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A blend of sulfonated poly(ether ether ketone) and poly(vinylidene fluoride) for DMFC

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ABSTRACT

This paper reports on the performance of direct methanol fuel cells (DMFCs) with the blend membranes of sulfonated polyether ether ketone (SPEEK)/ polyvinylidene fluoride (PVDF) as the electrolyte. The characteristic properties of the SPEEK/PVDF polymer membranes were investigated using thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), and the AC impedance method. The blend shows good thermal and mechanical properties and appreciable ionic conductivity. Though the ionic conductivity decreased with increasing content of PVDF, there is an improvement in the mechanical properties with the introduction of PVDF. As a result, the SPEEK/PVDF blends appear to be a good candidate as electrolytes for applications in DMFC. The performances of the membrane-electrode assembly (MEA) in DMFC, using the blend membranes of various percentages of PVDF (2-10%) were evaluated by single cell test and the maximum current density of 350 mA/cm^2 is observed around 0.25 V.

KEYWORDS

SPEEK;
PVDF;
Blends;
Polymer electrolytes;
Proton conductivity.

INTRODUCTION

Proton conductors are interesting materials due to their potential application as solid electrolyte in devices such as fuel cell, batteries, electrochromic glasses, etc.[1,2]. For more than one and half decades, there has been progressive interest in the development of ionic conducting membranes. With their excellent properties, they replace conventional liquid electrolyte systems leading to favourable substantial improvements in popular electronic devices such as batteries and fuel cells[3-6].

PEMs were initially used in fuel cells during the 1960s[7] in the form of a poly styrene sulfonic acid membrane. In the 1970s, DuPont Chemicals Nafion® was used in Polymer Electrolyte Membrane Fuel Cell (PEMFC) owing to its excellent proton conductivity and very good thermal stability[8]. After this, varieties of Polymer Electrolyte Membranes (PEMs) were developed for fuel cell applications. The work of Kerres[9] is the classification of the membranes according to their material. It includes perfluorinated ionomer membranes, partially fluorinated ionomer membranes, non-fluorinated ionomer membranes, high/ low molecular composite membranes and organic/ inorganic composite membranes. However, there are a few drawbacks associated with the perfluorinated membranes which include (i) high cost, (ii) non eco-friendly nature, (iii) loss of proton conductivity at elevated temperature, (iv) dependence on relative humidity in keeping proton conductivity, (v) high methanol permeability in the case of direct methanol fuel cell (DMFC) etc.

To overcome the drawbacks associated with the perfluorinated membranes, plenty of efforts were made in the last few years. To reduce the cost and to make the membrane eco-friendly several hydrocarbon based aromatic polymers[10-15], incorporation of heteropoly acids to improve the proton conduction[16-19], blend membranes[20-21] were considered for use as PEM in fuel cells. Among the poly(aryl ether ketone), sulfonated poly(ether ether ketone) was promising as reported earlier[16-18,20].

In the present study, blend membranes of sulfonated poly(ether ether ketone) (SPEEK) and poly(vinylidene fluoride) (PVDF) was synthesized. PVDF is a kind of hydrophobic material, and can reduce the water absorption[22]. Though the proton conductivity of membranes modified with PVDF decreased, good cell performance was reported earlier in the literature[23,24]. The percentage composition of PVDF in the SPEEK polymer matrix was varied from 2% to 10% and the blend membranes were characterized by various techniques like FT-IR, TGA, proton conductivity, UTM. The selectivity ratio of the blend membranes was better than SPEEK indicating that they can be successful candidate for applications in DMFC.

EXPERIMENTAL

Materials

PEEK was procured from Victrex, England and was dried overnight before use. PVDF was obtained from Sigma-Aldrich. Catalysts (Pt/Vulcan XC-72 and Pt-Ru/Vulcan XC-72) were purchased from Arora Matthey, India. Sulfuric acid and N-methyl pyrollidone were obtained from SRL chemicals, India. All the materials were used as received.

Sulfonation of PEEK

About 10g of dry PEEK was taken in a 3-necked RB flask. To this, required amount of sulphuric acid was added and the contents of the flask were stirred at room temperature in the presence of an inert atmosphere. After the desired time, the contents of the flask were poured into crushed ice. The innumerable number of fibres that were formed was recovered by filtration and it was washed plenty of times with deionised water until the pH of the washwater falls above 6.5. The precipitate was then dried in an oven at 100°C overnight. The final product obtained is the sulfonated form of poly(ether ether ketone) (SPEEK).

Preparation of blend membranes

Initially, SPEEK was dissolved in NMP at 60°C. Then, PVDF dissolved separately in NMP was added slowly to the SPEEK solution under constant stirring. After the addition of PVDF, stirring was continued for another six hours. The solution was then filtered and cast onto a clean, dry petri dish. It was then dried at 90°C for about 8 hours and then at 110°C for another 5 hours. The membrane obtained was pale brown in color and was peeled off from the petri dish. The dosage of PVDF in the blend membrane was varied between 0 and 10 while a 10% w/v solution was maintained for casting.

Characterization techniques

The ion exchange capacity (IEC) indicates the number of milli equivalents of ions in 1g of the dry polymer. It was determined by titration method. The membrane in its acid form was weighed and then soaked in an aqueous solution containing a large excess of KCl in order to extract all the protons from the membrane. The electrolyte solution was then neutralized using a very dilute Na_2CO_3 solution of known concentration (0.01N). The EW (equivalent weight) values were calculated from the dry weight of the membrane divided by the volume and the normality of the Na_2CO_3 solution. The IEC values were expressed as number of meq. of sulfonic groups per gram of dry polymer.

The amount of solvent uptake by the membranes was studied. The dried membranes were weighed and soaked in water and methanol separately and allowed to get equilibrated at room temperature for 24 hours, above which the weight was constant. The swollen membranes were then quickly weighed after blotting the surface water and the values noted. The swelling degree was determined using the formula,

$$SW = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100\%$$

Where, M_{wet} = Weight of wet membrane; M_{dry} = Weight of dry membrane.

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

TGA analysis is mainly carried out to determine the thermal stability of the blend membranes. The change in weight of the membrane with increase in temperature at a heating rate of 20°C/min in the range of the temperature between 30°C and 800°C is followed using a SDT Q600 US analyser.

The FT-IR spectra (450cm^{-1} – 4000cm^{-1}) for the dried membranes were recorded using a Perkin Elmer FT-IR spectrometer at 25 ± 2°C. Prior to the measurement, the samples were dried at 100°C for an hour in order to remove moisture.

The methanol permeability is a serious factor which reduces the efficiency of the fuel cell particularly in Direct Methanol Fuel Cell (DMFC). The permeation not only allows the methanol fuel to the cathodic compartment but also mixing of the fuel and the incoming gas at the cathode. This drastically reduces the performance of the fuel cell. The methanol permeability of the blend membranes was analyzed using a diaphragm diffusion cell, consisting of two glass bottles that can be interconnected with a capacity of 50cm^3. The membrane can be clamped between the two compartments. Initially 25ml of deionised water was taken in compartment A and 25ml of 20% v/v methanol was taken in the compartment B. As a result of concentration difference between the two compartments, methanol flux arises across the membrane. The increase in the methanol concentration with respect to time in compartment A was followed using a PAL II digital refractometer.

The measurements of proton conductivity, σ (S/cm) of the membranes were carried out using Autolab Potentiostat Galvanostat impedance analyser. Membranes with required dimensions were cut and pretreated with 0.01N sulphuric acid and kept in water for 100% hydration. Then it was placed between two silver electrodes with an area of 1.33cm^2 with a uniform pressure applied to hold the system. The resistance offered by the membrane was calculated and then converted to conductivity values using the formula,

$$\sigma = L/(R \times A)$$

Where, σ is the conductivity in S/cm; R is the resistance offered by the membrane in ohms; L is the thickness of the membrane in cm and A is the area of the membrane in cm^2.

The surface morphology of the blend membranes was investigated using Scanning Electron Microscope (JEOL 6360 instrument). A piece of membrane was vacuum sputtered with a thin layer of gold prior to SEM examination.

The mechanical properties were obtained from Hounsfield Universal Testing Machine. The samples were cut into a size of 5 mm x 50 mm as reported by D. H. Dung et al[25]. The cross head speed was set at a constant speed of 10 mm/min. For each testing reported, at least three measurements were taken and the average value was reported.

MEA preparation

Membrane electrode assembly (MEA) was obtained by sandwiching the SPEEK/PVDF blend membrane between the anode and cathode. For DMFC, the electrocatalysts used were 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, isopropy alcohol (IPA), deionized water and Nafion solution as binder and was coated on the carbon cloth. The electrodes were of 5 cm x 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.

Single cell test

Performance of the membranes was measured with DMFC test station. A single cell with a 25 cm^2 active area was used for the experiment. The external load was applied by means of an electronic load which is manually controlled. The fabricated MEA was placed in the test cell and the bolts were tightened with an equal torque on each bolt. The experiment has been conducted with 2M methanol at a flow rate of 20 mL/min in the anode side and in the cathode side O_2 with a flow rate of 40 mL/min is maintained.

RESULTS AND DISCUSSION

The results of IEC are given in TABLE 1. The IEC of Nafion 117 was also given for comparison. In the coding given for the blend membranes SP X, S stands for SPEEK, P stands for PVDF and X denotes the percentage of PVDF in the blend.

TABLE 1 : IEC and proton conductivity of blend membranes

S. No.	Membrane Code	IEC, mequiv/g	Absorption, %		Proton Conductivity, mS/cm
			Water	Methanol	
1	SPEEK	2.23	15.18	17.89	8.73
2	SP 2	2.16	13.67	14.71	7.98
3	SP 4	2.05	10.44	11.84	7.01
4	SP 6	1.95	8.78	9.59	6.36
5	SP 8	1.85	5.13	6.26	5.74
6	SP 10	1.69	3.22	4.57	5.15

The IEC value is maximum for virgin SPEEK, which was found to be 2.23 mequiv/g. When PVDF was introduced, there is a reduction in the IEC values. This is due to the fact that there is a reduction in the number of labile H^+ ions present in the sulfonic acid groupings of SPEEK that are responsible for the exchange of ions. When the concentration of PVDF in the blend is increased, in others words, when the quantity of SPEEK in the blend is decreased, there is a reduction in the number of sulfonic acid groupings and hence the number of replaceable H^+ ions. This accounts for the decreasing trend in the IEC values.

Both the water and methanol absorptions were found to be higher for SPEEK when compared to the blend membranes. In the case of SPEEK, hydrophilic character was introduced upon the addition of sulfonic acid groupings. Because of the presence of the hydrophilic groups, SPEEK exhibits a higher absorption. On the other hand, PVDF is highly hydrophobic in nature. Hence, the introduction of PVDF in SPEEK decreases the net hydrophilic character of the blend membranes. As a result, a gradual decrease in the absorption capacity with increase in the content of PVDF was observed.

The proton conductivity of SPEEK as well as the various blend membranes is given in TABLE 1. With increase in the concentration of PVDF in the blend membranes, there is a decrease in the proton conducting ability. This kind of attitude may be the result of the following factors,

(i) There is a decrease in the ion exchange capacity with increase in the concentration of PVDF. This is due to the reduction in the net SO_3H concentration when the amount of PVDF is increased,

(ii) There is a reducing trend in the water absorption as the content of PVDF is increased. PVDF is a well-known hydrophobic polymer and hence with increase in PVDF, there is a decrease in the water absorption of the blend membranes. The absorbed water acts like a canal for the passage of protons through the membrane. Hence, any reduction in the absorption capacity may lead to decreased proton conducting ability.

The methanol permeability is a crucial factor which decides the performance of the DMFC. With an increase in the content of PVDF, the methanol permeability decreases and the results are shown in TABLE 2. This may be due to the hydrophobic nature of PVDF as illustrated by the methanol absorption that prevents methanol from transferring through the membrane. The decrease in the methanol permeability makes these blends as a possible low cost alternative to Nafion® 117 for applications as electrolytes in DMFC.

TABLE 2 : Methanol permeability values of the blend membranes

Membrane Code	Methanol Permeability, %	Selectivity Ratio, Sscm^{-3}
SP 0	21.0	5.97 x 10^2
SP 2	17.5	8.27 x 10^2
SP 4	14.3	1.41 x 10^4
SP 6	11.9	2.22 x 10^4
SP 8	10.9	24.74 x 10^4
SP 10	10.1	6.97 x 10^3

The selectivity ratio of pristine SPEEK was 5.97 x 102 Sscm^{-3}. The blend membranes exhibited a selectivity ratio of 1-2 order higher than SPEEK. The higher selectivity ratio indicates that the blend membranes are better electrolytes for applications in DMFC.

In the durability study, the time taken for the physical disintegration of the various blend membranes was studied and the results are shown in TABLE 3. It is evident from the result that there is a gradual decrease in the withstanding ability of the blends with increase in the PVDF content. The possible reason could be that the continuity in the polymer matrix is lost due to the introduction of PVDF between the host SPEEK matrix.

TABLE 3 : Durability and mechanical properties

Membrane Code	Durability, hours	Tensile Strength, MPa	Percentage Elongation, %
SP 0	2.5	24.6	28.7
SP 2	2.2	30.2	25.2
SP 4	2.0	35.9	23.9
SP 6	1.5	38.1	20.1
SP 8	1.3	40.2	15.7
SP 10	1.1	44.6	10.3

The mechanical properties of the blend membranes are given in TABLE 3. There is an increase in the tensile strength as the content of PVDF increases. This shows a good compatibility between the individual constituents of the blend and as a result the blends were found to be stiffer and stronger.

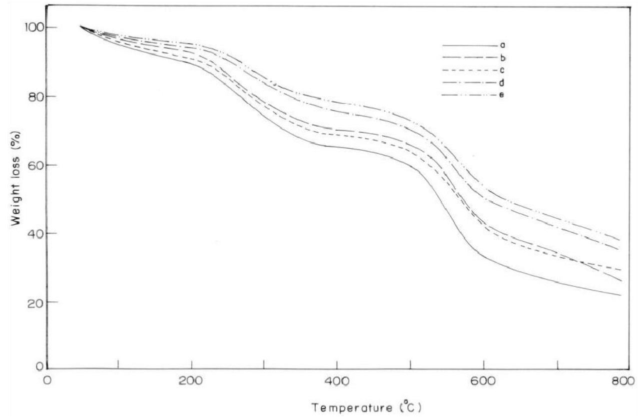

Figure 1 : TGA thermogram of SPEEK blended with (a) 2% PVDF (b) 4% PVDF (c) 6% PVDF (d) 8% PVDF and (e) 10% PVDF

The TGA spectra of the blend membranes were shown in figure 1. A three-step thermal degradation was observed in the thermal studies. The initial weight loss between 75°C and 175°C may be due to the loss of adsorbed water along with trace amount of solvent present in the membrane. The second weight loss ranging from 200°C to 350°C may be due to the splitting off of the sulfonic acid grouping from the SPEEK matrix. The final loss between 400°C and 600°C could be due to the cleavage of the polymer backbone. There is an increase in the thermal stability with increase in the content of PVDF. The blends were found to be thermally stable up to 200°C, which makes them suitable as electrolytes for fuel cell applications.

The FTIR spectrum of the blend membranes are shown in figure 2. There is a broad envelope in the high energy region lying between 2100 and 3900 cm^{-1}. It includes the OH stretch of SO_3H group of SPEEK and C-H vibrations of the aromatic ring. The fine structure bands at 2609 and 2428 cm^{-1} are due to hydrogen bonding of different OH groupings in the bulk material. These hydrogen bonds are responsible for the interaction between the PVDF and the polymer matrix, because of which the blends are said to be homogenous. The C=O vibration gives its peak close to 1600 cm^{-1}.

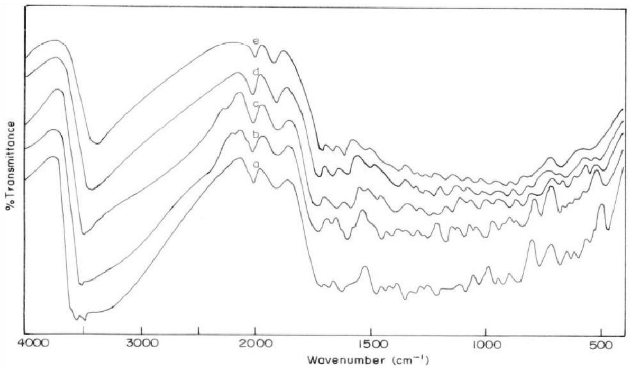

Figure 2 : FT-IR spectra of SPEEK blended with (a) 2% PVDF (b) 4% PVDF (c) 6% PVDF (d) 8% PVDF and (e) 10% PVDF

The SEM images of SPEEK and two blend membranes are given in figure 3. The SEM images confirmed a homogenous membrane without any pores. The absence of phase separation indicates a good compatibility between the constituents.

Single cell performance in DMFC

Figure 4 shows the polarization curve of the single cell (25 cm^2) SPEEK/PVDF blend membranes with different PVDF (2-10%) content. The performance of the single cell was measured with increasing content of PVDF from 2% to 10%. The performance of the single cell increased with increase in PVDF content. It can be seen that the highest cell current density of 350 mA/

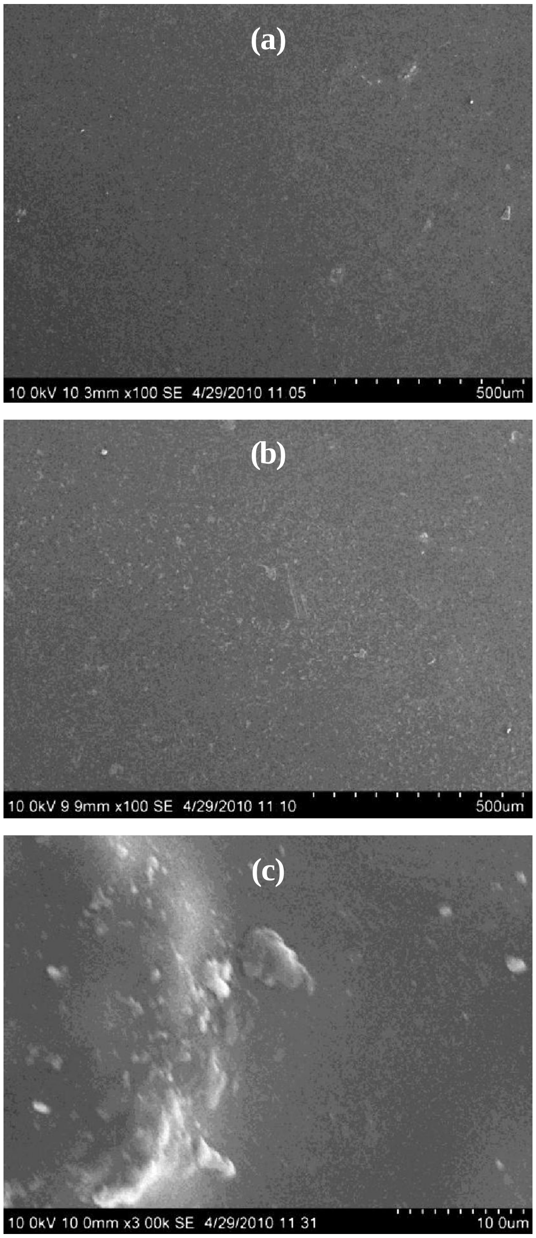

Figure 3 : SEM images of a) SPEEK, b) SP 6 and SP 10

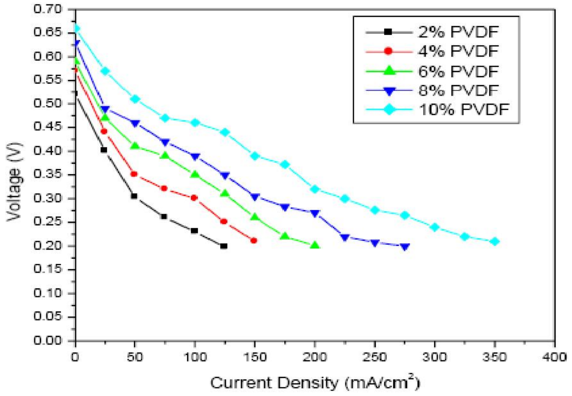

Figure 4 : Polarization curves of SPEEK/PVDF (2-10%) blend at room temperature

cm^2 is observed around 0.25 V. The results clearly indicate that the blending of PVDF with PEEK decreases the methanol crossover thereby increasing the performance of the fuel cell.

CONCLUSION

In the present study, blend membranes with SPEEK and PVDF were synthesized. The blends were found to be mechanically stable. FT-IR studies confirmed the interaction between the constituent polymers. The SEM images revealed good compatibility between the constituents of the blend. The prepared membranes were found to be thermally stable upto 200°C, which is highly suitable for fuel cell applications. Though there is a reduction in the water retention capacity as well as the proton conductivity, there is a significant improvement in blocking methanol and hence a better selectivity ratio was observed with the blend membranes. The performances of the membrane-electrode assembly (MEA) using the blend membranes of various percentages of PVDF (2-10%) were evaluated by single cell test and the maximum current density of 350 mA/cm^2 is observed around 0.25 V.

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