

Preparation and Properties of Phosphorylated and Crosslinked Poly(vinyl alcohol)/Bisphenol A–Epoxy Resin Membranes for Fuel Cell Applications

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ABSTRACT: To overcome the strong dependence of the conductivity on the relative humidity and the lower thermal stability at high temperature of perfluorosulfonate polymers and the leaching-out problem of phosphoric acid doped membranes, a series of phosphorylated and crosslinked poly(vinyl alcohol) (PVA)/bisphenol A–epoxy resin [diglycidyl ether of bisphenol A (DGEBA)] membranes were prepared. The membrane properties were characterized by Fourier transform infrared spectra, solubility, thermogravimetric analysis, water uptake, swelling ratio, ion-exchange capacity (IEC), small-angle X-ray scattering, and proton conductivity measurements. The results show

that the crosslinked PVA/DGEBA membrane had a higher thermal stability ($T_d \geq 250^\circ\text{C}$) than the pure PVA membrane ($T_d \geq 220^\circ\text{C}$) and that the phosphorylated and crosslinked PVA/DGEBA membranes (IEC = 5.54 mmol/g) with a low volume swelling ratio (7.21%) could achieve a maximum proton conductivity of 2.51×10^{-3} S/cm at a temperature as high as 150°C in anhydrous conditions © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3071–3079, 2011

Key words: crosslinking; membranes; SAXS

INTRODUCTION

A proton-exchange membrane (PEM) is one of the key components in a fuel cell system. Current state-of-the-art PEMs used in practical systems are sulfonated perfluoropolymers, typically DuPont's Nafion, which has a high proton conductivity, good mechanical properties, and chemical stability.¹ However, these membranes have some weak aspects, such as strong dependencies of the conductivity on the relative humidity (RH) and water content, a lower thermal stability at high temperature, and a high cost. Therefore, many efforts have been made to develop a PEM that shows less humidity dependence, good thermal stability at elevated temperature, and low cost.

The concept is mainly based on the doping of the polymers bearing basic sites with H_3PO_4 because of its very high degree of self-dissociation (H_2PO_4^- and H_4PO_4^+), along with some condensation (H_3O^+ and $\text{H}_2\text{P}_2\text{O}_7^{2-}$). Phosphoric acid doped polybenzimidazole

(PBI) membranes exhibit a high proton conductivity under low water content,^{2–7} good mechanical properties,⁸ and excellent thermal stability at temperatures up to 200°C .⁹ Extensive studies have been conducted at Case Western Reserve University^{10–14} on PBI complexes. Li et al.¹⁵ characterized phosphoric acid doped PBI. The conductivity of the doped PBI membrane showed less humidity dependence in contrast to the Nafion membrane but was sensitive to the doping level and the temperature. At a 4.50 doping level and a temperature of 165°C , the conductivity of the phosphoric acid doped PBI membrane achieved a conductivity of 4.6×10^{-2} S/cm. Ye et al.¹⁶ prepared and characterized $\text{H}_3\text{PO}_4/\text{PMIH}_2\text{PO}_4/\text{PBI}$ membranes, which were homogeneous, flexible, and freestanding and had good thermal stability and a wide temperature range of single-phase behavior. Their membranes had acceptable ionic conductivities of up to 2.0×10^{-3} S/cm at 150°C under anhydrous conditions. Wainright et al.² reported a conductivity of 2.2×10^{-2} S/cm at 190°C for a PBI membrane with an H_3PO_4 doping level of 5.01. Despite these interesting properties of PBI– H_3PO_4 membranes for high-temperature fuel cells, the phosphoric acid leaching out of the membrane limits the long-term utilization of PBI– H_3PO_4 membranes.

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Considering the strong dependence of the conductivity on RH and the lower thermal stability at high temperature of perfluorosulfonated membranes and the leaching-out problem of the phosphoric acid doped membranes, we designed crosslinked poly(vinyl alcohol) (PVA)/diglycidyl ether of bisphenol A (DGEBA) as a matrix membrane, which had good thermal stability, and used poly(phosphate acid) (PPA), which connected to the matrix membrane in the form of covalent bond and was not easily leached out. The membrane properties were characterized by Fourier transform infrared (FTIR) spectroscopy, solubility, thermogravimetric analysis (TGA), water uptake, swelling ratio, ion-exchange capacity (IEC), small-angle X-ray scattering (SAXS), and proton conductivity measurements. This information will be useful for phosphorylated and crosslinked PVA/DGEBA membranes used as PEMs for high-temperature fuel cells.

EXPERIMENTAL

Materials

The PVA (polymerization degree = 1850, hydrolysis degree = 98–99%) was supplied by Hunan Xiangda Chemical Co. (Loudi, Hunan, China). DGEBA (E_{44} , epoxy value = 0.41–0.47) was purchased from Yueyang Petrochemical Co. (Yueyang, Hunan, China). Dimethyl sulfoxide (DMSO; purity $\geq 99.5\%$) and PPA (content of $P_2O_5 \geq 80\%$) were supplied by Kermel Chemical Co. (Tianjin, China). All of the materials were commercial products and were used as received. We obtained the deionized water by passing the water through several ion-exchange resin columns in our college.

Preparation of the crosslinked PVA/DGEBA membranes

The crosslinked PVA/DGEBA membranes were formed by a solution cast method. The PVA/DGEBA solution was made by the mixture of a stoichiometric amount of DGEBA/DMSO solution and PVA solution under magnetic stirring. The DGEBA/DMSO solution was prepared by the dissolution of DGEBA in DMSO with a density of 0.11 g/mL. The PVA solution was prepared by the dissolution of 0.88 g of PVA in 20 mL of DMSO and then heating it to 80°C with continuous stirring until a homogeneous solution was obtained. The selected blend ratios of DGEBA/PVA were 0.2 : 1, 0.3 : 1, 0.4 : 1, 0.5 : 1, and 0.6 : 1 mol/mol. The DGEBA/PVA solution was stirred for 2 h at room temperature, and the resulting solution had a homogeneous, transparent, and highly viscous appearance. After removal of the air by a vacuum technique, the resulting solution was

cast on a polytetrafluoroethylene plate and dried for 24 h in a conventional oven at desired temperatures of 60 and 80°C, respectively. Finally, the membrane was placed in a vacuum oven at 120°C for 12 h to remove the last traces of the solvent and the DGEBA laterally crosslinked with the PVA. The crosslinking reaction took place between the hydroxyl groups of PVA and the epoxy group of DGEBA. When visually dry, the membrane was peeled from the polytetrafluoroethylene plate and had a thickness of 30–90 μm .

Preparation of the phosphorylated and crosslinked PVA/DGEBA membranes

Square sample pieces of the crosslinked PVA/DGEBA membranes ($4 \times 4 \text{ cm}^2$) were soaked separately in PPA at 80°C in an N_2 atmosphere for different phosphorylation times (e.g., 20%- x , where x is the phosphorylation time). Excess PPA was eliminated after several washings with deionized water until the pH of the filtrate was neutral, and then, the membrane was dried in a conventional oven at 80°C for 24 h. The phosphated reaction between the crosslinked PVA/DGEBA membrane and PPA is shown in Scheme 1.

FTIR spectra

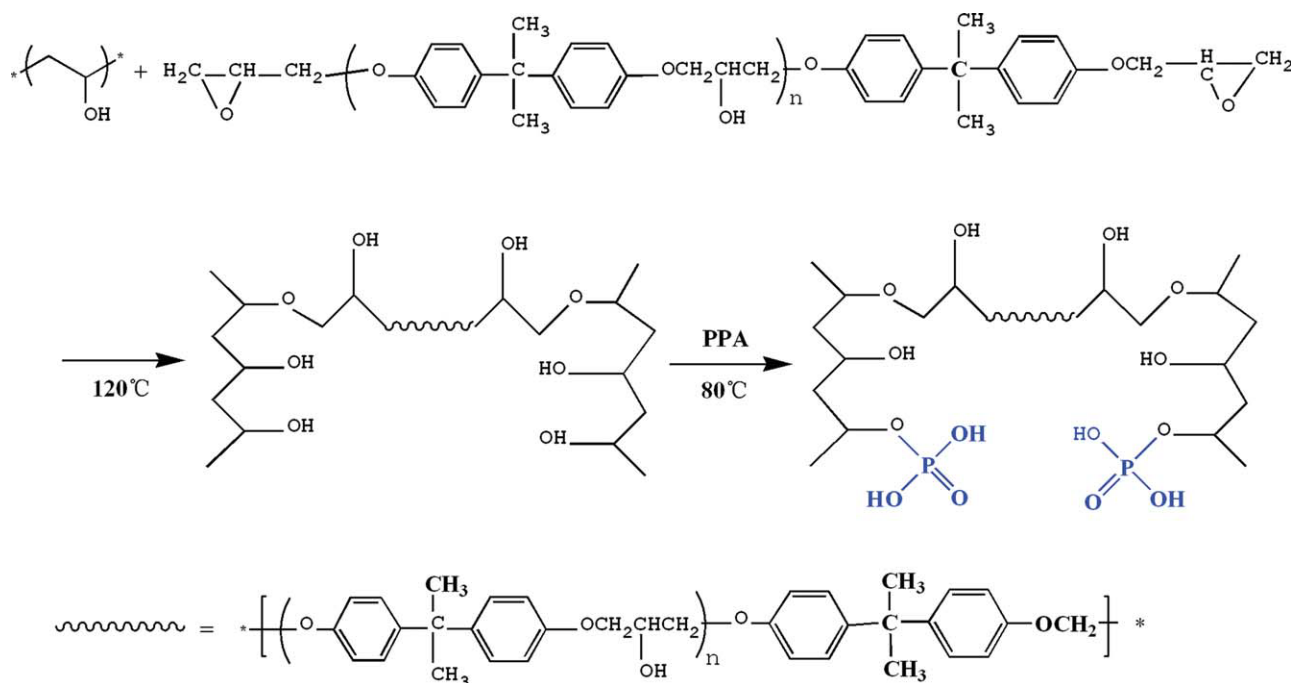
The prepared membranes were examined by FTIR spectroscopy on a spectrometer (PerkinElmer Paragon 1000PC spectrometer) (Perkin-Elmer Inc., Waltham, Massachusetts) with a wave-number resolution of 4 cm^{-1} in the range $400\text{--}4000 \text{ cm}^{-1}$. The pretreatment of the crosslinked PVA/DGEBA membrane was done by immersion of the membrane in a large volume of DMSO for 24 h at 80°C to extract unreacted PVA and DGEBA; then, it was washed with deionized water to remove DMSO and dried *in vacuo*.

Solubility

Both the pure PVA membrane and crosslinked PVA/DGEBA membranes were soaked in ethanolamine, DMSO, and H_2O at 80°C for 24 h to obtain their solubility data. If the crosslinked PVA/DGEBA membranes showed better solvent resistance than the pure PVA membrane, the crosslinking reaction could be confirmed.

TGA

The thermal stability of the membranes was analyzed with TGA (model STA409PC) (Netzsch Co., Bavaria, Germany) from 50 to 670°C at a rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere (N_2 flow



Scheme 1 Phosphorylation of the crosslinked PVA/DGEBA membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

rate = 50 mL/min). Before testing, the samples were dried for 2 h at 100°C *in vacuo* to remove moisture.

Water uptake and swelling ratio

The ability of the membrane to absorb water was estimated by gravimetric analysis. A previously weighed membrane sample was immersed in deionized water at 25°C for 24 h. The liquid water on the surface of the wet membranes was removed quickly with filter paper, and then, the weight and dimensional volumes of the wet membranes were measured.

The water uptake of the films was calculated from

$$\text{Water, uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

where W_{wet} is the weight of the water-swollen film sheet and W_{dry} is the weight of the dry membrane sample.

The membrane swelling was calculated from

$$\text{Swelling} = \frac{V_{\text{wet}} - V_{\text{dry}}}{V_{\text{dry}}} \times 100\% \quad (2)$$

where V_{wet} and V_{dry} are the volumes of the wet and dry membranes, respectively.

IEC

The IEC of each sample was determined by a titration method. The dried membrane in H^+ form was

weighed and then equilibrated in a saturated NaCl solution for 48 h. The amount of protons released in the filtrate was determined by titration with a 0.01 mol/L NaOH solution until the pH reached 7, where phenolphthalein was used as an indicator. IEC (mmol/g) was calculated with the following equation:

$$\text{IEC} = \frac{C_{\text{NaOH}} V_{\text{NaOH}}}{W_{\text{dry}}} \quad (3)$$

where W_{dry} (g) is the mass of the dry membrane and C_{NaOH} (mol/L) and V_{NaOH} (L) are the concentration and volume, respectively, of the NaOH solution.

SAXS

The SAXS experiments were performed on a Rigaku Nano-viewer (Micromax 007HF) (Rigaku Corporation, Tokyo, Japan) with an image plate system equipped with a $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation generator. The scattering vector (\mathbf{q}) was defined as follows:

$$\mathbf{q} = 4\pi \sin \theta / \lambda$$

where \mathbf{q} is the magnitude of the reciprocal lattice vector (\AA^{-1}), 2θ is the diffraction angle, and λ is the X-ray wavelength. The average size of the hydrophilic domain was estimated with Bragg's law:

$$2d \sin \theta = \lambda$$

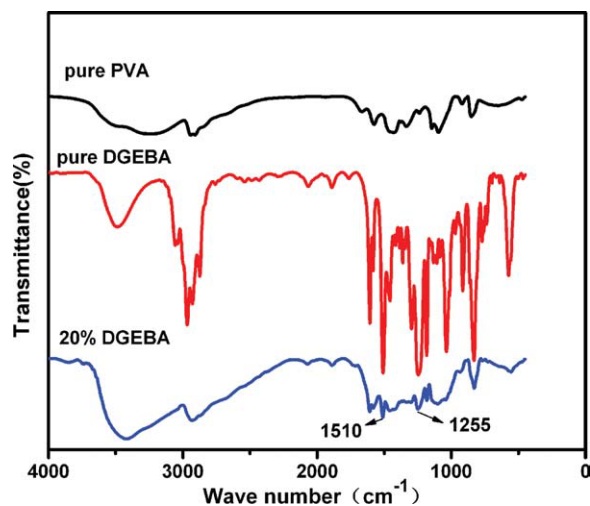


Figure 1 FTIR spectra of pure PVA, DGEBA, and the 20% crosslinked PVA/DGEBA membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

where d is the size of the scattering feature (\AA^{-1}). The combination expression relating q to d was obtained as

$$d = \frac{2\pi}{q} \quad (4)$$

Conductivity measurement

The proton conductivity of the membrane was measured by the alternating-current impedance method with a Solartron S-1296 electrochemical interface analyzer and a Solartron S-1260 frequency response analyzer (Solartron Analytical Co., Farnborough, Hampshire, UK) over the frequency range from 10^7 to 10^{-2} Hz, and the amplitude was 100 mV. Membrane samples ($1 \times 4 \text{ cm}^2$) were sandwiched between four platinum plate electrodes set in a Teflon cell. The resistance value related to the membrane proton conductivity was determined from the low intersect of the high-frequency semicircle on a complex impedance plane with the real axis. The proton conductivity (σ ; S/cm) was calculated from the impedance data with the following relationship:

$$\sigma = \frac{L}{RA} \quad (5)$$

where L is the distance between the electrodes used to measure the potential ($L = 1 \text{ cm}$), R is the impedance of the membranes, and A is the surface area required for a proton to penetrate the membranes (cm^2).

RESULTS AND DISCUSSION

Preparation and characterization of the crosslinked PVA/DGEBA membrane

FTIR spectra

Figure 1 shows the FTIR spectra of the pure PVA, DGEBA, and 20% crosslinked PVA/DGEBA membrane. A broad peak at a wave number ranging between 3000 and 3400 cm^{-1} , representing the hydroxyl group of PVA, was observed. In addition, a small sharp peak at 1700 cm^{-1} was noted. This was attributed to the presence of some residual vinyl acetate repeating units in the 99.5% hydrolyzed PVA molecules.¹⁷ The pure epoxy resin showed peaks at 912 and 841 cm^{-1} due to the oxirane group of epoxy resin.¹⁸ There were two new peaks at 1255 and 1510 cm^{-1} in the spectrum of the crosslinked PVA/DGEBA membrane. These two absorption peaks were characteristic of C—O—C bonds and phenylene, respectively. The peak at 1510 cm^{-1} was caused by the stretching vibration of aromatic C=C, and the peak near 1250 cm^{-1} was due to the aromatic aryl ether unit.¹⁹ The results indicated that the 20% crosslinked PVA/DGEBA membrane had the characteristic absorption band of DGEBA even after pretreatment. Although not quantitative, these observations proved that the PVA membrane was crosslinked by DGEBA.

Solubility

The solubility of the PVA membrane before and after crosslinking could also be used to prove the occurrence of the crosslinking reaction. Figures 2–4 show the swelling degree of the crosslinked PVA/DGEBA membrane in H_2O , DMSO, and ethanalamine at 80°C for 24 h. The pure PVA membrane readily dissolved in various solvents. After crosslinking, the crosslinked PVA/DGEBA membrane would swell and not dissolve in the solvents, which proved that the crosslinking reaction did occur inside of the PVA/DGEBA membranes.

Also, in Figures 2–4, we can see that the increasing amount of DGEBA strongly restricted the movement of polymer chains, so as to considerably restrain the swelling. With increasing time, the thickness and area were mostly unchanged.

TGA

Figure 5 shows the TGA curves of the pure PVA membrane and the crosslinked PVA/DGEBA membranes. For the pure PVA membrane, the decomposition began at about 220°C because of the loss of the hydroxyl group. The TGA curve of pristine PVA had two weight loss steps, in which the former was attributed to $-\text{OH}$ collapse and partial main-chain

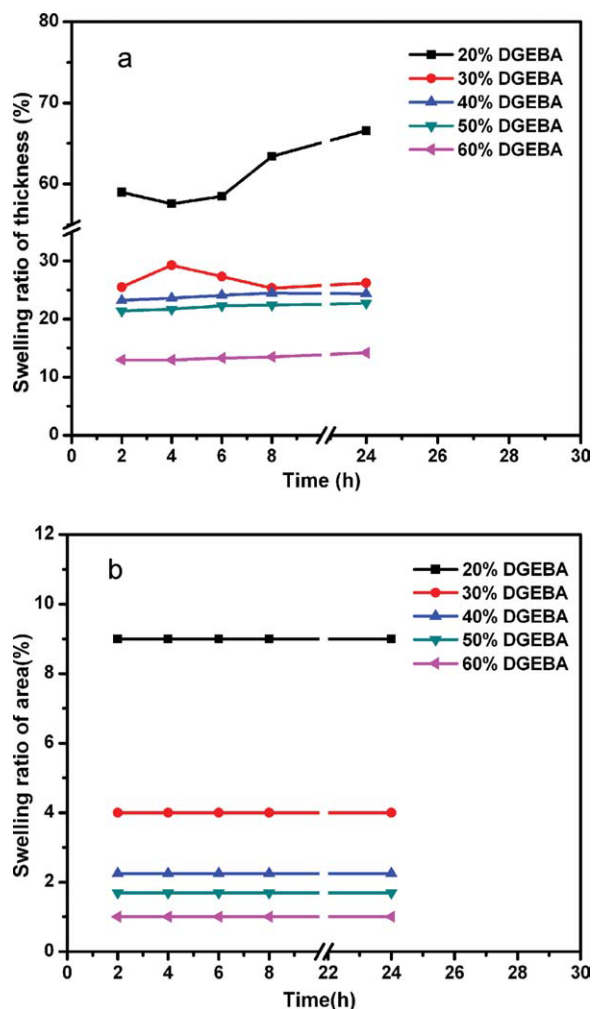


Figure 2 Swelling degree of the crosslinked PVA/DGEBA membranes in water at 80°C: (a) swelling of thickness and (b) swelling of area. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decomposition, and the latter was due to the residual main-chain decomposition.²⁰ The thermal stability of the PVA membrane was improved after crosslinking with DGEBA. The crosslinked PVA/DGEBA had three weight loss steps: the first step was caused by solvent release, the second step was assigned to $-OH$ collapse, and the last step was due to main-chain decomposition. The crosslinked PVA/DGEBA membrane became stable up to 250°C because of complexation between PVA and DGEBA.

Preparation and characterization of the phosphorylated and crosslinked PVA/DGEBA membranes

FTIR spectra and membrane appearance

Figure 6 shows the FTIR spectra of the 20% crosslinked PVA/DGEBA membrane and the phosphorylated and 20% crosslinked PVA/DGEBA membranes

(for simplicity, we use P-C-20 to represent phosphorylated and 20% crosslinked PVA/DGEBA hereafter). After the PVA/DGEBA was blended with poly(phosphoric acid), the intensity of $(P-O)H$ stretching at about 1000 cm^{-1} increased with increasing amount of poly(phosphoric acid). This peak shifted to lower wave numbers with increasing poly(phosphoric acid). The intense peaks at 998 cm^{-1} and small peak at 802 cm^{-1} were due to the stretching vibrations of $P=O$ for H_3PO_4 and $\nu(P(OH)_2)$ for $H_2PO_4^{4-}$, respectively.²¹ It was observed that the 20% crosslinked PVA/DGEBA membranes exhibited almost similar (but not identical) characteristics to those of the P-C-20 membranes. The peak at 1000 cm^{-1} shifted to lower wave numbers with increasing poly(phosphoric acid), evidence that the PPA was complexed with the 20% crosslinked PVA/DGEBA membrane.

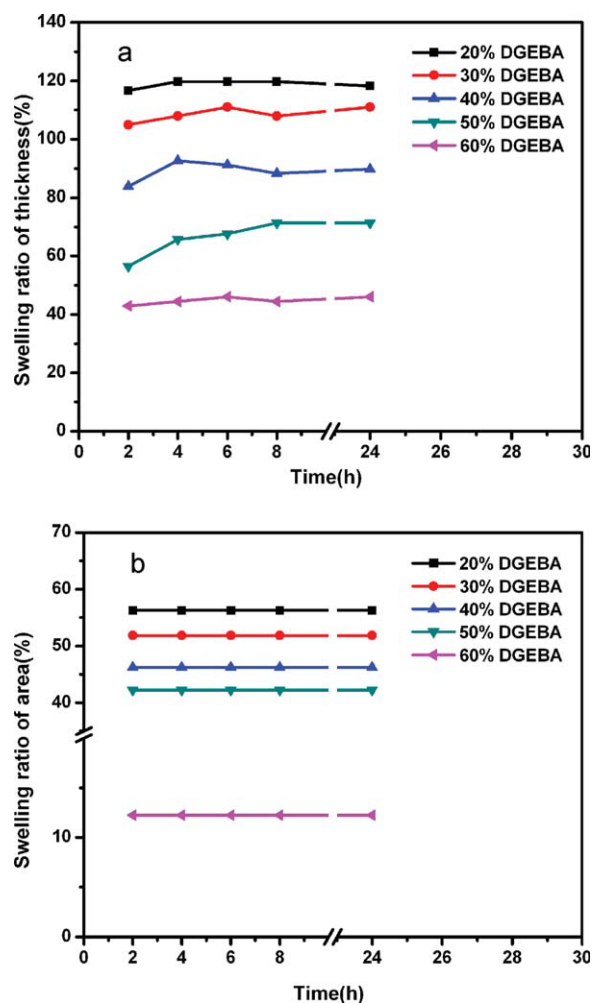


Figure 3 Swelling degree of the crosslinked PVA/DGEBA membranes in DMSO at 80°C: (a) swelling of thickness and (b) swelling of area. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

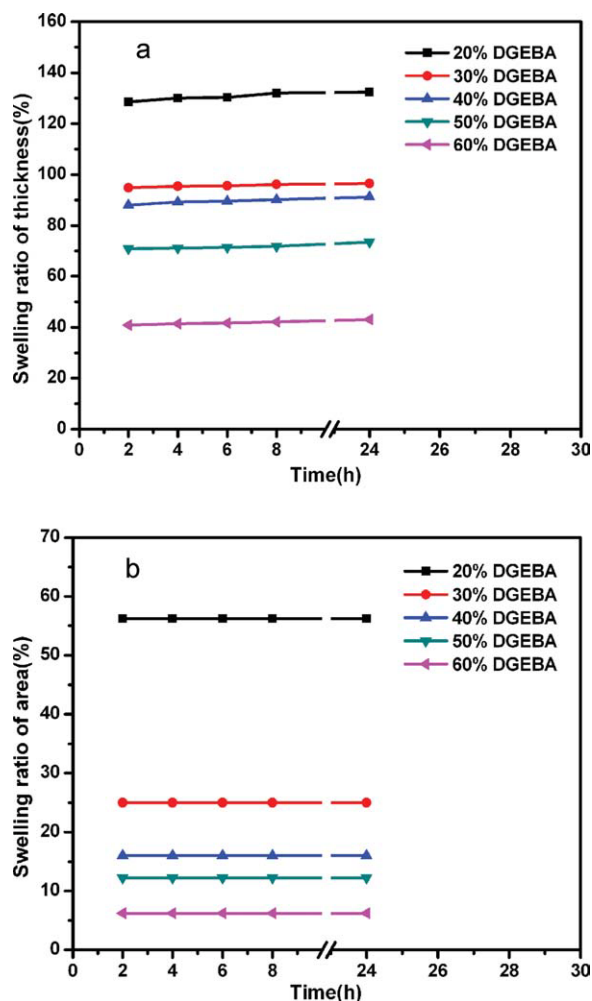


Figure 4 Swelling degree of the crosslinked PVA/DGEBA membranes in ethanolamine at 80°C: (a) swelling of thickness and (b) swelling of area. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

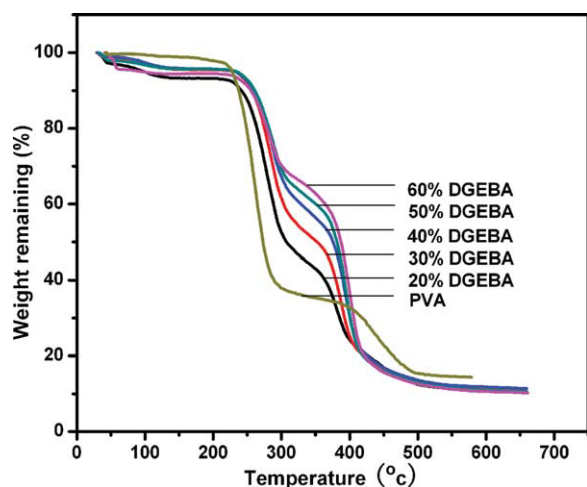


Figure 5 TGA curves of the pure PVA membrane and crosslinked PVA/DGEBA membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

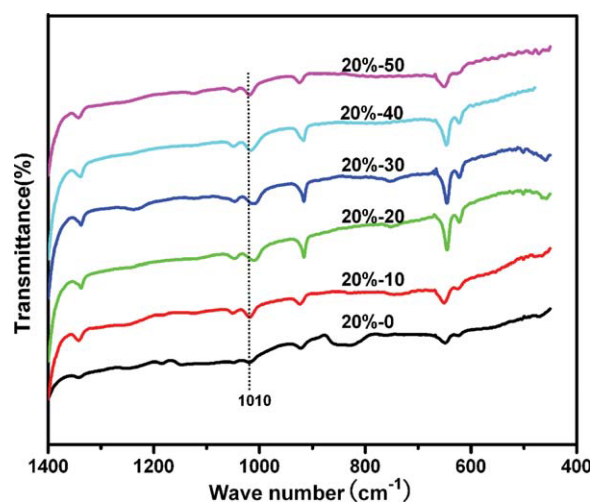


Figure 6 FTIR spectra of the 20% crosslinked PVA/DGEBA membrane and P-C-20 membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Figure 7 showed the photographs of 20% crosslinked PVA/DGEBA membrane and P-C-20 membrane. The appearance [Fig. 7(a)] of the 20% crosslinked PVA/DGEBA membrane was uniform and transparent and became opaque and dark after phosphorylation [Fig. 7(b)]. The reason was that PPA complexed with the 20% crosslinked PVA/DGEBA membrane, which resulted in this phenomenon.

TGA

Figure 8 shows the TGA curves of the P-C-20 membranes. The initial weight loss around 100°C was caused by the evaporation of the absorbed water within the membranes. The secondary weight loss, starting from around 200°C, was due to the loss of phosphoric acid groups and hydroxyl groups. The last weight loss started from around 350°C and was due to main-chain decomposition. In comparison with Figure 5, it could be seen that the final weight remaining for all phosphoric acid membranes examined at 700°C was around 40%, whereas that in Figure 5 was less than 20%. The reason was that the temperature of inorganic phosphorus was very high, so a high weight remained in Figure 8.

Water uptake and swelling ratio

The water uptake of the membrane could be increased by an increase in the ionic group content in the polymer chain, but most often, the uptake of more water would increase the swelling of a membrane. The relationship between the IEC and the phosphorylation time are shown in Table I.

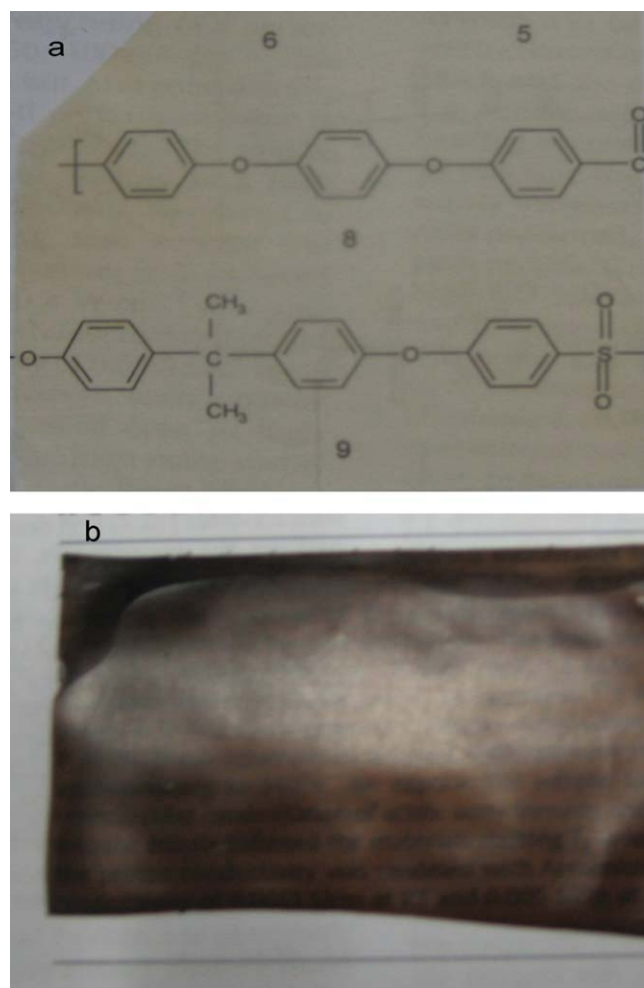


Figure 7 Photographs of the membranes: (a) 20% cross-linked PVA/DGEBA and (b) P-C-20 membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

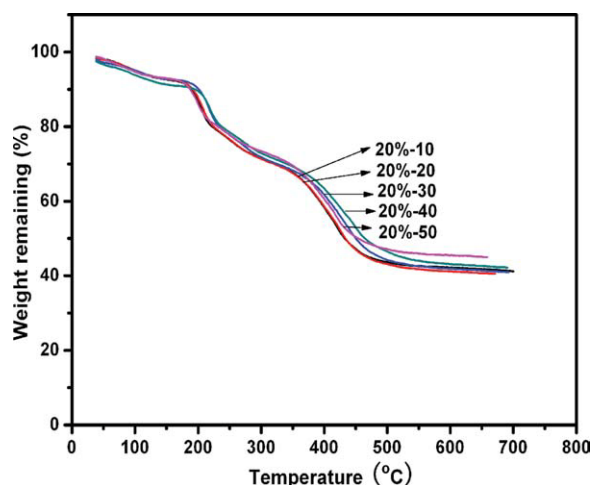


Figure 8 TGA curves of the P-C-20 membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
IECs of the P-C-20 Membranes

Sample	20%-10	20%-20	20%-30	20%-40	20%-50
IEC (mmol/g)	3.09	4.58	4.77	5.18	5.54

Both the water uptake and volume swelling ratio of the membranes are shown in Figure 9. As expected, higher IEC membranes absorbed more water, and the tendency of volume swelling was similar to that of the water uptake curves because the phosphoric acid groups enhanced the hydrophilic properties of the membranes. Membrane 20%-50, with the highest IEC of 5.54 mmol/g, showed the highest water uptake of 118% and a relatively low volume swelling ratio of 7.21%.

SAXS

The SAXS patterns of the relative scattering intensity and SAXS curves of the P-C-20 membranes are shown in Figures 10 and 11. From these two figures, we can obtain the ionic channel size information, which is connected with proton transfer. In the Nafion film, q of the ionic cluster in the dry state of the Nafion film was 0.31 nm^{-1} ; the Bragg spacing of the Nafion film was 3.22 nm ,²² as determined by calculation of the domain size of ionic cluster through Bragg spacing. Here, the scattering maximum generally appeared at $q = 0.07717 \text{ nm}^{-1}$, which was attributed to the difference in the electron density between the ionic domains and the surroundings or backbone group. From the Bragg law, it was obtained that the ionic channel size of the P-C-20 membrane was 81.38 nm , quite different from that of the Nafion film.

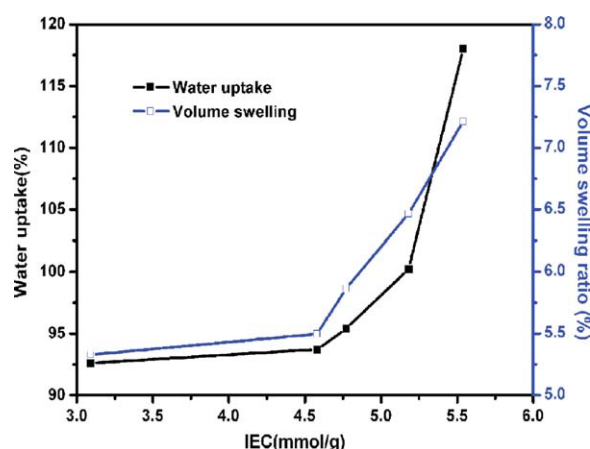


Figure 9 Water uptake and volume swelling ratio of the P-C-20 membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

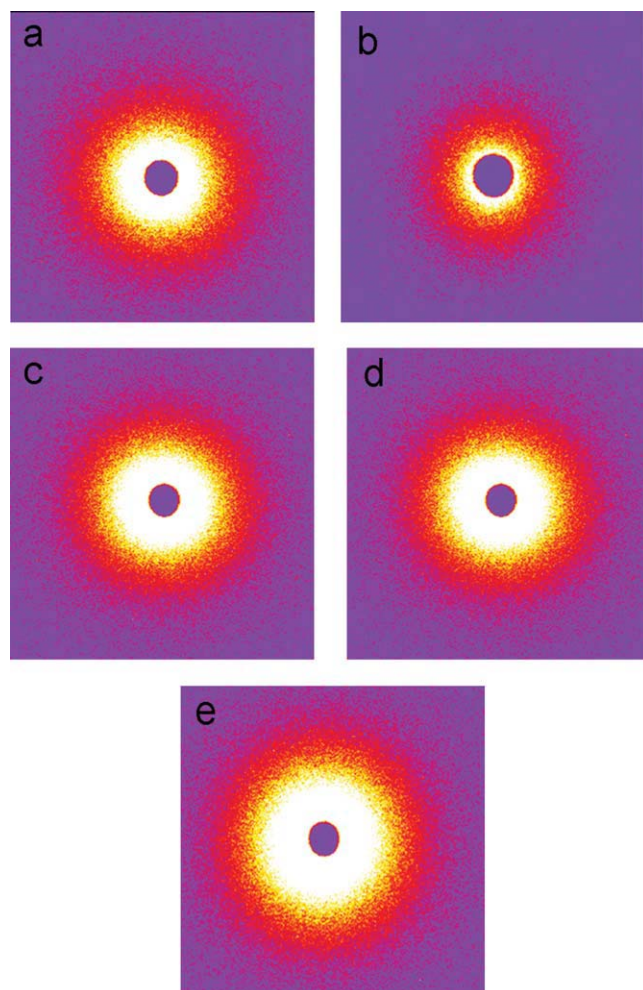


Figure 10 SAXS pattern of the P-C-20 membranes: (a) 20%-10, (b) 20%-20, (c) 20%-30, (d) 20%-40, and (e) 20%-50. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

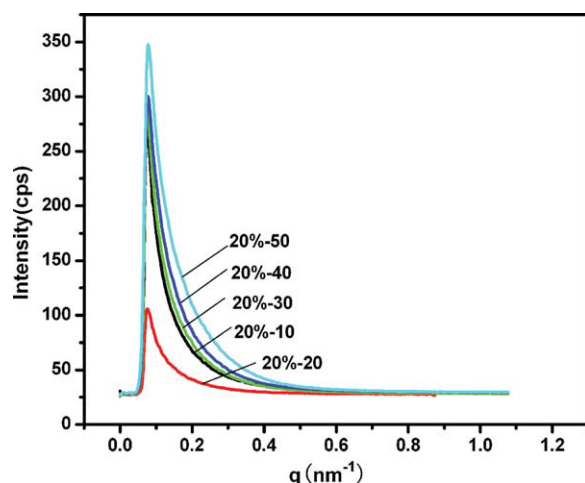


Figure 11 SAXS curves of the P-C-20 membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

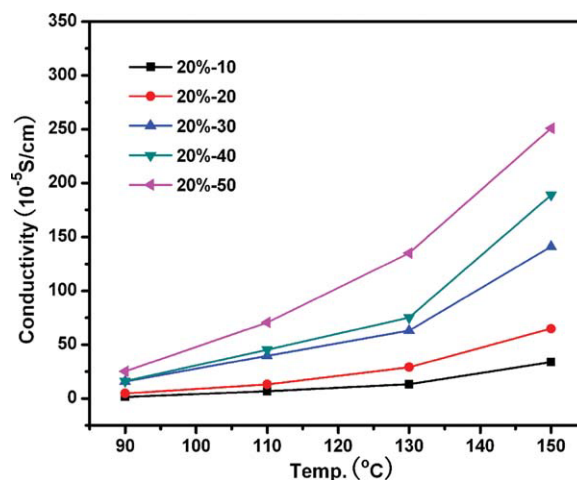
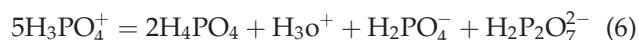


Figure 12 Proton conductivity of the P-C-20 membranes in anhydrous conditions at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Proton conductivity

It is well known that the mobility of protons in the Nafion membrane was strongly associated with water molecules absorbed inside the membranes. The strong dependence of the conductivity on the content and the nature of water inside the polymer membrane limited the operational temperature of the sulfonated polymer membranes. Consequently, the conductivity of the Nafion membranes decreased dramatically at higher temperatures, say, above 100°C under atmospheric pressure. As a widely used doping acid, H_3PO_4 exhibited effective proton conductivity, even in an anhydrous form, because of its unique proton conduction mechanism by self-ionization and self-dehydration:⁶



The conduction mechanism was suggested to be proton migration along the mixed $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ anionic chain by successive proton transfer and anion reorientation steps. As seen from Figure 12, the conductivity was found to increase with increasing temperature from 90 to 150°C and the acid content of the membrane. The membrane exhibited an acceptable ionic conductivity of about 2.51×10^{-3} S/cm under anhydrous conditions at 150°C. The main reason may have been that not only the phosphorylated and crosslinked PVA/DGEBA membrane maintain a high IEC (5.54 mmol/g) but also that the phosphoric group of the membrane had higher activation energies at high temperature.

CONCLUSIONS

A series of phosphorylated and crosslinked PVA/DGEBA membranes were prepared by immersion of

crosslinked membranes into PPA within a certain time. The properties of the crosslinked PVA/DGEBA membranes and phosphorylated and crosslinked PVA/DGEBA membranes were characterized with respect to FTIR, solubility, TGA, water uptake, swelling ratio, IEC, SAXS, and proton conductivity measurements.

The crosslinking reaction was confirmed by FTIR spectra and solubility change. The crosslinked membranes showed a higher thermal stability (20 wt % weight loss temperature (T_d) $\geq 250^\circ\text{C}$) than the pure PVA membrane ($T_d \geq 220^\circ\text{C}$).

The complexation of PPA and the crosslinked PVA/DGEBA membrane was confirmed by FTIR spectra and the exterior appearance change of the phosphorylated and crosslinked PVA/DGEBA membrane. TGA showed that the P-C-20 membranes began to decompose when the temperature reached 200°C . The water uptake (92.6–118%) of the membranes increased with increasing IEC. All of the volume swelling ratios of the membranes were at low levels (5.3–7.21%), which reflected that the phosphorylated and crosslinked PVA/DGEBA membrane had proper dimensional stability. Our SAXS study showed that the ionic channel size of the phosphorylated and crosslinked PVA/DGEBA membranes was 81.38 nm. The proton conductivity of the membrane (IEC = 5.54 mmol/g) achieved 2.51×10^{-3} S/cm at a temperature as high as 150°C in anhydrous conditions. This research demonstrated that the membranes maybe good candidates for PEMs for high-temperature fuel cells.

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