Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 3, Issue, 7, pp.192-198, July, 2011

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

PROTON EXCHANGE MEMBRANES BASED ON SPSEBS/PSEBS FOR FUEL CELL APPLICATION

Perumal Bhavani and Dharmalingam Sangeetha*

Department of Chemistry, Anna University Chennai, Chennai–25

ARTICLE INFO

Article History:
Received 22nd April, 2011
Received in revised form
17th May, 2011
Accepted 19th June, 2011
Published online 16th July 2011

Key words:
SPSEBS,
Conducting polymer,
PEMFC.

ABSTRACT

Proton–conducting polymer membranes are used as an electrolyte in the so - called proton exchange membrane fuel cells. Current commercially available membranes are perfluosulfonic acid polymers, a class of high –cost ionomers. This paper examines the potential of polymer blends, namely those of sulfonated poly styrene ethylene butylene poly styrene (SPSEBS) and poly styrene ethylene butylene poly styrene (PSEBS), in the proton exchange membrane application. SPSEBS / PSEBS blends were prepared by solvent evaporation method. SPSEBS membranes exhibited good conductivity, flexibility and chemical stability while they had poor mechanical stability. In an effort to improve the mechanical properties of SPSEBS while maintaining the initial conductivity, it was incorporated with PSEBS. The obtained membranes were characterized in terms of conductivity, ionic exchange capacity and water uptake. Blend membranes were studied by FTIR spectroscopy and X-ray diffraction. The morphology of the membranes was studied by scanning electron microscope (SEM). Thermal stability of the membranes was studied by TGA and DSC. Fuel cell performance studied by PEMFC and DMFC.

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 cell (PEMFC) and direct methanol fuel cell (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 PEMFC due to a poor catalyst. High proton conductivities have attracted considerable attention, as they are the main components in polymer electrolyte membrane fuel cells (PEMFCs). They are environment friendly and are efficient power sources for different applications. Commercially available Nafion membrane is a perflourosulphonic acid polymer electrolyte membrane, and is currently 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 perflourinated 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 and 4]. In 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 the –OH on the surface of silica nano particles could enhance the hydrophilicity of clusters inside the membranes and improve the proton conductivity at elevated temperatures [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 blended with different proportions of PSEBS, characterized by XRD, FTIR, SEM, etc., and their results are discussed.

MATERIALS AND METHODS

Polystyrene–block poly (ethylene butylene)-block-polystyrene (PSEBS, M_w = 89,000) and poly styrene ethylene butylene poly styrene (PSEBS) 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.

***Corresponding author:** *sangeetha@annauniv.edu*

Sulphonation of PSEBS

25g 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 3h 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 hours [8].

Preparation of blend membranes

The blend membranes were prepared by solvent evaporation method. Initially, a desired amount of SPSEBS was dissolved in THF. PSEBS was added to it in different proportions and the mixture was kept under vigorous stirring for 8 hours 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 by10% H_2SO_4 and finally washed with boiling water.

Table 1.

Membrane code	Composition by weight percentage SPSEBS: PSEBS
M 1	98:02
M 2	96:04
M 3	94:06
M 4	92:08
M 5	90: 10

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 0.01N sodium carbonate solution. Phenolphthalein was used as the indicator. The IEC was calculated using the following formula.

$$\text{IEC} = \frac{\text{Normality of sodium carbonate X volume of sodium carbonate}}{\text{Weight of dry membrane}}\ \text{meq /g}$$

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

$$\text{Percentage uptake} = \frac{\text{Wet M} - \text{Dry M}}{\text{Dry M}} \text{ X } 100$$

Where, Wet M – Weight of wet membrane
Dry M – Weight of dry membrane

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

Methanol Permeability

Experiment to evaluate methanol permeability was carried out using a testing cell, consisting of two reservoirs separated by an electrolyte membrane with a dense layer of SPSEBS or composite membranes to reproduce a phenomenon of methanol crossover in DMFC system. The two compartment glass cell 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 2M methanol solution and the receptor compartment with 50 ml of deionized water. The solution in each bath was stirred using magnetic stirrer during measurement to keep uniform concentration. Due to the presence of liquid water on either side of the cell, the membrane remains hydrated. Equal amount of solution in both the 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 one hour, few drops of solution from receptor compartment was withdrawn by syringe and placed in a prism of a refractometer. The permeability was determined from refract meter readings. The refractometer directly gives the percentage of methanol present in the solution. The methanol permeability experiments were carried out at room temperature (~30^0C). Methanol permeability was calculated by plotting methanol concentration in receptor compartment (C_B) as a function of time using the following formula,

$C_B = (AP/V_BL)\ C_A\ (t)$ and
$P = m \text{ x } (V_B/AC_A)$

Where 'm' is the slop of the linear plot of C_B versus time '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 and 't' is time (s). A, L and V_B are the area of membrane, the thickness of membrane and the volume of Cell B respectively. 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 30^0C.

Instrumental characterization

The XRD spectra of the membranes were recorded on "X" Pert Pro diffractometer. The scanning angle was from 1° to 80° with a scanning rate of 2° per minute. The FTIR spectra of SPSEBS and blend membranes were recorded using Perkin Elmer FTIR spectrometer. The differential scanning calorimetry (DSC) analysis of blend membranes was carried out on NETZSCH- Geratebu model DSC 200PC. Measurements were performed between 28 and 300º C at a heating rate of 10º C/min in hermetically sealed aluminum pans. Thermal stability of polymer films was examined using NETZSCH-Geratebu GMBH from 27 to 900º C and at a heating rate of 20ºC/min in nitrogen atmosphere. The surface morphology was studied by scanning electron microscopy

(SEM) using a JOEL JSM 6360 microscope. The proton conductivity was determined by AC impedance technique in the frequency range of 10 Hz to 40 KHz in the hydrated condition. The conductivity of sample (σ) was measured 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 Universal Testing Machine possessing a load cell of 5KN, at room temperature. The gauge length and breadth of all membranes were 50mm and 5mm, respectively. Tests were conducted with a constant strain rate of 10mm/min and up to failure of the sample.

Preparation of membrane electrode assembly (MEA)

Diffusion layer preparation

The preparation of the diffusion slurry ink included mixing 70 wt.% Vulcan XC – 72, 30 wt.% PTFE binder solution, and a suitable amount of double distilled water and isopropyl alcohol. The resulting black mixtures were first ultra sonicated for one hour. The black ink was then coated onto the carbon cloth and it was dried in a vacuum oven at 100°C for 2 hours and then kept in muffle furnace at 350°C for 6 hours [9].

Preparation of the anode and cathode electrodes

After preparation of the diffusion layer, the catalyst slurry ink for anode and cathode were fabricated with the help of carbon supported platinum black with platinum loading of 0.375 mg/cm^2 and 0.125 mg/cm^2, respectively. Then suitable amount of double distilled water and isopropyl alcohol were mixed by the help of ultra sonicator. After the ultra sonication, the black catalyst slurry was coated on to the respective diffusion layers. The prepared anode and cathode was dried in a vacuum oven at 100°C for 2 hours and then in muffle furnace at 350°C for six hours. For PEMFC fuel cells, the platinum loading of cathode was thrice greater than anode due to the water molecules produced at the cathode side [10].

Hot pressing

The proton conducting membrane sandwiched between the prepared anode and cathode electrodes were hot pressed at 80°C and 1.5 ton pressure for 2 minutes. Finally MEA was ready to use in PEMFC membrane fuel.

MEA Preparation for DMFC

Membrane electrode assembly (MEA) was obtained by sandwiching the SPSEBS/PSEBS 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 (IPA), deionized water and Nafion solution as binder and 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.

RESULTS AND DISCUSSION

Ion Exchange Capacity

Though the IEC values were found to be decreasing with the content of PSEBS all the membranes exhibit an IEC value better than Nafion® 117 (Figure 1) which was found to be 0.91 mequiv/g. Actually, the protons that are available in the sulfonic acid groupings of SPSEBS were responsible for the exchange of ions. When the concentration of PSEBS is increased, the concentration of SPSEBS decreases and in other words, the effective concentration of the sulfonic acid grouping decreases. This obviously account for the lowering of IEC values [11].

Water and Methanol absorption

Figure 2 and 3 shows the water and methanol absorption of the synthesized blend membranes. The water uptake of Nafion® 117 was found to be 28.51% and in the case of the blend membranes, the water absorption was found to be decreasing with increasing content of PSEBS. The methanol absorption was also found to follow a similar trend like water absorption. This may be due to the reduction in the number of hydrophilic sulphonic acid groupings as the content of PSEBS is increased. The decreased methanol absorption content revealed that the blend membranes can be a suitable candidate for use in direct methanol fuel cell (DMFC), wherein methanol is used as the fuel [12].

Methanol permeability

The methanol permeability of blend membrane given in figure 4 The methanol permeability of Nafion 117 was $35.2 \times 10^{-7} cm^2/S$. The introduction of PSEBS into the matrix of SPSEBS, there is a remarkable decrement in the methanol permeability. The blend membranes because of the presence of hydrophobic PSEBS offer better resistance to the flow of methanol.

Durability test

It was found that all the blend membranes were withstanding the condition for more than 8 hours, without any chemical disintegration.

XRD

Figure 5 shows the XRD pattern of SPSEBS and blend membranes. Three sharp diffraction peaks appeared at $2\theta = 45^0$, 52^0, and 74^0 illustrated the various crystalline forms of SPSEBS. There is an intense Pattern at 74^0 and weak pattern at 45^0 and 52^0. Combinations of both amorphous and crystalline phases are evident from the spectrum. In the blend, the content of PSEBS increases intensity slightly increases [13].

FT-IR

Figure 6 shows the FT-IR spectra of both SPSEBS and PSEBS blend membranes. Appearance of broad envelop around 3000-

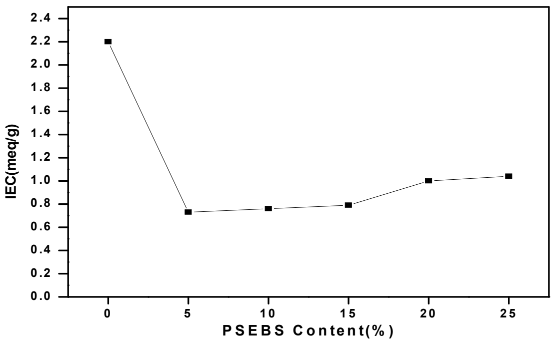

Fig. 1. Ion Exchange Capacity of SPSEBS/PSEBS blend membranes

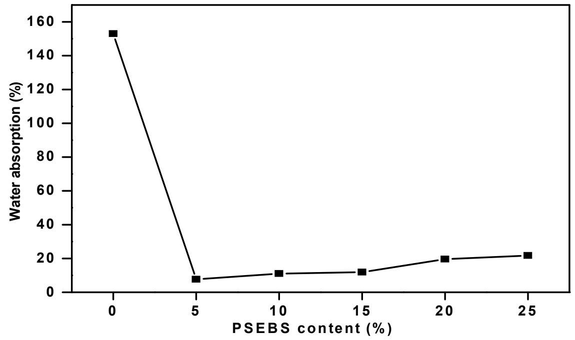

Fig. 2. Water uptake of SPSEBS/PSEBS blend membranes

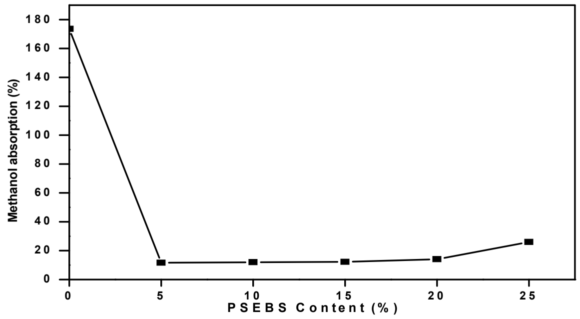

Fig. 3. Methanol uptake of SPSEBS/PSEBS blend membranes

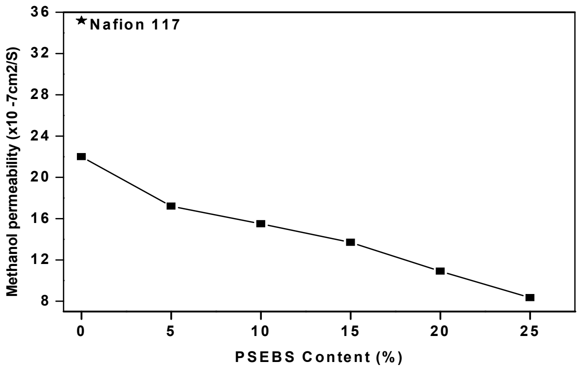

Fig. 4. Methanol permeability of SPSEBS/PSEBS blend membranes

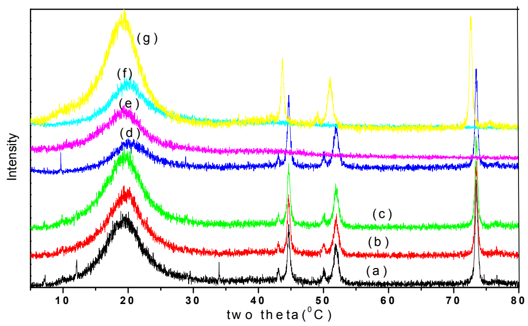

Fig. 5. XRD patterns of (a) SPSEBS, (b) M 1 (c) M 2, (d) M 3 (e) M 4(f) M 5 (g) PSEBS

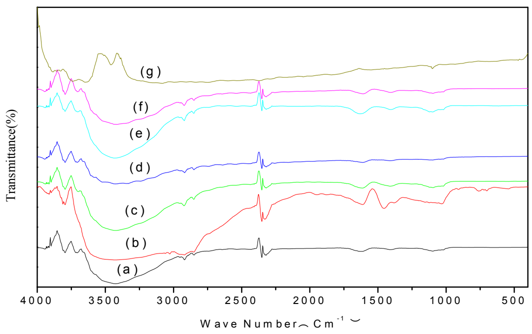

Fig. 6. FTIR Spectra of (a) SPSEBS, (b) M 1 (c) M 2, (d) M 3 (e) M 4(f) M 5 (g) PSEBS

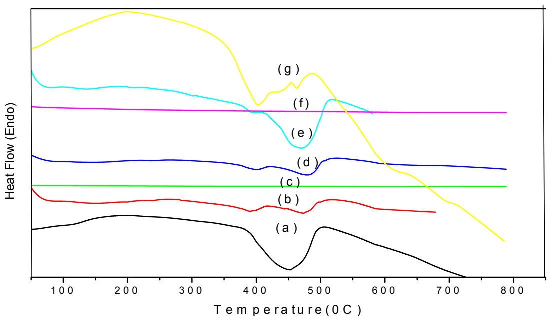

Fig.7. DSC curves of (a) SPSEBS (b) M 1 (c) M 2, (d) M 3 (e) M 4(f) M 5 (g) PSEBS

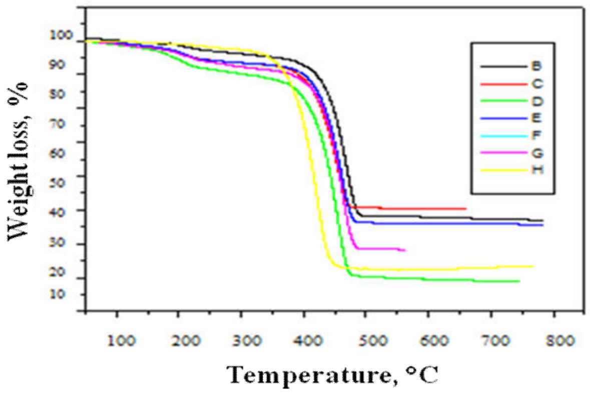

Fig. 8. TGA curves of (a) SPSEBS (b) M 1 (c) M 2, (d) M 3 (e) M 4 (f) M 5 (g) PSEBS

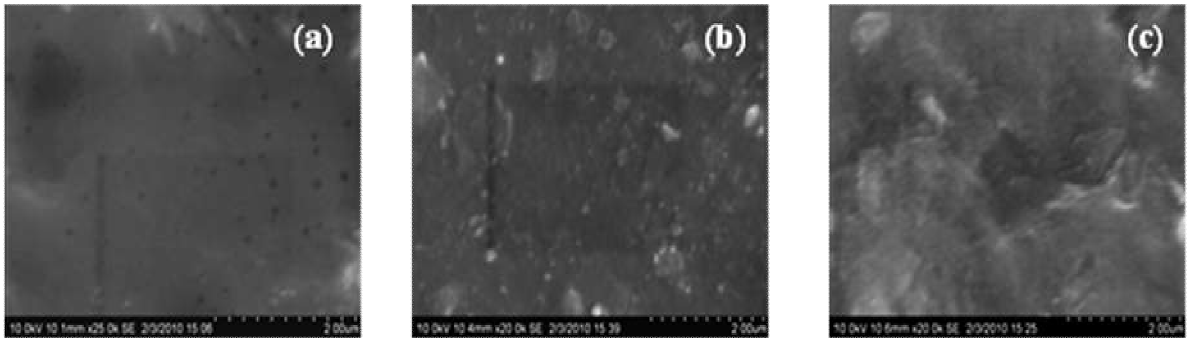

Fig. 9. SEM images of (a) M1 (b) PSEBS (c) M5

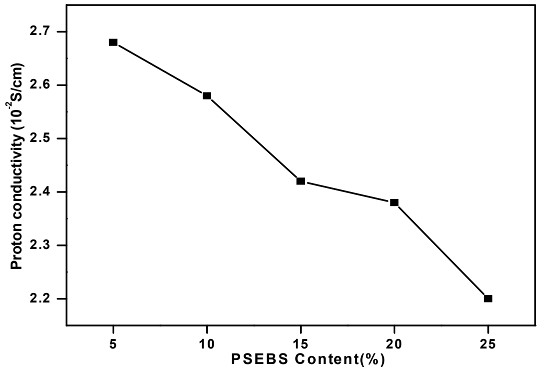

Fig. 10. Proton conductivity of SPSEBS/PSEBS blend membranes

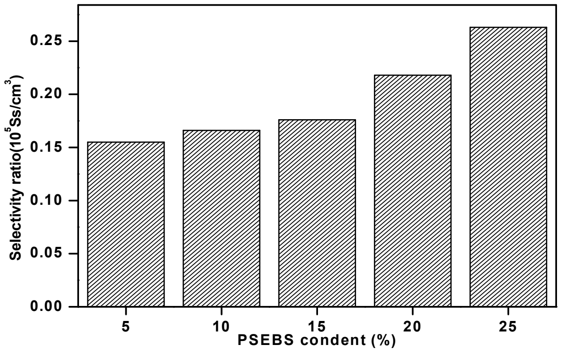

Fig. 11. Selectivity ratio of SPSEBS/PSEBS blend membranes

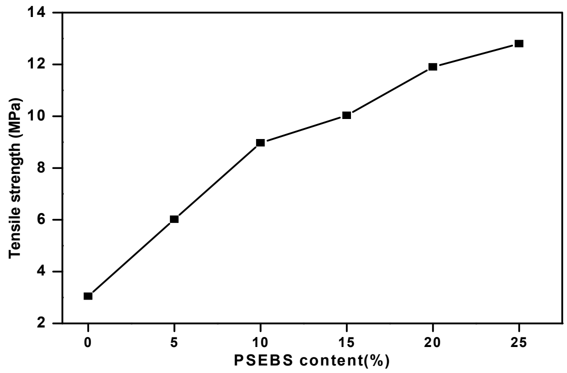

Fig. 12. Tensile strength of SPSEBS/PSEBS blend membranes

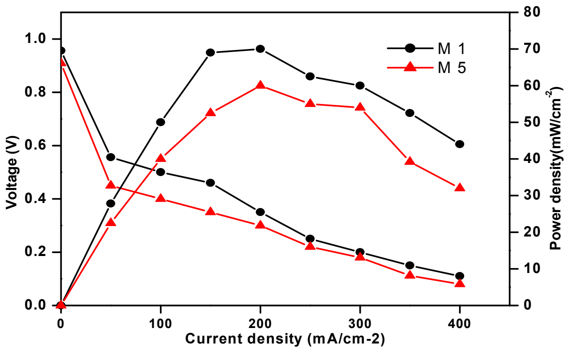

Fig. 13. Polarization and power density curves of blend membranes in PEMFC

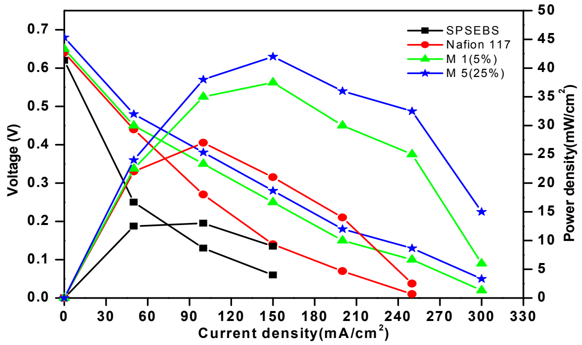

Fig. 14. Polarization and power density curves of SPSEBS, Nafion 117 and blend membranes in DMFC

3600cm^{-1} was assigned to -OH stretch of sulphonic acid group. Appearance of peak around 1125 and 1020cm^{-1} were assigned to the O=S=O (asymmetric stretch). Which is due to the presence of SO_2 stretching and thus confirms that the polymer PSEBS has been sulphonated. In the blend membrane the peak is slightly shifted to 1250 cm^{-1} [14 and 15].

DSC

Figure 7 shows the DSC curves of SPSEBS and PSEBS blend membranes. The inflection of point of the slope change of heat capacity plot was taken as the T_g and it was around 100°C to 164°C for SPSEBS. The T_g decrease with increasing content of PSEBS. This is because decrease in concentration of SPSEBS. This means that blend membranes could be easily fabricated for MEA preparation at a relatively lower temperature, conveniently without undergoing any chemical decomposition. In MEA preparation, the membrane is subjected to high pressure and fit in between the electrodes. DSC shows that the thermal stability of blend membrane is lower than SPSEBS [16].

TGA

The TGA curves of SPSEBS and PSEBS blend membranes are shown in figure 8. Thermal decomposition temperature of membrane is a function of sulphonation. The PSEBS sample display thermal stability up to 450 and 350°C respectively. The SPSEBS membrane losses its stability beyond 200°C. A small transition around 100°C is observed, which correspond to the weight loss of absorbed water. The transition around 200°C is due to the degradation of sulphonic acid groups. The transition around 400°C is attributed to main chain groups. Thermal stability of blend membrane decreased with the increase in the content of PSEBS due to segmental motion of the polymer chain [17 &18].

SEM

The SEM images of blend membranes shown in Figure 9 SPSEBS were found to be uniformly distributed over the SPSEBS matrix which facilitates a desirable and efficient matrix for continuous conduction pathway in all direction [19].

Proton conductivity

Proton conductivity of blend membrane is shown in figure 10. The proton conductivity tends to decrease with the addition of PSEBS. Three possible reasons could be attributed to the decrease in the proton conductivity as follows:

(i) With increase in the concentration of the PSEBS in the blend membranes, there is a decrease in the effective concentration of –SO_3H groupings. The protons present in the sulphonic acid groupings are labile and are responsible for the conduction of protons. Hence, there is a decrease in the proton conductivity.

(ii) With increase in the content of PSEBS in the blend membranes, there is a decrease in the ion exchange capacity of the membranes and so is the proton conductivity decreases.

(iii) With increase in the concentration of PSEBS there is an increase in the hydrophobic character when compared with virgin SPSEBS membrane. The hydrophobic nature results in low water absorption. The adsorbed water act like a canal for the transport of protons from the anode to the cathode. Hence with decrease in the water absorption, there is a decrease in the proton conducting ability also.

Selectivity ratio

The selectivity ratio of blend membrane is given in figure 11. The blend membranes exhibited a higher ratio. The higher selectivity ratio of the blend membranes when compared with Nafion ($0.5x10^5 Ss/cm^3$) and pristine SPSEBS ($0.54x10^5 Ss/cm^3$) indicate that they are better suitable as electrolyte membranes for DMFC.

Mechanical properties

Figure 12 shows the mechanical properties of blend membranes. With the increase in PSEBS the tensile strength of the blend membrane increased from 6.02 MPa to 12.8 MPa. The blend membranes exhibited excellent mechanical properties, indicating that the blend membranes are potential candidates for usage in PEMFC and DMFC [20and 21].

Single cell performance of PEMFC

Figure 13 compares the polarization curves of SPSEBS/PSEBS blend membranes (5 and 25 wt %) with those of plain SPSEBS and Nafion 117 membranes at room temperature in PEMFC [22] At 0.4V, the maximum power reached for the cell constructed with SPSEBS/PSEBS membranes are 70 and 60 mW/cm^2 for the membranes with PSEBS loading of 5% and 20%, respectively, whereas, at the same operating condition, the maximum power density offered by Nafion 117 and SPSEBS (0% PSEBS) membrane is 32 and 50 mW/cm^2, respectively, at room temperature. These features led to an enhancement of cell performance of the blend membrane, pointing out those SPSEBS/PSEBS membranes are a promising electrolyte for PEMFC [23].

Single cell performance of DMFC

Figure 14 compares the polarization curves of SPSEBS/PSEBS blend membranes (5 and 25 wt %) with those of plain SPSEBS and Nafion 117 membranes at room temperature in DMFC. The blend membranes show better performance in DMFC than plain SPSEBS membrane due to higher proton conductivity and lower methanol crossover. The lower methanol crossover suppresses the catalyst poisoning and lowers the mixed potential resulting in an increase in the OCV at steady state. The lower methanol crossover in the blend membrane could not only help lead to a better long-term stability and performance but also to lower the Pt catalyst loading at the cathode. At 0.3 V, the maximum power density reached for the cell constructed with SPSEBS/PSEBS membranes are 37.5 and 42 mW/ cm^2 for the membranes with PSEBS loading of 5% and 25%, respectively, whereas, at the same operating condition, the maximum power density offered by Nafion 117 and SPSEBS (0% PSEBS) membrane is 27 and 13 mW/cm^2, respectively, at room temperature with 2 M methanol solution. This could be due to the higher selectivity ratio of the blend membranes when compared with Nafion 117 and Virgin SPSEBS [24].

Acknowledgement

The authors would like to thank the University Grant commission (UGC), INDIA for funding this project.

REFERENCES

1. Nolte R, Ledjeff K, Bauer M, and Mulhaupt R, 1993. "Partially sulfonated poly (aryleneether sulfone) – A versatile proton conducting membrane material for modern energy conversion technologies. *Journal of Membrane Science,* 83: 211-220.
2. Sangeetha D, 2006. Sulphonated polyether ether ketone membrane electrolytes for fuel cells. International Journal of Plastic Technology, vol.10, pp. 645-654.
3. Shen Y, Qiu X, Shen J, Xi J, Zhu W, 2006. PVDF-g-PSSA and Al_2O_3 composite proton exchange membranes. *Journal of Power Sources*, 161, pp. 54–60.

4. Kadirgan F, Savadogo O, 2004. Methanol Crossover through Modified Nafion Proton exchange Membrane. *Russian Journal of Electrochemistry,* 40: 1141-1145.
5. Panero F, Ciuffa A, Epifano D, Scrosati B, 2003. "New concepts for the development of lithiumand proton conducting membranes. *Electrochim. Acta,* 48: 2009-2014.
6. Mauritz, K A, Moore R B, Deng Q, 1998. **"**Nafion®/(SiO_2, ORMOSIL, and dimethyl siloxane) hybrids via *in situ* sol-gel reactions: Characterization of fundamental properties. *J. Appl. Polym. Sci.,* 68: 747-763.
7. Lehtinen T, Sundholm G, Holmberg S, Sundholm F, Bjornborn P, Burdell, M. 1998. Electrochemical characterization of PVDF based proton conducting membranes for fuel cells. *Electrochim. Acta,* 43: 1881-1890.
8. Sangeetha D, 2004. Sulphonated polystyrene-block-poly (ethylene-ran-butylene)-block polystyrene as polymer electrolytes for proton exchange membrane fuel cells. *International Journal of Plastic Technology,* 8: 313-321.
9. Frederic Faverjon et al, "Electrochemical study of a hydrogen diffusion anode-membrane assembly for membrane electrolysis" Electrochemica Acta 51(2005) 386-394.
10. Th. Frey**,** 2004. Effects of membrane electrode assembly preparation on the polymer electrolyte membrane fuel cell performance. *Electrochemica Acta,* 50: 99-105.
11. Hansung Kim, 2004. Preparation of PEM fuel cell electrodes using pulse electrodeposition separation and purification technology. Journal of Power Source, 138: 14-24
12. Zhao C, Wang Z, Bi D, Lin H, Shao K, Fu T, Zhong S, Na H, 2007. Blend membranes based on disulfonated poly (aryl ether ether ketone)s (SPEEK) and (amide imide) (PAI) for direct methanol fuel cell usages. *Polymer*, 48: 3090-3097.
13. Xue S, Yin G, 2006. Proton exchange membranes based on poly (vinylidene fluoride) and sulfonated poly (ether ether ketone)", Polymer, vol. 47, pp. 5044-5049.
14. Mokrini A, Huneault M A, 2006. Proton exchange membranes based on PVDF/SEBS blends. *Journal of Power Sources,* 154: 51-58.
15. Jung H Y, Park J K, 2007. Blend membranes based on sulfonated poly (ether ether ketone) and Poly (vinylidene fluoride) for high performance direct methanol fuel cell. *Electrochimica Acta,* 52: 7464-7468.
16. Fu T, Zhao C, Zhong S, Zhang G, Shao K, Zhang H, Wang J, Na H, 2007. SPEEK/epoxy resin composite membranes in situ polymerization for direct methanol fuel cell usages. *Journal of Power Sources*, 165: 708 -716.
17. Choi W H, Jo W H, 2009. Preparation of new proton exchange membrane based on self- assembly of poly (styrene-co-styrene sulfonic acid)-b-poly (methyl methacrylate)/poly (vinylidene fluoride) blend. *Journal of Power Sources*, 188: 127-131.
18. Kim Y W, Lee D K, Lee K J, Kim J H, 2008. Single-`step synthesis of proton conducting poly (vinylidene fluoride) (PVDF) graft copolymer electrolytes. *European Polymer Journal,* 44: 932-939.
19. Wang P, Tan K L, Kang E T, Neoh K G, 2002. "Preparation and characterization of semi-conductive poly (vinylidene fluoride)/polyaniline blends and membranes. *Applied Surface Science*, 193: 36-45.
20. Yang M C, Liu T Y, 2003. The permeation performance of poly acrylonitrile/poly vinylidine fluoride blend membranes. *Journal of Membrane Science*, 226: 119-130.
21. Jung H Y, Park J K, 2009. Long-term performance of DMFC based on the blend membrane of sulfonated poly (ether ether ketone) and poly (vinylidene fluoride). *International Journal of Hydrogen Energy,* 34: 3915-3921.
22. Barbara Mecheri et al., 2007. Sulfonated polyether ether ketone and hydrated tin oxide proton conducting composites for direct methanol fuel cell application. *Journal of power source,* Press.
23. M. Helen, 2006. Fabrication and properties of hybrid membranes based on salt of heteropolyacid, zirconium phosphate and polyvinyl alcohol. Jounal of Power Source, 163: 433-439.
24. Ho-Young Jung, Jung-Ki Park, 2007. Blend membranes based on sulfonated poly(ether ether ketone) and poly (vinylidene fluoride for high performance direct methanol fuel cell" *Electrochemica Acta.*, 52: 7464-7468.

****