

# A new anhydrous proton conductor based on polybenzimidazole and tridecyl phosphate

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## Abstract

Most of the anhydrous proton conducting membranes are based on inorganic or partially inorganic materials, like SrCeO<sub>3</sub> membranes or polybenzimidazole (PBI)/H<sub>3</sub>PO<sub>4</sub> composite membranes. In present work, a new kind of anhydrous proton conducting membrane based on fully organic components of PBI and tridecyl phosphate (TP) was prepared. The interaction between PBI and TP is discussed. The temperature dependence of the proton conductivity of the composite membranes can be modeled by an Arrhenius relation. Thermogravimetric analysis (TGA) illustrates that these composite membranes are chemically stable up to 145 °C. The weight loss appearing at 145 °C is attributed to the selfcondensation of phosphate, which results in the proton conductivity drop of the membranes occurring at the same temperature. The DC conductivity of the composite membranes can reach  $\sim 10^{-4}$  S/cm for PBI/1.8TP at 140 °C and increases with increasing TP content. The proton conductivity of PBI/TP and PBI/H<sub>3</sub>PO<sub>4</sub> composite membranes is compared. The former have higher proton conductivity, however, the proton conductivity of the PBI/H<sub>3</sub>PO<sub>4</sub> membranes increases with temperature more significantly. Compared with PBI/H<sub>3</sub>PO<sub>4</sub> membranes, the migration stability of TP in PBI/TP membranes is improved significantly.

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**Keywords:** Proton conductivity; Polybenzimidazole; Tridecyl phosphate; Migration stability

## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) operating at intermediate temperature (100–200 °C) have received increasing attention due to the problem of CO poisoning to catalyst. Besides this, an intermediate temperature operation eventually increases the efficiency of PEMFC. Since the high proton conductivity of conventional hydrated sulfonic acid membranes is closely related to high levels of hydration, the performance of hydrated proton conducting membranes, such as Nafion, is insufficient above 100 °C due to the loss of water [1–3]. There has been considerable interest in developing anhydrous proton exchange membranes on the basis of acid–base complex electrolytes. Most of anhydrous proton conducting membranes are based on inorganic or partially inorganic materials, like SrCeO<sub>3</sub> membranes or polybenzimidazole (PBI)/H<sub>3</sub>PO<sub>4</sub> composite membranes [4–8]. Polymers based on

nitrogen-containing heterocycles, such as polybenzimidazole, poly(4-vinylimidazole), and poly(vinylpyrrolidone), have been found to exhibit a high proton conductivity under anhydrous and intermediate-temperature condition after being blended with inorganic acids, such as H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> [7–13]. Especially, the amphoteric behavior and the ability to form complex or intermolecular hydrogen bonds in these blends are important for the proton transport [14–16]. Particularly, pure PBI has an excellent thermal stability and is one of the most promising polymers for anhydrous polymer electrolyte membranes [17,18]. However, when blended with large amounts of H<sub>3</sub>PO<sub>4</sub> high proton conductivities are obtained, but the materials suffer from rather poor mechanical properties. The nitrogen-containing heterocycles in PBI possess both proton donating and accepting sites that are helpful for proton transport in acid doped membranes [19,20]. However, elution of the water soluble acids such as phosphoric acid from the membrane and dilution of the acid in the membrane can occur when the vapor produced at the cathode in the operation process of fuel cells is not eliminated. In this way, the stability of the membranes will be destroyed and the proton conductivity will be reduced. Tridecyl phosphate has

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a detergent-like structure containing a hydrophilic and acidic moiety as well as an aliphatic and hydrophobic flexible spacer. This specific structure may offer both high local mobility of protons via hydrogen bonds and low long-range diffusivity due to the spacers. In present work, anhydrous proton conducting membranes based on fully organic components of PBI and TP are prepared. The thermal stability, proton conductivity, and the intermolecular interaction between two components are mainly discussed.

## 2. Experimental

Polybenzimidazole (PBI) was purchased from Aldrich Chemical Company, Inc. and tridecyl phosphate (TP) from Fluka Co. Fig. 1 shows the chemical structure of PBI and TP. Both PBI and TP were used as received.

PBI is difficult to be dissolved, however, 1% (w/v) solution in *N*-methyl-2-pyrrolidone (NMP) was prepared by heating to 160 °C for 5 h, with stirring to affect the dissolution of PBI. TP was then added into the PBI solution directly. The mixture was stirred with a magnetic stirrer at 50 °C for 1 h to make it homogeneous. The composite membrane of PBI and TP was prepared by direct casting from the solution of PBI and TP. A polished polytetrafluoroethylene (PTFE) plate was used as a mold. The solvent in the membranes was first evaporated at 100 °C for 3 h, and then the membranes were further dried under vacuum at 190 °C for at least 24 h. The PBI/*x*TP blends, where *x* is the moles of TP per mole repeat unit of PBI, were prepared by adding certain amount of TP into PBI solution before casting. PBI/H<sub>3</sub>PO<sub>4</sub> composite membrane was prepared according to a method reported previously [7].

FTIR spectra of the membranes were measured in reflection mode with a PerkinElmer Paragon 1000 spectrometer in the range of 4400–500 cm<sup>-1</sup>. Thermal stability of the membranes was investigated by thermogravimetric analysis (TGA) (model STA 449C, Netzsch Co.). The samples were heated from room temperature to 700 °C with a heating rate of 10 °C/min under nitrogen atmosphere. Weight loss was measured and reported as a function of temperature. The proton conductivity of the membranes in anhydrous state was measured by an EG & G potentiostat/galvanostat (model 273, Princeton Applied Research Co.), which worked in the galvanostatic mode, and produced a proton current across the membrane. The gold electrodes

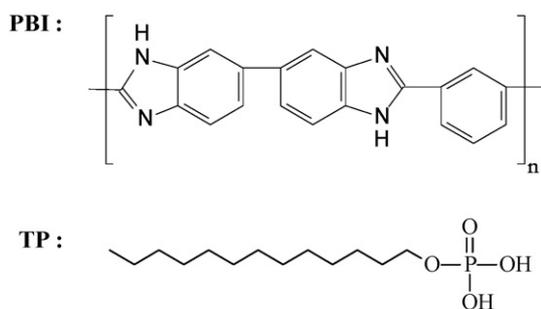


Fig. 1. Chemical structures of polybenzimidazole (PBI) and tridecyl phosphate (TP).

were employed. The applied current was typically of the order of 5 mA in the frequency range from 10<sup>-2</sup> to 10<sup>5</sup> Hz. DC conductivities were obtained from Cole–Cole plots (*Z''* vs. *Z'*) and identical values were obtained from the low-frequency plateau of the AC conductivity. The migration stability of TP and phosphoric acid in the composite membranes can be characterized by the weight loss percentage (*R*) of the membranes under the water vapor condition for several hours, which was carried out by putting the membrane over the vapor at 100–110 °C for a certain period of time and measuring the weight of the dry membrane (*w<sub>i</sub>*) at different time. If the original weight of the dry membrane is *w<sub>0</sub>*, then  $R = (w_0 - w_i/w_0) \times 100\%$ .

## 3. Results and discussion

### 3.1. Chemical structure of the composite membranes

FTIR spectra of pure PBI, TP and their blends are shown in Fig. 2. For PBI, the peaks corresponding to the free N–H stretch and the N–H···H hydrogen bond interaction can be found in the region of 3500–2500 cm<sup>-1</sup>. According to the results of Musto [21,22], absorption peak of free N–H stretch in PBI should appear near 3415 cm<sup>-1</sup> and that of N–H···H hydrogen bond interaction appears at 3145 cm<sup>-1</sup>. After being blended with TP, the peak around 3400 cm<sup>-1</sup> of PBI becomes a little broader which indicates the presence of hydrogen bonding between phosphonic acid moieties and the ‘free’ nitrogen side of the heterocycles. For TP, the broad band near 2800–3000 cm<sup>-1</sup> represents the stretching of –OH [23], while in PBI blends, these peaks become weaker and broader which indicates the formation of hydrogen bond between –OH and nitrogen atoms. In the spectrum of TP the broad peak at 1209 cm<sup>-1</sup> corresponds to P=O stretching, while this peak moves to 1145 cm<sup>-1</sup> in the PBI blends. It is reported that the absorption peak of the P=O stretching will reduce 50–80 cm<sup>-1</sup> if there are hydrogen bonds formed between P=O and other electronegative atoms such as nitrogen

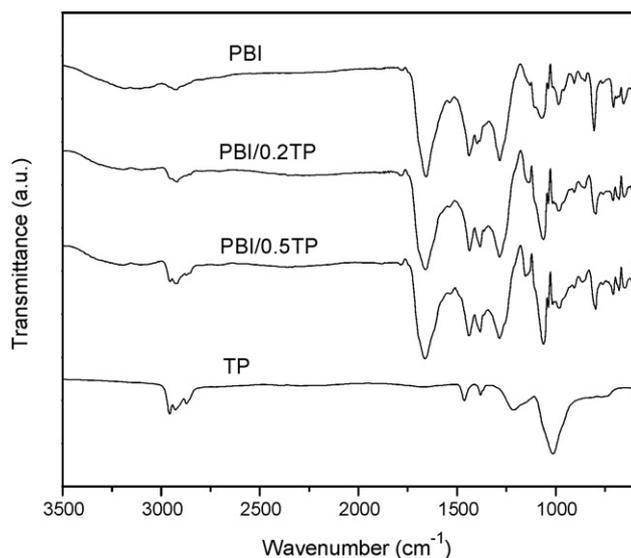


Fig. 2. FTIR spectra of pure PBI, TP, and PBI/*x*TP composite membranes (*x*=0.2, 0.5, respectively).

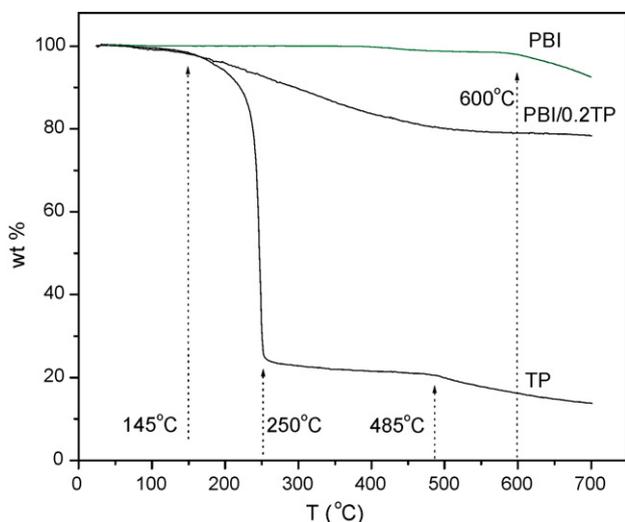


Fig. 3. Thermal gravimetric analysis of pure PBI, TP and PBI/0.2TP composite.

atom [24]. So, it is indicated in the infrared spectra that there is P=O...H-N hydrogen bond interaction between PBI and TP.

### 3.2. Thermal stability of the composite membranes

Fig. 3 shows the thermal stability of pure PBI, TP and PBI/0.2TP composite membrane. For pure PBI, the weight loss appears around 600 °C, which can be attributed to the degradation of the polymer. For both TP and the composite membrane ( $x=0.2$ ), they are thermally stable up to 145 °C, the first weight loss can be observed above 145 °C which can be attributed to the selfcondensation of TP [9]. For TP the sharp weight loss around 250 °C represents the decomposition of TP. At this temperature the molecular chain of TP degrades and the aliphatic part of hydrocarbon disappears with the phosphonic acid moiety remaining in the membrane, which can be calculated by the weight loss of TP. However, in the composite membrane ( $x=0.2$ ), this weight loss appears gradually ranging up to 500 °C, which indicates that TP is kinetically stable in PBI blends. For pure TP, the weight loss starting at 485 °C can be attributed to further selfcondensation of the remnant phosphonic acid moieties. Compared with the weight losses at 485 °C for pure TP and at 600 °C for pure PBI, there is no further weight loss observed at the range of 500–700 °C in the composite membrane which indicates the presence of strong interactions between phosphonic acid moieties and PBI molecules.

### 3.3. AC conductivity of the composite membranes

The proton conductivity of PBI/TP blend membranes was measured by impedance spectroscopy. Figs. 4 and 5 display the frequency dependence of the alternating current (AC) conductivities ( $\sigma_{ac}$ ) of PBI/TP blends with  $x=0.2$  and  $x=0.5$  respectively. In both samples the curves comprise the frequency-independent conductivity plateau regions, which are well developed at low frequencies and at low temperatures and expand and shift toward higher frequencies with increasing temperature. The irregularities on low frequency side at higher temperatures, i.e.  $T > 50$  °C

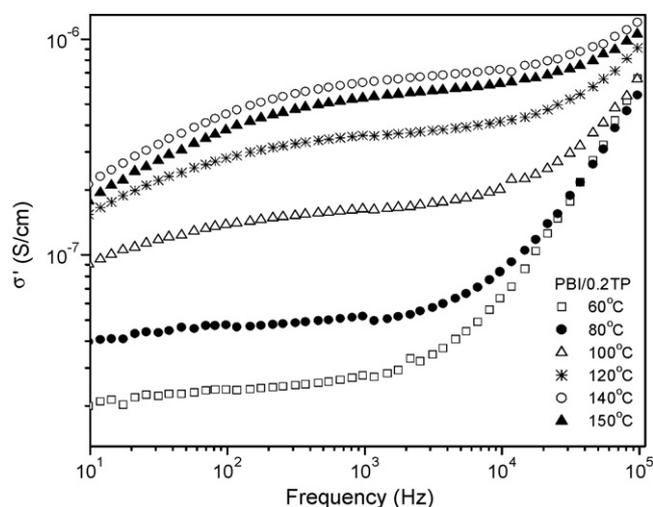


Fig. 4. The frequency dependent AC conductivity of PBI/0.2TP composite.

for  $x=0.5$  and  $T > 100$  °C for  $x=0.2$  are caused by electrode polarization due to blocking effect of the platinum electrodes [25]. For both samples, the AC conductivity drop around 150 °C can be attributed to the selfcondensation of TP, which can also be observed at the TGA curves.

Fig. 6 shows the frequency dependent AC conductivities of PBI/TP blends with different content of TP ( $x=0.2, 0.5, 1.8$ ) at the same temperature (70 °C). It can be found that the AC conductivity of PBI/TP blends increases with increasing content of TP. The frequency-independent conductivity plateau regions expand and shift toward higher frequencies with increasing content of TP.

### 3.4. DC conductivity of the composite membranes

Direct current (DC) conductivity ( $\sigma_{DC}$ ) of all the samples is calculated from the results of AC conductivity measurements. The temperature dependence of the DC conductivities of the membranes with  $x=0.2, 0.5$  and 1.8 are compared in Fig. 7. A

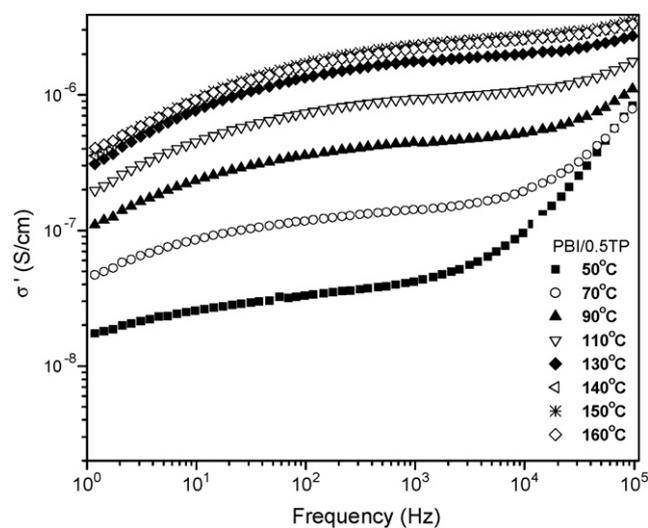


Fig. 5. The frequency dependent AC conductivity of PBI/0.5TP composite.

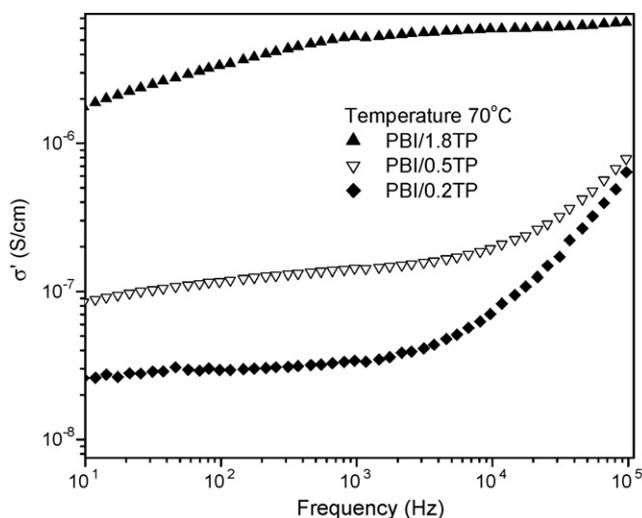


Fig. 6. The frequency dependent AC conductivity of PBI/ $x$ TP blends with  $x=0.2, 0.5, 1.8$  at  $70^\circ\text{C}$ .

conductivity drop at  $145^\circ\text{C}$  can be observed in both  $x=0.2$  and  $x=0.5$  which can be attributed to the selfcondensation of TP. Around  $145^\circ\text{C}$ , the selfcondensation of TP reduces the number of  $-\text{OH}$  groups which results in the reduction of proton carrier in PBI/TP membranes and thus the proton conductivity. This result should be understood in terms of Eq. (1)

$$\sigma(T) = n(T)\mu(T)e \quad (1)$$

where  $n$  is the number of charge carriers,  $\mu$  their mobility, and  $e$  the unit electric charge.

Below  $145^\circ\text{C}$ , the function of proton conductivity vs. temperature of all the PBI/TP composite membranes exhibits a simple Arrhenius behavior according to Eq. (2),

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{RT}\right) \quad (2)$$

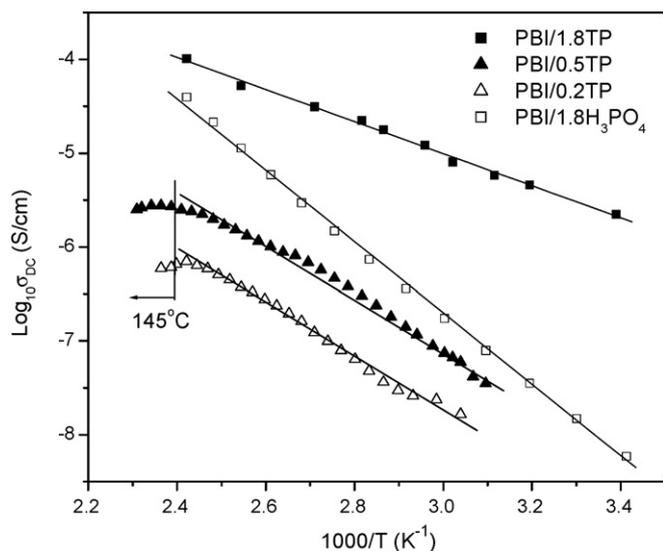


Fig. 7. Temperature dependence of DC conductivity of PBI/ $x$ TP composite membranes,  $x=0.2, 0.5, 1.8$ .

where  $\sigma_0$  is pre-exponential factors;  $E_a$  is apparent activation energy for proton transport;  $R$  is the Boltzmann constant;  $T$  is the temperature of polymer electrolytes. PBI is a fairly rigid polymer with glass transition temperature ( $T_g$ ) above  $400^\circ\text{C}$  [7,13,15]. Under the temperature investigated, the segmental motion of PBI is frozen. Kreuer [26] suggested that proton transport in acid–base blend materials under anhydrous or low humidity condition occurs by a Grotthuss mechanism, in which only protons move from site to site without the presence of diffusible water molecules, such as  $\text{H}_3\text{O}^+$  or  $\text{H}_5\text{O}_2^+$ . Similarly, the proton conductivity of PBI/TP composite membrane is mainly contributed by the moving of proton from site to site rather than the segmental motion of the polymer. According to Eq. (1), the proton conductivity is determined by the number of charge carriers and their mobility. The proton conductivity of the PBI/TP composite membrane can reach  $\sim 10^{-4}$  at about  $140^\circ\text{C}$  for  $x=1.8$  and increases with increasing content of TP according to its tendency. Practically, in the PBI/TP system the TP molecules cannot move effectively for a long distance because of the long flexible spacer and strong interaction with PBI molecules. The proton conductivity of PBI/TP composite membranes is based on a continuous ‘forming–breaking–forming’ process of complex or hydrogen bonds between PBI and TP, which allows for the proton transport in the membranes. The DC conductivity of PBI/TP composite membrane was also compared with PBI/ $\text{H}_3\text{PO}_4$  membrane at the same doping level of  $x=1.8$  to interpret the proton transport mechanism at anhydrous state. Fig. 7 indicates that PBI/TP blend has higher proton conductivity than PBI/ $\text{H}_3\text{PO}_4$  membrane at the same doping level of  $x=1.8$  under all the temperatures investigated. However, the proton conductivity of PBI/ $\text{H}_3\text{PO}_4$  membrane increases with increasing temperature more significantly. Although both TP and  $\text{H}_3\text{PO}_4$  are easy to form complexes or strong hydrogen bonds with PBI, it is more difficult for  $\text{H}_3\text{PO}_4$  to break from the complex or hydrogen bond and form new one at low temperatures under anhydrous condition. While in PBI/TP blend, a dynamic hydrogen bond network is easy to form, this can be attributed to the flexible structure of TP and the segmental motion of TP. So PBI/TP blend has higher proton conductivity than PBI/ $\text{H}_3\text{PO}_4$  membrane at lower temperature (e.g.  $<140^\circ\text{C}$ ). With the increment of temperature,  $\text{H}_3\text{PO}_4$  molecules gain high energy to break the complex or hydrogen bond and a dynamic hydrogen bond network is easy to form. Along with the better mobility, its proton conductivity increases more significantly than PBI/TP blend with increasing temperature.

### 3.5. Migration stability of TP and phosphoric acid in the composite membranes

As shown in Fig. 8, the migration stability of TP and  $\text{H}_3\text{PO}_4$  in the composite membranes can be characterized by the weight loss percentage of the composite membranes under the water vapor condition at  $100\text{--}110^\circ\text{C}$  for several hours. For comparison, the weight loss of PBI/1.8 $\text{H}_3\text{PO}_4$  membrane is much larger than that of PBI/1.8TP membranes. It is found that the weight loss of PBI/1.8 $\text{H}_3\text{PO}_4$  membrane is about 15 wt%, the doped  $\text{H}_3\text{PO}_4$  in PBI is almost leached out completely by the vapor.

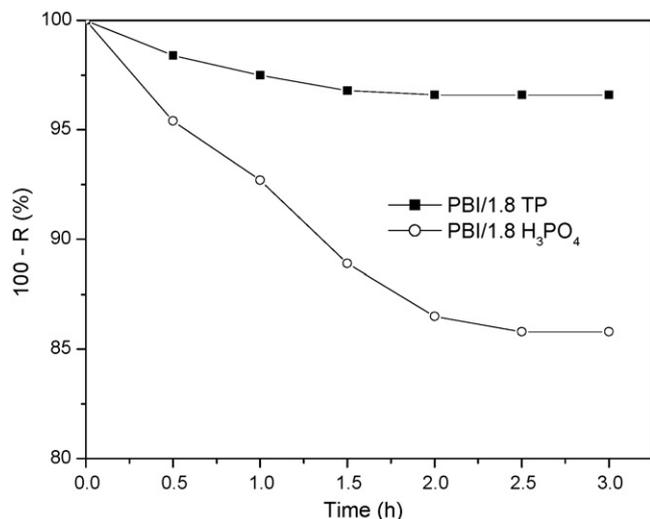


Fig. 8. Time-dependence of the weight loss of PBI/1.8TP and PBI/1.8H<sub>3</sub>PO<sub>4</sub> composite membranes in vapor with a temperature of 100–110 °C.

Meanwhile the mechanical strength of PBI/1.8H<sub>3</sub>PO<sub>4</sub> membrane becomes worse and worse with increasing time. TP in the PBI/1.8TP membrane shows high stability with the existence of long hydrophobic part, which improves the lifetime of the membranes in the fuel cells.

#### 4. Conclusions

A new kind of anhydrous proton conducting polymer based on fully organic components of PBI and tridecyl phosphate has been proposed. FTIR results prove the presence of the strong hydrogen bond interaction between TP and PBI. Thermogravimetric analysis (TGA) illustrates that these composite membranes are chemically stable up to 145 °C. The weight loss appearing at 145 °C is attributed to the selfcondensation of phosphate, which results in a proton conductivity drop of the composite membrane starting at the same temperature. The temperature dependence of the proton conductivity of the sample can be fitted by Arrhenius relation. The proton conductivity of PBI/TP composite membranes can reach  $\sim 10^{-4}$  S/cm at about 140 °C for  $x = 1.8$  and increases with increasing content of TP. The proton conductivity of PBI/TP composite membranes is mainly contributed by the hopping of proton from site to site rather than the segmental motion of the polymer. The proton transport in the membranes is mainly based on the continuous ‘forming–breaking–forming’ process of hydrogen bonds

between PBI and TP. Dynamic hydrogen bond networks are necessary for proton transport in anhydrous polymer electrolytes such as PBI/TP and PBI/H<sub>3</sub>PO<sub>4</sub> composite membranes. Compared with PBI/H<sub>3</sub>PO<sub>4</sub> membranes, the migration stability of TP in PBI/TP membranes is improved significantly.

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