

Sulfonated poly(ether ether ketone)-based composite membrane for polymer electrolyte membrane fuel cells

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Abstract

The solid proton conductor zirconium phosphate sulfophenylphosphonate of composition $Zr(HPO_4)_{0.65}(SPP)_{1.35}$ where SPP denotes metasulphophenylphosphonate was prepared in the amorphous gel form in dimethyl formamide (DMF) and characterized by ^{31}P NMR. The composite membranes of SPEEK up to 50 wt.% of zirconium phosphate sulfophenylphosphonate content were prepared by introducing the solid proton conductor from the gel. The composite membranes were characterized using FT-IR, powder X-ray diffraction, SEM, DSC/TGA. The proton conductivity of the membranes was measured under 100% relative humidity up to 70 °C. The composite membranes had better thermal stability when compared with that of SPEEK. A three-fold increase in proton conductivity at 70 °C was observed for the composite membrane with 50 wt.% of solid proton conductor. Furthermore, the conductivity results imply that a critical percentage of proton conductor is needed to establish conduction pathways in the polymer matrix.

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1. Introduction

Fuel cells promise to be clean alternative energy sources for variety of power applications ranging from mobile phones, note book computers, residential power production and traction for transportation purposes [1,2]. Polymer electrolyte membrane (PEM) fuel cell technology is on the forefront of commercialization efforts in comparison with other fuel cell technologies. Even though fuel efficiency, reliability, wider temperature operation, etc., of the PEM fuel cells have been established, cost is the main factor on the way of their widespread use. The commonly used perfluorinated solid polymer electrolyte membrane, Nafion, is an expensive component of the PEM fuel cell and contributes to the higher cost. Many research groups are actively engaged in developing alternative membranes with less expensive chemistries.

The engineering plastics like poly(ether ether ketone) (PEEK) [3–5], polysulfone (PSU) [6], polybenzimidazole (PBI)

[7], etc., are being evaluated for their suitability in fuel cell application. Among them, PEEK is very promising since it is cheap, possesses good mechanical properties and high thermal stability. The PEEK can be converted to sulfonated poly(ether ether ketone) (SPEEK), a proton conducting polymer, by the electrophilic substitution of sulfonic acid groups in the polymer backbone. The proton conductivity of SPEEK is directly related to the degree of sulfonation (DS). Even though conductivity of highly sulfonated SPEEK membranes (DS ~ 75%) will approach closer to that of Nafion membrane, they will not be suitable for fuel cell application since the mechanical stability of the membrane is also affected by DS. The highly sulfonated membranes will swell excessively under the humidified conditions of fuel cell environment and lose their dimensional stability. The membranes with DS in the range 45–55% can have satisfactory mechanical properties but their conductivity is not sufficient enough for good fuel cell performance.

The proton conductivity of SPEEK membranes can be improved by incorporating fast proton conductors in the polymer matrix. The composite membranes based on SPEEK and solid proton conductors like heteropolyacids [4], boron phosphate [5], etc., have been reported in the literature. The solid proton

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conductor zirconium phosphate sulfophenylphosphonate was thoroughly investigated as a promising candidate for the preparation of composite membranes due to its high proton conductivity and hydrophilic character [8,9]. It can be prepared in crystalline as well as amorphous state [9]. The crystalline form is layered and can exist as α or γ layered type with the general formula $(\text{Zr}(\text{HPO}_4)_{2-x}(\text{SPP})_x)$ or $\text{Zr}(\text{PO}_4)[\text{O}_3\text{P}(\text{OH})_2]_{1-x}(\text{SPP})_x$ where SPP denotes metasulfophenylphosphonate. The composition of amorphous compound is the same as that of α layer type. It is an organo-inorganic compound where the organic moieties are bridged through phosphorous atoms to an inorganic two-dimensional matrix. The presence of sulfonic acid groups in the organic framework will facilitate proton transfer on the surface as well as in the interlayer region. This class of compounds has an interesting property of exfoliation and can form colloidal suspensions or gels in the suitable organic solvents. Recently, Alberti et al. [10] have prepared amorphous zirconium phosphate sulfophenylphosphonate (hereafter referred as $(\text{ZrSPP})_x$) in the form of gel in organic solvents and incorporated in sulfonated polyether ketone (SPEK) polymer matrix. Conductivity of SPEK membranes increased from 9×10^{-4} to $8 \times 10^{-3} \text{ S cm}^{-1}$ for the composite membrane having 20 wt.% of $(\text{ZrSPP})_x$. Since SPEEK and its composite membranes are being widely studied for fuel cell application, it would be interesting to follow this approach to prepare composite membranes with SPEEK since it may be possible to prepare true nano-composite membranes with improved mechanical properties as well as conductivity. There is one published report in the literature where Bonnet et al. [11] have employed colloidal suspensions of amorphous $(\text{ZrSPP})_x$ to prepare composite membranes with SPEEK. However, the effect of $(\text{ZrSPP})_x$ loading on the membrane properties as well as thermal stability of the membranes were not reported. The aim of the present study is to incorporate $(\text{ZrSPP})_x$ into SPEEK matrix from $(\text{ZrSPP})_x$ gel and to study thermal as well as conductivity behavior of the membranes. The results are discussed in this communication.

2. Experimental

2.1. Chemicals

Poly(ether ether ketone) (PEEK) from Victrex was dried overnight at 110°C under vacuum and used for the reaction. Sulfuric acid (95 wt.%), barium chloride (99 wt.%), phosphoric acid (85 wt.%), dimethyl formamide all from Junsei Chemicals Co., Ltd., Japan, and phenyl phosphonic acid (98 wt.%), sulfur trioxide (99 wt.%), zirconyl chloride octahydrate (98 wt.%), Dowex-50WX8-100 cation exchange resin all from Aldrich chemicals were used as received without further purification.

2.2. 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 wt.% 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. The reaction was continued for further 5 h. The polymer solution was cooled down to 10°C to arrest the reaction and dropped over ice-cold demineralised (DM) water through 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.

2.3. Preparation of $(\text{ZrSPP})_x$ in gel form

2.3.1. Preparation of *m*-sulfophenyl phosphonic acid (SPPA)

Sulfonation of phenyl phosphonic acid (PPA) was carried out as per the reported method by Montoneri et al. [12]. Phenyl phosphonic acid (10.13 g, 63.5 mmol) was suspended in 50 ml of 1,2-dichloroethane. Sulfur trioxide (6.25 ml, 150 mmol) was added at 0°C and the two-phase viscous mixture was heated to reflux and maintained for 15 h. The lower viscous layer was reacted with barium chloride to remove the free sulfates and to convert the *m*-sulfophenyl phosphonic acid to its barium salt form. The acid was regenerated by ion exchange over Dowex-50WX8-100 cation exchange resin bed. The product was characterized by FT-IR and NMR spectral techniques.

2.3.2. Preparation of $(\text{ZrSPP})_x$ gel

The method reported by Alberti et al. [10] was followed for the preparation of $(\text{ZrSPP})_x$ gel. The SPPA (3.0 g, 12.5 mmol) was dissolved in 15 ml DM water and mixed with 0.70 g (6.0 mmol) of 85 wt.% H_3PO_4 . This was added to a solution containing 3.0 g (9.32 mmol) of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 15 ml DM water under vigorous stirring. The mass thickened in 30 min and could not be stirred. It was kept as such for 3 days during which time it became a transparent gel. The gel was dissolved in 200 ml DMF, water along with DMF was distilled out in a rotary evaporator to get transparent gel in DMF. An aliquot sample of the gel was dried in a vacuum oven to calculate the percentage of solids in the gel and was found to be 4.7 wt.%.

2.4. Composite membranes

The SPEEK was dissolved in DMF to make 5.0 wt.% solution and filtered through $0.1 \mu\text{m}$ filter. Required quantity of 4.7 wt.% gel was mixed with the polymer solution. The resulting mixture was stirred with magnetic stirrer for 30 min followed by sonication for the same duration. The homogeneous solution was degassed under vacuum and poured over flat bottom Petri dish. The solvent was removed at 60°C for 12 h followed by further drying at 120°C under vacuum.

2.5. Characterizations

2.5.1. NMR

The NMR spectra were recorded on 300 MHz Bruker DRX300 spectrometer. The ^1H NMR of SPPA was recorded in

D₂O against TMS as the reference. The ³¹P NMR of Zr(SPP)_x was recorded by dissolving the dried solid sample in 3 M HF. The shift positions were calculated with respect to 85 wt.% D₃PO₄ in D₂O [10].

2.5.2. FT-IR

The FT-IR spectra of the solid samples were obtained from KBr pellets on BOMEM-MB154 spectrophotometer in the range 400–4000 cm⁻¹.

2.5.3. XRD

The XRD patterns were recorded in the range 1.2–90° with a RIGAKU D/MAX-IIIC diffractometer using Cu Kα (λ = 1.4518 Å) radiation filtered through Ni.

2.5.4. SEM

The morphology of the composite membranes was investigated using a scanning electron microscope (JSM-849, JOEL). Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of Au prior to the analysis.

2.5.5. Thermal analysis

The DSC and TGA analyses were carried out on DSC 2010 and TGA 2050 instruments, respectively, from TA instruments, USA. For the DSC analysis, the sample (~10 mg) was preheated under nitrogen from room temperature to 160 °C at 10 °C min⁻¹ to remove moisture, cooled to 80 °C and reheated from that temperature to 320 °C. For TGA, the heating rate was 10 °C min⁻¹ under nitrogen atmosphere.

2.5.6. Conductivity

The proton conductivity of the membranes was measured by ac impedance spectroscopy using the 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 to 10 MHz with oscillating voltage of 5 mV. The home made four-probe conductivity cell configuration is similar to that reported in the literature [13]. 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.

3. Results and discussion

Sulfonation of SPEEK using 95–98 wt.% H₂SO₄ is the well established process since it avoids degradation and cross-linking reactions which occur on sulfonation with 100 wt.% H₂SO₄ or with chlorosulfonic acid [14]. The DS can be controlled by vary-

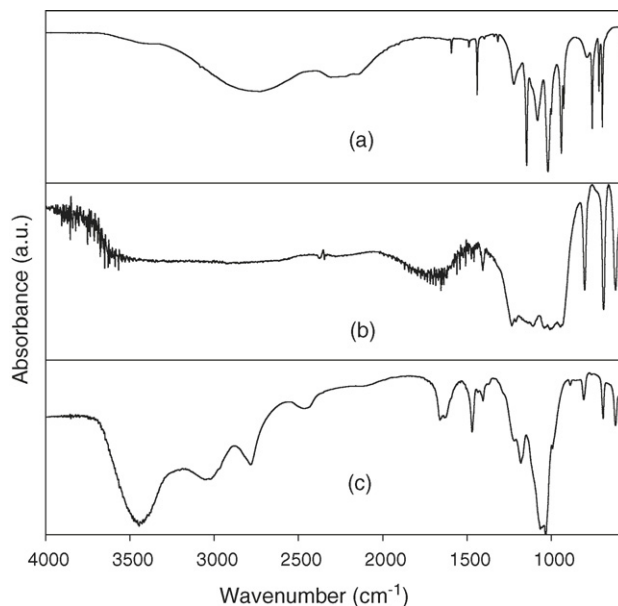


Fig. 1. FT-IR spectra: (a) phenyl phosphonic acid, (b) *m*-sulfophenyl phosphonic acid and (c) (ZrSPP)_x.

ing the temperature or the reaction time. The sulfonation reaction was carried out for various time durations and the dried polymer samples were analyzed for ion exchange capacity (IEC). Weighed quantity (1–2 g) of the polymer was kept in 1.0 M NaCl solution under stirring for 24 h and titrated with 0.1 M NaOH using phenolphthalein indicator. The IEC is calculated as the ratio of total charge by the dry polymer weight. The DS is calculated from IEC as, $DS = M_{w,p}IEC / (1 - M_{w,f})IEC$ where $M_{w,p}$ is the molecular weight of the non-functional polymer repeat unit, and, $M_{w,f}$ is the molecular weight of the functional group with the counter ion (–SO₃Na) [15].

The FT-IR spectra for PPA, SPPA and (ZrSPP)_x are given in Fig. 1. The aromatic C–C stretching vibration is observed at 1143 cm⁻¹ in PPA. The C–H out of plane bending vibrations is seen at 696, 715 and 756 cm⁻¹ as sharp peaks [12]. The broad band at 2500–2250 cm⁻¹ is due to the O–H stretching in phosphonic acid group [16]. Apart from this, the spectrum also has bands in the region 1250–750 cm⁻¹ due to phosphonic acid. There are noticeable differences in the spectrum of SPPA in comparison with PPA. The C–H out of plane bending vibrations falls at 688.53 and 800 cm⁻¹. The peaks for the O=S=O vibration of sulfonic acid group (SO₃H) could not be observed due to peak broadening in the region 1350–1000 cm⁻¹ which is attributed to hydrogen bonding between the sulfonic acid and phosphonic acid functions [12]. The peaks in the spectrum of (ZrSPP)_x are very broad and featureless which is due to the amorphous nature of the compound [17]. The peak for the O=S=O symmetric vibration at 1032 cm⁻¹ [18] could be observed as a shoulder along with the phosphonic acid bands. The aromatic C–C band appears at 1469 cm⁻¹ as a broad one. Apart from the broad phosphonic acid vibrations in the region 2500–2250 cm⁻¹, a large O–H stretching band centered at 3455 cm⁻¹ could be observed. This band is due to the water present in the compound [17].

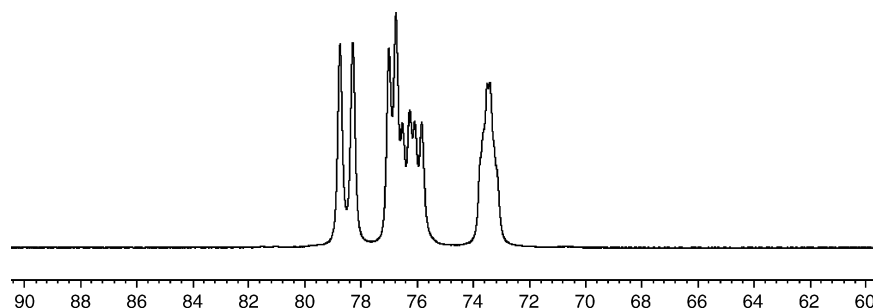


Fig. 2. ^1H NMR spectrum of *m*-sulfophenyl phosphonic acid.

The ^1H NMR spectrum of SPPA is presented in Fig. 2. The spectrum is complex due to the overlapping multiplets and ^1H - ^{31}P coupling. However, the signal consists of four multiplets corresponding to the four different protons in SPPA. The spectrum exactly matches with the one reported for SPPA in the literature [12]. The phosphate/sulfophenylphosphonate molar ratio was determined by liquid ^{31}P NMR. The shift position of the phosphoric acid and sulfophenylphosphonate signals with respect to 85 wt.% D_3PO_4 in D_2O were 2.7 and 17.3, respectively [10]. The calculated sulfophenylphosphonate/ HPO_4 molar ratio was 2.09 which corresponds to $\text{Zr}(\text{HPO}_4)_{0.65}(\text{SPP})_{1.35}$ as the exact molar composition of $\text{Zr}(\text{SPP})_x$.

Preparation of composite membranes by this approach is advantageous as well as simpler to adopt. The SPEEK solution and the $(\text{ZrSPP})_x$ gel form almost homogeneous dispersion. Formation of membrane from such a homogeneous solution may lead to uniform distribution of the proton conductor in the membrane matrix. Apart from this, very small particles with higher surface area for proton conduction, molecular level contact between the components and improved mechanical properties, etc., can be anticipated. The membranes were almost transparent which is indicative of good dispersion of solid proton conductor in the membrane matrix. The membranes with even 50 wt.% of $(\text{ZrSPP})_x$ were almost transparent, flexible and had good mechanical strength. However, Alberti et al. [10] have reported that the SPEEK + $(\text{ZrSPP})_x$ composite membranes become brittle if the $(\text{ZrSPP})_x$ content is above 20 wt.%, this may be due to the difference in the properties of the two polymers, i.e. SPEEK and SPEEK.

The powder XRD patterns of dried $(\text{ZrSPP})_x$ along with SPEEK and two of the composite membranes having 40 and 50 wt.% of $(\text{ZrSPP})_x$ are shown in Fig. 3. The XRD pattern of $(\text{ZrSPP})_x$ reveals few broad peaks at 2θ values of 4.8, 12.2, 22.0 and 34.50° due to its amorphous nature. The first peak at 4.8° is due to (200) reflexion. The SPEEK presents a broad peak which is the composite of amorphous and crystalline reflexions. In the composite membranes, the $(\text{ZrSPP})_x$ reflexions are overlaid by SPEEK reflexions to show broad features. However, the (200) reflexions are clearly observed in the composite membranes. The domain size of the $(\text{ZrSPP})_x$ in the composite membranes was calculated from (200) reflexion using the Debye–Sherrer formula with Warren correction for the instrumental effects. The domain size for the composite membranes

having 40 and 50 wt.% of $(\text{ZrSPP})_x$ were calculated as 72 and 64 \AA , respectively.

The membrane samples were fractured by keeping in liquid nitrogen and the cross-sections were observed in SEM. The SEM images for SPEEK as well as the composite membranes are given in Fig. 4. The cross-section of the SPEEK shows that the membrane matrix is somewhat porous with few voids. But the composite membranes reveal compact cross-sections which may be the result of intimate mixing of the components during membrane formation. A gradual reduction of voids in the composite membranes with increase in the content of $(\text{ZrSPP})_x$ can also be observed. The membrane surface is completely covered with $(\text{ZrSPP})_x$ at 50 wt.% level and no voids could be observed. The $(\text{ZrSPP})_x$ particles are hardly visible at 10 wt.% level (Fig. 4a) probably due to their dispersion with nano-scale dimensions in the membrane matrix. However, the particles are visible at higher loading (Fig. 4b and c), vary in size and are in the range of 20–30 and $\sim 100 \text{ nm}$ for 30 and 50 wt.% of $(\text{ZrSPP})_x$, respectively. Probably these are aggregates of particles having smaller dimensions as determined from the X-ray analysis.

Thermal properties of the membranes were studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The DSC graphs for SPEEK as well as the composite membranes are depicted in Fig. 5. The DSC curve for SPEEK shows glass transition (T_g) around 195°C . The T_g of

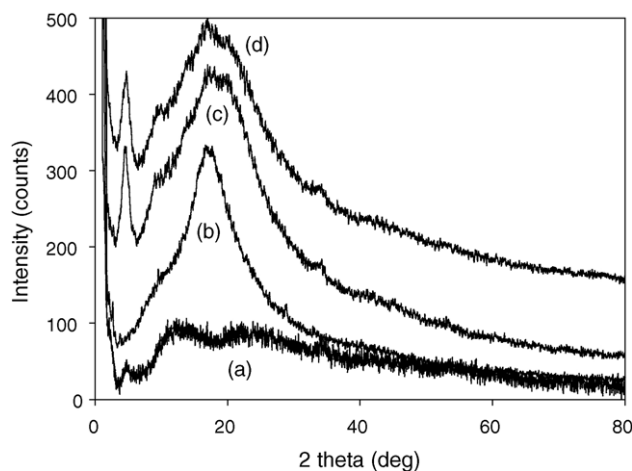


Fig. 3. Powder XRD pattern of: (a) $\text{Zr}(\text{SPP})_x$, (b) SPEEK, (c) 40 wt.% $\text{Zr}(\text{SPP})_x/\text{SPEEK}$ composite membrane and (d) 50 wt.% $\text{Zr}(\text{SPP})_x/\text{SPEEK}$ composite membrane.

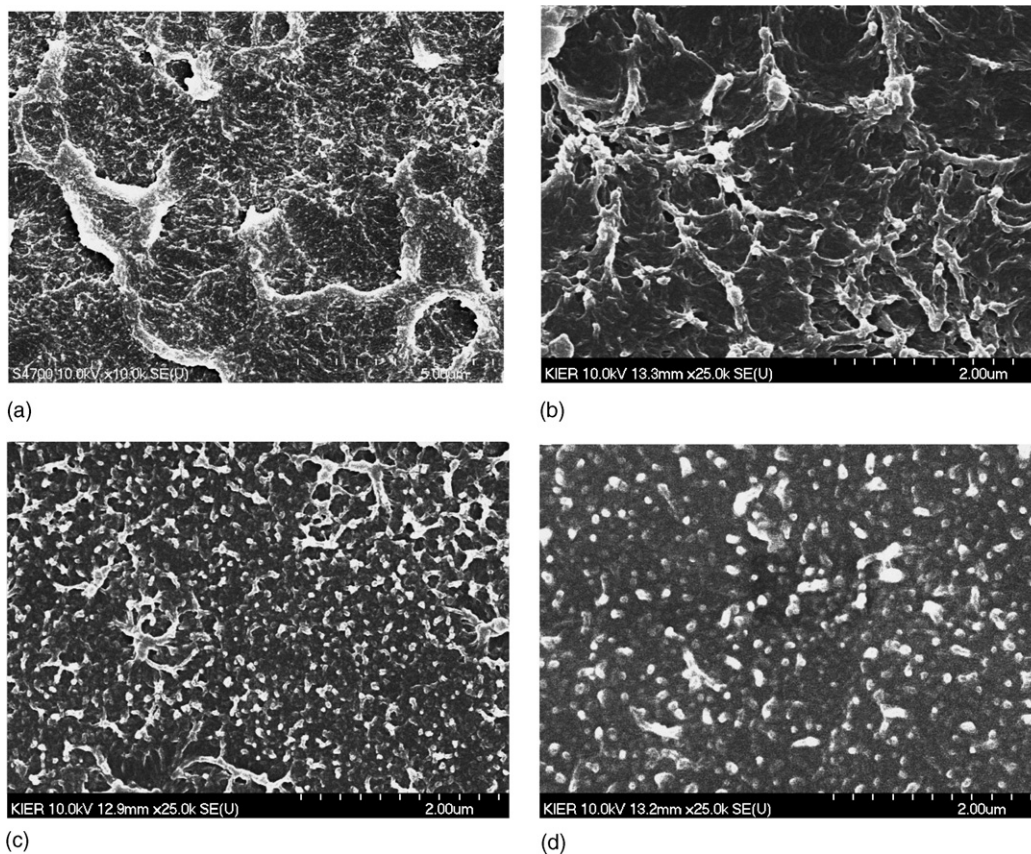


Fig. 4. SEM micrographs of the cryogenic fractures: (a) SPEEK, (b) 10 wt.% Zr(SPP)_x/SPEEK, (c) 30 wt.% Zr(SPP)_x/SPEEK and (d) 50 wt.% Zr(SPP)_x/SPEEK.

the composite membranes have increased by about 25 °C. This is due to restrictive segmental motion of the polymer chains in the composite membranes as the result of strong ionic interaction between SPEEK and (ZrSPP)_x. This is in consistent with the SEM micrographs which reveal good adhesion between the two components. A second glass transition around 270–280 °C is observed in the composite membranes before the onset of

sulfonic acid group decomposition around 280 °C. The second glass transition may be related to (ZrSPP)_x.

The TGA thermograms for the composite membranes along with SPEEK are presented in Fig. 6. It can be clearly seen that the thermal stability of composite membranes is improved when compared with that of SPEEK. The onset temperature for the thermal degradation is shifted to higher temperature with increase in concentration of Zr(SPP)_x up to 30 wt.%. Thermal stability is getting reduced at higher concentrations probably due to the formation of bigger aggregates. But still decomposition temperature of composite membrane with even 50 wt.% of (ZrSPP)_x is slightly higher than that of SPEEK. The TGA curves also show a difference in the degradation pattern of SPEEK and the composite membranes. The degradation of sulfonic acid groups in SPEEK occurs approximately in the temperature range 280–350 °C and then degradation of polymer backbone begins around 450 °C. But in the case of composite membranes, thermal degradation begins around 300 °C and continuous weight loss occurs with increase in temperature. This is due to the simultaneous decomposition of sulfonic groups in (ZrSPP)_x along with the sulfonic acid groups attached to the polymer backbone [19].

The results of proton conductivity measurement are plotted in Fig. 7. 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 hydrated membranes give a zero phase angle with no imaginary

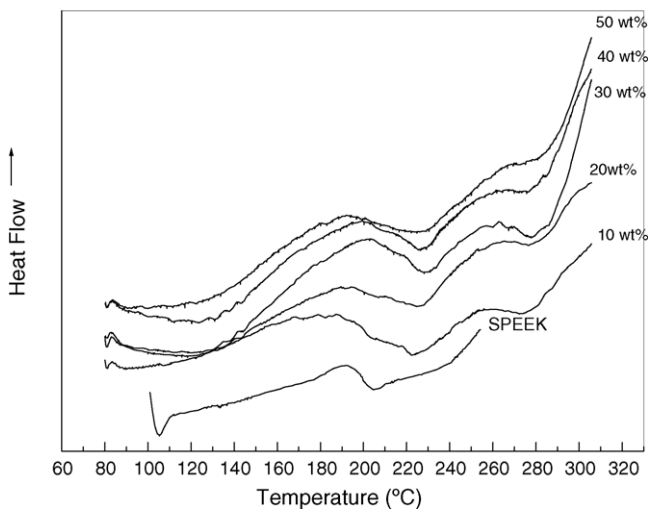


Fig. 5. DSC curves for SPEEK and composite membranes.

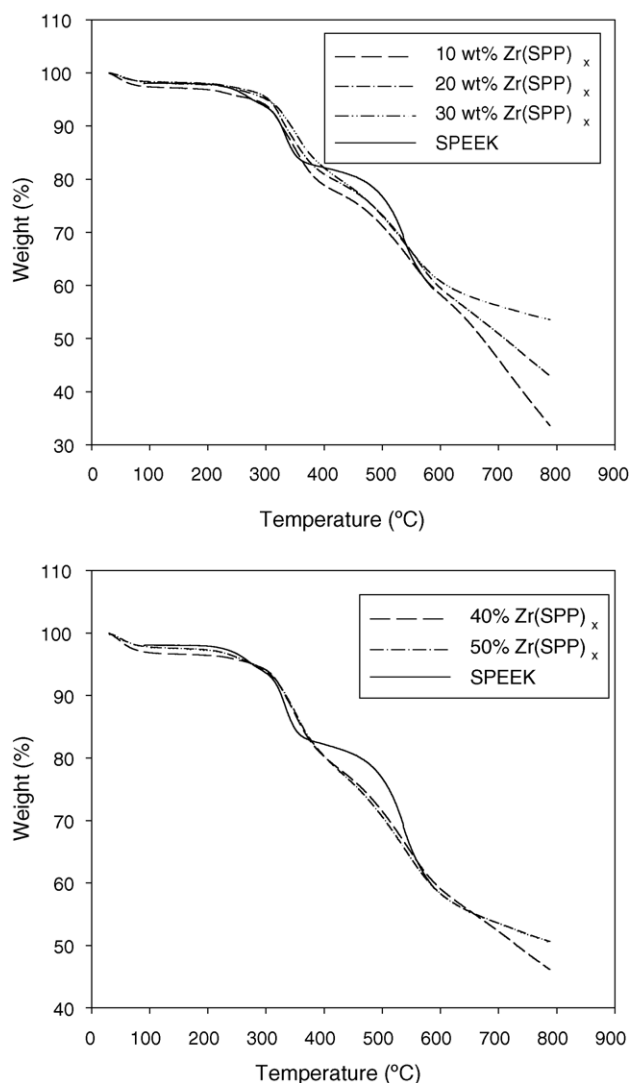


Fig. 6. Thermogravimetric weight loss curves for SPEEK and composite membranes.

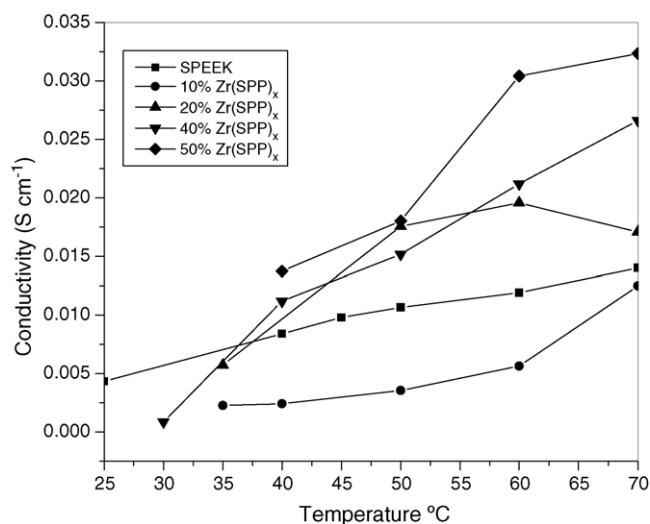


Fig. 7. Proton conductivity of SPEEK and SPEEK + Zr(SPP)_x composite membranes at different temperatures under 100% relative humidity.

response over a wide frequency range in the impedance spectrum thus behaving as true resistors. The conductivity of the composite membrane with 10 wt.% (ZrSPP)_x is always lower than that of SPEEK. Probably the concentration of proton conductor at this level is not sufficient enough to establish continuous conduction pathway for proton transfer. However, the conductivity increases with increase in concentration of proton conductor up to 50 wt.%. This shows the compatibilization of the SPEEK and (ZrSPP)_x. The solid proton conductor has not baffled the conduction process of the polymer even at high concentration, instead enhanced the conductivity by establishing conduction channels. A three-fold increase in conductivity was observed for the composite membrane with 50 wt.% (ZrSPP)_x.

4. Conclusions

The amorphous layered proton conductor (ZrSPP)_x was prepared in gel form. Composite membranes of SPEEK and (ZrSPP)_x were prepared up to 50 wt.% of (ZrSPP)_x by introducing the proton conductor from the gel. This is a simple and easier approach to prepare composite membranes having nano-scale dimensions of the component phases.

However, concentration of (ZrSPP)_x higher than 10 wt.% is needed to establish continuous conduction pathway in the composite membranes. Furthermore, the conductivity continuously increases with increase in concentration of (ZrSPP)_x up to 50 wt.% which is mainly due to mutual compatibility between the two components in establishing conduction pathways.

The composite membranes exhibited increased thermal stability and improved electrochemical properties when compared with that of SPEEK, which was mainly due to the ionic interaction of the component phases. A three-fold increase in conductivity was observed for the composite membrane having 50 wt.% of (ZrSPP)_x.

A distinct change in the morphology of the composite membranes could be observed with increased compactness of the matrix when compared with that of SPEEK. Due to the presence of compact membrane matrix, these membranes will have reduced methanol crossover and worth investigating for DMFC applications.

Acknowledgements

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