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High performance porous polybenzimidazole membrane for alkaline fuel cells

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ABSTRACT

In this study, a highly ion-conductive and durable porous polymer electrolyte membrane based on ion solvating polybenzimidazole (PBI) was developed for anion exchange membrane fuel cells (AEMFCs). The introduction of porosity can increase the attraction of electrolytic solutions (e.g., potassium hydroxide (KOH)) and ion solvation, which results in the enhancement of PBI's ionic conductivity. The morphology, thermo-physico-chemical properties, ionic conductivity, alkaline stability, and the AEMFC performance of KOH-doped PBI membranes with different porosities were characterized. The ionic conductivity and AEMFC performance of 70 wt.% porous PBI was about 2 times higher than that of the commercially available Fumapem[®] FAA. All KOH-doped porous PBI membranes maintained their ionic conductivity after accelerated alkaline stability testing over a period of 14 days, while the commercial FAA degraded just after 3 h. The excellent performance and good durability of KOH-doped porous PBI membrane makes it a promising candidate for AEMFCs.

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Introduction

Using alkaline medium instead of acidic in hydrogen fuel cells is preferred because the occurrence of corrosion is mitigated and cheaper construction materials can be used [1]. In anion exchange membrane fuel cells (AEMFCs), because of the alkaline environment, the reduction and oxidation kinetics of the oxidants and fuels (e.g., air and hydrogen) are inherently much faster for the cathode and anode electrodes, respectively, enabling higher power densities and energy conversion

efficiency. Thereby, employing non-precious metal electrocatalysts such as nickel and silver are feasible in such systems, making them a potentially low-cost technology. Moreover, due to the less corrosive nature of an alkaline medium, longer lifetime is expected for AEMFCs [2–7]. However, the major barrier to commercialize AEMFCs is the anion exchange membrane (AEM) which suffers from low performance and physico-chemical stability. Thus, it is vitally required to develop a cost effective AEM, possessing excellent ionic conductivity and high thermo-physico-chemical stability [6,8–11].

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Generally, AEMs are categorized according to various types of polymeric backbones and ion-exchange groups [12–14]. Depending on ion-exchange groups, AEMs can be classified into (i) ion-doped membranes, in which the polymers are doped with electrolytic solutions (e.g., KOH, LiOH etc.); (ii) composite membranes, where the incorporated inorganic materials are in charge of ion transfer; and (iii) blended membranes, in which another polymer acts as the ion-exchange group. The most studied polymers, so far, are polybenzimidazole [7,15–20], polyphenylene oxide [21,22], polyetherketone [23], cardo polyetherketone [24], polyethersulfone [25,26], poly(vinyl alcohol) [27], poly(ethylene-co- tetrafluoroethylene) [28–31] and poly(arylene ether sulfone) [32]. However, at the current state of AEM technology, there are still major challenges that must be resolved, including low ion conductivities, chemical instabilities in concentrated alkaline environments, and fast thermal degradation.

In this study, the developed AEM is based on ion-doped membranes. Among the examined polymeric structures in literature, poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) is an inexpensive amorphous homo-polymer, having outstanding physico-chemical and thermal stability [4,33–39], promising candidate for the backbone of ion-doped membranes [40–44]. An unmodified PBI is an ionic and electronic non-conductor [39,45–48]. However, due to the existence of amine (–NH–) and imide (–N) groups in the imidazole rings of PBI, it turns into an excellent ionic conductor by doping with strong alkaline (e.g., KOH) [39–41,49] or acidic (e.g., phosphoric acid) [50–52] solutions, yet maintains its electronic non-conducting properties after doping. Xing et al. [39] have shown ionic conductivities between $5 \times 10^{-5} \text{ S cm}^{-1}$ and $1 \times 10^{-1} \text{ S cm}^{-1}$ for PBI using KOH with a concentration of 6 M at 70–90 °C. However, the reported high ionic conductivity for PBI was measured when the membrane was in the electrolytic solution at elevated temperatures. In this work, a unique approach has been taken to introduce porosity into the morphology of PBI and then dope it with KOH, which makes it to function without the requirement of being submerged in the electrolytic solution. The existence of pores can increase the uptake of KOH, leading to the increase of ionic conductivity [53,54]. To the best of our knowledge, although there are a few examples of proton-conducting porous PBI membranes for proton exchange membrane fuel cells (PEMFCs) [16,19,20,55–60], there are no reports on the development of KOH-doped porous PBI membranes for AEMFCs. In order to make the membrane porous, the synthesized PBI was mixed with an appropriate amount of a low molecular weight pore-forming agent (dibutyl phthalate, DBP), which could be removed after synthesis by immersion in methanol solution. DBP was selected among various phthalate-based porogens due to its aliphatic chains. It has been shown that aliphatic structure of phthalates exhibit more interconnected and

larger pore size than fully aromatic ones such as diphenyl phthalate [16]. Accordingly, the authors chose dibutyl phthalate (DBP) as a candidate for porogen in their study. Then, the obtained porous membrane was doped with a highly concentrated KOH solution. The morphology, chemical analysis, mechanical properties, thermal stability, electrolyte absorption, hydroxide conductivity, alkaline stability, and AEMFC performance of the KOH-doped PBI membranes with different porosities were characterized and compared to commercially available AEM (Fumapem® FAA from FuMA-Tech GmbH) using different spectroscopic and microscopic analysis methods, including proton nuclear magnetic resonance ($^1\text{H NMR}$), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) mapping, Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA) and differential thermal analysis (DTA), tension testing, contact angle measurement, and electrochemical impedance spectroscopy (EIS).

Experimental section

Synthesis of polybenzimidazole (PBI)

The synthesis of PBI is well described in the literature [61]. In this study, according to Fig. 1, 4.7 mmol of 3,3'-diaminobenzidine (DAB, Aldrich) with an equivalent molar amount of isophthalic acid (IPA, Aldrich) were dissolved into polyphosphoric acid (PPA, Alfa Aesar) in a round-bottom flask with a magnetic stirrer under a slow flow of nitrogen gas. After stirring for 7 h at 200 °C, the reaction mixture turned dark reddish brown and became viscous. The reaction was quenched by pouring the hot solution into a large amount of cold water. The formed PBI fibers were stirred and washed for 48 h in distilled deionized (DDI) water and subsequently for 7 h in 2 M KOH solution followed by drying in an oven at 100 °C overnight.

Preparation of KOH-doped porous PBI membranes

A schematic of fabricating KOH-doped porous PBI is displayed in Fig. 2. As shown, 1 wt.% dried PBI polymer with different amounts of DBP (Aldrich) were dissolved in dimethyl sulfoxide (DMSO, Aldrich) under stirring and heating until an orange homogeneous solution was obtained. Then, it was spread onto a glass plate and placed in an oven. The temperature ramp was from 60 to 190 °C over 12 h in order to slowly evaporate the solvent. After the heating was finished, the glass plate was immersed in DDI water in order to detach the membrane from the plate. Then, DBP was extracted by immersing the membranes in methanol for 1 h. The porous PBI was dried at 80 °C until a constant weight was achieved. Then, all membranes were doped with KOH by keeping them in 6 M KOH solution for

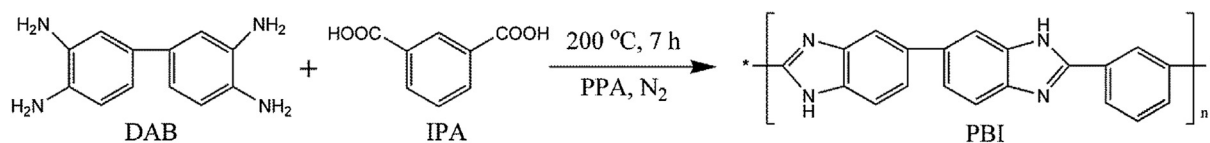


Fig. 1 – The synthesis and chemical structure of PBI.

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