RESEARCH ARTICLE

EVALUATION OF SULFONATED TRI-BLOCK COPOLYMER/ HETEROPOLY ACID COMPOSITE MEMBRANES FOR FUEL CELL APPLICATIONS

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ABSTRACT

A novel composite membrane was prepared by incorporation of phosphotungstic acid (PWA) and silicotungstic acid (SWA) into sulfonated polystyrene ethylene butylene polystyrene (SPSEBS) by solution casting method. The interactions of SPSEBS with heteropoly acids (HPA) were studied by Fourier transform infrared (FTIR). From the thermogravimetric analysis (TGA), the thermal stability of the composite membranes was found to be increased with increased inorganic content and the X-ray diffraction study proved the crystalline structure of HPA in the membrane. SEM and AFM images of composite materials showed evidence uniform distribution of HPA in SPSEBS. The IEC and proton conductivity of the composite membranes increased with the increase in HPA content and in contrast the water absorption, methanol absorption and methanol permeability values decreased with increasing HPA. The performance of the SPSEBS and composite membranes was studied and compared with Nafion 117 in both proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) single cell setup.

Key words: sulfonation, composite membranes, fuel cells, heteropoly acids, SPSEBS

INTRODUCTION

Fuel cells are electrochemical energy converters, which directly transform chemical energy in to electricity (Sangeetha, 2007). PEMFCs are believed to be the best type of fuel cell as the vehicular power source to eventually replace the gasoline and diesel. However, current PEMFCs still suffer from the severe conditions e.g., low humidity, high temperature and excessive gas contaminants. A proton exchange membrane (PEM) is a semi permeable membrane generally made from ionomers and designed to conduct protons while being impermeable to gases such as oxygen and hydrogen. Separation of reactants and transport of protons are their essential functions when incorporated into a proton exchange membrane fuel cells. PEMs can be made from either pure polymer membranes or from composite membranes where other materials are embedded in a polymer matrix. One of the most common and commercially available PEM materials is Nafion. Nafion is a perfluoro sulfonic acid polymer invented in the late 1960s by WalterGroth of DuPont de Nemours. Perfluoro sulfonated ionomer membrane is a successful PEM as proton conducting separator in fuel cells. Nafion has received a considerable amount of attention as a proton conductor for PEMFCs because of its excellent proton conductivity, thermal and mechanical stability. The chemical basis of Nafion's superior conductive properties remains a focus of research. However, it is well known that application of Nafion membrane to DMFC, which uses methanol as fuel, causes the problem of methanol cross over lowering DMFC performance (Li-Chun Chen *et al.,* 2008). To address these limitations, the development of low cost and high performance

polymer as alternative materials is strongly desired. Instead of the well established different polymer electrolyte such as modified perfluorinated, partially perfluorinated and non perfluorinated polymer electrolytes are under development for fuel cell application (Antonios Kelarakis *et al.,* 2010). Composite membranes must exhibit high ionic conductivity and mechanical strength and low methanol permeability. Their use in fuel cell system is very attractive because they will enhance the efficiency of the cell significantly.

HPAs will solvate the proton of the stronger sulfonic acid, creating the ion network cluster for conduction. This type of acid does not have the volatility problems of water. When HPAs are incorporated into the membranes, the composite membrane can also conduct protons through self ionization. The HPAs, including phosphotungstic acid and silicotungstic acid has been proposed as solid electrolyte for PEMFCs application due to its high proton conductivity (Colicchio *et al.,* 2009, Giordano *et al.,* 1996). It is believed that the incorporation of HPA in an electrolyte could increase the proton conductivity of the electrolyte. The interest lies in the potential of these composite materials in the manufacture of fuel cells as they have improved operating characteristics. HPA is a class of acid made up of a particular combination of hydrogen and oxygen with certain metals and non-metals. Metal atoms linked by oxygen atoms form a cluster with the hetero-atom inside bonded via oxygen atoms. The possibilities of being in different combinations of metal atoms and different types of hetero atoms results in a number of HPA. Two of the better known groups of these are based on the Keggin, $H_nXM_{12}O_{40}$, and Dawson, $H_nX_2M_{18}O_{62}$, structures. The heteropolyacids based on the Keggin structure can possess qualities such as good thermal stability, high acidity and high oxidizing ability. The Keggin unit consists of a

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central atom in a tetrahedral arrangement of oxygen atoms surrounded by 12 oxygen octahedra connected with tungsten or molybdenum (Zhang *et al.,* 2006). Kreuer has suggested that the heteropoly acid act as a bronsted acid towards the water of hydration, which is generally loosely bound in the structure, resulting in high proton conductivity (Kim *et al.,* 2003).

This paper describes the preparation of composite membrane of a tri block copolymer with phosphotungstic acid (PWA) and silicotungstic acid (SWA). In recent years, lot of organic – inorganic composite membranes were investigated for PEMFC and DMFCs. The main purpose of this work is to provide a general method for increasing the thermal stability without decreasing proton conductivity in proton conductive polymer by inorganic modification. Phosphotungstic acid (PWA), a heteropoly acid with the chemical formula $H_3PW_{12}O_{40}$, is the strongest of heteropolyacids. It is normally present in a hydrated state. These interesting aspects of the phosphotungstic acid electrolyte justified the orientation of research activity towards the fixation of the heteropolyacids in stable structures so that they could become water-insoluble while retaining their high proton conductivity (Mosa *et al.,* 2008). PWA is an interesting compound to be incorporated as dopant in membranes to provide high proton conductivity (Mioč *et al.,* 1991, Honma *et al.,* 2002, Staiti *et al.,* 1999, Chuang *et al.,* 2007, Lavrenčič Štangar *et al.,* 2001, Aparicio *et al.,* 2005, Uma *et al.,* 2006, Park *et al.,* 2000). The silico tungstic acid (SWA) molecular formula with $H_4[W_{12}SiO_{40}]$ was also chosen as an inorganic proton conductor material. It was preferred because it forms more stable material and displays higher proton conductivity (Mosa *et al.,* 2008, Sangeetha, 2004). The silicate network also improves the mechanical strength and chemical durability (Mioč *et al.,* 1991).

EXPERIMENTAL

Materials

Polystyrene-block-(ethylene-ran-butylene)-block-polystyrene (PSEBS) (Mw = 89,000; 29% styrene) and phospho tungstic acid (PWA) and silicotungstic acid (SWA) were purchased from SRL. Chlorosulphonic acid (CSA) was purchased from Spectrochem and used without further purification. Tri-butyl phosphate (TBP) was purchased from Lancaster. The solvent used for membrane casting was Tetrahydro furan (THF) and was purchased from Merck.

Sulfonation of PSEBS

Polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene (PSEBS) (M_w = 89,000; 29% styrene) from Aldrich (Germany) was sulfonated as reported in the literature.[18]

Preparation and purification of composite membranes

The appropriate weights of SPSEBS ionomer and heteropoly acid were dissolved in THF separately and the solutions were mixed and allowed for stirring to obtain a homogeneous mixture. Then the polymer solution was cast in to a clean glass plate and the membrane was prepared by solvent evaporation method.[19] Membranes containing 1, 2, 5 and 7.5 wt% of PWA and SWA in SPSEBS were prepared.

Distribution and the effect of heteropoly acid loading in the membranes were studied by various analysis. The purification test is generally conducted to remove the impurities from the membranes before feeding into the fuel cell. The membranes were allowed to boil in 3% H_2O_2, then allowed in boiling water for 15 minutes and then for half an hour in 10% H_2SO_4. Finally, it was washed with boiling water.

Water and methanol absorption

Swelling studies were carried out on the dry samples. The dry membrane samples were weighed and immersed in water and methanol separately and equilibrated for one day. The wet weights of the swollen membranes were measured after wiping the surface solvents on either sides of the membrane. The water/ methanol absorption was calculated using the given formula

$$H_2O/ MeOH\ Uptake = \frac{W_{wet}\ -\ W_{dry}}{W_{dry}}\ x100\% \qquad (1)$$

Where W_{wet} and W_{dry} are the wet membrane weight and dry membrane weight respectively

Ion Exchange Capacity (IEC)

Ion exchange capacity measurements of the composite membranes were determined by titration method. A desired area of the membrane was equilibrated in 2M KCl solution for overnight to ensure that the membranes were fully converted from H^+ form into K^+ form. The amount of H^+ liberated was estimated by acid-base titration with sodium carbonate (titrant) solution of known concentration (0.01N) with phenolphthalein as indicator. IEC is then calculated using the formula given below

$$IEC= \frac{Titre\ value\ (ml)\ x\ Normality\ of\ titrant\ (N)}{Wt.\ of\ the\ dry\ polymer\ membrane\ (g)}\ meq/g \quad (2)$$

Durability test

For checking the durability of the SPSEBS membrane as well as composite membranes, the following procedure was adopted. Initially, a 4 ppm ferrous ammonium sulfate, 3% H_2O_2 was freshly prepared and the temperature was maintained at 80 °C. The membrane with the dimension of 0.5 cm^2 was cut and placed in the solution. The time required for the physical degradation is carefully noted down and reported.

Characterization

FTIR spectra were recorded in absorbance mode on a Perkin–Elmer FTIR spectrometer. The spectra were obtained for both SPSEBS and composite membranes. The TGA was carried out using a thermo balance SDT Q600 US analyzer at a heating rate of 20 ºC/min under nitrogen atmosphere. The tensile properties of the membranes were determined at ambient condition by HOUNSFIELD UTM. The samples were cut into a size of 5 mm x 50 mm of thickness 300 microns and the speed of moving cross heads was set to 10 mm/min (Linkous *et al.,* 1993). The membrane morphology was investigated by field emission scanning electron microscopy in a JEOL JSM-

6360 equipment. The samples were coated with platinum for observation in the microscope. To know the level of dispersion of the inorganic content in the polymer membranes and to know the amount of crystallinity, XRD measurements were performed using a X' pert pro diffractometer.

Methanol permeability

Experiment to evaluate methanol permeability was carried out by using a testing cell, consisting of two reservoirs separated by the sample membrane. The two-compartment glass cell used in this experiment has been previously described (Ding *et al.,* 2007); the PEM is sandwiched between donor (Chamber A) and receptor (Chamber B) compartments as shown in Fig. 1. Initially, the donor compartment was filled with 50 ml of aqueous 2M methanol solution and the receptor compartment with 50 ml of deionized water. The change in concentration of methanol in receptor compartment was measured as a function of time. The two compartments were kept under stirring conditions. For every one hour interval, few drops of solution from receptor compartment was withdrawn by syringe and placed in a prism of refractometry. The permeability was determined from refractive index meter [ATAGO, Japan (model PAL-3)] readings.
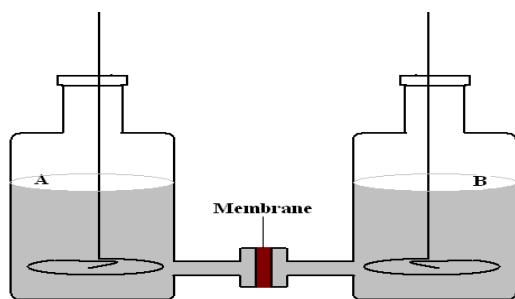

Fig. 1. Schematic diagram of the setup used for methanol permeability study

Proton conductivity

Proton conductivity of the membrane samples were measured in a measurement cell using complex impedance spectra, obtained using Volta lab dynamic-EIS voltammetry model PGZ 301. Studies were carried out using a 2-compartment electrochemical cell using platinum foil electrodes and 1M sulphuric acid solution as the electrolyte.

Fuel cell performance

Membrane electrode assembly (MEA) was constructed as reported in the literature (Bhavani *et al.,* 2011).

RESULTS AND DISCUSSION

The thickness of all the membranes was maintained at approximately 130 µm. The IEC values of the SPSEBS and the composite membranes with various compositions (1, 2, 5, 7.5 and 10 wt%) of PWA and SWA content were tabulated in Table 1 and 2. The IEC is usually defined as the moles of fixed -SO_3H sites per gram of polymer. It is observed that IEC of the composite membranes increased continuously with the increment in HPA content. This may be due to the fact that the HPA itself acts as the major proton source (Kim *et al.,* 2003).

Table 1. IEC and Absorption of the SPSEBS/PWA composite membranes at ambient condition

PWA content (wt %)	IEC (meq/g)	Absorption (%) Water	Absorption (%) Methanol	Tensile strength (MPa)
0	2.07	134	104	1.5
1	2.40	134	102	1.5
2	2.53	123	89	1.5
5	2.72	96	83	1.5
7.5	2.90	95	75	1.5
10	2.95	93	61	3.5

Table 2. IEC, Absorption and tensile strength of the SPSEBS/SWA composite membranes at ambient condition

SWA content (wt %)	IEC (meq/g)	Absorption (%) Water	Absorption (%) Methanol	Tensile strength (MPa)
0	2.07	134	104	1.5
1	2.42	131	101	1.5
2	2.50	127	99	3.0
5	2.67	116	88	4.5
7.5	2.81	99	81	5.5
10	2.94	91	73	6.0

The water and methanol uptake of the various composite membranes are also shown in Table 1 and 2. PEMFCs use a proton-conducting polymer membrane as an electrolyte, which is typically a poor proton conductor unless water is present. Therefore the hydration of a PEM is very important to the performance of the fuel cell. In the present case the water and methanol uptake of the composite membranes decreased with the increase in HPA content. This is due to the interaction developed between the sulfonic acid moiety of the polymer chain and the hydroxyl group of HPA molecules, which in turn may reduce the capacity of holding water (or methanol) molecules (Lin *et al.,* 2005).

Methanol permeability

In DMFCs, the methanol permeability results in a significant loss of fuel cell performance. The transport of methanol in PEMs may require well-connected channels, which are formed by hydrophilic sulfonic functional groups (Staiti, *et al*., 2001). The measured methanol permeability of the composite membranes versus the HPA loading in the membrane are shown in Fig.2. Initially, the methanol permeation in all the membranes increased as a function of time and it reached the maximum level over a period of time. The maximum stable value of methanol permeation was reached at about 6-7 hours for all the composite membranes. It is clear from the figure that the methanol permeability decreased with the increase in HPA loading in to the SPSEBS membrane. The decrease in methanol permeability may be attributed to the interaction between the hydroxyl groups of HPA and sulfonic acid groups of the polymer. These interactions reduce the ionic channels, and hence decrease the methanol permeability. Also, the non ionic block of the polymer can act as a barrier for methanol permeation and the block copolymer ionomer have the ability to self assemble into nanostructured morphologies that may lead to different transport properties compared to random ionomer. The decrease in permeability of methanol with increase in HPA content is consistent due to the fact that the composite membrane possesses a better compatibility and a good dispersion of inorganic material in the polymer membrane is obtained.
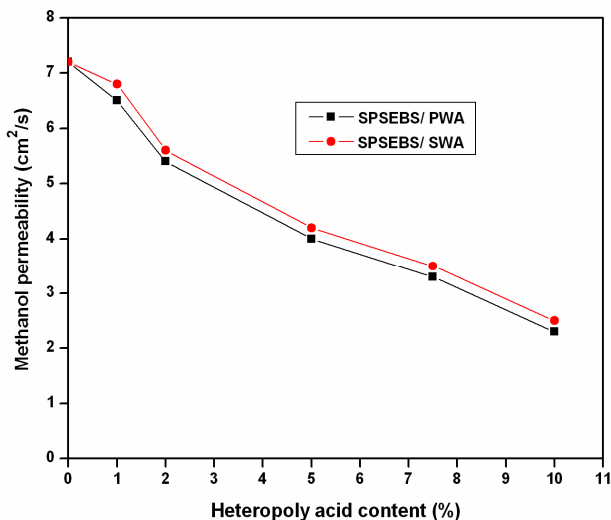
Fig. 2. Methanol permeability with the increase of HPA content

FTIR

The specific interaction in HPA/sulfonated polymer represents one of the most important factors including the miscibility and mechanical property of the composite membrane. The specific interaction was elucidated by means of FTIR spectroscopy, primarily on the basis of two frequency regions: (i) The SO_3 symmetric stretching region (1000-1050 cm^{-1}) and (ii) The W-O stretching region (700 - 850, 870 - 1010 cm^{-1}) (Lin *et al.,* 2005). The FTIR spectra of 1, 2, 5, 7.5 and 10 wt% PWA composite membrane is shown Fig. 3. Appearance of broad envelope around 3000-3600 cm^{-1} was assigned to -OH stretch of sulfonic acid group. The symmetric stretch of SO_3 is obtained at 1031.8 cm^{-1} in pure SPSEBS and red shifted to 1029.9 cm^{-1} when blended with PWA. The symmetric stretch of sulfone group at 1126 cm^{-1} in both the composites remains insensitive to the incorporation of HPA. This indicates that the PWA particles interact primarily with the sulfonic acid group. In SPSEBS/SWA (Fig. 4) composite membrane, peaks between 800 -1100 cm^{-1} is responsible for the S – O – Si linkage (Kim *et al.,* 2003).
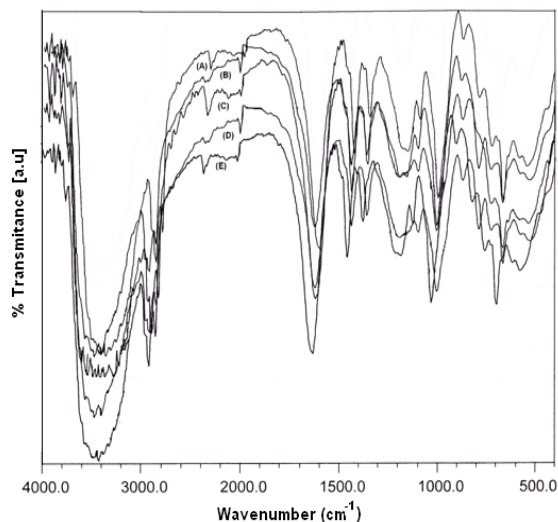

Fig. 3. FTIR spectra of (A) to (E) SPSEBS/PWA composite membranes of 1, 2, 5, 7.5 and 10% of PWA content
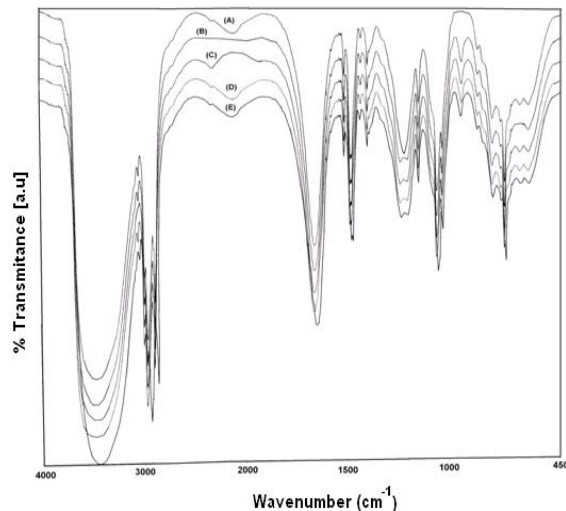

Fig. 4. FTIR spectra of (A) to (E) SPSEBS/SWA composite membranes of 1, 2, 5, 7.5 and 10% of SWA content

Appearance of peak in this region is an evidence for the silica chemically bonded with the sulfonic acid group. The symmetric stretch of SO_3 is obtained at 1031.8 cm^{-1} in pure SPSEBS and red shifted to 1035 cm^{-1} when blended with SWA. This confirms the chemical linkage between the sulfonic acid group and silica.

Thermogravimetric analysis

The TGA thermograms of the treated and untreated membranes are displayed in Fig. 5 and 6. It is seen that all the membranes retain more than 75% of their weight up to a temperature of about 400 $^\circ$C. The TGA curves can be divided in to regions corresponding to different weight loss. Two weight loss steps were observed for the composites, which are reflected by two broad peaks in the DTA curve.
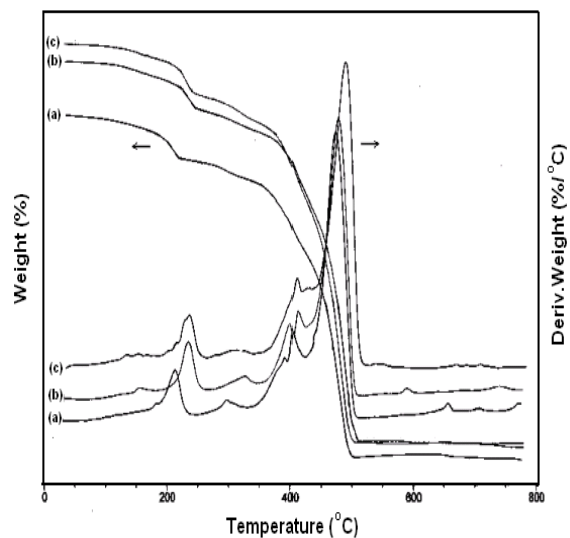

Fig. 5. TGA – DTA curve of (a) SPESBS and (b) composite membrane (5 wt% PWA) before boiling water treatment (c) composite membrane (5 wt% PWA) after boiling water treatment
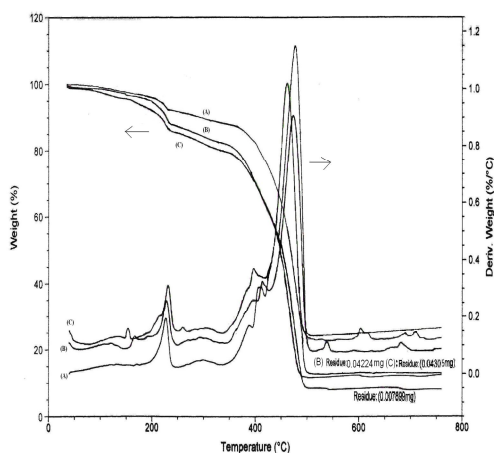
Fig. 6. TGA – DTA curve of (a) SPESBS and (b) composite membrane (5 wt% SWA) before boiling water treatment (c) composite membrane (5 wt% SWA) after boiling water treatment

The first decomposition around the region of 220 ^{o}C shows the weight loss attributed to splitting-off of sulfonic acid groups. This decomposition accounts for the loosening of sulfonic acid groups present in the composite membranes. A similar observation was made for all the composite membranes. The second decomposition was found to be around 400 ^{o}C. Above 400 ^{o}C all the membranes started to decompose in a rapid manner. This weight loss is assigned to the final thermal decomposition of polymeric network. In the thermal degradation of SPSEBS/SWA and SPSEBS/PWA composite membranes the final degradation temperature shifted to around 460 ^{o}C. It may be due to the crystallization of PWA and SWA frame works in the hybrid membranes. The broad exothermic peak between 400 and 500 ^{o}C observed in the DTA curve agrees with this continuous weight loss. Judging on this, the composite materials can be considered thermally stable up to 220 ^{o}C and will be stable enough within temperature range for PEMFC and DMFC applications.

UTM studies

The tensile strength of the SPSEBS and HAP composite membranes are shown in Table 1 and 2. The tensile strength of the composite membranes was increased with the addition of HPA in the polymer matrix, because the ionic channel interactions was slightly reduced.

Membrane morphology

SEM was used to characterize the structural morphologies of the SPSEBS/PWA and SPSEBS/SWA composite membranes. The morphology of the composite membranes is shown in Fig.7 and 8. It can be seen that the solid PWA is uniformly well distributed over the membrane and do not form any agglomerated like structures. It is difficult to find the significant interfaces between inorganic and organic compounds. As shown in Fig. 7(c), the membrane with 5 wt% PWA shows uniform distribution of the PWA particles throughout the polymer matrix. The homogeneity of the composite membrane indicates no phase separation suggesting that the organic and the inorganic compounds were blended at molecular level. Based on these results, it may be concluded

that PWA treatments to make SPSEBS better proton conduction have proved positively. Whereas, in the case of SPSEBS/SWA as seen in Fig. 8, there are two visible phase regions indicating the phase separation between the organic polymer and inorganic SWA component.
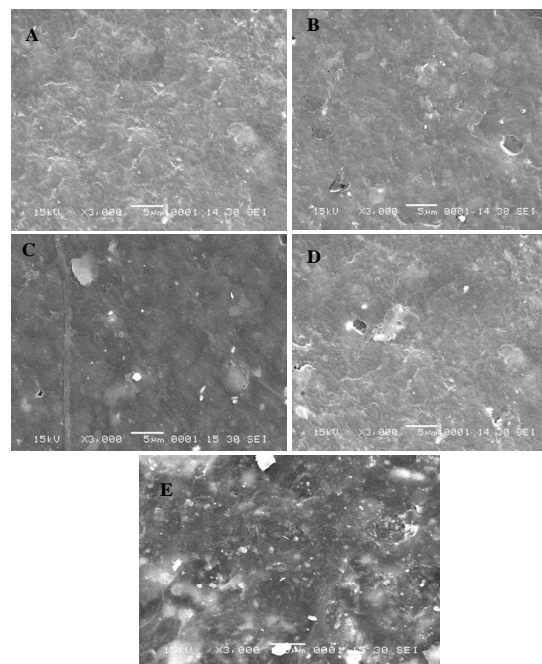

Fig. 7. SEM images of (A) to (E) SPSEBS/PWA composite membranes of 1, 2, 5, 7.5 and 10% of PWA content
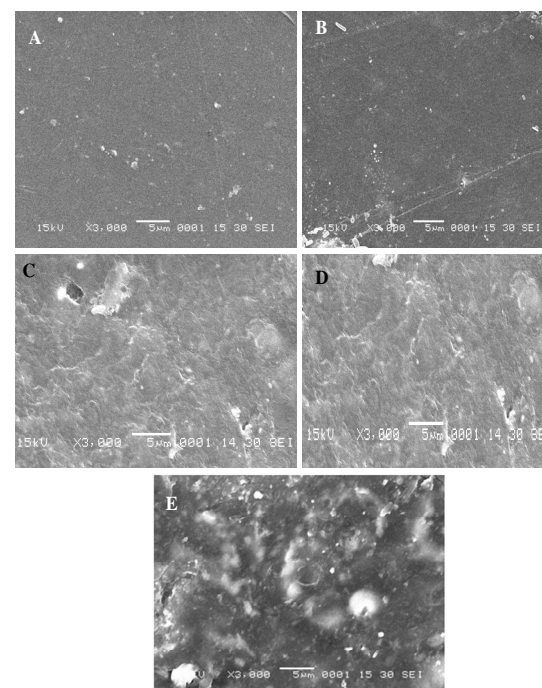

Fig. 8. SEM images of (A) to (E) SPSEBS/SWA composite membranes of 1, 2, 5, 7.5 and 10% of SWA content

XRD studies

The purpose of XRD is to investigate the relation between the structural changes such as, crystallinity and formation of new crystalline regions in the polymer matrix. In the crystalline

and the partially crystalline polymer, the periodic repeating crystalline layer gives rise to well defined sharp diffraction peaks. On the other hand, non crystalline (or) amorphous material generates broad peaks. Crystallinity was evaluated quantitatively for the cast SPSEBS and composite membranes and the incorporation effect of HPA was investigated. The diffraction pattern of the SPSEBS and composite membranes are shown in Fig. 9 and 10. The broad peak ranging from 15° to 25° in SPSEBS is believed to be the amorphous region of polymer membrane. According to the literature this broad peak can be divided into two peaks assigned to be amorphous ($2\theta = 16^o$) and crystalline ($2\theta = 17.5^o$). In the case of SPSEBS/PWA composite membranes, figure 9 compares the XRD pattern of the PWA, SPSEBS and the composite membranes (Elamathi *et al.,* 2009, Costamagna *et al.,* 2002, Staiti *et al.,* 2001, Dimitrova *et al.,* 2002). PWA (a) shows an intense peak at 54° (2θ), which faded with the addition of sulfonated polymer material. It confirms the good dispersion of the PWA in the polymer matrix. The X-ray diffraction pattern of SPSEBS (b) shows an intense pattern at $2\theta = 72.61^o$ and weak patterns at $2\theta = 43.74^o$ and 50.94^o. Combination of both amorphous and crystalline phases is evident from the spectrum. Amorphous phase appears to be dominating over the crystalline phase.
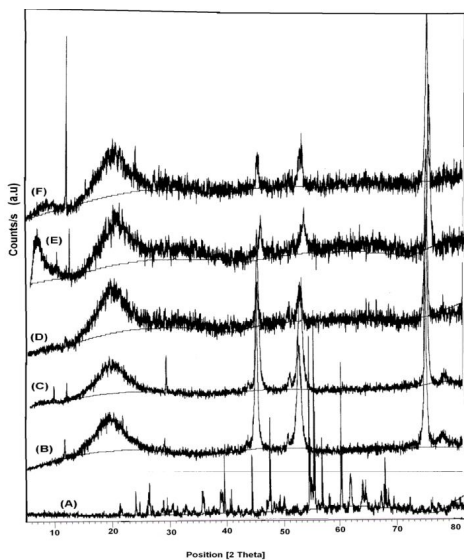

Fig. 9.   XRD patterns of (A) PWA, and (B) to (F) SPSEBS/PWA composite membranes of 1, 2, 5, 7.5 and 10% of PWA content

In the XRD pattern of SPSEBS/PWA composite membrane, all the patterns of PWA are not observed. Though some patterns are appearing, selective missing of certain patterns illustrates a strong interaction of the plane corresponding to this pattern of PWA with the polymer matrix. Hence the diffracted rays from this plane might be completely false scattered by the polymer matrix. Hence the entire PWA grains might be completely well surrounded by polymer matrix in order to completely suppress the patterns of PWA. From the Fig. 10, for the pattern of SWA the crystalline peak at $2\theta = 8.26^o$ was found. In the case of PSEBS/SWA composite membranes, it is note worthy that the new crystalline peak corresponding to the crystalline peak of SWA appears in the amorphous region of SPSEBS membrane at $2\theta = 12^o$. It indicates that the SWA crystalline region seems to be newly

formed in the amorphous structure of cast polymer in composite membranes. This suggests that SWA may cause structural modification, indicating that new type crystalline region may be created in the amorphous region of polymer matrix or possibly at the interface of HPA and polymer. It can be seen that the crystallinity of the composite membranes were increased by increasing inorganic content.
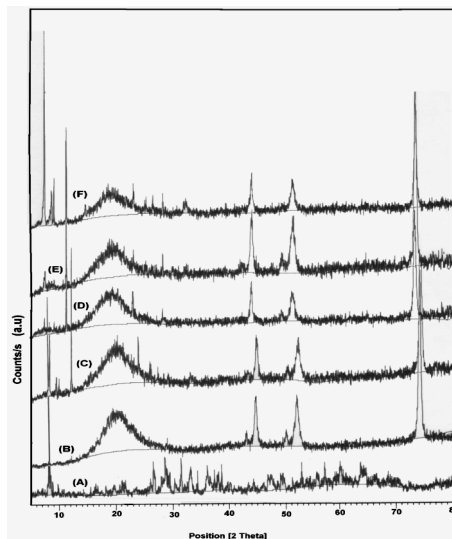

Fig. 10.   XRD patterns of (A) SWA and (B) to (F) SPSEBS/SWA composite membranes of 1, 2, 5, 7.5 and 10% of SWA content

Proton conductivity

The conductivities of all composite membranes using PWA and SWA are slightly higher than that of the host polymer membrane and increases with the increase in the content of HPA is shown in Table. 3. The condensed HPA in the composite membranes might decrease the distance between two sulfonate groups, resulting in an increased conductivity. It can be concluded that the homogeneous distribution of the two main components is crucial. The high proton conductivity of doped membranes at low temperature is attributed to the network containing PWA and SWA acid ions as proton donors and strongly hydrogen bonded hydroxyl groups. The mechanism of conduction in these materials is likely to be promoted by proton jump from one to other position. Ionic conductivity measurements at ambient conditions were performed on samples of composite membranes with different wt% of PWA and SWA content in SPSEBS material. Among the measured samples the conductivity of the composite membranes with phosphotungstic acid and silicotungstic acid were increasing from 10^{-3} to 10^{-2} S/cm with the increase in HPA loading.

Table 3. Proton conductivity of SPSEBS/HAP composite

Sample	Conductivity (S/cm)
SPSEBS	5.50×10^{-3}
PWA – 1	1.20×10^{-2}
PWA – 2	1.29×10^{-2}
PWA – 5	1.53×10^{-2}
PWA – 7.5	2.19×10^{-2}
PWA –10	3.07×10^{-2}
SWA – 1	1.31×10^{-2}
SWA – 2	1.65×10^{-2}
SWA – 5	1.89×10^{-2}
SWA – 7.5	2.09×10^{-2}
SWA – 10	2.15×10^{-2}

Although the water absorption was decreased with increase in HPA content, the composite membrane showed higher conductivity with the HPA loading. This may be due to the presence of larger number of labile protons of heteropoly acid that contributes to the proton conduction in the composite membranes when compared to the SPSEBS membranes.

Selectivity ratio

The selectivity ratio of composite membranes is given in Fig. 11. The HAP membranes exhibited a higher selectivity ratio when compared with pristine SPSEBS mambrane. Strong interaction between SPSEBS and HPA are believed to confer decrease of the methanol permeability. The presence of a HPA component provides additional beneficial effects like water retention, reduction of methanol cross over with increasing proton conductivity.
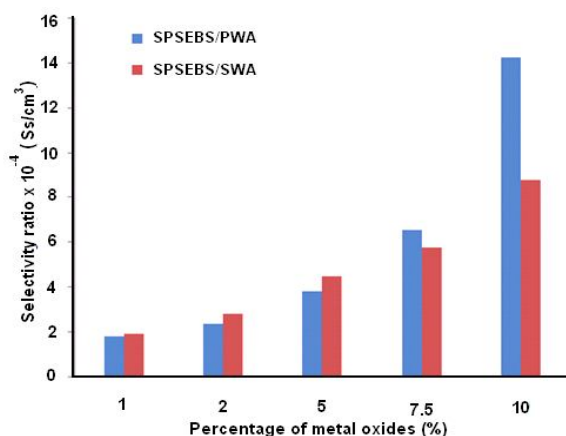
Fig.11. Selectivity of SPSEBS/HPA composite membranes

The increase of proton conductivity while decreasing methanol permeability shows high selectivity ratio. SPSEBS/PWA composite membrane showed higher selectivity than SPSEBS/SWA composite membranes.

Durability

The durability of SPSEBS as well as the composite membranes was determined in Fenton's reagent at 80 ºC. This gives an idea about the life time of the electrolyte membranes. All the membranes were found to be stable even after 8 hours, without any physical degradation. This indicates that the composite membranes are very well suitable for application as electrolytes in fuel cell.

Single cell performance in PEMFC

SPSEBS/PWA (5%) and SPSEBS/SWA (5%) composite membranes were used to prepare the MEA for single cell (25 cm^2) performance. The cell voltage data of single cell for PEMFCs operated at room temperature with hydrogen and oxygen feed concentration of 40 ml/min is shown in Fig.12. The open circuit voltage of SPSEBS/PWA membrane (0.846V) and SPSEBS/SWA (0.889V) is higher than that of pristine SPSEBS and commercially available Nafion 117 membrane. The maximum power density is achieved first in the case of SPSEBS/SWA (269.5 mW/cm^2) at a current density of 700 mA/cm^2 and SPSEBS/PWA (257.4 mW/cm^2) at a current density of 600 mA/cm^2 than the SPSEBS

(247.8 mW/cm^2) and Nafion (225.0 mW/cm^2) at a current density 600 mA/cm^2. This is due to the addition of HPA in the ionomer, because as mentioned above, HPA itself can act as a proton source.
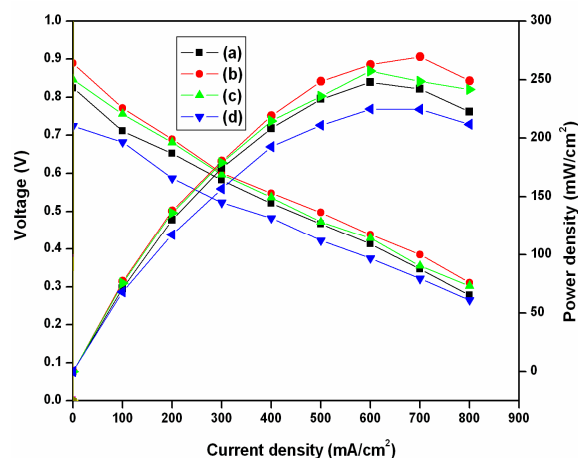
Fig. 12. Comparison of the polarization with power density curves of the (a) SPSEBS, (b) SPSEBS/SWA, and SPSEBS/PWA and Nafion 117 in single cell PEMFC. The data were collected with a H$_2$ flow rate of 40 mLmin^{-1} at the anode and an O$_2$ flow rate of 40 mLmin^{-1} at the cathode. Anode: 0.125 mg Pt cm^{-2}; cathode: 0.375 mg Pt cm^{-2}, at room temperature

Single cell performance in DMFC

The potential vs current density and the power density vs current density curves for the composite membrane in DMFC are shown in Fig.13. The maximum power density was 57.3 mW/cm^2 for the SPSEBS with PWA membrane compared to SPSEBS with SWA membrane (52.05 mW/cm^2) and pristine SPSEBS membrane (43.8 mW/cm^2). The Nafion membrane showed the maximum power density of 49.2 mW/cm^2 at a current density of 150 mA/cm^2 because of its higher methanol permeability. Compared to pristine SPSEBS and Nafion, the composite membranes showed higher power density because of its higher proton conductivity and lower methanol permeability.
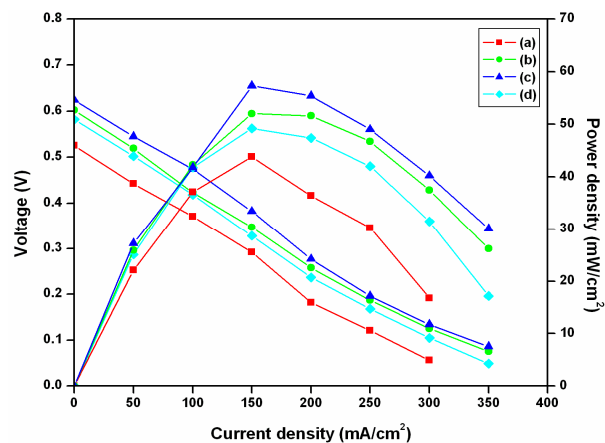
Fig.13. Comparison of the polarization with power density curves of (a) SPSEBS, (b) SPSEBS/SWA, (c) SPSEBS/PWA and (d) Nafion membranes in DMFC. The data were collected with a methanol flow rate of 20 mLmin^{-1} at the anode and an O$_2$ flow rate of 40 mLmin^{-1} at the cathode. Anode: 0.25 mg PtRu cm^{-2}; cathode: 0.375 mg Pt cm^{-2}, methanol concentration: 1M at room temperature

Conclusion

A series of composite membranes have been successfully prepared by solution mixing of PWA and SWA with sulfonated triblock copolymer. The composite membranes improved its water and methanol resistant properties with the addition of HPA and the stability test of the membranes with HPA content were able to withstand in a peroxide solution for more than 8 hours. The tensile strength results indicate the mechanical strength improvement of membranes for HPA composite membrane, than the pristine SPSEBS. TGA results concluded the composite membranes were thermally stable up to 240 ^{o}C and uniform dispersion of inorganic materials in polymer material was confirmed with SEM images and XRD spectra. These membranes exhibited the conductivity from 10^{-3} to 10^{-2} S/cm. Proton conductivity of the composite membranes increased with increase of the HPA. From these results, it is concluded that SPSEBS/PWA and SPSEBS/SWA composite membranes have great potential as electrolytic membranes and these membranes can be highly suitable for both PEMFC and DMFC application.

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