachloride hydrate (DAB.4HCl.2H₂O, 98%), isophthalic acid (IPA, 99%), polyphosphoric acid (PPA, 115%), phosphoric acid (H₃PO₄, 85%) and Silicon dioxide (SiO₂) nanoparticles were obtained from Sigma–Aldrich (USA) and N–N Dimethylacetamide (DMAc, Merck) was used as received. Titanium dioxide (TiO₂) was purchased from Degussa GmbH (Germany), zirconium hydrogen phosphate (ZrP) was obtained from ChemCruz[®] Biochemicals (USA). All solvents used were high grade materials without further need for purification.

PBI composite membrane preparation

In this study, polymer is synthesized according to the process that was explained in literature. By Ergun et al. [15]. The monomers were DAB.4HCl.2H₂O and IPA, while the solvent was PPA. Reaction setup consisted of a four-necked glass flask, mechanical stirrer with heater, nitrogen inlet and CaCl₂ drying tube. System temperature was controlled by the thermocouple of the stirrer-heater. Reaction was resumed for 24 h, at 200 °C, under constant nitrogen stream. PBI polymer with 82,000 g/mole molecular weight was obtained. In a previous work, PBI based composite membranes with SiO₂ particles were prepared and characterized [16]. The molecular weight of PBI polymer was used as 45,000. In this study, PBI based nanocomposite membranes were prepared by using PBI polymer with molecular weight as 82,000.

The PBI composite membranes were prepared by a solvent casting method. PBI polymer (2.5 wt. %) was dissolved in DMAc at atmospheric pressure and 80 °C temperature. Subsequently, proper amounts of the inorganic particles (5 wt. %) were dispersed by ultrasonication in the PBI polymer solution to obtain homogenous solution. The homogeneous solution was cast onto petri dish and DMAc was evaporated in a ventilated oven in a temperature range from 80 to 120 °C for 24 h. Membrane was stripped from the petri dish. The PBI membrane without filler was also prepared with the same procedure for comparative study. Membranes were treated in boiled water for 6 h to remove residual solvent, and then dried

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