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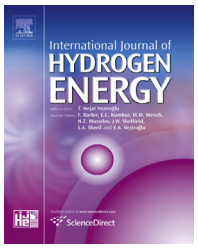

Polybenzimidazole/SiO_2 hybrid membranes for high temperature proton exchange membrane fuel cells

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ABSTRACT

Polybenzimidazole/Silicon dioxide (PBI/SiO_2) hybrid membranes were prepared and characterized as alternative materials for high temperature proton exchange membrane fuel cell (HT-PEMFC). The PBI/SiO_2 membranes were cast from a PBI polymer synthesized in the laboratory and contained 5 wt. % SiO_2 as inorganic filler. Scanning electron microscopy (SEM) analysis showed that the uniform and homogeneous distribution of SiO_2 particles in the hybrid membrane. The existence SiO_2 has improved the acid retention and proton conductivity properties. A maximum conductivity of 0.1027 S/cm at 180 °C was obtained for the PBI/SiO_2 hybrid membrane. Gas diffusion electrodes (GDE) were fabricated by ultrasonic coating technique with 1 mg Pt/cm^2 catalyst loading for both anode and cathode. The membranes were tested in a single HT-PEMFC with a 5 cm^2 active area operating at the temperature range of 140 °C–180 °C. Single HT-PEMFC tests indicated that PBI/SiO_2 hybrid membrane was more stable and also performed better than pristine PBI membrane. Maximum current density was observed for PBI/SiO_2 membrane at 165 °C and cell voltage of 0.6 V as 0.24 A/cm^2. The results suggested that PBI/SiO_2 hybrid membrane is promising electrolytes for HT-PEMFC with improved fuel cell performance.

Introduction

Fuel cell technology is expected to become one of the key technologies of the 21st century because the fuel utilization in fuel cell engines is markedly higher than in internal combustion and diesel engines [1,2]. Nafion®, manufactured by DuPont is the most well-known proton exchange membrane for PEMFC. However, maintaining proton transport properties of Nafion membrane above 90 °C is very difficult because proton transport is highly dependent on the hydration condition. Moreover it has a comparative short lifetime if hydrogen containing traces of carbon monoxide (CO) is fed to the electrolyte because CO is poison for the platinum (Pt) anode catalyst at low working temperature [5]. It is known that the resistance of Pt catalyst to the CO poisoning needs higher operation temperature of proton exchange membrane fuel cell (PEMFC) and thus stable membranes working at high

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temperatures more than 100 °C [3]. To solve this problem, different systems are currently under development. Sulphonated poly(arylene ether)s (SPAES, e.g., SPEEK), sulphonated polyimides (SPI), sulphonated poly(phenylene oxide) (SPPO), and have attracted considerable attention for moderate temperature PEMFC whereas polybenzimidazoles (PBIs) doped with phosphoric acid were investigated as potential candidates for high-operating-temperature and anhydrous PEMFCs [4].

PBI have achieved more and more attention for their high ionic conductivity at higher temperature up to 200 °C under anhydrous conditions, and excellent oxidative/thermal stability [5,6] and the fuel impurities tolerance at temperatures up to 200 °C. However, some drawbacks, such as acid leaching problem, insufficient proton conductivity, and mechanical property under HT-PEMFC operation condition, somewhat limit the performance PBI based membranes for HT-PEMFC [7,8]. To achieve adequate proton conductivity for HT-PEMFC operation, PBI needs to be doped with acid because its conductivity is very low (about 10^{-12} S/cm) [9]. Various inorganic acids have been investigated such as H_2SO_4, H_3PO_4, $HClO_4$ and HNO_3 [10]. Among these is H_3PO_4 (phosphoric acid) of special interest because of its unique proton conductivity, also under anhydrous conditions, as well as its excellent thermal stability and very low vapor pressure at elevated temperatures. But higher H_3PO_4 loading level has some drawbacks i.e., loss of the mechanical property as well as leaching out of unbound acid from the membrane by water during HT-PEMFC operation [11]. In order to solve this problem, modification of the PBI matrix by addition of inorganic filler is required. Inorganic fillers are typically added to increase the proton conductivity and/or acid uptake of PBI membranes. The combine of hydrophilic inorganic nanomaterial with a PBI creates favorable results, because of their affinity to interact with the water and acid and turn out to be more hydrophilic [12,13]. Most types of HT-PEMC membranes have successfully been doped with inorganic fillers such as hygroscopic oxides (SiO_2, TiO_2, ZrO_2, Al_2O_3), montmorilonite, clays, heteropolyacids and zirconium phosphates (ZrP) [14].

Ublekov et al. worked on p-PBI phosphoric acid doped membranes, containing high levels of protonated montmorilonite (MMT-H). They observed the incorporation of MMT-H results in drastic increase (over 100%) of proton conductivity and mechanical properties [15]. Shabanikia e al. investigated novel nanocomposites membranes were prepared using different amounts of $SrCeO_3$ nano powders dispersed into PBI by solution casting method. The phosphoric acid-doped PBI/$SrCeO_3$ nanocomposite membranes were tested in a fuel cell and showed 0.44 W/cm^2 power density and 0.88 A/cm^2 current density in 0.5 V at 180 °C [16].

Among different inorganic additives SiO_2 is well known for its barrier property towards gases and solvents along with its strong H-bonding capability to acids, which is beneficial to prevent the acid leaching and improve the proton conductivity of the resulting hybrid membranes compared to the virgin membrane. Suryani et al. reported PBI-functionalized silica nanoparticles have been prepared through an ozone-mediated process using N-(p-carboxyphenyl) maleimide modified silica as precursors. They observed the PBI/SNP-PBI membrane demonstrates a maximum power density of 0.650 W/cm^2 in a single cell test with H_2 and O_2 gases, compared to the value of 0.530 W/cm^{-2} read from the test for PBI membrane [17]. Linlin et al. [18] investigated the performance of poly(2,5-benzimidazole) (ABPBI)-Silica membranes for application in HT-PEMFC. They reported the synthesis of poly(2,5-benzimidazole) (ABPBI) membranes and fabrication of ABPBI–silica nanocomposites by an ex situ technique using methanesulfonic acid as the solvent. The introduction of sulfonated silica particles into the ABPBI matrix improved the thermal stability of membranes that is important for HT-PEMFC application The maximum proton conductivity of 0.038 S/cm was obtained from phosphoric acid-doped ABPBI nanocomposite membrane containing 10 wt. % modified silica at 140 °C and 1% relative humidity in comparison to 0.01523 S/cm for virgin phosphoric acid-doped ABPBI membrane.

In this study, we report the preparation and characterization of hybrid membranes based on a PBI with SiO_2 nanoparticles. SiO_2 was used as an inorganic additive to enhance to properties of PBI membrane at high temperature and non-humidified HT-PEMFC conditions. It is pointed out that there are few papers reporting the development of PBI/SiO_2 hybrid membranes for H_2/Air HT-PEMFC. We have detail studied the size effect of SiO_2 on the membrane properties, including membrane morphology, thermal stability, mechanical strength, acid leaching, proton conductivity and HT-PEMFC performance. As a result, the PBI/SiO_2 membranes have exhibited improved mechanical strength, high proton conductivities, and single HT-PEMFC performance compared to the pristine PBI membrane.

Experimental

Materials

PBI polymers were prepared by polycondensation of 3,3′-diaminobenzidine and isophtalic acid in polyphosphoric acid in our laboratory according to the reported method [19]. To achieve the required phosphoric acid doping level, it is advantageous to cast the membrane from a PBI polymer with a high molecular weight. The molecular weight of PBI polymer was selected as 45,000. N–N dimethylacetamide ($CH_3C(O)N(CH_3)_2$ DMAc), sulfuric acid (98%), and o-phosphoric acid (85%) were used as received. SiO_2 in diameter of 10–20 nm were received from Sigma–Aldrich and used as received. All solvents were used high-grade reagents and without further purification.

Preparation of PBI/SiO_2 hybrid membranes

The PBI and PBI hybrid membranes were prepared by a solution-casting method [20]. In this method, the hybrid membranes were fabricated using DMAc as a solvent. An appropriate amount of 5 wt. % PBI solution was mixed with 5 wt. % SiO_2 powders in an ultrasonic bath for 30 min. The use of high inorganic material often gives rise to a non-homogenous distribution and undesirable aggregation of the inorganic material in polymer matrices. The homogeneous