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Anhydrous proton exchange membranes at elevated temperatures: effect of protic ionic liquids and crosslinker on proton conductivity

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A series of novel anhydrous proton exchange membranes (poly(vinyl alcohol)–citric acid–ionic liquid (PVA– CA–IL)) were prepared using the low cost ionic liquids ethylammonium nitrate (EAN), diethylammonium nitrate (DEAN), and triethylammonium nitrate (TEAN) as conductive fillers in PVA support membrane. The properties of the PVA–CA–IL membranes can be controlled by changing the molar ratio of the PVA, ILs and CA. The thermal stability of PVA–CA–IL membrane was measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the microstructure was investigated using scanning electron microscopy (SEM) and the Anton-paar SAX Sess mc2 system (SAXS). The effects of temperature, ILs and crosslinker dosage on proton conductivity were also systematically investigated. The results showed that the PVA–CA–IL membranes had excellent performance. The proton conductivity of PVA–CA–EAN (mole ratio = 1: 0.05: 0.4) could reach up to 7.8 mS cm⁻¹ at 140 °C. The introduction of ionic liquid into PVA membrane constituted a new and efficient kind of anhydrous proton exchange membrane.

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1. Introduction

With the development of industry and the inadequacy of energy resources, the sustainable energy generation by proton exchange membrane fuel cells (PEMFCs) has received widespread interest among the researchers.^{1,2} In the past years, PEMFCs have been widely applied in a number of areas, such as aerospace, transportation, and as mobile power stations.³⁻⁵ The proton exchange membrane (PEM) serves as the electrode separator in addition to its primary role as a continuous medium for conducting protons from anode to cathode.6-10 The perfluoride-based membrane of Nafion® is the most common commercial PEM, which shows an outstanding chemical stability and excellent proton conductivity.11,12 However, the proton conductivity decreases significantly at temperatures above 80 °C due to the evaporation of water from the membranes, thus limiting proton mobility.13,14 In addition, the membrane has very high cost and high fuel permeability.^{15,16} These drawbacks of Nafion® hinder its future application. Therefore, the novel PEMFCs need to be developed in earnest.

In order to develop excellent PEMs, polymers such as polyimides, polybenzimidazole, poly(ether ether ketone)¹⁷ and poly(vinyl alcohol) (PVA) have been investigated.¹⁸⁻²⁰

membrane material because of its low cost, excellent fuel barrier, controllable physical properties and microstructures.²¹⁻²³ Won Rhim et al.²⁴ reported a novel crosslinked PVA membrane. The PEMs were prepared using poly(styrene sulfonic acid-co-maleic acid) (PSSA_MA) (PVA: PSSA_MA = 1:7) and clay 15A, which achieved an excellent inhibition methanol performance $(2.19 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1})$ and outstanding proton conductivity (0.023 S cm⁻¹). Gomes and Filho²⁵ successfully prepared a series of hybrid membranes using PVA, phosphotungstic acid and (diethylenetriamine)pentaacetic acid and found that the maximum conductivity could reach 8.59 imes10³ S cm⁻¹. Thanganathan and Nogami²⁶ synthesized a new class of hybrid nanocomposite membranes by sol-gel method, which contained PVA, phosphotungstic acid, 3-glycidyloxypropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane and glutaraldehyde, and the maximum conductivity was 2.5 imes 10^{-2} S cm⁻¹. All these membranes showed excellent proton conductivities, which were measured under a certain relative humidity. The proton transport in these PVA membranes is due to the mobility of water molecules in the water channel of these membranes. The proton conductivity would decrease significantly at high temperatures, due to the evaporation of water from the membranes, limiting proton mobility. The development of membranes, which can be applied at high temperatures under anhydrous conditions, is the need of the hour.27

Admittedly, PVA has attracted a lot of attention as an excellent

Ionic liquids (ILs) can not only replace water to maintain a channel for proton transfer, but can also donate protons. ILs are receiving considerable attention due to their unique properties,

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such as high thermal stability, high ionic conductivity and environmental friendliness.28 These advantages of ILs can overcome the restrictions imposed by temperatures. In other words, the PEMs with ILs can be used at higher temperatures and can also meet the demand of environmental protection. Ven et al.²⁹ prepared a high-temperature proton conductive membrane based on the IL 1-H-3-methylimidazolium bis(trifluoromethanesulfonyl)imide with polybenzimidazole (PBI). The highest proton conductivity could reach to 1.86 mS cm^{-1} at 190 °C. Eguizábal et al.30 reported a new kind of high temperature proton exchange membrane, which was composed of the 1-H-3-methylimidazolium bis(trifluoromethanesulfonyl) IL imide, NH₄BEA, NaY and PBI. In this, a proton conductivity of 54 mS cm⁻¹ was attained at 200 °C. However, the costs of these polymer matrices are high, so a membrane with low cost and high operating temperature is needed.

In this work, anhydrous proton exchange membranes of PVA have been prepared by the low cost protic ionic liquids (ethylammonium nitrate (EAN), diethylammonium nitrate (DEAN) and triethylammonium nitrate (TEAN)). The controllable structure of the membrane is provided by the PVA support and the proton conductivity can be achieved by the protic ionic liquids. The excellent properties of novel anhydrous proton exchange membranes are based on the properties of the above materials. The effects of temperature, ILs and crosslinker dosage on proton conductivity have also been systematically investigated.

2. Experimental

2.1. Materials

PVA (average MW 88 000–97 000 g mol⁻¹; 98–99% hydrolyzed), CA (\geq 99.8%) were provided by Alfa Aesar. Nitric acid, ethylamine (\geq 99%), diethylamine (\geq 99%) and triethylamine (\geq 99%) were purchased from Beijing Chemical Reagent Co. All chemicals were used without further purification.

2.2. Preparation of ILs

EAN, DEAN and TEAN (Fig. 1) were synthesized according to literature.³¹ In a typical preparation, 50 ml nitric acid was added to a round bottom flask and 83 ml ethylamine solution slowly dropped into it with vigorous stirring at 0 °C. Then, the mixture was purified with a rotary evaporator for removing the water and excess ethylamine. DEAN and TEAN were produced in a similar way.

2.3. Preparation of PVA-CA-IL membranes









Fig. 2 Possible reaction mechanism of cross-linked PVA-IL membrane. CA serves as a crosslinker; IL as proton conductor.

solution with concentrations ranging from 20 to 55 wt%. Then, an appropriate amount of CA was added into the mixture solution. The composite membranes were prepared by solution casting method at room temperature. The homogeneous hot solutions were poured into a specific mold,²⁵ and then dried at room temperature. The composite membranes were peeled off and cross-linked in a vacuum drying oven at 120 °C for 2 h. The crosslinking reaction is shown in Fig. 2. After cooling, the crosslinked PVA–IL membranes (PVA–CA–IL) were cut into pieces (*ca.* 1.5 × 2 cm).

2.4. Structure and morphology characterization

Fourier transform infrared (FT-IR) spectra were recorded on VERTEX-70 FT-IR spectrometer in the range of 4000 to 500 cm⁻¹. ¹H NMR spectroscopy was performed on a Bruker Avance II 300 NMR spectrometer at a resonance frequency of 300 MHz, using D₂O as the solvent and tetramethylsilane (TMS) as an internal standard. The morphologies of composite membranes were characterized using the scanning electron microscopy (SEM, JSM-7600F, EOL, Ltd., Japan). The structures of the membranes were investigated using Anton-paar SAX Sess mc2 system (SAXS) with Ni-filtered Cu K α radiation (0.154 nm) operating at 50 kV and 40 mA. The DSC curves were measured on a Perkin Elmer DSC-8500 instrument at a heating rate of 10 °C min⁻¹ under dry nitrogen.

2.5. Thermal stability

Thermogravimetric analysis (TGA) was carried out using a Rheometric Scientific TGA1500 (Piscataway, NJ) to investigate the thermal properties of samples. Studies were conducted under inert atmosphere of nitrogen using 8–10 mg samples with a heating rate at $10 \,^{\circ}$ C min⁻¹ from ambient temperature to 600 $^{\circ}$ C.

2.6. Proton conductivity

The proton conductivities of the membranes were measured using the electrochemical workstation (660D, CH Instruments, Co., China) using two copper electrodes, over the frequency range 1×10^6 Hz to 1×10^{-4} Hz, after placing in a nitrogen atmosphere under anhydrous conditions from 40 to 140 °C for 2 h before each measurement. The bulk resistance (R_b) was determined from the equivalent circuit analysis by using a frequency response analyzer. The proton conductivity was calculated according to the following equation:

$$\sigma = \frac{L}{R_{\rm b}A} \tag{1}$$

where σ is the proton conductivity, *L* is the distance between the electrodes, *A* is the area of the sample.³²

2.7. Mechanical property

Mechanical tensile tests were performed using a Universal Testing Machine (Yashima Works Co Ltd., model RTM-IT) at room temperature. The crosshead displacement speed of testing was set at the rate of 5 mm min⁻¹. The membranes with size of 6 mm \times 25 mm were used for testing in 35% RH.

Tensile strength $(T_s)^{33}$ is the stress at the maximum in the plastic portion of the stress–strain curve that may be sustained by the membrane. Tensile strength was calculated as follows:

$$T_{\rm s} = F/A_0 \tag{2}$$

Moreover, ductility is another important mechanical property. It is a measure of the degree of plastic deformation that has been sustained at fracture. Ductility (% EL) may be expressed as the percentage of elongation, which was the plastic strain percent at fracture and calculated as follows:

% EL =
$$(l_{\rm f} - l_0)/l_0$$
 (3)

where F is the maximum load, A_0 is the cross section area, l_f and l_0 are the fracture length and original gauge length, respectively.

3. Results and discussion

3.1. Composite membranes characterization

The Fourier transform infrared attenuated total reflection (FT-IR-ATR) spectra of the membranes were examined by FT-IR,



Fig. 3 FT-IR spectra of PVA-CA-IL membranes (molar ratio 1:0.02:0.2).





equipped with an ATR accessory, which measured both the top and bottom surfaces. As shown in Fig. 3, all membranes that we prepared exhibited strong absorbances at 1231 and 1718 cm⁻¹, which are ascribed to the stretching vibrations of C–O–C and of C=O, respectively. This indicates the occurrence of esterification.^{34,35} The stretching vibrations of C–N around 1100 cm⁻¹ were also observed in all membranes, which indicate the presence of ILs. Moreover, all membranes showed a very strong broad peak around 3300 cm⁻¹ for the hydroxyl (O–H) stretching vibration. From these results, it could be demonstrated that the PVA–CA–ILs membranes were prepared successfully.

Fig. 4 shows the TGA curves of PVA-CA (molar ratio 1 : 0.02), PVA-CA-EAN, PVA-CA-DEAN, and PVA-CA-TEAN (molar ratio 1:0.02:0.2) composite membranes. It is obvious that all membranes exhibit three main weight loss regions, which can be attributed to the thermal salvation, thermal dehydroxylation and deamination, and thermo oxidation.³⁶ Compared with PVA-CA membrane, the other membranes (PVA-CA-EAN, PVA-CA-DEAN and PVA-CA-TEAN) exhibit an initial weight loss (2-3%) between 50 and 160 °C, which is attributed to water desorption, indicating the presence of free water loaded by ionic liquids and the strong hydrogen-bond interactions between PVA and ILs.37 The second weight loss occurs at 160-300 °C, which can be attributed to the decomposition of ester bond,38 N-H,39 and NO₃⁻.⁴⁰ It is obvious that the weight loss of the PVA-CA-EAN membrane is more than those of the PVA-CA, PVA-CA-DEAN, and PVA-CA-TEAN membranes. It may be due to the molecular structure of EAN, which possesses more N-H groups per molecule than the others. Moreover, the starting decomposition temperatures (160-300 °C) of all the membranes we prepared are higher than those of traditional PVA membranes, which are usually below 80 °C.41 Finally, the weight loss at 300-500 °C is attributed to the decomposition of the PVA backbone.42 This TGA result illustrates that the composite membranes could be used up to 160 °C.

The morphologies of the PVA–CA–EAN membrane's surface and cross-section are shown in Fig. 5. The surface morphology of the composite membranes is smooth, homogeneous and dense (Fig. 5a). The morphologies of membrane surfaces



Fig. 5 SEM images of PVA–CA–EAN membrane: (a) surface; (b) crosssection.



Fig. 6 SAXS spectra of PVA-CA and PVA-CA-IL membranes.

indicate the formation of continuous conducting channels essential for enhancement of proton conductivity.⁴³ Fig. 5b shows the cross-section image. It is obvious that many little holes are on the cross-section, which could have resulted from the crosslinking reaction at high temperature. Due to the high temperature, the free water could get out of the composite membranes through these little holes. But the membrane was denser, indicating the importance of crosslinking reaction.⁴⁴

In order to further investigate the structure of the composite membranes, SAXS was used as the appropriate tool for elucidating the formation of the composite membrane. Fig. 6 shows the SAXS curves of four different composite membranes (PVA-CA, PVA-CA-EAN, PVA-CA-DEAN, and PVA-CA-TEAN). The SAXS curve of the PVA-CA membrane displays a 'knee' type shape. It is a single peak and the maximum value of scattering vector q is located at 0.18 nm⁻¹, which indicates that PVA-CA membrane is a semi-crystalline structure.⁴⁵ For the model of isolated domains embedded in a continuous matrix, the average distance between domains, d, can be estimated by the equation below.

$$D = 2\pi/q \tag{4}$$

From this equation, the average distance of the PVA–CA nano-crystallites is 34.9 nm, which is higher than that of pure PVA nano-crystallites (7–20 nm).⁴⁶ This demonstrates that the cross-linking reaction destroys the hydrogen bonds present in the poly(vinyl alcohol) chain, which are important to stabilize the polymer crystals.⁴⁷ When ILs are added into the PVA–CA membranes, the SAXS curves show shoulder peaks. The average values of q increase and the peaks become wider. These results





could be due to the intermolecular hydrogen bonds between OH (PVA) and N (ionic liquids), which shorten the average distance between domains.⁴⁸ This shortened distance is beneficial for proton conduction, which means that the ionic liquids play a dominant role in the formation of the proton exchange membrane. The incorporation of DEAN and TEAN cause the single peaks to become much broader than that of PVA-CA-EAN membrane, which indicates better homogeneity of EAN in the PVA structure. The heterogeneous distributions of DEAN and TEAN and TEAN in the PVA matrix lead to a relatively poor conductivity compared to that of PVA-CA-EAN membrane.⁴⁸

DSC was used to elucidate the dispersed state of IL in the crosslinked PVA-IL membranes. The PVA-CA-TEAN membrane and pure TEAN were selected for investigation because of the highest melting point of TEAN among the three ionic liquids, which makes it easier to observe the changes between the PVA-CA-TEAN membrane and pure TEAN. In the DSC curve of TEAN, the endothermic peak at *ca.* 117 °C (Fig. 7) is the melting peak of TEAN. However, it is obvious that the melting peak disappears after inserting TEAN into the crosslinked PVA structure. This implies that the TEAN embedded inside the membrane is well-dispersed with very small size. The highly dispersed state of TEAN likely results from interactions between TEAN and the polymer matrix. These interactions significantly reduce the size of the IL nanoaggregates.⁴⁹

3.2. Proton conductivity of PVA-CA-IL membranes

The proton conductivity is one of the most crucial parameters for characterizing a proton conducting membrane.⁵⁰ Fig. 8a shows the proton conductivity of the PVA–CA–IL (molar ratio 1:0.02:0.2) composite membranes. The proton conductivities increase sharply with the increase of the tested temperature. The membrane conductivities of PVA–CA–EAN, PVA–CA–DEAN, and PVA–CA–TEAN membranes could reach values of 1.1, 1.5, and 0.4 mS cm⁻¹ at 140 °C, respectively. It is obvious that the conductivity of PVA–CA–DEAN is higher than that of PVA–CA– EAN though the distributions of the DEAN are poorer than that of EAN. This may be attributed to higher ionicity of DEAN, which is beneficial for the proton conductivity.⁵¹ The proton conductivity of PVA–CA–TEAN is lowest among the three PVA–



Fig. 8 (a) Proton conductivities of PVA-CA-IL membranes as a function of temperature (molar ratio PVA : CA : IL = 1 : 0.02 : 0.2) and (b) temperature dependence of proton conductivity.

Table 1 E_a values of PVA-CA-IL membranes and Nafion 117

Composite membrane	Slope	Activation energy (kJ mol ^{-1})	
PVA-CA-TEAN	-7.24	60	
PVA-CA-DEAN	-9.17	76	
PVA-CA-EAN	-9.58	80	
Nafion 117	—	13	

CA-IL composite membranes. This is attributed to the great steric hindrance, which hinders the proton transfer.³

The apparent activation energy (E_a) for PVA-CA-IL composite membranes was estimated using the following equation:⁵²

$$\ln \sigma = -\frac{E_{\rm a}}{RT} \tag{5}$$

where σ is the proton conductivity, *R* is the universal gas constant, and *T* is the absolute temperature.

As shown in Fig. 8b, the ln σ depends almost linearly on 1/*T*. The E_a values of three PVA–CA–IL membranes are shown in Table 1. All the E_a values are higher than that of Nafion 117.⁵³ This indicates that the proton mobility in PVA–CA–IL composite membrane is limited, which can be attributed to the bulky size of the IL.⁵⁴

3.3. Effect of IL dose

In order to investigate the effect of IL dosage on the proton conductivity, we measured the conductivities of PVA-CA-EAN (molar ratio PVA : CA = 1 : 0.1) membranes with different dosage of IL at 100 °C. As shown in Fig. 9, with the increase of IL dosage, proton conductivity increases sharply when the mass percent of IL is higher than 42.4%. This may be due to the higher proton density (the proton number per unit volume), which can lead to an increase of proton conductivity of PVA-CA-IL composite membrane.⁵⁵ The maximum conductivity is 6.5 mS cm⁻¹ at 100 °C, which is higher than those of diethylethylammonium trifluoromethanesulfonate (IL) doped hybrid membrane (5.4 mS cm⁻¹) at 100 °C,⁵⁶ 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide doped sulfonated



Fig. 9 Effect of IL dosage on proton conductivity of PVA–CA–EAN membrane measured at 100 $^\circ\text{C}.$

poly(ether ketone) membrane (1.3 mS cm⁻¹)⁵⁷ at 100 °C and H_3PO_4 doped PVA/PAM membrane (5.25 mS cm⁻¹) at 180 °C.⁵⁸

3.4. Effect of CA dose

The crosslinker (CA) plays an important role in the preparation of PVA-IL composite membrane. First, the crosslinker can make the membrane more compact and rigid, which is beneficial to the Young's modulus, tensile strength and oxidative stability of membrane.^{59,60} Second and notably, the degree of crosslinking of the polymer could affect the proton conductivity of the PVA-IL composite membrane. Therefore, it is important to investigate CA dosage in PVA-IL (molar ratio PVA : EAN = 1 : 0.4) composite membranes. When the mole ratio of CA-PVA is 0.1: 1, with increase of temperature, the increase in the proton conductivity becomes relatively slow (Fig. 9a). This indicates that the mobility of the proton is limited by the highly crosslinked composite membrane. In other words, the high degree of crosslinking hinders the proton mobility.61 When the mole ratio of CA-PVA was changed to 0.05 : 1, the curve shows a sharp increase (Fig. 10a) with increasing temperature. The maximum conductivity reaches 7.8 mS cm⁻¹ at 140 °C. This implies that the lower degree of crosslinking is beneficial for the proton conductivity. However, it is to be noted that the tensile strength



Fig. 10 (a) Effect of CA dosage on proton conductivity of PVA–CA–EAN membrane measured at different temperatures and (b) temperature dependence of proton conductivity (ln σ –1000/*T*).

Table 2 $E_{\rm a}$ values and mechanical stability of PVA–CA–EAN membranes with different molar ratios and Nafion 117

Composite membrane	Slope	Activation energy (kJ mol ⁻¹)	Tensile strength (MPa)	Elongation (%)
PVA-CA-EAN	-8.97	75	10.7	320.4
(1:0.1:0.4) PVA-CA-EAN	-3.73	31	8.8	314.7
(1:0.05:0.4) PVA-CA-EAN	-9.58	80	_	_
(1:0.05:0.2) Nafion 117	_	13	14.2	_

decreases upon decreasing the mole ratio of CA–PVA (Table 2). When the degree of crosslinking is low enough, the structures of the membrane possibly cannot maintain a fixed shape at high temperature due to poor mechanical property. Thus, it is important to choose the optimal CA dosage for balancing the proton conductivity and mechanical property of the membranes.

Fig. 10b shows a linear relationship between $\ln \sigma$ and 1/T. The calculated values are shown in Table 2. Comparing the membrane with different CA dosages, the E_a of PVA-CA-EAN (mole ratio = 1 : 0.05 : 0.4) is lower. The lowest E_a value of proton conductivity indicates the least energy needed for proton transfer in the membranes.⁶² Upon fixing the CA dosage, the dosage of EAN is reduced by half. The result shows that the E_a of PVA-CA-EAN (mole ratio = 1 : 0.05 : 0.2) reaches up to 80 kJ mol⁻¹ (Table 2). All these results indicate the importance of CA and EAN doses for elevating the proton conductivity.

4. Conclusion

A series of novel anhydrous proton exchange membranes (PVA-CA-IL) were prepared using the low cost ionic liquids EAN, DEAN, TEAN, and the polymer PVA. All the composite membranes PVA-CA-IL could be used at high temperatures, and also had smooth morphologies of surfaces, capable of establishing continuous conducting channels to enhance the proton conductivity. ILs played an important role in the PVA-CA-IL anhydrous proton exchange membrane and were not

present alone in the composite structure. The IL and crosslinker dosages had an important effect on proton conductivity. The maximum conductivity was 7.8 mS cm⁻¹ at 140 °C, which was higher than reported values. This work may provide a new approach for the research and development of new anhydrous proton exchange membranes.

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