J Mater Sci (2011) 46:1741–1748
DOI 10.1007/s10853-010-4993-3

Synthesis, characterization of novel silicotungstic acid incorporated SPEEK/PVA-co-ethylene-based composite membranes for fuel cell

Baskar Ramaganthan · P. M. Sivakumar · Sangeetha Dharmalingam

Received: 2 July 2010 / Accepted: 7 October 2010 / Published online: 30 October 2010

Abstract Sulfonated polyether ether ketone (SPEEK) is prepared by the sulfonation of polyether ether ketone (PEEK). Five of the composite membranes (PSW1–PSW5) with various percentage compositions of the SPEEK, PVA-co-ethylene, and silicotungstic acid (SWA) were prepared. The prepared composite membranes were characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Surface morphology of the composite membranes was analyzed using scanning electron microscopy (SEM). Other evaluations related to conductivities (ion exchange capacity, IEC), proton conductivity), absorptivity (water and methanol absorption), durability and mechanical properties (tensile strength and percentage elongation) were also evaluated for the composite membranes. Among the five composite membranes, composite membrane with higher SWA content, PSW5 (which has 10% SWA) showed more conductivity compared to other membranes. These composites also showed very good conductivities, mechanical properties, and durabilities. Hence, these composite membranes have the potential to be used in the development of newer proton exchange membrane fuel cells (PEMFCs).

B. Ramaganthan (✉) · S. Dharmalingam
Department of Chemistry, Anna University,
Chennai 600 032, India
e-mail: baskchem@yahoo.co.in

P. M. Sivakumar
Department of Biotechnology, Indian Institute of Technology
Madras, Chennai 600 036, India

Introduction

Proton exchange membrane fuel cells (PEMFCs) are found to be excellent and most promising energy conversion devices for automotive, stationary, and portable devices [1, 2]. It has several advantages like low cost construction materials, its relative simplicity of design and operation, being environmentally clean, highly efficient, etc. [3–5]. Nafion is found to be an effective membrane used in PEMFC due to its mechanical and chemical stability and excellent proton conductivity. Though it has many excellent favorable properties, it has a few limitations too. To name a few, high cost, difficulty in synthesizing, loss of conductivity at elevated temperature, necessity of humidification, difficulty in recycling and disposal of these fluorinated membranes which can cause environmental problems, etc. [6–8].

Hence, there is a need for newer electrolyte polymer membrane to be developed for higher temperature PEMFCs without fluorine-based backbone [9]. Aromatic polymer, poly (ether ether ketone) (PEEK), has very excellent thermal stability, high electrical and mechanical performance and high chemical resistance even at elevated temperatures. PEEK is hydrophobic in nature and after sulfonation of PEEK to sulfonated PEEK (SPEEK), the hydrophilicity of the membrane is higher which also helps in the proton conductivity of the membrane [10].

PVA-co-ethylene acts as a backbone. SO_3H^- group in sulfonated PEEK conducts protons and also interacts with the OH group of PVA-co-ethylene. Incorporation of the PVA-co-ethylene increases the mechanical stability (durability) and prevents the SO_3H^- ions present in the SPEEK from the attack of the free radicals. Earlier Helen et al. used PVA as polymeric matrix in the preparation of composite membranes [11]. Optimal quantity of heteropoly acid if incorporated into the membrane to form a stable structure prevents leaching of molecules when the membrane is immersed in water [11]. Silicotungstic acid (SWA) is one such heteropoly acid, has been incorporated into these membranes and its properties have been thoroughly studied [12]. It has been observed that after incorporation of SWA, the membrane has higher proton conductivity and increased thermal stability. Earlier Staiti et al. has already used SWA as inorganic proton conductor [12].

When compared to the homopolymeric membranes, blends and composites are superior, as their properties can be altered by varying the composition. Kerres et al. [13] synthesized and characterized novel acid–base blend membranes based on PEEK–PSU (polysulfone) as acid, and poly benzimidazole (PBI) and poly (ethylene imidazole) (PEI) as base. The acid–base blend membranes showed good proton conductivities, ion exchange capabilities (IEC), and excellent thermal stabilities. Soczka-Guth et al. [14] has reported (poly ether ketone) PEK–PBI blend. Helen et al. [11] also has studied the properties of PVA matrix composite membranes doped with other inorganic contents like SWA and zirconium phosphate. The composite materials have lesser methanol cross over compared to Nafion 115.

Present work comprises of various important improvements in the physical properties of the composite membranes. The UTM measurements of the membranes developed (e.g., PSW1–PSW5) have shown a clear enhancement in elasticity (% elongation) to an extent of 20%. Swelling due to water and methanol makes our membranes better proton conductive material which is favorable for fuel cells. The green chemistry used in the procedure makes the system environment friendly. Probably one of the most important achievements is in cost reduction in the process.

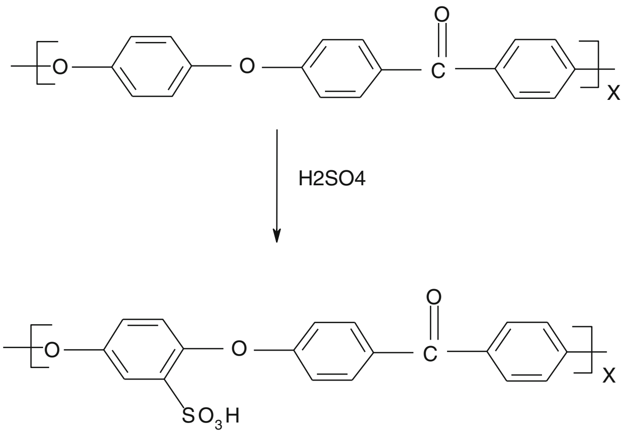
Materials and methods

PEEK was purchased from Victrex, England, PVA-co-ethylene was purchased from Aldrich Chemicals, *N*-methyl pyrollidone (NMP) and SWA were purchased from SRL chemicals, Mumbai, India. Solvents and other chemicals used in the studies were purchased from SRL chemicals, Mumbai, India.

Preparation of the composite membrane

Sulfonation of PEEK

About 10 g of the PEEK powder was dried overnight at 100 °C to eliminate any traces of moisture. It was then accurately weighed and quickly transferred into round bottom flask. The flask was equipped with a nitrogen inlet and outlet. Required quantity of sulfuric acid was then added and the reaction contents were vigorously stirred. After the stipulated time, the entire contents of the flask were poured into a tray containing a large excess of water with crushed ice. The innumerable fibers obtained were recovered by filtration and then washed repeatedly until the pH of the wash water fell close to 7. It is important to remove even the last trace of acid as it may affect the properties of the product. It was then dried in an oven at 100 °C for about 10 h. The final product obtained was the sulfonated form of PEEK and is denoted as SPEEK. The sulfonation occurs exclusively on the hydroquinone segment which is consistent with the result of Xing et al. [15]. Scheme 1 shows the sulfonation of the PEEK.



Scheme 1 Sulfonation of the PEEK

Preparation of composite membrane

PVA-co-ethylene was initially dissolved in NMP at 50 °C. Appropriate amount of SPEEK was then added and it is stirred until a homogenous solution was obtained. The SWA ($2H_2O{\cdot}SiO_2$, $12WO_3{\cdot}30H_2O$) heteropoly acid was then added over a period of time with constant stirring. The resulting solution was stirred for about 8 h and the temperature was maintained at 50 °C. The homogenous

Table 1 Membrane code, its composition, durability and tensile strength

S. no.	Membrane code	Composition, wt% PVA-co-ethylene: SPEEK:SWA	Durability (h)	Tensile strength (MPa)
1	PSW 1	49:49:02	8.50	23.5
2	PSW 2	48:48:04	8.35	21
3	PSW 3	47:47:06	8.20	17
4	PSW 4	46:46:08	8.00	15
5	PSW 5	45:45:10	7.45	12

solution obtained was then cast onto a clean dry petri dish. Membranes were obtained by drying the contents of the petri dish at 80 °C for another 10 h [16]. Five different membranes (PW1–PW5) were prepared by varying the weight percentage composition of ingredients (SPEEK: PVA-co-ethylene: SWA). The composition of the membranes is shown in Table 1.

Characterization of composite membranes

Fourier transform infrared spectroscopy (FT-IR)

The IR spectra (450–4000) for the dried membranes were recorded with a Perkin Elmer FT-IR spectrometer at 25 ± 2 °C. The samples were dried at 100 °C for an hour before recording the spectrum. The interactions between the inorganic hetero poly acid and the polymer matrix were studied.

Thermogravimetric analysis (TGA)

The TGA was carried out to determine the thermal stability of the membrane. The loss in weight of the membrane with increase in temperature at a heating rate of 10 °C/min in the range of temperature between 30 and 800 °C was recorded using a SDT Q600 US analyzer.

X-ray diffraction (XRD)

The XRD measurement was done using the "X"pert pro diffractometer. The dried membrane sample was mounted on an aluminum sample holder and the scanning angle was varied from 1° to 80° with a scanning rate of 2° per min. All the spectra were taken at ambient temperatures (25 ± 2 °C).

Scanning electron microscopy (SEM)

The surface morphology of the composite was investigated using scanning electron microscope (JEOL 6360 instrument). A piece of membrane was vacuum sputtered with a thin layer of platinum prior to SEM examination. The nature of pores, the level of dispersion, and the crystal formation of the SWA were examined.

Evaluation of composite membranes

Ion exchange capacity (IEC)

The number of replaceable H^+ ions in the membrane is called IEC. The SPEEK/PVA-co-ethylene/SWA blend composite membrane was placed in saturated KCl solution, for at least 24 h. With in this time, all the H^+ ions in the membrane was replaced by K^+ ions and the H^+ in the solution was determined by titrating with 0.01 N sodium carbonate solution [17].

$$\text{IEC} = \frac{\text{Strength of sodium carbonate} \times \text{volume of sodium carbonate}}{\text{Weight of the membrane}} \tag{1}$$

Proton conductivity

The proton conductivity was measured by AC impedance technique (auto lab), under the frequency range of 10 Hz–40 kHz in the hydrated condition. The conductivity (σ) of the composite membrane was obtained from the resistance offered by the membrane using the relationship [18]

$$\sigma = L/RA, \tag{2}$$

where L is the thickness of the membrane in cm, R is the resistance of the membrane in Ω, and A is the area of the membrane under study in cm^2.

Water and methanol absorption

Measurement of solvent (water/methanol) uptake was determined by finding out the difference between the weight of the wet membrane and dry membrane. The dry membrane was weighed and then soaked in the corresponding solvent for a minimum period of three days, to ensure complete absorption. After the stipulated time, the membrane was taken out and excess solvent on the surface was quickly removed with the help of tissue paper, and the sample was weighed. The percentage absorption was calculated using the following formula [18].

$$\%\ \text{absorption} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100, \tag{3}$$

where M_{wet} is the weight of wet membrane and M_{dry} is the weight of dry membrane.

Durability test

3% Hydrogen peroxide, 4 ppm ferrous ammonium sulfate solution was freshly prepared and the temperature was maintained at 80 °C. The membrane was soaked in this solution and the time required for the physical disintegration was carefully noted.

Mechanical properties

The mechanical properties of the membranes were studied using Houns field universal testing machine (UTM). The samples were cut into 0.5 × 7 cm, as reported by Ding et al. [19].

Results and discussion

The composite membranes were synthesized, characterized, and evaluated. Table 1 shows the composition of the membranes (PSW1–PSW5).

Characterization of composite membranes

FT-IR

Synthesized SPEEK gave characteristic peaks at 3450 (O–H vibration from HSO_3 group interact with water molecules), 1219, 1076, 1018 (sulfonic group in SPEEK), and 1644 (C=O stretching). Similar peaks were also observed for SPEEK by Yang [20].

FT-IR spectra measurement for PVA-co-ethylene showed characteristic peaks at 3257 (OH stretching), 2924 (CH_2 stretching), and 1443 (CH_3 bending). Characteristic peaks were also observed for SWA, which were similar to the earlier report of Helen et al. [11]. The composite membranes (PSW1–PSW5) showed characteristic peaks for its components (PVA-co ethylene, SWA, and SPEEK). The detailed vibrational frequencies for the composite membranes (PSW1–PSW5) and their components (PVA-co-ethylene, SWA, and SPEEK) are shown in Table 2. The FT-IR spectrum PSW5 is shown in Fig. 1.

XRD

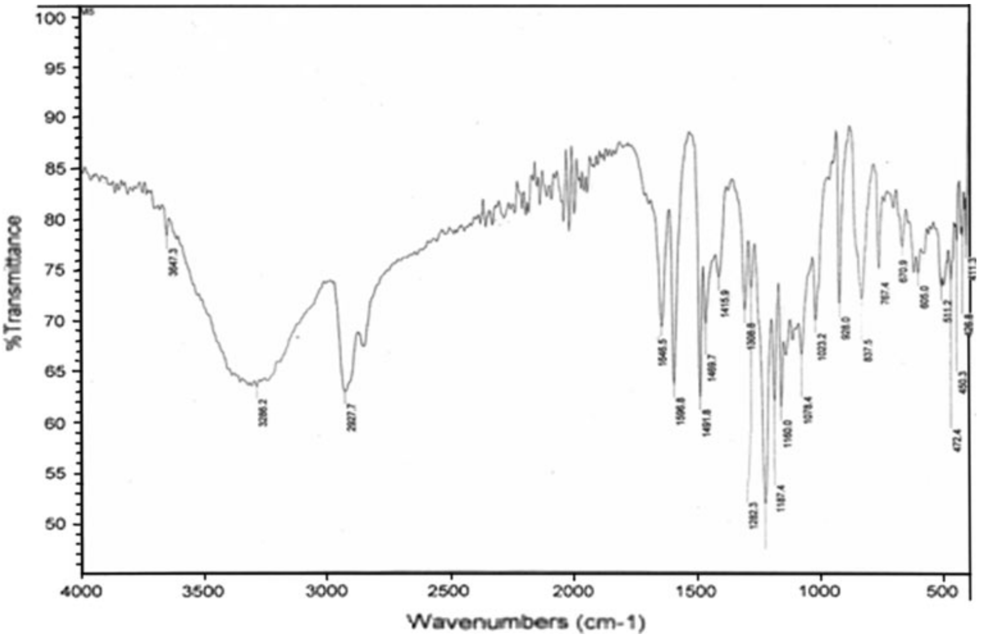
Figure 2 shows the XRD patterns of the membranes SPEEK, SWA, PVA-co-ethylene and two representative composite membranes (PSW3–6% SWA and PSW5–10% SWA) taken in dry state. Observation of the XRD pattern gives an idea about the change in crystallinity with the addition of SWA. SWA is a highly crystalline nature, and can be understood from the characteristic peak pattern ($2\theta = 10°–40°$). The SPEEK is semi-crystalline nature [17], which is understood from the slightly broadened peak

Table 2 Vibration frequencies for the composite membranes (PSW1–PSW5) and their components

Composite membranes (cm^{-1})	PVA-co ethylene (cm^{-1})	SWA (cm^{-1})	SPEEK (cm^{-1})
3285 (OH stretching), 2928 (CH_2 stretching), 1647 (C=O stretching), 1416 (CH_3 bending), 1225, 1079, 1023 (sulfonic group in SPEEK), 982 (W–O_t), 767 (W–O_b–W), 924 (Si–O)	3257 (OH stretching), 2924 (CH_2 stretching), 1443 (CH_3 bending)	758 (W–O_b–W), 906 (Si–O), 972 (W–O_t)	3450 (O–H vibration from HSO_3 group interact with water molecules), 1219, 1076, 1018 (sulfonic group in SPEEK), 1644 (C=O stretching)

O_b bridged oxygen, O_t terminal oxygen

Fig. 1 FT-IR Spectrum of PSW5



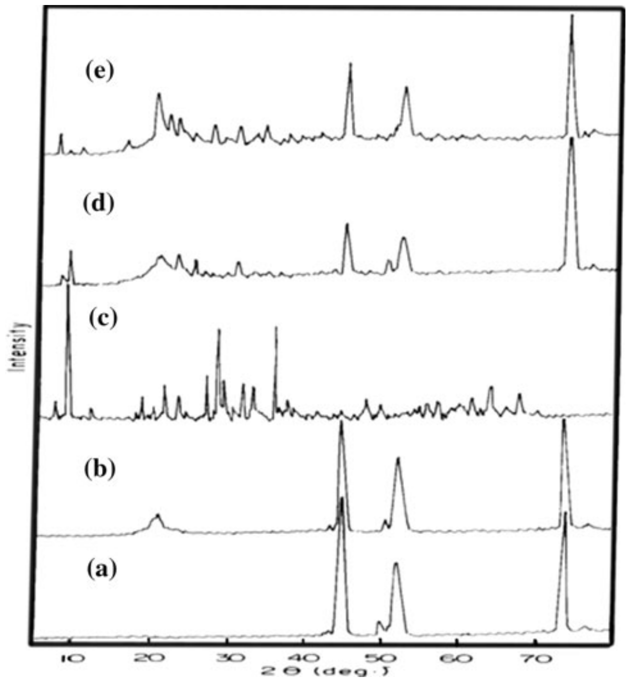


Fig. 2 XRD patterns of (*a*) SPEEK, (*b*) PVA-co-ethylene, (*c*) SWA, (*d*) PSW3, and (*e*) PSW5

pattern ($2\theta = 40°–80°$). Compared to SWA, PVA-co-ethylene is a semi-crystalline polymer with regular conformation and hydrogen bonding with polymeric chain and can be differentiated by the presence of peak at $2\theta = 20°$ from that of SPEEK. The composite membranes (PSW3–6%SWA and PSW5–10%SWA) in Fig. 1d, e show the presence of peaks at $2\theta = 10°–40°$ (characteristic peaks of SWA) and $2\theta = 20°$, $45°–75°$ (characteristic peaks of PVA-co-ethylene and SPEEK) showing the incorporation of SWA in PVA-co-ethylene and SPEEK. However, the incorporation of 6 and 10% SWA to the composite membrane influence the crystallinity of the membrane. Variation of peak broadening observed from the diffraction pattern of PSW3–6%SWA and PSW5–10%SWA ($2\theta = 15°–30°$) shows the decrease in crystallinity nature of SWA in the composite membrane. These kinds of changes from crystalline to amorphous nature of SWA in the composite membrane are also observed by other researchers [11, 17].

Thermogravimetric studies

The TGA patterns (percentage weight vs. temperature) of SPEEK and the composite membranes (PSW1–PSW5) are shown in Fig. 3. It was observed that the onset temperature of the composite membranes increased when compared to SPEEK alone. The degradation pattern of the SPEEK and composite membranes are also different. SPEEK shows the initial degradation which is responsible for the degradation of sulfonyl groups in SPEEK and the second degradation response for the rest of the polymer. The percentage residue at 800 °C was found to be more in the case of SPEEK when compared to the composite membranes. The initial degradation for pristine PVA-co-ethylene exerts two of the decomposition patterns, the first degradation was from 150 °C due to the PE Ahn et al. [21], and the second decomposition was usually at 460–573 °C due to PVA [11]. The composite membranes showed two of the degradation patterns at 150–350 °C, which is responsible for the initial degradation. Degradation starts because of the polyethylene in PVA co-ethylene copolymer and it extended due to the degradation of sulfonyl groups in SPEEK and the second degradation approximately in the range of 430–570 °C due to the PVA and the polymeric content of the SPEEK and it was also accompanied by the conversion of heteropoly acid into its respective metal oxides. This was observed earlier by the Helen et al. [11].

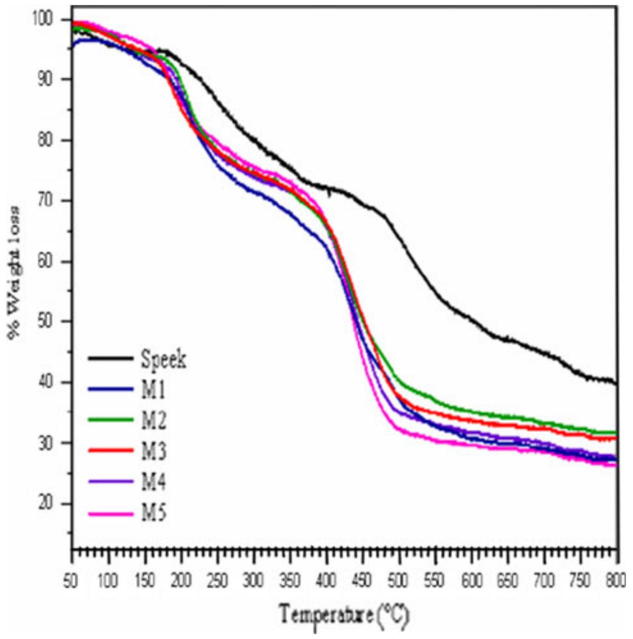


Fig. 3 TGA curve for composite membranes (PSW1–PSW5) and their components

SEM

Surface morphology of the membranes was analyzed using SEM studies. SEM photomicrographs of some of the membranes, namely PSW3 and PSW5 were taken at magnification levels 5 µm and it is shown in Fig. 4. These photomicrographs clearly revealed uniform distribution of the inorganic material (SWA) in organic matrix of the composite membranes. Since the SEM images are focused on higher resolution, we are able to see the even

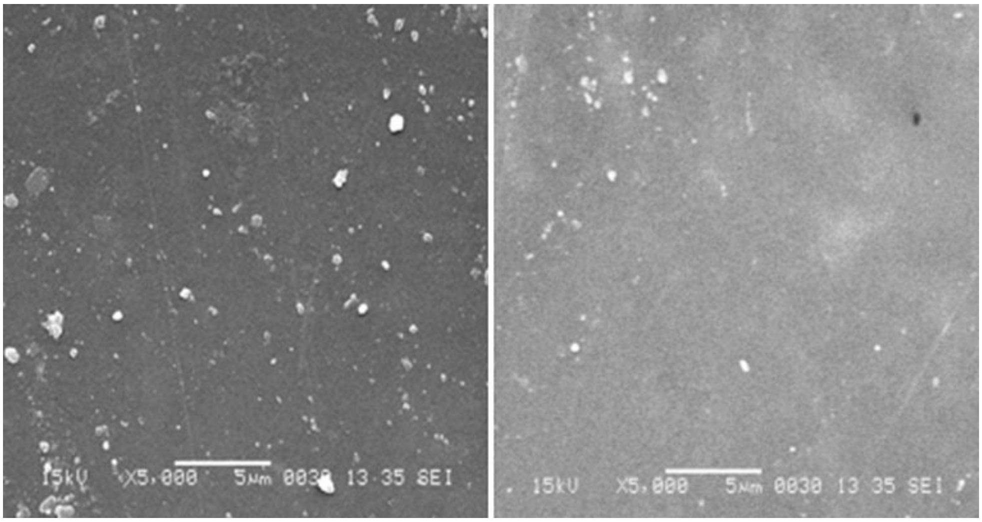


Fig. 4 SEM photomicrographs of membranes PSW5 and PSW3

distribution of the SWA on the membrane surfaces. The surface of the membranes was found to be smooth and homogeneous. These two membranes were less porous and highly dense.

Evaluation of composite membranes

IEC

The IEC is directly related to the proton exchanging ability of the membrane. The values of IEC for the composite membranes (PSW1–PSW5) and SPEEK are shown in Fig. 5. As the concentration of SWA is increased, it is evident that there will be an increase in the IEC values. This is because the heteropoly acid not only acts as a Lewis acid, but also acts as a rich proton carriers [22]. These protons are capable of getting exchanged and hence the increase in the IEC values with increase in the content of SWA was in according to the expected trend. However, the IEC values of the composite membranes (PSW1–PSW5) were found to be lower than the virgin SPEEK membrane which may be due to the presence of PVA-co-ethylene. Moreover, SO_3^- ions are in the polymeric site responsible for the proton conductivity, since in the composite membranes the SPEEK amount was reduced to half, the SO_3^- ions amount also reduced to half. Hence, the IEC values of the composite membranes have lesser values than the virgin SPEEK. Yang et al. also observed similar reduction in IEC values of SPEEK blends with PVA when compared to SPEEK [18].

Proton conductivity

The conductivity values were obtained by impedance spectroscopy method. The conductivity values are shown in Fig. 6. It was observed that the proton conductivity of

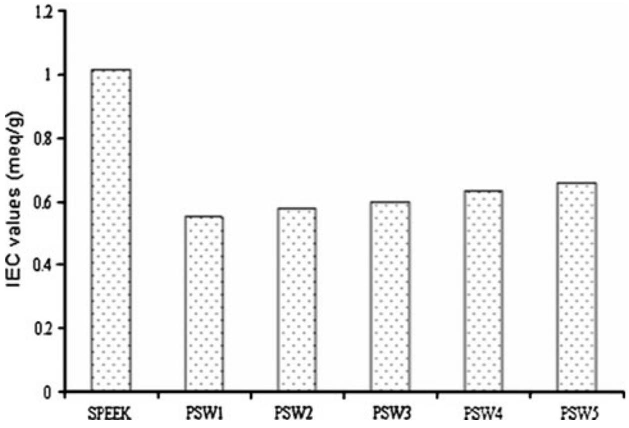


Fig. 5 Ion exchange capabilities of composite membranes (PSW1–PSW5)

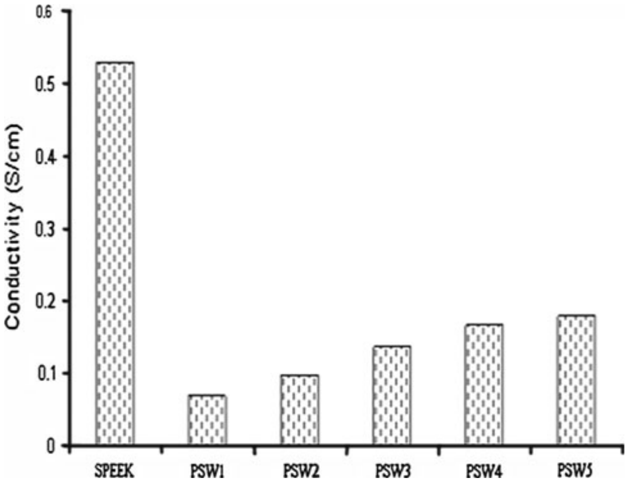


Fig. 6 Proton conductivities of composite membranes (PSW1–PSW5) and its component (SPEEK)

the composite membranes (PSW1–PSW5) reduced when compared to the SPEEK pristine sample due to the reduction of SO_3^- ions (almost 50%, due to 50% and lesser SPEEK used in the PSW1–PSW5) and the introduction which are all the good IEC values. With in the composite membranes, the amount of SWA increased from 2 to 10%. There was an increase in the conductivity values which was in accordance with the IEC values. A positive and good correlation (correlation coefficient $(r) = 0.98$) was obtained between the percentage increase in SWA (2–10%) and the proton conductivities which again shows that the percentage increase in SWA will result in increase in conductivities. Usually inorganic proton conductors such as heteropoly acids like SWA were used to improve the conductivity and thermal stability of the membranes [12].

Water/methanol absorption

For an excellent proton conducting ability, the membranes should have some appreciable water absorbing property. The absorbed water molecule acts like a canal for the passage of protons and the proton conductivity is largely dependent on the connectivity of the hydrated domains which in then increases the mobility of ions. However, excessive swelling in water results in a loss of mechanical and dimensional stability which can weaken the contact between the electrolyte membrane and the catalyst [11, 20]. The water uptake of the SPEEK is totally dependent upon the sulfonation, hence SPEEK and their blends are preferred. Other components PVA [20] and SWA [11] are also useful water absorbing agents.

In our research, both water and methanol absorption increased with increase in the content of SWA and was found to be higher than virgin SPEEK membrane. Though the SPEEK can absorb very good amount of water and methanol, blends with HPAs outperform. The HPAs are known to hold a very large amount of solvent especially water since they are highly hydrophilic in nature. This also confirms an increase in the amount of SWA in the composite membranes from PSW1 to PSW5. Similar results were observed by Teli et al. [23].

Durability

Due to the chemical or mechanical degradation or deterioration, the durability of the membrane is affected. The stability studies of the membrane toward peroxide solutions give an idea about the life (durability of membrane) of the membrane. The degradation time required for the series of composite membranes and SPEEK are shown in Table 1. The durability decreases with an increase in the content of SWA. This may be due to the space occupied by the SWA molecules between the adjacent polymer chains thereby reducing the amount of interaction between them. Though it may be argued that there is a kind of interaction between SWA and the individual polymer chains, it may not be sufficient to hold all the polymer chains together. Moreover, hydrophilic component SWA and the SO_3^- ions in the aromatic rings of the SPEEK are more sensitive to the radical attack and the PVA-co-ethylene is less prominent to the peroxide radicals generated by the H_2O_2 [17]. Hence, the incorporation of PVA-co-ethylene with SPEEK will enhance the durability of the membrane, but in our case due to the presence of SWA with PVA-co-ethylene and SPEEK reduces the durability of the blend membranes.

Mechanical properties

The UTM results are shown in Table 1. The tensile strength and percentage elongation values gradually decreasing when the concentration of SWA increased, because the inorganic materials (SWA) occupied the space between the adjacent polymer layers, reducing the amount of interaction between the adjacent polymeric chains. As a result, tensile strength and percentage elongation values of the composite membranes decreased with increasing concentration of SWA.

Conclusion

In conclusion, the composite membranes (PSW1–PSW5) were prepared by using SPEEK, SWA, and PVA-co-ethylene. The prepared membranes were characterized spectrophotometrically using FT-IR. Thermal characteristics of the membranes were studied using TGA. Surface characterization was carried out using SEM studies and the sample was mechanically characterized in terms of percentage elongation and tensile strength. The membranes was also characterized for IEC, water/methanol absorption, durability, XRD and for proton conductivity. The membranes with SWA showed predominated IEC and proton conductivity. The durability of these membranes was appreciable with high thermal stability. The SEM analysis revealed uniform distribution of the composite membrane. The water and methanol absorption values increased with increase in the dosage of SWA. Introduction of inorganic materials also resulted in the increase of thermal stability. The increase in the water absorption assists in a better proton conductivity. The incorporation of PVA-co-ethylene improved the mechanical properties (which acts as cover to protect the SPEEK from the free radicals) of the resulting composite membranes. Though the prepared composite membranes has lesser conductivity compared to Nafion due to their durability and thermostability of these membranes, they can be used as membrane for PEMFC.

References

1. Sun H, Zhang G, Guo L, Liu H (2009) Int J Hydrogen Energy 34:5529
2. Song C (2002) Catal Today 77:17
3. Yilanci A, Dincer I, Ozturk HK (2008) Int J Hydrogen Energy 33:7538
4. Hasani-Sadrabadi MM, Emami SH, Ghaffarian R, Moaddel H (2008) Energy Fuels 22:2539
5. Famouri P, Gemmen RS (2003) In: Proc. IEEE power engineering society general meeting, vol 3, pp 1436–1440
6. Colomer MT (2006) J Solid State Electrochem 10:54
7. Yu J, Dong C, Liu J, Li C, Fang J, Guan R (2010) J Mater Sci 45:1017. doi:10.1007/s10853-009-4033-3
8. James PJ, Elliot JA, MCMaster TJ, Newton JM, Elliot AMS, Hanna S, Miles MJ (2000) J Mater Sci 35:5111. doi:10.1023/A:1004891917643
9. Chen J, Zhai M, Asano M, Huang L, Maekawa Y (2009) J Mater Sci 44:3674. doi:10.1007/s10853-009-3490-z
10. Lakshmi RTSM, Choudhary V, Varma IK (2005) J Mater Sci 40:629. doi:10.1007/s10853-005-6300-2
11. Helen M, Viswanathan B, Srinivasa Murthy S (2007) J Membr Sci 292:98
12. Staiti P, Minutoliv M (2001) J Power Sour 94:9
13. Kerres J, Ullrich A, Meier F (1999) Solid State Ionics 125:243
14. Soczka-Guth T, Frank G, Baurmeister J, Pawlik J, Knauf R (2003) US Patent 6,632,847B
15. Xing P, Robertson GP, Guiver MD, Mikhalenko SD, Wang K, Kaliaguiene S (2004) J Membr Sci 95:229
16. Chang J-H, Park JH, Park G-G, Kim C-S, Ok Park O (2003) J Power Sour 124:18
17. Zhang L, Mukerjee S (2006) J Electrochem Soc 153:A1062
18. Wang H, Holmberg BA, Huang L, Wang Z, Mitra A, Norbeck JM, Yan Y (2002) J Mater Chem 12:834
19. Ding FC, Wang SJ, Xiao M, Meng YZ (2007) J Power Sour 164:488
20. Yang T (2008) Int J Hydrogen Energy 33:6772
21. Ahn SH, Lee DK, Seo JA, Kim JH, Lee KB (2010) Ionics. doi:10.1007/s11581-009-0412-7
22. Mustarelli P, Carollo A, Grandi S, Quartarone E, Tomasi C, Leonardi S, Magistris A (2007) Fuel Cells 6:441
23. Teli SB, Gokavi GS, Sairam M, Aminabhavi TM (2007) Sep Purif Technol 54:178