



## Recent advances in alkali-doped polybenzimidazole membranes for fuel cell applications

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### ABSTRACT

Polybenzimidazole (PBI), with a well-known excellent thermal stability, has been recognized as an alternative for anion exchange membrane fuel cells (AEMFC), primarily because it can serve as an ionic conductor after doping with inorganic hydroxides (typically KOH/NaOH) and thus allows fuel cells to be operated at high temperatures (currently as high as 120 °C). In addition, alkali-doped PBI membranes also offer many other favored physicochemical properties, such as high ionic conductivity. The objective of this article is to provide a review of recent research on the alkali-doped PBI membranes and their applications in fuel cells, including mechanisms of ion conduction through the alkali-doped PBI membranes, stability of the PBI membranes doped with alkali, strategies aiming at improving the ionic conductivity of the PBI membranes doped with alkali, as well as the performance of alkali-doped PBI membrane based fuel cells. Additionally, future perspectives relating to the development of alkali-doped PBI membranes and their applications in fuel cells are also highlighted.

### 1. Introduction

Anion exchange membrane fuel cells (AEMFCs) are generally regarded as an emerging energy conversion technology that has the potential to overcome many obstacles of proton exchange membrane fuel cells (PEMFC) in cost, stability, and durability of materials [1–10]. The typical structure design of AEMFC systems is analogous to that of PEMFCs, where the ion transport pathways are established between the cathode and anode. It is attributed to the dispersed ionomers with a network inside the electrodes, which are interfaced with the membrane [11–16]. Nevertheless, the performance of such a fuel cell system where transporting the hydroxide ions through the membrane purely relies on an AEM and ionomers in the electrodes is not satisfactory, primarily due to the low conductivity of state-of-the-art AEMs and corresponding ionomers [17–21]. In addition, another obstacle limiting the cell power output of AEMFCs is that current AEMs fabricated into fuel cells are not capable to be operated at high temperatures (< 60 °C) [22–24]. It has been recently demonstrated that polybenzimidazole (PBI) can withstand the high-temperature operation, and after doping with inorganic acid, the membranes can conduct protons and thus be used in fuel cells [25–37]. Among them, Wainright et al. [31] firstly introduced PBI membranes doped with acid for high-temperature PEMFCs. Similarly, Xing et al. [37] examined alkali-doped PBI membranes for AEMFCs.

The highest conductivity of KOH-doped PBI ( $9 \times 10^{-2} \text{ S cm}^{-1}$  at 25 °C) was higher than those of H<sub>2</sub>SO<sub>4</sub>-doped PBI membrane ( $5 \times 10^{-2} \text{ S cm}^{-1}$  at 25 °C) and H<sub>3</sub>PO<sub>4</sub>-doped PBI membrane ( $2 \times 10^{-2} \text{ S cm}^{-1}$  at 25 °C). More impressively, they showed that the hydrogen/oxygen fuel cells with an alkali-doped PBI membrane and a Nafion 117 membrane exhibited the same performance [37].

Since the pioneering work done by Xing et al. [37], extensive attentions have been paid to the alkali-doped PBI membranes, which become an alternative to the conventional QA-based AEMs in AEMFCs over the past decade [37–43]. As a consequence, great progress has been made in facilitating the large-scale utilization of this membrane in practical applications, but several critical issues are still remaining to be resolved, such as alkali leakage, high fuel permeability, and poor mechanical stability. This review focuses on recent advances and development of alkali-doped PBI membranes for fuel cell applications. In this article, we start with the mechanisms of ion conduction through the alkali-doped PBI membranes and the chemical structure change after doping, followed by the detailed discussion about the stability of the alkali-doped PBI membranes, including thermal stability, mechanical stability, and liquid uptake. Moreover, the strategies to promote the ionic conductivity of the PBI membranes doped with alkali are also summarized and compared. Meanwhile, the effects of the doping time, alkali type and concentration, carbonate presence, temperature, and

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soaking time on the ionic conductivity are described and discussed, respectively. Finally, we summarize and discuss the single-cell performance achieved by using the alkali-doped PBI membranes in fuel cells running on various fuels, including hydrogen, methanol, ethanol, and other alcohols.

## 2. Mechanisms of ion conduction through the alkali-doped polybenzimidazole membrane

The ion exchange membranes used in fuel cells are expected to meet the following requirements: high performance, high durability, but low cost. The function of the ion exchange membranes installed in fuel cells is to separate two electrodes (electron insulator), conduct ions (ion conductor), and be impermeable to fuels (fuel insulator). In AEMFCs, a barrier that limits their performance is that current AEMs fabricated into fuel cells are not capable to be operated at high temperatures (typically  $< 60\text{ }^{\circ}\text{C}$ ). It has been recently demonstrated that alkali-doped PBI membranes can offer the good thermal property and high ionic conductivity. For this reason, much attention has been extensively paid to this type of membrane. In fact, the pristine PBI membrane is primarily an electron and ion insulator (ionic conductivity:  $1 \times 10^{-12}\text{ S cm}^{-1}$  [44]) and its chemical structure is shown in Fig. 1. Like doping with inorganic acid, adding the pyrrole-type nitrogen (-NH-) and the pyridine-type nitrogen (-N=) in the benzimidazole rings is in favor of absorbing and interacting with the free inorganic base, which is capable of conducting ions [45]. Generally, the pristine PBI membrane is pre-treated to form the ion-conductive membrane by immersing it in an alkaline electrolyte solution (typically NaOH/KOH [37,38,45]) or in an alkaline fuel-electrolyte-mixed solution (typically ethanol/methanol + NaOH/KOH [39,46]), for a certain period of time. Zeng et al. [45] investigated the morphology change of the PBI membrane doped with alkali comparing to the PBI membrane via SEM-EDS. It was shown that the membrane possessed a uniform, dense and smooth structure after doping. In addition, it was also shown that after doping, the potassium and oxygen that were derived from the doped alkali were distributed through the whole membrane uniformly. They further investigated the morphology change during doping via AFM. It was found that the original PBI membrane was hydrophobic as a result of showing a bright field; while, the hydrophilic domains appeared after doping. Also, Hou et al. [39] studied the PBI membranes doped with alkali through the cross-sectional SEM images and its corresponding EDX mappings for elements of K, O, and N. Similarly, it was demonstrated that the elements of K, O, and N were distributed homogeneously. They explained that the presence of potassium was attributed to the reaction between KOH and -NH- in addition to the free KOH in the matrix, both of which were beneficial to the ion conduction.

In addition, the doping process also changes the chemical structure of the membrane. Zeng et al. [45] investigated the chemical structure change of the membrane doped with alkali comparing to the PBI membrane via FTIR. The results showed that the -NH- stretching vibration ( $1284\text{ cm}^{-1}$ ) was replaced by -NK- deformation ( $1510\text{ cm}^{-1}$ ) and bending vibration ( $1120\text{ cm}^{-1}$ ), indicating that the reaction between cations ( $\text{K}^+$ ) and benzimidazole segments in the PBI skeleton caused partial fracture of the hydrogen bonds. They further confirmed the chemical structure change of the membrane doped with alkali comparing to the PBI membrane via XPS, and found that after doping,

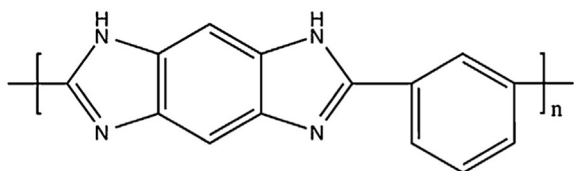


Fig. 1. Chemical structure of the pristine polybenzimidazole membrane [59]. Reproduced with permission from Elsevier.

the emergence of the potassium peaks indicated the successful formation of the PBI membrane doped with alkali.

Based on the above-mentioned characterizations before and after doping, there are a few mechanisms proposed for formation of the alkali-doped PBI membrane [39,45,47]. For example, Hou et al. [39] proposed a doping mechanism for alkali-doped PBI membranes, as shown in Fig. 2a. Firstly, the interaction between  $\text{K}^+$  and -NH- in imidazole ring occurred due to neutralization. Secondly, the existence of hydrogen bonding was detected between -N- and  $\text{OH}^-$  in imidazole ring; meanwhile,  $\text{K}^+$  was brought into the polymer to balance  $\text{OH}^-$ . They also confirmed this result via DFT calculations [47]. Based on the DFT results, they proposed a detailed mechanism, as illustrated in Fig. 2b. (i) -NH- can dissociate into  $\text{H}^+$  and -N-; (ii) the dissociated  $\text{H}^+$  can combine with  $\text{OH}^-$  to form  $\text{H}_2\text{O}$ ; and (iii)  $\text{K}^+$  has to combine with -N- to form -NK-. Recently, Zeng et al. [45] also proposed a similar doping mechanism for the PBI membrane immersed in alkaline solutions, as illustrated in Fig. 2c. Firstly, the pyrrole-type nitrogen (-NH-) in pristine PBI membrane dissociated protons and then the dissociated protons reacted with the hydroxide ions ( $\text{OH}^-$ ). Hence, the first step can be presented by a neutralization reaction. Secondly, the potassium cations ( $\text{K}^+$ ) are functioned in bridging nitrogen atoms that are negatively charged. In addition, the hydrophilic ionic clusters will establish to conduct the hydroxide ions by combination between the KOH solution and the PBI matrix, as illustrated in Fig. 2d. With a higher KOH concentration, the hydrophilic ionic clusters will become larger, which is the reason that the conductivity of the PBI membranes doped with alkali increases with higher KOH concentration [45].

In a fuel cell system, positively or negatively charged ions act as charge carriers to form the ionic current by transporting through ion exchange membranes. In alkali-doped PBI membranes, there are free  $\text{K}^+$  and  $\text{OH}^-$  in the PBI matrix, as well as bonded  $\text{K}^+$  and  $\text{OH}^-$  in the PBI skeleton, creating an anion-cation co-existing system in the PBI membrane after doping. To determine the charge carrier for the ion exchange membrane, An et al. [57] designed an experimental setup and determined the charge carrier of the three different types of commercial membrane, i.e., AEM (A201), CEM (Nafion 211), and NaOH-doped PBI membrane, as shown in Fig. 3a and b. It was found that the  $\text{Na}^+$  flux through the AEM was almost zero at the whole current density region; while,  $\text{Na}^+$  fluxes through the CEM and NaOH-doped PBI membrane were, respectively, 32% and 28% of the theoretical  $\text{Na}^+$  flux, meaning that  $\text{OH}^-$  fluxes through the CEM and NaOH-doped PBI membrane are 68% and 72% of the total ionic current, respectively. Hence, it was indicated that both  $\text{Na}^+$  ions and  $\text{OH}^-$  ions contributed to the ionic current, but the main charge carrier was the  $\text{OH}^-$  ion.

## 3. Stability of the alkali-doped polybenzimidazole membrane

The physiochemical properties of ion exchange membranes can significantly affect the fuel cell performance and thus much attention has been paid to the physiochemical characterizations of alkali-doped PBI membranes. This section will summarize and discuss the past research on the thermal and mechanical properties, as well as liquid uptake.

### 3.1. Thermal stability

The thermal stability of an ion exchange membrane during fuel cell operation is an important property, which significantly affects the stability and durability of the fuel cell system. Radically different from the conventional functional groups based AEMs, the striking feature of the utilization of the PBI membranes fabricated in fuel cells is that they are capable to be operated at a high temperature due to the good thermal stability [35,36]. After doping with an alkali, however, many physiochemical properties will be changed, such as the ionic conductivity. For this reason, much attention has been paid to the thermal stability of alkali-doped PBI membranes via thermogravimetric analysis

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