

## Research Article

# 3D Network Structural Poly (Aryl Ether Ketone)-Polybenzimidazole Polymer for High-Temperature Proton Exchange Membrane Fuel Cells

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Poor mechanical property is a critical problem for phosphoric acid-doped high-temperature proton exchange membranes (HT-PEMs). In order to address this concern, in this work, a 3D network structural poly (aryl ether ketone)-polybenzimidazole (PAEK-*cr*-PBI) polymer electrolyte membrane was successfully synthesized through crosslinking reaction between poly (aryl ether ketone) with the pendant carboxyl group (PAEK-COOH) and amino-terminated polybenzimidazole (PBI-4NH<sub>2</sub>). PAEK-COOH with a poly (aryl ether ketone) backbone endows superior thermal, mechanical, and chemical stability, while PBI-4NH<sub>2</sub> serves as both a proton conductor and a crosslinker with basic imidazole groups to absorb phosphoric acid. Moreover, the composite membrane of PAEK-*cr*-PBI blended with linear PBI (PAEK-*cr*-PBI@PBI) was also prepared. Both membranes with a proper phosphoric acid (PA) uptake exhibit an excellent proton conductivity of around 50 mS cm<sup>-1</sup> at 170°C, which is comparable to that of the well-documented PA-doped PBI membrane. Furthermore, the PA-doped PAEK-*cr*-PBI membrane shows superior mechanical properties of 17 MPa compared with common PA-doped PBI. Based upon these encouraging results, the as-synthesized PAEK-*cr*-PBI gives a highly practical promise for its application in high-temperature proton exchange membrane fuel cells (HT-PEMFCs).

## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have drawn much attention as clean power generation devices due to their many attractive features, such as high efficiency, high power density, and environmental friendliness for potential application as power sources in stationary transportation and portable devices [1–5]. Proton exchange membranes (PEMs) are key components of the PEMFCs, which play the main role of proton transport and fuel isolation. Compared with conventional low-temperature PEMFCs, high-temperature PEMFCs (HT-PEMFCs) operate at above

100°C, which made it possess many advantages, such as simple water and heat management, high CO tolerance, and less dependence on platinum catalysts [6–8].

Among all the types of HT-PEMs, phosphoric acid-doped polybenzimidazole (PA-PBI) membranes have been considered to be the most promising candidates for a high-temperature proton exchange membrane owing to its good chemical and thermal stability and excellent proton conductivity under anhydrous conditions at high temperature [9–12]. In order to obtain high proton conductivity, it is necessary to dope an excess amount of phosphoric acid (PA) in the membrane [13]. However, due to the strong plasticization

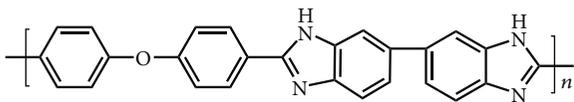


FIGURE 1: The molecular structure of poly (4,4'-(diphenyl ether)-5,5'-bibenzimidazole) (PBI).

of PA molecules, high proton conductivity is usually at the expense of the mechanical strength of the membrane [14–17]. Besides, the preparation of a high-strength PA-PBI membrane requires high molecular weight of PBI, which exhibits poor solubility in organic solvents and makes it fairly hard to prepare uniform casting solution [18]. Therefore, to realize high-performance HT-PEMs and high-efficiency HT-PEMFCs, it is one of the important issues to settle the balance between proton conductivity and mechanical properties of phosphoric acid-doped polymer membranes.

In fact, several strategies have been proposed to deal with the issue. Crosslinking is considered an effective strategy to enhance the properties of PA-doped membranes for HT-PEMFCs [19–23]. In the past few decades, a variety of crosslinkers have been widely studied, including small molecular and macromolecular crosslinkers. Small molecular crosslinkers such as epoxides [24, 25] and halides [26–28] are more frequently used for the improvement of the membrane properties. Compared with small molecular crosslinkers, macromolecular crosslinkers will give higher overall performance to HT-PEMs. Recently, Yang et al. [29] studied the covalently crosslinking PBI membrane using chloromethyl polysulfone as the macromolecular crosslinker. Their results show that the properties of the crosslinked membranes with high PA doping level are almost unchanged during the test. In addition, other macromolecular crosslinkers such as poly (vinyl benzyl chloride) [30] and bromomethylated poly (aryl ether ketone) [31] have also been adopted to prepare crosslinked PBI membranes. Unfortunately, most of these methods are based on the sacrifice of N-H sites on the imidazole ring of the PBI main chain, which ultimately impedes the absorption of phosphoric acid and proton transport [32]. All in all, it is an urgent demand to design a reasonable polymer framework and a suitable covalent crosslinker to satisfy the actual requirements of HT-PEMs. To our knowledge, poly (aryl ether ketone) (PAEK) is extensively used in the preparation of various electrolyte membranes in fuel cells due to its good thermal, mechanical, and chemical stability [33–36].

In this work, we prepared a 3D network structural poly (aryl ether ketone)-PBI (PAEK-*cr*-PBI) through crosslinking reaction between PAEK with the pendant carboxyl group (PAEK-COOH) and amino-terminated imidazole (PBI-4NH<sub>2</sub>). For the purpose of enhancing the mechanical strength of a PA-doped membrane without the sacrifice of proton conductivity, a new crosslinker (PBI-4NH<sub>2</sub>, polybenzimidazole terminated with amino groups) was designed and synthesized. This kind of crosslinked membrane gets rid of the binding of PBI as a polymer framework. Besides, poly (aryl ether ketone) has good thermal stability to meet the test requirements of HT-PEMFCs, and the 3D network structure of the membrane can maintain good mechanical properties

after phosphoric acid doping. In addition, we also prepared the composite membrane PAEK-*cr*-PBI@PBI, which was obtained by blending PAEK-*cr*-PBI and PBI polymers. In order to better evaluate the performance of the as-synthesized PAEK-*cr*-PBI and PAEK-*cr*-PBI@PBI membranes, we compared the well-documented PBI membrane with it. The properties of these membranes, including their solubility in common solvent, morphology analysis, thermal stability, oxidative stability, proton conductivity, and mechanical strength, were studied and compared.

## 2. Experiment

### 2.1. Materials and Chemicals

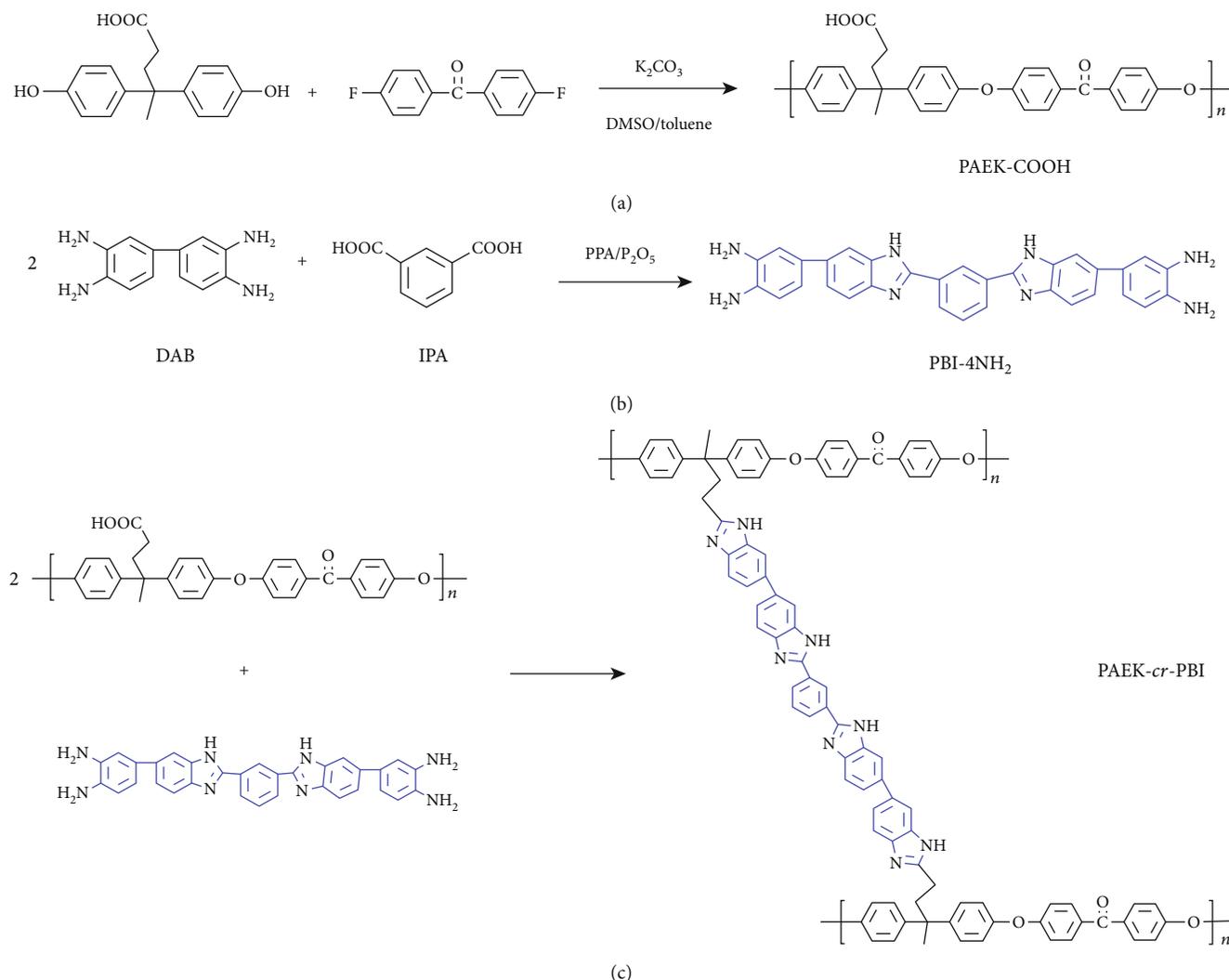
**2.1.1. Materials.** Poly (4,4'-(diphenyl ether)-5,5'-bibenzimidazole) (PBI, 6000 Pa-S) was obtained from Shanghai Shengjun Plastic Technology Co., Ltd. Figure 1 shows the molecular structure of PBI.

**2.1.2. Chemicals.** 4,4-Bis(4-hydroxyphenyl)-valeric acid (98%), phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>), polyphosphoric acid (PPA), phosphoric acid solution (85 wt%), and 1-methyl-2-pyrrolidinone (NMP) were obtained from Aladdin Chemistry Co. Ltd. 4,4'-Difluorobenzophenone (99%), isophthalic acid (IPA), and 3,3'-diaminobenzidine (DAB, 97%) were obtained from Shanghai Macklin Biochemical Co. Ltd. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), toluene, isopropyl alcohol, tetrahydrofuran (THF), and hydrochloric acid (HCl) were purchased from Guangzhou Chemical Reagent Factory. Ammonia solution (25 wt%) was purchased from Tianjin Fuyu Fine Chemical Co. Ltd.

### 2.2. Synthesis

**2.2.1. Synthesis of PAEK-COOH.** Poly (arylene ether ketone) with the pendant carboxyl group (PAEK-COOH) was synthesized via the step condensation polymerization [33, 37, 38]. The synthetic pathway of PAEK-COOH is shown in Scheme 1(a); in a 250 mL three-neck round-bottom flask equipped with a magnetic stirrer, a condenser, a Dean-Stark trap, and a nitrogen inlet, 4,4-bis(4-hydroxyphenyl)-valeric acid (2.86 g, 0.01 mol) and 4,4'-difluorobenzophenone (2.18 g, 0.01 mol) were dissolved in 40 mL DMSO and 45 mL toluene. Then, K<sub>2</sub>CO<sub>3</sub> (3.46 g, 0.025 mol) was added to the reaction flask. Under an atmosphere of nitrogen, the mixture was heated to 145°C and maintained at this temperature for 4 h until the water was totally separated by means of a Dean-Stark trap using toluene. Then, the system temperature was elevated to 170°C to render polymerization for 22 h.

Purification of the polymers was done by decantation of the supernatant from the reaction mixture after cooling to room temperature; then, HCl and THF were added at a ratio of 1:4; thus, the mixture was stirred until the solid polymer was completely dissolved. After the stirring, the orange-colored polymer layer floating on the top of the liquid phase was collected. The PAEK-COOH solution in THF (orange-colored polymer layer) was precipitated by dropping it into 500 mL of isopropyl alcohol in a 1 L beaker. The obtained white polymer was washed with isopropyl alcohol, followed



SCHEME 1: Synthesis of (a) PAEK-COOH, (b) PBI-4NH<sub>2</sub>, and (c) PAEK-cr-PBI.

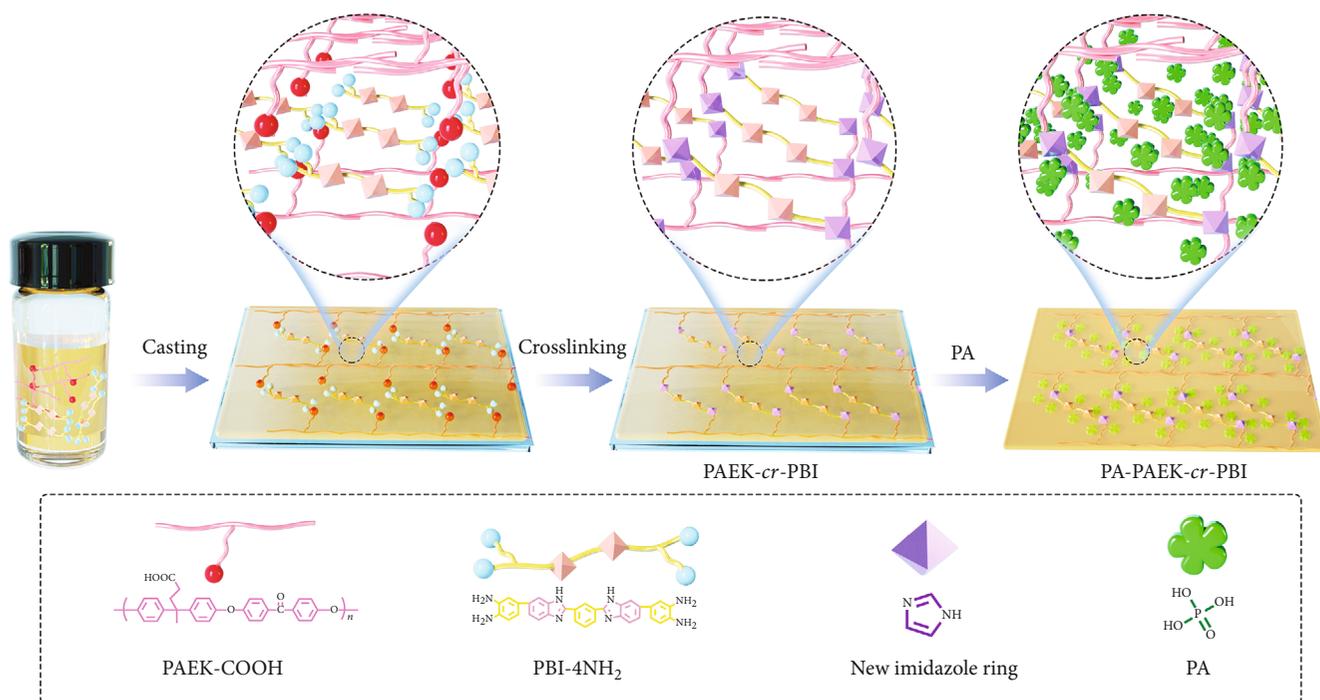
by deionized water. Then, the purified product, PAEK-COOH, was dried in a 100°C dry oven for 24 h.

**2.2.2. Synthesis of the Crosslinker (PBI-4NH<sub>2</sub>).** The amine-terminated polybenzimidazole (PBI-4NH<sub>2</sub>) was synthesized by the condensation reaction of 3,3'-diaminobenzidine (DAB) with isophthalic acid (IPA) in polyphosphoric acid (PPA) [39, 40], as shown in Scheme 1(b). In a 100 mL dry three-neck flask equipped with a nitrogen inlet and a nitrogen outlet, 27 g of PPA and 7 g of phosphorus pentoxide were heated at 120°C under nitrogen flow and mechanically stirred about 4 h till a clear solution was observed. After cooling to room temperature, DAB (1.2856 g, 6 mmol) and IPA (0.4985 g, 3 mmol) were added; then, the reaction mixture was mechanically stirred, slowly heated to 190°C, and kept at this temperature for 20 h. After cooling to about 80°C, the viscous solution was slowly poured into the ice deionized water and then was neutralized to pH 7 with dilute solution of ammonium hydroxide solution (5 wt%). The product was filtered and washed with deionized water several times and dried

in a freeze dryer for 2 days at minus 60°C to remove the residual solvents completely.

### 2.3. Preparation of Membranes

**2.3.1. Preparation of the PAEK-cr-PBI Membrane.** The synthesis route of PAEK-cr-PBI is shown in Scheme 1(c), and the PAEK-cr-PBI membrane was fabricated by a solution casting method, as shown in Scheme 2. The calculated result of the carboxyl equivalent in PAEK-COOH is 2.15 mmol/g. Firstly, PAEK-COOH (300.0 mg) was dissolved in 2–3 mL 1-methyl-2-pyrrolidinone (NMP) to form a uniformly transparent solution. Then, the PBI-4NH<sub>2</sub> (168.6 mg, the molar ratio of diamino to carboxyl is 1:1) was dissolved completely in 2 mL NMP. The total polymer concentration was controlled to be 8–15% (*w/v*). After that, the solution of PBI-4NH<sub>2</sub> was added dropwise into the solution of PAEK-COOH in NMP and then stirred for 4 h to obtain a uniform solution. The resulting polymer solution was cast onto a clean glass plate followed by heating at 80°C for 5 h to remove residual solvent and then a further thermal treatment at 150°C for 2 h and then put in a



SCHEME 2: Schematic diagram of the preparation procedure of the PA-doped 3D network structural PAEK-cr-PBI membrane.

vacuum at 190°C for 12 h for further crosslinking. The obtained membrane was then peeled off, washed thoroughly with deionized water, and dried at 100°C for 24 h.

**2.3.2. Preparation of the PAEK-cr-PBI@PBI Membrane.** Similar to the PAEK-cr-PBI membrane, the composite PAEK-cr-PBI@PBI membrane was also fabricated by a solution casting method. What needs to be explained here is that the mass ratio between PAEK-cr-PBI and PBI is 4:1; the detail of the preparation process is as follows: PAEK-COOH (300.0 mg) and PBI (117.2 mg) were dissolved in 3 mL 1-methyl-2-pyrrolidinone (NMP) to form a uniformly transparent solution. Then, the PBI-4NH<sub>2</sub> (168.6 mg) was dissolved completely in the 1-2 mL NMP. The rest of the procedure is the same as the preparation process of the PAEK-cr-PBI membrane.

**2.3.3. Preparation of the PBI Membrane.** The preparation method of the PBI membrane is the most convenient: 0.5 g PBI was dissolved in 5 mL NMP and stirred for 24 h at room temperature to obtain a homogeneous solution. Then, the polymer solution was cast on a flat glass plate and then dried at 80°C for 24 h.

## 2.4. Characterizations

**2.4.1. Structural Characterization.** <sup>1</sup>H NMR spectra of the PAEK-COOH and PBI-4NH<sub>2</sub> were recorded on a Bruker DRX-500 NMR spectrometer with deuterated DMSO (DMSO-d<sub>6</sub>) as the solvent and tetramethylsilane (TMS) as the standard at room temperature. The molecular weight of synthesized PAEK-COOH was measured using a gel permeation chromatography (GPC) system (Waters 515 HPLC Pump, Waters 2414 detector), and the measurement was carried out at 30°C with the THF solvent. The surface and cross-

section morphologies of the membranes were recorded on scanning electron microscopy (FE-SEM, Quanta 400F).

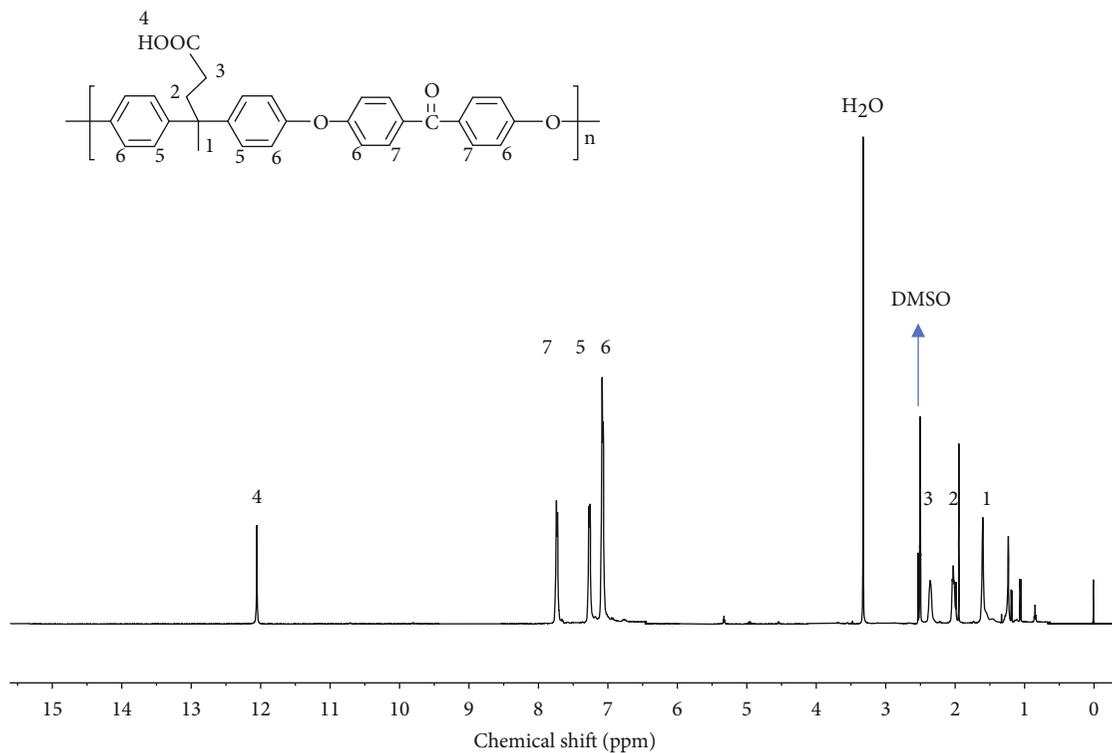
**2.4.2. Solubility Test.** The crosslinking degree was characterized by measuring the solubility of the PAEK-cr-PBI and PAEK-cr-PBI@PBI membranes in common solvents. The membranes were immersed in NMP for 12 h at 90°C. Then, the residual samples in the NMP solution were collected, dried, and weighed. The weight residue of the membranes was calculated by the following equation:

$$\text{Gel content(\%)} = \frac{W_A}{W_B} \times 100\%, \quad (1)$$

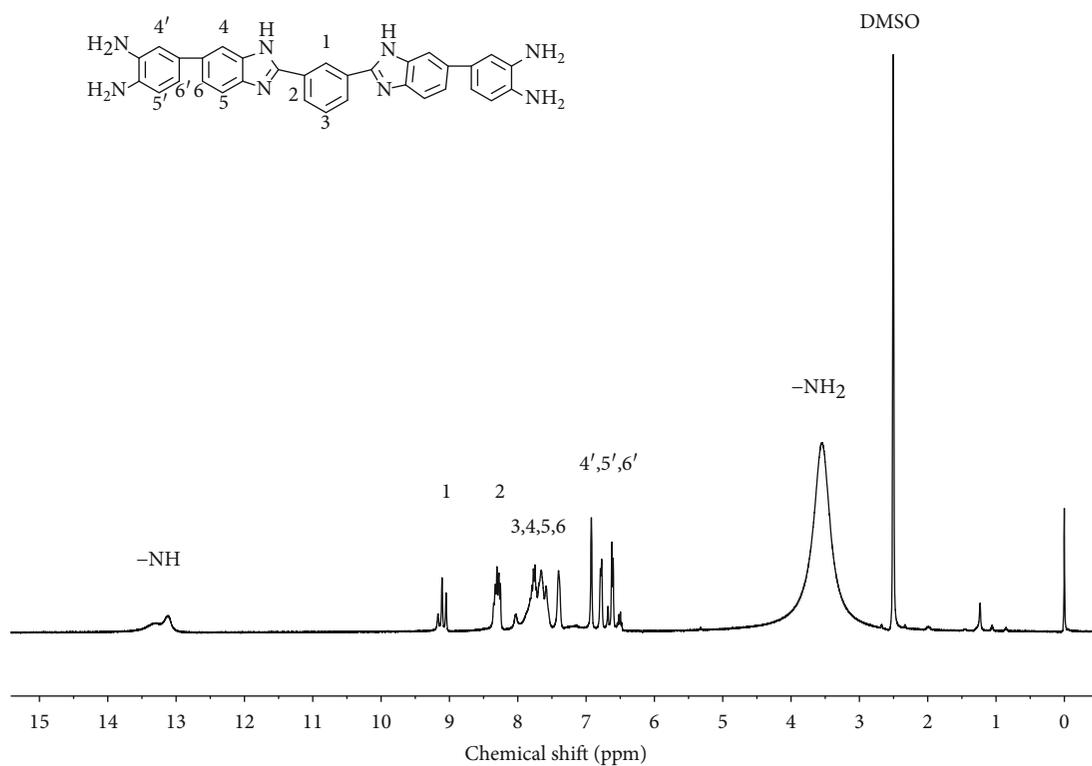
where  $W_A$  is the weight of membranes after the test and  $W_B$  is the weight of membranes before the test.

**2.4.3. PA Uptake and Swellings.** The PBI, PAEK-cr-PBI, and PAEK-cr-PBI@PBI membranes were dried in a vacuum oven at 80°C for 12 h. After measuring the weight, length, width, and thickness, they were immersed in 85 wt% phosphoric acid solution at 120°C for 15 h. The membranes were taken out and wiped with tissue wipes. After drying at 100°C for 12 h, PA uptake and the length, width, and thickness of each sample were measured immediately. Each type of membranes was tested for three samples, and the average value was reported. The PA uptake ratio of the membrane was calculated by the following equation:

$$\text{PA uptake(\%)} = \frac{W_{PA} - W_D}{W_D} \times 100\%, \quad (2)$$



(a)



(b)

FIGURE 2: <sup>1</sup>H NMR spectra of (a) PAEK-COOH and (b) PBI-4NH<sub>2</sub>.

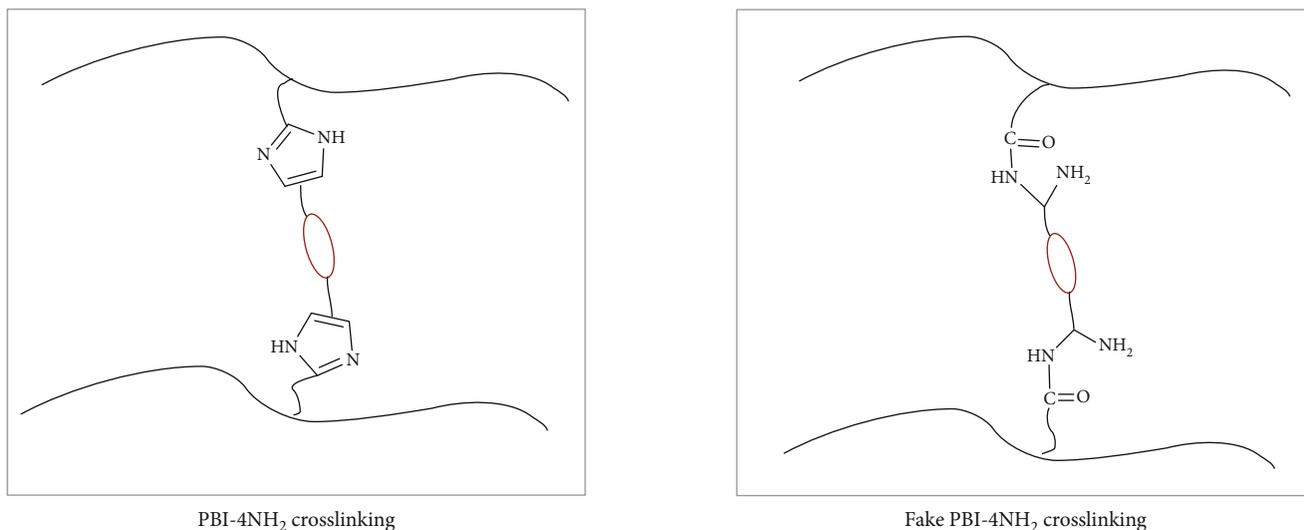


FIGURE 3: Schematic representation of the possible crosslinking structures of the PAEK-*cr*-PBI membrane.

where  $W_{PA}$  is the weight of the PA-doped membrane and  $W_D$  is the weight of the undoped dry membrane. The dimensional swelling ratio of the membrane was calculated by the following equations:

$$S_{\text{area}} (\%) = \frac{A_{PA} - A_D}{A_D} \times 100\%, \quad (3)$$

$$S_{\text{volume}} (\%) = \frac{V_{PA} - V_D}{V_D} \times 100\%,$$

where  $A_D$  and  $V_D$  represent the area and volume of the dry membrane, respectively, and  $A_{PA}$  and  $V_{PA}$  represent the area and volume of the wet membrane, respectively, after being immersed in 85 wt% phosphoric acid solution at 120°C.

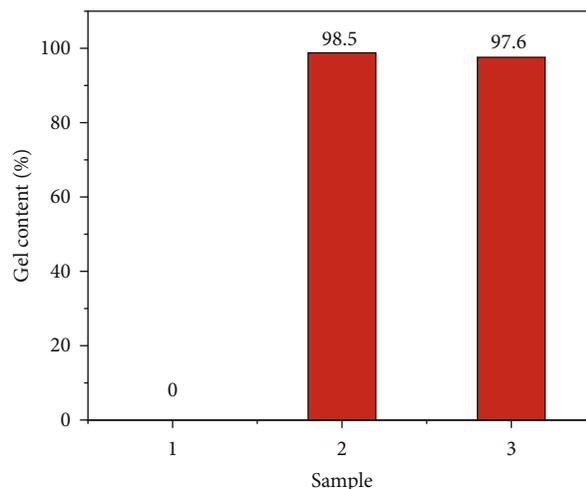
**2.4.4. Thermal Stability.** The thermogravimetric (TGA) curves of membranes were obtained by Pyris 1 TGA (PerkinElmer) under the nitrogen atmosphere. All the samples were preheated at 100°C for 2 h to eliminate the absorbed water and organic solvents before testing. Then, the samples were tested from 50 to 800°C with a heating rate of 10°C min<sup>-1</sup>.

**2.4.5. Oxidative Stability.** To test oxidative stability, the undoped membrane samples were immersed into Fenton's reagent (3% H<sub>2</sub>O<sub>2</sub> solution containing 4 ppm Fe<sup>2+</sup>) at 80°C for 40 h; then, the samples were removed from the solution and dried in a vacuum oven at 120°C for 12 h. Each type of membranes was tested for 3 samples, and the average value was reported. The residual weight of the samples represented the oxidative stability [18, 41].

**2.4.6. Proton Conductivity.** The proton conductivities of PBI, PAEK-*cr*-PBI, and PAEK-*cr*-PBI@PBI membranes were measured by electrochemical impedance spectroscopy (EIS) using a PGSTAT204 electrochemical workstation (AUT50992, AUTOLAB). The membrane sample was immersed in 85 wt% PA solution for 12 h at room temperature before testing. The impedance measurement was performed under anhy-



(a)



(b)

FIGURE 4: (a) Photographs and (b) gel content of membranes after the solubility test in NMP at 90°C for 12 h. (1) PBI, (2) PAEK-*cr*-PBI, and (3) PAEK-*cr*-PBI@PBI.

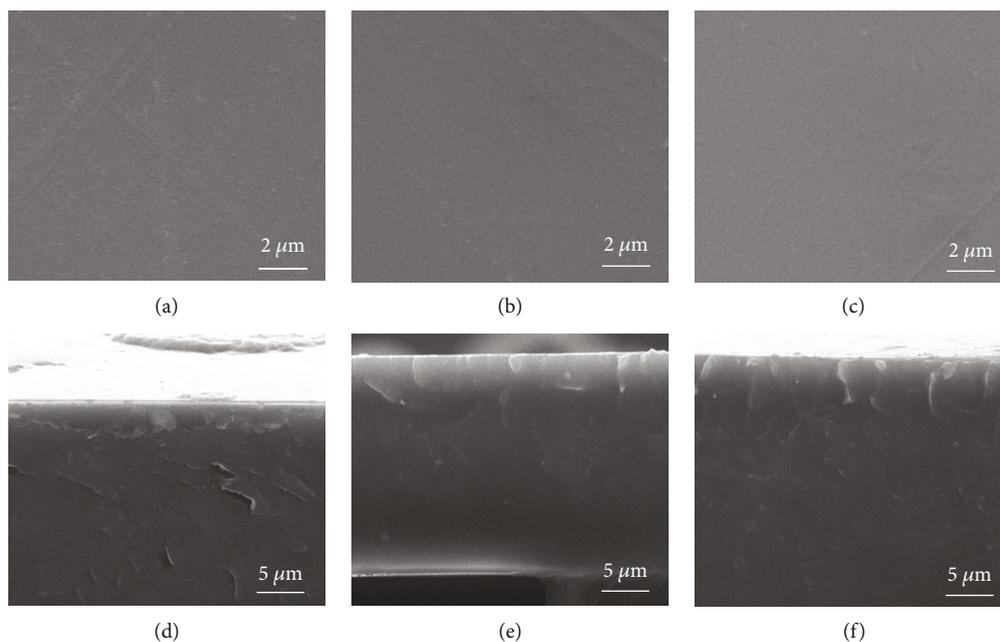


FIGURE 5: SEM micrographs of the surface (up) and cross-section (down) of PA-undoped membranes: (a, d) PBI, (b, e) PAEK-*cr*-PBI, and (c, f) PAEK-*cr*-PBI@PBI.

drous conditions from 120°C to 170°C in the frequency range of 0.1 Hz to 100 kHz. The conductivity is calculated by the following equation:

$$\sigma = \frac{L}{R \times W \times T}, \quad (4)$$

where  $L$  (cm) is the distance between two electrodes,  $R$  ( $\Omega$ ) is the membrane resistance obtained by a Nyquist plot, and  $W$  (cm) and  $T$  (cm) are the width and thickness of the membrane, respectively.

**2.4.7. Mechanical Properties.** The mechanical properties of PA-doped membranes were evaluated on a tensile tester (New SANS, Shenzhen, China) with a stretching speed of 10 mm/min under an ambient atmosphere. The size of all the samples is 6 mm  $\times$  40 mm. Before testing, the PA-doped membranes were dried in a vacuum oven at 100°C for 24 h to remove any absorbed water or organic solvents. Each type of membranes was tested for 4 samples, and the average value was reported.

### 3. Results and Discussion

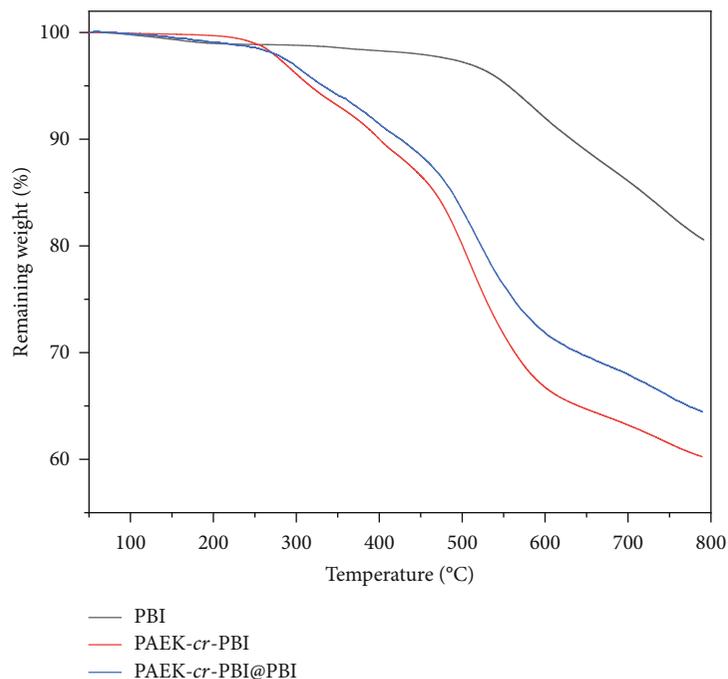
**3.1. Chemical Structure Identification.** From the GPC analysis, the number and weight average molecular weights of PAEK-COOH were 40,000 and 92,000 g mol<sup>-1</sup>, respectively. This result suggests that the polymer possesses a high enough molecular weight to form a membrane.

The synthesized PAEK-COOH and PBI-4NH<sub>2</sub> were analyzed using <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>), and the presence of carboxyl and amino groups was confirmed as shown in Figure 1. As it can be seen in Figure 2(a), the protons in the benzene ring of the polymer main chain show chemical shifts

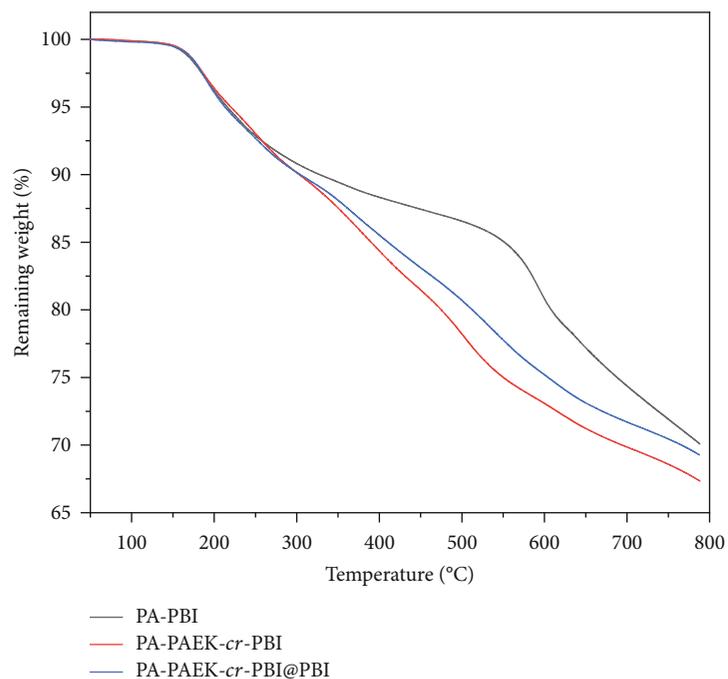
at 7.06, 7.27, and 7.73 ppm; the NMR peak at 12.05 ppm comes from the proton in the carboxyl group of PAEK-COOH. In Figure 2(b), the broad peak at 13.10 ppm is attributed to the -NH proton of the benzimidazole groups. Peaks of 9.05-9.16 ppm are assigned to protons (H1) near the two benzimidazole groups. Peaks in the range of 6.93-6.50 ppm are ascribed to aromatic protons of benzene rings (H3', H4', and H5') at both ends. Peaks in the range of 8.28-7.41 are attributed to the remaining aromatic protons (H2-6). The broad peak at 3.55 ppm is attributed to protons of the terminal amino group. The results of peak distribution indicate that the desired PBI-4NH<sub>2</sub> was prepared successfully.

The schematic representation of the possible crosslinking structures of the crosslinked membrane is shown in Figure 3. Because of the insolubility of the crosslinked membrane (PAEK-*cr*-PBI), it is difficult to confirm the imidazolization between PAEK-COOH and PBI-4NH<sub>2</sub> by the conventional analysis.

The solubility test was carried out to ascertain the crosslinking degree of PAEK-*cr*-PBI and PAEK-*cr*-PBI@PBI successfully. It is easy to know that if a complete dissolution of the membrane occurs, there is no crosslinking in the membrane. On the other hand, if the membrane has a residual sample after a period of immersing, the membrane is approved to be crosslinked. As shown in Figure 4, PAEK-*cr*-PBI and PAEK-*cr*-PBI@PBI membrane samples maintained the structural integrity after immersing in NMP at 90°C for 12 h. The weight of the PAEK-*cr*-PBI and PAEK-*cr*-PBI@PBI sample was over 97% after treatment. These results confirm that the crosslinking occurred between PAEK-COOH and PBI-4NH<sub>2</sub>. In addition, there was no significant dissolution of PBI in the PAEK-*cr*-PBI@PBI membrane, which may be owing to the network structure of PAEK-*cr*-PBI suppressing PBI molecular



(a)



(b)

FIGURE 6: TGA curves of (a) PA-undoped and (b) PA-doped membranes under the  $N_2$  atmosphere.

chain movement. On the contrary, the noncrosslinked membranes (PBI) completely dissolved in NMP in 2 h.

**3.2. Morphology Analysis.** The surface and cross-section morphologies of the prepared membranes were studied using SEM micrography. In Figure 5, it is observed that PAEK-cr-PBI and PAEK-cr-PBI@PBI membranes show a completely homogenous and compact structure without pores as well as the PBI membrane, which is essential for separating the

fuel and oxidant during fuel cell operation and benefits the fuel cell performance.

**3.3. Thermal Stability.** Thermal stability of polymer electrolytes is one of the most critical features for long-term durability of fuel cells, especially in high-temperature operation. The thermal stability of PA-undoped and PA-doped membranes was studied by TGA under the nitrogen atmosphere. As shown in Figure 6(a), two-step degradation can be observed

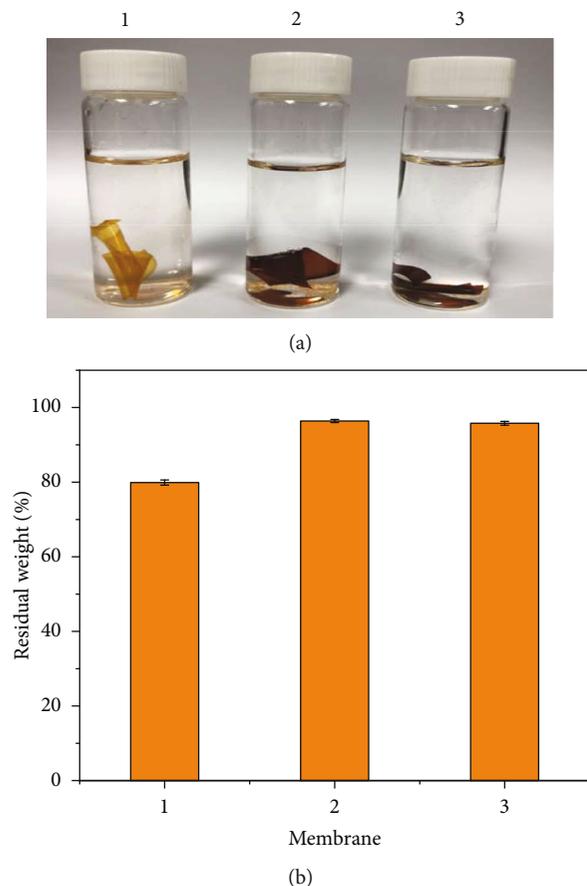


FIGURE 7: (a) Photographs and (b) residual weight of the membranes after the Fenton test: (1) PBI, (2) PAEK-cr-PBI, and (3) PAEK-cr-PBI@PBI.

in both undoped PAEK-cr-PBI and PAEK-cr-PBI@PBI membrane samples. The first weight loss beginning at around 250°C was attributed to the degradation of imidazole groups and carboxyl groups on the side chains, which suggested that the amino and carboxyl groups do not react completely. The second step observed at about 470°C was due to the degradation of the polymer main chain, including poly (aryl ether ketone) (PAEK) and poly (4,4'-(diphenyl ether)-5,5'-bibenzimidazole) (PBI). On the other hand, the undoped PBI membrane decomposed only in one step at around 500°C. After doping with PA, as shown in Figure 6(b), for all the membranes, weight loss appeared earlier at about 160°C because of the dehydration of phosphoric acid. Nonetheless, the degradation of polymer membranes itself was observed in the temperature range similar to that of PA-undoped polymer membranes. The TGA results show that both PAEK-cr-PBI and PAEK-cr-PBI@PBI membranes exhibit excellent thermal stabilities and can be used for HT-PEMFCs.

**3.4. Oxidative Stability.** To estimate the long-term stability of PEMs, the oxidative stability of the membranes was measured by the Fenton test. During the fuel cell operation, the incom-

TABLE 1: PA doping behavior of the membranes.

Membrane	PA uptake (%)	$S_{\text{area}}$ (%)	$S_{\text{volume}}$ (%)
PBI	231 ± 8	50 ± 2	136 ± 7
PAEK-cr-PBI	193 ± 5	37 ± 2	79 ± 4
PAEK-cr-PBI@PBI	224 ± 6	43 ± 2	124 ± 5

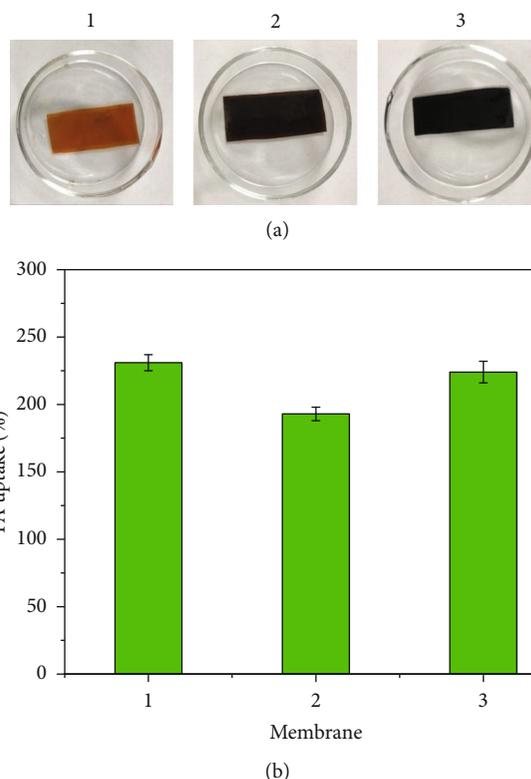


FIGURE 8: (a) Photographs of the PA-doped membrane and (b) PA uptake of the membranes: (1) PBI, (2) PAEK-cr-PBI, and (3) PAEK-cr-PBI@PBI.

plete reduction of oxygen produces  $\text{HO}^\bullet$  and  $\text{HO}_2^\bullet$  radicals. Subsequently, these lively radicals attack the skeleton of the polymer membrane, which causes membrane degradation. The degradation of the membranes was investigated by determining the weight loss. As shown in Figure 7, the PAEK-cr-PBI and PAEK-cr-PBI@PBI membranes show superior oxidative stabilities as compared to the PBI membrane. It is because the densely crosslinked structure reduces the possibility of radical species to attack the polymer chain. After 40 h of the Fenton test, only 79.9% of the initial weight of the linear PBI membrane remained. However, the residual weight values of PAEK-cr-PBI and PAEK-cr-PBI@PBI are both more than 95%. The results indicated that the polymer PAEK-cr-PBI exhibited excellent oxidative stability.

**3.5. PA Uptakes and Swellings.** The proton transport of HT-PEMs depends on the dissociation of phosphoric acid, so the content of free phosphoric acid has a direct impact on proton conductivity of HT-PEM materials. The PA-doped membranes were obtained by immersing the dried membranes into 85 wt% phosphoric acid solution at 120°C for 15 h, and the PA

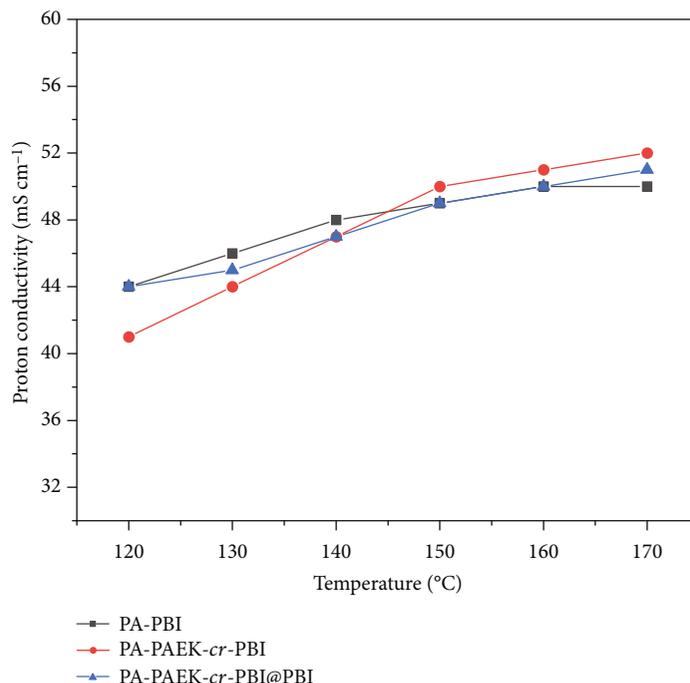


FIGURE 9: Proton conductivity of PA-doped membranes.

uptake and swelling ratio of the membrane are summarized in Table 1. To make it easier to follow, the photographs of the PA-doped membranes and histogram of PA uptake of the PBI, PAEK-*cr*-PBI, and PAEK-*cr*-PBI@PBI membranes are shown in Figure 8.

As it can be seen in Figure 8, the highest PA uptake was obtained by the PBI membrane. However, the PA uptakes of the membranes synthesized in this study are not disappointing. As it can be seen in Table 1, the PAEK-*cr*-PBI and PAEK-*cr*-PBI@PBI membranes have a PA uptake of 193% and 224%, respectively. Obviously, the PAEK-*cr*-PBI@PBI membrane, which is the membrane PAEK-*cr*-PBI blended with some PBI, did absorb more phosphoric acid than the PAEK-*cr*-PBI membrane without PBI.

In respect to the swelling of the membrane caused by doping PA molecules, the PAEK-*cr*-PBI membrane showed a volume swelling of below 80% and an area swelling of below 40%. The low swelling of the PA-doped PAEK-*cr*-PBI membrane probably benefited from its crosslinked structure and the skeleton stability of the poly (aryl ether ketone) matrix. However, the swelling of the membrane with PBI (PAEK-*cr*-PBI@PBI) was higher than that of the pristine PAEK-*cr*-PBI membrane. That may be due to the enhancement of PA uptake of the membrane or the plasticizing effect of phosphoric acid on the PAEK-*cr*-PBI framework.

**3.6. Proton Conductivities.** The proton conductivity measurement was carried out from 120 to 170°C in anhydrous condition. In order to evaluate the proton conductivity of crosslinked PAEK-*cr*-PBI and PAEK-*cr*-PBI@PBI membranes, the well-documented PBI membrane was selected as the comparison. In Figure 9, the proton conductivities of all the membranes increase with the increase in the testing temperature as we expected. It is interesting to see that these

three kinds of membranes have almost the same proton conduction ability, which demonstrates that the proton conductivity of the PAEK-*cr*-PBI and PAEK-*cr*-PBI@PBI membranes is comparable to that of the traditional PBI membrane. However, there is a change observed in the slope above 150°C for the proton conductivity curves of all membranes, which may be due to the transformation of a proton conducting mechanism, because the condensed phosphoric acids such as the dimer (pyrophosphoric acid ( $H_4P_2O_7$ )), trimer (meta- or tripolyphosphoric acid ( $H_5P_3O_{10}$ )), and larger fused structures were formed when the temperature is over 150°C [1]. Obviously, when the temperature is over 150°C, the PAEK-*cr*-PBI membrane with the lowest PA uptake exhibits the highest proton conductivity, which illustrates that the 3D network structure of the membrane is conducive to proton conduction.

**3.7. Mechanical Properties.** It is well known that the excellent mechanical properties of HT-PEMs are essential for practical application. The typical stress-strain curves of the membranes at room temperature are shown in Figure 10, and the mechanical properties are displayed in Table 2. As shown in Figure 10, the PA-doped PAEK-*cr*-PBI membrane exhibits the best tensile strength of 17 MPa among the three kinds of membranes as expected. In the meanwhile, the PA-doped PAEK-*cr*-PBI@PBI membrane also showed fairly excellent mechanical strength of over 10 MPa. However, the tensile strength of the PA-doped PBI membrane is only about 3.5 MPa. These results show that the PA-doped 3D network structural PAEK-*cr*-PBI membrane has outstanding mechanical properties; moreover, it can be used as a support material to improve the mechanical properties of PA-doped PBI membrane without reducing the proton conductivity.

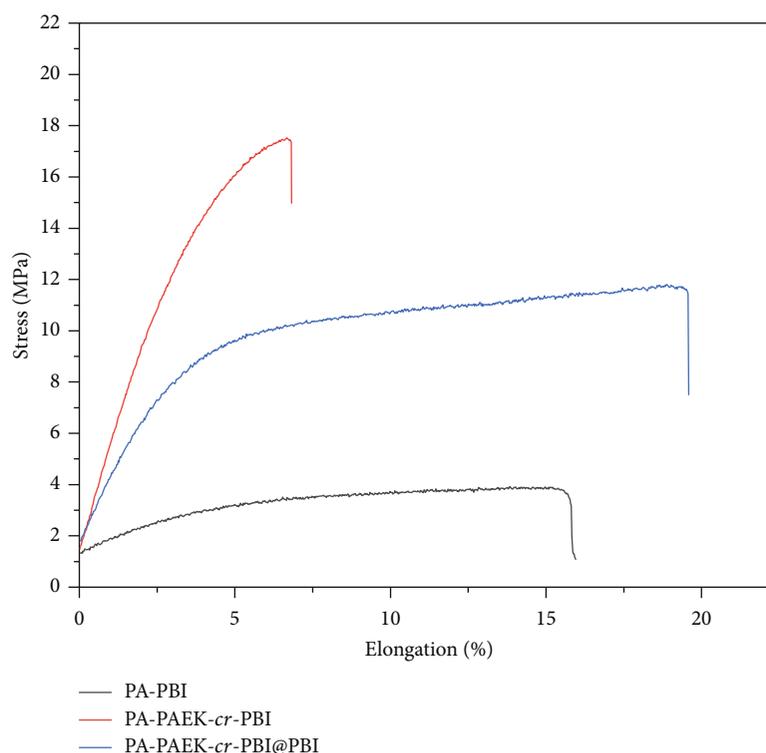


FIGURE 10: Mechanical properties of PA-doped membranes at room temperature.

TABLE 2: Summary of proton conductivities and mechanical properties of PA-doped membranes.

Membrane	PA uptake (%)	Proton conductivity ( $\text{mS cm}^{-1}$ ) <sup>a</sup>	Tensile strength (MPa) <sup>b</sup>	Elongation (%) <sup>b</sup>
PBI	$231 \pm 8$	50	$3.5 \pm 0.4$	$15.8 \pm 2.4$
PAEK- <i>cr</i> -PBI	$193 \pm 5$	52	$17.0 \pm 0.4$	$9.7 \pm 1.1$
PAEK- <i>cr</i> -PBI@PBI	$224 \pm 6$	51	$11.4 \pm 0.3$	$19.7 \pm 3.2$

<sup>a</sup>Measured at 170°C and under anhydrous condition. <sup>b</sup>Measured at room temperature.

## 4. Conclusions

In this work, a 3D network structural PAEK-*cr*-PBI membrane was prepared and investigated as HT-PEMs for HT-PEMFCs. The 3D network structural membrane PAEK-*cr*-PBI and the composite membrane PAEK-*cr*-PBI@PBI both showed excellent thermal stability which is suitable for operation in the high-temperature range of 120~180°C. Moreover, the PAEK-*cr*-PBI and PAEK-*cr*-PBI@PBI membranes exhibit excellent proton conductivities of about  $50 \text{ mS cm}^{-1}$  at 170°C, which are comparable to those of the traditional PBI membrane. As an encouraging result, the PA-doped PAEK-*cr*-PBI membrane showed superior mechanical properties of 17 MPa than the PA-doped linear PBI membrane, which is only 3.5 MPa. These results show that the as-synthesized PAEK-*cr*-PBI gives a highly practical promise for its application in HT-PEMFCs.

## Data Availability

All of the data used to support the findings of this study are included within the article.

## Conflicts of Interest

There is no conflict of interest.

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