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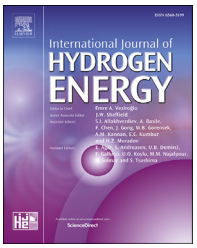

Composite membranes based on polybenzimidazole and ionic liquid functional Si–O–Si network for HT-PEMFC applications

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ABSTRACT

Polybenzimidazole (PBI)/ionic liquid (IL) functional Si–O–Si network composite membranes are prepared from PBI with 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride. The IL can be hydrolyzed to form Si–O–Si network structure under acidic conditions. And such IL functional Si–O–Si network (NP) in the composite membranes could improve phosphoric acid doping levels and proton conductivities simultaneously. The ability of retaining more PA is also reflected in the high proton conductivity value of PBI/NP-15% membrane which shows almost three-fold increment compared to the pristine PBI. All the PBI/NP-X composite membranes display excellent chemical stability and improved mechanical strength. This is attributed to Si–O–Si network structure. Moreover, PBI/NP composite membranes have demonstrated high thermal stability up to 250 °C, which is attractive for high-temperature (>200 °C) proton exchange membrane fuel cells.

Introduction

Proton exchange membrane fuel cells (PEMFCs) have become one of the most promising clean energy-shift devices because of their high power density, good efficiency and low pollutant generation, and polymer electrolyte membrane (PEM) is the important component in proton exchange membrane fuel cells (PEMFCs) [1–3]. PEM should not only separate H_2 from O_2 to prevent cross-permeation but also transport the protons toward a specific direction. Perfluorosulfonated membranes are commonly used as PEM in PEMFCs, such as Nafion®. This kind of PEM is thermally and mechanically stable [4–6]. However, they still have several shortcomings, such as poor CO tolerance, a high methanol diffusion, and a low proton conductivity at high operation temperature (above 80 °C).

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Hence, the development of low-cost, low methanol crossover, high-temperature-resistant alternative PEMs for high temperature PEMFCs (HT-PEMFCs) have received a lot of attention [7–10]. Polybenzimidazole (PBI) has been widely investigated, because of their excellent thermal stability and good mechanical properties [11–13]. However, pristine PBI has low proton conductivity. Therefore, it has been investigated the preparation of PBI composite membranes combined with various inorganic acids to enhance the conductivity of PBIs. Acid-doped PBI membranes were first suggested for fuel cell applications by Wainright et al. [14–17]. Thereafter, various inorganic acids were reported, such as sulfuric acid, phosphoric acid, perchloric acid, hydrochloric acid and nitric acid as doping agents in membranes. Among these acids, phosphoric acid is the most extensively studied by researchers. Phosphoric acid-doped polybenzimidazole (PA/PBI) membranes exhibit high proton conductivity at high temperatures ranging from 100 to 200 °C under anhydrous conditions, as well as having good mechanical properties [18–21]. Higher doping levels result in higher proton conductivity and degrade mechanical strength [22–25]. The higher operation temperatures in the PEMFC could be accompanied with higher CO tolerance and faster reaction kinetics [26,27]. Recently, ionic liquids (ILs) have attracted considerable attention in electrochemical applications [28–30]. ILs are liquid molten salts at ambient temperature. They are composed of ions and are non-volatile substances. As we all know, ILs have unique properties such as high thermally stable within a wide temperature range [31]. Thus, they are likely to be good electrolyte alternatives for high-temperature PEMFCs. Doyle et al. reported a PEM based on Nafion® and ionic liquid (IL) in order to improve the conductivity and thermal stability [32–34]. It exhibited excellent conductivity of 0.1 S cm^{-1} at 180 °C. The continuing improvements in IL-based PEM have led to many effective results and a lot of research studies [27,29,31,35].

In this study, the preparation and characterization of composite membranes based on PBI and ionic liquid functional Si–O–Si network, PBI/NP-X is investigated. As mentioned above, we expect that the introduction of Si–O–Si network structure will improve mechanical properties and proton conductivity at high temperatures. This novel type of composite membranes can be a promising proton exchange membrane candidate for HT-PEMFC applications.

Experimental

Materials

Isophthalic acid (IPA) was purchased from Aladdin Industrial Corporation. Polyphosphoric acid (PPA), Phosphorus pentoxide (P_2O_5), 1-Methylimidazole, (3-chloropropyl)trimethoxysilane were commercially obtained from Shanghai Macklin Biochemical Co., Ltd. N, N-Dimethylacetamide (DMAc), calcium chloride anhydrous ($CaCl_2$), sodium hydrogen carbonate ($NaHCO_3$) were supplied by Tianjin Guangfu Technology Development Co., Ltd. All the other chemicals were obtained commercially and used without further purification.

Synthesis of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride

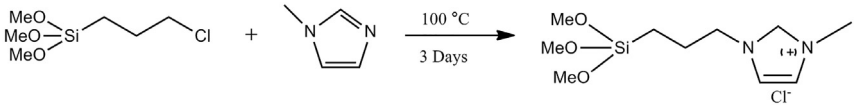
As shown in Scheme 1, 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride was synthesized from 1-methylimidazole and 3-(chloropropyl) trimethoxysilane. Briefly, a mixture of 1-methylimidazole (3.19 ml, 0.04 mol) and 3-(chloropropyl) trimethoxysilane (7.87 ml, 0.04 mol) was heated under nitrogen atmosphere at 110 °C for three days. To remove unreacted material, the viscous liquid mixture was washed with toluene several times at room temperature. Finally, the ionic liquid was maintained in vacuum oven at 50 °C to remove excess toluene. The resulting viscous ionic liquid was light yellow.

Synthesis of PBI

As depicted in Scheme 2, PBI was synthesized from 3, 3′-diaminobenzidine (DAB) and isophthalic acid (IPA) with a molar ratio of 1.0:1.0 in polyphosphoric acid (PPA). In a 100 ml, four-necked round-bottom flask equipped with a mechanical stirrer under a nitrogen atmosphere, DAB (3.2141 g, 15 mmol) was first dissolved in 75.808 g PPA at 140 °C. After the DAB was completely dissolved in PPA, IPA (2.4920 g, 15 mmol) was added into the solution. When obtaining a homogeneous mixture, the temperature was elevated to 200 °C and maintained for 5 h under stirring. The completely reacted viscous solution was poured into water and was neutralized with sodium bicarbonate solution. Afterwards, the polymer powder was washed several times with deionized water and dried under vacuum for 12 h at 120 °C.

Preparation of PBI/NP-X composite membranes

In this work, PBI/NP-X composite membranes were obtained by the solution-casting and evaporation method, as shown in Scheme 3. The ratio percent of the IL in the PBI matrix was 3, 5, 7, 10, 15 and 20 wt%, respectively. The resulting composite membranes were denoted as PBI, PBI/IL-3%, PBI/IL-5%, PBI/IL-7%, PBI/IL-10%, PBI/IL-15% and PBI/IL-20%, respectively. A detailed preparation procedure was as follows: a certain amount of PBI powder was dissolved in N, N-dimethylacetamide (DMAc) to achieve a 2 wt % solution. Then a fixed amount of IL was added into the PBI solution under vigorous stirring for 24 h. The homogeneous solution was poured on a clean glass plate and dried in a vacuum oven at 80 °C for 24 h to evaporate the DMAc solvent. Then the dry membranes were immersed in 1 M H_2SO_4 solution at 80 °C for 24 h to obtain



Scheme 1 – Synthetic process of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride.

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