



Fabrication and characterization of phosphoric acid doped imidazolium ionic liquid polymer composite membranes



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ABSTRACT

Phosphoric acid (PA) doped imidazolium ionic liquid polymer composite membranes were fabricated using the approach of immersing the membranes based on imidazolium ionic liquids and polymers of sulfonated poly (ether ether) ketone (SPEEK) or polyvinylidene fluoride (PVDF) into pure phosphoric acid at room temperature. Imidazolium ionic liquids of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) or 1-butyl-3-methylimidazolium dihydrogenphosphate (BMIMH₂PO₄) link phosphoric acid molecules to polymer matrix. SPEEK is suitable to capture imidazolium ionic liquids owing to the strong interaction between imidazolium ionic liquid cations (BMIM⁺) and sulfonic acid group (–SO₃[–]). So the composite membranes based on SPEEK show promise as high temperature proton exchange membranes. Although all the components influence the conductivity values of these composite membranes, phosphoric acid molecular chains play a dominant role in the proton conduction. Proton conductivity of SPEEK/50%BMIMPF₆/4.6PA membrane at a level of $3.0 \times 10^{-2} \text{ S cm}^{-1}$ was achieved at 160 °C under anhydrous conditions. Although the tensile stress at break decreased from 3.12 MPa to 0.10 MPa when the temperature increased from room temperature to 160 °C, SPEEK/50%BMIMPF₆/4.6PA membrane still possesses a stable conductivity of $2.0 \times 10^{-2} \text{ S cm}^{-1}$ more than 600 h at 160 °C.

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1. Introduction

Research in high conducting membrane exploitation is fuelled by diverse technological needs. Clean energy technology, energy storage device, portable electronics and other power facilities require materials with high conductivity over the complex environment [1–4]. Owing to the high power density, high efficiency, fast start-up and low emission, proton exchange membrane fuel cells (PEMFCs) as a favorable candidate have attracted a wide attention in the field of clean energy sources [5]. Although PEMFCs have made a great progress, some key problems including high price in economy and low operation temperature in technology hindered their practical application [6]. At present, developing PEMFCs that can work at elevated-high temperature, close to or above 100 °C, was believed as an effective strategy to solve these difficult situations. Indeed, PEMFCs working at elevated-high temperature could bring about some advantages: enhancement of Pt catalyst tolerance of CO poison; simplification of the water management; heat recovered and elevation of the heat efficiency; and increment of the reaction rate of cathode and anode, thus improving the ionic conductivity [7,8]. So, encouraged by these merits, many attempts including modified Nafion® membranes [9], acid–base polymer membranes [10,11],

alternative sulfonated aromatic polymers and their inorganic composite membranes [12], blend polymer membranes [13] and ionic liquid/polymer membranes [14–16] have been made to develop advanced electrolyte membranes durable in an intermediate temperature range (100–200 °C) to meet the demands from high temperature PEMFCs.

Ionic liquids initially appeared as molten salts in use of liquid electrolyte at room temperature due to the special characteristics of extremely high ionic conductivity under anhydrous conditions, negligible vapor pressure, high thermal and chemical stability and a large electrochemical window [17–19]. Until the late 1990s, J. Fuller explored the freestanding membranes by incorporating ionic liquids of 1-ethyl-3-methylimidazolium (EMIM⁺) cation with trifluoromethane sulfonate (Tf[–]), tetrafluoroborate (BF₄[–]) and hexafluorophosphate (PF₆[–]) anions into polyvinylidene fluoride–hexafluoropropylene PVdF(HFP) copolymer [20], which made ionic liquids as a favorable candidate for the task of anhydrous conducting membrane explanation. After these, many efforts were made in the development of membranes based on ionic liquids with high conductivity at low relative humidity. D. Doyle demonstrated that the perfluorinated ionomer membranes such as Nafion® membrane can be doped with ionic liquid of EMIMTf, and the conductivity of membrane exceeded 0.1 S cm^{-1} at 180 °C. But the primary charge carriers in the polymer membranes were indeterminate [21]. Next, S.S. Sekhon deemed that cations and anions are mobile in electrolytes and they both contribute to conductivity through the

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research on line narrowing in the variation of ^1H and ^{19}F NMR line width with temperature in membranes [22]. Previous researches in our group yielded more information to prove that the ion mobility of ionic liquids played a dominant role to the whole conductivity of membranes [23]. Afterwards, H.N. Zhang and C. Huang revealed that the hydrophilic ionic domains were formed in the SPEEK/BMIMBF₄ membrane. These ionic domains were connected by small ionic channels that facilitate proton transporting process [24]. The reported high conductivity values of membranes owe to high conductivity of ionic liquids and the ordered structures. More dynamic systems with greater freedom for ordered array such as continuous conduction pathways for ion migration were propitious to gain high conductivity value [25]. In addition, polymerization ionic liquid (PIL) membranes through unsaturated bonds in ionic liquid monomer polymerizing also contributed to the development of membrane electrolytes [16,26–28]. Unfortunately, PIL membranes had to face a dilemma of the drop in conductivity by several orders of magnitude due to the confined ion mobility after polymerization.

Undoubtedly, these reported membranes succeed in conducting proton under anhydrous conditions, however, the improvement on conductivity is needed to cater for practical application yet. Inspired by phosphoric acid (PA) favoring the proton conduction in membranes as reported [10,11,29–31], we ever prepared PA doped membranes by introducing PA into imidazolium doped SPEEK membranes and the proton conductivity could reach $2.0 \times 10^{-2} \text{ S cm}^{-1}$ at 160 °C under anhydrous conditions for more than 350 h [29]. However, the effects of polymer structure, cations and anions of ionic liquids on the proton conduction in membranes were needed to be investigated comprehensively. Here we report our continued work to study the effects of all the components on the performance of PA doped ionic liquid polymer membrane systematically. As a model system, we selected imidazolium ionic liquids of BMIMPF₆ or BMIMH₂PO₄ and polymers of SPEEK or PVDF as contrastive studies. Ionic liquids based on imidazolium cations as the most important candidates have been extensively investigated to promote the safety and performance of solar cells, fuel cells, capacitors and lithium batteries [32–34]. Sulfonated hydrocarbon-based polymers as a substitute of Nafion® gained wide attention. Especially, SPEEK has been considered as a promising candidate material because of its unique features, showing lower cost, excellent mechanical properties and easy preparation [35]. In addition, PVDF as a semi-crystalline, hydrophobic and an engineering thermoplastic could offer many favorable properties like durability, mechanical integrity, stability and chemical resistance-properties [13]. These prepared membranes are denoted as SPEEK/BMIMPF₆/PA, SPEEK/BMIMH₂PO₄/PA and PVDF/BMIMPF₆/PA. Membranes based on ionic liquids and polymers were firstly fabricated with solution casting method, and then PA molecules were loaded via intermolecular hydrogen bonds. Through contrastive researches on the conductivity values of these prepared membranes, we confirmed that the imidazolium ionic liquid and sulfonic groups from polymer favored the ion conduction, yet these formed free PA molecular chains as channels dominated the proton conduction for these prepared PA doped membranes. Importantly, these prepared membranes showed the tunability characteristic of the content of ionic liquids with PA loading. Although the conductivity-mechanical property dilemma was frustrated, we expected to find ideal membranes with high-performance in integral property by optimizing these components.

2. Experimental

2.1. Synthesis and purification of BMIMPF₆ and BMIMH₂PO₄

N-methylimidazole, 1-chlorobutane and ethyl acetate as starting materials to synthesize the intermediate of 1-butyl-3-methylimidazolium chloride (BMIMCl) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals were used as received without further

purification. BMIMPF₆ was synthesized referring to the literature [36]. Nuclear magnetic resonance spectra were obtained using a Bruker Avance 600 MHz NMR Spectrometer. Dimethylsulfoxide (DMSO)-*d*₆ was used as the solvent. Tetramethyl silicane (TMS) for ^1H NMR spectra and H₃PO₄ for ^{31}P spectra were used as the internal standard. For BMIM⁺ cation, ^1H NMR, δ (ppm): 0.890 (t, 3H, CH₃); 1.263 (h, 2H, CH₂); 1.771 (m, 2H, CH₂); 3.838 (s, 3H, CH₃); 4.146 (t, 2H, CH₂); 7.615 (s, 1H, CH); 7.678 (s, 1H, CH); 9.020 (s, 1H, CH). For PF₆⁻ anion, ^{31}P NMR, δ (ppm): –152.90; –149.97; –147.04; –144.11; –141.18; –138.26; –135.33. BMIMH₂PO₄ was synthesized referring to the literature [37], but pure PA was adopted instead of 85% PA in the literature (the processes were shown in supporting information). The prepared viscous ionic liquids of BMIMPF₆ and BMIMH₂PO₄ were stored in sealed containers in order to prevent the moisture.

2.2. Membrane preparation

SPEEK polymer was synthesized by PEEK polymer (Jida High Performance Materials Company, Ltd., China) sulfonation with concentrated sulfuric acid and the degree of sulfonation (DS) of SPEEK was 47.2 mol%. SPEEK solution was prepared by dissolving SPEEK polymer in N,N-dimethylacetamide (DMAc) at 50 °C under magnetic stirring. Then ionic liquid was added into SPEEK solution under continuous stirring for additional 6 h. Membrane was obtained by spreading the solution on leveled glass plates and evaporating DMAc at 120 °C for 24 h. The preparation of membranes based on PVDF polymer (Guangzhou Zi De Fluoroplastics Co. Ltd., China) also followed the above process. The thicknesses of all membranes were at the range of 80–100 μm as checked by a microcalliper (5 measurements). PA doped membranes were prepared by immersing the membranes into pure PA (62.6 g polyphosphoric acid was dissolved in 10 g de-ionized water) in a sealed container for 72 h at room temperature.

2.3. Thermal and chemical stability

Thermal stabilities of ionic liquid and membranes were measured by a thermogravimetric analyzer (HCT-2, Henven Company, China) with 10 °C min⁻¹ heating rate under air atmosphere. All samples were preheated at 100 °C overnight before the test. Chemical stabilities of membranes were tested by immersing these samples into Fenton reagent (H₂O₂, 3 wt.%; Fe²⁺, 4 ppm) at 68 °C for 72 h.

2.4. Fine surface structure

The surface morphology of these membrane samples was observed with a Shimadzu SSX-550 scanning electron microscope. Gold nanoparticles were sprayed on the surface of membrane samples.

2.5. Methanol permeability

For these membrane samples, the ability to resist methanol permeation was measured using a home-made diffusion cell. The cell consists of two conical flasks (denoting as flask A and flask B) and each flask (about 100 cm³) has a columniform side-arm (about 0.41 cm²) to clamp membrane sample. Flask A was filled with methanol source (1 M, 3 M, 10 M or pure methanol) and flask B was filled with de-ionized water. Magnetic stirring was used to ensure the uniformity of solution. The change in methanol concentration of solution in flask B (*C*_B) was monitored using a gas chromatograph (GC-6820, Agilent, USA) with the column of 30 m in length, 0.32 mm wide bore and film of 0.25 μm in thickness (DB-FFAP, Agilent, USA). The methanol permeability *P* (cm² s⁻¹) was calculated in Eq. (1) [38]:

$$P = \frac{I C_B V_B}{A C_A t} \quad (1)$$

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