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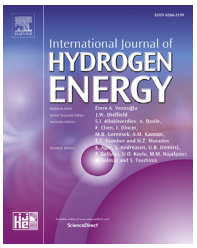

Novel perovskite structured calcium titanate-PBI composite membranes for high-temperature PEM fuel cells: Synthesis and characterizations

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ABSTRACT

We report the incorporation of nanoCTO (nanoCaTiO$_3$), prepared by sol-gel methods into the synthetic m-PBI to develop nanoCTO-PBI composite membranes. The macromolecular structure of the membrane shows high conductivity and good oxidative stability. The acid doping level in the membrane was estimated by the amount of phosphoric acid (PA) per specific volume. Increase in the content of nanoCTO results in the increase in conductivity as well as the oxidative stability of the membrane. Higher conductivity observed for 15% nanoCTO-PBI composite membrane as 32.7 mS cm^{-1}, whereas that of 5% nanoCTO-PBI is only 20.2 mS cm^{-1}. The power density and current density of 10% nanoCTO-PBI composite membrane at 0.6 V and 160 °C obtained are 251.4 mW cm^{-2} and 419 mA cm^{-2} respectively. Thus, the composite membranes are found to be potential electrolytes for HT-PEM fuel cells with enhanced proton conductivity.

Introduction

Nowadays fuel cells are considered greatly for clean, renewable, pollution-less and highly efficient energy source, which are utilized in stationary, automotive and mobile applications [1]. Among the fuel cells, proton exchange membrane fuel cell (PEMFC) shows better performance than other fuel cells because of their simplicity, high power density, and quick start up [2]. In PEMFC process at low temperature window 60–80 °C, Nafion membrane was mostly used as electrolyte and separator due to their several advantageous qualities. Nafion membrane has many limitations such as reduced carbon dioxide tolerance, low performance, humidification, and high expense due to low temperature operation temperature below 100 °C [3–6]. Because of many advantages such as faster chemical kinetics at the electrode, heat utilization, reduced CO/CO$_2$ catalyst poisoning, simple thermal and water management [7], more research is expected on the development of high temperature polymer electrolyte membranes (HT-PEM) that operates at 100–200 °C. The acid doped polssy [2,2-(m-phenylene)-5,5-bibenzimidazole] (m-PBI) is a

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promising HT-PEM due to its high proton conductivity, high thermal stability, and high fuel cell performance up to 200 °C [8]. Sulfuric and phosphoric acids are considered as doping agents in membranes which act as both donors and acceptors in proton transfer and, then, allow proton migration along the anionic chain. Of the two acids, phosphoric acid shows interesting results due to its conductivity, mechanical properties, and thermal stability at temperatures greater than 150 °C [8–11]. Various types of phosphoric acid-doped PBI membranes have been studied extensively [12–15]. To avoid acid leaching problem of m-PBI membranes, unusual PBI composite have been studied. Introduction of inorganic fillers such as phosphotungstic acid, silicotungstic acid, boron phosphate, zirconium tricarboxybutylphosphonate, titanium oxide, titano-silicates, clay, aluminum oxide and silica introduced into PBI membranes can improve the ionic conductivity by increasing the amount of the doping acid in the PBI membrane as well as long-term strength by reducing the acid leaching [16–29]. The proton conductivity of the membrane can be enhanced by metal oxides which show good affinity and interaction with phosphoric acid [29–32].

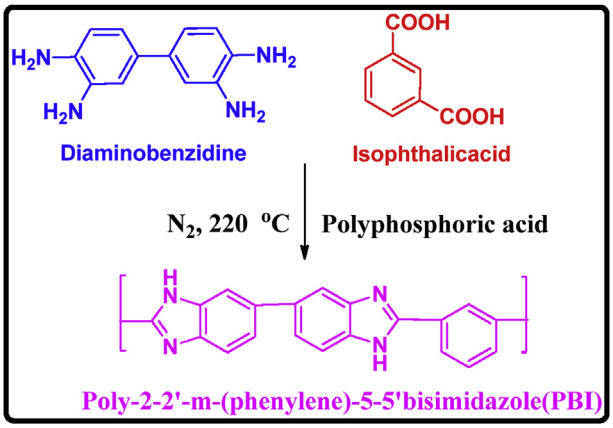
Hence, in the present work, a novel nanoCTO-PBI composite membrane has been prepared by nano$CaTiO_3$ by incorporating into synthetic m-PBI. The morphology of the nanoCTO-PBI composite membranes as well as FTIR analysis, XRD analysis and measurement of proton conductivity, oxidative stability and thermal characteristics were studied. The characteristics of the membrane were compared with synthetic m-PBI membranes.

Experimental section

Materials and methods

The ^{13}C and ^{15}N spectral studies were carried out at 300 and 75 MHz respectively using Bruker spectrometer. Morphology of the membrane was examined by a high resolution scanning electron microscopy (HRSEM) (FEI Quanta 250 Microscope, Netherland). Fourier transform infrared (FTIR) spectra were recorded using KBr pellet using Nicolet 5700 spectrophotometer (Thermo Electron Co., USA). Poly[2,2′-(*m*-phenylene)-5,5′-benzimidazole] (m-PBI) was synthesized in the laboratory using the method described earlier [33–35] and the dried polymer has an inherent viscosity value of 0.526 dL g^{-1} in H_2SO_4 (98%) at 30 °C. TGA experiments were carried out using TA instruments Inc., model SDT Q600 by heating under nitrogen atmosphere at 10 °C min^{-1}.

Scheme 1 shows the sequence of chemical reaction in the polymer synthesis. m-PBI was prepared by condensation polymerization of 3,3′-diaminobenzidine (DAB) and isophthalic acid (IPA) in the presence of polyphosphoric acid (PPA, Aldrich). 3.24 g (15.1 mmol) of DAB was first dissolved in 60 g PPA at 120 °C. Then 2.51 g (15.1 mmol) IPA was added. The mixture was stirred at 220 °C in nitrogen (N_2) atmosphere for 24 h for polymerization to take place. Progressive increase in viscosity was observed as the reaction proceeded. After the reaction, the product was poured into de-ionized water to isolate the polymer. The excess acid contained in the polymer was neutralized by washing the polymer in dilute sodium bicarbonate solution. The polymer was the filtered and washed thoroughly with water and methanol, successively, followed by drying in vacuum oven and grinded to obtain the polymer powder.



Scheme 1 – Synthetic route of m-PBI.

Synthesis of calcium titanate (CTO) and nanoCTO-PBI composites

In a 500 mL three neck round-bottom flask 4.2 g of CaO was dissolved in 10 mL of concentrated acid. Methanol (20 mL) was added to the solution [36]. The reaction mixture was added drop wise to a solution of 21.293 g titanium (IV) isopropoxide dissolved in the same volume of dried n-butanol at room temperature for 3 h. Then the precipitate was filtered under vacuum, thoroughly washed with deionised water followed by methanol. White powders were obtained from gel by drying at 100 °C in oven. The gel powder was calcined in air at temperature up to 500 °C.

The nanoCTO-PBI hybrid composite membranes were prepared by a solution-casting method [37]. 2 wt% m-PBI solution in DMSO was mixed with 5–15 wt% nanoCTO powders in an oil bath for 30 min at 120 °C. Then, solution was poured onto Petri dishes (diameter 17 cm), by drying at 80 °C for 24 h. The resultant membranes were then peeled off and soaked in distilled water at 80 °C for 2 h and further dried at 100 °C for 1 h.

Physico-electrochemical characterizations

Synthesized composite membranes were immersed in 14.0 M phosphoric acid (PA) at 90 °C for 12 h [38]. After that, the membranes were cleaned with a tissue paper to eliminate the extra acid on the membrane surface and dried at 110 °C for 4 h. The PA doping of the membrane (%) was determined by weight gain from the doping and calculated according to the following Eq. (1):

$$PA\ doping\ level(\%) = \left[\frac{W_{PA} - W}{W}\right] \times 100 \quad (1)$$

where W_{PA} and W, are the weight of dried membrane after doping and before doping, respectively.

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