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Preparation and characterization of proton-conducting sulfonated poly(ether ether ketone)/phosphatoantimonic acid composite membranes

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Abstract

The solid proton conductor, phosphatoantimonic acid, $HSbP_2O_8 \cdot H_2O$ was prepared by ion exchange of the corresponding potassium salt. The composite membranes of SPEEK with up to 40 wt% of $HSbP_2O_8 \cdot H_2O$ were prepared by introducing the solid proton conductor from the aqueous suspension. The composite membranes were characterized using FT-IR, powder X-ray diffraction, SEM, DSC/TGA. Thermal stability of the composite membranes was slightly lower than that of SPEEK. The composite membranes had higher water uptake when compared with SPEEK and the membranes exhibited controlled swelling up to 50 °C. The proton conductivity of the membranes was measured under 100% relative humidity up to 70 °C. The composite membranes showed enhanced proton conductivity up to 20 wt% of $HSbP_2O_8 \cdot H_2O$ and the conductivity was reduced with further increase of $HSbP_2O_8 \cdot H_2O$ loading. A maximum of four-fold increase in proton conductivity at 70 °C was observed for the composite membrane with 20 wt% of solid proton conductor.

Keywords: Phosphatoantimonic acid; SPEEK; Composite membrane; Proton conducting membranes

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1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are widely investigated as clean energy devices for various applications such as portable power, residential as well as transportation purposes [1,2]. However, the present manufacturing cost of PEM fuel cell power systems is much higher than that of conventional internal combustion (IC) engine based power generation devices. The cost of PEM fuel cells has to be brought down to the level of IC engines for their widespread market penetration. As of now, the solid polymer electrolyte membrane Nafion®, manufactured by DuPont is the industrial standard for making PEM fuel cell stacks. Though, Nafion® has excellent mechanical properties to withstand the fuel cell environment, higher cost, limited operating temperature of around 80 °C

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and high methanol crossover rate are the disadvantages associated with Nafion membrane. Various engineering plastics like polyether ether ketone (PEEK) [3,4], polysulfone (PSU) [5], polybenzimidazole (PBI) [6] etc. are being evaluated as Nafion® alternatives to circumvent the problems associated with Nafion® membrane. Among the above mentioned polymers, PEEK is very promising, since it is cheap, possesses good mechanical properties and high thermal stability. The PEEK can be converted to sulfonated polyether ether ketone (SPEEK), a proton-conducting polymer, by the electrophilic substitution of sulfonic acid groups in the polymer back bone. The proton conductivity of SPEEK is directly related to the degree of sulfonation (DS). The membranes with DS in the range of 45–55% can have satisfactory mechanical properties, but their conductivity is not sufficient enough for good fuel cell performance.

The proton conductivity of polymer electrolyte membranes can be considerably improved by incorporating fast proton conductors in the membrane matrix [7]. The proton conductors improve the conductivity of composite membranes by providing additional proton-conducting channels. The composite membranes of SPEEK with fast proton conductors like zirconium phosphate sulphophenylen phosphonate [8], heteropolyacids [9] and boron phosphate [10], etc. are reported in the literature. Phosphatoantimonic acids are a class of proton conductors represented by the general formula $H_nSb_nP_2O_{(3n+5)} \cdot H_2O$, where n is an odd integer, 1, 3, 5 etc. and x varies depending on the degree of hydration [11]. They have layered network structure made of SbO_6 octahedra and PO_4 tetrahedra. The network could be either bidimensional ($n = 1$, 3) or three dimensional ($n = 5$). The proton conductivity is mainly due to the water adsorbed on the grain boundaries as well as intercalated between the layers and the hydronium ions present in the interlayer regions [11,12]. Hence, the conductivity is a strong function of relative humidity. The lower members of the series $HSbP_2O_8 \cdot H_2O$ (H1) and $H_3Sb_3P_2O_{14} \cdot H_2O$ (H3) are good proton conductors and conductivity close to $0.001\ \text{Scm}^{-1}$ is reported for H1 at 20 °C under 100% relative humidity [12]. Since they are insoluble in water under acidic conditions [13], they are ideal candidates for the preparation of composite membranes. The phosphatoantimonic acids swell extensively in the presence of water forming stable suspensions from which they can be uniformly incorporated into the membrane matrix. Baradie et al. [14] have prepared the composite membranes of sulfonated polysulfone and H3 up to 35 wt% of H3. They have observed a maximum in conductivity with 7.1% H3 and the conductivity decreased with further increase of H3 in the composite membranes. Dimitrova et al. [13] have prepared composite membranes of sulfonated polysulfone and H3 up to 12% of H3. They have used H3 in the form of aqueous gel for its uniform dispersion in the membrane. A three-fold increase in conductivity at 80 °C under 100% relative humidity has been reported for the composite membrane with 8% of H3. However, no literature reference on the introduction of either H1 or H3 in SPEEK membrane matrix is available. Hence, the aim of the present work was to prepare the solid proton conductor H1 from suitable precursors and to prepare the composite membranes of SPEEK and H1. The results of membrane preparation and characterization are discussed in the present communication.

2. Experimental

2.1. Materials

PEEK (Victrex®) from Victrex plc was dried overnight at 110 °C under vacuum and used for the reaction. Antimony pentoxide (Sb_2O_5) 85%, ammonium dihydrogen phosphate ($NH_4H_2PO_4$) 98%, potassium dihydrogen phosphate (KH_2PO_4) 99% from Aldrich, sulfuric acid (H_2SO_4) 95%, nitric acid (HNO_3) 99% and *N,N*-dimethyl formamide (DMF) 99% from Junsei Chemicals Co. Ltd., Japan, were used as received without further purification.

2.2. Characterization

XRD patterns of dry membrane samples were recorded in the 2θ range 2–80° at the scan rate of 3°/min with a RIGAKU D/MAX – IIIC X-ray diffractometer using Cu Kα ($\lambda = 1.4518$ Å) radiation filtered through Ni. FT-IR spectra of dry membrane samples in ATR mode were recorded in the frequency range 4000–650 cm^{-1} on a JASCO FT-IR 470 plus instrument. The spectrum was recorded as the average of 50 scans with the resolution of 4 cm^{-1}. Equal pressure was applied for all samples to avoid differences caused by pressure and penetration depth. Morphology of the membranes was investigated using a scanning electron microscope

(SEM) S-4700 from HITACHI. The membranes were fractured by briefly immersing in liquid nitrogen. Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of Pt/Pd prior to the analysis.

Differential scanning calorimetry (DSC) analysis was carried out on a DSC instrument DSC-2000 from TA instruments, USA, calibrated with indium. The sample (~10 mg) was loaded in hermetically sealed aluminium pans, pre-heated under nitrogen from room temperature to 160 °C at 10 °C/min, cooled to 100 °C and reheated from 100 °C to 250 °C at the rate of 10 °C/min. Thermal gravimetric analysis (TGA) was carried out on TGA 2050 instrument from TA instruments, USA. Initially, the samples were heated under nitrogen up to 150 °C, cooled down to 90 °C and reheated till 600 °C at the rate of 10 °C/min, under nitrogen atmosphere.

Water uptake of the membranes at different temperatures was determined from the difference in weight before and after hydration. Membrane samples were dried at 110 °C under vacuum until constant weight, which is recorded as W_{dry}. The samples were then immersed in DM water for 4 h at a given temperature, removed from water, surface-attached water was wiped off with filter paper and immediately weighed (W_{wet}). Water uptake was recorded as weight percent absorbed water, with respect to dry membranes:

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

The proton conductivity of the membranes was measured by ac impedance spectroscopy using a Solartron 1260 gain phase analyzer interfaced to Solartron 1480 multistat. The measurement was carried out in the potentiostatic mode over the frequency range 0.1 Hz–10 MHz with oscillating voltage of 5 mV. The home made four-probe conductivity cell configuration is similar to that reported in the literature [16]. The cell had two platinum foils for carrying the current and two platinum wires at 1 cm apart to sense the potential drop. The membrane sample (2 cm length, 1 cm wide) was placed over the platinum foils in the lower compartment; the upper compartment along with the potential sensing platinum wires was clamped. The cell was kept in a temperature controlled sealed off vessel. Water was kept inside the vessel to maintain 100% relative humidity. The conductivity of the samples was calculated from the impedance data using the relation $\sigma = d/RS$, where d and S are the thickness and the face area of the samples, respectively and R is derived from the impedance value at zero phase angle.

2.3. Sulfonation of PEEK

Sulfonation of PEEK was carried out following the reported literature procedure [3]. The reaction was carried out in a four-neck round bottom flask fitted with a mechanical stirrer. About 500 ml of 95% H_2SO_4 was transferred to the reaction flask and heated over water bath to 50 °C under N_2 atmosphere. Then, 25 g of PEEK was slowly added under stirring. The mass remained heterogeneous initially and the polymer completely dissolved in 1 h and the reaction was continued for further 5 h. The polymer solution was cooled to 10 °C to arrest the reaction and dropped over ice cold demineralised (DM) water using a separating funnel as thin stream. The fibers were then washed with DM water till the neutral pH and stirred overnight to remove the residual acid. The polymer was dried at 60 °C for 12 h followed by overnight drying at 110 °C under vacuum.

2.4. Preparation of phosphatoantimonic acid

Preparation of crystalline $KSb(PO_4)_2$ was carried out via solid state reaction of the suitable precursors [15]. The precursors namely Sb_2O_5(s), $NH_4H_2PO_4$(s) and KH_2PO_4(s) were intimately mixed in the stoichiometric ratio 0.5:1:1. The mixture was then heated in a ceramic crucible as per the reported heating programme. The crystalline $K(SbPO_4)_2$ was then ion exchanged using 9 M HNO_3 at 50 °C for 24 h. The resultant solid H1 was then filtered over a sintered crucible (G4). It was washed with aliquots of deionised water and the material turned into gel, while washing due to its swelling nature in water. The gel was dried at 60 °C under vacuum and used for the preparation of composite membranes.

2.5. Preparation of composite membranes

SPEEK was dissolved in DMF to make 5 wt% solutions and filtered through 0.1 μm filter, the H1 was suspended in DM water to make a 2.2% suspension. The suspension remained reasonably stable without settling at the bottom and could be conveniently used for the preparation of composite membranes. The SPEEK solution was taken in a round bottom flask, required quantity of 2.2 wt% of H1 suspension was added and the solution was concentrated in a rotary evaporator with the simultaneous removal of water. The thick solution was cast onto flat bottom Petri dishes for membrane formation. The membranes were dried at 60 °C for 12 h followed by vacuum drying at 120 °C. The composite membranes up to 40 wt% of H1 were prepared and referred as SPEEK/H1X in the following text, where "*X*" denotes wt% of H1. The membranes were almost transparent without any pinholes.

3. Results and discussion

The SPEEK with DS 65% was prepared as per the procedure outlined in the experimental section. The introduction of sulfonic acid groups in the polymer chain was confirmed by FT-IR and ion exchange capacity measurement. The SEM-EDX analysis of H1 showed 3.0% $KSb(PO_4)_2$, probably due to incomplete ion exchange. Powder X-Ray diffraction pattern for the $KSb(PO_4)_2$ as well as that of H1 are given in Fig. 1. The XRD pattern for the $KSb(PO_4)_2$ exactly matches with the rhombohedral pattern reported in the literature (JCPDS Card No. 39-0153). The XRD spectrum of H1 shows all the reflections reported for H1 in the literature (JCPDS Card No. 40-0219). The H1 shows poor crystallinity, which is reported to be due to the changes in the layer structure leading to a monoclinic or triclinic distortion in the lattice [17]. Apart from this, reflections corresponding to $KSb(PO_4)_2$ are also observed in the XRD spectrum of H1, which is due to the presence of 3.0% of $KSb(PO_4)_2$ in H1.

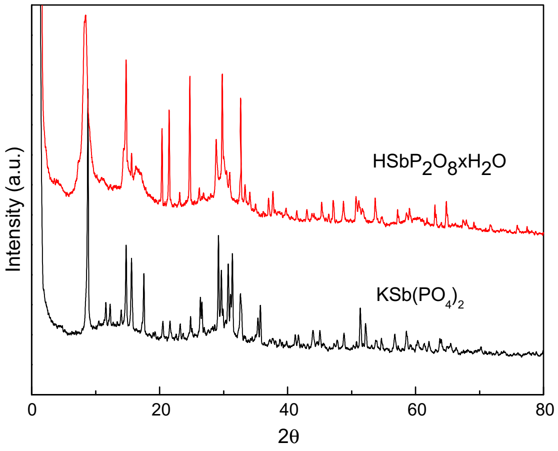

Fig. 1. Powder XRD pattern of KSb $(PO_4)_2$ and $HSbP_2O_8 \cdot H_2O$.

The surface morphology of $KSb(PO_4)_2$ and H1 as revealed by SEM is shown in Fig. 2. The $KSb(PO_4)_2$ depicts the 'deck of cards' morphology as reported in the literature [15]. Since these compounds have layered structure, the individual lamella join together to produce the structure similar to that of a randomly oriented deck of playing cards. The micro porosity within the lamella and void spaces between the individual lamella could be observed. The changes to the $KSb(PO_4)_2$ lamella caused by the ion exchange treatment are clearly visible in the morphology of H1. Even though main features of $KSb(PO_4)_2$ are maintained in H1, effective delamination is evident [15,17].

The X-ray diffraction patterns for SPEEK as well as the composite membranes are given in Fig. 3. PEEK is a semi-crystalline polymer showing sharp crystalline peaks corresponding to (1 1 0), (1 1 1), (2 0 0) and (2 1 1) planes in the 2*θ* range of 20–30° [18]. Sulfonation strongly decreases crystallinity

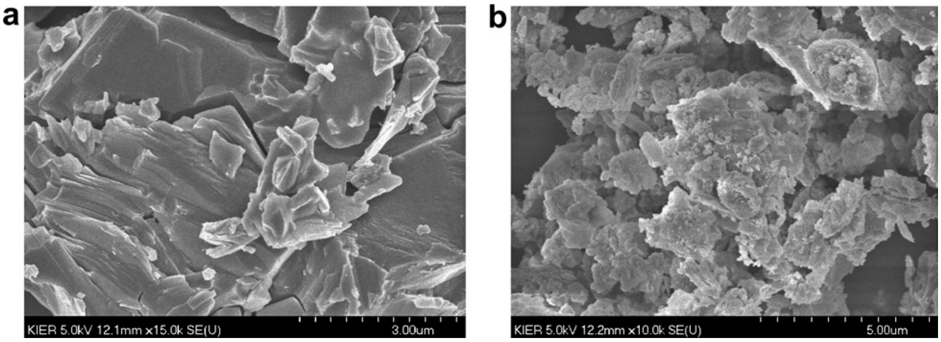

Fig. 2. SEM micrographs of (a) $KSb(PO_4)_2$ and (b) $HSbP_2O_8 \cdot H_2O$.

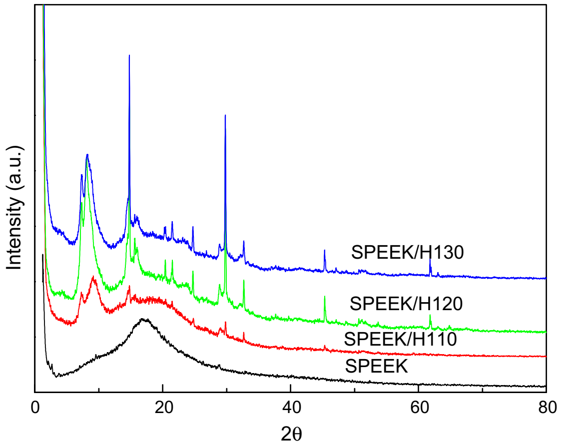

Fig. 3. Powder XRD pattern of (a) SPEEK, (b) SPEEK/H110, (c) SPEEK/H120 and (d) SPEEK/H130 membranes.

and highly sulfonated SPEEK is reported to be totally amorphous [19]. However, XRD pattern of SPEEK used in the present study indicates presence of a crystalline peak probably the one due to (1 1 0) plane, which is overlaid on the broad amorphous halo. Sharp reflections of H1, except that due to (2 0 0) plane are not visible for SPEEK/H110 membrane suggesting some degree of polymer percolation between the H1 particles, i.e. the H1 clusters are fixed in the polymer matrix without long range ordering [20]. But sharp reflections of H1 are clearly observed in the case of SPEEK/H120 and SPEEK/H130 membranes showing long range ordering of H1 in these membranes. The particle size of H1 in the composite membranes was calculated from (2 0 0) reflection using the Debye–Sherrer formula with Warren correction for the instrumental effects. The particle size of H1 in the three composite membranes was 9.3, 13.7 and 16.5 nm, respectively. The particle size increased with increase in the concentration of H1 in the composite membranes.

The FT-IR spectra of SPEEK as well as that of the composite membrane SPEEK/H130 are given in Fig. 4. The spectrum of SPEEK shows characteristic peaks for symmetric as well as asymmetric stretching vibrations of O=S=O group present in the sulphonic acid. These bands appear at 1020.15, 1074.15 and 1215.89 cm^{-1} in SPEEK [3] and were shifted to 1019.19, 1075.12 and 1218.79 cm^{-1} respectively in SPEEK/H130. Apart from the above, peak position of majority of the peaks in SPEEK were shifted to either lower or higher values in SPEEK/H130 indicating interaction between the sulfonic acid functional group and the H1. The stretching vibration of O–H group present in sulfonic acid occurs as a broad band around 3070 cm^{-1} in SPEEK mainly due to the intermolecular hydrogen bonding [21]. This is further shifted to 3050 cm^{-1} and broadened in SPEEK/H130 due to the presence of additional water in the composite membrane. It has been reported that H1 shows a sharp peak around 700 cm^{-1}, broad bands around 1000, 1600 and 3400 cm^{-1} in the IR spectrum [15]. The peaks at 700 and 1000 cm^{-1} could be clearly observed in the spectrum of SPEEK/H130 (Fig. 4b). There are noticeable differences in the spectrum of composite membrane in the range 650–1000 cm^{-1} when compared with that of SPEEK. Hence, the composite membrane reflects the spectral features of SPEEK as well as that of H1.

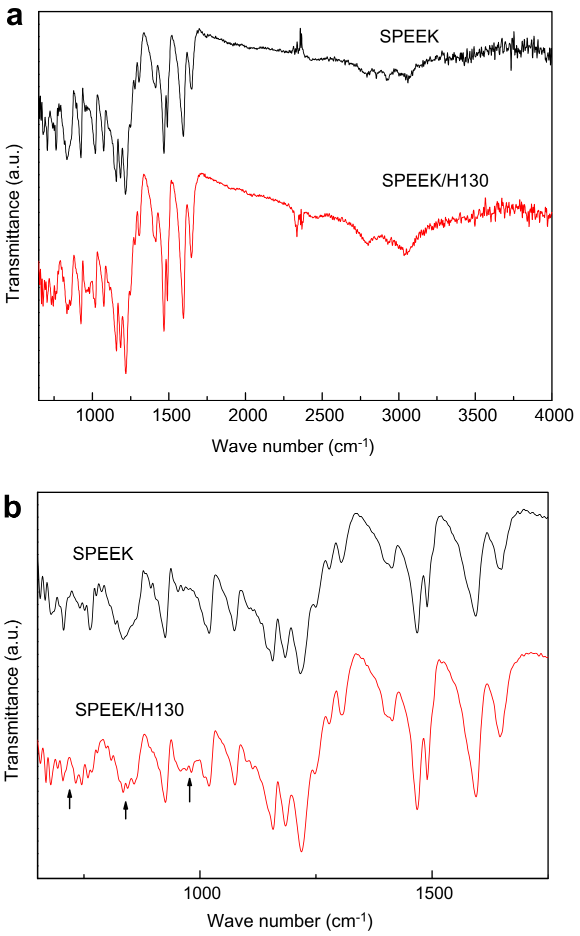

Fig. 4. FT-IR of SPEEK and SPEEK/H130 membranes; (a) 650–4000 cm^{-1}, (b) 650–1750 cm^{-1}.

The membrane samples were fractured by briefly immersing in liquid nitrogen and the cross-sections were observed in SEM. The SEM images of SPEEK

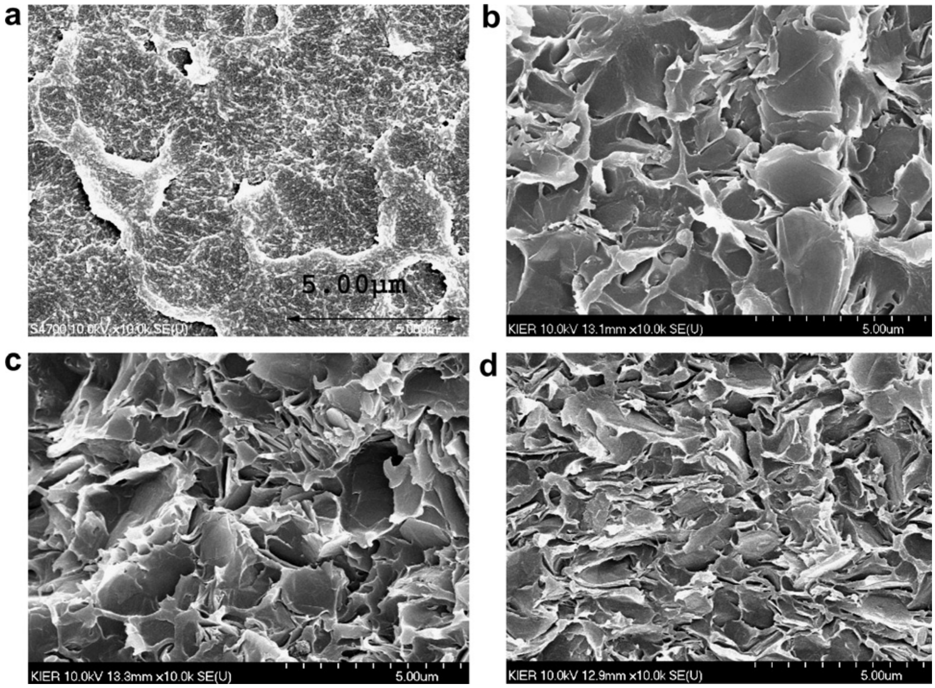

Fig. 5. SEM micrographs of (a) SPEEK, (b) SPEEK/H110, (c) SPEEK/H120 and (d) SPEEK/H130 membranes.

as well as the composite membranes are given in Fig. 5. The cross-section of the SPEEK reveals the porous structure of membrane matrix. Whereas, the cross-sections of composite membranes represent a rough morphology. The whole membrane cross-section was observed at low magnifications (not shown here), which did not indicate segregation of H1 on bottom face of the membrane as observed in the earlier study [14]. But intimate interfacial adhesion between the components phases normally provide composite membranes with improved properties. The SEM pictures show that the interfacial adhesion is not very good in the composite membranes which are mainly due to the layered nature of H1. The continuous H1 lamella is visible in all the composite membranes, which may be beneficial for establishing conduction pathways through the composite membrane. But this may block the conduction channels of polymer at higher concentrations [22].

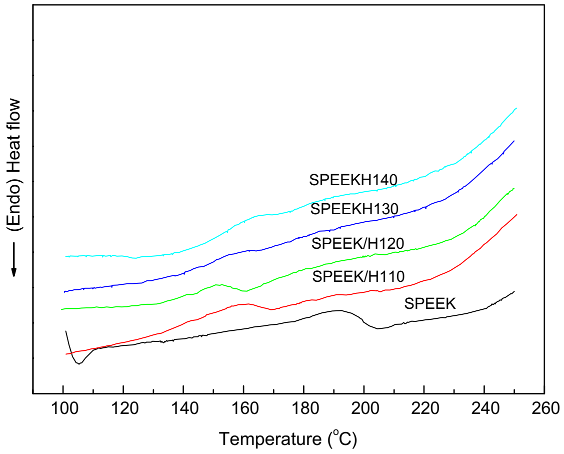

Fig. 6. DSC curves for SPEEK and composite membranes.

Thermal properties of the membranes were studied by DSC and TGA. The DSC graphs for SPEEK as well as the composite membranes are presented in Fig. 6. The DSC curve for SPEEK shows glass transition (T_g) around 198 °C. But T_g for the composite membranes was reduced to lower values. The T_g for SPEEK/H110 and SPEEK/H120 membranes was 167 and 159 °C, respectively. The reduction in T_g indicates increased mobility of the polymer chain [23]. But the T_g increased with further increase in H1 percentage. The T_g for the SPEEK/H130 and SPEEK/H140 membranes was 162 and 169 °C respectively. The increase in T_g at very high content of H1 was mainly due to stiffening of segmental motion of the polymer chain [24]. Another noticeable difference is that the T_g peak height and area of the composite membranes were lesser than that of SPEEK and progressively decreased with increasing H1 percentage. This shows the increased crystallinity of the composite membranes with increasing concentration of H1 [25]. The crystalline nature of composite membranes was evident from the XRD studies as discussed earlier. The reduction of T_g of the composite membranes reveals that their thermal stability is reduced when compared with SPEEK. The reduced thermal stability might be due to inefficient interfacial contact between the phases. The thermal properties of the membranes could be improved by improving the interfacial compatibility of the polymer matrix and the solid proton conductor.

Thermal decomposition behavior of the membranes was studied by TGA. The TGA thermograms for the composite membranes along with SPEEK are presented in Fig. 7. A detailed analysis of the degradation behavior of the membranes is given in Table 1. Three decomposition steps could be observed in all the membranes. The first weight loss (T_d^1) is due to the loss of water from the membranes. The percentage weight loss during this step is higher in the case of composite membranes due to adsorption and holding of excess water by H1 in the composite membranes. The decomposition of sulfonic acid groups (T_d^2) in SPEEK begins around 295 °C and the decomposition of polymer backbone (T_d^3) begins at 480 °C. The decomposition of sulfonic acid groups begins around 277–287 °C in the composite membranes, which is about 10–20 °C lesser than that observed in SPEEK.

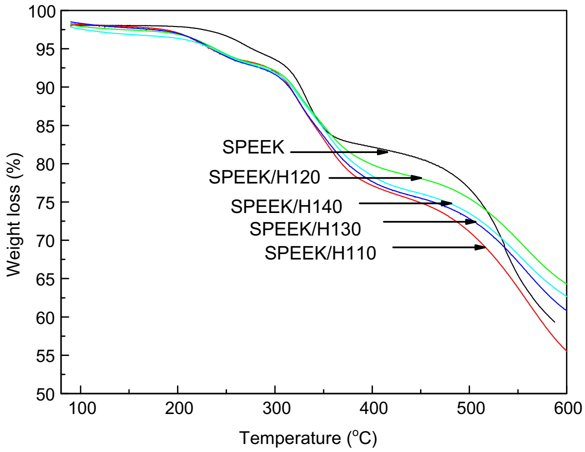

Fig. 7. Thermogravimetric weight loss curves for SPEEK and composite membranes.

Table 1
Thermal properties of SPEEK and SPEEK/H1 composite membranes

Polymer	T_g (°C)	T_d (5%)	T_d^1 (°C)	T_d^2 (°C)	T_d^3 (°C)
SPEEK	198	276	205	297	480
SPEEK/H110	167	233	178	277	450
SPEEK/H120	159	238	178	284	450
SPEEK/H130	162	235	192	282	457
SPEEK/H140	169	235	192	287	462

The results of water uptake studies are presented in Fig. 8. Since H1 swells in the presence of water, we could expect the composite membranes to uptake excess water when compared with that of SPEEK. Water uptake of composite membranes is higher than that of SPEEK, which is due to the incorporation of water in the H1 matrix. The water uptake increased with increase in the content of H1. But all the membranes exhibited a controlled water uptake and swelling up to 50 °C. However, the water uptake increased more steeply at higher temperatures.

The results of proton conductivity measurement are plotted in Fig. 9. Since the SPEEK membranes with 65% DS will swell excessively above 70 °C under 100% relative humidity conditions, the proton conductivity was measured up to 70 °C. The conductivity of SPEEK as well as that of the composite membranes increases with increase in temperature. The conductivity pattern is almost same for all the membranes up to 60 °C. However, higher conductivity in some of the composite membranes might be due to holding of excess water as discussed earlier. The sharp increase in conductivity of the composite membranes beyond 60 °C indicates a

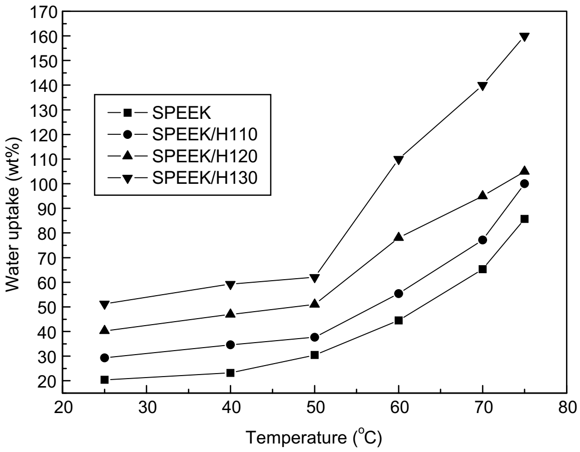

Fig. 8. Water uptake of SPEEK as well as the composite membrane samples.

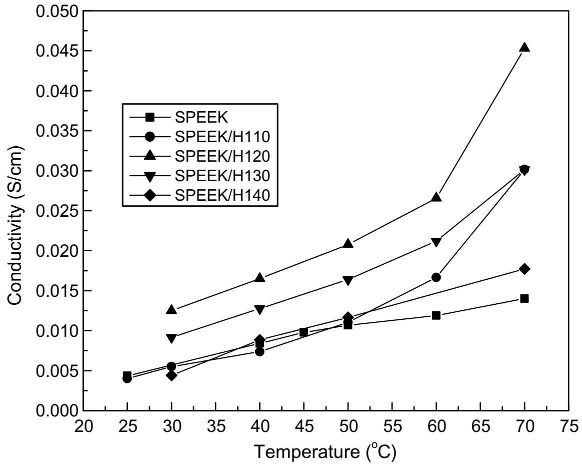

Fig. 9. Conductivity of the membranes under 100% relative humidity.

change in conduction mechanism. Probably at temperatures beyond 60 °C, the protogenic groups present in the interlayer region as well as in the grain boundaries of H1 also might be taking part in the proton conduction process. Thus, the adsorbed water as well as the protogenic groups might be contributing to the enhanced conductivity in the composite membranes, SPEEK/H110 and SPEEK/H120. The conductivity of the composite membranes increases up to 20% loading of H1, similar observation has been reported earlier for the composite membranes of sulfonated polysulfone and H3 [14]. The conductivity of the composite membranes beyond 20% loading of H1 is reduced which might be due to blocking of the polymer conduction channels by the solid proton conductor [24]. A good four-fold increase in conductivity was obtained for the SPEEK/H120 membrane. In the next step, composite membranes of SPEEK with DS in the range of 50–60% and H1 loading up to 20% will be prepared and tested for PEM fuel cell application.

4. Conclusions

The fast proton conductor, i.e. phosphatoantimonic acid (H1) was prepared from suitable precursors. Composite membranes of SPEEK and H1 were prepared up to 40 wt% of H1.

Thermal stability of the composite membranes is slightly inferior when compared with that of SPEEK, which is due to in-efficient compatibilization between SPEEK and H1 in the composite membranes. However, decomposition temperature of the composite membranes (280 °C) is quite sufficient for any intended membrane application.

The conductivity of the composite membranes increased up to 20% loading of the H1 and decreased at higher H1 loadings due to blocking of the polymer conduction channels by H1. An impressive four-fold increase in conductivity was observed for the composite membrane having 20 wt% of H1.

The composite membranes might have reduced methanol cross over which warrants further study with respect to direct methanol fuel cell (DMFC) application.

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