

Sulfonated Dextran/Poly(vinyl alcohol) Polymer Electrolyte Membranes for Direct Methanol Fuel Cells

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Abstract: Polymer electrolyte membranes, featuring ionic channels, were prepared from sulfonated dextran/poly(vinyl alcohol) (sD/PVA) membranes. A stiff sulfated dextran was chosen as the route for ionic transport, since ionic sites are located along the stiff dextran main chain. The sD/PVA blend membranes were annealed and then chemically crosslinked. The characteristics of the crosslinked sD/PVA membranes were investigated to determine their suitability as proton exchange membranes. The proton conductivity was found to increase with increasing amounts of sD inside the membrane, which reached a maximum and then decreased when the sD content exceeded 30 wt%, while the methanol permeability increased with increasing sD content. The good dispersion of sD inside the membrane, which serves as an ionic channels mimic, played a significant role in proton transportation.

Keywords: polymer electrolyte membranes, direct methanol fuel cells, poly(vinyl alcohol), dextran.

Introduction

Attention has been paid to proton electrolyte membranes (PEM) as key components of polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). Nafion has been used in both fuel cell types because this perfluorinated ionomer membrane has high chemical and electrochemical resistances as well as high proton conductivity under the harsh conditions of fuel cell operation. However, it has been found that the methanol can transport across the Nafion membrane in DMFCs, leading to excessive membrane swelling^{1,2} and resulting in lower power density in DMFCs. These drawbacks have prompted research on PEMs aimed at decreasing the methanol permeability, either through the development of new polymer electrolytes³ or by modifying conventional membranes.⁴ Most attempts to develop new PEMs have been centered on membranes containing aromatic polymers, such as poly(ethersulfone), poly(ether ether ketone), polyphenylquinoxaline, or polybenzimidazole.^{3,5,6} Investigations of ways to reduce methanol permeation in conventional polymers have focused on

modification of the membrane surface, including grafting of other monomers⁷ or making composites with inorganic^{4,8-10} and organic¹¹ particles.

In order to reduce methanol transport through the membrane, it is important to understand its mechanism. It is generally accepted that the ionic channels, which are formed by water swollen clusters inside the Nafion membrane, play a role in proton as well as methanol transport. The size of the clusters in the Nafion membrane increases with increasing methanol content due to a combination of expansion in cluster size and redistribution of the sulfonate sites. Swelling-induced disentanglement inside the polymer matrix is the dominant factor responsible for the enlargement of the ionic channels and, consequently, for the enhanced methanol transport. Ionic channel size is largely dependent upon the swellability of the membrane within both the ionic cluster and the polymer matrix itself. Therefore, it is necessary to control the cross-sectional size of the ionic channels as well as to reduce the matrix swellability. This is a challenge in PEM research for DMFCs.

We selected a stiff sulfated dextran (sD) as an ionic transport route, since the ionic sites are located rather regularly along the stiff dextran chain and the fixed ionic sites do not

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involve the redistribution in methanol solution, sD also provides a well-dispersed, stiff barrier inside the polymer matrix and a tortuous path for the methanol to travel. Poly(vinyl alcohol) (PVA) was used as a matrix polymer because PVA has a good compatibility with sD.¹² In addition, PVA can be crosslinked in order to reduce methanol transport.¹³ The goal of this research was to investigate the effects on proton transport of the regular distance of the ionic sites along the stiff dextran chain. Although PVA itself may not be suitable under the harsh conditions operated in fuel cells, its miscibility with sD and simple crosslinking make it a good model to prove the concept.

In our previous study, good proton transport was obtained from membranes that had ionic channel structures rather than ones that lacked ionic channels but did have comparable ion exchange sites.¹⁴ Therefore, the addition of stiff ionic chains of sD inside the polymer membranes was expected to facilitate proton transport through the ionic sites neighboring each other on the stiff dextran chains. In this study, the membranes were prepared by casting a membrane from a sD/PVA solution, followed by annealing and crosslinking the membrane. The characteristics of the crosslinked sD/PVA membranes were investigated for use as PEMs.

Experimental

Materials. PVA (99 + % hydrolyzed, average M_w 89,000–98,000; Aldrich) and sulfated dextran sodium salt (M_w = 10,000, ca. 17% sulfur; Sigma) were used as membrane materials. Sulfated dextran sodium salt was pretreated using ion exchange resins in order to change from the Na^+ to the H^+ form. Glutaraldehyde (GA; 50 wt% in water), HCl, and acetone were also purchased from Aldrich. All analytical grade reagents from commercial sources were used without further purification.

Preparation of Membranes. PVA was dissolved in water with heating at 95 °C to make a 5 wt% solution, and was mixed with various amounts of sD complexes (10, 15, 20, 25, 30, 35, and 45 wt%) and vigorously stirred to achieve complete dissolution. The membranes were prepared by pouring the homogeneous solution onto Petri dishes and evaporating the solvent at 25 °C for more than 5 days.

The prepared membranes were annealed at 100 °C in an oven for 2 h. After this treatment, the membranes were soaked in a solution of 1.9 wt% GA in acetone/HCl (70 : 2 w : w) solution for 4 h at 50 °C, in order to reduce the membrane swellability by chemical crosslinking.¹³ All membranes were washed many times with cold, deionized water, and stored in deionized water before the measurements.

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

Swelling of the membranes was determined by water

uptake measurements. Membranes were completely dried under vacuum at 30 °C for 24 h and then weighed. The dried membranes were then placed submerged in water for 1 week at 25 °C. The membranes were then removed from the vessel, wiped quickly with absorbent paper, and weighed. The water uptake, as a percentage, was calculated using the following relationship,

$$\text{Water Uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100,$$

where W_{wet} and W_{dry} are the weights of the wet and dried membrane, respectively.

Proton conductivity of the membranes was assessed using a four-point probe method, which employed a home-made cell consisting of two platinum plates carrying the current and two platinum wires monitoring the potential drop across the membranes.^{14,15-17} Further details of the cell configurations have been described previously.^{14,15-17} Before conductivity measurements commenced, the membranes were equilibrated with deionized water. Complex impedance measurements were carried out in the frequency range 1 Hz to 8 MHz using an impedance analyzer (IM6; Zahner). During the impedance measurements, humidity (100% RH) and temperature (25 °C) were constantly maintained using a home-made humidity/temperature controlling chamber.²⁰

Methanol permeability of the membranes was determined using a diffusion cell as described previously.^{14,18,19} This cell consists of two reservoirs, of volume approximately 48 cm^3 , separated by a vertical membrane.¹⁵ The contents of the reservoirs in the diffusion cell were slowly stirred during the experiment. Prior to testing, the membranes were equilibrated in deionized water. Initially, one reservoir contained a 10 wt% methanol aqueous solution and the other only deionized water. The increase in the concentration of methanol in the water reservoir was measured as a function of time using a refractive index detector (RI750F, Young In Co.). All experiments were carried out at room temperature.

The ion-exchange capacity (IEC) of the prepared membranes was measured by exchange of protons with Na^+ ions in NaCl solution (acid-base titration). The quantity of exchanged H^+ ions was determined using a pH meter, and the IEC values [meq per g dry membrane] were calculated using the following equation,

$$\text{IEC} = \frac{C_H V_{\text{sol}}}{W_{\text{dry}}},$$

where C_H is the concentration of H^+ ions [$\text{mmol cm}^{-3} \cong \text{meq cm}^{-3}$] determined by the pH measurements, V_{sol} is the volume of the extraction solution [cm^3], and W_{dry} is the weight of dried membrane [g]. All data were averaged for at least three samples. For comparison, the proton conductivity, methanol permeability, water uptake, and IEC values of the Nafion 117 membrane were 0.09 S cm^{-1} , $1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, 29%, and 0.91 meq g^{-1} , respectively.

Wide-angle x-ray diffraction (WAXS) measurements were performed using a conventional diffractometer that employed Ni-filtered Cu-K α radiation. The dried sample membranes were mounted on an aluminum sample holder, and the scanning angle was varied from 5° to 55° at a scanning rate of 5°/min. The d -spacing was calculated using Bragg's law, $d = \lambda/2\sin\theta$, where θ is the broad peak maximum. All spectra were measured at ambient temperature.

The cross-sectional morphology of the membranes was studied using a scanning electron microscope (Hitachi S-4700, Japan).

Results and Discussion

All crosslinked PVA composite membranes with different amounts of sD afforded solid films.

Figure 1 shows FT-IR spectra of crosslinked PVA and crosslinked sD/PVA membranes containing different amounts of sD. The absorption band assigned to the O-H stretching vibration was observed in the range of 3600-3200 cm^{-1} . It is known that the intensity of the O-H stretching vibration band is reduced following crosslinking,²¹ with a concomitant band shift to a higher wavenumber. This suggests that the hydrogen bonding between the OH groups of PVA is weaker in the chemically crosslinked PVA membranes than in pure PVA due to a diminution in the number of OH groups. The shift in wavenumber in sD/PVA membranes from 3287 to 3368-3375 cm^{-1} is due to hydrogen bond formation between the OH groups of PVA and the SO₃H groups of sD. The absorption band associated with the formation of ether bonds (C-O-C) derived from the alcohol groups of PVA and the aldehyde groups of GA generally appears in the range of 1280 to 1230 cm^{-1} .²¹ The crosslinking reaction of GA would involve the OH groups of the sD. The presence of the sulfonic acid group was confirmed by

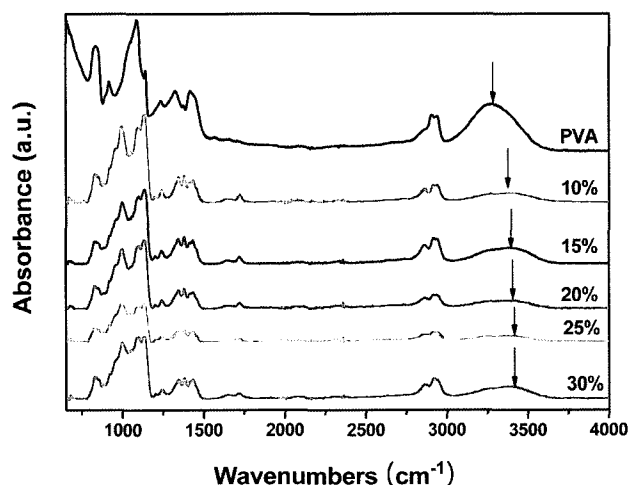


Figure 1. FT-IR spectra of crosslinked PVA and crosslinked sD/PVA membranes having different amounts of sD.

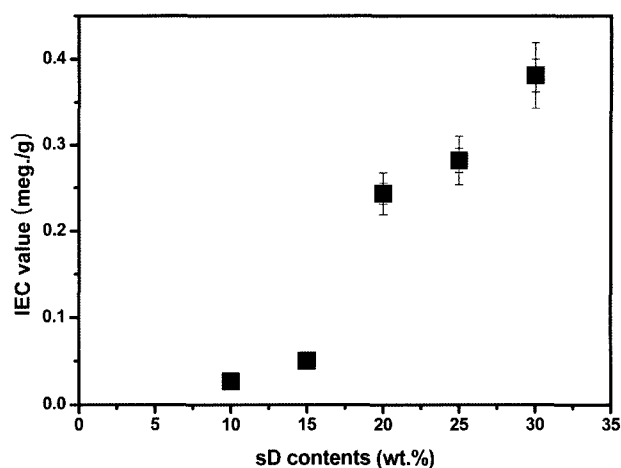


Figure 2. IEC of crosslinked sD/PVA membranes.

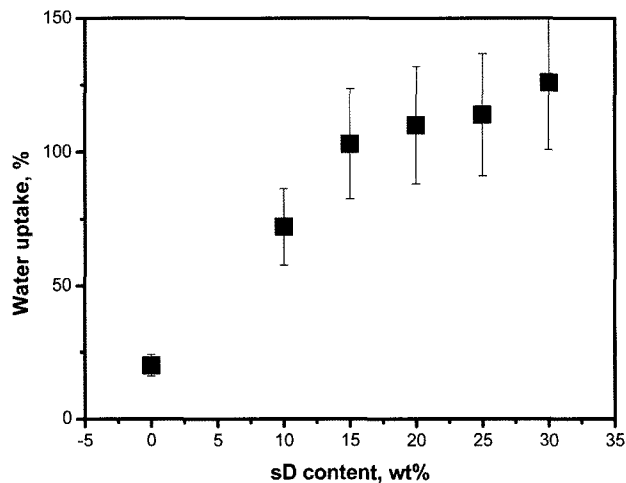


Figure 3. Water uptake of crosslinked sD/PVA membranes.

the absorption bands assigned to the sulfonic acid group at $\sim 1146 \text{ cm}^{-1}$ (asymmetric O=S-O stretch), $\sim 1011 \text{ cm}^{-1}$ (S=O stretch), and $\sim 862 \text{ cm}^{-1}$ (S-O stretch). It is obvious that the relative intensity of these characteristic peaks increased with increasing content of the corresponding component.

The IEC change and water uptake of the crosslinked sD/PVA membranes are shown in Figures 2 and 3, respectively. The IEC values as well as the water uptake of the sD/PVA membranes increased with the amount of sD in the membrane. The water uptake of crosslinked sD/PVA membranes reached 130% for membranes with 30 wt% sD. This implies that the addition of sD inside PVA affects the crosslinking reaction, although there is a possibility that the OH group in sD participates in the crosslinking reaction with GA.

Crosslinked sD/PVA membranes with concentrations $> 35 \text{ wt}\%$ sD showed inhomogeneities in the membranes, observed via the SEM images, while the solutions were homogeneous.

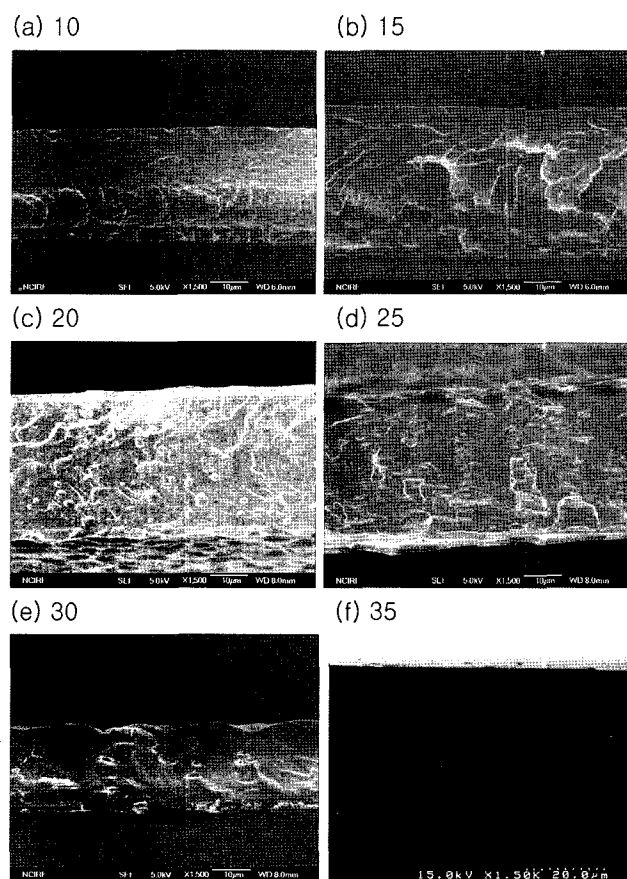


Figure 4. SEM images of crosslinked sD/PVA membranes having different amounts of sD.

SEM images of cross sections of sD/PVA membranes with increasing contents of sD are shown in Figure 4. Cross-linked sD/PVA membranes containing less than 25 wt% sD showed no significant phase segregation between PVA and sD on this scale. On the other hand, some open voids appeared for blend membranes having higher amounts of sD.

The proton conductivities of crosslinked sD/PVA blend membranes are shown for different amounts of sD in Figure 5. The proton conductivity increased for sD values up to ca. 30 wt%, and then decreased for larger amounts of sD. Obviously the enhanced IEC values of the membranes should contribute to the proton mobility through the membrane. Segregation would prevent proton transport through the membrane for large amounts of sD, although it has a high IEC.

The conductivity was maximal for membranes containing ca. 30 wt% sD; the proton conductivity was 1.2×10^{-2} S/cm. The IEC values were ~ 0.4 meq/g, implying that the advantage of the stiff ionic channel. In order to see the structural effect of the ionic channel, we prepared randomly sulfonated PVA. In order to obtain the proton conductivity reached ca. 1×10^{-2} S/cm; at least, the IEC had to be higher than 0.5 meq/g. [The proton conductivity was 1.06×10^{-2} S/

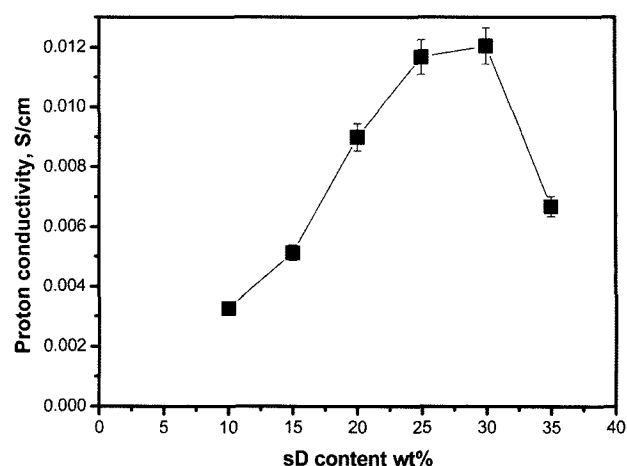


Figure 5. Proton conductivity of crosslinked sD/PVA membranes.

cm at 0.52 meq/g for the randomly sulfonated PVA].²² For the 30 wt% sD membrane, the water uptake value was over 130%, and the conductivity was higher than the proton conductivity of randomly sulfonated crosslinked PVA. sD is hydrophilic, so that the well-dispersed sD in the PVA membrane increased water absorption, and the connectivity of the ionic channels led to the higher value of water uptake as well as the higher proton conductivity. Therefore, structural modifications to the membrane, due to both the addition of stiff dextran components and the new interfacial polymer-dextran properties, can be expected to affect the proton mobility and can facilitate proton transport under optimal conditions. Obviously the enhanced water uptake of the membranes should contribute to the proton mobility through the membrane.

For crosslinked sD/PVA membranes with higher amounts of sD (> 30 wt%), the proton conductivity decreased, which may be due to inhomogeneity of the membranes. Protons would be expected to travel through the ionic channels formed by sD, while the crosslinked PVA region would act as a barrier. Although the sD in the matrix provides a route for proton transport, the proton transport route was interrupted by segregation for large amounts of sD (over 30 wt%).

Adding stiff dextran with ionic groups would be expected to affect the methanol permeability. The methanol permeability derived from a 10 wt% aqueous solution was measured and the results are presented in Figure 6. Although PVA is a good material for blocking methanol transport, methanol may permeate through the ionic channels and the swollen matrix, and the general trend for methanol permeability is an increase with increasing numbers of ionic sites. The methanol permeability of the crosslinked sD/PVA membranes of 25 wt% sD was on the order of 10^{-7} cm² s⁻¹.

WAXS measurements were used to investigate the morphological properties and structural changes of the PVA-

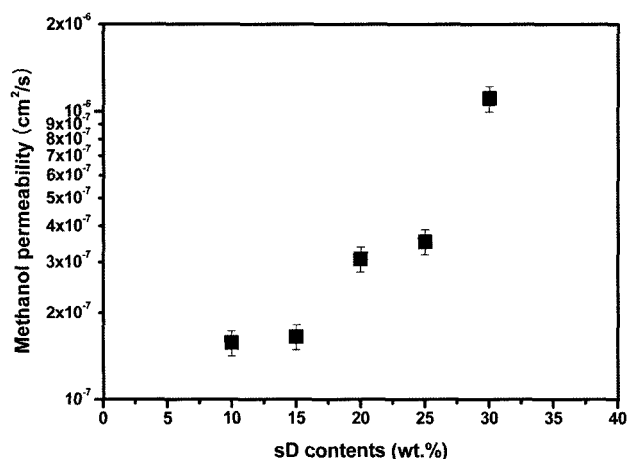


Figure 6. Methanol permeability of crosslinked sD/PVA membranes.

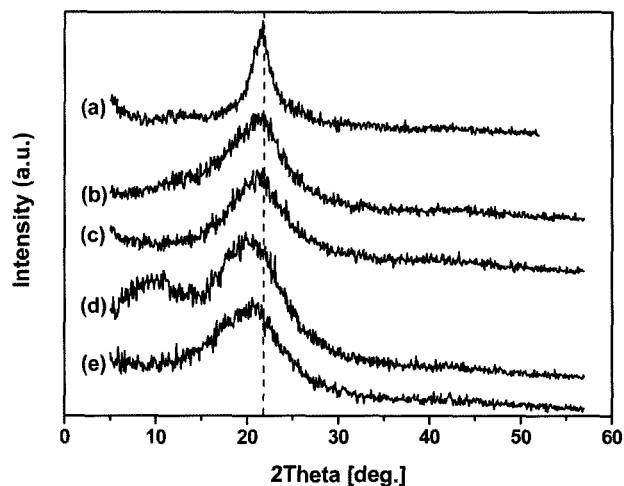


Figure 7. WAXS data for crosslinked sD/PVA blend membranes. (a) pure PVA, (b) 15 wt% sD, (c) 25 wt% sD, (d) 35 wt% sD, and (e) 45 wt% sD for sD/PVA blend membranes.

based composite membranes with increasing sD amounts; the results are shown in Figure 7. The PVA membranes containing no sD displayed a sharp diffraction feature at $2\theta = 21.64^\circ$, which shifted to lower angles and broadened as the wt% of sD increased. The Bragg d -spacing, which usually reflects the interchain distance, was calculated from Bragg's law using the broad peak maximum.¹¹ The d -spacing increased from 4.10 Å for 0 wt% sD to 4.38 Å for 35 wt% sD in PVA. This result indicates that the addition of sD distorts the membrane morphology, leading to an increase in the interchain distance and reduced crystallinity, implying the increase of free volume. Increased swelling of the membrane increases the free volume for diffusion across it for both methanol and hydrated protons, which therefore affects both the proton conductivity and the methanol per-

meability.

One of the methods used to assess membrane performance is the selectivity parameter, Φ [S s cm^{-3}], calculated using,²³

$$\Phi = \sigma / P_{\text{methanol}}$$

where σ is the proton conductivity [S cm^{-1}] and P_{methanol} is the methanol permeability [$\text{cm}^2 \text{s}^{-1}$] through the membrane. The selectivity parameters of the crosslinked sD/PVA membranes as a function of the amount of sD were ca. $3 \times 10^4 \text{ S s cm}^{-3}$, which is in the same order of magnitude as those of Nafion 117 (Φ is about $5 \times 10^4 \text{ S s cm}^{-3}$), although crosslinked sD/PVA membranes have a lower IEC to provide proton exchange, implying the role of the facilitated transport of protons along the stiff dextran chains.

Conclusions

Polymer electrolyte membranes containing stiff ionic channel structures were prepared by blending water-soluble PVA and sD to form sD/PVA blend membranes, followed by crosslinking to provide ion exchange sites.

The crosslinked blended membranes showed good properties in terms of proton conductivity and methanol permeability. We found that the conductivity increased with the addition of sD and then decreased for higher amounts of sD. The proton conductivity increased with the addition of sD and depended upon the water uptake of these membranes. A membrane with 25 wt% sD showed an ionic conductivity of 0.01 S cm^{-1} , a methanol permeability of $3.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

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