

Chitosan–poly(vinyl pyrrolidone) blends as membranes for direct methanol fuel cell applications

B. Smitha, S. Sridhar, A.A. Khan*

Membrane Separations Group, Chemical Engineering Division, Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500007, India

Received 19 September 2005; received in revised form 7 December 2005; accepted 7 December 2005

Available online 24 January 2006

Abstract

Blend membranes made of chitosan (CS) and poly(vinyl pyrrolidone) (PVP), were synthesized and characterized for their ion exchange capacity (IEC) and Swelling Index to investigate their applicability in direct methanol fuel cells (DMFC). These membranes were assessed for their intermolecular interactions and thermal stability using FT-IR, X-ray diffraction methods, and TGA. Their methanol permeability and proton conductivity were also estimated and compared to that of Nafion 117. In addition to being effective methanol barriers, the membranes have a high ion exchange capacity (IEC) and possess adequate thermal stability. Crosslinking the polymer blend using glutaraldehyde and sulfuric acid has been particularly effective in producing a reduction of methanol permeability from $9.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for CS/PVP blend to $7.3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for crosslinked CS/PVP blend (GS-CS/PVP) and enhancing the conductivity from 0.019 S cm^{-1} for CS/PVP blend to 0.024 S cm^{-1} for GS-CS/PVP, thereby rendering it more suitable for a DMFC. Low methanol permeability, excellent physico-mechanical properties and above all, the cost effectiveness could make their use in DMFC quite attractive.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Fuel cells; CS blend membranes; DMFC; Ion exchange capacity; Methanol permeability

1. Introduction

Fuel cells have emerged strongly as a viable option for electrical power owing to their high energy efficiency and environmental cleanliness [1,2]. Amongst the various types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) has been well established for over five decades and is successfully used as a source of electrical power in spacecraft and submarines [3]. The direct methanol fuel cell (DMFC), a variant of a PEMFC, also uses a polymer membrane as the electrolyte wherein the fuel, methanol, is oxidized catalytically at the anode, producing protons [4]. These protons migrate through the membrane and react catalytically with oxygen to produce water at the cathode.

The major functions of the membrane in DMFCs can be classified as (1) a proton conductor, (2) a fuel barrier, and (3) a mechanical separator between the anode and cathode [5–8]. PEMs (e.g. Nafion, DuPont) utilized in current DMFCs typically have a phase-separated structure comprising of a hydropho-

bic matrix and interconnected hydrophilic ionic clusters, called ionic channels [9,10]. It has been known that proton conduction occurs through the ionic channels formed by micro- or nanophase separation between the hydrophilic proton exchange sites and the hydrophobic domains [11,12]. As is well known, however, the membranes do not seem to be applicable to DMFCs because an abundant amount of methanol (MeOH) is easily transported across the membrane to the cathode, which is known as methanol crossover [13,14]. It is known that methanol permeates the membranes primarily through ionic channels, and thus the cross-sectional size of these channels determines methanol permeability. This size is largely dependent upon the swellability of the membrane. Thus, swelling facilitates the permeation of both methanol and water as well as that of protons to some extent [15,16]. The swelling induced disentanglement behavior in a polymer matrix is responsible for the enlargement of the ionic channels and consequently for the observed methanol crossover phenomena. Therefore, it is also necessary to reduce the swellability by fixing the microdomain structure of the membrane [9]. Reduction in the swellability of a PEM can be achieved by adequate crosslinking of the polymer matrix.

* Corresponding author. Tel.: +91 40 27193139; fax: +91 40 27193626.
E-mail address: aakhan_iict@rediffmail.com (A.A. Khan).

Table 1
Literature survey on using chitosan composites for fuel cell applications

Sl no.	Membrane	Proton conductivity	Methanol permeability	Reference
1.	Crosslinked chitosan	0.05 S cm ⁻¹ at 30 °C	8 × 10 ⁻⁷ cm ² s ⁻¹	[21,22]
2.	Composite of chitosan–methanediphosphonic acid	5 × 10 ⁻³ at 150 °C	–	[23]
3.	Crosslinked chitosan–sodium alginate blend	0.042 S cm ⁻¹ at 30 °C	4.6 × 10 ⁻⁸ cm ² s ⁻¹	[24]
4.	Phosphorylated chitosan	1.2 × 10 ⁻³ at 30 °C	–	[25]
5.	Di- <i>o</i> -butyrylchitosan	1.2 × 10 ⁻³ at 30 °C	–	[26]
6.	Crosslinked blend of PVA and chitosan	0.009 S cm ⁻¹ at 30 °C	9.45 × 10 ⁻⁸ cm ² s ⁻¹	[27]
7.	Ionically crosslinked blend of PAAc and chitosan	0.038 S cm ⁻¹ at 30 °C	3.9 × 10 ⁻⁸ cm ² s ⁻¹	[28]

Reduction of methanol crossover in PEMs can be achieved by (1) appropriate selection of membrane materials, (2) morphology (microstructure) control, and (3) adequate crosslinking [9,10]. The selection of a polymer matrix for the PEM of DMFCs is very important because the proton conductivity and methanol permeability are largely dependent upon the properties of polymers.

Hydrophilic membranes such as chitosan (CS) are widely used in membrane based applications due to its high hydrophilicity, good chemical and thermal resistance properties. Since it has both hydroxyl and amino groups, it can be modified chemically into many forms and can participate in chemical reactions resulting in salt formation. These hydrophilic groups are considered to play an important role in preferential water sorption and diffusion through the chitosan membrane [17,18]. CS is generally blended with other hydrophilic polymers to overcome the disadvantage of the loss in mechanical strength in the wet state. Poly(vinyl pyrrolidone) (PVP), on the other hand, is a tough hydrophilic polymer and gets fairly well dispersed in a CS matrix when doped into it [19]. PVP, upon blending with chitosan followed by crosslinking with glutaraldehyde, forms a semi-interpenetrating network [20]. Table 1 lists the literature reports on chitosan composites as fuel cell membrane candidates [21–28].

The present study reports the formation of a blend of PVP/chitosan (CS), which is crosslinked by glutaraldehyde followed by further crosslinking with sulfuric acid to improve the membrane resistance to excessive swelling during interaction with water without causing loss of hydrophilic groups which aids in the transport of protons. These membranes were characterized for their physico-thermal properties using FT-IR and TGA. Their methanol permeability as well as proton conductivity is also estimated.

2. Experimental

2.1. Materials

Chitosan having an average molecular weight of 500,000 and degree of deacetylation of 84% was purchased from Aldrich Chemical Company Ltd. PVP of molecular weight 125,000 was purchased locally. Sulfuric acid, hydrochloric acid, glutaraldehyde was purchased from s. d. Fine Chemicals, Mumbai. Isopropanol, Methanol and Glacial acetic acid was purchased from Loba Chemie, Mumbai.

2.2. Membrane preparation

The 2 wt.% solution of CS in 2% (v/v) aqueous acetic acid was prepared, stirred and filtered to remove the undissolved matter. A 2 wt.% PVP solution was prepared by continuous stirring of PVP in water. A blend of PVP/chitosan (1:4) was prepared by physically mixing both the solutions. The solutions were then cast onto a clean glass plate and dried at 30 °C in a convection oven for over 24 h. The membranes were then crosslinked in a glutaraldehyde bath (the solution used for crosslinking the dry polymer films at room temperature was an isopropanol–water (90/10 vol.%) mixture containing 5 vol.% of glutaraldehyde and 1 vol.% of hydrochloric acid as a catalyst) for a period of 40 min. The membranes were then dried thoroughly and sulfonated with 1N sulfuric acid in methanol/water bath (90:10) for a period of 60 min. The prepared membranes were stored in a 50 wt.% methanol/water bath.

2.3. Membrane characterization

2.3.1. FT-IR studies

The FT-IR spectra of chitosan, PVP, in their unmodified and crosslinked blends were scanned using a Nicolet-740, Perkin-Elmer-283B FT-IR Spectrometer. These spectra are shown in Fig. 1.

2.3.2. XRD studies

A Siemens D 5000 powder X-ray diffractometer was used to study the solid state morphology of the blend membranes in powdered form. X-rays of 1.5406 Å wavelength were generated by a CuK source. The angle of diffraction was varied from 2° to 65° to identify the change in the crystal structure and the intermolecular distances between the intersegmental chains upon blending PVP/CS and the results are shown in Fig. 2.

2.4. Thermal gravimetric analysis (TGA)

The thermal stability of the polymer blends was examined to determine the thermal stability and their decomposition characteristics using a Seiko 220TG/DTA analyzer from 40 to 300 °C at a heating rate of 10 °C min⁻¹ with continuous flushing using pure nitrogen gas at 200 ml min⁻¹. The TGA spectra of the PVP/CS blend both before and after crosslinking are displayed in Fig. 3.

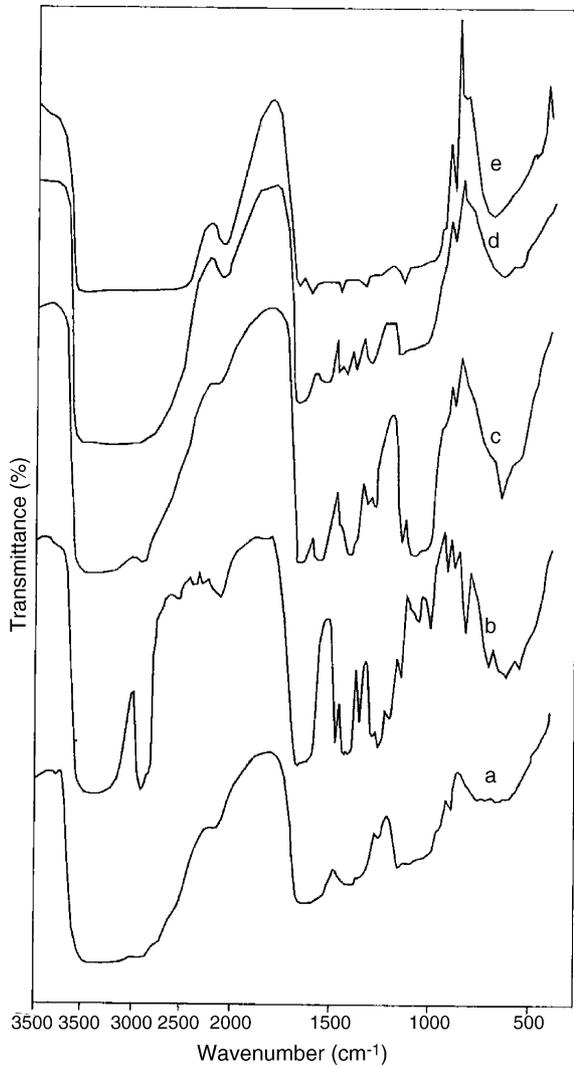


Fig. 1. FT-IR spectra of (a) CS, (b) PVP, (c) PVP/CS, (d) G-PVP/CS and (e) GS-PVP/CS.

2.5. Water and methanol uptake

In order to determine for polymer–liquid interaction, circular pieces of (3 cm dia.) membrane samples were subsequently weighed and soaked in deionized water as well as methanol. The swollen samples were taken out after different soaking periods and weighed immediately after carefully blotting away of the excess feed mixture to estimate the amount absorbed at a particular time “*t*”. Films were then quickly placed back in the solvent. The percentage sorption and the degree of swelling was calculated using the following equations:

$$\text{Uptake (\%)} = \frac{M_s - M_d}{M_d} \times 100 \quad (1)$$

where M_s is the mass of the swollen polymer (in g) and M_d is the mass of the dry polymer (in g).

2.6. Permeability

The methanol permeability of the films was determined and calculated by the method described by Pivovar et al. [29]. Prior

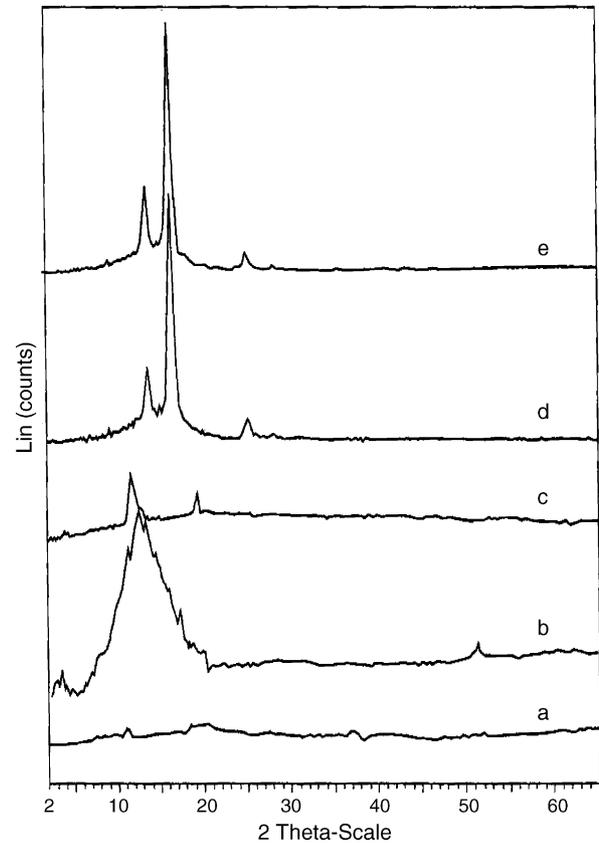


Fig. 2. XRD spectra of (a) CS, (b) PVP, (c) PVP/CS, (d) G-PVP/CS and (e) GS-PVP/CS.

to testing, membranes were hydrated in deionized water for at least 24 h. The concentration of methanol in the samples was determined by using gas chromatography (GC). The samples were analyzed using a Shimadzu GC-15A gas chromatograph fitted with a DEGS packed column. A view of the cell used for methanol permeability is shown in Fig. 4.

2.7. Proton conductivity

The proton conductivity in water-equilibrated membranes was determined by a four-electrode electrochemical impedance spectroscopy (EIS) method [30] using a PGSTAT20 frequency analyzer from EcoChemie B.V. Spectra and were recorded between 1 MHz and 0.1 Hz with 10 points per decade at a maximum perturbation amplitude of 10 mV. The impedance spectra were fitted on the basis of the equivalent circuit shown by Haufe and Flemming [31]. The Zview 2.1b software by Scribner Associates Inc. was used for the curve fitting procedure. In order to measure the temperature dependence of the conductivity, the cell was placed in a sealed, tempered, double-walled vessel and the temperature recorded in close proximity to the membrane with a K-type thermocouple. To avoid changes in the humidification levels during the measurements, a Teflon[®] bowl filled with water was placed at the bottom of the vessel. Measurements were carried out in a conductivity cell at temperatures ranging from 30 to 150 °C. Fig. 5 gives the schematic view of the conductivity cell.

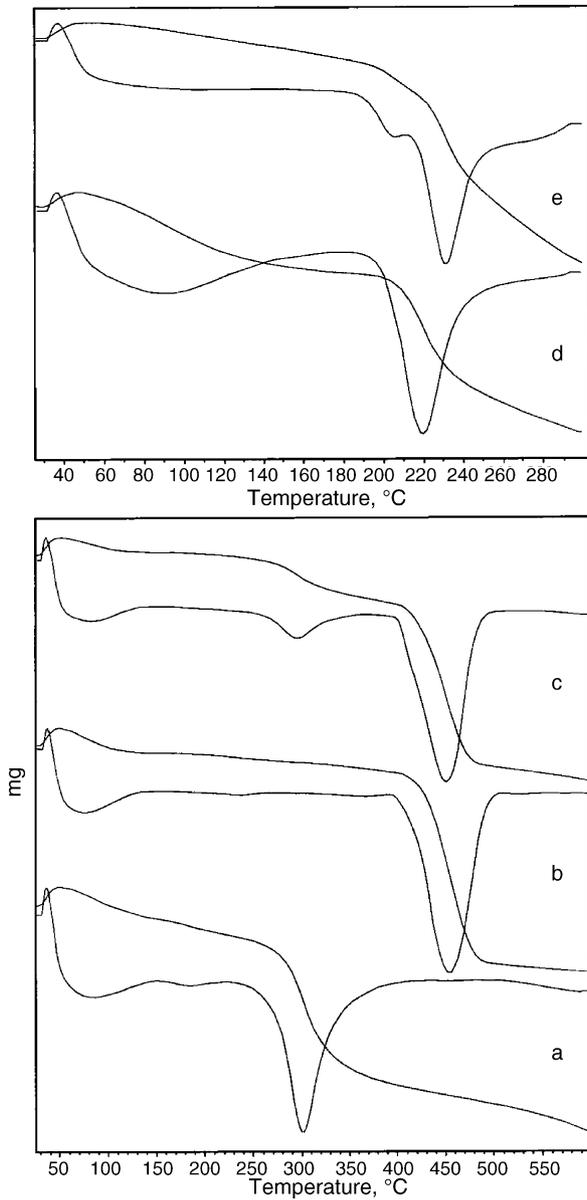


Fig. 3. TGA curves of (a) CS, (b) PVP, (c) CS/PVP, (d) G-CS/PVP, and (e) GS-CS/PVP.

2.8. Pervaporation experiments for diffusion co-efficient measurement

Experiments were carried out with an indigenously constructed pervaporation manifold operated under a vacuum as low as 0.9 mmHg in the permeate line. The membrane area in the pervaporation cell assembly was approximately 20 cm². The experimental procedure is described in detail elsewhere [32]. The test membrane was soaked in the feed mixture before starting the experiment for a period of 12 h. Permeate was collected after a period of 8–10 h. Experiments were carried out at room temperature (35 ± 2 °C) and repeated twice using fresh feed solution to check for reproducibility. The collected permeate was weighed after attaining room temperature in a Sartorius electronic balance (accuracy: 10⁻⁴ g) to determine the flux. Feed and permeate samples were analyzed using a Nucon Gas Chromatograph (GC Model 5765) installed with a thermal conductivity detector (TCD) and a Tenax packed column of 2 m length.

2.9. Flux

The flux *J* of a given species, say faster permeating component *i* of a binary liquid mixture comprising of *i* (water) and *j* (methanol) is given by

$$J_i = \frac{W_i}{At} \tag{3}$$

where *W_i* represents the mass of water in permeate (kg), *A* the membrane area (m²) and *t* represents the evaluation time (h).

2.10. Diffusion coefficient (*D_i*)

The diffusion co-efficient is computed at 30 °C using the below stated equation:

$$J_i = \frac{D_i C_i}{\delta} \tag{6}$$

where *C_i* is the concentration of water or methanol in the feed after the process, *J_i* the flux of the given species, and *δ* is the membrane thickness.

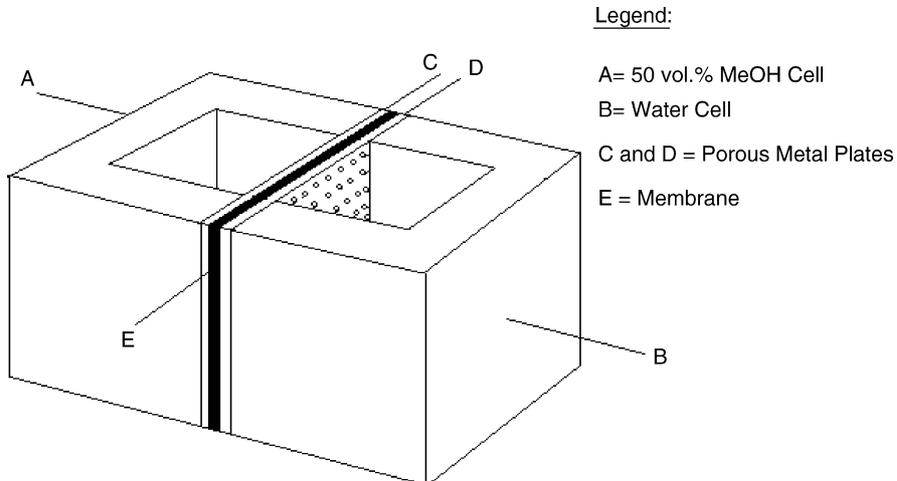
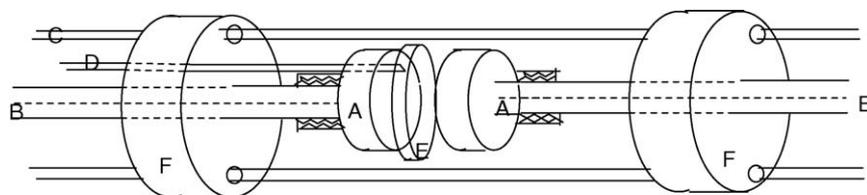


Fig. 4. Schematic of methanol permeability cell.



where

- A – Gold plated electrodes
- B – Platinum wire
- C – Adjustable Hylam screws
- D – Thermocouple
- E – Membrane
- F – PTFE disks

Fig. 5. Schematic of proton conductivity cell.

3. Results and discussion

Blend membranes of CS/PVP were chosen as potential candidates for fuel cell applications on the basis of the close proximity of Hansen's solubility parameter value of chitosan ($43.04 \text{ J}^{1/2} \text{ cm}^{-3/2}$) [33] and PVP ($46.45 \text{ J}^{1/2} \text{ cm}^{-3/2}$) to that of water ($47.9 \text{ J}^{1/2} \text{ cm}^{-3/2}$) [34] such that the resulting blend has sufficient polar groups to aid proton transport.

4. Membrane characterization

4.1. Interaction with crosslinking agents

Glutaraldehyde and sulfuric acid were used as crosslinking agents to crosslink the CS/PVP blend membranes. It was observed that the blend membrane on crosslinking with glutaraldehyde (G-PVP/CS) exhibited considerable swelling but remained insoluble in water. This non-solubility of the blend can be due to the formation of imine linkage between the amino group of chitosan and the aldehyde groups of GA as well as the existence of weak force of attraction between amine groups of CS and carbonyl group of PVP. Further crosslinking with sulfuric acid (GS-PVP/CS) should enable the interaction between the sulfate ions of sulfuric acid and residual amine groups of CS. An estimation of the number of groups present before and after crosslinking gives an idea of the extent of crosslinking.

The ion exchange capacity (IEC) of the unmodified and crosslinked blend was determined to estimate the amount of residual amine and hydroxyl groups present after crosslinking. It was noted that the unmodified blend showed an IEC of $1.42 \text{ mequiv. g}^{-1}$ whereas the crosslinked polymer exhibited an IEC of $0.54 \text{ mequiv. g}^{-1}$. The IEC, which is equivalent to the total number of free amino groups (considering the fact that amino groups are more interactive when compared to hydroxyl groups), R-NH_2 present in the membrane decreased upon crosslinking because some amino groups were consumed with the reaction of the crosslinker during the prepara-

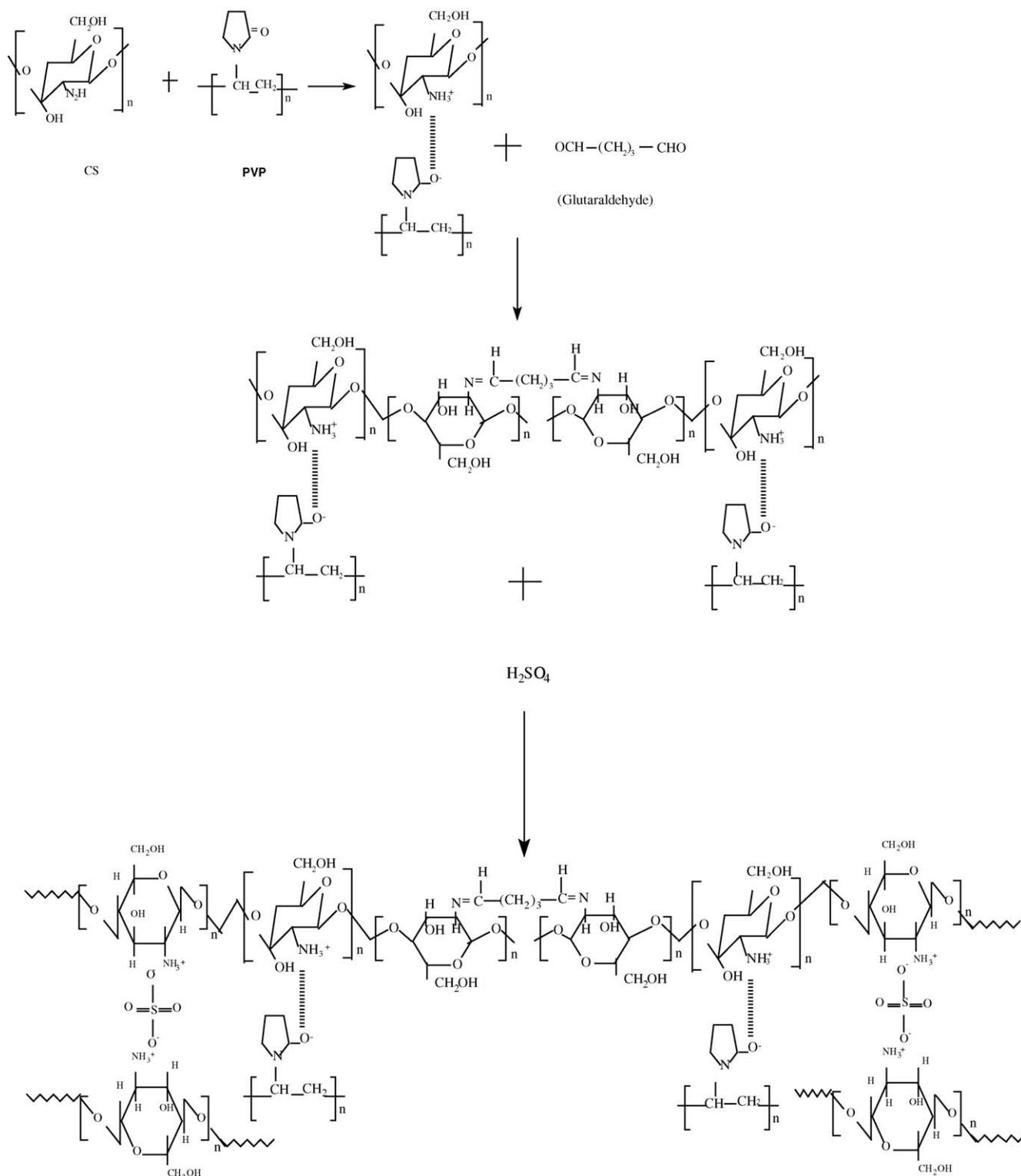
tion of the crosslinked membrane [35]. This shows that almost 61% of the amine groups present in the unmodified chitosan formed crosslinks with glutaraldehyde and sulfuric acid and there were still a few amine and hydroxyl groups left to aid the proton transfer. Scheme 1 shows the possible interaction between CS and PVP and with the crosslinking agents. The occurrence of crosslinking is proved by the IEC and FT-IR studies.

4.2. FT-IR analysis

FT-IR is a very powerful technique to detect the intermolecular interactions between two polymers. Fig. 1 shows the FT-IR spectra of plain PVP, chitosan and their PVP/CS (1:4) blend membranes both crosslinked as well as uncrosslinked Fig. 1(a)–(e). The spectrum of CS film shows peaks in the range $700\text{--}850 \text{ cm}^{-1}$, indicating the presence of benzene ring. The spectra of pure CS (Fig. 1(a)), shows a broad peak at wave numbers $1570\text{--}1655 \text{ cm}^{-1}$, which indicates the presence of amide I and II. The peaks at 1639 and 3342 cm^{-1} can be attributed to the amide carbonyl band and free hydroxyl groups, respectively.

PVP shows the amide carbonyl band at 1688 cm^{-1} (Fig. 1(b)) higher than that observed for pure CS. The blend of CS/PVP (Fig. 1(c)) also shows absorbance in the amide carbonyl band of PVP at 1688 cm^{-1} . As a result, each of the chitosan/PVP blends shows a single carbonyl band at 1660 cm^{-1} indicating the interaction between CS and PVP. The intermolecular interaction through hydrogen bonding can be characterized by FT-IR, because the specific interaction affects the local electron density and the corresponding frequency shift can be observed. The shifting of the characteristic peaks of chitosan to higher frequencies suggests an interaction between chitosan and PVP through hydrogen bonds. Chitosan, which is a hydrogen donor forms a hydrogen bond with the carbonyl group of PVP. The pyrrolidone rings in PVP contain a proton accepting carbonyl moiety, while chitosan presents hydroxyl and amine groups as side chains. Therefore, a hydrogen bond interaction may take place during

Weak interaction between CS and PVP



Scheme 1. A model depicting the formation of semi-IPN and interaction of the blend with crosslinking agents.

the interaction between chitosan and PVP. The formation of hydrogen bonds between two macromolecules competes with the formation of hydrogen bonds between molecules of the same polymer.

The PVP/CS blend crosslinked with glutaraldehyde (G-PVP/CS) (Fig. 1(d)) shows the disappearance of a peak at 1570–1655 cm⁻¹ [characteristic of -NH₂ bending in chitosan] and appearance of a new peak at 1675 cm⁻¹ resulting due to

the formation of imine linkage ($-C=N-$). Further crosslinking with sulfuric acid (GS-PVP/CS) (Fig. 1(e)), showed the formation of a new peak at 1550 cm^{-1} in the spectra of the crosslinked blend membrane. This may be assigned to the symmetric $-NH_3^+$ deformation resulting from the crosslinking reaction occurring between the amino groups of chitosan and sulfate ions of sulfuric acid which have a Coulombic interaction.

4.3. XRD analysis

From the spectra of unmodified and crosslinked CS–PVP blend (Fig. 2), it can be noted that the XRD patterns of the plain and crosslinked blend suggest semi-crystallinity with sharp peaks at around 10° and 20° of 2θ , indicating the average intermolecular distance of the amorphous part. It can also be seen that there are two distinct bands having their maxima at $2\theta = 9-11^\circ$ and 2θ at 20° , the former corresponding to the reactive functional groups present in the polymer. A reduction in effective d-spacing value from 9.45 \AA for uncrosslinked to 9.41 \AA for the glutaraldehyde crosslinked polymer (G-PVP/CS) to 9.38 \AA (GS-PVP/CS) gives an indication of shrinkage in cell size or inter-segmental spacing resulting from crosslinking. This reduction suggests an improvement in selectivity of the crosslinked blend.

4.4. Thermogravimetric analysis (TGA)

The TGA curves of CS (Fig. 3(a)) and PVP (Fig. 3(b)) show a single weight loss stage ranging from 270 to 350 and 400 to 490°C followed by a final decomposition at 550°C . The blend (Fig. 3(c)) on the other hand shows two weight loss stages at $270-340$ and $410-480^\circ\text{C}$ corresponding to the decomposition of CS and PVP, respectively. The final decomposition of the blend appeared at 550°C .

The TGA curve of G-PVP/CS (Fig. 3(d)) blend showed a single weight loss stage at $205-240^\circ\text{C}$ followed by final decomposition of the crosslinked blend. On the other hand, the GS-PVP/CS (Fig. 3e) blend showed two weight loss stages at $200-220$ and $230-250^\circ\text{C}$. The first weight loss stage may have corresponded to the degradation of the side chain followed by the main chain degradation of the polymer.

Hence from the thermal stability studies it can be said that the crosslinked blends can be safely used for pervaporation applications at temperatures up to 150°C .

Table 3
Diffusion coefficient of methanol and water for different feed compositions

Sl. no	Concentration of water in feed mixture (wt.%)	Diffusion coefficient ($\text{m}^2\text{ s}^{-1}$)	
		Water, D_w ($\times 10^{-6}$)	Methanol, D_M ($\times 10^{-6}$)
1	2.28	2.28	0.0045
2	4.92	1.54	0.0067
3	9.96	0.98	0.0084
4	28.52	0.62	0.0116
5	40.38	0.45	0.0132
6	50.78	0.22	0.0171
7	99.98	0.44	0.101

4.5. Water and methanol uptake

Table 2 shows the equilibrium percentage sorption of water/methanol obtained by soaking the membrane in their respective solutions at room temperature. The crosslinked CS/PVP membrane (GS-CS/PVP) exhibited the least water uptake of 52.1% , followed by a negligible sorption in methanol of 0.11% . Despite crosslinking, it can be noted that the blend has interacted extensively with the water molecules showing a higher selective tendency to water than to methanol. Water molecules having relatively small molecular size can diffuse through the denser membrane more easily than the methanol, having large molecules.

4.6. Diffusion coefficient measurements

A diffusion coefficient study is a prelude to measurement of the permeability and indicates the phenomenon of transport of water/methanol molecules through the cross-section of the membrane. From Table 3, it can be seen that the diffusion co-efficient values decreased from 2.28×10^{-6} to $0.22 \times 10^{-6}\text{ m}^2\text{ s}^{-1}$ for feed containing $2-50\text{ wt.}\%$ water and showed a further increment to $0.44 \times 10^{-6}\text{ m}^2\text{ s}$ for feed containing $100\text{ wt.}\%$ water, whereas the diffusion co-efficient values for that of methanol were remarkably low and ranged from 0.0045×10^{-6} to $0.101 \times 10^{-6}\text{ m}^2\text{ s}^{-1}$ for feed containing $2-50\text{ wt.}\%$ water, indicating a higher interaction between the membrane and water.

It is interesting to note that the diffusion coefficients of water decreased for all the membranes with increasing the amount of water in the feed. This suggests that up to $50\text{ wt.}\%$ of water, the water transport through the membrane depends more on

Table 2
% Water and methanol uptake, methanol permeability and proton conductivity of the membranes used in this study

Membrane	%Water uptake	%Methanol uptake	Methanol permeability ^a ($\text{cm}^2\text{ s}^{-1}$)	Proton conductivity ^b (S cm^{-1})
CS/PVP	^c	1.8	9.2×10^{-8}	0.019
GS-CS/PVP	52.1	0.11	7.3×10^{-8}	0.024
Nafion 117	33.3	9.32	21.6×10^{-8}	0.086

^a Measurements carried out at 30°C , using $50\text{ wt.}\%$ methanol.

^b Conductivity measured at room temperature using 4-probe conductivity cell.

^c Highly swollen in water, not measurable.

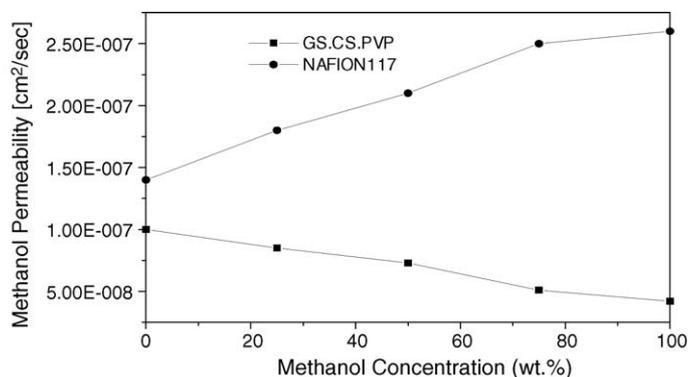


Fig. 6. Methanol permeability vs. concentration.

sorption than diffusion, beyond which sorption plays the role of transportation of the water molecules. Such an effect is not observed in the case of methanol, where its diffusion coefficients increased continuously for all the membranes with increasing water concentration in the feed.

4.7. Permeability

The values of methanol permeability for the test membranes are shown in Table 2. The notable feature is the permeability of Nafion 117 ($21.6 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) at 50 wt.% methanol concentration, which is three times higher than that observed in this work. This shows that a significant reduction in methanol crossover could be achieved by using the present membranes, which are much less permeable to methanol. It is known that the methanol permeability in Nafion increases with increasing methanol concentration [29], but for the blends used in this study, the trend is entirely reversed. From Fig. 6, it can be noted that the methanol permeability in Nafion increases with the increasing concentration of methanol. Thus, at higher methanol concentrations, Nafion acts as a poor barrier, whereas the blend membranes exhibit quite good barrier properties. Also, the lack of significant chemical interaction between methanol and the ionic clusters, introduced into the blend membrane after crosslinking with sulfuric acid, could result in a drop in its permeability.

4.8. Proton conductivity measurements

Measurement of conductivity is important to assess the contribution of various ionic groups in the blends. According to literature, on suitable modification, polymers containing hydroxyl and amine groups exhibit good conductivities [36]. A membrane yielding a proton conductivity value greater than $1 \times 10^{-5} \text{ S cm}^{-1}$ is considered applicable for fuel cell operation. The conductivity of the unmodified and the crosslinked blend (GS-CS/PVP) membranes as a function of temperature in the range of 30–120 °C is shown in Fig. 7. From the graph, it can be noted that the crosslinked blend of CS and PVP showed better conductivity (0.024) performance than the unmodified CS/PVP blend (0.019). The proton conductivity of the membranes used in the study is much lower when compared to Nafion 117 (0.086 S cm^{-1}). Furthermore, the crosslinked blend exhib-

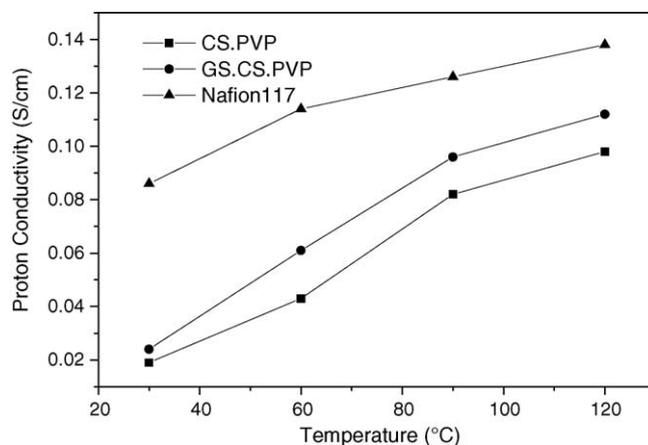


Fig. 7. Proton conductivity vs. temperature at 100% R.H.

ited a conductivity equal to that of Nafion (room temperature conductivity) at the fuel cell operating temperature of 80 °C. However, the blend membranes in a way compensate for the lower proton conductivity by exhibiting better barrier properties to methanol in comparison with Nafion, thereby limiting fuel losses. Moreover, these membranes allow a sizable reduction in fabrication cost. There also exists a possibility of attaining conductivities close to Nafion, by doping these membranes with acids [37].

The Arrhenius plot in Fig. 8 is an indication of the mechanism of proton transport. From the plot it can be said that the proton transport might have occurred by two mechanisms. The first of these, a Grotthuss or “jump” mechanism, which can be idealized as the proton being passed down a chain of water molecules. The second transport mechanism, called a vehicle mechanism, assumes a proton combines with the solvent molecules, yielding a complex like H_3O^+ or CH_3OH_2^+ . This complex then diffuses intact. In Nafion both the mechanisms are believed to exist [38]. In the present work, the vehicle mechanism is the most likely one because CH_3OH_2^+ or some similar methanol containing complex is responsible for transportation of protons. When glutaraldehyde and sulfuric acid are used for partial crosslinking of CS/PVP blend, a fraction of the amine and hydroxyl groups

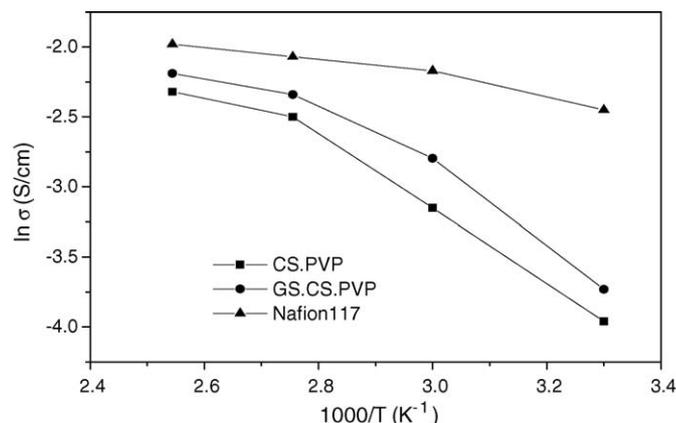


Fig. 8. Arrhenius plot of conductivity and temperature.

get chemically bonded, although the majority of them are still available for proton exchange.

5. Conclusions

This study reveals the possibility of preparing low cost CS-based membranes having high IEC values but relatively lower methanol permeabilities compared with Nafion. The results imply that an improvement in fuel utilization efficiency could be realized using proton exchange membranes that control the magnitude of fuel by-pass. Crosslinking of the CS/PVP blend with glutaraldehyde and sulfuric acid appears promising in terms of attaining a better methanol barrier property.

Characterization revealed adequate thermal stability of the membranes, which is essential for fuel cell applications. FT-IR spectroscopy clearly indicated an interaction between CS–PVP and the crosslinking agents. Although these membranes do not offer significant advantages over Nafion, as far as proton conductivity is concerned, a significant reduction in methanol permeability makes these polymers appear to be suitable for DMFCs.

Acknowledgments

The authors would like to thank Council of Scientific and Industrial Research, India for funding the Fuel Cell Project (ES/P 81-1-03, EMR Head). The contribution of Ms. Srigowri and Ms. Anjali Devi of Membrane Lab is acknowledged. Help rendered by Mr. Sai Babu, of Design section, Mr. Murari Lal, Instrumentation for FT-IR analysis is gratefully acknowledged.

References

- [1] H. Voss, J. Huff, J. Power Sources 5 (1997) 155.
- [2] A. Heinzl, R. Nolte, K. Ledjeff-Hey, M. Zedda, Electrochim. Acta 43 (1998) 3817.
- [3] H.R.A. Magnet, in: C. Berger (Ed.), Handbook of Fuel Cell Technology, Prentice-Hall, Englewood Cliffs, New Jersey, USA, 1967.
- [4] J. Kjaer, S. Yde-Anderson, N.A. Knudsen, E. Skou, Solid State Ionics 46 (1991) 169.
- [5] J. Won, H.H. Park, Y.J. Kim, S.W. Choi, H.Y. Ha, I.-H. Oh, H.S. Kim, Y.S. Kang, K.J. Ihn, Macromolecules 36 (2003) 3228–3234.
- [6] J. Won, S.W. Choi, Y.S. Kang, H.Y. Ha, I.-H. Oh, H.S. Kim, K.T. Kim, W.H. Jo, J. Membr. Sci. 214 (2003) 245–257.
- [7] J. Ding, C. Chuy, S. Holdcroft, Macromolecules 35 (2002) 1348–1355.
- [8] J.M. Serpico, S.G. Ehrenberg, J.J. Fontanella, X. Jiao, D. Perahia, K.A. McGrady, E.H. Sanders, G.E. Kellogg, G.E. Wnek, Macromolecules 35 (2002) 5916–5921.
- [9] M.K. Ravikumar, A.K. Shukla, J. Electrochem. Soc. 143 (1996) 2601–2606.
- [10] A. Kruver, W. Vielstich, J. Power Sources 74 (1998) 211–218.
- [11] K.D. Kreuer, W. Weppner, A. Rabenau, Angew. Chem. Int. Ed. Engl. 21 (1982) 208–209.
- [12] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29–39.
- [13] C. Pu, W. Huang, K.L. Ley, E.S. Smotkin, J. Electrochem. Soc. 142 (1995) 119–120.
- [14] G.T. Burstein, C.J. Barnett, A.R. Kucernak, K.R. Williams, Catal. Today 38 (1998) 425–437.
- [15] V. Tricoli, N. Carretta, M. Bartolozzi, J. Electrochem. Soc. 147 (2000) 1286–1290.
- [16] J. Kerres, W. Cui, R. Disson, W. Neubrand, J. Membr. Sci. 139 (1998) 211–225.
- [17] T. Urugami, K. Takigawa, Polymer 31 (1990) 372–668.
- [18] M. Hara (Ed.), Polyelectrolytes, Science and Technology, Marcel Dekker, New York, 1993 (Chapter 4).
- [19] Chitosan and Poly(vinyl pyrrolidone): Compatibility and Miscibility of Blends, Enrico Marsano, Silvia Vicini, Joanna Skopiska, Marcin Wisniewski, Alina Sionkowska, Macromolecular Symposia, vol. 218 (1) pp. 251–260.
- [20] M. Faragalla, D.J.T. Hill, A.K. Whittaker, Polym. Bull. 47 (2002) 421–427.
- [21] P. Mukoma, B.R. Jooste, H.C.M. Vosloo, J. Power Sources 136 (2004) 16–23.
- [22] P. Mukoma, B.R. Jooste, H.C.M. Vosloo, J. Membr. Sci. 243 (2004) 293–299.
- [23] M. Yamada, I. Honma, Electrochim. Acta 50 (2005) 2837–2841.
- [24] B. Smitha, S. Sridhar, A.A. Khan, Eur. Polym. J. 41 (2005) 1859–1866.
- [25] Y. Wan, K.A.M. Creber, B. Peppley, V. Tam Bui, Macromol. Chem. Phys. 204 (2003) 5–6.
- [26] Y. Wan, K.A.M. Creber, B. Peppley, V. Tam Bui, J. Appl. Polym. Sci. 94 (2004) 2309–2323.
- [27] B. Smitha, S. Sridhar, A.A. Khan, J. Appl. Polym. Sci. 95 (2005) 1154–1163.
- [28] B. Smitha, S. Sridhar, A.A. Khan, Macromolecules 37 (2004) 2233–2239.
- [29] B.S. Pivovar, Y. Wang, E.L. Cussler, Membr. J. Sci. 154 (1999) 155–162.
- [30] B.D. Cahan, J.S. Wainright, J. Electrochem. Soc. 140 (1993) 185.
- [31] S. Haufe, U. Flemming, J. Electrochem. Sci. 185 (2001) 95–103.
- [32] S. Sridhar, R. Ravindra, A.A. Khan, Ind. Eng. Chem. Res. 39 (2000) 2485–2490.
- [33] Available on <http://scholar.lib.vt.edu/theses/available/etd-42198-13329/unrestricted/ch3-5.pdf>.
- [34] M. Zeng, F. Zhengping, C. Xu, J. Membr. Sci. 230 (2004) 175–181.
- [35] X.F. Zeng, E. Ruckenstein, Biotech. Prog. 15 (1999) 1003–1008.
- [36] X.Y. Zhou, M.A. Hoffmann, J.A. Weston, E. Chalkova, H.R. Allock, S.N. Lvov, in: S. Narayana, T. Zawadzinski, S. Gottesfeld (Eds.), Proceedings of the Electrochemical Society Series on Direct methanol Fuel Cells, Pennington, New Jersey, USA, 2003.
- [37] Akita, Hiroshi, Ichikawa, Masao, Iguchi, Masaru, Oyanagi, Hiroyuki, US Patent 6,523,699 (2003).
- [38] T. Okada, S.K. Ratjke, H. Hanche-Olsen, J. Membr. Sci. 66 (1992) 179–192.