

# Chitosan-Polyvinyl Alcohol-Sulfonated Polyethersulfone Mixed-Matrix Membranes as Methanol-Barrier Electrolytes for DMFCs

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**ABSTRACT:** Chitosan (CS)-polyvinyl alcohol (PVA) cross-linked with sulfosuccinic acid (SSA) and modified with sulfonated polyethersulfone (SPES) mixed-matrix membranes are reported for their application in direct methanol fuel cells (DMFCs). Polyethersulfone (PES) is sulfonated by chlorosulfonic acid and factors affecting the sulfonation reaction, such as time and temperature, are studied. The ion-exchange capacity, degree of sulfonation, sorption, and proton conductivity for the mixed-matrix membranes are investigated. The mixed-matrix membranes are also characterised for their mechanical and thermal properties. The methanol-cross-over flux across the

mixed-matrix membranes is studied by measuring the mass balance of methanol using the density meter. The methanol cross-over for these membranes is found to be about 33% lower in relation to Nafion-117 membrane. The DMFC employing CS-PVA-SPES mixed-matrix membrane with an optimum content of 25 wt % SPES delivers a peak power-density of 5.5 mW cm<sup>-2</sup> at a load current-density of 25 mA cm<sup>-2</sup> while operating at 70°C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: E73–E82, 2012

**Key words:** mixed-matrix membrane; SPES; degree of sulfonation; methanol cross-over; DMFCs

## INTRODUCTION

Direct methanol fuel cells (DMFCs) have been found to be attractive option for various portable power applications.<sup>1</sup> DMFCs employ perfluorinated membranes, such as Nafion or Flemion, as electrolyte. Although these membranes have good physical and chemical stability along with their high proton-conductivity, these are prone to methanol crossover from anode to the cathode that poisons the cathode and, consequently, affects the performance of the DMFCs.<sup>2,3</sup> Such a situation demands the development of membrane electrolytes for DMFCs that are impervious to methanol.

In the literature,<sup>4,5</sup> efforts have been expended to develop methanol impervious membrane electrolytes for DMFCs. In recent years, natural and synthetic-polymer composite membranes have made significant impact as polymer electrolytes for DMFCs.<sup>6,7</sup> Among these, natural polymer chitosan (CS) and synthetic polymer poly(vinyl alcohol) (PVA) have drawn considerable attention in the past decade.<sup>8,9</sup> CS is the second most abun-

dant natural biopolymer obtained by alkaline deacetylation of chitin, a major component in exo-skeleton of crustaceans.<sup>10</sup> Because of its low cost of production, natural abundance and ecocompatibility, CS is a preferred membrane material for ultrafiltration, reverse osmosis, and pervaporation.<sup>11–13</sup> It is also reflected that CS-based natural polymeric composite membranes can help reducing methanol crossover in DMFCs.<sup>14–16</sup> PVA can also be used as an attractive material for membrane electrolyte in DMFCs owing to its good mechanical and chemical stability.<sup>17</sup> PVA-based blends or composite membranes can also offer high electrochemical selectivity in DMFCs.<sup>18,19</sup> Ironically, however, CS and PVA suffer from high modulus of elasticity with low strain-to-break and high crystallinity, and hence need to be blended with each other to improve hydrophilicity and mechanical properties.<sup>20–23</sup> In the literature,<sup>20</sup> CS-PVA blend membranes have been prepared and used for pervaporative dehydration of isopropanol and ethylene glycol. Carboxyethyl CS-PVA nanofibrous membranes have also been used as wound-dressing materials for skin regeneration.<sup>21</sup> The effect of chemical crosslinking and formation of single and dual-network structures in CS-PVA films have also been studied.<sup>22</sup> Wu et al.<sup>23</sup> have reported that CS-PVA blend has higher selectivity, mechanical strength and stability than the pristine PVA membranes.

Our recent findings suggest that PVA-PSSA,<sup>24</sup> modernite (MOR)-incorporated PVA-PSSA with varying

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degree of sulfonation and PVA-sulfosuccinic acid (SSA)-heteropoly acid (HPA) composite membranes exhibit attractive mechanical stability and provide promising DMFC performance.<sup>25,26</sup> It is also found that chitosan (CS)-hydroxyethyl cellulose (HEC), CS-gelatin (GL), and sodium alginate (NaAlg)-PVA blends with their modification by incorporating HPAs can be successfully employed as electrolyte membranes for DMFCs owing to their low cost and excellent methanol-barrier properties in relation to commercially available membranes.<sup>27-29</sup>

Recently, a variety of hydrocarbon-based sulfonated polymers have been synthesized and used as membrane electrolytes in fuel cells to mitigate the problems associated with perfluorinated polymers or less stable self-supported membranes.<sup>30-35</sup> In particular, sulfonated poly (ether sulfone) (SPES),<sup>30</sup> sulfonated poly ether ether ketone (SPEEK),<sup>31</sup> sulfonated polyimides,<sup>32</sup> sulfonated polysulfones,<sup>33</sup> sulfonated polyphthalazinones,<sup>34</sup> and sulfonated polybenzimidazoles<sup>35</sup> have been widely used to prepare polymer electrolyte membranes for fuel cell applications. Among these polymers, polyethersulfone (PES) exhibits high mechanical, chemical, and biological stabilities.<sup>30</sup> Sulfonation of PES can also be performed by chemical modification method and negatively charged sulfonic groups can be chemically introduced into PES backbone using chlorosulfonic acid or sulfuric acid as sulfonating agent.<sup>36</sup>

In the literature, studies on mixed-matrix membranes of CS-PVA with SPES as a methanol-barrier electrolyte in DMFC are rather scanty. In the present study, PES is sulfonated with chlorosulfonic acid as sulfonating agent and is incorporated with CS-PVA blend wherein CS-PVA polymer networks are interconnected through the cross-linked covalent bonds by an ion-conducting crosslinker SSA to provide additional proton-conducting groups. In the study, SPES is incorporated based on the limitations experienced with PVA-PSSA-MOR and PVA-SSA-HPA on account of proton conductivity in the case of the former and the problem of leaching, which is circumvented to certain extent by stabilizing the heteropolyacids with cesium ions, in the latter. SPES is mainly incorporated for enhancing proton conductivity in CS-PVA matrix. Taking in to account the advantage of the hydrophilicity of the polymer chains and stability of these blends, SPES can easily be incorporated in the matrix to help mitigating the methanol cross-over in DMFCs.

## EXPERIMENTAL

### Membrane and electrode materials

Polyether sulfone (PES,  $M_w = 132,000$ ,  $M_n = 94,000$ ) was obtained from Gharda Chemicals, India. Chlorosulfonic acid and dimethylacetamide (DMAc) were procured from Acros Organics, India. Toray TGP-H-120 was procured from E-tek (US). Vulcan XC-72R

carbon was procured from Cabot Corporation (US). Pt-Ru (60 wt % in 1 : 1 atomic ratio) and Pt/C (40 wt % Pt on Vulcan XC-72R carbon) were obtained from Alfa Aesar (Johnson Matthey). Chitosan (CS) flakes with  $M_w$  of 100,000 (degree of deacetylation > 95%) and 70 wt % sulfosuccinic acid (SSA) in water solution were procured from Aldrich Chemicals. Polyvinyl alcohol (PVA) with  $M_w$  of 133,000, glacial acetic acid and concentrated sulphuric acid (98%) were procured from Loba Chemicals. All chemicals were used as received. Deionized water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) was used during the study.

### Sulfonation reaction

Sulfonation reaction was performed as reported in the literature.<sup>36</sup> In brief, 5 g of PES was dissolved in 20 mL of concentrated sulfuric acid (98 %) under continuous stirring at room temperature to form a homogeneous solution. Required amount of chlorosulfonic acid was added dropwise to the PES solution with rigorous stirring. The resulting reaction mixture was stirred further for 10 h at 30°C. After optimizing the reaction time, the mixture was gradually precipitated into ice-cold deionized water under agitation, and the resulting precipitate was recovered by filtration and washed with deionized water until the pH value was neutral. The dried sample was further used for determination of its ion-exchange capacity and degree of sulfonation. The yield obtained for the SPES was 70%.

### Ion-exchange capacity (IEC)

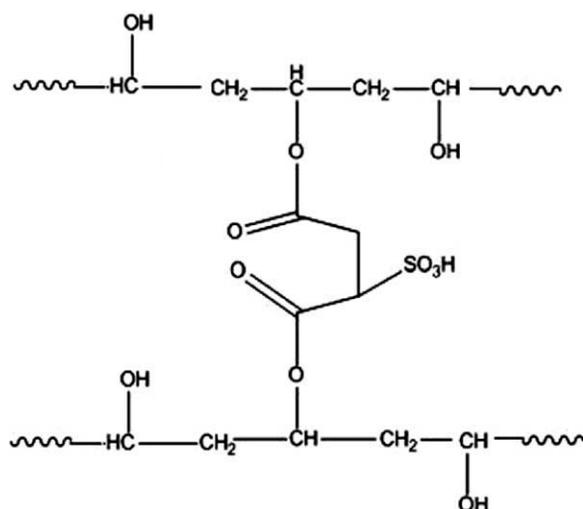
Ion-exchange capacity (IEC) indicates the number of milli-equivalents of ions in 1 g of dry polymer. IEC of SPES was determined by titration method using the procedure described elsewhere.<sup>37</sup> In brief, required amount of SPES sample was soaked in 50 mL of 3M sodium chloride (NaCl) solution for 24 h, to convert SPES-H<sup>+</sup> into SPES-Na<sup>+</sup>. Nearly 10 mL of the above solution was titrated against 0.01N sodium hydroxide (NaOH) solution using phenolphthalein as the indicator. By measuring the amount of NaOH consumed in the titration, the molar quantity of the sulfonic acid groups (–SO<sub>3</sub>H) contained in the SPES-H<sup>+</sup> sample was determined. By using this value, IEC was estimated by eq. (1).

IEC

$$= \frac{\text{Volume of NaOH consumed} \times \text{Normality of NaOH}}{\text{Dry weight of SPES}} \quad (\text{meq/g}) \quad (1)$$

### Degree of sulfonation (DS)

DS is defined as the average number of sulfonated groups per repeat unit. DS could be related to IEC by eq. (2).<sup>38</sup>



Scheme 1 Cross-linking reaction between SSA and PVA.

$$DS = \frac{232 \times IEC}{(1000 - 80 \times IEC)} \quad (2)$$

In eq. (2), 232 is the molecular weight of one repeat unit of PES, and 80 is the molecular weight of  $\text{SO}_3\text{-group}$ .

### Membrane preparation

About 1 wt % CS was dissolved in deionized water with 2 wt % aqueous acetic acid to form a homogeneous viscous-solution. Nearly 10 wt % PVA aqueous solution was prepared by dissolving PVA in water at 60°C. And 25 wt % of SSA in relation to PVA is added *in situ* for crosslinking. When PVA is crosslinked with SSA, an introduction of negative charged ion group in PVA by the chemical modification through crosslinking with SSA occurs. Cross-linking does not occur soon after SSA is mixed with PVA as SSA is diluted to avoid immediate gelation or precipitation. After a certain period of time, the crosslinking occurred and homogeneous membranes were obtained after drying the crosslinked solution. Cross-linking reaction between PVA and SSA is represented in Scheme 1. CS and PVA solutions were mixed in different proportions under stirring for 24 h to form a compatible blend (Table I). Required wt % of SPES dissolved in DMAc solution in relation to PVA and CS was added to the blend to form a mixed matrix. Solution was poured on a flat Plexiglas plate and the solvent was evaporated at room temperature (30°C). The resultant membrane was peeled off and immersed in a cross-linking solution of 1M sulphuric acid for 4 h to ionically cross-link CS. Cross-linking occurred when the sulfuric acid content in the chitosan membrane was synchronous with protonation.  $\text{SO}_4^{2-}$  ions located between two  $\text{NH}_3^+$  groups on the chitosan chains bring about

ionic cross-linking. As the reaction time increases, more and more  $\text{SO}_4^{2-}$  ions diffused to locations bridging two  $\text{NH}_3^+$  groups, increasing the degree of ionic crosslinking. Accordingly, ionic crosslinking is dependent on the mobility of  $\text{SO}_4^{2-}$  ions in the membrane. The membranes were boiled with deionised water for 5 h to ensure complete removal of any residual acid. The pH was regularly monitored until it showed the neutral value. Membranes were again dried under ambient conditions. The thickness of the membranes was  $\sim 180 \mu\text{m}$ . On higher addition of SPES, i.e., more than 25 wt %, an aggregation of SPES particles in the membrane matrix was observed causing membrane brittleness. However, at lower wt %, such aggregation was not found and it was easier to maintain the rigidity of the matrix.

### Sorption measurements

Sorption measurements were carried out using circularly cut (diameter = 2.5 cm) CS-PVA blend and CS-PVA-SPES mixed-matrix membranes. Dry membrane sample weights ( $W_d$ ) were measured and dipped separately in deionized water for 24 h to attain equilibrium at room temperature. The membranes were surface blotted and sorbed membranes were weighed ( $W_s$ ). Water sorption and swelling ratio values for aforesaid membranes were calculated using eqs. (3) and (4).

$$\text{Swelling ratio (\%)} = \frac{W_s}{W_d} \times 100 \quad (3)$$

$$\text{Sorption (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (4)$$

In eqs. (3) and (4),  $W_s$  and  $W_d$  refer to the weights of sorbed and dry membranes, respectively.

For water-methanol mixture, sorption measurement carried out at 30°C and the feed composition was 2M aqueous methanol. Preweighed dry membranes ( $W_d$ ) were dipped in feed solution for 24 h to attain equilibrium. The equilibrated membranes were surface blotted and final weights ( $W_s$ ) were recorded at ambient temperature (30°C) and water/methanol

TABLE I  
Compositions of Blended Chitosan and PVA Membranes

Abbreviations	wt %	
	Chitosan	PVA
CS	100	0
CS PVA 75:25	75	25
CS PVA 50:50	50	50
CS PVA 25:75	25	75
PVA	0	100

sorption and swelling ratio was calculated from eqs. (3) and (4), respectively.

### Proton-conductivity measurements

Proton-conductivity measurements were performed on CS-PVA-SPES mixed-matrix membranes in a two-probe cell by AC impedance technique. The conductivity cell comprised two stainless-steel electrodes, each of 20-mm diameters. The membrane sample was sandwiched between these two electrodes mounted in a Teflon block and kept in a closed glass-container. The ionic conductivity data for the membranes were obtained under fully humidified condition ( $\sim 100\%$ ) by keeping deionized water at the bottom of the test container and equilibrating it for  $\sim 24$  h. Subsequently, conductivity measurements were conducted between 303 and 373 K in a glass container with provision to heat. The temperature was constantly monitored with a thermometer kept inside the container adjacent to the membrane. AC impedance spectra of the membranes were recorded in the frequency range between 1 MHz and 10 Hz with 10 mV amplitude using Autolab PGSTAT 30. The resistance ( $R$ ) of the membrane was determined from the high-frequency intercept of the impedance with the real axis and the membrane conductivity was calculated from the membrane resistance,  $R$ , from eq. (5).

$$\sigma = \frac{L}{RA} \quad (5)$$

In eq. (5),  $\sigma$  is the proton conductivity of the membrane in  $S\text{ cm}^{-1}$ ,  $L$  is the membrane thickness in centimeter and  $A$  is the cross-sectional area of the membranes in  $\text{cm}^2$ .

### Physicochemical characterization

Universal testing machine (UTM) (Model AGS-J, Shimadzu, Japan) with an operating head-load of 10 kN was used to study the mechanical properties of the membranes. For the study, cross-sectional area of the sample from the known width and thickness of the membrane sample was calculated. The test samples were prepared in the form of dumb-bell shaped object as per ASTM D-882 standards. The membranes were then placed in the sample holder of the machine. The film was stretched at a cross-head speed of  $1\text{ mm min}^{-1}$  and its tensile strength was calculated using the eq. (6).

$$\text{Tensile strength} = \frac{\text{Maximum load}}{\text{Cross-sectional area}} (\text{MPa}) \quad (6)$$

The tensile strength and elongation-at-break measurements were conducted for CS-PVA blend

and CS-PVA-SPES mixed-matrix membranes. Thermo-gravimetric analysis (TGA) for CS-PVA-SPES mixed-matrix membranes were conducted using a SDT Q600 V8.2 TGA/DTA instrument in the temperature range between 273 and 973 K at a heating rate of  $10\text{ K min}^{-1}$  with nitrogen flushed at  $200\text{ mL min}^{-1}$ . Surface morphologies for CS-PVA blend membrane and CS-PVA-SPES mixed-matrix membrane were obtained using JEOL JSM 35CF Scanning Electron Microscope (SEM). Gold film of thickness  $<100\text{ nm}$  was sputtered on the membrane surfaces using a JEOL fine coat ion sputter-JFC-1100 unit, prior to their examination under SEM.

### Methanol-permeation studies

Methanol crossover can be measured by measuring the  $\text{CO}_2$  concentration in cathode exhaust gases by: (a) mass spectroscopy, (b) gas chromatography, (c) gas analyzer, and (d)  $\text{CO}_2$  gas sensor. These measurements do not account for  $\text{CO}_2$  permeation across the membrane and hence could be erroneous. The density measurement is free from the above problem. Determination of methanol crossover using density measurement method has already been reported elsewhere.<sup>28</sup>

The permeated methanol from anode to cathode was measured by determining the methanol concentration based on the mass balance between the methanol supplied to the cell, methanol utilized for the electrochemical reaction and unutilized methanol during the DMFC operation. The approach follows Faraday's law<sup>39</sup> where concentration of methanol varies with the load current-density with one mole of methanol being equivalent to 96485 Coulombs. Accordingly, the amount of the methanol cross-over ( $\text{MeOH}_{\text{cross-over}}$ ) was taken as the difference between amounts of methanol circulated inside the cell ( $\text{MeOH}_{\text{cir}}$ ) for the reaction and the methanol consumed during the Faradaic reaction to produce electrical energy ( $\text{MeOH}_{\text{rxn}}$ ).

The 2M aqueous methanol was initially supplied to the DMFC and the cell was allowed to equilibrate. After attaining steady state, the difference in the amount of methanol supplied to the cell and the methanol collected at the anode outlet for a particular time ( $t$ ) was measured under OCV condition at  $70^\circ\text{C}$ . The densities of methanol collected from the inlet and outlet of the cell anode were measured using a density meter (Mettler Toledo DE51) with 20 mL of the collected methanol sample. Subsequent to each measurement, the density meter was purged with water and isopropanol followed by aqueous methanol solution. The molarity of the methanol was calculated from the measured density values using eq. (7).<sup>40</sup>

$$\text{Molarity} = 10 \times \text{wt \% of Methanol} \left( \frac{\rho}{M} \right) \quad (7)$$

In eq. (7),  $\rho$  is the density of methanol ( $\text{g cm}^{-3}$ ) and  $M$  is the molecular weight of methanol ( $\text{g mol}^{-1}$ ).

Inlet methanol concentration ( $C_1$ ) and volume ( $V_1$ ) of methanol, and the outlet methanol concentration ( $C_2$ ) and volume ( $V_2$ ) were measured separately after the cell operation was stopped. It is noteworthy that under OCV condition, methanol supplied at the inlet ( $\text{MeOH}_{\text{in}}$ ) is equal to the sum of the methanol collected at the outlet ( $\text{MeOH}_{\text{out}}$ ) and the methanol crossed-over ( $\text{MeOH}_{\text{cross-over}}$ ) from anode to cathode side of the cell. Accordingly,

$$\text{MeOH}_{\text{cross-over}} = \text{MeOH}_{\text{in}} - \text{MeOH}_{\text{out}} \quad (8)$$

At a particular current density ( $I$ ), methanol consumed during the electrochemical oxidation reaction over a time ( $t$ ) was calculated to be  $4.19 \times 10^{-3} \text{ mL}/(A \times \text{min})$ . Hence from eq. (9),

$$\text{MeOH}_{r \times n} = I \times 4.19 \times 10^{-3} \times t \quad (9)$$

In eq. (9),  $I$  is in  $A$ ,  $t$  is in  $\text{min}$ . Cross-over methanol was calculated using eqs. (8) and (9).

Accordingly,

$$\text{MeOH}_{\text{cross-over}} = \text{MeOH}_{\text{cir-in/out}} - \text{MeOH}_{r \times n} \quad (10)$$

In eq. (10),  $\text{MeOH}_{\text{cir-in/out}}$  is the difference in methanol volume at the inlet and outlet of the anode. From eq. (10), equivalent current ( $i_{\text{pmtMeOH}}$ ,  $\text{mA cm}^{-2}$ ) for methanol cross-over from anode to cathode side was determined.<sup>41</sup> The aforesaid procedure was carried out under OCV condition, and the corresponding methanol permeation currents and methanol crossover rates were estimated. Based on the results of proton conductivity and methanol permeability, the electrochemical selectivity values for all the membranes were obtained using eq. (11).<sup>41</sup>

$$\beta = \frac{\sigma}{\rho_{\text{MeOH}}} \quad (11)$$

In eq. (11),  $\rho_{\text{MeOH}}$  is the methanol permeability ( $\text{cm}^2 \text{ s}^{-1}$ ) and  $\sigma$  is the proton conductivity ( $\text{S cm}^{-1}$ ).

### Membrane-performance evaluation in DMFC

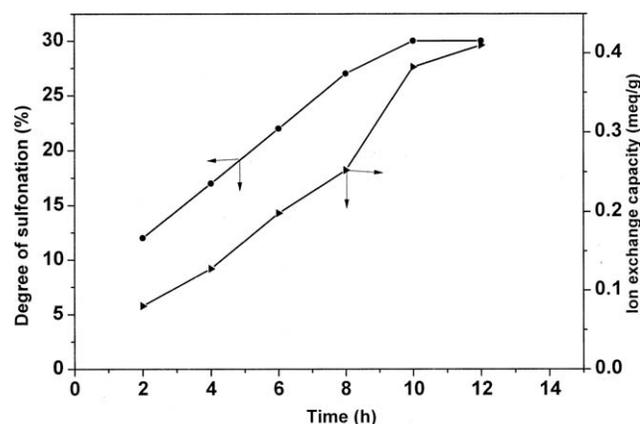
The aforesaid membranes were performance evaluated in a DMFC by making membrane electrode assemblies (MEAs). In brief, 15 wt % teflonized Toray-TGP-H-120 carbon paper of 0.37 mm thickness was used as the backing layer. To prepare the gas-diffusion layer (GDL), Vulcan XC-72R was sus-

ended in cyclohexane and agitated in an ultrasonic water bath for 30 min. To this solution, 15 wt % polytetrafluoroethylene (PTFE) suspension in 2 mL ammonia was added with continuous agitation to form slurry that was coated onto the backing layer uniformly until the required loading of  $1.5 \text{ mg cm}^{-2}$  carbon was attained. GDL thus obtained was sintered in muffle furnace at  $350^\circ\text{C}$  for 30 min. For anode reaction layer, 60 wt % Pt-Ru (1 : 1 atomic ratio) supported on Vulcan XC-72R carbon mixed with binder and coated on to one of the GDL constituted the catalyst layer on the anode while 40 wt % Pt catalyst supported on Vulcan XC-72R carbon mixed with binder coated on to the other GDL constituted the catalyst layer on the cathode. The catalyst loading on both the anode and cathode was kept at  $2 \text{ mg cm}^{-2}$ . The active area for the DMFC was  $4 \text{ cm}^2$ . MEA comprising CS-PVA-SPES mixed-matrix membrane was obtained by sandwiching between the two electrodes followed by its hot-pressing at  $100^\circ\text{C}$  for 3 min at a pressure of  $60 \text{ kg cm}^{-2}$ . MEA was evaluated using a conventional fuel-cell fixture with parallel serpentine flow-field machined on graphite plates. The cells were tested at 343 K with 2M aqueous methanol at a flow rate of  $2 \text{ mL min}^{-1}$  at the anode side and air at the cathode side at a flow rate of  $300 \text{ mL min}^{-1}$  at atmospheric pressure. Measurements of cell potential as a function of current density were conducted galvanostatically using a Fuel Cell Test Station (Model PEM-FCTS-158541) procured from Arbin Instruments (US).

## RESULTS AND DISCUSSION

### IEC and Degree of sulfonation

IEC is an indirect but reliable estimate of proton conductivity that provides information on the ion-exchangeable groups present in a membrane for proton conduction.<sup>42</sup> It is seen from the data in Figure 1 that IEC can be directly related to degree of sulfonation. IEC of SPES is varied between 0.08 and 0.41  $\text{meq g}^{-1}$  with time for different SPES samples taken at each time interval. The IEC for SPES is low because of the low reactivity of the aromatic rings directly attached to the sulfone groups.<sup>43</sup> It is noteworthy that the degree of substitution of  $-\text{SO}_3\text{H}$  group increases with time with concomitant increase in the degree of sulfonation from 12 to 30% and reaches a steady state value after 10 h; the reaction is affected by both the electrophilicity of the sulfonating agent and the electron-donating characteristic of SPES.<sup>36,44</sup> There may also be the electron withdrawing effect of the sulfone linkages that deactivates the adjacent aromatic rings for electrophilic substitution.<sup>44</sup> Polymer degradation occurs as the postsulfonation is performed under harsh conditions.

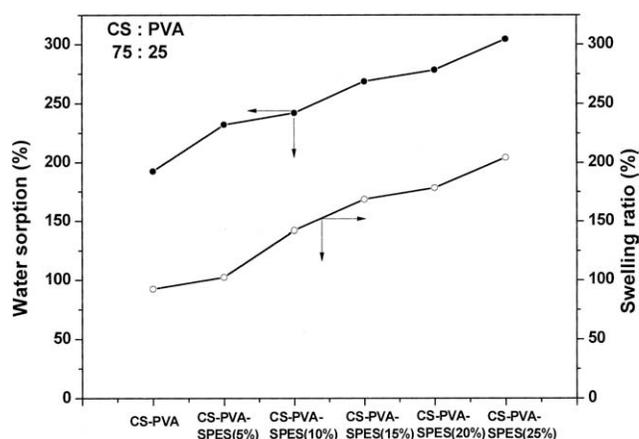


**Figure 1** Degree of sulfonation and ion-exchange capacity vs. time for PES polymer.

IEC values for the mixed-matrix membranes are given in Table II. IEC values for the CS-PVA blend and mixed-matrix membranes of CS-PVA-SPES are higher in relation to pristine SPES. This is due to the presence of sulfonic acid groups present in SSA used for crosslinking CS-PVA that facilitates the additional ion exchange groups and affects the membrane sorption and proton conductivity.

### Sorption for the membranes

The water sorption and swelling ratio for CS-PVA-SPES mixed-matrix membranes increases with increase in SPES content as shown in Figure 2. This is due to the higher sulfonic acid group of SPES and its strong affinity to water. The hydrophobic backbone and hydrophilic sulfonic acid groups of SPES are principally responsible for the water uptake.<sup>45,46</sup> It is conjectured that at low percentage of SPES, the hydrophilic part is isolated in continuous hydrophobic phase. When SPES content is increased, the hydrophilic ionic domains become continuous and form large channels.<sup>47,48</sup> Figure 3 shows the effect of water-methanol sorption and swelling ratio in CS-PVA blend, CS-PVA-SPES mixed-matrix membranes. Interestingly, as SPES content is increased in the CS-PVA membranes, water-methanol uptake and swel-



**Figure 2** Water sorption (number of percentage) and swelling ratio (number of percentage) for CS-PVA blend and CS-PVA-SPES (5–25 wt %) mixed-matrix membranes.

ling ratio decreases contrary to increase in water uptake and swelling ratio for water sorption. It is conjectured that water sorption trend is reversed in water-methanol sorption. Hence, it is conjectured that in aqueous methanol solution the membrane has preference for water sorption in relation to methanol. This assumption is validated by methanol permeability and polarization studies.

### Scanning electron microscopy for the membranes

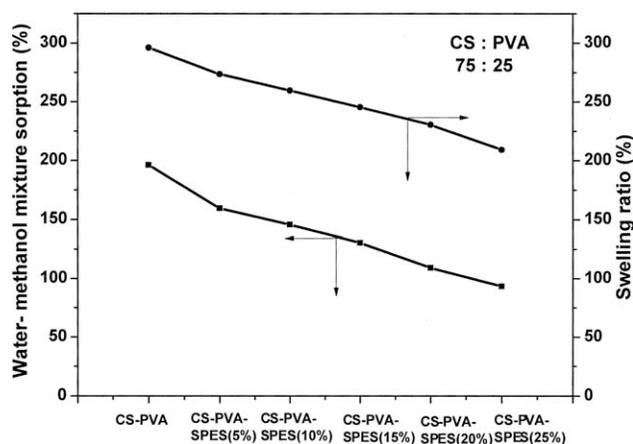
Figures 4(a–d) shows surface and cross-sectional SEM micrographs for CS-PVA blend and CS-PVA-SPES mixed-matrix membranes. It is noteworthy from the surface morphology that SPES is uniformly distributed in the CS-PVA matrix. It can be seen from the cross-sectional micrographs that voids of CS-PVA matrix are filled by SPES and there is a molecular level distribution. It is noteworthy that uniform morphology of the membrane is desirable for its use in DMFCs.

### Mechanical properties of the membranes

The tensile strength of pristine SPES, CS-PVA blend and CS-PVA-SPES mixed-matrix membranes under

**TABLE II**  
Properties of Blend and Mixed-Matrix Membranes

Membrane type	Ion exchange capacity (meq g <sup>-1</sup> )	Tensile strength (MPa)	Elongation at-break (%)	Activation energy (kJ mol <sup>-1</sup> )	Electrochemical selectivity (×10 <sup>-4</sup> S cm <sup>-3</sup> s <sup>-1</sup> )
CS-PVA	0.47	1.8	4.7	31.9	0.24
CS-PVA-SPES (5 wt %)	0.52	4.0	1.6	21.6	0.06
CS-PVA-SPES (10 wt %)	0.58	5.1	5.9	18.4	0.21
CS-PVA-SPES (15 wt %)	0.61	11.8	9.2	15.5	0.34
CS-PVA-SPES (20 wt %)	0.63	10.4	4.4	10.2	1.89
CS-PVA-SPES (25 wt %)	0.69	8.3	5.7	8.1	2.41
SPES	0.41	8.2	0.6	–	–
Nafion-117	0.90	18	32	7.46	3.69



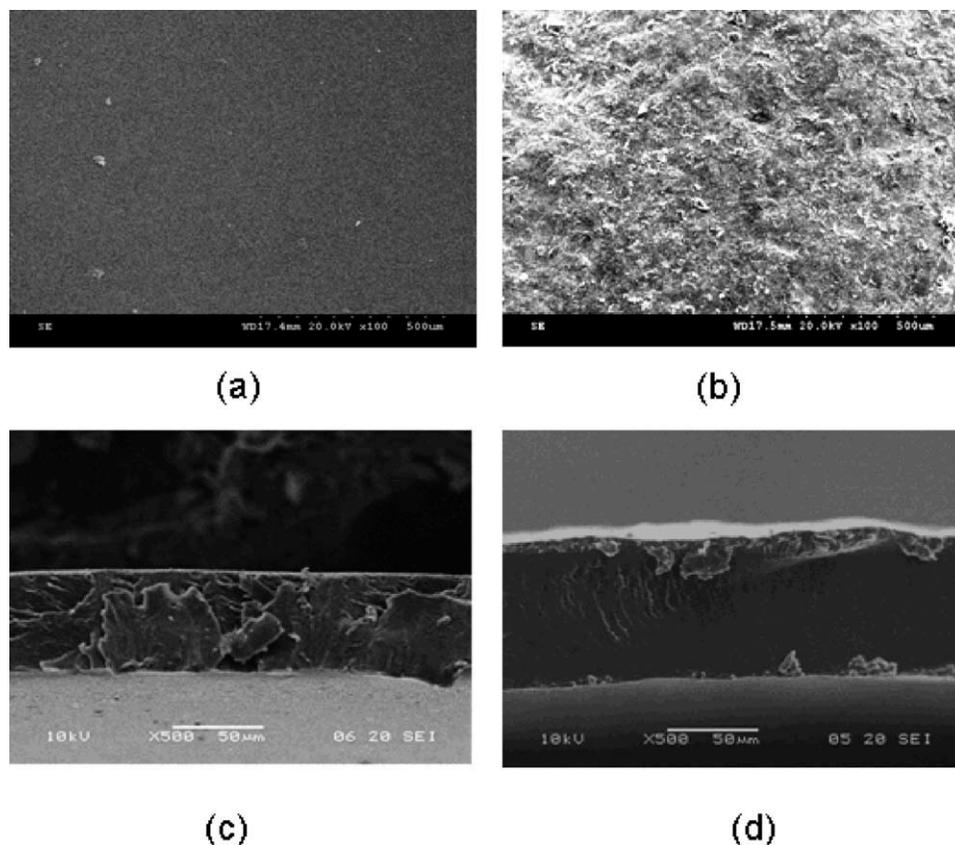
**Figure 3** Water-methanol mixture sorption (number of percentage) and swelling ratio (number of percentage) for CS-PVA blend and CS-PVA-SPES (5–25 wt %) mixed-matrix membranes.

sorbed conditions are shown in Table II. On incorporation of SPES content the CS-PVA matrix exhibits improved tensile strength. Morphological study for CS-PVA and CS-PVA-SPES also clearly shows that on incorporation of SPES, surface homogeneity is maintained and there are no defects. It is noteworthy that tensile strength increase in relation to percentage of SPES, i.e., up to 15 wt %. However, it

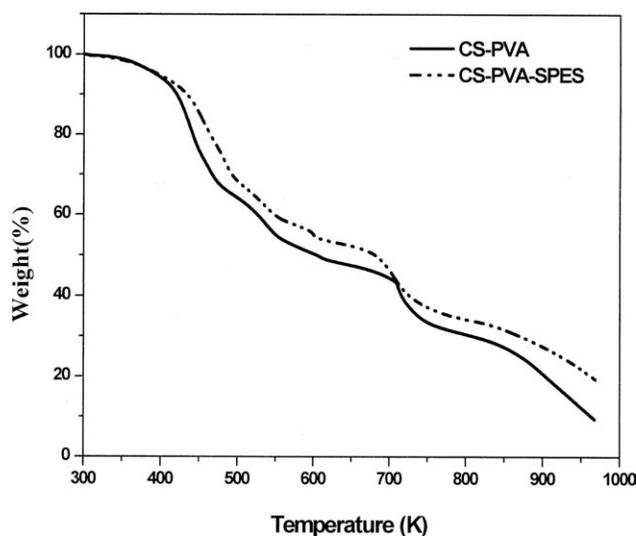
decreases when the % of SPES increases beyond 15 wt % in relation to the similar membranes studied in the literature.<sup>48</sup> This is attributed to the flexible chain mobility of the CS-PVA-SPES mixed matrices. In contrast, there is a restriction in chain mobility due to the higher addition of SPES which affects its tensile strength. However, for pristine SPES, in sorbed condition, elongation is less in relation to all the other membranes. It is also attributed to the force/stress applied in sorbed membranes. The force/stress applied to attain the maximum load for CS-PVA-SPES is more that in turn affects the elongation. The membranes are more rigid at higher wt % of SPES, i.e., up to 15 wt % of SPES in sorbed condition, and thereby elongation is higher at maximum load. However, beyond 15 wt % of SPES, elongation is lower at maximum load. In case of Nafion-117 membrane, both tensile strength and elongation are higher at maximum load.

#### Thermal properties for the membranes

The thermal stabilities for the CS-PVA blend and CS-PVA-SPES mixed-matrix membranes are studied by TGA and the data are presented in Figure 5. Three main degradation stages occur due to the processes of thermal dehydration, thermal degradation and



**Figure 4** Surface and cross sectional SEM micrographs for (a and c) CS-PVA blend and (b and d) CS-PVA-SPES (25 wt %) mixed-matrix membranes.

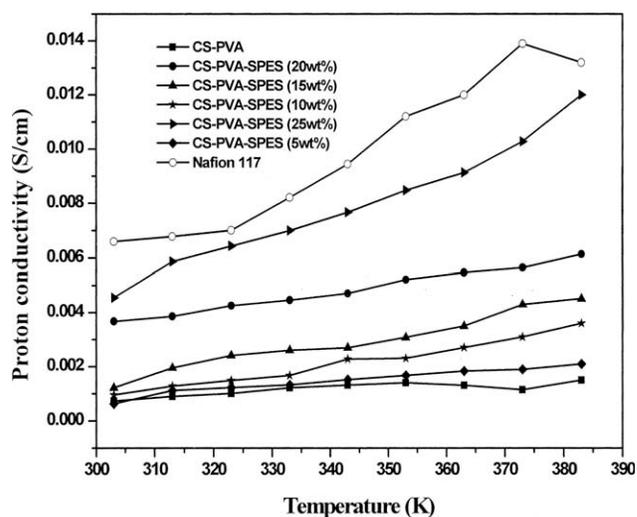


**Figure 5** TGA for CS-PVA blend and CS-PVA-SPES mixed-matrix membranes.

thermal decomposition of the polymeric backbone and mixed matrices as reported for similar kind of membranes.<sup>25,27,49,50</sup> The first weight loss between 343 and 393 K is due to the loss of absorbed water molecules from the CS-PVA matrix. The second weight loss between 393 and 673 K is due to the thermal degradation of CS-PVA matrix. In addition, the second transition occurring over the temperature range between 600 and 723 K is attributed to the loss of sulfonic acid ( $-\text{SO}_3\text{H}$ ) group, i.e., desulfonation in SPES.<sup>37</sup> The third weight loss observed between 673 and 973 K is due to the decomposition of main chains of CS and PVA. However, the weight loss observed beyond 900 K is for the decomposition of SPES main chain.<sup>37</sup> There is a decrease in weight loss for CS-PVA-SPES mixed-matrix membranes during three stages of degradation due to the introduction of SPES which in turn increases its intermolecular ionic interaction and thermal stability.

### Proton conductivity for the membranes

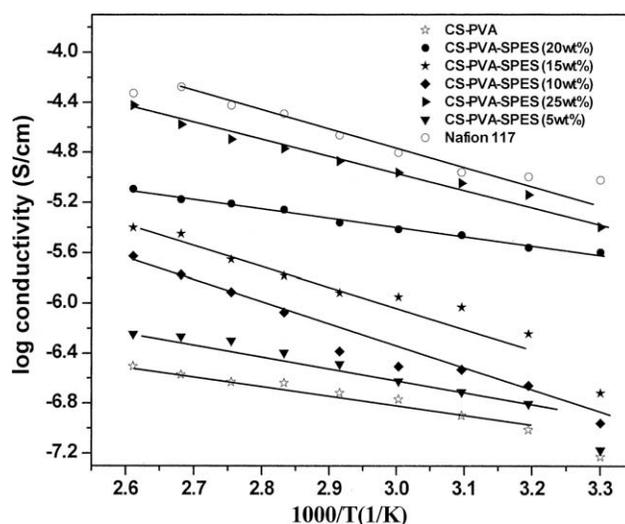
The proton conductivity for Nafion-117, CS-PVA blend and CS-PVA-SPES mixed-matrix membranes increases with increase in temperature as shown in Figure 6. It is observed that the proton conductivity increases with increase in SPES content from 5 to 25 wt %. Both the water/methanol sorption and IEC have profound effect on membrane conductivity. At room temperature, high water sorption helps protons to transport suggesting involvement of intermolecular proton transfer during the mobility of protons; a process termed as structural diffusion. In all the mixed-matrix membranes of CS-PVA-SPES, molecular diffusion dominates intermolecular proton transfer with increasing temperature.<sup>26,51,52</sup> How-



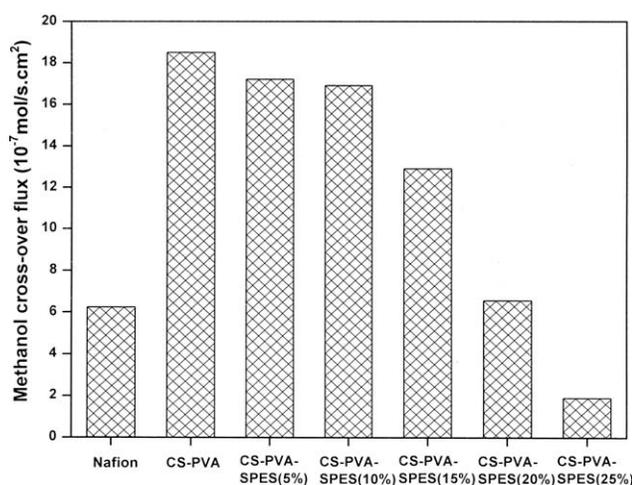
**Figure 6** Proton conductivity vs. temperature for Nafion-117, CS-PVA blend, and CS-PVA-SPES (5–25 wt %) mixed-matrix membranes.

ever, proton conductivity for Nafion-117 is higher in relation to mixed-matrix membranes due to the more conducting pathways compared to mixed-matrix membranes.

Figure 7 shows the Arrhenius plots for the proton conductivity as a function of temperature for CS-PVA blend and CS-PVA-SPES mixed-matrix membranes. It is noteworthy that activation energy is lower for CS-PVA-SPES mixed matrices than for CS-PVA blend membrane as shown in Table II, suggesting that lower energy is required for proton transport as seen clearly from the conductivity data for the CS-PVA-SPES mixed-matrix membrane. However, activation energy of Nafion-117 is lower than all the membranes. All membranes exhibit Arrhenius-type



**Figure 7** Log conductivity vs.  $1000/T$  plot for Nafion-117, CS-PVA blend and CS-PVA-SPES (5–25 wt %) mixed-matrix membranes.



**Figure 8** Methanol cross-over flux for Nafion-117, CS-PVA blend, CS-PVA-SPES (5–25 wt %) mixed-matrix membranes.

temperature dependence and the minimum energy required for proton transport is obtained from eq. (12).

$$\sigma = \sigma_0 e^{-(E_a/RT)} \quad (12)$$

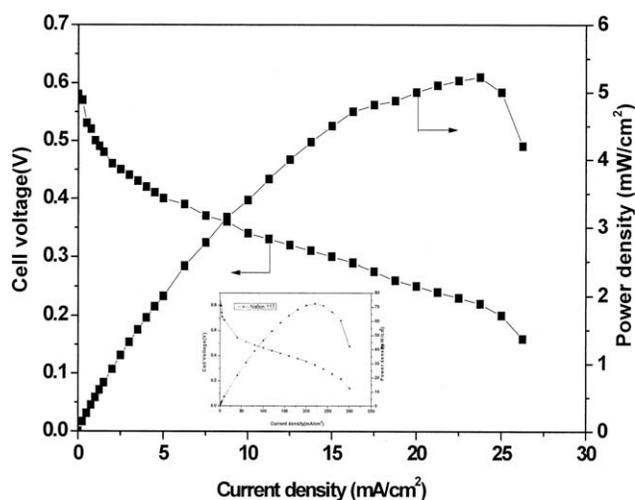
In eq. (12),  $\sigma$  is the proton conductivity ( $S\text{ cm}^{-1}$ ),  $\sigma_0$  is the preexponential factor,  $E_a$  is the activation energy in  $\text{kJ mol}^{-1}$ ,  $R$  is the gas constant ( $8.314\text{ J mol}^{-1}\text{ K}^{-1}$ ), and  $T$  is the absolute temperature (K).

### Methanol crossover and performance evaluation of membranes in DMFCs

Figure 8 shows methanol crossover-flux for the Nafion membrane, CS-PVA blend membrane and CS-PVA-SPES mixed-matrix membranes at open-circuit potential (OCP). It is noteworthy that the methanol crossover flux gradually decreases with increasing SPES content in CS-PVA-SPES mixed-matrix membranes. Under OCP conditions, the electro-osmotic drag for methanol is higher than that for water providing an accurate comparison for all the membranes studied. From Figure 8, it can be clearly seen that methanol cross-over flux for Nafion-117 is lower in relation to CS-PVA blend membrane as electro-osmotic drag for methanol is higher for CS-PVA blend membrane at OCP conditions. The hydrophilicity for CS depends on hydroxyl groups ( $-\text{OH}$ ) and amino groups ( $-\text{NH}_2$ ), while that for PVA depends on only hydroxyl groups ( $-\text{OH}$ ). Accordingly, for CS-PVA blend membrane, hydroxyl group can form stronger hydrogen bonds with water as well as methanol molecules<sup>20</sup> thereby increasing the methanol cross-over for CS-PVA blend membrane. However, when

SPES is incorporated into CS-PVA matrix, methanol cross-over gradually decreases due to the higher electro-osmotic drag of water in presence of  $-\text{SO}_3\text{H}$  groups, and at 25 wt % of SPES, it is found to be lower than that for Nafion-117. Proper balance of proton conductivity and methanol crossover is essential for better electrochemical selectivity of the membranes.<sup>53</sup> However, in CS-PVA blend membrane and CS-PVA-SPES mixed-matrix membranes, proton conductivity as well as methanol crossover rate is decreased, which affects its electrochemical selectivity, as shown in Table II. Methanol permeability in Nafion-117 membrane is observed due to the strong fluorinated structural hydrophobic backbone that attracts the methanol molecules along with water without affecting its proton conductivity and increasing its electrochemical selectivity.<sup>54</sup> However, dual hydrophilic interactions of CS-PVA blend and SPES decreases the methanol permeability at increased content of SPES. However due to the lower proton conductivity of the mixed matrix membranes than Nafion, the electrochemical selectivity is lower.

Polarization curve for the fuel cell with Nafion MEA at  $60^\circ\text{C}$  using air as oxidant is compared with CS-PVA-SPES mixed-matrix membranes. Peak power density of  $70\text{ mW cm}^{-2}$  at load current density of  $225\text{ mA cm}^{-2}$  is observed for Nafion-117 membrane. By contrast, CS-PVA-SPES (25 wt %) mixed-matrix membrane electrode assemblies used for DMFC operation with methanol as a fuel and air as an oxidant exhibit area-specific resistance ( $I$ ) of  $2\ \Omega\text{ cm}^{-2}$  in the ohmic region of Figure 9. The cell polarization for the MEA using the CS-PVA-SPES mixed-matrix membrane is  $0.23\text{ V}$  at load current-density of  $25\text{ mA cm}^{-2}$  at  $60^\circ\text{C}$  with power density output of  $5.5\text{ mW cm}^{-2}$  as shown in Figure 9. This reflects that these membranes can be used in



**Figure 9** Cell polarization data for DMFC with Nafion 117 and CS-PVA-SPES (25 wt %) mixed-matrix membranes.

DMFCs. However, a proper balance between proton conductivity and methanol permeability needs to be optimized to achieve higher DMFC performance. As the blend membranes of CS-PVA exhibit substantially low open-circuit voltage, the polarization data for CS-PVA blend could not be obtained. The present study is based on controlling the degree of sulfonation of SPES in relation to time and its effect on DMFC performance. Studies are in progress to optimize the DMFC performance and further improvements are highly likely.

## CONCLUSIONS

Sulfonated-polyether sulfone (SPES) is prepared using chlorosulfonic acid as sulfonating agent with 30% degree of sulfonation. CS-PVA-SPES mixed-matrix membrane is found to be a methanol-barrier electrolyte in DMFCs. Simple and cost-effective preparative method for CS-PVA-SPES mixed-matrix membrane is attractive for its use in DMFCs. However, the durability and the performance of these membranes need to be improved.

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