

Highly Anion-Conducting Porous Polymer Electrolyte Membrane for Alkaline Fuel Cells

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A highly anion-conductive porous polymer electrolyte membrane based on polybenzimidazole (PBI) was developed for alkaline fuel cells. The pores are introduced by leaching out the pore-forming agent (dibutyl phthalate), after making the membrane, comprised of it. The porosity increase the attraction of electrolytic solutions (e.g., potassium hydroxide), which results in the enhancement of plasticized PBI's ionic conductivity. The morphology, physico-chemical properties, thermal stability, and the hydroxide conductivity of the KOH-doped porous PBI membranes were characterized, using different spectroscopic and microscopic analysis methods. It was observed that the hydroxide conductivity of 70 wt.% porous PBI was 6 times higher than that of commercial FAA anion exchange membrane. The excellent performance of KOH-doped PBI makes it a promising membrane material for alkaline fuel cells.

Introduction

Recently anion exchange membrane fuel cells (AEMFCs) have absorbed considerable attention, primarily due to their distinct advantages over polymer electrolyte membrane fuel cells (PEMFCs). The preferences of operating fuel cells in an alkaline environment are fast kinetics of oxygen reduction reaction (ORR) at cathode, facile oxidation kinetics of fuels at anode, feasible using of non-precious metal electro-catalysts such as silver and nickel, higher durability and reduced fuel crossover (1-3). However, AEMFCs need to overcome strenuous technical and economic challenges which are specifically associated with the fabrication of a cost-effective anion exchange membrane (AEM) possessing (i) high anionic conductivity, (ii) interfacial compatibility with catalyst layer, and (iii) exemplary physico-chemical and temperature stability, especially at elevated temperatures (1-4).

The commercially available AEMs are usually based on quaternary ammonium (QA) cross-linked polystyrene, which cannot be used for AEMFCs due to their low chemical and thermal stability, as well as weak mechanical property. Distinctively, the polystyrene backbone is too rigid to produce flexible thin films, and the QA functional group attached on polystyrene tends to degrade at 40–60 °C (4). To conquer the above-mentioned issues, several types of quaternized polymeric structures have been used to produce AEMs for application in AEMFCs (5). Nevertheless, the performance and durability of SAFCs based on them is still low due to the decay of the hydroxide exchange groups (e.g., QA functional groups) at elevated temperatures (>60 °C) (6).

Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) is an inexpensive amorphous homo-polymer, having outstanding physico-chemical and thermal stability (6-13). An unmodified PBI is an ionic and electronic non-conductor (13-17). However, because of the existence of amine (–NH–) and imide (–N) groups in imidazole rings of PBI, it turns into an excellent ionic conductor by doping with strong alkaline (e.g., potassium hydroxide) (13, 18-20) or acidic (e.g., phosphoric acid) (21-23) solutions, yet it keeps its electronic non-conductivity property after doping. Therefore, PBI membranes can be the promising candidates for energy conversion devices such as fuel cells, showing good performance (13, 18, 19, 24, 25). For instance, Xing et al (13) have shown ionic conductivities between $5 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ and $1 \times 10^{-1} \text{ S} \cdot \text{cm}^{-1}$ for

PBI using KOH with a concentration of 6 M at 70–90 °C. However, the obtained high anion conductivity for PBI was achieved only at elevated temperatures.

In this study, a different approach has been taken to develop hydroxide-doped porous PBI membranes. Generally, the existence of pores can increase the uptake of an electrolytic solution, leading to the increase of ionic conductivity (26, 27). To the best of our knowledge, although there are two examples for proton-conducting porous membrane, doped with highly concentrated phosphoric acid (28, 29), there is no evidence for hydroxide-conducting porous polymer electrolytes for AEMFCs. In this work, in order to introduce the porosity into the membrane, the synthesized PBI was mixed with an appropriate amount of a pore-forming agent, i.e., porogen. Then, the obtained porous membrane was doped with a highly concentrated KOH solution. A schematic of fabricating KOH-doped porous PBI has been shown in Figure 1. The morphology, physico-chemical properties, thermal stability, and the hydroxide conductivity of the KOH-doped porous PBI membranes were characterized, using different spectroscopic and microscopic analysis methods, including scanning electron microscopy (SEM), proton nuclear magnetic resonance (^1H NMR), Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), and electrochemical impedance spectroscopy (EIS).

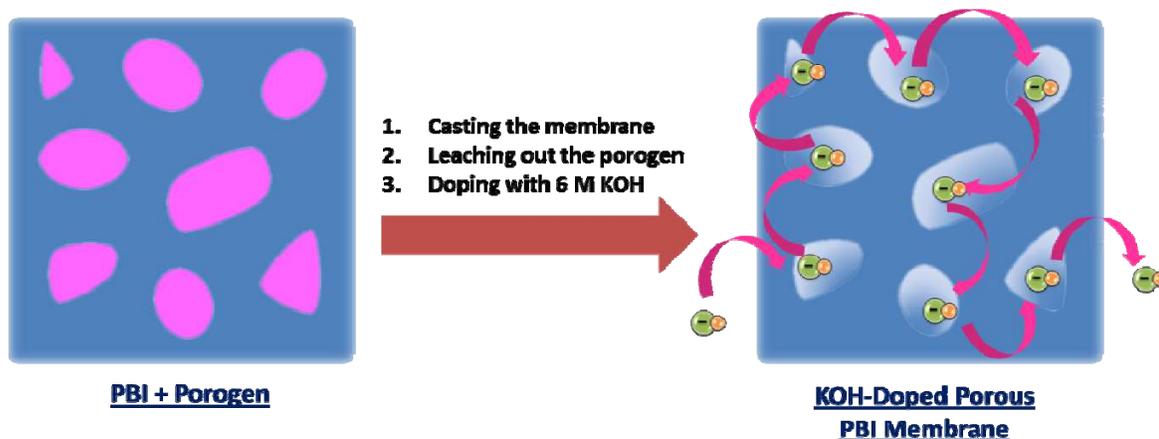


Figure 1. A schematic of fabricating KOH-doped porous PBI.

Experimental

Synthesis of Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI)

1 g 3,3'-diaminobenzidine (DAB, Aldrich), 776 mg isophthalic acid (IPA, Aldrich), and 20 g polyphosphoric acid (PPA, Alfa Aesar) were loaded into a round-bottom flask fitted with a magnetic stirrer under a slow flow of nitrogen gas. After stirring for 7 h at 200 °C, the reaction mixture turned dark 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 water and 7 h in 300 mL of a 10% KOH solution, and then dried in an oven at 100 °C overnight.

Fabrication of KOH-Doped Porous PBI Membrane

1 wt.% dried PBI polymer and an appropriate amount of porogen, i.e., dibutyl phthalate (DBP, Aldrich), were dissolved in dimethyl sulfoxide (DMSO) 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 in order to evaporate slowly the solvents for 12 h. After the

heating was finished, the glass plate was immersed in DI water in order to detach the membrane from the plate. Then, the porogen-plastisizer was extracted by immersing the membranes in methanol for 1 h. The porous PBI was dried at 80 °C until constant weight was achieved. Then, all membranes were doped with KOH by immersion in 6 M alkaline solution for 2 days and finally, stored in DI water until future characterization tests.

Characterization Tests

The presence of PBI was shown by proton nuclear magnetic resonance (¹H NMR, 500 MHz Bruker Analytik GmbH) and Fourier transform infrared spectroscopies (FT-IR, Avatar 320). The overall morphology of all samples was examined by using scanning electron microscopy (SEM, LEO FESEM 1530). Thermogravimetric analysis (TGA) was performed under nitrogen with a TGA Q500 V20.10 instrument in the temperature range from 25 to 900 °C at the heating rate of 10 °C min⁻¹.

Water Uptake and Swelling Ratio. The water uptake and swelling ratio of the membranes were evaluated by first drying the films in a vacuum oven at 80 °C until constant dry weight (W_d) and length (L_d) were obtained. The dried membranes were immersed in deionized water at room temperature for 48 h. The surface water was swabbed away with tissue paper before weighing. The weight and length were measured several times until constant weight (W_w) and length (L_w) were achieved. Then, the water uptake (WU) and swelling ratio (SWR) were calculated by using equations 1 and 2:

$$WU (\%) = \frac{W_w - W_d}{W_d} \times 100 \quad [1]$$

$$SWR (\%) = \frac{L_w - L_d}{L_d} \times 100 \quad [2]$$

Ionic Conductivity. The ion conductivity of all PBIs was characterized in in-plane direction of the membranes, using 4-electrode AC impedance spectroscopy in Princeton Versastat MC potentiostat, and a simple home-made four-point cell made from four stainless-steel strips and Teflon plates. The outer stripes were the current source and sink, while the inner ones (reference electrodes) were used for the voltage measurements. The impedance was measured in the frequency range between 0.1 MHz and 0.1 kHz with perturbation voltage amplitude of 10 mV. The cell was placed in a thermo-controlled chamber in DI water for measurement. All samples were equilibrated in water for at least 24 h prior to the conductivity measurement. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements (at least three times) were then taken at that given temperature with 10 min interval until no more change in conductivity was observed. The hydroxide conductivity (σ) of all samples was then determined along the longitudinal direction, using equation 3:

$$\sigma = \frac{L}{RA} \quad [3]$$

Results and Discussion

Figure 2 represents ¹H NMR and FT-IR spectroscopies, which confirm the successful synthesis of PBI. The proton chemical shifts according to ¹H NMR are 9.14 (Ha), 8.28 (Hb), 7.85 (He), 7.8 (Hc), 7.67 (Hd), 7.53 (Hf). C=N, C=C, and the imidazole ring were characterized by FT-IR spectrum.

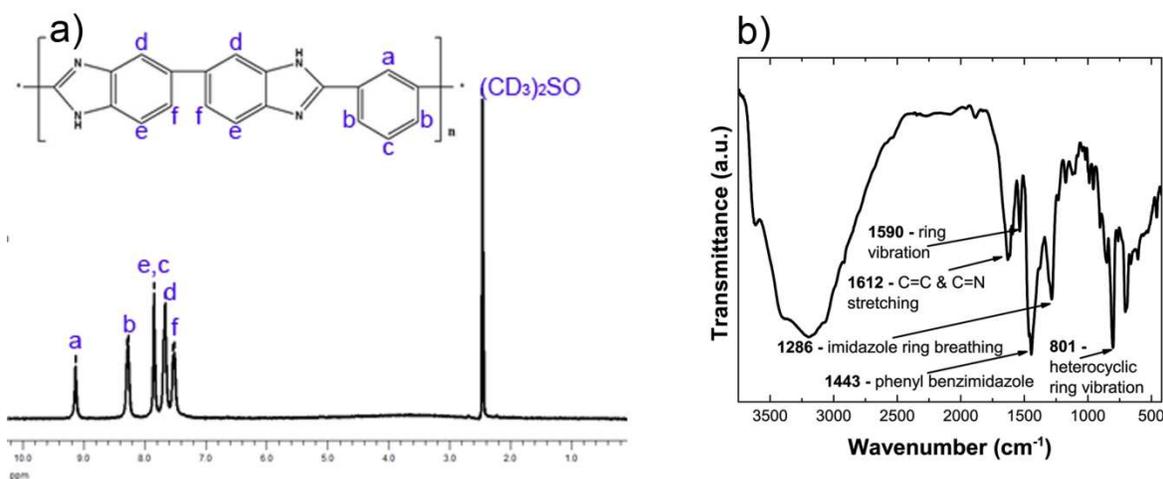


Figure 2. a) Proton chemical shifts of PBI in ^1H NMR, where the solvent was $(\text{CD}_3)_2\text{SO}$. b) FT-IR spectrum of PBI

The cross-section SEMs in Figure 3 show the morphology of the non-porous and 70 wt.% porous PBI membranes. The non-porous PBI has a smooth structure whereas; the open pores have been introduced in the porous membrane. It is observed that the pore size distribution is uniform and its average is around $1\ \mu\text{m}$.

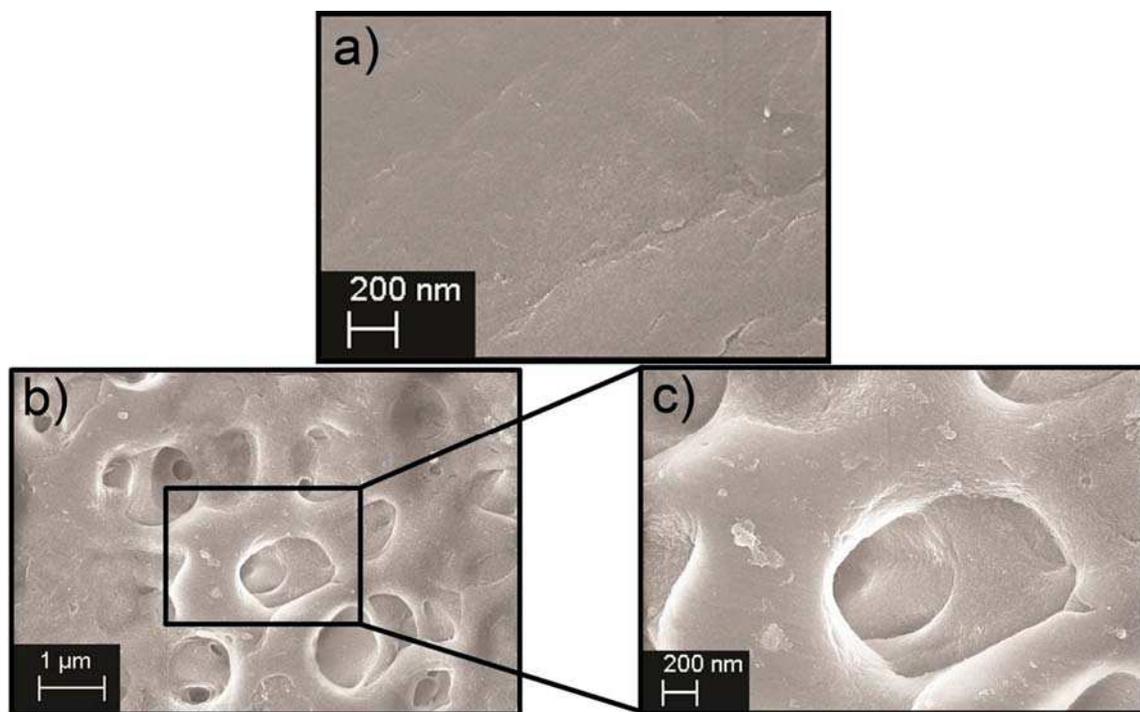


Figure 3. Cross-section pictures from SEM for a) non-porous PBI membrane, b) 70 wt.% porous PBI in low resolution, and c) 70 wt.% porous PBI in high resolution.

Table 1 exhibits the enhancement of water affinity by increasing the porosity from 0 to 70 wt.%, which was 53%. At the same time, the swelling ratio was increased to 75%.

TABLE I. Water uptake and swelling ratio of KOH-doped non-porous and porous PBI membranes.

Porosity of KOH-doped PBI membrane	Water uptake (%)	Swelling ration (%)
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0	28	6
70	59	24

The thermal stability of the membranes is illustrated in Figure 4. According to TGA and DTA, the introduction of porosity has not affected the thermal stability of the membrane. For both non-porous and porous membranes, the degradation temperature has started after 500 °C.

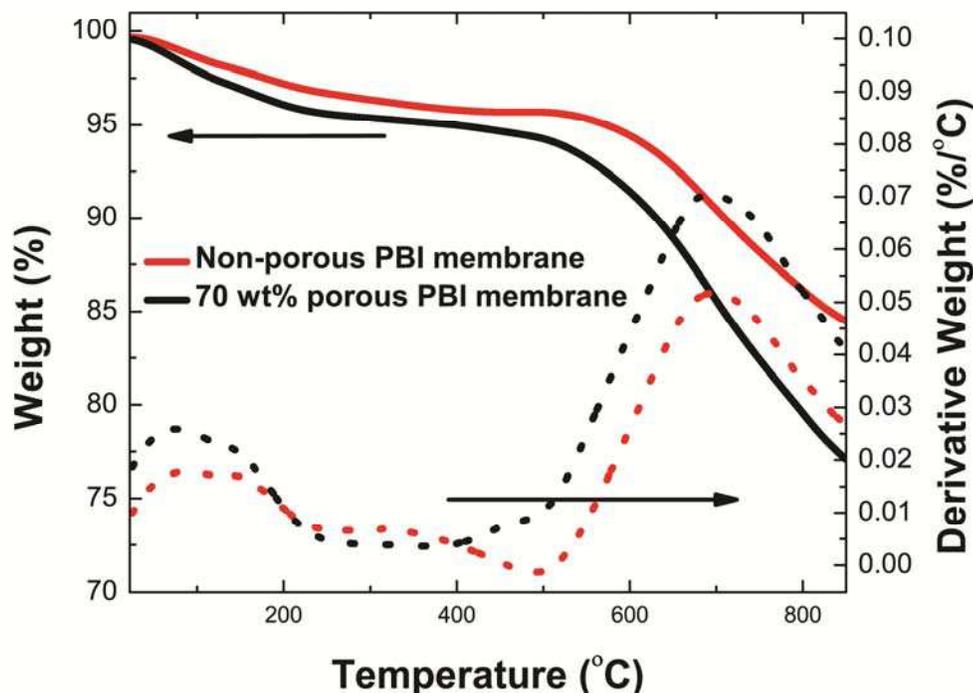


Figure 4. TGA and DTA curves of non-porous and 70 wt.% porous PBI membranes

Figure 5 shows the enhancement of ionic conductivity at different temperatures for the 70 wt.% porous PBI membrane, compared to that of non-porous PBI and the commercial FAA membranes. Fumapem® FAA from FuMA-Tech GmbH (35–40 μm thickness, resistivity of $0.59 \Omega \cdot \text{cm}^2$ at 20°C , IEC of $1.2 \text{ mmol} \cdot \text{g}^{-1}$) is an anion exchange membrane made of aminated polyarylene (polysulfone) chloride, hydroxide and carbonate salts, used for alkaline fuel cells. The “FAA” is just the name of the membrane, coined by the producer (i.e., FuMA-Tech GmbH). Both KOH-doped non-porous and porous PBI membranes have exhibited higher ionic conductivity at all temperatures in comparison with FAA. The maximum hydroxide conductivity was achieved for 70 wt.% porous PBI at 65°C , which was $3.5 \times 10^{-1} \text{ S} \cdot \text{cm}^{-1}$. Generally, it was observed that the highest ionic conductivity was at 65°C for both non-porous and porous PBI membranes and a decrease in performance occurred at 85°C . This may indicate that the temperature dependence and ion conduction mechanism in KOH doped PBI is different from other types of electrolytic membranes. This behavior was also seen in the work of Xing, B. and Savadogo¹³, where they tested the hydroxide conductivity of KOH-doped PBI

membrane. However, no mechanism was published so far to explain such a behavior. Determination of the hydroxide conduction mechanism in non-porous and porous PBI membranes is currently being pursued in our research for which various hypothesis and experiments are under study. For instance, in one of them, we observed that the swelling ratio of PBI membranes increases considerably in an aqueous medium by increasing the temperature. This may cause the closure of some pores in the membrane, leading to less available paths for hydroxides to be transferred. However, it seems obvious that the concentrated KOH adsorbs better inside the porous membrane, leading to a higher water uptake and therefore to a higher ionic conductivity.

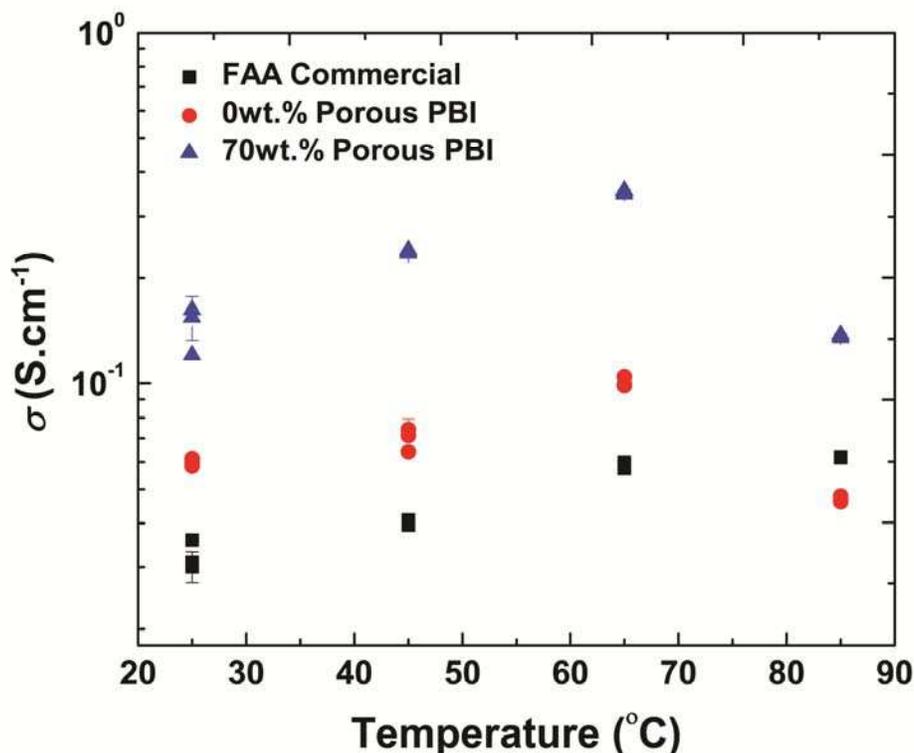


Figure 5. The hydroxide conductivity of non-porous and 70 wt.% porous PBI membranes, compared to the commercial FAA membrane at different temperatures in 100% relative humidity conditions.

Conclusion

The aspect of this study was the formation of KOH-doped porous polymeric membrane for alkaline fuel cells. The polymeric backbone of the membrane was based on polybenzimidazole (PBI). Dibutyl phthalate (DBP), which is a non-solvent material, was employed as the plasticizer and porogen to form the pores in PBI membrane. The pores are introduced by leaching out DBP, after making the membrane, comprised of the porogen. The introduction of porosity into the polymeric membrane creates more open path as well as higher surface area for ion transfer and electrolytic solution affinity, respectively. The enhancement of doping level and uptake of the electrolytic solution (e.g., potassium hydroxide), results in a plasticized porous polymer, which significantly helps the increase of ionic conductivity. It was seen that the hydroxide conductivity of 70 wt.% porous PBI was 6 times higher than that of commercial FAA anion exchange membrane. The excellent performance of KOH-doped PBI makes it a promising membrane material for alkaline fuel cells.

Acknowledgments

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