

BLEND MEMBRANES FOR DIRECT METHANOL AND PROTON EXCHANGE MEMBRANE FUEL CELLS*

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Abstract Sulphonated polystyrene ethylene butylene polystyrene (SPSEBS) prepared with 35% sulphonation was found to be highly elastic and enlarged up to 300%–400% of its initial length. It absorbed over 110% of water by weight. A major drawback of this membrane is its poor mechanical properties which are not adequate for use as polymer electrolytes in fuel cells. To overcome this, SPSEBS was blended with poly(vinylidene fluoride) (PVDF), a hydrophobic polymer. The blend membranes showed better mechanical properties than the base polymer. The effect of PVDF content on water uptake, ion exchange capacity and proton conductivity of the blend membranes was investigated. This paper presents the results of recent studies applied to develop an optimized in-house membrane electrode assembly (MEA) preparation technique combining catalyst ink spraying and assembly hot pressing. Easy steps were chosen in this preparation technique in order to simplify the method, aiming at cost reduction. The open circuit voltage for the cell with SPSEBS is 0.980 V which is higher compared to that of the cell with Nafion 117 (0.790 V). From this study, it is concluded that a polymer electrolyte membrane suitable for proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) application can be obtained by blending SPSEBS and PVDF in appropriate proportions. The methanol permeability and selectivity showed a strong influence on DMFC performance.

Keywords: Fuel cell; Impedance; Polymer blend; Proton conductivity.

INTRODUCTION

A fuel cell is an electrochemical energy conversion device that combines a fuel (hydrogen, natural gas, methanol, gasoline *etc.*) with an oxidant (air or oxygen), and converts a fraction of their chemical energy into electrical energy^[1]. Polymer electrolyte membranes (PEMs) are one of the key components for polymer electrolyte membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). Configuration of DMFC is almost the same as that of PEMFC, except for using different species of feeding fuel and catalyst. The performance of DMFC system is known to be lower than that of PEMFC due to its poor catalyst.

High proton conductivity electrolytes have attracted considerable attention, as they are the main components in polymer electrolyte membrane fuel cells (PEMFCs). They are environment friendly and efficient power sources for different applications. Commercially available Nafion membrane is a perfluorosulphonic acid polymer electrolyte membrane and the most commonly used electrolyte in PEMFC^[2]. Though this membrane has high proton conductivity, good mechanical and chemical stabilities, its high methanol permeability and cost are the main obstacles in using it for DMFC applications.

There have been many investigations on the development of novel proton conducting membranes in order to substitute the perfluorinated membrane. A reduction in methanol permeability was achieved by modifying the surface of the Nafion membrane with a film of poly(methyl pyrrole) by an electrochemical method^[3, 4]. In

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another study, polyelectrolytes were prepared by swelling a ceramic added composite PVDF based membrane in a H_3PO_4 solution^[5]. A novel Nafion/silica hybrid membrane suggested that the $-\text{OH}$ on the surface of silica nano particles could enhance the hydrophilicity of clusters inside the membranes and improve the proton conductivity at elevated temperature^[6]. PVDF grafted polystyrene sulphonic acid proton exchange membranes based on a radiation grafting technique showed higher proton conductivity and higher water uptake ability compared to Nafion membranes^[7].

In the present study PSEBS was sulphonated separately to make it proton conducting. It exhibited good conductivity, flexibility and chemical stability but its mechanical properties were not adequate for direct application in fuel cell. Hence it was planned to blend SPSEBS with different proportions of PVDF which was reported to have high mechanical, particularly, tensile properties. As it has fluoro groups, it can get compatibilized, and can confer dimensional stability to other systems carrying hydrogen bonding groups. In this study the support SPSEBS membrane carries sulphonic acid groups, hence it can very well interact with PVDF by hydrogen bonding and can acquire dimensional stability^[8].

EXPERIMENTAL

Materials

Polystyrene-*block* poly(ethylene butylene)-*block*-polystyrene (PSEBS, $M_w = 89000$) and poly(vinylidene fluoride) (PVDF) were purchased from Aldrich and used as received. Chlorosulphonic acid (CSA), tributylphosphate (TBP), tetrahydrofuran (THF) and chloroform were obtained from Spectrochem India, Lancaster, Merck and SRL, respectively.

Sulphonation of PSEBS

25 g of PSEBS was dissolved in few ml of chloroform with continuous stirring. Tributyl phosphate was added to it and the mixture was allowed to cool to 0°C in an ice bath. Chlorosulphonic acid was then added drop-wise over a period of time. After 3 h the reaction was terminated by adding a lower aliphatic alcohol. The sulphonated PSEBS was recovered after removing all the solvents by evaporation. The product was washed several times with water until neutral pH was obtained and then dried at 75°C for 24 h^[9].

Preparation of Blend Membranes

The blend membranes were prepared by a solvent evaporation method. Initially, a desired amount of SPSEBS was dissolved in THF. PVDF was added to it in different proportions and the mixture was kept under vigorous stirring for 8 h to attain homogenization. The polymer solutions were then cast into clean and dry petridishes and the membranes formed by solvent evaporation technique. The weight percentage of blend membranes is given in Table 1. All the prepared membranes were treated with 3% H_2O_2 followed by 10% H_2SO_4 and finally washed with boiling water.

Table 1. Composition of SPSEBS/PVDF blends

Membrane code	Weight percentage (%) SPSEBS:PVDF
PVDF-A	95:5
PVDF-B	90:10
PVDF-C	85:15

Ion Exchange Capacity, Water and Methanol Uptake

Ion exchange capacity (IEC) depends on the number of sulphonic acid groups that are bonded to the membrane. The SPSEBS blend membrane was immersed in saturated potassium chloride solution over night to allow exchange of protons with K^+ ions. The protons released from the membrane were neutralized by 0.005 mol/L sodium carbonate solution. Phenolphthalein was used as the indicator. The IEC was calculated using the following formula.

$$\text{IEC} = \frac{\text{Titre value (in mL)} \times \text{Normality of the titrant (Na}_2\text{CO}_3)}{\text{Weight of the dry polymer membrane (in grams)}}$$

Water and methanol uptake was determined gravimetrically. Previously dried membranes were immersed in respective solvents at room temperature. Percentage uptake was calculated using the formula

$$\text{Percentage up take} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100\%$$

where, M_{wet} -weight of wet membrane, M_{dry} -weight of dry membrane.

The stability of membranes was examined by immersing them in freshly prepared Fenton's reagent at 80°C. The mixture was stirred with a glass rod every 10 min. The stability of the membranes was determined by noting down the time required for the physical disintegration of the membranes.

Methanol Permeability

Experiments for evaluating methanol permeability were carried out by using a testing cell, consisting of two reservoirs separated by an electrolyte membrane with a dense layer of SPSEBS or a composite membrane to reproduce a phenomenon of methanol crossover in DMFC system. The two compartment glass cell was used in this experiment. The PEM is sandwiched between donor (Chamber A) and receptor (Chamber B) compartments. Initially the donor compartment was filled with 50 mL of aqueous 2 mol/L methanol solution and the receptor compartment with 50 mL of deionized water. The solution in each bath was stirred using magnetic stirrer during the measurement to keep uniform concentration. Due to the presence of liquid water on either side of the cell, the membrane remains hydrated. The equal amount of solution in both compartments ensures that equal hydrostatic pressure is maintained. The change in concentration of methanol in receptor compartment was measured as a function of time. For every 1 h, few drops of solution from receptor compartment was withdrawn by syringe and placed in a prism of a refractometer. The permeability was determined from refractometer readings. The refractometer directly gives the percentage of methanol present in the solution. The methanol permeability experiments were carried out at room temperature (*ca.* 30°C). Methanol permeability was calculated by plotting methanol concentration in receptor compartment (c_B) as a function of time using the following formulae,

$$c_B = (AP/V_B L)c_A t$$

$$P = m (V_B L / A c_A)$$

where m is the slope of the linear plot of c_B versus time t (s), P is the methanol permeability (cm^2/s), A is the membrane area (cm^2), V_B is the volume of compartment B (mL), L is the film thickness (cm), c_A and c_B are the concentrations of methanol (mol) in Cell A and Cell B, D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The product DK is the methanol permeability P , which was calculated from the slope of the straight-line plot of methanol concentration vs. permeation time. The measurements were carried out at 30°C.

Instrumental Characterization

The XRD spectra of the membranes were recorded on an "X" Pert Pro diffractometer. The scanning angle was from 1° to 80° with a scanning rate of 2° per min. The FTIR spectra of SPSEBS and blend membranes were recorded using a Perkin Elmer FTIR spectrometer.

Thermal stability of polymer films was examined using a NETZSCH-Geratebu GMBH from 27°C to 900°C and at a heating rate of 20 K/min in nitrogen atmosphere.

Dynamic mechanical analysis was performed using a 242 Dynamic Mechanical Analyzer (TA Instrument) at a frequency of 1.0 Hz.

The surface morphology was studied by scanning electron microscopy (SEM) using a JOEL JSM 6360 microscope.

The proton conductivity was measured by AC impedance technique in the frequency range of 10 Hz to 40 kHz in the hydrated condition. The conductivity of samples (σ) was determined using the following formula,

$$\sigma = L/RA$$

where, L is the thickness of the membrane in cm, A is the area of the membrane in cm^2 , R is the resistance in Ω and σ is conductivity in S/cm.

Tensile strength of the membranes was measured using a Universal Testing Machine possessing a load cell of 5 kN, at room temperature. The gauge length and breadth of all membranes were 50 mm and 5 mm, respectively. Tests were conducted with a constant strain rate of 10 mm/min and up to failure of the sample.

Preparation of Membrane Electrode Assembly (MEA)

Diffusion layer preparation

The slurry for the gas diffusion layer is prepared by mixing 70 wt% Vulcan XC-72, 30 wt% poly(tetra fluoroethylene) (PTFE) binder, double distilled water and isopropyl alcohol. The resulting black mixture was then ultrasonicated for 15 min. The resultant slurry made of carbon was then coated onto the carbon cloth, and it was sintered in the muffle furnace for 3 h at 350°C^[10].

Preparation of the anode and cathode electrodes

The catalyst layer was prepared by mixing 20% Pt/C with IPA and PTFE binder. The catalyst loading for anode and cathode were 0.125 mg/cm^2 and 0.375 mg/cm^2 , respectively. The black catalyst slurry was then coated on to the respective diffusion layers and dried in a muffle furnace at 350°C for 3 h. Since the oxygen reduction kinetics is slow at the cathode, the cathode catalyst loading is thrice than that of the anode side where the kinetics for hydrogen oxidation is relatively fast^[11].

Hot pressing

The proton conducting membrane is sandwiched between the anode and the cathode by hot pressing at 80°C for 2 min with an applied pressure of 1.5 ton. Finally the membrane electrode assembly (MEA) was ready to use in PEMFC membrane fuel.

MEA Preparation for DMFC

Membrane electrode assembly (MEA) was obtained by sandwiching the SPSEBS/PVDF blend membrane between the anode and cathode. For DMFC, the electrocatalyst used was 40 wt% Pt:Ru (1:1) on Vulcan XC-72 and 20 wt% Pt on Vulcan XC-72 in the anode (loading 0.5 mg/cm^2) and cathode (loading 0.5 mg/cm^2), respectively. The catalyst layer is obtained by mixing the catalyst, isopropyl alcohol, deionised water and Nafion solution as binder and coated on the carbon cloth. The electrodes were of 5 cm $\times$ 5 cm (area = 25 cm^2). The MEA was fabricated uniaxially by hot pressing the anode and cathode onto the membrane at 100°C with a pressure of 150 kg/cm^2 for 3 min^[12].

RESULTS AND DISCUSSION

IEC, Water and Methanol Uptake of Blend Membranes

Ion exchange capacity (IEC) provides an indication of the acid groups present in a polymer matrix, which are responsible for the conduction of protons and provide a reliable approximation of the proton conductivity.

It has been widely reported in literature that the proton conductivity of sulphonated polymers is associated with the water uptake and IEC of the membranes. In general, proton conductivity depends on the number of available sulphonic acid groups and their dissociation capability in water. Water uptake is an important parameter in studying PEMs, because water that resides in the hydrophilic domains facilitates the transport of protons. However, too much of water uptake will result in loss of mechanical stability. The IEC and water uptake values of SPSEBS/PVDF blend membranes are shown in Figs. 1 and 2. The IEC of the blends decreased with increase in the weight fraction of PVDF. The decreasing trend may be attributed to the decrease in the concentration of SPSEBS or in other words decrease in the effective concentration of the sulphonic acid groups

in the blend. In addition, that the surface became more and more hydrophobic as a result of introduction of PVDF might also play a major role in reducing IEC^[11].

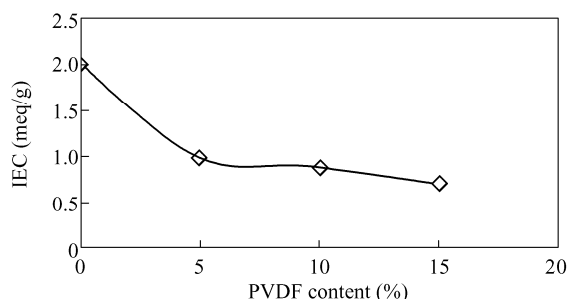


Fig. 1 Ion exchange capacity of SPSEBS, PVDF A, PVDF B and PVDF C

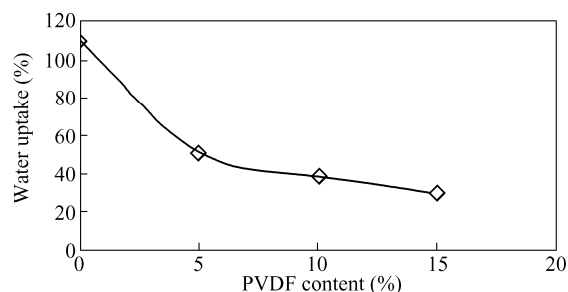


Fig. 2 Water uptake of SPSEBS, PVDF A, PVDF B and PVDF C

As expected, the water uptake values decreased with increase in the weight fraction of PVDF in the membrane. The water uptake of pure SPSEBS membrane was 110%, whereas the blend membranes containing 5%, 10% and 15% PVDF showed water uptake of 51.4%, 39.0% and 30.5% respectively. This decrease in the water absorption is due to the incorporation of hydrophobic PVDF in the hydrophilic SPSEBS membrane.

The methanol uptake of the blend membranes is shown in Fig. 3. It decreased considerably when compared to the pure SPSEBS membrane. With increase in the content of PVDF, the methanol absorption of the blend membranes decreased. The decrease in the methanol absorption is postulated to be the result of interaction between the SPSEBS and PVDF which restricts the formation of large ionic clusters or transport channels in the blend membrane^[13].

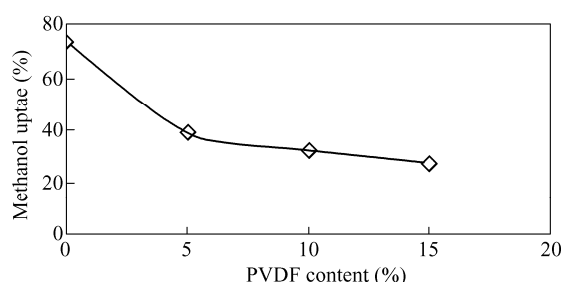


Fig. 3 Methanol uptake of SPSEBS, PVDF A, PVDF B and PVDF C

Stability Test

SPSEBS and blend membranes withstood the test conditions, without any physical degradation. All the membranes were found to withstand the condition without any disintegration for more than 8 h. Hence the membranes can be safely used in the fuel cell up to temperatures 80°C.

Methanol Permeability

The methanol permeability of blend membranes is given in Fig. 4. When compared with Nafion, the permeation of methanol in the case of SPSEBS is lower. But with the introduction of PVDF, there is a remarkable decrease in the methanol permeability. The resistivity of the blend membranes to the flow of methanol becomes better than that of Nafion when the concentration of PVDF goes beyond 5%.

XRD

Figure 5 shows the XRD patterns of PVDF, SPSEBS and blend membranes (SPSEBS/PVDF) with various weight percentages of PVDF. Three sharp diffraction peaks appeared at $2\theta = 45^\circ$, 52° and 74° which illustrated the various crystalline forms of SPSEBS. However, these peaks became less prominent in the presence of PVDF. Two sharp diffraction peaks that appeared at $2\theta = 18.5^\circ$ and 20.0° illustrated the various crystalline forms of PVDF. It was found that these sharp crystalline diffraction peaks in PVDF became less prominent in the

membranes. This suggests that the blending of the two polymers induced significant disorderliness^[14]. It was essentially due to hydrogen bonding between sulphonic acid groups of SPSEBS and the C—F bonds of PVDF.

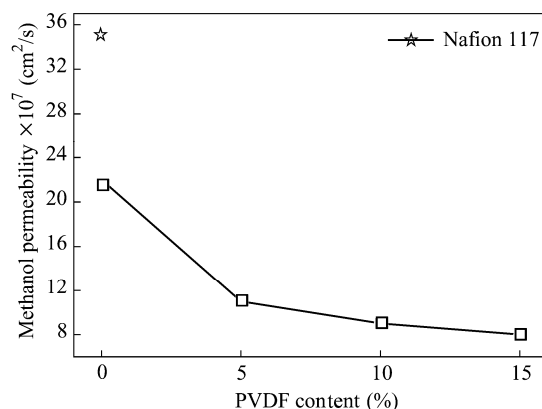


Fig. 4 Methanol permeability of SPSEBS, PVDF A, PVDF B and PVDF C

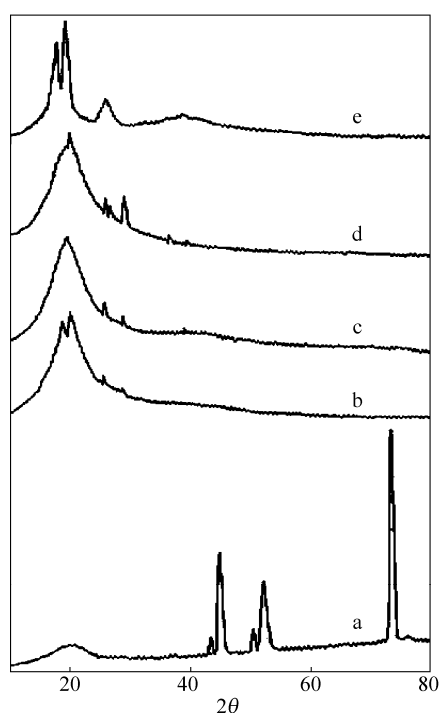


Fig. 5 XRD patterns of (a) SPSEBS, (b) PVDF A, (c) PVDF B, (d) PVDF C and (e) PVDF

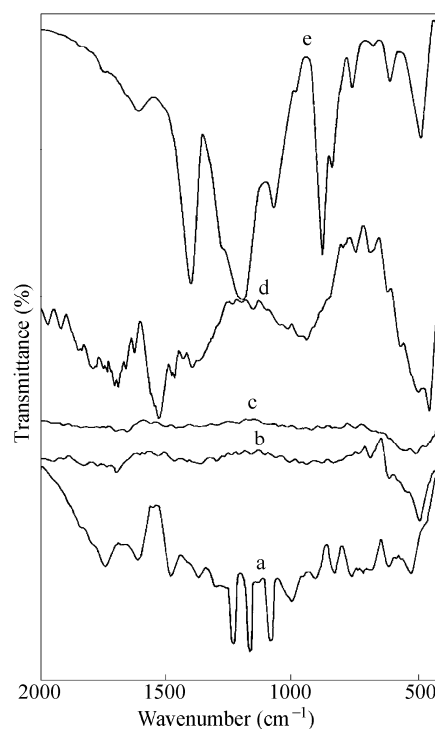


Fig. 6 FTIR Spectra of (a) SPSEBS, (b) PVDF A, (c) PVDF B, (d) PVDF C and (e) PVDF

FT-IR

Figure 6 shows the FT-IR spectra of blends as a function of PVDF content in the 500–2000 cm^{-1} region. For the pure PVDF, the spectrum exhibits characteristic absorption bands at 1403 cm^{-1} associated with the CH_2 scissoring of the PVDF. It is observed for the blends containing 5%, 10%, and 15% PVDF, the bands shift to 1369, 1431 and 1464 cm^{-1} respectively which is indicative of the presence of intermolecular interaction between PVDF and SPSEBS polymers^[15, 16].

TGA

The TGA results of SPSEBS, PVDF and their blend membranes are illustrated in Fig. 7. While the thermogram of PVDF showed a single stage weight loss at around 430°C, that of SPSEBS showed a three stage decomposition. The first weight loss of SPSEBS was marginal and it occurred between 80°C and 150°C. This was attributed to the loss of physically bound water. The second loss that occurred between 180°C and 260°C was due to the loss of sulphonic acid groups from the polymer chains. The final weight loss that occurred between 340°C and 520°C was due to the degradation of polymer backbone. The polymer blends also exhibited a three stage degradation. The initial two weight losses of the blend membranes were similar to those of SPSEBS. The final weight loss was found to be at a higher temperature. Since the loss of sulphonic acid occurred around 180°C the polymer blends can be exploited as polymer electrolyte for fuel cell up to a maximum of 160°C. Since blending did not stabilize sulphonic acid groups, their weight loss occurred at the same temperature of the base polymer. Though the final degradation occurred between 380°C and 520°C it did not have any significance on the use of blend membranes^[17–19].

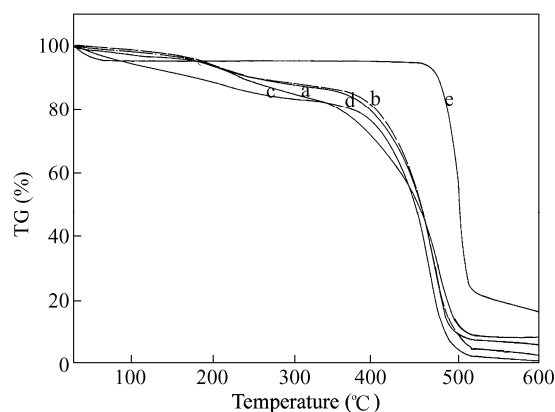


Fig. 7 Thermo gravimetric curves of (a) SPSEBS, (b) PVDF-A, (c) PVDF-B, (d) PVDF-C and (e) PVDF

Dynamic Mechanical Analysis

The results of dynamic mechanical analysis of the polymers and their blends are illustrated in Fig. 8. DMA data can be used to complement data obtained from thermal analysis techniques such as DSC and TMA. The T_g of SPSEBS polymer occurred at 164°C. It indicates that the material stores most of the energy supplied to it. Hence it possesses low damping properties and elastic behavior. In the case of blend membranes, PVDF-A and PVDF-B, the T_g was lowered to 150°C and 155°C, respectively. On the other hand the blend PVDF-C showed an increase of the T_g to 192°C. Hence only in the last blend the interaction between the chains might be maximum to yield high T_g . Hydrogen bonding between the chains could possibly be the major force for such variations in T_g ^[20].

SEM

The SEM images of SPSEBS, PVDF, PVDF-A, PVDF-B, and PVDF-C membranes are shown in Fig. 9. While SPSEBS membranes showed aggregates of fine granules, PVDF showed spherical sponge like morphology. In all the blends, thorough miscibility of both the polymers was clearly evident. The major driving force for miscibility was the hydrogen bonding between sulphonic acid groups and C-F groups of SPSEBS and PVDF, respectively. None of the blend membranes showed any mesopores which also has importance for electrolyte applications^[12].

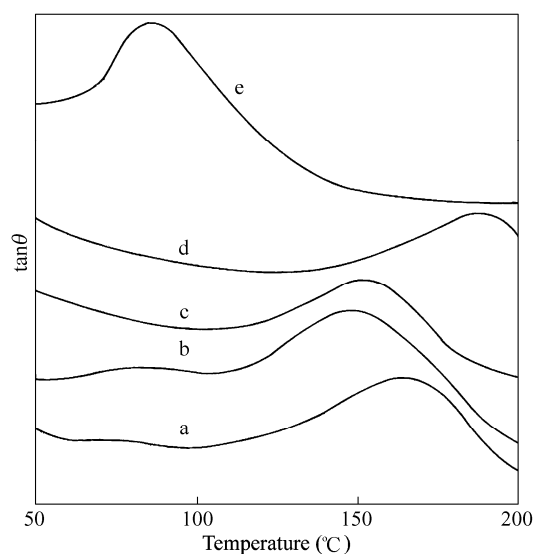


Fig. 8 DMA of (a) SPSEBS, (b) PVDF-A, (c) PVDF-B, (d) PVDF-C and (e) PVDF

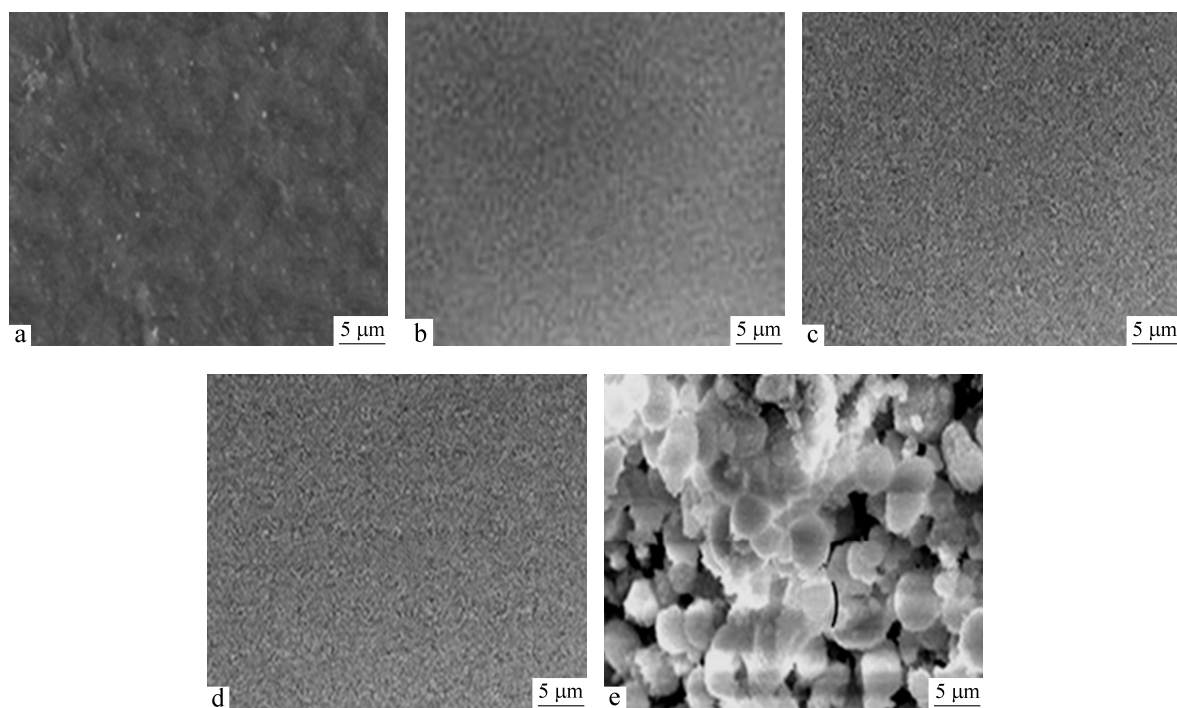


Fig. 9 SEM images of (a) SPSEBS, (b) PVDF-A, (c) PVDF-B, (d) PVDF-C and (e) PVDF

Proton Conductivity

The proton conductivity of SPSEBS/PVDF blend membranes as a function of PVDF content is presented in Table 2. The proton conductivity decreased with the increase in the content of hydrophobic PVDF. With the increase in the content of PVDF the SPSEBS content decreased with the consequent dilution of sulphonic acid groups. This is the main cause for the decrease in the conductivity of the blends. It is also in line with the suppression of electron hopping mechanism of conductivity. Hence on comparison of the conductivities of the membranes, PVDF-A is better than both PVDF-B and PVDF-C.

Table 2. Proton conductivity of blend membranes

Membrane code	Proton conductivity (S/cm)
SPSEBS	1.09×10^{-1}
PVDF-A	1.99×10^{-3}
PVDF-B	1.64×10^{-3}
PVDF-C	4.02×10^{-4}

Mechanical Properties

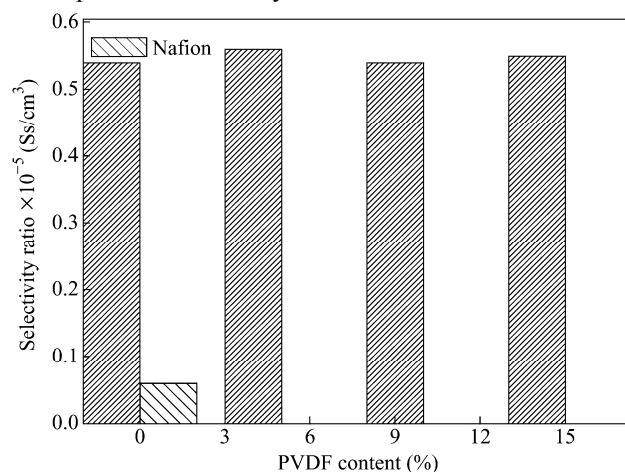
The tensile strength of the various blend membranes are given in Table 3. The tensile strength increased with increase in the content of PVDF. This suggests that PVDF might favour strong association of chains together to confer such properties. The tendency of PVDF to exhibit hydrogen bonding interaction with the sulphonic acid protons might be the main cause for such chain association. Hence, it could be predicted that both the sulphonic acid groups and C—F bonds of SPSEBS and PVDF, respectively might be close and favourably oriented for such interactions. Strong interaction between sulphonic acid groups and C—F bonds was also reported for related polymers^[21, 22].

Table 3. Tensile strength of blend membranes

Membrane code	Tensile strength (MPa)
SPSEBS	5.05
PVDF	20.00
PVDF-A	22.50
PVDF-B	28.00
PVDF-C	33.00

Selectivity Ratio

The selectivity ratios of Nafion, pristine SPSEBS as well as the blend membranes are given in Fig. 10. The pristine SPSEBS electrolyte membrane exhibited a selectivity ratio of 0.50×10^5 Ss/cm³ which is higher when compared to Nafion (0.06×10^5 Ss/cm³). It indicates that there is an excellent reduction in the methanol permeation at the expense of meagre amount of proton conductivity.

**Fig. 10** Selectivity ratio of SPSEBS and blend membranes

Single Cell PEMFC Performance of the Blend Membranes

To check the functioning of the blend membrane in a real device, the electrochemical performance of the membranes was tested in a PEMFC single cell. Figure 11 shows the polarisation and power density for the blend membrane in a PEMFC test at room temperature compared with Nafion 117 membrane. The open circuit voltage (OCV) for the SPSEBS (0.980 V) was larger than that of Nafion 117 (0.790 V). The OCV value of PVDF-A is 0.56 V which is lesser than that of Nafion 117, similarly the OCV value of PVDF-C is 0.52 V which is lesser than that of Nafion 117^[23].

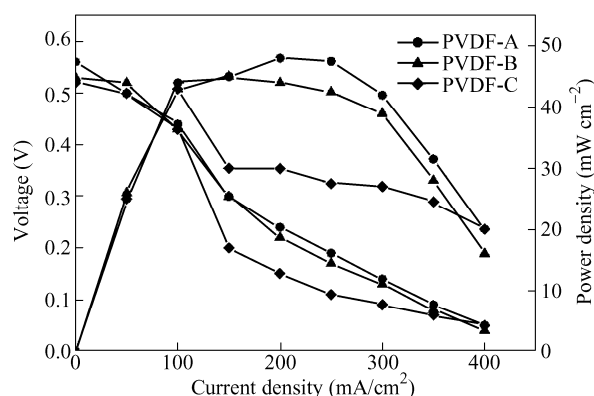


Fig. 11 Polarization and power density curves of blend membranes in PEMFC testing at room temperature

In the whole voltage range investigated, the current values of the SPSEBS membrane were always larger than the values obtained with Nafion 117 membrane. The maximum power density value reached at room temperature with the SPSEBS was 50 mW cm^{-2} , whereas, the maximum power density of Nafion 117 was 32 mW cm^{-2} with the same operating condition. In the case of blend membranes, the maximum power density values are 48, 45 and 43 mW cm^{-2} respectively. These results indicate that SPSEBS and blend membranes are promising electrolytes for fuel cell^[24, 25].

The PEMFC performance of SPSEBS and blend membrane at 60°C is given in Fig. 12. The polarisation and power density for the blend membranes in a PEMFC test at 60°C were compared with those of Nafion 117 membrane. The open circuit voltage (OCV) of SPSEBS (0.995 V) was larger than that of Nafion (0.790 V). The OCV value of PVDF-A was 0.60 V which was less than that of Nafion 117, similarly the OCV value of PVDF-C was 0.54 V which was less than that of Nafion 117. In the whole voltage range investigated, the current values of the SPSEBS membrane were always larger than the values obtained with Nafion 117 membrane. The maximum power density value reached at 60°C with the SPSEBS was 90.5 mW cm^{-2} whereas the maximum power density of Nafion 117 was 48 mW cm^{-2} with the same operating conditions. In the case of blend membranes the maximum power density values were 70, 42.5 and 37.5 mW cm^{-2} respectively. These results indicate that SPSEBS and blend membranes are promising electrolytes for PEMFC fuel cell^[28, 29].

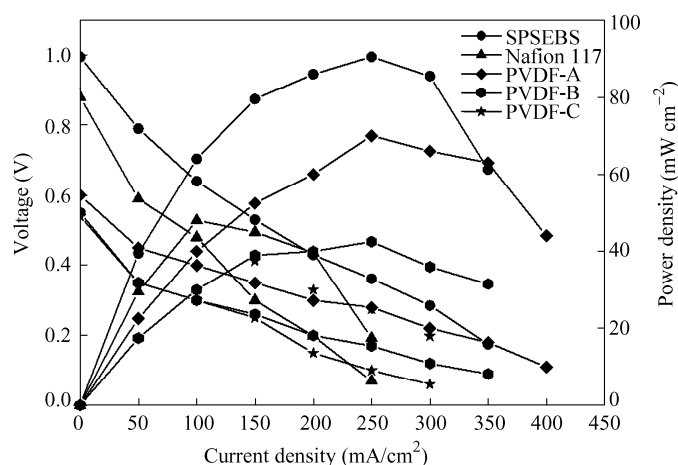


Fig. 12 Polarization and power density curves of SPSEBS and blend membranes in PEMFC testing at 60°C

DMFC Performance of Blend Membranes

Figure 13 represents the cell performance based on the blend membranes containing 5%, 10% and 15% of PVDF at room temperature. The open circuit voltage (OCV) of the SPSEBS was (0.62 V). The OCV of blend

membranes were always larger than that of Nafion 117 (0.64 V). The OCV value of PVDF-A was 0.62 V which was slightly closer to that of Nafion 117, whereas the OCV value of PVDF-C was 0.65 V which was higher than that of Nafion 117. In the whole voltage range investigated, the current values of the blend membrane were larger than the values obtained with Nafion 117 membrane. The maximum power density value reached at room temperature with the SPSEBS was 13 mW cm^{-2} whereas the maximum power density of Nafion 117 was 27 mW cm^{-2} with the same operating condition. In the case of blend membranes the maximum power density values are 58, 60 and 72 mW cm^{-2} respectively. The results indicate that the performance of the cell based on these blend membranes is comparable to that based on Nafion 117 membrane. The performance of the blend membranes was tested three times for the constancy of maximum power density. The values were same illustrating the stability and uniformity in properties of the membranes. This is mainly attributed to good compatibility of the membrane with the electrode and also its high-dimensional stability.

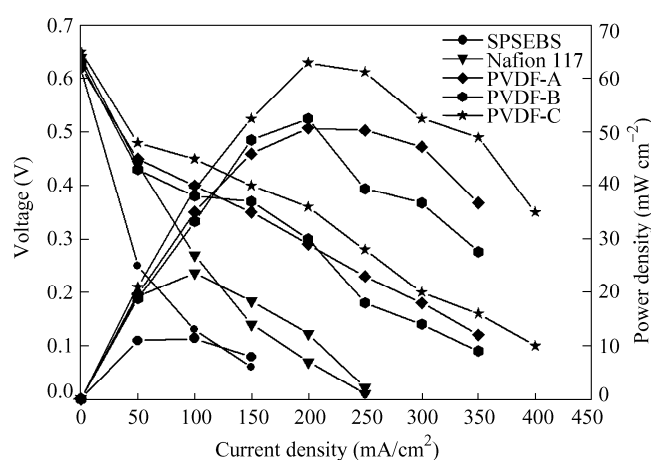


Fig. 13 Polarization and power density curves of SPSEBS and blend membranes in DMFC testing at room temperature

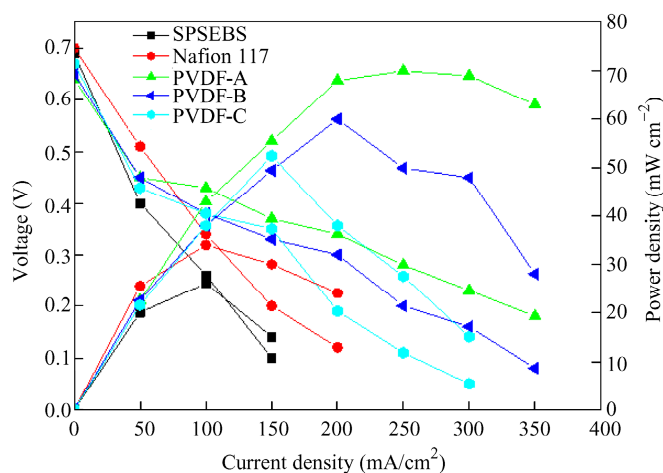


Fig. 14 Polarization and power density curves of SPSEBS and blend membranes in DMFC testing at 60°C

Figure 14 represents the cell performance of the blend membrane containing 5%, 10% and 15% of PVDF at 60°C . The open circuit voltage (OCV) for the SPSEBS (0.69 V) membranes was always close to that of Nafion 117 (0.70 V). The OCV value of PVDF-A was 0.64 V which was less than that of Nafion 117, whereas the OCV value of PVDF-C was 0.67 V which was less than that of Nafion 117. In the whole voltage range investigated,

the current values of the blend membranes were larger than the values obtained with Nafion 117 membrane. The maximum power density value reached at 60°C with the SPSEBS was 26 mW cm⁻² whereas the maximum power density of Nafion 117 was 34 mW cm⁻² with the same operating condition. In the case of blend membranes the maximum power density values are 70, 60 and 72 mW cm⁻² respectively. The results indicate that the performance of the cell based on these blend membranes is comparable to that based on Nafion 117 membrane. Here again the performance of the blend membranes was tested three times, and the maximum power density remained the same illustrating its stability and uniformity in properties of membranes. This is mainly attributed to the good compatibility of the membrane with the electrode and also its high-dimensional stability. These results indicate that SPSEBS and blend membranes are promising electrolytes for DMFC fuel cell^[28].

CONCLUSIONS

This work demonstrated that sulphonation of PSEBS can be carried out with the conventional procedure involving the use of chlorosulphonic acid. Sulphonation also aids thorough miscibility with PVDF through hydrogen bonding. It was found to be the major bonding force to influence the properties of the blends. This study revealed that any suitably designed polymer carrying aromatic rings in the back bone can also be made to show similar properties for applications as electrolytes in fuel cells. Although the blends showed slightly reduced proton conductivity, IEC, water and methanol uptake, their mechanical properties increased significantly. The interaction between fluorine and SO₃H groups of the blend membranes was proved by FTIR. A maximum power density of 50 mW cm⁻² was obtained from SPSEBS. The open circuit voltage for the cell with SPSEBS was 0.980 V at room temperature, which was higher compared to that of the cell with Nafion 117 (0.790 V). Maximum power density of blend membranes was also very high compared to that of Nafion 117.

Polymer blends based on SPSEBS/PVDF were investigated for their application as membranes of direct methanol fuel cell. The blends were only compatible in the limited range of composition due to high hydrophobic characteristic of PVDF in the blend. The maximum power density value of blend membranes was higher than that of Nafion 117. This simple hydrocarbon blend membrane with the advantage of lower cost is suggested to be very promising for practical application to direct methanol fuel cell.

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