High Temperature Polymer Electrolyte Membranes Based on Poly(2,5-benzimidazole) (ABPBI) and POSS Incorporated Ionic Liquid

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Abstract-This paper reported a method to modify polyhedral oligomeric silsesquioxane (POSS) particle into POSS ionic liquid (POSS-IL) and its incorporation into ABPBI/H_3PO_4 system to enhance the proton conductivities and mechanical properties of the membranes simultaneously. It was found that good dispersion of POSS-IL in the polymer matrix increased the tensile strength and Young's modulus of the membranes. For membranes with the same H_3PO_4 content, the incorporation of POSS-IL increased the conductivities of the membranes by about two orders of magnitude. The highest conductivity was achieved by ABPBI/10 wt% POSS-IL composite membrane, which was 7.6×10^{-2} S/cm at 200 ℃.

Keywords- POSS Incorporated Ionic Liquid; High Temperature PEM; Hydrogen Fuel Cell

I. INTRODUCTION

Polymer electrolyte membrane fuel cell (PEMFC) is regarded as an environmentally friendly technology with high efficiency [1]. The operation of the PEMFC at high temperatures (>120 ℃) is desirable because of the enhanced electrochemical reaction kinetics, reduced poisoning effect of fuel impurities, and better water and heat management [2]. One of the most promising membranes is acid-doped poly(2,5-benzimidazole) (ABPBI), due to the high thermal stability, good mechanical properties and low methanol crossover [1, 3, 4].

Polyhedral oligomeric silsesquioxanes (POSS) are silsesquioxanes with cage structures and have a formula of $(RSiO_{1.5})_n$, where R refers to an organic group or hydrogen [5]. In previous work done by Q. Liu [6, 7], POSS was incorporated into the H_3PO_4 doped ABPBI system, and the resulting composite membranes showed superior mechanical properties, high H_3PO_4 doping levels, and excellent proton conductivities.

Ionic liquids (ILs) are salts that exist in the liquid state at room temperature, which are composed of bulky, asymmetric cations (imidazolium, ammonium, etc.) and anions (CH_3COO^-, Cl^-, BF_4^-, etc.) [4]. Recent research found that ILs can be used in high temperature PEMs, due to their high thermal stability and high conductivity [8]. According to literatures, ILs based Nafion® [8] and PBI [4, 9] membranes showed excellent conductivities at high temperatures, and are considered to be promising membranes for high temperature PEM application. However, the incorporation of ILs caused reduced mechanical properties of the membranes, as well as a potential ILs leakage problem in fuel cell systems [4, 8, 9].

These drawbacks can be solved by incorporating fillers that can form "links" with the IL molecules. Until now, there is very limited information regarding the combination of nanofiller and ILs for PEM application. This paper reports the preparation of a POSS incorporated ionic liquid (POSS-IL) and its embedding into ABPBI/H_3PO_4 system to enhance the proton conductivities and mechanical properties of the membranes. The mechanical and thermal properties, microstructures, and proton conductivities of the ABPBI/POSS-IL composite membranes will be discussed.

II. EXPERIMENTAL

A. Materials

1) Chemicals

3,4-Diaminobenzoic acid (DABA), phosphorus pentoxide, 1-Butyl-3-methylimidazolium chloride [BMIM]Cl and dichloromethane were purchased from Sigma-Aldrich, UK. Methanesulphonic acid (MSA) was purchased from Fisher Scientific, UK. Octa Ammonium POSS (AM-POSS) was purchased from Hybrid Plastic, USA. Succinic anhydride was purchased from Acros Organic, UK. All the chemicals were used directly for the synthesis without further purification.

ABPBI was synthesized using the method reported by Kim et al [1]. 6.6 mmol (1.000 g) of DABA was mixed with 10 mL of methanesulphonic acid (MSA) and 1.0~1.5 g of phosphorus pentoxide (P_2O_5) in a 50 mL two-neck reaction flask with a magnetic oval stir bar (see Fig. 1). The synthesis was carried out at 140~160 ℃ for 3 hours with a rotary speed of 400 rpm under nitrogen (N_2) atmosphere. At the end of the reaction, a viscous polymer solution was obtained and sealed in a flask.
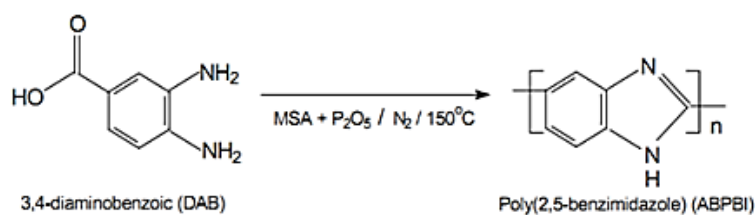
Fig. 1 Synthesis of ABPBI from DABA in MSA

2) Synthesis of POSS-IL

[BMIM]OH was synthesized as illustrated in Fig. 2. 25.0 g of [BMIM]Cl (0.14 mol) was mixed with 6.0 g of NaOH (0.15 mol) in dichloromethane and the mixture was then stirred vigorously at 25 ℃ for 24 hours. The precipitated NaCl deposition was removed by filtration, and the solvent was evaporated using a vacuum rotary evaporator. After washed with ethyl acetate for 3 times and vacuum evaporated again, the obtained product was dried in a vacuum oven at 70 ℃ for 24 hours.
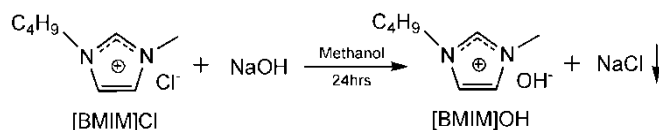

Fig. 2 Synthesis of [BMIM]OH from [BMIM]Cl via anion exchange in methanol

Fig. 3 shows the reaction route of synthesising POSS-IL. Octa-substituted carboxy-termini POSS (C-POSS) was synthesized using the method reported by Tanaka et al [10]. 2.0 g of AM-POSS (0.0017 mol) and 2 mL of trimethylamine were dissolved in 40 mL methanol. 3.0 g of succinic anhydride (0.0030 mol) was then added, and the reaction mixture was stirred at room temperature for 2 hours. After the reaction, the mixture was poured into chloroform, and the precipitates were collected by filtration. The precipitates were further purified by repeatedly washing with chloroform and drying at 80 ℃, until the weight remained constant to obtain C-POSS white powders [10].
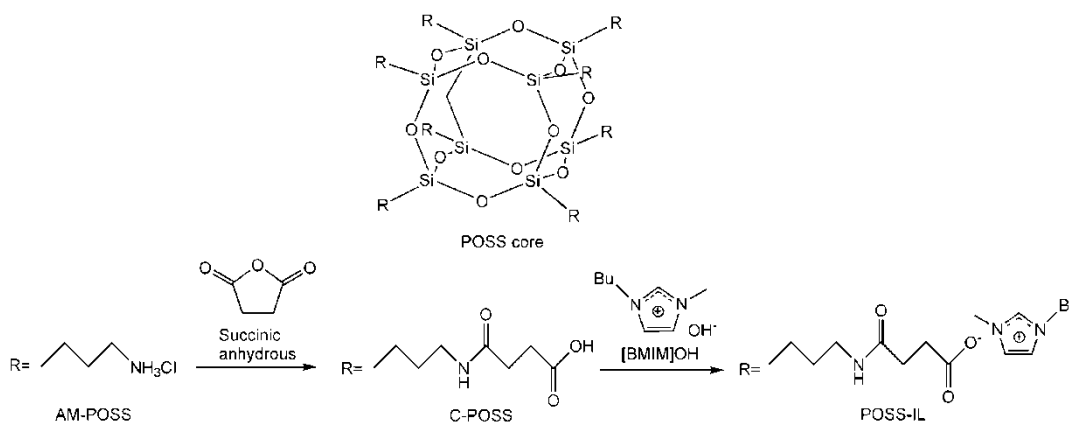

Fig. 3 Synthesis of POSS-IL from a two-step reaction

The preparation of POSS-IL was acid-base neutralization [11]. C-POSS was dissolved in methanol to form a homogeneous suspension, the reaction was then performed by titration of the suspension with 10 % [BMIM]OH-methanol solution. The methanol and water formed during the reaction were removed using vacuum rotary evaporation, followed by drying at 60 ℃ in vacuum for 24 hours to obtain POSS-IL.

3) Preparation of ABPBI-POSS Ionic Liquid Membrane

Different amounts of POSS [BMIM] (Table 1) were dissolved in MSA, and were added into the as-synthesized ABPBI-MSA solutions. The mixtures were then stirred at 70 ℃ for overnight to form a homogeneous composite solution. The solutions were poured into Petri dishes, and heated gradually to 150 ℃. Membranes were obtained after the solvent was fully evaporated.

TABLE 1 POSS-IL CONTENTS IN THE ABPBI MEMBRANES

POSS-IL, g	0.00	0.05	0.10	0.15	0.25
ABPBI, g	1.00	0.95	0.90	0.85	0.75
POSS-IL contents, wt%	0	5	10	15	25

B. Characterizations

1) Fourier Transform Infrared (FTIR) Spectroscopy

IR spectra were recorded by using an FT-IR spectrometer (FTIR-8400, Shimadzu Corp., Japan) with 64 scans in the region of 4000-600 cm^{-1}.

2) Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) instrument (2960 SDT V3.0F, TA Instruments Inc., USA) was used to measure the thermal degradation of [BMIM]OH, POSS-IL and its composite ABPBI membranes. Samples were heated under nitrogen and their weights were measured from 25 ℃ to 600 ℃ at a heating rate of 10 ℃/min.

3) Tensile Tests

Mechanical properties of the membranes were measured using a universal tensile test machine (Model Lr50K Plus, Lloyd Instrument, UK). According to ASTM D638, the gauge length was 10 mm, width was 2.5 mm, the crosshead speed was 50 mm/min and the load cell was 1.0 kN). To ensure the membrane reaches a steady state, all samples were held at ambient condition for 30 minutes before tests.

4) Conductivity Tests

The impedance of the membranes was measured using Electrochemical impedance Spectroscopy (EIS), where a Solartron Analytical 1280 Electrochemical Measurement Unit (1280 EMU, Solartron Analytical Ltd.) was employed. The frequency range was 1M to 100 Hz and the AC amplitude was 100 mV. The samples were sandwiched between two circular platinum (Pt) electrodes (diameter 2.00 mm, purity 99.95 %, Goodfellow Cambridge Ltd.), and were fixed firmly into a PTFE cell with two springs. A piece of pressure indicating film (Pressurex®) was used to measure the compression pressure applied on the membrane, which was between 350 psi and 1400 psi. The cell was then placed into a tube furnace to conduct the impedance measurement at elevated temperatures. The proton conductivity (σ) of an electrochemical cell was calculated using Eq. (1).

$$\sigma = d/(R \times A) \tag{1}$$

where d is the distance between two electrodes, i.e. the membrane thickness in this case, cm; R is the bulk resistance of the sample with the unit Ω; A is the contact area.

III. RESULTS AND DISCUSSIONS

A. FTIR Measurement

The synthesis of POSS-IL was characterized using FTIR as shown in Fig. 4. For POSS-IL and [BMIM]OH, the peaks related to imidazolium ring are found at 1566 cm^{-1} (in-plane C-C/C-N stretching vibrations of imidazolium ring) and 1250 cm^{-1} (symmetrical C-H vibration of imidazolium ring) [12]. The peaks related to symmetrical stretching and deformation vibrations of alkyl chains are found at around 2971 cm^{-1} and 1390 cm^{-1}, respectively. The peak at 1456 cm^{-1} is owing to the C-H bending vibrations of –CH_3 groups.
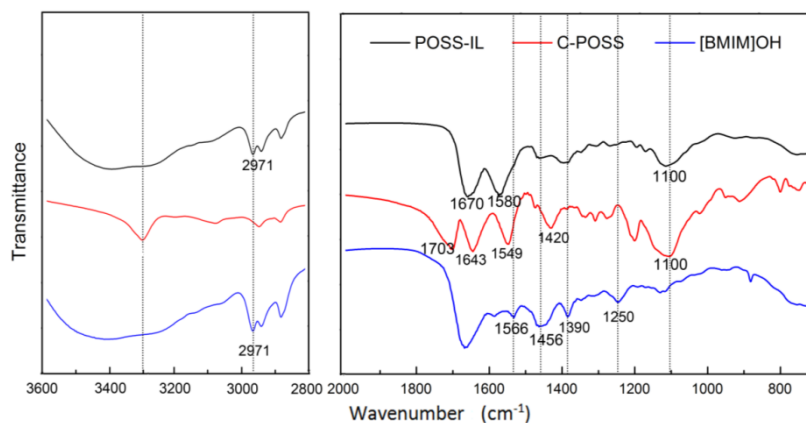

Fig. 4 FTIR spectra of POSS-IL, C-POSS and [BMIM]OH

For C-POSS compound, the presence of amide groups is proven by the peaks at about 3300 cm^{-1} (stretching vibration of secondary NH groups), 1643 cm^{-1} (stretching vibration of C=O groups) and 1549 cm^{-1} (bending vibration of NH groups). The peaks at around 1703 cm^{-1} (stretching vibration of C=O groups) and 1420 cm^{-1} (bending vibration of O-H groups) indicate the presence of COOH groups. The silicon cage is determined by a broad peak at around 1100 cm^{-1} which refers to the vibration of Si-O-Si structure [13].

For POSS-IL, the presence of Si-O-Si cage structure is confirmed by a broad peak at around 1100 cm^{-1} [13]. The peaks referred to the amide groups left shift to 1670 cm^{-1} (stretching vibration of C=O groups) and 1580 cm^{-1} (bending vibration of NH groups). The peaks of O-H bending at 1420 cm^{-1} and C=O in carboxylic acid group at 1703 cm^{-1} disappear after the reaction, owing to the ionic reaction between COO$^-$ and [BMIM]$^+$.

The FTIR spectra of ABPBI/POSS-IL composite membrane are shown in Fig. 5. For all of these membranes, the typical peaks of $H_2PO_4^{1-}$ are found, including the symmetrical P-O(H) stretching at 866 cm^{-1}, owing to the presence of H_3PO_4 in the membrane. For both types of POSS-ILs incorporated ABPBI membranes, their FTIR spectra are combinations of those of ABPBI and POSS-ILs. Most peaks of POSS-ILs are overlapped by those of the ABPBI, such as the amide C=O in POSS-IL being overlapped by C=C and C=N in ABPBI polymer. Compared to 0 wt% membrane, the new peaks in the spectra of ABPBI/POSS-IL composite membranes at 2971 cm^{-1} and 1070 cm^{-1} are assigned to the stretching of C-H and vibration of Si-O, respectively.
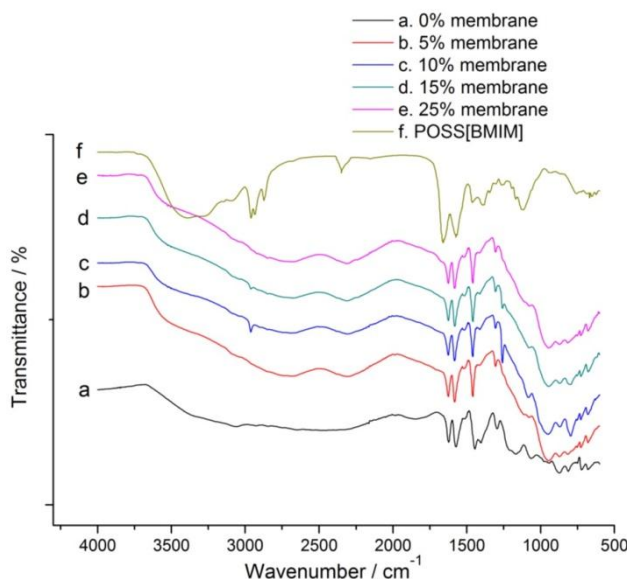

Fig. 5 FTIR spectra of ABPBI membranes with (a)0 wt%, (b)5 wt%, (c)10 wt%, (d)15 wt% and (e)25 wt% POSS-IL, and FTIR spectrum of (f)POSS-IL

B. Thermal Stability of ILs

According to the TGA results illustrated in Fig. 6, the decomposition of [BMIM]OH happened at around 150-300 ℃, while the decomposition of POSS-IL took place at around 200-300 ℃, which was slightly higher than [BMIM]OH, indicating that the incorporation of POSS anion (POSS-(CH$_2$)$_3$NHC(=O)(CH$_2$)$_2$COO$^-$) improved the thermal stability of the original ionic liquid. The AM-POSS part of POSS-IL can withstand temperature up to 300 ℃.
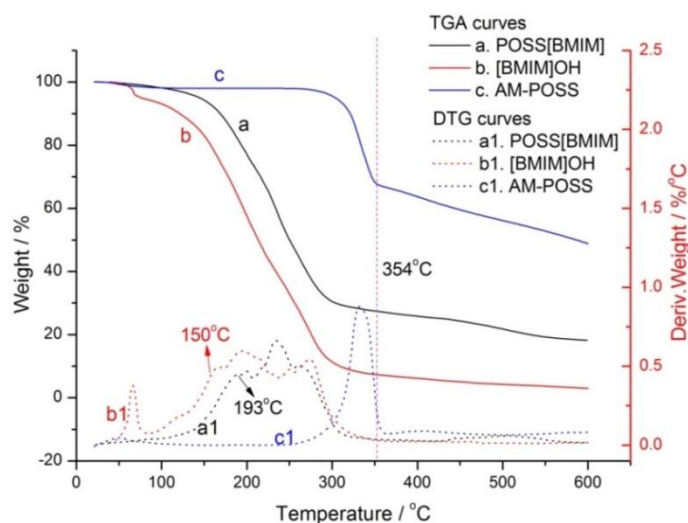

Fig. 6 TGA and DTG curves of (a) POSS-IL, (b) [BMIM]OH and (c) AM-POSS

Fig. 7 illustrates the TGA/DTG curves of ABPBI/10 wt% POSS-IL membrane and pristine ABPBI membrane. Their TGA/DTG curves were roughly divided into three regions. The weight losses of POSS-IL incorporated ABPBI membranes

below 193 ℃ was attributed to the decomposition of H_3PO_4 and evaporation of water, including free surface water and hydrogen bonded water. The weight losses, which started at 193 ℃ and ended at 600 ℃, were mainly due to the decomposition of POSS-IL. The weight losses after 600 ℃ were attributed to the decomposition of ABPBI polymer, remaining pyrophosphoric acid and POSS cores [14]. These results implied that the thermal stability of this POSS-IL incorporated ABPBI membrane was sufficient for high temperature PEM application.
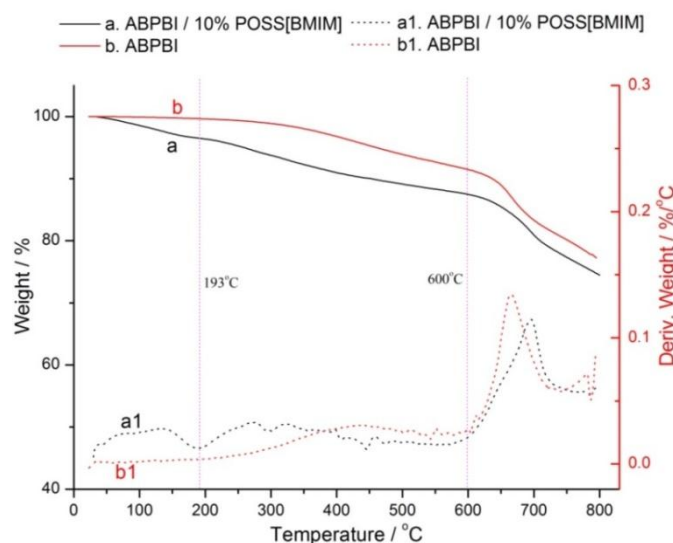

Fig. 7 TGA and DTG curves of (a) ABPBI/10 wt% POSS-IL and (b) ABPBI membranes

C. Mechanical Properties

Fig. 8 shows the mechanical properties obtained from the stress-strain (s-s) curves for the POSS-IL incorporated ABPBI membranes. The Young's modulus was increased significantly with the addition of POSS-IL from 28.8 MPa for pure ABPBI membrane to 146.7 MPa for the membrane containing 25 wt% POSS-IL. As the modulus of the POSS particle was much higher than that of the polymer ($E_f \gg E_m$), therefore a higher volume fraction of POSS-IL resulted in a higher Young's modulus.
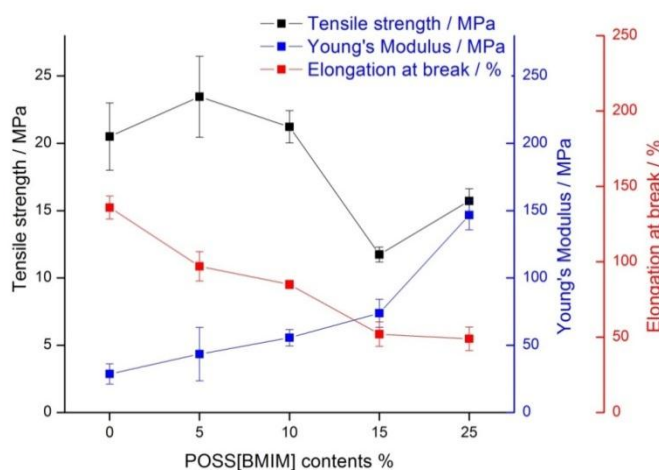

Fig. 8 Effects of the POSS-IL content on the mechanical properties of the membranes

With the increasing POSS-IL content, the elongation at break decreased dramatically, from 136 % to 49 %. This decrease was because that the POSS particles and interactions between ionic liquid inhibited the movement of the polymer chains, which embrittled the membranes, leading to reduced value of elongation at break.

A 18 % increase in the ultimate tensile strength of the membrane was observed with the addition of 5 wt% of POSS-IL, which was mainly due to the good dispersion of the fillers in the polymer matrix. A good dispersion results in intimate contacts between the fillers and the polymer matrix, which helps in transferring the local stress from the matrix to rigid POSS particles. The nanofiller in the composites interrupted and delayed the propagation of micro-cracks by stress distribution, contributing to the improvement of the tensile strength. However, the tensile strength of the composites was decreased when more POSS-IL was added, owing to the agglomeration of the POSS-IL fillers in the polymer matrix, resulting in more defects and stress concentrations in the composites.

D. Microstructures of POSS-IL Incorporated ABPBI Composite Membranes

The SEM images of ABPBI membranes with (a) 5 wt%, (b) 10 wt% and (c)25 wt% POSS-IL are shown in Fig. 9. For membranes with over 10 wt% POSS-IL, roughness and "cracks" appeared on the membranes' surface, because hydrophilic IL molecules tent to aggregate and form a domain within the polymer matrix.

The dispersion of the POSS-IL in ABPBI membrane was characterized by creating silicon distribution maps using EDX modulus as shown in Fig. 9 (d-f). The bright areas of the EDX map indicated the presence of Si, and in 10 wt% and 25 wt% samples, agglomerations with diameters over 3 μm were observed. For 5 wt% samples, Si was distributed well in the polymer matrix and no bright area was found from the EDX map, due to the good dispersion of fillers that was normally obtained at relatively low filler content.
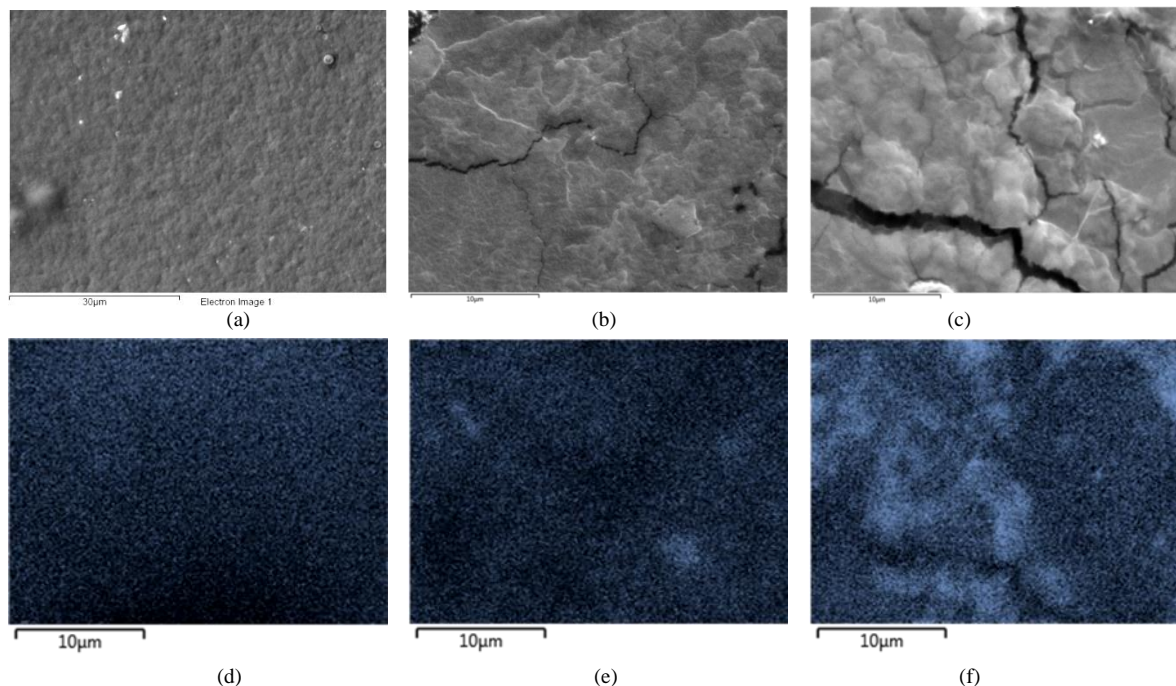

Fig. 9 SEM images of (a) 5 wt%, (b) 10 wt% and (c) 25 wt% POSS-IL incorporated ABPBI composite membranes (top), and the corresponding EDX mapping results of Silicon in (d) 5 wt%, (e) 10 wt% and (f) 25 wt% membranes (bottom)

E. Ionic Conductivity of POSS-IL Incorporated ABPBI Membranes

Proton conductivities of the ABPBI/POSS-IL composite membranes at different temperatures are illustrated in Fig. 10. Theoretically, these composite membranes contained the same amount of P_2O_5, which might absorb moisture from air during the membrane preparation to form $H_4P_2O_7$ and H_3PO_4 (Eq. (2)). The enhancement of POSS-ILs on the conductivities was analyzed by comparing the conductivities of POSS-ILs incorporated ABPBI membranes (Fig. 10 b-e) with that of ABPBI membrane without POSS-ILs (Fig. 10 a). All membranes were dried at 100 ℃ before test to remove the free water.

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \tag{2}$$

The conductivity of the (a) 0 wt% membrane came from the H_3PO_4 within the membrane. It was observed that the conductivities of POSS-IL incorporated ABPBI membranes were about two orders of magnitude higher than the membrane without POSS-IL, suggesting the incorporation of POSS-IL greatly enhanced the conductivity of the membrane. However, the conductivity was not proportional to the POSS-IL content.

As shown in Fig. 10, a linear relationship was found in the temperature range from 80 ℃ to 200 ℃ (2.9 to 2.1), and the corresponding activation energy E_a was calculated through Arrhenius equation (Eq. (3)) [15-18] and tabulated in Table 2.

$$\ln(\sigma) = \ln A - \frac{E_a}{RT} \tag{3}$$

where E_a is Arrhenius activation energy, σ_0 and A are pre-exponential factors, R is gas constant (8.314 J/mol•K), T is absolute temperature, whilst σ is the conductivity at temperature T.

The activation energy (E_a) is the sum of the enthalpies of defect pair (charge carrier) formation (ΔH_f) and migration (ΔH), which indicates the grade of difficulty for proton hopping and rotation of the donor and the acceptor [15], in another word, the potential barrier for proton conduction. A large value of E_a indicates a high enthalpy required for proton transfer, which results in low conductivity.
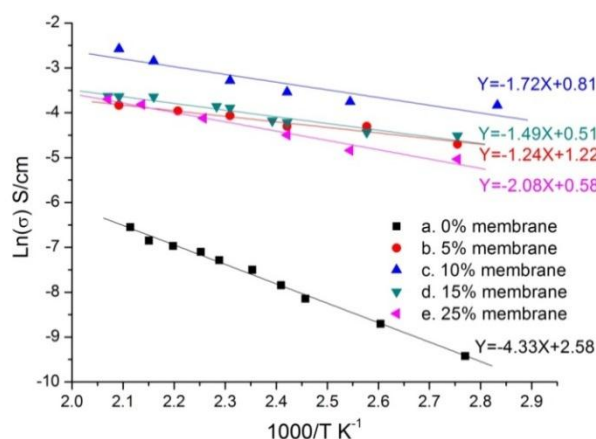
Fig. 10 Conductivities of (a)0 wt%, (b)5 wt%, (c)10 wt%, (d)15 wt% and (e)25 wt% POSS-IL incorporated ABPBI composite membranes

As shown in Table 2, the incorporation of POSS-IL greatly reduced the activation energy of the membrane, from 36.0 kJ/mol to 10~18 kJ/mol, suggesting that POSS-IL reduced the potential barrier for proton conduction. Ionic channel theory [19-21] was used to explain this ABPBI/POSS-IL system, as illustrated in Fig. 11. The hypothesis was that the interaction between the C=O and COO$^-$ groups from the POSS-IL and the N-H groups from the ABPBI formed hydrophilic ionic channels within the polymer matrix. These hydrophilic channels contained increased amount of hydrogen bonded water, which greatly enhanced the mobility of charge carriers (H_3PO_4, H_2O, etc.), and hence reduced the E_a value and increased the conductivity of the membrane.

TABLE 2 ACTIVATION ENERGY OF CONDUCTIVITIES OF ABPBI/POSS-IL COMPOSITE MEMBRANES

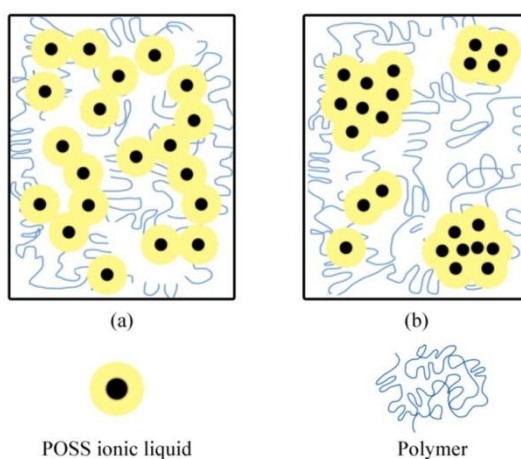| Membrane	Activation energy (E_a) (kJ/mol)	Temperature range (T) (℃)
0 wt% ABPBI	36.0	80~200
5 wt% ABPBI	10.3	80~200
10 wt% ABPBI	14.3	80~200
15 wt% ABPBI	12.4	80~200
25 wt% ABPBI	17.3	80~200

Fig. 11 The schematic illustration of ABPBI/POSS-ILs ionic channel system

Dispersion of the POSS-IL was crucial to the formation of ionic channels in the polymer matrix. As shown in Fig. 11, the membrane containing 10 wt% POSS-IL showed the highest conductivity (7.6×10^{-2} S/cm at 200 ℃), while the membrane with 25 wt% POSS-IL the lowest, owing to the poor dispersion of the fillers in the polymer matrix. According to the EDX mapping results shown in section D, good dispersions of the fillers were obtained by 5 wt% and 10 wt% samples, where POSS-IL filled the whole space within the membrane, and ionic channels were well connected to each other throughout the polymer matrix. Filler agglomeration took place when the filler content was over 10 wt%, which led to lower surface-area-to-volume ratio of the POSS-IL and isolated ionic liquid channels. At current stage, no strong evidence can be provided to explain the exact proton conduction mechanism. However at least, ABPBI membrane with modified nanofiller can be a promising candidate to produce high temperature PEMs, and the incorporation of nanofiller with IL may be a good approach to improve the current ILs based PEMs.

IV. CONCLUSIONS

The synthesized POSS incorporated ionic liquid showed good thermal stability up to 200 ℃, and was successfully embedded into ABPBI/H_3PO_4 membrane system. Good dispersion of POSS-IL increased the membrane's ultimate tensile strength and Young's modulus, but reduced the elongation at break. For membranes with the same H_3PO_4 content, the incorporation of POSS-IL enhanced their conductivities by about two orders of magnitude, owing to the formation of ionic channels in the polymer matrix. The highest conductivities were achieved by ABPBI/10 wt% POSS-IL composite membrane (7.6×10^{-2} S/cm a t 200 ℃), due to the good dispersion of POSS-IL and well-connected ionic channels throughout the polymer matrix.

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