Physicochemical properties of alkaline doped polybenzimidazole membranes for anion exchange membrane fuel cells

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Alkaline doped PBI membranes are investigated for their physicochemical properties when employed in alkaline direct alcohol fuel cells. Alkali uptake, water uptake, alcohol permeability, ion conductivity, mechanical strength, and evolution of the morphology for the alkaline doped PBI membranes are measured. It is demonstrated that the alkaline doping process has a profound influence on the physicochemical properties of PBI membranes. With a high alkaline doping level, the alkali uptake of alkaline doped PBI membranes reaches 14%. The high alkaline uptake results in a separation of the polymer backbones and partial cleavage of hydrogen bonds, which leads to a reduction in the mechanical strength and an increase in the alkali permeability of alkaline doped PBI membranes. However, the high alkaline doping level is beneficial to the ion conductivity. The conductivity of alkaline doped PBI membranes increases to 96.1 mS cm\(^{-1}\) at 363.15 K after PBI membranes are doped with 6 M KOH solution. Based on these investigations, a mechanism is proposed to interpret the chemical interaction during the alkaline doping process and its influence on physicochemical properties. The existence of a neutralization reaction and the re-establishment of hydrogen bonding networks should be attributed to the property transformation during the alkaline doping process.

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1. Introduction

Alkaline direct alcohol fuel cells (ADAFCs) have been widely investigated in the last few decades for their numerous merits and interesting properties [1–3]. An alkaline medium can dramatically improve the kinetics of both oxygen reduction reaction (ORR) and alcohol oxidation reaction (AOR) [1,4]. Therefore, non-precious metal catalysts based on abundant transition metals, such as nickel [5] and silver [6], can be employed as catalysts, without compromising reaction rate and dramatically reducing system cost. In addition, the conductive ions (typically OH\(^{-}\)) in the anion exchange membranes (AEMs) transfer from the cathode to the anode, in an opposite direction to that of alcohol crossover. Thus, the electro-osmotic effect in ADAFCs can be mitigated, particularly at high currents. Finally, alcohols are liquid fuels and exhibit high volumetric energy densities [7]. They are also reusable fuels and can be produced in large quantities from biomass or agricultural products.

As a crucial component of ADAFCs, AEMs are particularly indispensable to anion conduction and fuel/oxidant separation. Heterogeneous membranes containing ionic exchange materials and inert compounds have recently been widely investigated [8–10]. In particular, much attention has been focused on alkaline doped polybenzimidazole (PBI), due to its high hydroxide ion conductivity and excellent chemical stability in alkaline media. Although PBI is an electronic and ionic insulator, the pyridine-type nitrogen (\(\text{N}^{-}\)) and pyrrole-type nitrogen (\(\text{N}^{+}\)) in the benzimidazole rings allow absorption and interaction with the free inorganic base (i.e., KOH), contributing to the ion conductivity. For instance, Hou et al. [11] reported that KOH-doped PBI membrane for AEM direct methanol fuel cells (AEM DMFCs) exhibited high thermal stability, low methanol permeability and an ionic conductivity of 18.4 mS cm\(^{-1}\) recorded at room temperature; however, the power density obtained at 363.15 K was as low as 31 mW cm\(^{-2}\). Hou et al. [12] also demonstrated that a peak power density of 60.9 mW cm\(^{-2}\) was achieved at 363.15 K when the anode was fed with 2 M ethanol and 2 M KOH solution. Modestov et al. [13] studied the MEAs fabricated with alkali-doped PBI membranes and non-platinum electrocatalysts; a power density of 100 mW cm\(^{-2}\) was reached at 353.15 K using 2 M ethanol and 3 M KOH as the fuel for a single cell. The PBI-derivate membranes [14–17] were also synthesized and the ionic conductivity was tested; the PBI with pendant quaternary ammonium groups [16] exhibited a hydroxide conductivity of 56 mS cm\(^{-1}\) at 353.15 K.
Recently, Aili et al. [18,19] measured the membrane composition and ionic conductivity of three types of alkaline doped PBI membranes (linear, crosslinked and thermally cured PBI); it was demonstrated that the PBI membrane compositions were not significantly changed while the conductivities of PBI membrane after the cross-linking process and thermal-curing process were essentially lower than that of linear PBI membrane. In addition to the ionic conductivity, the alcohol crossover in alkaline doped PBI membranes [20,21], the assembly of PBI, supporting materials and metal nanoparticles for fuel cell catalysts [22–24], and the durability of alkaline-doped PBI [25] were also investigated. Our literature review indicates that the alkaline doping process has a profound influence on the performance of PBI membranes, whereas a systematic study of the influence of the alkaline doping process on the physicochemical properties in terms of the ionic conductivity, thermal stability and mechanical properties, has not yet been addressed.

The objective of this work is to prepare solution-cast PBI membranes and systematically characterize the physicochemical properties of the alkaline doped PBI membranes. The surface/phase morphologies of PBI membrane before and after the alkaline doping process were examined, and the chemical structure of the alkaline doped PBI was characterized. The alkaline uptake, water uptake, ionic conductivity, alcohol permeability and the mechanical properties of the PBI membrane doped by KOH solutions of various concentrations were also tested. Finally, based on these characterizations, a mechanism was proposed to elucidate the interaction between the doped alkali and the PBI membrane.

2. Experimental

2.1 PBI membrane casting

PBI solution of concentration 26 wt% (intrinsic viscosity: 0.73 dL g⁻¹) was purchased from PBI Performance Products Inc. Based on the intrinsic viscosity, the molecular weight of PBI membrane calculated from Mark–Houwink expression is 123,798 Da [26]. Concentrated PBI solution was diluted with dimethylacetamide (DMAC) to make a solution with a concentration of 4 mg mL⁻¹. The PBI solution was cast upon a clean glass plate using a micrometer. Room temperature was dwelled at 363.15 K for 4 h, 393.15 K for 4 h, forced convection oven. To completely evaporate the solvents, the closed vessel (then dried at 383.15 K for 2 h in an oven and quickly weighed in a water wiped off with tissue paper. The PBI samples were thereafter measured. Accordingly, water uptake (WU), alkali uptake (AU) and swelling ratio (SR) were determined by

\[ WU = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \]  

(1)

\[ AU = \frac{m_{\text{dry}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \]  

(2)

\[ SR = \frac{A_{\text{wet}} T_{\text{wet}} - A_{\text{dry}} T_{\text{dry}}}{A_{\text{dry}} T_{\text{dry}}} \times 100\% \]  

(3)

2.2 Water uptake, alkali uptake and swelling ratio measurement

The PBI membrane samples were doped in KOH solutions of various concentrations. During the doping process, a piece of pristine PBI membrane was immersed in deionized (DI) water for the purpose of comparison. The alkaline doping process lasted for 10 days to ensure that the doping process was complete. Subsequently, the wet weight \( m_{\text{wet}} \), surface area \( A_{\text{wet}} \) and thickness \( T_{\text{wet}} \) of the membranes were then measured at room temperature after the excess alkaline solution on the PBI membrane surface was quickly wiped off with tissue paper. The PBI samples were then dried at 383.15 K for 2 h in an oven and quickly weighed in a closed vessel \( m_{\text{dry1}} \) to prevent possible interference from CO₂ in the air [19]. The PBI samples were then treated in DI water at 363.15 K for 2 h to remove the residual KOH and dried at 383.15 K for 2 h in an oven and quickly weighed in a closed vessel \( m_{\text{dry2}} \). The surface area \( A_{\text{dry}} \) and thickness \( T_{\text{dry}} \) of the doped PBI samples were thereafter measured. Accordingly, water uptake (WU), alkali uptake (AU) and swelling ratio (SR) were determined by

\[
\sigma = \frac{L}{R_{\text{et}} \times A}
\]  

(4)

where \( L \) represents the thickness of the membrane and \( A \) represents the surface area of the membrane [27,28].

After the ion conductivity was measured at a given temperature, the alkaline doped PBI membranes were taken out, quickly wiped off the surface water and submerged in the corresponding KOH solutions for 1 h and resembled to measure the ionic conductivity in the N₂-saturated DI water. In such a short time interval, the conductivity of alkaline doped PBI membranes can be considered as stable and the influence of the alkali leaching out from the doped PBI matrix can be ignored.

2.3 Physical characterization

The surface morphology and the cross-section of the PBI membrane before and after the alkaline doping process were determined by scanning electron microscopy (JEOL–6300F). SEM-energy-dispersive X-ray spectroscopy (SEM–EDS) mapping was operated at 15 kV. FTIR spectra were collected between wavenumbers ranging from 4000 to 400 cm⁻¹ by Fourier transform infrared spectroscopy (FTS 600, Bio–Rad) with ATR accessory. X-ray photoelectron spectroscopy (XPS) were performed on a Physical Electronics PHI5600 with X-ray source operated at 12 kV and 350 W. Survey spectra and high resolution spectra for each element were all obtained at pass energy of 187.85 eV and 23.5 eV, respectively. All membranes were dried under a vacuum oven at 373.15 K overnight before the surface analysis.

The phase image of atomic force microscopy was performed in a Nanoscope-MultiMode/Dimension (Digital Instruments). The instrument was equipped with a NanoWizard scanner. For tapping-mode AFM, a commercial Si cantilever of about 320 kHz resonant frequency was used. The set-point used for imaging varied between 1.0 and 1.5 V. All AFM phase images were shown as recorded without any additional image processing.

2.4 Ionic conductivity measurement

The ionic conductivity of the PBI membrane was determined with a potentiostat (EG&G Princeton, model M2273) through a two electrode conductivity clamp using an AC impedance method. The membranes were sandwiched by a pair of Au-coated stainless steel electrodes. The electrodes were then sandwiched between two PTFE plates and placed in a home-made container filled with N₂–saturated DI water to prevent possible interference from CO₂. A frequency range from 100 kHz to 1 Hz with a wave amplitude of 10 mV was applied to the conductivity clamp to obtain the AC impedance spectra. The membrane resistance \( R_{\text{et}} \) can be obtained by calculating the intercept of the high frequency region. The ionic conductivity \( \sigma \) can be obtained from:

\[
\sigma = \frac{L}{R_{\text{et}} \times A}
\]  

(4)
with a home-made apparatus. The membrane was tightly sandwiched between two chambers with the same volume (40 ml). Chamber A was filled with 3 M methanol + 6 M KOH or 3 M ethanol + 6 M KOH while Chamber B was filled with 6 M KOH. The alcohol permeability of pristine PBI membrane was measured for the purpose of comparison when Chamber A was filled with 3 M methanol or 3 M ethanol while Chamber B was filled with DI water. The concentration of ethanol/methanol in Chamber B due to permeation was measured by gas chromatography (6890 GC Instrument, Agilent Technologies). Each chamber contained a magnetic stirrer during the measurement. The alcohol concentration in Chamber B can be determined by [26,29]

\[ C_B(t) = \frac{A DK}{V L} C_A(t-t_0) \]  

where \( C \) is the concentration of the alcohol, \( A \) and \( L \) are the area and thickness of the membrane, respectively, \( D \) and \( K \) stand for the alcohol diffusivity and partition coefficient, \( V \) is the volume of chamber, and \( t_0 = \frac{L^2}{D} \) is the time lag. The alcohol permeability \( P = DK \) is determined by the slope of the variation in alcohol concentration with time.

2.6 Mechanical property measurement

The mechanical properties were measured with a micro-force testing machine (Alliance RT/5, MTS) with a crosshead speed of 5 mm min\(^{-1}\) at room temperature. All the PBI membranes were doped by KOH solutions of various concentrations for 10 days. Prior to the measurement, the alkaline doped PBI membranes were taken out and wiped with tissue paper to remove the free alkaline solution on the surface. All samples were cut into a size of 40 mm in length × 5 mm in width, which were supported by a pair of fixture assemblies. The average values of modulus and the stress at break were determined from load–deformation curves of three tensile measurements. All the measurements were performed at room temperature with 60% relative humidity.

3. Results and discussion

3.1 Morphology evolution of the alkaline doped PBI membrane

The morphologies of PBI membranes before and after the alkaline doping process were determined by SEM-EDS, as presented

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**Fig. 1.** (a) surface morphology of pristine PBI; (b) surface morphology and (c) cross-section morphology of the alkaline doped PBI (6 M); (d)–(f) EDS mapping of potassium, oxygen and nitrogen elements.
in Fig. 1. It is seen that a uniform, dense and smooth membrane without the existence of pores is formed both before and after the alkaline doping process (Fig. 1a and b). The results of element mapping are presented in Fig. 1d–f. The signals of potassium and oxygen, derived from the doped alkali, are uniformly distributed on the entire membrane while the signal of nitrogen results from the original PBI membrane. This result indicates that the alkali is well dispersed through the alkaline doped PBI membrane.

AFM was employed to further investigate the morphology evolution during the alkaline doping process. The AFM phase images of pristine PBI and PBI doped with KOH solutions of various concentrations were recorded using a tapping mode under ambient conditions, as presented in Fig. 2a–d. The dark areas and the bright areas in AFM phase images are ascribed to the hydrophilic (ionic) domains and hydrophobic domains, respectively [30–33]. The pristine PBI membrane exhibits a bright field, clarifying pristine PBI membranes possess hydrophobic property. In contrast, in alkaline doped PBI membranes, the hydrophilic domains appear and the boundaries between the hydrophilic and hydrophobic domains become more apparent as the alkaline concentration is increased. Meanwhile, the hydrophilic domain shows an interconnected phase morphology, which is beneficial to the hydroxide ion transportation. It should be noted that AFM measurement was performed in the ambient environment with the relative humidity of about 60%. Very little amount of water molecule might be absorbed on the surface of pristine PBI membrane. However, the dark fields in pristine PBI membrane are lighter than that in alkaline doped PBI membranes, indicating that the water molecules were absorbed on the surface, instead of being doped in the PBI matrix.

3.2 Chemical structure of the alkaline doped PBI membrane

FTIR spectra of PBI membrane before and after alkaline doping treatment are presented in Fig. 3. The pristine PBI membrane exhibits an absorption peak at 1600 cm⁻¹ attributing to C–N stretching, 1544 cm⁻¹ arising from –N–H stretching, and 1284 cm⁻¹ from the breathing mode of imidazole ring. After doped by 6 M KOH, the PBI membrane exhibits absorption peaks located at 1625 cm⁻¹, 1510 cm⁻¹ and 1120 cm⁻¹, corresponding to –O–H stretching in the absorbed water, –N–K deformation and the –N–K out of plane bending. It is apparent that the –N–H stretching vibration (1284 cm⁻¹) is replaced by –N–K deformation (1510 cm⁻¹) and bending vibration (1120 cm⁻¹) [34], implying that the hydrogen bonds are partially fractured while the cations (K⁺) react with benzimidazole segments in the PBI skeleton.
The chemical structure of PBI membrane before and after the alkaline doping process was further confirmed by XPS (Fig. 4a). After the alkaline doping process, the emergence of the K peaks (376.8 eV for K 2 s, 291.8 eV for K 2 p, 32.8 eV for K 3 s and 16.8 eV for K 3 p) indicates that the alkali has successfully been doped on the PBI membrane. The N 1s high-resolution spectra of PBI membrane before and after the doping process is shown in Fig. 4b, from which it is seen that N 1s spectra can be deconvoluted into two peaks (Fig. 4c) due to the double-bonded and single-bonded nitrogen in the benzimidazole rings [35,36]. However, the binding energy for N 1s core level spectra in the alkaline doped PBI membrane is negatively shifted (0.25 eV) when compared with that of in the pristine PBI membrane, indicating that the benzimidazole segments are delocalized with some electrons and negatively charged [37,38]. This result demonstrates that benzimidazole segments are deprotonated to form a polymeric salt.

3.3 Water uptake, alkali uptake and swelling ratio

The water uptake, alkali uptake were measured at room temperature. As shown in Fig. 5a, the WU of PBI membrane treated by DI water is limited to 10 wt%. At low KOH concentrations (≤ 1.0 M), the WU and AU are also relatively low. Actually, the pristine PBI membrane can be neutralized with the doped alkaline solution with the KOH concentration above 0.063 M assuming that the dissociation constant (pK_a = 12.8 at 298.15 K) of benzimidazole in an aqueous solution [39] is applied for PBI membrane. But the alkali concentration in the alkaline doped PBI membranes is lower than that of in the bulk solution, hence the AU and WU is low when the PBI membranes are doped with KOH solutions with a low concentration. It should be noted that the measured WU of PBI membrane treated by DI water and low KOH concentrations (≤ 1.0 M) is lower than that of results reported in the literature [40,41], which is likely induced by the different molecular weight/structure and membrane thickness. However, the WU and AU almost linearly increase when the KOH concentration is higher than 1.0 M. The WU and AU respectively reach 45 wt% and 15 wt% when PBI membranes are doped with 6 M KOH. With the similar calculation adopted by Glipa et al. [42], the KOH concentration in the PBI membrane doped by 6 M KOH is about 25 wt%, which is almost the same content of the liquid phase alkaline solution. When being doped by 6 M KOH, the amount of doped alkali in the alkaline doped PBI membrane normalized to each PBI repeating unit is 0.84, which is relatively lower than that of values reported in the literature [18,19]. Similarly, the differences of AU might be caused by the different molecular weight/structure of PBI membranes. When the concentration of KOH was further increased to 8 M, PBI membranes crumbled or even dissolved in the alkaline solution. The high WU will cause an increase in the water affinity of the alkaline doped PBI membranes. To determine the changes in hydrophilicity, the water contact angle was measured, as illustrated in Fig. 5b. It can be seen that the contact angle decreases with an increase in the doped KOH concentration, indicating an increase in the hydrophilicity of the alkaline doped PBI membranes. As shown inset in Fig. 5b, the alkaline doped PBI membrane exhibits high wettability when PBI membrane is doped with 6 M KOH.

The swelling ratio of the PBI membrane doped by KOH solutions of various concentrations at room temperature were measured, as shown in Fig. 6. The tendency of swelling ratio is similar with that of AU, i.e., a low swelling ratio is achieved at a low doping level while the swelling ratio of alkaline doped PBI membranes almost linearly increases with an increase in KOH concentration (≥ 1.0 M). Interestingly, the swelling ratio in the thickness direction is larger than that of in the length/width direction, which is an indicative of asymmetric swelling of alkaline doped PBI membranes. Although the mechanism of asymmetric swelling is still unclear, the low swelling ratio in the length/width direction is beneficial to the dimensional stability during the fuel cell operation.
3.4 Ionic conductivity

Ionic conductivity of alkaline doped PBI membranes is highly dependent on the AU (Fig. 7a). It is seen that the ionic conductivity of alkaline doped PBI membranes is extremely low when the PBI membrane is doped by a low alkaline concentration (i.e. 0.5 M KOH). An increase in the KOH concentration significantly enhances the ionic conductivity of the alkaline doped PBI membranes since the amount of associated KOH absorption in the molecular networks is increased. After being doped in 6 M KOH, the alkaline doped PBI membrane possesses an ionic conductivity of 34.1 mS cm\(^{-1}\) at 303.15 K. Meanwhile, the ionic conductivity increases with elevated temperatures. The highest ionic conductivity of PBI doped by 6.0 M KOH reaches 96.1 mS cm\(^{-1}\) at 363.15 K, which is in the same range as previously reported for the KOH doped PBI membrane [19,43]. This result can be explained as follows. First, the intermolecular interaction reduces with the elevated temperature, resulting in an incompact structure and increased free volumes. Hence, the ionic conducting channels expand, contributing to ion mobility. Meanwhile, the water uptakes of membranes increases with the elevated temperature, resulting in further promotion of ionic conductivity. It should be noted that massive water uptake would dilute the ionic strength of ionic conducting channels, thereby reducing the ionic conductivity of the membrane. However, this issue was not present in the alkaline doped PBI membranes.

Fig. 7b presents the Arrhenius plots of PBI membranes doped by KOH solutions of various concentrations. It is seen that ln $\sigma$ vs. 1000/T fits linearly for all samples while the slopes for each of the sample differ. The activation energy ($E_a$) can be obtained from the fitted slope through the following equation: $E_a = -\frac{b}{R}$. Here, $R$ is the gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)) and $b$ is the fitted slope. Based on the evaluation, the activation energy is 23.22 kJ mol\(^{-1}\), 16.92 kJ mol\(^{-1}\), 16.00 kJ mol\(^{-1}\), 15.87 kJ mol\(^{-1}\), corresponding to the PBI membranes doped by 0.5 M KOH, 2.0 M KOH, 4.0 M KOH and 6.0 M KOH, respectively. The decline of $E_a$ with an increase in the doped KOH concentration testifies that the membrane’s ionic channels are well-established, thereby reducing the dependence of ionic conductivity on temperature. The activation energy values are also close to the acid-doped PBI membranes [44,45], which is the indicative of the similar transportation mechanism, i.e., the Grotthuss mechanism.

3.5 Alcohol permeability

The alcohol permeability in the pristine PBI and the alkaline doped PBI membrane at different temperatures was measured and the calculated permeability is summarized in Table 1. The pristine PBI exhibits a low methanol and ethanol permeability. Ethanol and methanol are required to be hydrated and diffused through the membrane with the aid of absorbed water, which has a significant influence on the diffusivity [46,47]. The pristine PBI has a low water uptake, thereby resulting in a low alcohol permeability. After doped with 6 M KOH, the permeability of methanol and ethanol significantly increases. For instance, the alkaline doped PBI membrane has an ethanol permeability of $21.57 \times 10^{-7}$ cm\(^2\) s\(^{-1}\), which is much larger than that of the pristine PBI membrane ($0.67 \times 10^{-7}$ cm\(^2\) s\(^{-1}\)) at 363.15 K. The increased permeability results from the reduced intermolecular interaction as a result of established ionic channels [48]. On the other hand, the permeability of methanol is higher than that of ethanol due to methanol has a smaller hydrated molecular size, leading to a relatively low resistance for methanol across the alkaline doped PBI membranes [49]. However, the methanol permeability of alkaline doped PBI membrane ($27.05 \times 10^{-7}$ cm\(^2\) s\(^{-1}\)) at 363.15 K is in the same range as previously reported for the alkaline doped PBI membrane ($28.7 \times 10^{-7}$ cm\(^2\) s\(^{-1}\) at 333.15 K) [21] and lower than that of...
3.6 Mechanical property

Excellent mechanical properties are essential for AEMs to counteract harsh processes in the course of fuel cell assembling and operating conditions. It is generally considered that the mechanical strength of polymer membranes is determined by the attractive forces among polymer molecules, such as dipole–dipole interaction (including hydrogen bond), induction forces and dispersion forces between non-polar molecules. When a polymer is doped with alkali, the ionic bonding and ion-dipole interactions also contribute to the mechanical strength [48]. The tensile–strain curves of pristine PBI and alkaline doped PBI membrane are shown in Fig. 8 and the calculated results are summarized in Table 2. For pristine PBI membranes, the mechanical strength is predominantly determined by the hydrogen bond between –N= and –NH– segments. In our experiments, the pristine PBI membrane has a tensile strength at break as high as 92.98 MPa with an elongation of 5.6%, indicating that the pristine PBI membrane possesses a superior mechanical strength. When the alkali is introduced, the originally hydrogen bonds are partially cleaved, resulting in the swelling ratio in the cross-section direction and increased separation of PBI backbones. These interactions decrease molecular cohesion and deteriorate the PBI membrane’s mechanical strength [48]. As seen in Fig. 8, the tensile strength at break dramatically decreases with the increased KOH concentrations. After the PBI membrane was doped by 6 M KOH, the tensile strength at break and Young’s modulus reduce to 14.75 MPa and 0.27 GPa, respectively. The percentage of reduction in the tensile strength and Young’s modulus are approximately 84.1% and 87.1%, respectively, when compared with that of the pristine PBI membrane. However, the tensile strength demonstrated in this work is still higher than that of AEMs reported in the literature [52–54] and satisfies the mechanical requirement in ADAFCs.

![Fig. 8. The stress–strain curves of pristine PBI membrane and the alkaline doped PBI membrane.](image)

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile strength at break (MPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBI</td>
<td>92.98</td>
<td>2.09</td>
<td>5.6</td>
</tr>
<tr>
<td>2 M KOH-doped PBI</td>
<td>65.16</td>
<td>1.32</td>
<td>36.5</td>
</tr>
<tr>
<td>4 M KOH-doped PBI</td>
<td>25.12</td>
<td>0.45</td>
<td>72.1</td>
</tr>
<tr>
<td>6 M KOH-doped PBI</td>
<td>14.75</td>
<td>0.27</td>
<td>81.5</td>
</tr>
</tbody>
</table>

Interestingly, the elongation at break of the alkaline doped PBI membrane increases with an increased KOH concentration. The elongation at break for pristine PBI membrane is 5.6% when PBI membrane was saturated with DI water despite the low water uptake, while the elongation at break is significantly increased to 81.5% when PBI membrane was doped by 6 M KOH. This behavior indicates that the alkaline doped PBI membranes exhibit an improved plasticity.

### 3.7 Mechanism

As discussed in the aforementioned sections, the alkaline doping process has a profound influence on the physicochemical properties of PBI membranes. While He et al. [48] studied the effects of phosphoric acid doping process on the mechanical properties and proton conductivity, the current literature lacks a systematic investigation on the properties of PBI membrane after the alkaline doping process.

Actually, the pristine PBI exhibits a weak alkalinity in aqueous solutions, which can be proven by the dissociation constant ($K_w$=12.8 at 298.15 K) of benzimidazole in an aqueous solution [39]. Due to the high concentration of alkaline solutions, however, PBI will fulfill the role of an acid by dissociating protons from the pyrrole-type nitrogen ($–N\equiv$). Subsequently, the hydroxide ions impregnated in the polymer matrix react with the dissociated protons. This neutralization reaction is presented in Scheme 1a. The high KOH concentration promotes this reaction, resulting in more –NH groups being substituted by the free alkali. This can be demonstrated from the increased alkali uptake as shown in Section 3.3. Meanwhile, the strong hydrogen bonds are partially cleaved due to the introduction of the polar bond ($–\equiv$–K) and the pyrrole-type nitrogen ($–N\equiv$) atoms are negatively charged. The potassium cations are then involved in the bridging negatively charged nitrogen atoms and the doped alkali, as illustrated in Scheme 1b. The combination between KOH solution and PBI will establish hydrophilic ionic clusters to transport the hydroxide ions. The proposed hydroxide ion transport pathway is illustrated in Fig. 9. With high KOH concentrations, the size of hydrophilic ionic clusters will increase and interconnect, as demonstrated by AFM measurement. Hence, the ionic conductivity of the alkaline doped PBI membrane improves with the increased KOH concentration as shown in Section 3.4.

The increase in alcohol permeability in the alkaline doped PBI membrane can be also explained with the proposed mechanism. Since the water uptake increases accompanying with the increased alkali uptake, the size of well-established ionic clusters will be enlarged. Therefore, the alcohols dissolved in water enable to be facilely transported through the alkaline doped PBI membranes.

In regard to the mechanical property, the high mechanical strength of pristine PBI results from strong hydrogen bonds between the pyrrole-type nitrogen ($–N\equiv$) and the pyridine-type nitrogen ($–N\equiv$) (Fig. 9a). However, the strong hydrogen bond networks are partially cleaved in the course of the alkaline doping process, leading to the decrease in the mechanical strength. Although the hydrogen bonds among the bridging negatively charged nitrogen atoms and the doped alkali will be formed, this interaction is much weaker than that of hydrogen bond between the pyrrole-type nitrogen ($–N\equiv$) and the pyridine-type nitrogen ($–N\equiv$) (Fig. 9a). Therefore, the tensile strength at break and Young’s modulus of alkaline doped PBI membranes are significantly reduced with the increased KOH concentration. Meanwhile, the elongation at break increases after the alkaline doping process, indicating that the membranes with high alkali content in the polymer matrix become more plastic. This plasticizing effect results from an increased flexibility of PBI backbones due to the reduction of molecular cohesion.
4. Conclusions

In summary, the influence of the alkaline doping process on the physicochemical properties of PBI membrane was systematically studied and a mechanism was proposed. After being doped by KOH solutions of various concentrations, the morphology of the alkaline doped PBI membrane remained unchanged while a hydrophobic/hydrophilic phase separation was established as a result of the formation of hydrophilic ionic clusters in the PBI skeleton. The modification of PBI membrane by KOH solution was also investigated by FTIR, demonstrating that the strong hydrogen-bonded networks were partially fractured while the cations (K⁺) reacted with benzimidazole segments (–NH) in the PBI skeleton. This modification has a profound influence on the ionic conductivity, alcohol permeability and mechanical properties. We experimentally testified that the ionic conductivity of the alkaline doped PBI membrane reached 96.1 mS cm⁻¹ at 363.15 K when PBI membrane was doped by 6 M KOH. Although the increase in the alcohol permeability and the deterioration of mechanical properties were also induced by the decreasing the molecular cohesion, these properties of the alkaline doped PBI membranes still met the requirement for the application in ADAPCs. Finally, a mechanism was proposed to interpret the interaction and their influence on physicochemical properties. The existence of a neutralization reaction and the re-establishment of hydrogen bonding networks resulted in the property transformation during the alkaline doping process.

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