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PAPER

High-temperature proton exchange membranes from ionic liquid absorbed/doped superabsorbents[†]

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The development of high-temperature proton exchange membranes (HTPEMs) operated over 120 °C under anhydrous conditions is pursued worldwide in order to solve some core problems of current PEM fuel cells based on Nafion (CO tolerance, improved kinetics, water management, *etc.*). In the current work, two classes of HTPEMs based on absorbing and doping of the protic ionic liquid, 1-methylimidazolium trifluoromethanesulfonate ([MIm][Tfo]), into a 3D framework of poly(acrylic acid)–poly(ethylene glycol) (PAA–PEG) superabsorbent are successfully synthesized. The resultant membranes show high proton conductivity, good thermal stability and excellent mechanical strength due to the unique absorption property and interpenetrated polymer network of PAA–PEG, and good conduction of [MIm][Tfo]. Proton conductivities as high as 40.4 and 19.4 mS cm⁻¹ at 200 °C under anhydrous conditions are obtained in [MIm][Tfo] doped and absorbed PAA–PEG membranes, respectively. The long-term stability of the superabsorbent-based membranes at high-temperatures, in combination with simple preparation, low cost, scalable host and proton conductor, demonstrates the potential use of these materials in HTPEMs.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are electrochemical devices used for the conversion of chemical energy directly into electrical power having a high efficiency and a low environmental impact.^{1,2} At the heart of PEMFCs are the membrane materials, which show low conductivity at low humidity. The state-of-art Nafion-based or sulfonated membranes cannot function well at high temperatures (>80 °C) or low humidity (<80% RH) because of the required mechanism of proton transfer in water.^{3,4} These membranes have to be fully hydrated to maintain a high proton conductivity. This is accomplished by pre-hydrating the inlet gases in a precise and controlled manner. However, this hydration requirement brings about issues with flooding of the electrodes. Furthermore, fuel humidification of these membranes usually leads to increased proton conductivity, but also to extreme water swelling which is adverse for minimizing the interface resistance and improving the mechanical strength.⁵ By addressing these questions, the development of PEMs capable of operating above 100 °C is possible,⁶⁻⁹ since it will accelerate electrochemical reactions, avoid Pt catalyst poisoning, obviate unnecessary water management, simplify the design and reduce the cost of fuel cells.

One promising approach to elevate the operating temperature of PEMs is to employ anhydrous proton conductors as carriers for proton transport. Among these proton carriers, protic ionic liquids (PILs),^{10,11} and nonvolatile H₂SO₄ (ref. 12) or H₃PO₄ (ref. 13) are good candidates because of their thermal stability and high proton conduction. Great success has been achieved in elevating the operating temperature to >100 °C, although other adverse problems were generated, such as the leakage and corrosion of PILs^{10,11} and inorganic acids,^{12,13} resulting in the decline of the fuel cell performances. The combination of H₃PO₄ with polybenzimidazole (PBI) to fabricate PEMs operated at 200 °C is feasible,¹⁴ but the extremely difficult processability of PBIs due to their high melting temperature and limited solubility has hindered their large-scale use.¹⁵

Recently, PIL based PEMs have been developed as alternative membranes for high-temperature application.^{10,11,16-19} It is well known that the PILs can be easily produced through the combination of a Brønsted acid and Brønsted base, and they have a characteristic feature of forming hydrogen bonds *via* the Grotthuss mechanism. The protons are conducted by the intra-/ inter-molecular interactions.¹⁹ The resultant PEMs exhibit promising proton conductivity at temperatures above 100 °C under anhydrous conditions because of the negligible volatility and high thermal stability.²⁰ However, a major drawback is the long-term stability for these PEMs due to the PIL release and leakage. To enhance the proton conductivity of PEMs, one should increase the PIL loading, yielding free PIL in the membranes which can be more easily eluted by washing. Herein

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we introduce a new concept which employs the unique absorption and retention of the poly(acrylic acid)-poly(ethylene glycol) (PAA-PEG) superabsorbent material as a way to increase the proton conductivity of these membranes by either absorbing or doping 1-methylimidazolium trifluoromethanesulfonate ([MIm] [Tfo]), a typical PIL that can stably conduct protons at high temperatures. Superabsorbents, 3D networks of chemically or physically crosslinked polymers having a porous structure and absorbing a high percentage of solvents as well as the good solvent retention,²¹⁻²³ have attracted considerable interest because of the similar conduction mechanism and ionic conductivity to that of liquid systems.²⁴⁻²⁷ Using the unique absorption and [MIm][Tfo] retention, the resultant HTPEMs are expected to show high proton conductivity, good thermal stability, and reasonable mechanical strength. The focus of this article is on the microstructural characterization, proton conductivity, mechanical strength and [MIm][Tfo] retention of the new [MIm][Tfo] doped/ absorbed PAA-PEG membranes at high temperatures.

2. Experimental

2.1. Synthesis of 1-methylimidazolium trifluoromethanesulfonate

The [MIm][Tfo] was synthesized by stirring the mixture of 1-methylimidazolium with an equivalent molar amount of trifluoromethanesulfonic acid at 100 °C, as described in the literature.^{10,19} The resultant viscous oil was cooled to room temperature. The final [MIm][Tfo] (of high purity) is solid at room temperature and shows a melting point of around 88 °C.²⁸

2.2. Synthesis of the PAA-PEG superabsorbent material

The PAA-PEG hybrid was synthesized according to a simple twostep method which has been described in our previous reports.^{22,29,30} In detail, a mixture solution 1 consisting of an acrylic acid monomer (AA) and a crosslinker N.N'-(dimethylene) acrylamide (NMBA) was made by agitating deionized water (10 mL), AA (10 g) and NMBA (0.0025 g) in a water-bath at 80 °C. Under vigorous stirring, potassium persulfate (KPS) (0.025 g) was added to the above mixture. The AA monomers will be initiated by the thermal decomposition of KPS to form PAA prepolymers. As the polymerization proceeds, the viscosity increased gradually. When the viscosity of the PAA prepolymers reached around 140 mPa s⁻¹, another mixture solution 2 consisting of poly-(ethylene glycol) (PEG, $M_w = 20\ 000, 3\ g$) and NMBA (0.0025 g) was added. Under strong agitation, another 0.025 g of KPS was added into the above reagent solution until the viscosity of the system reached about 180 mPa s⁻¹. Finally, the reagent was poured into a Petri dish and cooled to room temperature for a subsequently gentle polymerization. After washing with deionized water, the product was dried under vacuum at 50 °C. The average thickness of the samples was in the range of 0.5-2 mm, which was measured before proton conductivity testing.

2.3. Preparation of [MIm][Tfo] absorbed PAA-PEG membranes

The dried PAA-PEG hybrid was immersed in [MIm][Tfo] aqueous solution (0.5-20 wt%). The absorption process was

carried out in a sealed bottle at room temperature for 3 days to reach absorption equilibrium. The resultant product was filtrated and dried under vacuum at 60 °C for 2 days to remove water to obtain [MIm][Tfo] absorbed PAA–PEG. The [MIm][Tfo] loading (g g^{-1}) was calculated according to eqn (1):

[MIm][Tfo] loading (wt%) =
$$\frac{m_{d1} - m_{d2}}{m_{d1}} \times 100\%$$
 (1)

where m_{d1} (g) is the mass of dried [MIm][Tfo] absorbed PAA–PEG, m_{d2} (g) is the mass of dried PAA–PEG composite, $m_{d1} - m_{d2}$ is the mass of [MIm][Tfo].

2.4. Preparation of the [MIm][Tfo] doped PAA-PEG membranes

The method is similar to that of synthesizing PAA-PEG. In detail, a mixture solution 1 of the AA monomer, crosslinker N,N'-(dimethylene)acrylamide (NMBA) and [MIm][Tfo] was prepared by agitating deionized water (10 mL), acrylic acid (10 g), NMBA (0.0025 g) and different amounts of [MIm][Tfo] (2-50 wt%) in a water-bath at 80 °C. Under vigorous stirring, KPS (0.025 g) was added to the above mixture. The polymerization reaction was carried out until the viscosity of the reactant system became 140 mPa s⁻¹. Another solution **2** of PEG of 4 g and NMBA of 0.0025 g was poured into the above prepolymerization solution, and initiator KPS (0.025 g) was added. Under stirring, the mixture solution was polymerized until the viscosity of the system reached about 180 mPa s⁻¹. The system was immediately cooled to room temperature for a subsequently gentle polymerization. After washing by deionized water, the product was dried under vacuum at 50 °C.

2.5. Measurement of proton conductivity

The proton conductivity of the sample was characterized by ACimpedance spectroscopy using an electrochemical potentiostat (VersaSTAT 3) in the frequency range of 0.01 Hz to 0.1 MHz and an AC amplitude of 10 mV in the temperature range of 25-200 °C.10,19,31 The resistance of the membranes was tested by a four-probe method with two Pt foils as the electrodes separated by 1 cm². The ohmic resistance associated with the membrane was determined from the high frequency intercept of the spectrum with the Z' axis, from which the proton conductivity can be calculated. The samples were cut into thin slices with the average thickness of around 100-500 µm and the system temperature was controlled from 25 to 200 °C by a thermocouple heating apparatus. All the measurements were carried out in a furnace with flowing dried air and thermally equilibrated at each temperature for at least 30 min prior to the measurements. The proton conductivity (σ) of the sample was then calculated from impedance spectra with eqn (2):

$$\sigma = \frac{l}{Rhd} \tag{2}$$

where *l* is the thickness (cm) of the membrane, *h* and *d* are the length (cm) and width (cm) of the sample, respectively. *R* (Ω) is the resistance of the sample obtained from the impedance plot. The measurements were done in duplicate with an error margin of 5%.

The conductivity stabilities of the [MIm][Tfo] doped PAA–PEG membrane at 21.4 wt% [MIm][Tfo] was examined by placing the membrane in the thermocouple heating apparatus for 90 h at 200 °C. The proton conductivity was measured by the same AC impedance method.

2.7. Dimension tests

To evaluate the dimension stability of the membranes against the temperature, the [MIm][Tfo] absorbed and doped PAA–PEG membranes at [MIm][Tfo] loadings of 24.5 and 21.4 wt%, respectively, were molded to a disc with a diameter of 2 cm. The specimen was kept in the temperature ranging from 25 to 200 °C for 30 min and the diameters were measured under anhydrous conditions because of the potential use in high-temperature PEMFCs.

2.8. Measurements of mechanical strength and gas permeation

The stress-strain tests of [MIm][Tfo] absorbed PAA-PEG were carried out using an Elastocon AB testing machine (Sweden) equipped with an oven such that the temperature can be adjusted in the range of -40 to 250 °C. The test conditions were as follows: the temperature was 120 °C, the length and crosssectional area of the specimens were around 8 cm and 0.75 mm², respectively. The tensile speed was controlled at 100 mm min⁻¹. The strain under stress is defined as the change in length relative to the initial length of the specimen. The tensile stress and strain at break of the [MIm][Tfo] doped PAA-PEG were calculated on the basis of the initial cross-sectional area. The tests were repeated five times and an average value was obtained. The tensile strength-elongation tests of the [MIm][Tfo] doped PAA-PEG membranes were carried out using an INSTRON Model 5583 testing machine (USA). The test conditions were as follows: the temperature is 25 °C, the size of the sample is 5 \times 5 \times 80 mm³, the distance between two square panels is 20 mm, and the crosshead speed is 20 mm min⁻¹. The strain under stress is defined as the change in length relative to the initial length of the specimen. The tensile strength and strain at break were calculated on the basis of the initial cross-sectional area.

The gas permeability was measured by the equal pressure method with a gas chromatograph (Hewlett-Packard Series II 5890), equipped with a packed-bed column and an integrator, monitoring the amounts of H_2/O_2 that permeated across the [MIm][Tfo] absorbed PAA–PEG membrane with [MIm][Tfo] loading of 24.5 wt% from one side to the other. A 158 µm thick membrane was set in a cell with a gas inlet and outlet, where the temperature (25–200 °C) was controlled. H_2/O_2 was supplied at a flow rate of 30 mL min⁻¹.

2.9. Characterizations

The morphology was observed and photographed by an S-4700 Hitachi cold field emission scanning electron microscopy (FESEM). The thermal gravimetric analysis (TGA) tests were conducted on a TA TGA 2050 instrument. The experimental procedure consisted of heating the samples in flowing nitrogen (99.999% purity, 100 mL min⁻¹) at a heating rate of 10 °C min⁻¹

from room temperature to 750 °C until all the samples were completely consumed. Fourier transform infrared (FTIR) spectra were identified using a Nicolet Nexus 470 FTIR spectrophotometer equipped with an IR data management system. The samples were milled to powders and made into pellets by adding to solid KBr, grinding and pressing. The curves of the samples were obtained using KBr as the background. The X-ray diffraction analyses of the samples were carried out using a D/MAX Uitima X-ray diffractometer of Rigaku Co., CuK α of 0.1540 nm wavelength, running at 40 kV and 30 mA, scanning from 2 to 65° at a speed of 5° min⁻¹.

3. Results and discussion

3.1. Synthesis of PAA-PEG superabsorbent material

The polymerization reaction of the PAA-PEG superabsorbent is an example of free radical initiated graft copolymerization, in which KPS is used as a thermal initiator. Homolytic cleavage of each peroxide bond (-O-O-) in the KPS provides two SO_4^{-} radical anions which react with water to form hydroxyl radicals (OH). The OH radicals have initiated the process of polymerization by generating the free radicals on the C = C' bonds of NMBA and acrylic acid and -OH of PEG. During the propagation step, crosslinking of PAA by NMBA has occurred and formed a 3D PAA network (A) because of the macrobiradical nature of NMBA. In the absence of the crosslinker NMBA, the resultant PAA would have a linear structure and less strength. In fact, the as-obtained PAA-PEG system is a complicated structure comprising of NMBA crosslinked PAA and NMBA crosslinked PAA-graft-PEG (B). The -OH groups in the PEG backbone can easily lose H atoms to form oxygen free radicals and subsequently form α -C free radicals. These radicals can be linked with the macrobiradicals on NMBA, and acrylic acid and NMBA, leading to the formation of a 3D network of PAA-graft-PEG (B). The plausible proposed mechanism for the synthesis of PAA-PEG superabsorbent is given in Fig. 1. Physical entanglement of the two networks in combination with the chemical bonds and hydrogen bonds results in the formation of a highmechanical strength PAA-PEG composite. The resultant PAA-PEG matrix can swell in [MIm][Tfo] aqueous solution and the closed pores would open because of the strong hydrophilicity of -COOH and -OH groups, resulting in the absorption of [MIm] [Tfo] solution into the 3D framework. The incorporation of [MIm][Tfo] aqueous solution into the PAA-PEG superabsorbent framework is primarily driven by the osmotic pressure present across the membrane.³² The absorption of [MIm][Tfo] aqueous solution by PAA-PEG causes the PAA-PEG framework to stretch and expand considerably in volume, the process of which can be briefly summarized by the following three steps:³³ (1) adsorption of H₂O on the surface of the PAA-PEG composite because of the hydrophilicity of -COOH and -OH groups; (2) relaxation of PAA-PEG macromolecule chains, and (iii) stretch of whole PAA-PEG macromolecule chains in [MIm] [Tfo] solution. After removal of H₂O, the remaining [MIm][Tfo] close to the PAA-PEG framework backbones form hydrogen bonds with -COOH and -OH groups. The [MIm][Tfo] away from the framework backbones are free.³⁴ In our studies, the samples with low [MIm][Tfo] loading exhibit rigidity but they



Fig. 1 Schematic of PAA-PEG superabsorbent material prepared by an aqueous solution polymerization route.

become more flexible at higher [MIm][Tfo] loading, indicating the presence of free [MIm][Tfo] within the membrane. The free [MIm][Tfo] plays an important role in proton conductivity of the membrane. and the PAA-PEG matrix. The observation of transverse patterns in the low magnification (Fig. 2d) and longitudinal nanochannels in the high-magnification SEM images (Fig. 2e)

3.2. Morphological characterization

The physical appearance of the as-synthesized PAA-PEG superabsorbent composite is shown in Fig. 2a, the microstructure of which is fully dense with no open pores. After the superabsorbent composite is soaked in a concentrated [MIm][Tfo] aqueous solution, its volume is appreciably enlarged due to the incorporation of water and [MIm][Tfo] molecules into the polymer framework. The internal 3D-interconnected porous microstructure of the superabsorbent revealed by the freezedrying technique is also shown in Fig. 2b. It is very interesting to note that all the pores are completely closed as the volume shrinks after drying at 60 °C, Fig. 2c, forming a dense membrane and preventing the loss of [MIm][Tfo]. At this stage, the electronegative atoms, such as N in enclosed [MIm][Tfo] molecules can form hydrogen bonds with -COOH and -OH groups abundant in the polymer framework of PAA-PEG. However, no pores are observed in the [MIm][Tfo] doped PAA-PEG membrane, indicating the molecular reaction of [MIm][Tfo]



Fig. 2 Cross-sectional microstructures of (a) as-synthesized PAA–PEG, (b) as-swollen in [MIm][Tfo] aqueous solution, (c) dried [MIm][Tfo] absorbed PAA–PEG membrane ([MIm][Tfo] loading: 24.5 wt%), and (d and e) [MIm][Tfo] doped PAA–PEG membrane ([MIm][Tfo] loading: 21.4 wt%) at low and high magnifications.

Downloaded by Texas A & M University on 24 March 2013 Published on 17 May 2012 on http://pubs.rsc.org | doi:10.1039/C2JM32637J indicates the successful design of an interpenetrated network structure.

3.3. Structural characterization

In the TGA analysis (Fig. 3a), the weight loss started at about ~400 °C for [MIm][Tfo], indicating a good thermal stability in high-temperature PEMs, while the PAA-PEG host shows a starting decomposition temperature of \sim 120 °C. However, the thermal stability is significantly enhanced by absorbing or doping [MIm][Tfo] into PAA-PEG, indicating a decomposition temperature of ~ 200 °C due to the loss of low molecular weight polymers.³⁵ In addition, the weight percent of [MIm][Tfo] absorbed PAA-PEG at ~500 to 700 °C is higher than that of [MIm][Tfo] doped PAA-PEG which may be the result of strong hydrogen bond interactions of [MIm][Tfo] with the PAA-PEG host in molecular scale.²¹ In the FTIR spectrum of the PAA-PEG host (Fig. 3b), for the peak at ~ 1248 cm⁻¹ corresponding to the O-H distortion in the carboxylic group, the peak intensity increases in both [MIm][Tfo] absorbed and doped PAA-PEG membranes.36 The weak peak at ~1160 cm⁻¹ for the C-O stretching vibration in PAA-PEG is shifted to 1170 cm⁻¹ in the PEMs. A new band at \sim 3460 cm⁻¹ appears in [MIm][Tfo] absorbed and doped PAA-PEG membranes. The new band and change in peak intensity and position indicate the bonded reaction between -COOH groups in PAA-PEG and [MIm][Tfo], showing that a hydrogen bond is formed between the hydroxyl (-OH) in -COOH of PAA-PEG and -N in [MIm][Tfo].37 Fig. 3c shows sharp diffraction peaks for powdered [MIm][Tfo] at $2\theta = 14.4^{\circ}$, 15.7°, 16.8°, 17.4°, 18.6°, 19.0°, 20.5°, 23.4°, 26.1°, 28.4°, 29.0°, and 35.6°. After incorporating with PAA–PEG, all the diffraction peaks disappear, indicating the molecular level interaction and complete coverage of [MIm][Tfo] by the PAA–PEG framework.³⁸

3.4. Absorption kinetics of [MIm][Tfo]

The most appealing properties of superabsorbents are their unique absorption to aqueous solution and the absorbed solution cannot be released even under some pressure. Using the absorption performances, superabsorbents have created a wide spectrum of applications, including tissue engineering,³⁹ artificial muscles,⁴⁰ contact lenses,⁴¹ drug delivery,⁴² sensors,⁴³ and dye reclamation.⁴⁴ Fig. 4 and Table 1 show the absorption kinetics of the PAA–PEG superabsorbent to the [MIm][Tfo] aqueous solution. The [MIm][Tfo] loading in PAA–PEG increases gradually with concentration. The highest [MIm][Tfo] loading of 24.5 wt% is obtained at the [MIm][Tfo] concentration of 20 wt%, indicating an excellent absorption ability of PAA–PEG for [MIm][Tfo]. The absorbed [MIm][Tfo] molecules are held in the 3D frameworks of the PAA–PEG host by H-bonding and physical interactions.

3.5. Proton conductivity of the membranes

An important feature of conductive composite materials is that their overall conductivity is strongly influenced by the contents of



Fig. 3 (a) TGA curves, (b) FTIR spectra and (c) XRD patterns of (i) [MIm][Tfo], (ii) PAA–PEG, (iii) 24.5 wt% [MIm][Tfo] absorbed PAA–PEG, and (iv) 21.4 wt% [MIm][Tfo] doped PAA–PEG membranes.



Fig. 4 [MIm][Tfo] loadings in the PAA–PEG superabsorbent at various concentrations of [MIm][Tfo] aqueous solution: (a) 0.5, (b) 1, (c) 2, (d) 3, (e) 5, (f) 6, (g) 10, (h) 15, and (i) 20 wt%.

Table 1 [MIm][Tfo] loadings in PAA-PEG superabsorbent material

| [MIm][Tfo] | 0.5 | 1 | 2 | 3 | 5 | 6 | 10 | 15 | 20 |
|--|------|-----|-----|-----|-----|-----|------|------|------|
| conc. (wt%) [MIm][Tfo] loading (wt%) | 0.57 | 1.2 | 2.2 | 3.7 | 7.7 | 9.6 | 17.4 | 22.1 | 24.5 |

conducting components in the materials.^{45,46} [MIm][Tfo] doped and absorbed PAA–PEG membranes with various [MIm][Tfo] loadings are fabricated and evaluated for their proton conductivity results. The proton conductivity of the membranes at 150 °C is shown in Fig. 5 as a function of the loading of [MIm] [Tfo]. The measured conductivity of the pure PAA–PEG is $\sim 10^{-8}$ S cm⁻¹ at room temperature and that of the membrane at 24.5 and 50 wt% [MIm][Tfo] for [MIm][Tfo] absorbed and doped PAA–PEG membranes is 15.2 and 19.1 mS cm⁻¹, respectively, indicating the main contribution of proton conduction from



Fig. 5 Proton conductivity of the [MIm][Tfo] doped and absorbed PAA–PEG membranes as a function of [MIm][Tfo] loadings. The proton conductivities were recorded at 150 $^{\circ}$ C under anhydrous conditions.

[MIm][Tfo]. An abrupt increase in conductivity is observed at around 3.7 and 21.4 wt% [MIm][Tfo] for [MIm][Tfo] absorbed and doped PAA–PEG membranes, respectively, indicating that the conducting channels from [MIm][Tfo] segments are almost isolated below the observed percolation threshold and conducting channels become interconnected at higher than these values. In the previous reports on graphite doped polyacrylate and Cu doped polyacrylamide conducting hydrogels, we have demonstrated the structure model of interconnected conducting-channels in the superabsorbent-based conductive composites (Fig. S1⁺);^{47,48} it is believed that the model is also suitable for [MIm][Tfo] absorbed and doped PAA–PEG membranes. Furthermore, Watanabe and co-workers have reported the potential proton transport mechanism, indicated by the intra-/ inter-molecular interactions.¹⁹

The relationship between the temperature and conductivity was expressed well with the activation energy (E_a) for the proton conduction behavior of [MIm][Tfo] absorbed PAA-PEG membranes derived from the Arrhenius equation as described: σ $= A \exp(-E_a/RT)$, where R is the gas constant, T is the absolute temperature, and A is the pre-exponential factor. For the proton conduction, it was found that the plots of log σ against 1/T gave straight lines in the temperature range of 25-200 °C for [MIm] [Tfo] absorbed PAA-PEG (Fig. 6), which was a typical anhydrous proton-conducting behavior. And a highest conductivity of 40.4 mS cm⁻¹ is observed for the [MIm][Tfo] doped PAA-PEG membrane at 200 °C, which is higher than the reported conductivity of PIL-based membranes.^{10,19} The activation energy, $E_{\rm a}$, which is the minimum energy required for proton conduction through the [MIm][Tfo] absorbed PAA-PEG membrane with [MIm][Tfo] loadings of 3.7 and 24.5 wt% was obtained from the slope in the linear fit, showing 16.57 and 12.75 kJ mol⁻¹, respectively, indicating that proton movement becomes easier in the membrane at high [MIm][Tfo] loading. The proton conduction in PIL has been ascribed to a combination of proton hopping (Grotthuss) and vehicular mechanisms.^{10,19,49} However,

88 °C conductivity(mS·cm⁻¹)] 0 -2 -3 24.5 wt% [MIm][Tfo] absorbed PEM log[3.7 wt% [MIm][Tfo] absorbed PEM 28.6 wt% [MIm][Tfo] doped PEM 1.8 wt% [MIm][Tfo] doped PEM 2.0 2.2 2.4 2.8 3.0 3.2 1.8 2.6 3.4 $1000/T (K^{-1})$

Fig. 6 Arrhenius plots for [MIm][Tfo] absorbed and doped PAA–PEG membranes. The thicknesses of 24.5 wt% [MIm][Tfo] absorbed PAA–PEG, 3.7 wt% [MIm][Tfo] absorbed PAA–PEG, 1.8 wt% [MIm][Tfo] doped PAA–PEG, and 28.6 wt% [MIm][Tfo] doped PAA–PEG membranes are 129, 175, 182, and 216 μm, respectively.





Fig. 7 Durabilities of proton conductivity for 17.4 wt% [MIm][Tfo] absorbed and 21.4 wt% [MIm][Tfo] doped PAA–PEG membranes. The measurement was carried out at 200 °C over 90 h. The membrane thicknesses are 153 and 268 μ m for absorbed and doped PEMs, respectively.

an obvious turn is observed for [MIm][Tfo] doped PAA-PEG membranes at around 88 °C, the melting point of [MIm][Tfo]. The E_a of the doped membranes at 1.8 wt% and 28.6 wt% [MIm] [Tfo] can be calculated as 10.64 and 9.51 kJ mol⁻¹ in the temperature range of 88–200 °C, respectively. The increased E_a in the temperature range of 25-88 °C indicates a dramatically decreased proton transport kinetics at low temperatures. The different trends may be explained from the different synthesis approaches and microstructure. In the [MIm][Tfo] absorbed PAA-PEG membranes, the [MIm][Tfo] is absorbed into the 3D framework in its aqueous solution. After drying, the water molecules are completely removed and the [MIm][Tfo] will bond onto the 3D framework of PAA-PEG in the molecular scale. In other words, [MIm][Tfo] and PAA-PEG would form a homogeneous phase, therefore the resultant membrane obeys the Arrhenius plots well. However, [MIm][Tfo] doped PAA-PEG membranes were synthesized by mixing [MIm][Tfo] with acrylic acid monomers and copolymerizing. The inevitable problems are the inhomogeneous incorporation of [MIm][Tfo] with 3D PAA-PEG, yielding separated phases from [MIm][Tfo] and [MIm] [Tfo] bonded PAA-PEG. The observed temperature-conductivity relationship is the result of competition between [MIm] [Tfo] and [MIm][Tfo] bonded PAA-PEG. In the temperature range of 22-88 °C, [MIm][Tfo] is in solid state and shows high activation energy for proton transport, and is in flowing state in the temperature higher than 88 °C, revealing a decrease in activation energy.

3.6. Conductivity stability

In order to study the stability of the proton conductivity at 200 °C and under anhydrous conditions, the [MIm][Tfo] doped PAA–PEG membrane at 21.4 wt% [MIm][Tfo] was left to operate at this temperature for 90 h. The results were depicted in Fig. 7, and it is obvious that no sign of degradation can be detected during the short 90 hour measurement, indicating promising membranes for HTPEMs.

3.7. Mechanical properties

The mechanical properties of the PEMs are an important factor for their practical application in fuel cells. Fig. 8a shows the representative stress-strain (σ - ε) plots of [MIm][Tfo] absorbed PAA-PEG membranes at various [MIm][Tfo] loadings at 120 °C. We can find that the [MIm][Tfo] absorbed PAA-PEG membrane shows good tensile stress and strain properties, which is due to the interpenetration and entanglement for the PAA network and the PEG network in PAA-PEG.^{21,22} The tensile stress at break increases with [MIm][Tfo] loading in the loading range of 0-3.7 wt% [MIm][Tfo], indicating that the [MIm][Tfo] can improve the mechanical properties by an interaction between the PAA-PEG matrix and the absorbed [MIm][Tfo]. However, the stress decreases in the loading range of 3.7-24.5 wt% [MIm] [Tfo] due to the plasticizing effect of [MIm][Tfo], which is consistent with H₃PO₄ doped PBI membranes.^{50,51} Differently, the strain at break increases with [MIm][Tfo] loading because the introduction of [MIm][Tfo] enhances the mobility of PAA-PEG molecular chains and flexibility. The maximum strain and stress at break in Fig. 8b are 709% and 13.19 MPa for the [MIm][Tfo] absorbed PAA-PEG at the [MIm][Tfo] loading of 24.5 $g \cdot g^{-1}$ and 3.7 wt%, respectively. Fig. 8c shows the σ - ε plots of [MIm][Tfo] doped PAA-PEG membranes at room temperature. There is a good correlation between the breaking stress and breaking strain, and the [MIm][Tfo] doped PAA-PEG membrane at [MIm][Tfo] of 7.1 wt% has a maximum breaking stress and breaking strain of 21.62 MPa and 821%, respectively (Fig. 8d), while those for pure PAA-PEG are 21.05 MPa and 620%, respectively. The slight increase may be ascribed to the strong hydrogen bonding interaction between [MIm][Tfo] and the PAA-PEG framework. The breaking stress decreases gradually but the breaking strain increases with [MIm][Tfo] loading. Combining mechanical properties and proton conductivity, the membrane at 28.6 wt% [MIm][Tfo] maybe the best, in which the maximum stress and strain at breaking are 12.72 MPa and 1214%, respectively.

3.8. Gas permeation and dimension stability

Increased fuel permeation in a hydrogen fuel cell not only results in inefficient fuel utilisation, but also leads to mixed electrochemical potentials and other fuel cell specific operational problems. The low fuel permeability is significant to enhance the fuel cell performances. Fig. 9a shows temperature dependence of H₂/O₂ permeability in the [MIm][Tfo] absorbed/ doped PAA-PEG membrane with [MIm][Tfo] loadings of 24.5 and 21.4 wt%, respectively. Compared with the reported data from Nafion 112 and PIL/sulfonated polyimide membranes,9,19 H2/O2 are less permeable in the hybrid membrane. For example, the H₂ and O₂ permeability coefficients for 24.5 wt% [MIm][Tfo] absorbed PAA-PEG at ~80 °C are both in the order of $\sim 10^{-13}$ cm⁻³ cm cm⁻² s⁻¹ Pa⁻¹ compared with that of $\sim 10^{-8}$ cm⁻³ cm cm⁻² s⁻¹ Pa⁻¹ for Nafion 112 and PIL/sulfonated polyimide membranes.¹⁹ H₂/O₂ permeability increases by orders of magnitude with increasing temperature. As a comparison, the H_2 permeability is little higher than O_2 . The significantly low fuel permeation is expected to enhance the fuel cell performances.



Fig. 8 (a) Stress–strain curves of the [MIm][Tfo] absorbed PAA–PEG at [MIm][Tfo] loadings (test temperature: $120 \,^{\circ}$ C): (i) 0.057, (ii) 1.2, (iii) 2.2, (iv) 3.7, (v) 7.7, (vi) 9.6, (vii) 17.4, (viii) 22.1 and (ix) 24.5 wt%, and (b) the plots of [MIm][Tfo] loading as a function of tensile strength and elongation. (c) Stress–strain curves of the [MIm][Tfo] doped PAA–PEG membranes at [MIm][Tfo] loadings (test temperature: $25 \,^{\circ}$ C): (i') 0, (ii') 7.1, (iii') 14.3, (iv') 21.4, (v') 28.6, (vi') 35.7, and (vii') 50 wt%, and (d) the plots of [MIm][Tfo] loading as a function of tensile strength and elongation.



Fig. 9 (a) H_2/O_2 permeability and (b) dimension stability as a function of temperature for [MIm][Tfo] absorbed and doped PAA-PEG membranes at [MIm][Tfo] loading of 24.5 and 21.4 wt%, respectively.

The dimension stability of the [MIm][Tfo] absorbed/doped PAA–PEG membrane against temperature is shown in Fig. 9b. The diameter remained unchanged at temperatures below 80 °C. Interestingly, there is a slight increase in diameter at temperatures higher than 100 °C. Generally, the PAA–PEG hybrid with high crosslinking degree is believed to be a thermosetting polymer composite. However, the [MIm][Tfo] absorbed or doped PAA–PEG membrane is thermoplastic because of the melting temperature of [MIm][Tfo] at around 88 °C. The characteristic feature of a thermoplastic resin is the thermal expansion at temperatures higher than its crystallization temperature. The little deviation is believed to have less influence on cell performances.

4. Conclusions

The high proton conductivity, low fuel permeation, good mechanical strength, [MIm][Tfo] retention and dimension

stability in combination with the long-term durability, simple preparation, low cost, scalable host and proton conductor demonstrate the potential use of these materials in hightemperature PEMs.

In summary, two new classes of [MIm][Tfo] absorbed and doped PAA-PEG membranes have been synthesized by incorporating [MIm][Tfo] into PAA-PEG superabsorbents as HTPEMs. The proton transfer is carried out via hydrogen bonds present in [MIm][Tfo] as well as those formed among [MIm][Tfo] and functional group hosts -OH in PAA-PEG. The open pores can be easily closed during the last step of the synthesis, effectively retaining the loaded [MIm][Tfo] during operation. Proton conductivities of as high as 19.4 and 40.4 mS cm⁻¹ at 200 °C under anhydrous conditions have been achieved for [MIm][Tfo] absorbed and doped PAA-PEG membranes, respectively. The maximum strain and stress of the membranes at break are 709% and 13.19 MPa for the [MIm][Tfo] absorbed PAA-PEG membrane and 12.72 MPa and 1214% for the [MIm][Tfo] doped PAA-PEG membrane, respectively. The new membranes also show good chemical stability at elevated temperatures under anhydrous conditions. The preliminary conductivity testing results show reasonable performance. Further optimization on membrane synthesis to enable thin-film fabrication and electrode configuration could lead to a commercially viable, low-cost, robust and high conductivity membrane for robust, high temperature PEMFC applications.

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