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Ionic Cluster Mimic Membranes Using Ionized Cyclodextrin

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Abstract: Ionic cluster mimic, polymer electrolyte membranes were prepared using polymer composites of crosslinked poly(vinyl alcohol) (PVA) with sulfated-β-cyclodextrins (β-$CDSO_3H$) or phosphated-β-cyclodextrins (β-$CDPO(OH)_2$). When Nafion, developed for a fuel cell using low temperature, polymer electrolyte membranes, is used in a direct methanol fuel cell, it has a methanol crossover problem. The ionic inverted micellar structure formed by micro-segregation in Nafion, known as ionic cluster, is distorted in methanol aqueous solution, resulting in the significant transport of methanol through the membrane. While the ionic structure formed by the ionic sites in either β-$CDSO_3H$ or β-$CDPO(OH)_2$ in this composite membrane is maintained in methanol solution, it is expected to reduce methanol transport. Proton conductivity was found to increase in PVA membranes upon addition of ionized cyclodextrins. Methanol permeability through the PVA composite membrane containing cyclodextrins was lower than that of Nafion. It is thus concluded that the structure and fixation of ionic clusters are significant barriers to methanol crossover in direct methanol fuel cells.

Keywords: polymer electrolyte membrane, direct methanol fuel cells, poly(vinyl alcohol), ionized cyclodextrin.

Introduction

Considerable attention has been directed towards the development of proton exchange membranes (PEM), key components in polymer electrolyte membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC), due to the desire to develop the portable energy sources.

Nafion, a commercially available PEM, is commonly used in low temperature fuel cell applications since the perfluorinated ionomer membranes exhibit high chemical and electrochemical resistance at the harsh operating conditions, as well as high proton conductivity. However, it has been found that over 40% of the methanol in DMFCs, leading to excessive membrane swelling and resulting in lower power density in DMFCs.[1-3]

It is generally accepted that the water-swollen morphology of Nafion is best represented as an inverted micellar structure, approximately spherical in shape,[4,5] which becomes distorted upon addition of methanol (see Nafion in Scheme I). The solvent molecules must necessarily diffuse across the amorphous fluorocarbon or interfacial regions between the swollen polar domains. The growth of the ionic clusters with increasing methanol content has been proposed to occur through a combination of cluster size expansion and a redistribution of the polymer chain.[5] The swelling-induced disentanglement behavior in the Nafion matrix is significantly responsible for the enlargement of the ionic channels composed of ionic clusters. The cross-sectional size of the ionic channels is largely dependent upon the swellability of the entire membranes, that is, including both the ionic cluster and the matrix itself. Methanol permeates membranes primarily through ionic channels, and thus the cross-sectional size of these channels determines the degree of permeability, so does the proton transport.

In this respect, it is therefore necessary to fix the ionic cluster as well as to reduce the swellability by fixing the microdomain structure of the membrane. This is a major challenge in polymer electrolyte membrane development for DMFCs.

Here, we mimic the ionic cluster structure of Nafion inside a polymer matrix that exhibits a relatively high tolerance towards methanol, such that no significant swelling of the ionic cluster would be expected to occur in the presence of the solvent. Cyclodextrins (CDs), cyclic oligosaccharides,

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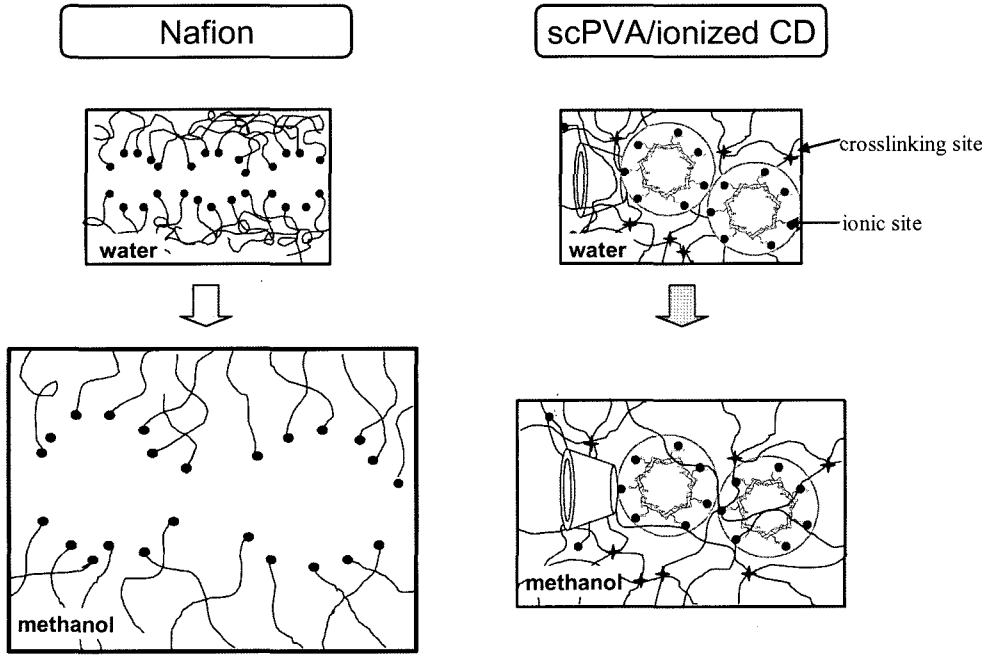
Scheme I



	Nafion		scPVA/Ionized CD	
	in Water	in Methanol	in Water	in Methanol
Characteristics of Matrix	Physically Crosslinked	Disentanglement	Chemically Crosslinked	Maintain Matrix Structure
Characteristics of Ionic Cluster	Inverted Micellar Structure	Significantly Swollen Structure	Intrinsic Cyclodextrin Structure	Maintain the Cyclodextrin Structure
Phenomena of the Membrane	Significantly Swelling		Maintenance	

were selected to mimic the structure of the ionic cluster for this study. The internal CD cavity, which is capable of accommodating various organic molecules with moderate affinity,[6] would also affect the transport.

The hydrophilic poly(vinyl alcohol) (PVA) was selected as the matrix polymer since it is reported to be highly compatibility with CD,[7-9] to prove the concept of this study, although PVA may not suitable to apply the harsh condition of fuel cell operation.

There have been several reports of PVA/CD membranes, in which the CD was primarily employed to selectively form inclusion complexes with a large number of organic molecules. For example, Yamasaki *et al.*, reported the preparation of a crosslinked PVA membrane containing a β-CD oligomer, and found the effects of this oligomer on the pervaporation characteristics of the composite membrane towards ethanol/water mixtures.[10,11] For the crosslinked PVA membrane comprising β-CD,[12,13] the solubility selectivity towards *p*-xylene/*m*-xylene mixtures increased from 1.18 to 4. These effects of the β-CD can be interpreted in terms of the inclusion strength in the cavity. Eddaoudi *et al.* also prepared PVA/CD membranes in order to construct a membrane-separation system using propanol isomers for extracting fullerene C_{60} molecules.[14]

In this work, an ionized β-CD was added to an aqueous viscous PVA solution. The membranes were formed using the casting method. The characteristics of the PVA/ionized CD membranes having fixed ionic clusters as PEM for DMFCs were investigated.

Experimental

Materials. Poly(vinyl alcohol) (PVA) (99% hydrolyzed; average Mw=89,000-98,000; Aldrich), β-cyclodextrin sulfated sodium salt (β-$CDSO_3H$, typical substitution 7-11 moles/mole β-CD; 8.0 from elemental analysis, Aldrich), β-cyclodextrin phosphated sodium salt (β-$CDPO(OH)_2$, degree of substitution 2-6; Aldrich) were purchased. Glutaraldehyde (GA) and HCl were purchased from Aldrich, and all other analytical grade reagents were used without further purification. The protonation of β-$CDSO_3H$ and β-$CDPO(OH)_2$ was performed using ion exchange resins (Na^+ form$\rightarrow H^+$ form).

Preparation of Membranes. A 5 wt% aqueous solution

of PVA was prepared with heating and then mixed with various amounts of either β-$CDSO_3H$ (15, 25, 30, 45 wt%) or β-$CDPO(OH)_2$ (5, 10, 15, 20 wt%). The mixtures were stirred vigorously at room temperature for 4 h, and then the corresponding PVA composite membranes were prepared by pouring the homogeneous solution into Petri dishes, and allowing the solvent to evaporate over a period of 5 days (at 25 °C). The prepared membranes were then annealed at 100 °C (or 70 °C) in an oven for 2 h. After thermal treatment, the membranes were soaked in a solution containing GA (6 g), acetone (300 g) and HCl (8 g) for 3 h at 50 °C to induce chemical crosslinking in order to reduce membrane swellability. This condition was optimized by our previous study.[15] Finally, the membranes were immersed in deionized water to remove any impurities. Crosslinked PVA membrane without ionized β-CD was also prepared as a reference material.

Characterization of Membranes. The swelling properties of the PVA composite membranes were determined by conventional water uptake measurements. The membrane was completely dried under vacuum at 30 °C for 24 h and then weighed. The dried membranes were then placed in deionized water for a week at 25 °C. After such time, the membrane was taken out of the vessel, wiped quickly with absorbent paper, and re-weighed. The water uptake was then calculated using the following relationship:

$$\frac{W_{wet}-W_{dry}}{W_{dry}}\times 100 \quad (1)$$

where W_{wet} and W_{dry} represent the wet and dried membrane weights, respectively. The temperature dependence as well as the swellability in methanol aqueous solution was not considered due to the experimental limitation of this measurement.

A four-point probe method, using a home-made cell consisting of two platinum plate charge carriers, and two platinum wires to monitor the potential drop, was employed to measure the proton conductivity of the membranes.[16-19] More detailed cell configurations have been described in previous articles.[16-18] Prior to taking conductivity measurements, the membranes were equilibrated with deionized water. Complex impedance measurements were performed using an IM6 impedance analyzer (ZAHNER, Germany) in the frequency range of 1 Hz to 8 MHz. During the impedance measurements, both humidity (100% RH) and temperature were held constant through the use of a home-made humidity/temperature controlled chamber.

The methanol permeability of the PVA composite membranes was determined using a diffusion cell of configuration described in previous articles.[16-18,20-22] This cell consists of essentially two reservoirs, each approximately 48 mL, separated by a vertical membrane.[17,18] The diffusion cell was slowly stirred during the experiment. Prior to testing, the membranes were equilibrated in deionized water. Initially, one reservoir is charged with a 10 wt% methanol aqueous solution while the other reservoir contains only deionized water. Increases in the methanol concentration in the water reservoir were measured against time using a refractive index detector (RI750F, Young In Co., Korea). The methanol permeability was calculated. All experiments were carried out at room temperature and the uncertainty of the obtained values was less than 2%.

The ion-exchange capacity (IEC) of the PVA/ionized CD membranes was determined using the acid-base titration method (exchanging H^+ for Na^+ ions) in NaCl solution, and monitoring the quantity of exchanged H^+ ions with a pH-meter. The corresponding IEC values were then calculated using the following equation:

$$\text{IEC(meq./g dry membrane)}=\frac{C_{H^+}V_{sol}}{W_{dry}} \quad (2)$$

where C_{H^+} represents the concentration of H^+ ions (mmol/$cm^3 \cong$ meq./cm^3), V_{sol} the volume of extraction solution (cm^3), and W_{dry} represents the weight of dried membrane (g).

Wide angle X-ray diffraction (XRD) measurements were performed using a conventional diffractometer employing Ni-filtered Cu-Kα radiation. The dried sample membranes were mounted on an aluminum sample holder, and the scanning angle was varied from 5 to 55 ° with a scanning rate of 5 °/min. The d-spacing values were calculated by means of Bragg's law ($d=\lambda/2\sin\theta$), using θ of the broad peak maximum. All spectra were taken at ambient temperature.

FTIR analysis was performed on a 6030 Galaxy Series FTIR spectrometer (Mattson Instruments): 256 scans were signal averaged at a resolution of 4 cm^{-1}.

Results and Discussion

All PVA membranes prepared using defined amounts of ionized β-CD (thickness≈100-150 μm) afforded solid films. The FTIR spectra of the PVA, β-$CDSO_3H$ and PVA/β-$CDSO_3H$ composite membranes are shown in Figure 1. The absorption band assigned to the O-H stretching vibration was observed in the range of 3600-3200 cm^{-1}, and was found to shift after thermal treatment, indicating that hydrogen bonds form between the -OH (PVA) and -SO_3H (β-$CDSO_3H$) groups.[22-25] It is known that the intensity of the O-H stretching vibration band is further reduced immediately following chemical crosslinking. This comes with a concomitant band shift to a higher wavenumber. This observation suggests that the hydrogen bonding between the OH groups of PVA are weaker in the chemically crosslinked PVA membranes than in pure PVA due to the diminution in the number of OH groups. A band observed at 1222 cm^{-1} is attributed to the SO_2 stretching vibrations.[26] The absorption band associated with the formation of ether bonds (C-O-C) between the alcohol groups of PVA and the aldehyde groups of GA generally appears in the range from 1280 to 1230 cm^{-1},

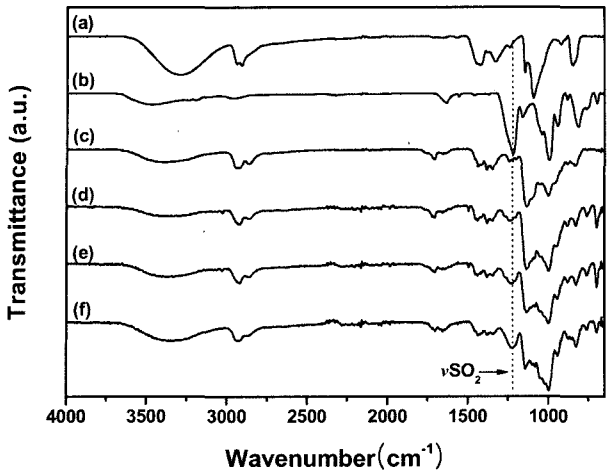


Figure 1. FTIR spectra of (a) PVA, (b) β-$CDSO_3H$, and PVA/β-$CDSO_3H$ composite membranes of (c) 15, (d) 25, (e) 30, and (f) 45 wt% of β-$CDSO_3H$.

but was seemingly masked by other bands in this region.[24]

The water uptake of the PVA/β-$CDSO_3H$ composite membranes annealed at 70 °C (O, low temperature in Figure 2) and 100 °C (●), and the PVA/β-$CDPO(OH)_2$ composite membranes annealed at 100 °C, are shown in Figure 2.

The water content in the composite membranes was found to increase with increasing content of ionized β-CDs, implying that the composite is more hydrophilic than the pure PVA membrane alone. The addition of sulfonic acid groups to the PVA membrane tends to decrease the degree of crystallization in PVA, as confirmed by XRD (*vide infra*). The crosslinking density of the PVA phases in the PVA/ionized β-CD membrane may be lower than that in the pure PVA membrane because the CDs are likely to retard the crosslinking reaction between PVA and glutaraldehyde.[12,13] Moreover, a higher concentration of sulfonic acid provides itself with more chances to react with the hydroxide groups in PVA (or sulfonic acid groups in β-$CDSO_3Hs$), which is well known in sulfonic acid system.[27,28] The water uptake of the PVA/β-$CDSO_3H$ composite membrane was found to be lower for membranes annealed at 100 °C then for those annealed at 70 °C. The sulfated CDs are vulnerable to esterification at high temperature and are thus believed to affect the degree of water swelling. The water swellability of the PVA/β-$CDPO(OH)_2$ membranes prepared at 100 °C is comparable with that for the PVA/β-$CDSO_3H$ membrane annealed at 70 °C. This compatibility is essentially due to the fact that esterification is not occurred in the PVA/β-$CDPO(OH)_2$ system. The reaction between β-$CDSO_3H$ and PVA, esterification between -SO_3Hs in β-$CDSO_3H$, producing a denser membrane, and thus higher resistance towards water diffusion, which lead to the lower swellability of the membranes annealed at high temperature.

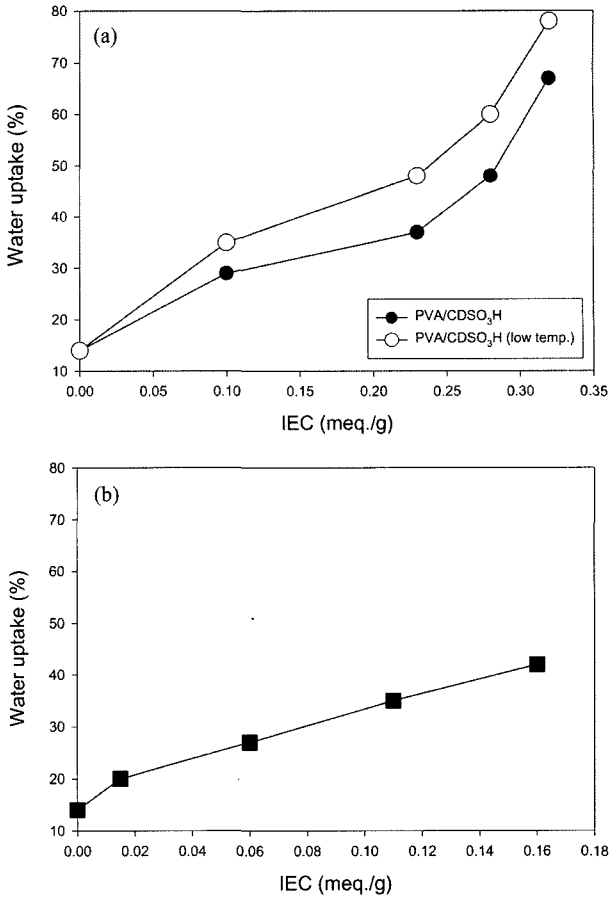


Figure 2. Water uptake of (a) PVA/β-$CDSO_3H$ and (b) PVA/β-$CDPO(OH)_2$ composite membranes.

The XRD patterns of the PVA composite membranes were measured in order to investigate the structural changes that occur upon addition of β-$CDSO_3H$ (Figure 3(a)). These XRD patterns present very broad peaks compared to the crystalline PVA in the range of 2θ, reflecting a loss in crystallinity, and an increase in the amount of amorphous regions within the composite membrane, due to the increased amounts of ionic CDs.

The characteristic XRD peaks of β-$CDSO_3H$ are not visible in the spectrum, implying that the CDs are uniformly distributed throughout the PVA composite membrane and no agglomeration has occurred during the preparation of the membranes. Indeed, these characteristic CD diffraction peaks are even absent from the spectrum of the highly loaded (45 wt%) PVA/β-$CDSO_3H$ composite membrane. It is also confirmed by the homogeneity from the scanning electron microscopy image (data is not shown) of the cross-section of the membranes.

The peaks corresponding to *d*-spacings of approximately 4.12 Å (calculated using the Bragg equation), have been assigned to the interchain distance.[25-29] When 15 wt% of β-

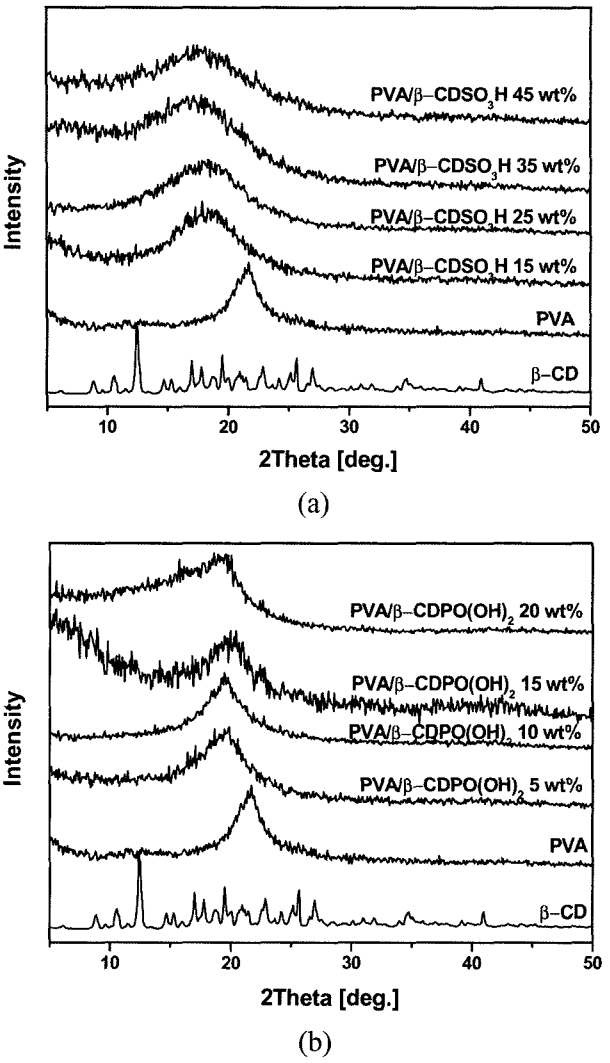


Figure 3. XRD patterns of (a) PVA/β-$CDSO_3H$ and (b) PVA/β-$CDPO(OH)_2$ composite membranes.

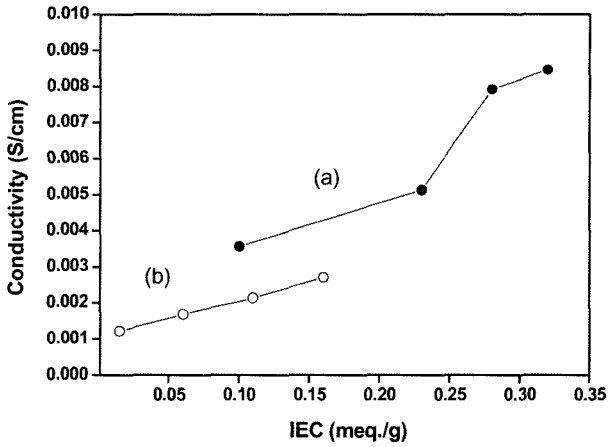


Figure 4. Proton conductivity of (a) PVA/β-$CDSO_3H$ and (b) PVA/β-$CDPO(OH)_2$ composite membranes.

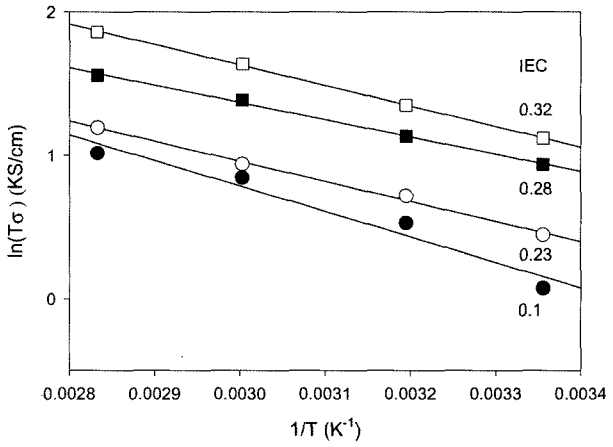


Figure 5. Temperature dependence of proton conductivity for PVA/β-$CDSO_3H$ composite membranes (membranes were crosslinked at 100°C).

$CDSO_3H$ was induced, the Bragg *d*-spacing of the composite membrane was observed to increase to 4.70 Å. This value is larger than that of PVA/β-$CDPO(OH)_2$ (4.45 Å). This implies that the substitution number for ionized β-CD is different (the number of substitution is higher in β-$CDSO_3H$ than in β-$CDPO(OH)_2$).

The proton conductivities for a number of PVA/β-$CDSO_3H$ and PVA/β-$CDPO(OH)_2$ composite membranes comprising varying amounts of CD, at 100% relative humidity, are shown in Figure 4. As shown in this figure, the proton conductivities are largely dependent upon the acidic group content within the CDs. The PVA membrane containing 45 wt% of β-$CDSO_3H$ is mechanically stable and gives a proton conductivity of 0.0085 S/cm at 0.32 IEC. A comparison of the proton conductivity values obtained at ca. 0.15 IEC reveals that the PVA/β-$CDSO_3H$ composite membranes show higher proton conductivities than those of the PVA/β-$CDPO(OH)_2$ composites. This finding is expected, since $-PO(OH)_2$ is an acid having lower pKa values than that of $-SO_3H$.

An increase in conductivity was observed when the temperature was increased (Figure 5). Here, the activation energy for proton conduction was estimated using the following expression:[30]

$$\ln(\sigma T) = \ln(\sigma_o) - \frac{E_a}{RT} \tag{3}$$

where R is the gas constant, σ is a proton conductivity, σ_o is a constant with respect to T, and E_a is the activation energy for proton conduction. Membranes show very similar temperature dependency of proton conduction to membranes in general. The following activation energies 14.8, 11.6, 11.0, and 11.9 kJ/mol correspond to the PVA/β-$CDSO_3H$ membranes with IEC values of 0.1, 0.23, 0.28, and 0.32 meq./g,

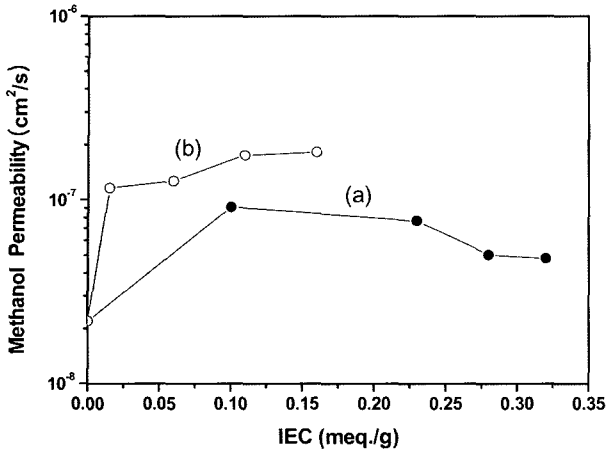


Figure 6. Methanol permeability in (a) PVA/β-$CDSO_3H$ and (b) PVA/β-$CDPO(OH)_2$ composite membranes.

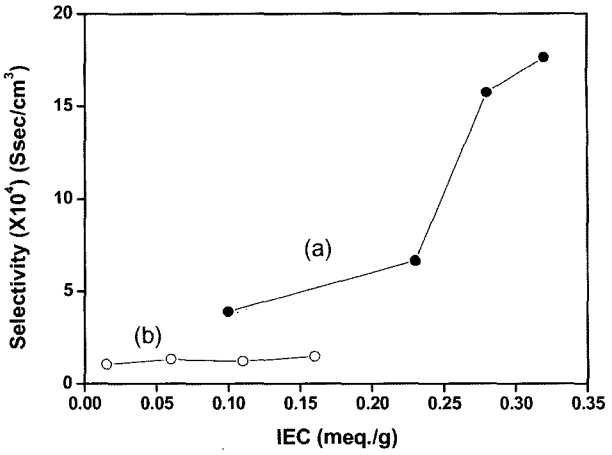


Figure 7. Selectivity of (a) PVA/β-$CDSO_3H$ and (b) PVA/β-$CDPO(OH)_2$ composite membranes.

respectively, and are somewhat higher than that observed for Nafion (i.e. E_a /Nafion = 10.50 kJ/mol).[15]

The permeability of a 10 wt% methanol aqueous solution through the PVA composite membranes was measured (Figure 6). Methanol permeability values for all samples are higher than PVA membranes without ionic CDs. Compared with Nafion 117 (1.9×10^{-6} cm^2/s), most PVA/ionized-β-CDs membranes measured show much stronger resistance towards methanol crossover. Methanol permeability is known to occur through ionic channels and swollen matrices, and is generally found to increase in accordance with increases in the number of ionic sites present within the membrane and swellability. The increment of the methanol permeability is rather low, even it showed a decreasing phenomena with increasing amount ionic CDs, therefore, another factor would exist in this composite membrane. The inclusion behavior of large amount of CD's cavity is likely to affect the permeance of methanol, since the CD cavity is hydrophobic and thus more attractive towards methanol than water.[10,11] In this respect, the permeation mechanism of methanol through PVA/β-$CDSO_3H$ would be also controlled by the existence of CDs.[11]

To compare the applicability of these different PVA composite model membranes as DMFCs, we calculated the selectivity parameter (Φ) using the following relationship:[16]

$$\Phi(\mathrm{S\ s\ cm^{-3}}) = \sigma / P_{Methanol} \quad (4)$$

where σ represents the proton conductivity (S cm^{-1}) and $P_{Methanol}$ represents the methanol permeability (cm^2 s^{-1}) through the membrane.

Figure 7 shows the selectivity parameters for PVA/ionized β-CD membranes as a function of the amount of ionized β-CD. The results show that the selectivity parameter of PVA/β-$CDSO_3H$ membrane containing 45 wt% of β-$CDSO_3H$ is at least 3.5-fold higher than that of Nafion 117 in the methanol concentration range considered (the selectivity parameter for Nafion 117 is *ca.* 50000).

Conclusions

In this study, a new concept of ionic cluster mimic membranes has been assessed by the preparation of crosslinked PVA composite membranes with β-$CDSO_3H$ (or β-$CDPO(OH)_2$), for PEM of future DMFCs application.

It is widely known that methanol is able to permeate through ionic channels and swollen polymer matrices. In addition, the structure of the ionic cluster and the polymer electrolyte membrane matrix are known to change and swell in the presence of methanol. The ionic micellar structure, which is formed by the intrinsic inverted micellar shape of β-$CDSO_3H$ (β-$CDPO(OH)_2$) in this composite membrane, is maintained in methanol aqueous solution. Therefore, the fixing of the ionic cluster structure using the permanent shape of CD as well as the PVA matrix through crosslinking has been shown to reduce the transport of methanol.

The proton conductivity in PVA membranes was observed to increase with addition of ionized CDs. Compared with Nafion 117, most of the prepared PVA/ionized β-CDs membranes show much stronger resistance towards methanol crossover. It is thus concluded that the structure and fixation of the proton transport sites are crucial in preventing methanol crossover in direct methanol fuel cells.

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