

Composite Polyphosphazene Membranes Doped with Phosphotungstic Acid and Silica

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Abstract Poly(bis(phenoxy)phosphazene) (SPBPP)/phosphotungstic acid (PWA)/silica composite membranes for fuel cells were prepared. The composite membranes were characterized by using FTIR, TGA and SEM techniques. Incorporation of PWA particles and silica particles into the SPBPP polymer matrix and a specific interaction between them were confirmed by FTIR spectra. TGA results showed that the composite membranes had high thermal stability. Homogeneous distribution of PWA and silica particles within the SPBPP matrix was verified by SEM micrographs. The doped membranes showed increased water uptake and proton conductivity.

Keywords: Sulfonated polyphosphazene; Composite membrane; Proton conductivity.

INTRODUCTION

The proton exchange membrane (PEM) in fuel cells performs a number of critical functions. It separates the fuel and oxidant, and provides the pathway for the protons transfer. DuPont's Nafion or other poly(perfluorosulfonic acid) membranes are widely studied as good fuel cell membranes, because their high proton conductivity combined with oxidative and chemical stability^[1]. However, the cost of the perfluorinated sulfonic acid membranes are too high for any serious (large-scale) commercialization for automotive or stationary power. A big part of the research efforts in the PEM is therefore devoted to the finding of suitable electrolytes that can be produced at moderate costs.

The heteropolyacid phosphotungstic acid (PWA) has been proposed as solid electrolyte membranes for fuel cell applications due to its high proton conductivity^[2–4]. Although the PWA in the solid state is a pure Brønsted acid and stronger than the conventional solid acids such as SiO₂, Al₂O₃, H₃PO₄, and zeolites, its use as electrolyte material is limited due to its inherent solubility in water^[5], which makes the membranes unstable and causes weak mechanical properties. It is believed that the incorporation of PWA in a host material such as SiO₂ and Al₂O₃ may circumvent the leaching problem while taking advantage of the high proton conductivity of this material^[6].

PWA has been incorporated into membranes to improve their structure and functionality and produce composite membranes. Sulfonated polymers that are typically used in PEMFC are suitable candidates as host materials for PWA as there are specific interactions between them that the inorganic conductor particles can embed into polymer matrix to improve the conductivity. The matrices of the sulfonated polymers include Nafion^[7–10], sulfonated polysulfone^[11–13], sulfonated poly(ether ether ketone)^[14] and sulfonated poly(arylene

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ether sulfone)^[15]. The hybrid polymer membranes had higher ionic conductivity than the native polymers. However, strong hydration and swelling of the membranes and the dissolution of PWA in water lead to detrimental consequences to fuel cells efficiency, therefore further stabilization of the PWA additive is necessary. This can be conveniently achieved by anchoring PWA on an oxidic support that is introduced into the polymeric matrix, and the modified PWA by SiO₂ and Al₂O₃ and their salt have been developed.

Polyphosphazenes are hybrid organic-inorganic polymers with a phosphorus-nitrogen chain backbone $-(RR'P=N)-_n$ and have valuable qualities as structural and functional materials. The potential uses of polyphosphazenes include membranes, biomedical materials, optical and electro-optical materials, solid polymer electrolytes and elastomers because of their many different chemical and physical properties depending on the tunable structure, which results from the two side-groups attached to each phosphorus atom. In order to improve the proton conductivity of polyphosphazene for using as proton exchange materials, in this paper, we prepared the sulfonated polyphosphazene-based composite membranes for proton exchange membrane fuel cells for the first time. SiO₂ and PWA were doped into the matrix of sulfonated poly(bis(phenoxy)phosphazene) (SPBPP) leading to a series of composite membranes. The silica is generated by using a tetraethylorthosilicate (TEOS) hydrolysis, which is promoted by the PWA particles, the PWA anchors on the SiO₂ to obtain further stabilization^[16]. We investigated the thermal and water uptake, proton conductivities of the composite membranes.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (NPCl₂)₃ was purchased from LanYin Chemical, China. Tetrahydrofuran (THF), dioxane, dimethylacetamide (DMAC), concentrated sulfuric acid (98%), phenol, phosphotungstic acid (PWA) and tetraethylorthosilicate (TEOS) were purchased from Aldrich Chemical Co. (NPCl₂)₃ was purified by two recrystallization processes from hexane and vacuum sublimation prior to use. Dioxane and THF were freshly distilled from sodium benzophenone ketyl. PWA was dried at 100 °C in an oven for 12 h before use (the number of hydrated water molecules per PWA molecule being 6)^[11]. Other chemicals were used as received.

Synthesis of Sulfonated Poly(bis(phenoxy)phosphazene) (SPBPP)

Poly(dichlorophosphazene) (PDCP) was prepared by ring opening polymerization of hexachlorocyclotriphosphazene ((NPCl₂)₃) at 250 °C in a sealed tube^[17, 18]. The resultant linear poly(dichlorophosphazene) (PDCP) was dissolved in dioxane, then 3 equivalents of sodium phenoxide was added to the solution. The reaction mixture was refluxed for 55 h, then it was poured into distilled water and the polymer was collected. The resulting polymer (PBPP) was purified by successive reprecipitation from THF to hexane. The obtained polymer was dried in a vacuum oven at 60 °C overnight. A known weight of the PBPP (2.0 g) was immersed in 80 mL of concentrated sulfuric acid, while stirring for 1 h at room temperature, the polymer dissolved, forming a viscous uniform solution. The solution was heated to 80 °C, with occasional stirring for 1 h, and then cooled to room temperature. Sulfonated polyphosphazene (SPBPP) was isolated by pouring the polymer/acid solution over ice and then filtering and washing the resulting precipitate. The degree of sulfonation (DS) of the obtained SPBPP estimated from ¹H-NMR was 25%, the ion exchange capacity (IEC) value was 1.1 mmol/g. The monomer structure of PBPP and SPBPP are shown in Fig. 1.

Preparation of the Composite Membranes

SPBPP was dissolved in DMAC to form 10 wt% solutions. PWA and TEOS were dissolved in DMAC, respectively. The PWA and the TEOS solutions were shortly mixed and then added to the SPBPP solution. The formed solution was mixed with a magnetic stirrer at RT for 24 h and poured into a Teflon plate. The solvent was evaporated under vacuum at 80 °C for 8 h, followed by 100 °C/24 h. The contents of SiO₂ in the hybrid membranes were 10% and 20% based on SPBPP, and the contents of PWA in the mixture were 5%, 10% and 15% based on SPBPP. The details of all the hybrid membranes are reported in Table 1.

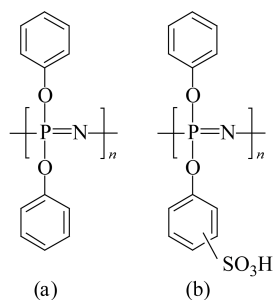


Fig. 1 (a) Poly[bis(phenoxy)phosphazene] and (b) sulfonated poly[bis(phenoxy)phosphazene]

Table 1. Details of membranes preparation

Sample name	SPBPP (g)	Silica (g)	PWA·6H ₂ O (g)	PWA/SPBPP (wt%)
SPBPP	0.40	—	—	—
SP-S10-P5	0.40	0.04	0.0208	5%
SP-S10-P10	0.40	0.04	0.0415	10%
SP-S10-P15	0.40	0.04	0.0623	15%
SP-S20-P15	0.40	0.08	0.0623	15%

FTIR

FTIR spectra were obtained by using a Horiba FT-720 Fourier transform spectrometer with a resolution of 2 cm⁻¹.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed with a TGA-Q500 instrument in a nitrogen atmosphere at a heating rate of 10 K/min over the range 20–700 °C.

Morphology

The cross section of membranes was examined with a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX). The samples were fractured by immersion in liquid nitrogen.

Water Uptake

The water uptake (WU) was determined by weight difference between fully hydrated membrane and dried membrane. The membranes were first equilibrated in water at 25 °C for 24 h, and then removed from water, subsequently wiped with blotting paper and weighed quickly. The water uptake of the membrane was calculated by the following equation:

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

where W_{wet} and W_{dry} were the weight of the wet and dry membranes, respectively.

PWA Extraction

The amount of PWA extracted from the composite membranes was characterized by the following experiment: the membranes were first dried in a vacuum oven at 100 °C for 24 h, then they were weighed to obtain an initial weight. The membranes were then immersed in deionized water at room temperature for 24 h, then they were finally dried in a vacuum oven at 100 °C for 24 h and weighted again. The extraction of PWA in membranes were studied by a weight loss percentage.

Proton Conductivity

Proton conductivity was measured by using a CHI660D impedance analyzer over the frequency range from 100 Hz to 0.1 MHz. It was calculated from the impedance data as follows:

$$\sigma = l / RS$$

σ , l , R and S denote the conductivity, distance between the electrodes to measure the potential, the impedance, the cross sectional area of the membrane perpendicular to the current flow, respectively.

RESULTS AND DISCUSSION

FTIR Analysis

FTIR spectra of PWA, SiO₂, SP-S10-P15 and SPBPP are given in Fig. 2. From spectrum (a), the characteristic bands of hydrated PWA can be noted at 1076 cm⁻¹, 974 cm⁻¹, 883 cm⁻¹ and 775 cm⁻¹, which are respectively attributed to the stretching vibrations band P—O, the terminal oxygen band W=O_t (O_t is the terminal oxygen atom), the bridging oxygen bands W—O_c—W (O_c is the corner-sharing oxygen atom) and W—O_e—W (O_e is edge-sharing oxygen atom)^[19]. As shown in the spectrum (b), the absorption bands at 1124 cm⁻¹ and 805 cm⁻¹ are due to the Si—O—Si asymmetric stretching vibration and Si—O symmetric stretching vibration. In the IR spectrum of the SP-S10-P15 composite membranes, the obvious absorption bands at 1077 cm⁻¹, 977 cm⁻¹ and 810 cm⁻¹ are contributed to the P—O stretching vibrations, W=O_t stretching vibrations and Si—O stretching vibrations. And these results indicate that PWA and silica have been successfully incorporated into the SPBPP polymer matrix. In addition, the symmetric stretching of SO₃ observed at 1025 cm⁻¹ for pure SPBPP gets shifted to 1020 cm⁻¹ when blended with PWA indicating that the PWA primarily interacts with the sulfonic acid moiety and is opposed to other functional units in the backbone of polymer.

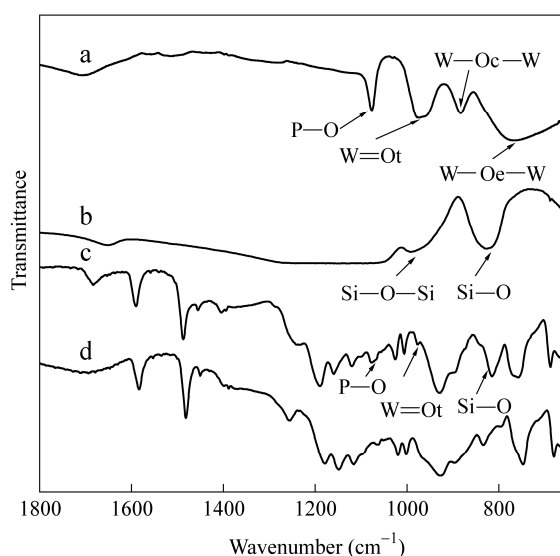


Fig. 2 FTIR spectra of (a) PWA, (b) SiO₂, (c) SP-S10-P15 and (d) SPBPP

Thermal Stability

The TGA curves of SPBPP membrane and composite membranes are shown in Fig. 3. The membranes exhibited four distinct weight losses in the thermal spectra. The weight loss of the membranes from 25 °C to 200 °C is attributed to desorption of water bonded to sulfonic groups of the polymers and the crystal water molecules of PWA particles. The second weight loss observed near 220 °C is attributed to the loss of sulfonic acid groups. It was observed that the temperature at which the splitting-off of the sulfonic acid groups was significantly increased for the two hybrid materials. This result suggests that the thermal stability of composite membranes was enhanced by the specific interactions between the sulfonic acid groups and the PWA particles. The third weight loss near 325 °C is due to the degradation of side chains of the polymer. Above 300 °C, the thermal decomposition of SP-S10-P15 increases compared to SPBPP, this maybe due to the degradation of the PWA. The last weight loss region occurs at 400 °C is due to degradation of the polyphosphazene backbone.

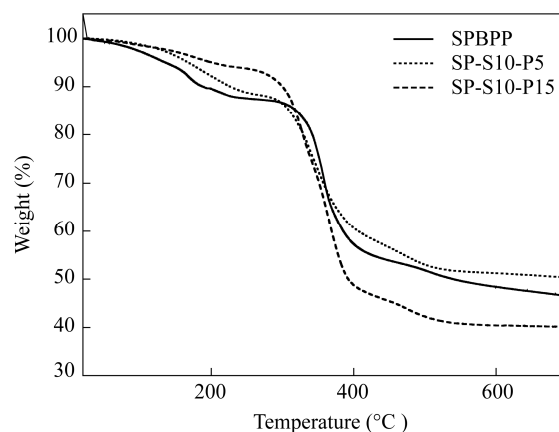


Fig. 3 Thermogravimetric curves of SPBPP and composite membranes

SEM Analysis

The SPBPP membrane shows a very homogeneous cross-section in the SEM image (Fig. 4a) while the solid silica particles were well dispersed in SPBPP matrix (Fig. 4b). EDX spectrum of the SP-S10-P10 membrane cross-section also shows the existence of PWA (P and W elements) and silica (Si element) in the SPBPP matrix (Fig. 5a). Further, PWA is homogeneously distributed within the SPBPP matrix which was confirmed by EDX mapping images (Figs. 5b and 5c), in which the Si and W elements are highlighted as bright dots.

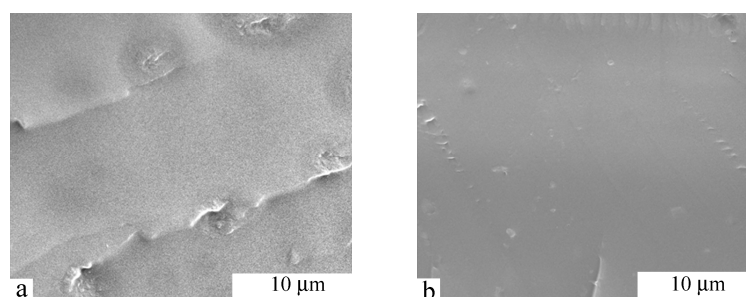


Fig. 4 Cross-section micrographs of (a) SPBPP and (b) SP-S10-P10 composite membrane

Water Uptake and Proton Conductivity

Water uptake of polymers has a great impact on proton conductivity, and high water uptake results in good proton conductivity. As shown in Table 2, the water uptake of the composite membranes including SP-S10-P5, SP-S10-P10, and SP-S10-P15 increases with the addition of PWA ranging from 5% to 15% and is greatly higher than that of the native membrane SPBPP. Subsequently, composite membranes SP-S10-P10 and SP-S10-P15 have significant improvements in the proton conduction test showing high conductivity values at 0.097 S/cm and 0.123 S/cm, respectively, compared with SPBPP (0.055 S/cm) and Nafion117 (0.09 S/cm). These results indicate the dependence of the proton conductivity on water uptake^[20] and then on the PWA addition. The increase in water uptake can be attributed to the distribution of PWA particles within the polymer matrix which makes aqueous phase in the composite membrane more continuous^[21]. However, PWA extraction test found the composite membranes treated in water showed elevated weight loss due to the water soluble material. Nevertheless, the PWA extraction could be reduced by increasing the load of silica as comparing two membranes SP-S10-P15 and SP-S20-P15 because PWA molecules were fixed up by silica network in membranes^[16]. Silica loading may also improve mechanical properties of membranes. As a result, membrane SP-S20-P15 containing 15% PWA and 20% silica displayed as good water uptake and proton conductivity as Nafion.

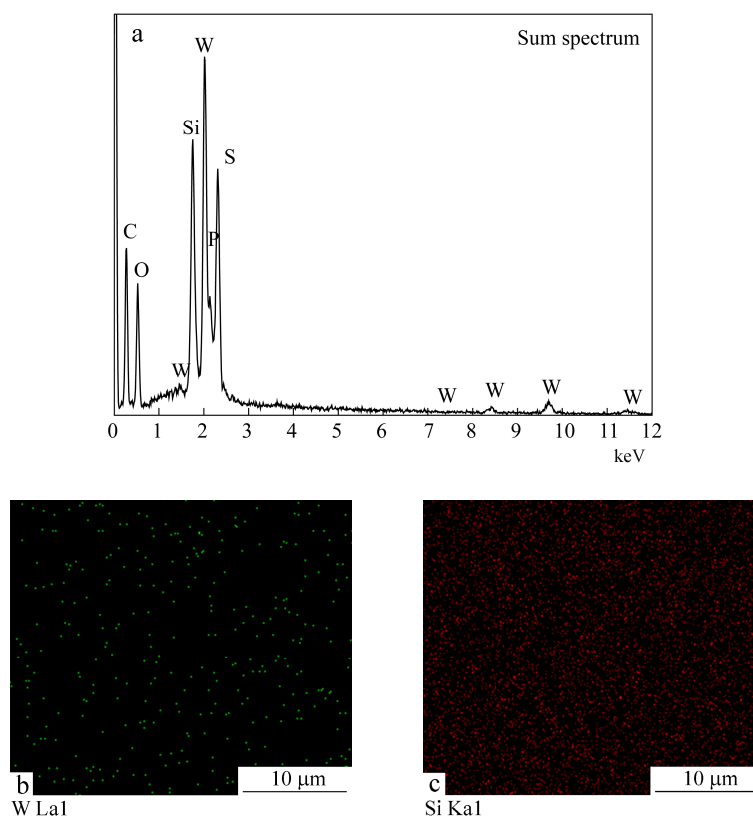


Fig. 5 (a) EDX measurement of the cross-section of SP-S10-P10 composite membrane; and EDX mapping images for the elements (b) W and (c) Si of the SP-S10-P10 cross-section

Table 2. PWA extraction amount, water uptake, proton conductivity for the composite membranes

Sample name	Weight loss (%)	Water uptake (%)	Conductivity (S/cm)
SPBPP	0.0	18	0.055
SP-S10-P5	1.3	25	0.053
SP-S10-P10	1.6	66	0.097
SP-S10-P15	1.9	110	0.123
SP-S20-P15	1.6	39	0.08
Nafion	0.0	35	0.09

CONCLUSIONS

Phosphotungstic acid and silica were successfully incorporated into polyphosphazenes and it resulted in the formation of SPBPP/SiO₂/PWA composite membranes. Well dispersion of the doped components in SPBPP matrix confirmed by FTIR and SEM indicated a specific interaction between PWA particles and the sulfonic acid of SPBPP polymer in the composite membranes. Consequently, the composite membranes showed elevated thermal stability compared to the native membrane SPBPP. In particular, the membranes SP-S10-P15 and SP-S20-P15 revealed significantly enhanced proton conductivity. These results suggest that the addition of PWA together with silica is an effective way for improvement of polyphosphazenes membranes in the application of PEM fuel cells.

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