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Poly(vinyl alcohol) (PVA)/sulfonated polyhedral oligosilsesquioxane (sPOSS) hybrid membranes for direct methanol fuel cell applications

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Organic/inorganic hybrid membranes based on poly(vinyl alcohol) (PVA) and sulfonated polyhedral oligosilsesquioxane (sPOSS), crosslinked by ethylenediaminetetraacetic dianhydride (EDTAD), were prepared as candidate materials for proton exchange membranes in direct methanel fuel cell (DMFC) applications. Fourier transform infrared (FT-IR) spectroscopy and ion exchange capacity measurements for the prepared networks clearly revealed sPOSS incorporation. We found that proton conductivity increased and methanol permeability decreased with increasing sPOSS content in the hybrid membrane. In particular, our hybrid membranes demonstrated proton conductivities as high as 0.042 S/cm, which is comparable to that of Nafion™, while exhibiting two orders of magnitude lower methanol permeability as compared to Nafion™. We postulate that the polar sulfonic acid groups of the incorporated sPOSS cages assemble to provide ion conduction paths while the hydrophobic portions of the same sPOSS cages combine to form a barrier to methanol permeation with improved thermal stability of the hybrid membrane. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: poly(vinyl alcohol) (PVA); sulfonated polyhedral oligosilsesquioxane (sPOSS); membrane; direct methanol fuel cell (DMFC)

INTRODUCTION

Fuel cell technologies based on polymer electrolyte membranes (PEMs) have received wide attention during the past decade, largely owing to the many advantages offered over existing energy technologies. Broadly speaking, fuel cell technologies produce no pollutants, are compact in size, can be easily transported, require minimal resources, and are cost and energy efficient. Direct methanol fuel cells (DMFCs), in particular, employing polymer electrolyte membranes are one of the most attractive power sources for a wide range of applications.[1] The most commonly used polymer for electrolyte membranes is the perfluorinated ionomer known by its trade name Nafion™. Despite its attractively high proton conductivity and chemical stability, Nafion™ is costly and has high methanol permeability. The high methanol permeability allows undesirable transport of methanol from the anode side of the fuel cell, through the membrane, to the cathode side, a phenomenon known as methanol crossover. As a consequence, excessive methanol permeability of any PEM leads to an unacceptable decrease in cell performance.[2–4]

To address the problem of methanol crossover, numerous membranes as alternatives to Nafion™ have been developed and studied. These include sulfonated polyetherether ketone,[5] sulfonated polyimide,[6] polybenzimidazole,[7] and sulfonated polyposphazene.[8] Additionally, organic/inorganic hybrid membranes have been investigated, motivated by the potential for inorganic particles which can provide a physical barrier against methanol crossover while simultaneously improving mechanical and thermal stability.[9–12] Recently, membranes based on poly(vinyl alcohol) (PVA) have been studied for application as DMFC membranes due to their low cost and good performance in water/alcohol separations. Proton conduction in this polymer is made possible by combining it with other materials bearing acid groups, such as poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS),[13–15] phosphor tungstic acid (PWA),[16] or

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by crosslinking it with sulfosuccinic acid (SSA)[17,18] or polyacrylic acid.[19]

Polyhedral oligosilsesquioxane (POSS) is a unique nanostructured organic/inorganic hybrid molecule allowing a synthetic "bottom-up" approach to the creation of nanomaterials. The POSS molecule, itself, features a well-defined nanosized Si–O cage structure (Si_8O_{12}) with additional organic functional groups covalently bonded to each vertex Si on the cage. Due to the organic functional groups, the POSS cage is naturally compatible with organic hosts, such as polymers, and can be incorporated into polymer systems by copolymerization or by chemical grafting. Improved thermal stability and mechanical properties have been reported for various polymer/POSS hybrid nanocomposites.[20–22]

In this study, we attempted to make membranes for DMFC applications from the hybridization of POSS with PVA. For this purpose, we prepared a POSS bearing both sulfonic acid groups and hydroxyl groups by reacting a POSS triepoxide—a POSS bearing three glycidyl groups—with three equivalents of 4-hydroxybenzene sulfonic acid. The resulting sulfonated POSS (sPOSS) was blended with PVA and the blend then crosslinked by ethylenediaminetetraacetic dianhydride (EDTAD)[23] to yield PVA/sPOSS hybrid membranes. It was expected that a high proton conductivity would be afforded by the addition of the sulfonic acid groups of sPOSS while low methanol permeability and durability would result from the combination of crosslinking and hydrophobic nature of sPOSS.

EXPERIMENTAL

Materials

The PVA used in this study (98–99% hydrolyzed, average $M_w = 85,000 \sim 146,000$), EDTAD (98%), and 4-hydroxybenzenesulfonic acid (65 wt% solution in water) were purchased from Sigma-Aldrich Chemical (Milwaukee, WI, USA). Triglycidyl isobutyl POSS (EP 0423) which has three glycidyl groups and seven isobutyl groups on the corners was obtained from Hybrid Plastics Co., USA. Tetrahydrofuran (THF), methanol (MeOH), and dimethyl sulfoxide (DMSO) were purchased from Junsei Chemical Co., Ltd. All chemicals were used as received without further purification.

Synthesis of sulfonated POSS (sPOSS)

Triglycidyl POSS (1 mmol) was weighed and dissolved in 10 ml THF in a 100 ml round-bottom flask with N_2 purging. After stirring vigorously for 1 hr at 50°C, 1.0 g of 4-hydroxybenzenesulfonic acid (3.7 mmol) was added to the POSS solution, resulting in a clear solution that was then stirred for an additional 5 hr at 50°C to allow a reaction between glycidyl group and phenoxyl group to form the sulfonated POSS. After the reaction, the solvent was removed by evaporation at room temperature for 24 hr and then dried in a vacuum oven at room temperature for 48 hr to isolate the sulfonated POSS. This product was finally washed with distilled water at 50°C to remove unreacted 4-hydroxybenzenesulfonic acid. Quantitative yields were obtained. Scheme 1 summarizes this synthetic method to prepare

sPOSS. To confirm the structure, sPOSS was characterized by ^{1}H-NMR and Fourier transform infrared (FT-IR). The ^{1}H-NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer (300 MHz) at room temperature. For each analysis, ~5 wt% sPOSS solution was dissolved in $CDCl_3$.

^{1}H-NMR spectra of the original triglycidyl POSS and sPOSS are shown in Fig. 1(a) and (b), respectively. It can be seen that peak 'e' in Fig. 1(a), which represents a glycidyl group, disappeared, while in Fig. 1(b), two new peaks 'i' and 'j' appear, which correspond to the protons of the aromatic ring. So it is thought that a benzene sulfonic acid group was successfully introduced into the POSS. Furthermore, it was observed that integration values of peaks 'b' (–CH_3 on isobutyl) and 'i' (aromatic H) are 21.73 and 2.86, respectively, i.e. the ratio of the integration value of the two peaks is 7.6. There should be three aromatic rings (six i's) for the seven isobutyl groups (42 b's) in sPOSS, as depicted in Fig. 1(b). The results indicate that more than 90% of the glycidyl groups on POSS are converted into benzene sulfonic acid groups.

To further assess the structure of synthesized sPOSS, infrared spectroscopy was employed. An FT-IR spectrum of sPOSS, alongside that of the triglycidyl POSS, is shown in Fig. 2. A broad band with minimum transmittance at about 3300 cm^{-1} and a sharp band at 1593 cm^{-1} are attributed to the presence of hydroxyls and aromatic rings, respectively. In addition, absorbance at 1359 cm^{-1} reflects the presence of isobutyl groups attached to each POSS vertex. Two absorbances at 1111 and 1050 cm^{-1} were observed and attributed to the Si–O–Si group cage structure. Together, ^{1}H-NMR and FT-IR analyses are entirely consistent with the sPOSS structure shown in Scheme 1.

Preparation of membrane

To prepare sPOSS/PVA membranes, a multistep protocol was required, which we now describe by way of an example. PVA was completely dissolved in 20 ml of DMSO at 80°C. Separately, sPOSS was dissolved in 10 ml of DMSO with the aid of ultrasonication. The resulting sPOSS solution was added to the PVA solution to yield PVA/sPOSS weight ratios of 80/20, 70/30, 60/40, or 50/50. The PVA/sPOSS mixture was stirred for 6 hr at room temperature. EDTAD was dissolved in 2 ml of DMSO at room temperature and added to PVA/sPOSS blend solution at the level of [OH]/[anhydride] = 1/0.025. The reaction mixture was stirred at room temperature for an additional 30 min, following which it was cast into a Teflon^{TM} dish for drying at 40°C for 24 hr. During this time, the EDTAD laterally crosslinked the PVA chains, as depicted in Scheme 2.[23] The crosslinked PVA/sPOSS films were next dried in a vacuum oven at room temperature for 48 hr, followed by immersion in a large volume of DMSO for 24 hr at 80°C to extract unreacted PVA and sPOSS. Finally, the crosslinked and extracted samples were immersed in deionized water to remove DMSO, with the water being changed at least three times, followed by exhaustive drying under vacuum.

The chemical bonding within the membranes was examined using attenuated total reflectance infrared (ATR-IR) spectroscopy (Varian 800 FT-IR) with a wavenumber resolution of 4 cm^{-1} and range of 400–4000 cm^{-1}.
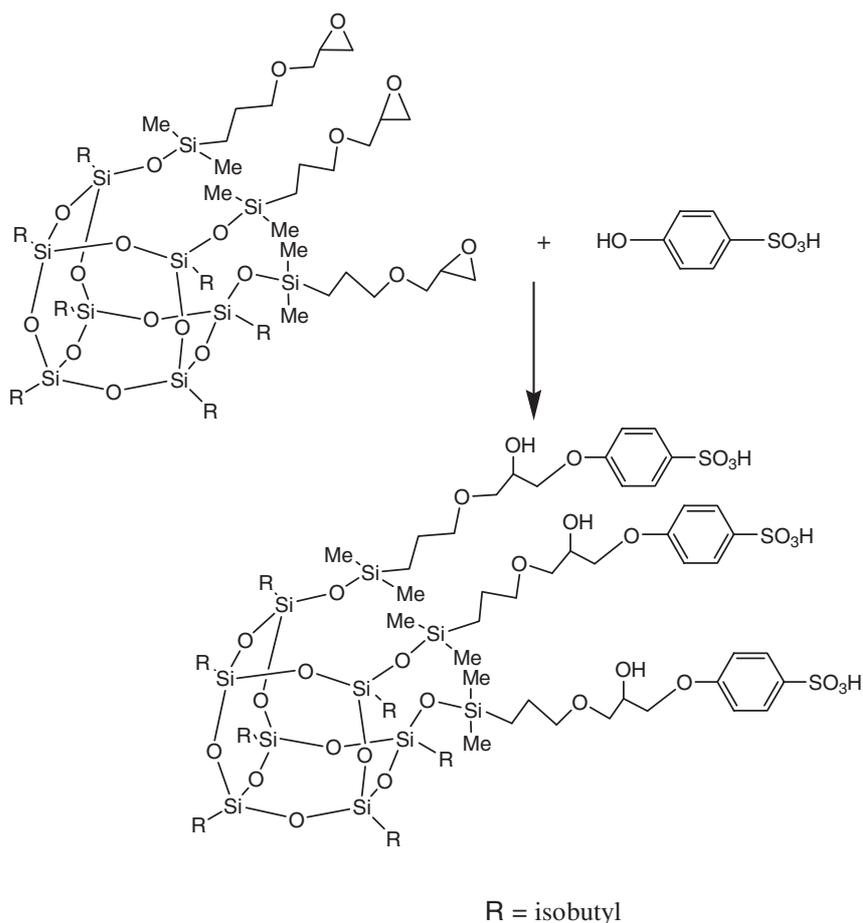
Scheme 1. Reaction of triglycidyl-POSS with 4-hydroxybenzene sulfonic acid to form trisulfonated POSS (sPOSS).

Water uptake

Samples for water swelling analysis were dried in vacuum at 40°C for 48 hr, and then cut into 2 cm × 2 cm squares, each sample then being weighed in the dry state before swelling in water at room temperature (20°C). Afterwards, samples were immersed in deionized water for at least 24 hr, dabbed for removal of surface water, and then immediately weighed. Water uptake was calculated by the following equation:

$$\text{Water uptake}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \qquad (1)$$

Ion exchange capacity

The ion exchange capacity (IEC) was measured using the classical titration method. After immersing samples in distilled water, they were soaked in a large volume of 0.1 M HCl solution to fully protonate the acid functionalities. They were then washed with distilled water to remove excess HCl and equilibrated with 20 ml of 2 M NaCl solution for at least 24 hr to effect ion exchange of Na^+ for H^+. The remaining solution was then titrated with a 0.1 M NaOH solution using phenolphthalein as an indicator, allowing measurement of the number of ionizable groups within the sample; i.e. those groups that released protons into solution during ion exchange. The IEC value (in meq/g) is defined as milliequivalents of sulfonic groups per gram of dried sample

and it is obtained from the following equation:

$$\text{IEC} = \frac{M_{\text{H}^+}}{W_{\text{dry}}} \qquad (2)$$

where $M_{\text{H}+}$ represents milliequivalents of H^+ released during ion exchange and W_{dry} is the weight of dried membrane (g).

Proton conductivity

The proton conductivity of membranes was measured using the four-point probe technique at relative humidity 95%. The impedance of the membranes was measured using a HP 4192A LF impedance analyzer. The impedance analyzer was operated in galvanostatic mode with AC current amplitude of 0.1 mA over a frequency range from 100 to 0.1 Hz. Each sample was cut into strips that were approximately 1.0 cm wide and 4.0 cm long prior to being mounted on the cell. Measurements were carried out at the room temperature and the proton conductivity (σ) was obtained using the following relation:

$$\sigma = \frac{l}{R \cdot S} \qquad (3)$$

where σ is the proton conductivity (S/cm), l the distance between the electrodes used to measure the potential (cm), R the measured impedance of membrane (Ω), and S is the cross-sectional area of the membrane (cm^2).
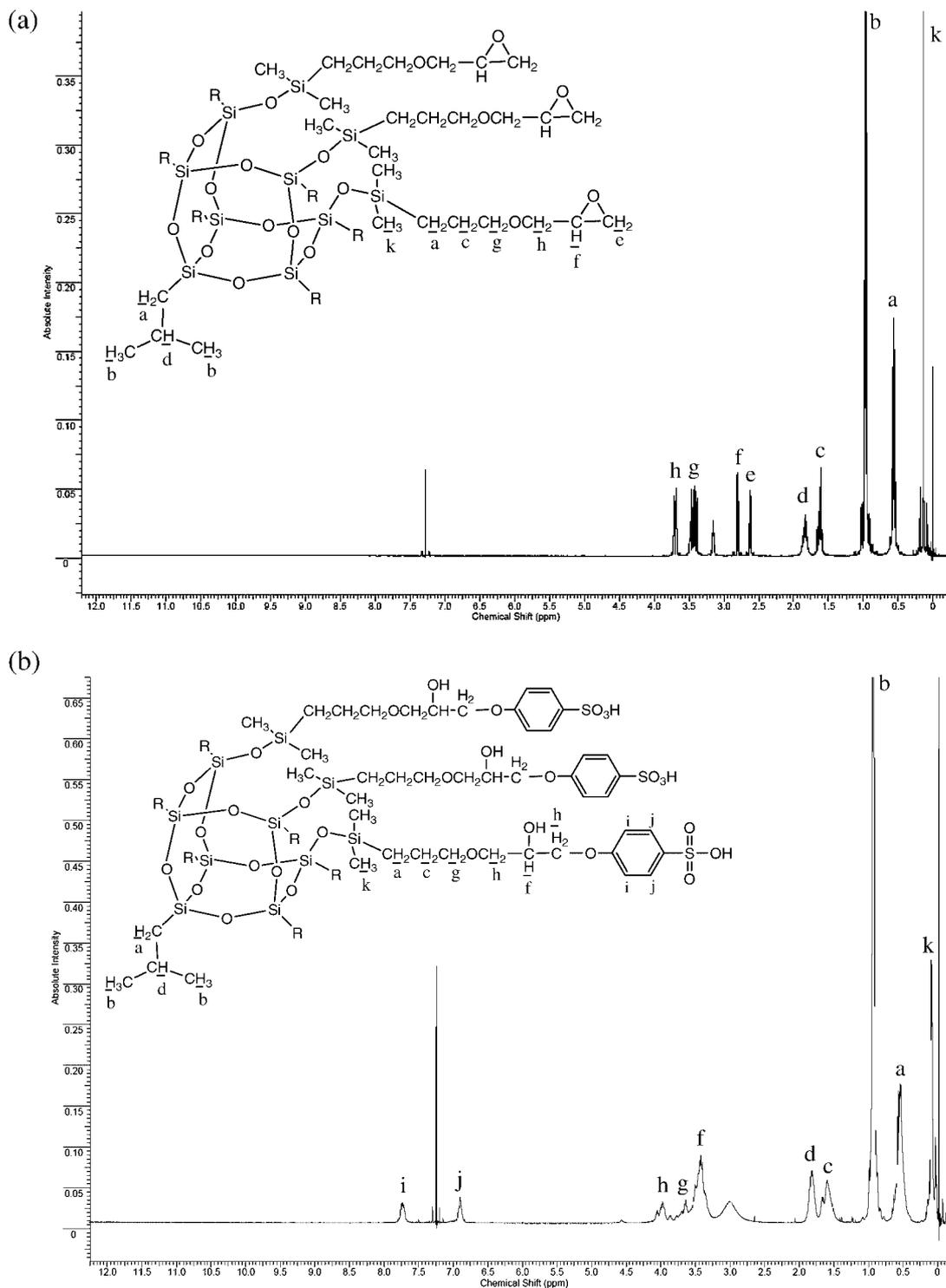
Figure 1. ^{1}H-NMR spectra of (a) triglycidyl POSS and (b) sPOSS.

Methanol permeability

Methanol permeability of the membranes was determined using a diffusion cell described by Rhim *et al.*[17,18] This cell consists of two reservoirs of distinct composition (discussed below), each approximately 48 ml, partitioned by a vertical membrane. Each reservoir of the diffusion cell was slowly stirred during the experiment. Prior to apparatus assembly, the partitioning membranes were equilibrated in distilled water for at least 24 hr. To drive methanol diffusion across the membranes, one reservoir contained a 2 M aqueous methanol solution while the other reservoir contained pure distilled water. As diffusion ensued, the concentration of methanol in the water reservoir increased with time, which was monitored using gas chromatography. The solutions in each cell were stirred vigorously to avoid concentration gradients near the membrane surface itself. The methanol
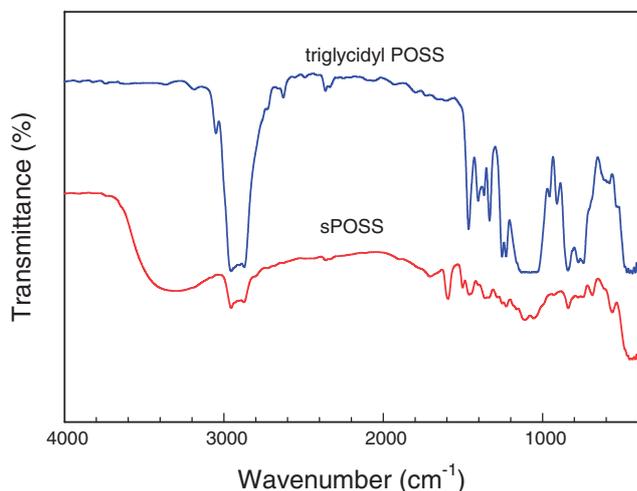
Figure 2. FT-IR spectra of triglycidyl POSS and sPOSS.

concentration in the receiving compartment as a function of time is given by

$$C_B(t) = \frac{A}{V_B}\frac{DK}{L}C_A(t - t_0) \qquad (4)$$

where C_B and C_A are the methanol concentrations of the two compartments, A, L, and V_B are effective area of membrane, membrane thickness, and volume of permeated compartment, respectively. D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The assumptions made in this study were that the value of D inside the membrane was constant and that the value of K did not depend upon the methanol concentration. The product DK denotes the membrane permeability (P in cm²/sec).

$$P = \frac{1}{A}\frac{C_B(t)}{C_A(t - t_0)}V_B L \qquad (5)$$
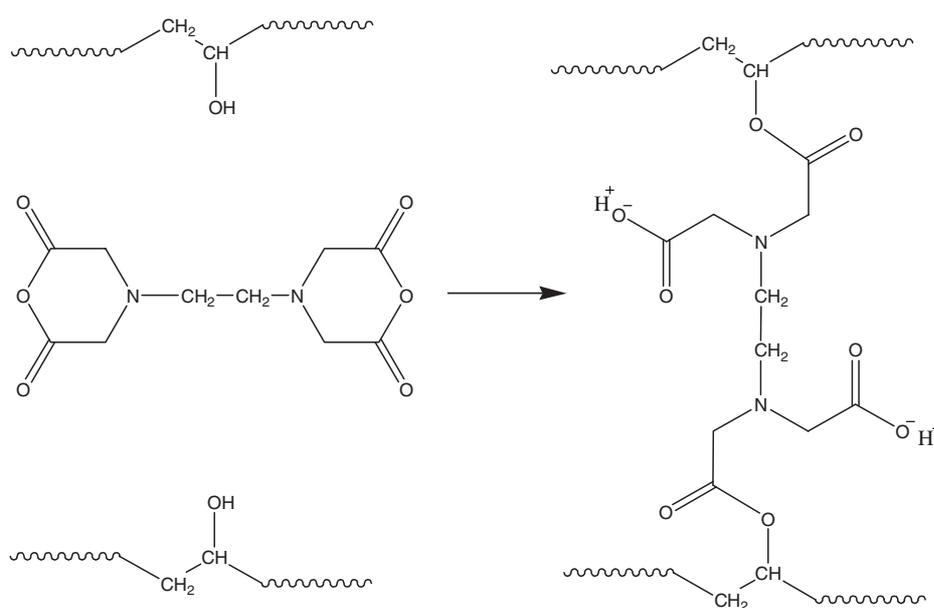
The value of C_B was measured several times during the permeation experiments, and the methanol permeability was calculated from the slope of the straight line obtained from plots of methanol concentration versus time. All experiments were carried out at 25°C.

Thermal stability of the membrane

Thermal stability of the membranes was characterized using thermogravimetric analysis (C-R4A, Shimadzu). The analysis was carried out by heating samples from 25°C to 700°C under nitrogen flow at a heating rate of 10°C/min. Temperatures for onset of decomposition and char yields were compared among the materials tested.
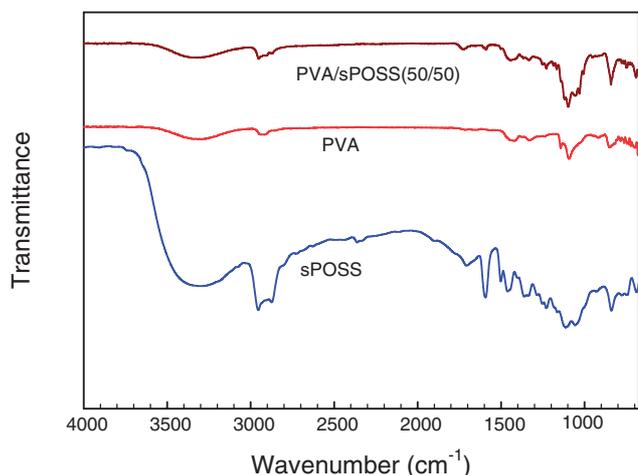
It is to be noted that these properties of the PVA/sPOSS hybrid membranes are demonstrated as a function of sPOSS content in the initial mixture of PVA and sPOSS.

RESULTS AND DISCUSSION

Formation of crosslinked hybrid membrane

The crosslinked structure in PVA/sPOSS membrane was examined by solubility change before and after crosslinking when it is immersed in DMSO for 24 hours. Before crosslinking, the polymer readily dissolved, but after crosslinking the membrane would not dissolve, but instead swelled, which confirms that the membrane was crosslinked by EDTAD. Gel fraction of the crosslinked PVA/sPOSS films, which was evaluated by the ratio of the weight of the dried sample after extraction at 80°C for 24 hr using DMSO to that of the sample before the extraction, is in the range 80–84% for all hybrid samples.

Figure 3 shows the FT-IR spectra of pure PVA and PVA/sPOSS hybrid crosslinked by EDTAD. The pure PVA sample shows a characteristic broad absorbance at 3297 cm⁻¹ (–OH stretching), at 2918 cm⁻¹ (symmetric –CH₂–), and at 1418 and

Scheme 2. Crosslinking of poly(vinyl alcohol) by EDTAD, resulting in the formation of two carboxylic acids per crosslink site.[23]

Figure 3. FT-IR spectra of PVA/sPOSS crosslinked by EDTAD.

Figure 4. Proton conductivity versus sPOSS content of the PVA/sPOSS hybrid membrane at 25°C.

1093 cm^{-1} for C–O group. In the crosslinked hybrid membrane, characteristic band at 1589 cm^{-1} due to aromatic ring and 1726 cm^{-1} due to ester group of EDTAD can be seen. Though not quantitative, these spectroscopically specific observations prove that sPOSS participated in the PVA/EDTAD network.

Proton conductivity

Proton conductivity of the PVA/sPOSS hybrid membrane as a function of sPOSS content is presented in Fig. 4. It is apparent that the proton conductivity of the PVA/sPOSS membrane increases with the amount of sPOSS in the hybrid. The proton conductivity of the hybrid membrane containing 20 wt% sPOSS is about 0.02 S/cm, comparable to Nafion 117,

then reaches about 0.042 S/cm when the sPOSS content is 50 wt % in the hybrid membrane. This must be due to the increase in concentration of sulfonic acid groups with the increase in sPOSS in the hybrid. This is in good agreement with the linear increase of IEC with sPOSS content in the hybrid membrane, which will be discussed in next section. The significant increase in proton conductivity with sPOSS content implies that the sPOSS is distributed uniformly in the PVA matrix. Figure 5 illustrates the proposed model structure of the hybrid membrane.

Water uptake and ion exchange capacity (IEC)

Water uptake is known to have a profound effect on the proton conductivity of the membrane. In general, the proton
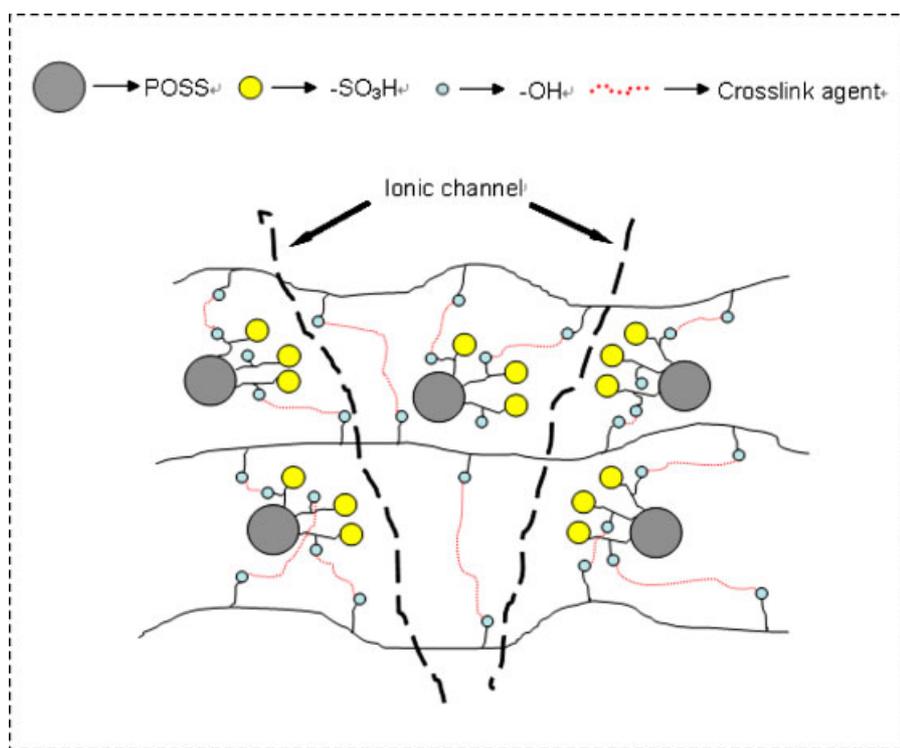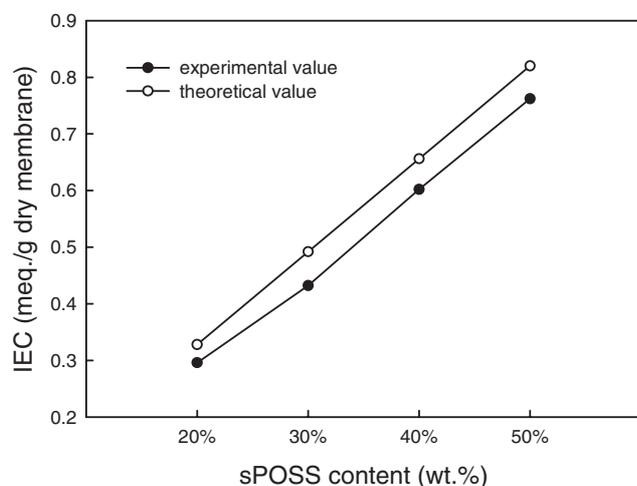

Figure 5. Proposed model structure of crosslinked PVA/sPOSS hybrid membrane.
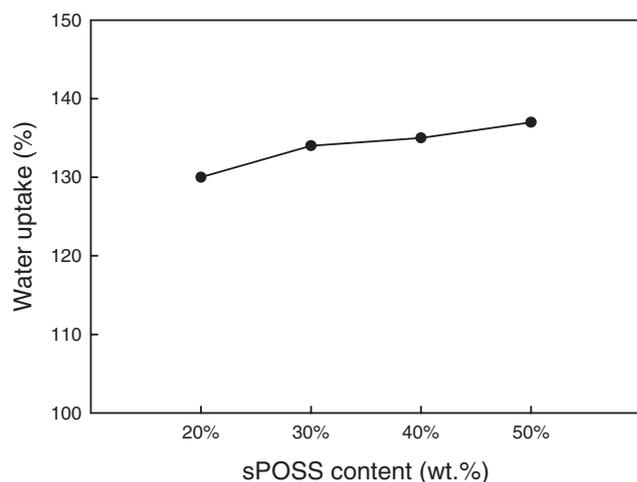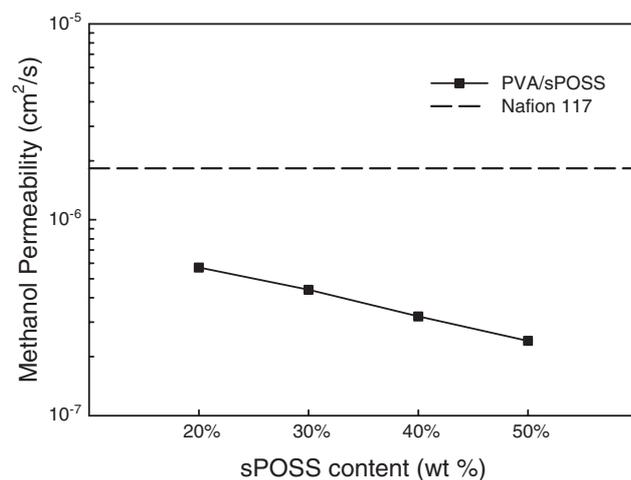
Figure 6. Water uptake versus sPOSS content of the PVA/ sPOSS hybrid membrane.

Figure 8. Methanol permeability versus sPOSS content of PVA/sPOSS hybrid membrane.

conductivity will increase with increasing water uptake because the mobility of hydronium ions in the water phase increases with increasing amount of water in the membrane.[4] Figure 6 presents the water uptake of the hybrid membranes as a function of sPOSS content. It can be seen that the water uptake increases only modestly with sPOSS content in the hybrid membrane. We attribute the slight increase in water uptake with sPOSS content to the increase in sulfonic acid groups, which has strong hydrophilicity, mediated by the competing hydrophobicity of sPOSS' isobutyl groups. These two characteristics of the sPOSS moiety act to offset each other so that the water uptake is not affected much by increasing the sPOSS content in the hybrid membranes.

To our surprise, a quite contrasting behavior was observed for IEC in the membranes. Figure 7 presents a plot of IEC of the hybrid membrane as a function of sPOSS content, where we observed that IEC increases linearly with increasing sPOSS content in the hybrid membranes. This trend coincides with the increase in proton conductivity with sPOSS content as shown in Fig. 4. These results indicate that

sPOSS contributes to proton conduction due to the increase in the sulfonic acid groups as a proton donor and carrier in the membrane. It should be noted further that the experimental values of IEC are comparable to the theoretical values (calculated based on composition and assuming complete protonation of sulfonate groups), which implies that sPOSS takes part in the PVA network by the reaction of hydroxyl groups of sPOSS with anhydride groups of EDTAD. Had sPOSS not been integrated in the network, extraction of it would have occurred during the DMSO extraction prior to IEC measurement, leading to an IEC value significantly lower than that based on composition.

Methanol permeability

In addition to their attractive proton conductivity values, the sPOSS-containing membranes also feature attractive methanol barrier properties. Figure 8 reveals the methanol permeability of the hybrid membrane as a function of sPOSS content. For a comparison, methanol permeability of Nafion 117 was measured under the same experimental conditions, yielding a value of $1.83 \times 10^{-6}\,cm^2/sec$, in good agreement with the value reported in the literature.[17] For the PVA/ sPOSS hybrid membranes, the methanol permeability is observed to decrease significantly with increase in sPOSS content. Thus, sPOSS content plays a key role in lowering methanol permeability, indicating that the sPOSS moieties may interfere with methanol permeation in some manner, while facilitating proton transport through the sulfonic acid groups. As mentioned above, the methanol permeability of Nafion 117 was also measured in an identical fashion for comparison and is shown by a broken line in Fig. 8. Clearly, the methanol permeability values of the PVA/sPOSS hybrid membranes are much lower than that of Nafion 117, indeed about one order of magnitude lower.

Thermal stability

Thermal stability of the PVA/sPOSS hybrid membranes was assessed using thermogravimetric analysis. TGA curves obtained for the series of membranes with increasing sPOSS content (under flowing nitrogen) are shown in Fig. 9. It can be

Figure 7. IEC versus sPOSS content of the crosslinked PVA/ sPOSS hybrid membrane.
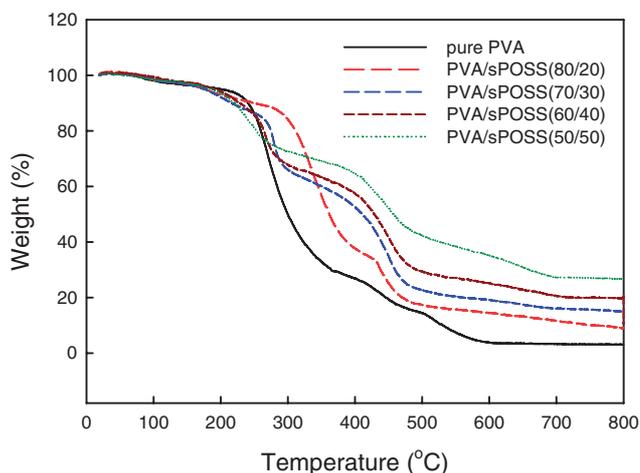
Figure 9. TGA curves of the PVA/sPOSS hybrid membranes.

seen that the first, minor, weight loss event occurs just above 100°C for all the samples in a nearly identical fashion. This weight loss is attributed to the loss of absorbed water molecules. Decomposition of the materials is similar for all samples, showing multistep decomposition events at temperatures near 280, 450, and 650°C. We speculated that these events involve loss of isobutyl groups, backbone fragments, and finally sintering of the ceramic char, respectively. In contrast, PVA completes most of its degradation, presumably via backbone fragmentation, over the broad range $250 < T_{dec} < 400$°C.[24] Interestingly, the PVA/sPOSS (80/20) hybrid membrane exhibits a distinct behavior from both PVA and the higher sPOSS-content materials. In particular, it does not commence significant decomposition until $T > 300$°C, above which temperature the hybrid material behaves similar to the other sPOSS materials. The decomposition behavior of the PVA/sPOSS hybrids is complex and deserves further study.

CONCLUSIONS

We have developed a method for the preparation of organic/inorganic hybrid membranes based on PVA and sulfonated POSS (sPOSS). This simple method involved solution blending of PVA and sPOSS, followed by crosslinking with EDTAD. We found attractive properties for the membranes thus formed: the proton conductivity increased while methanol permeability decreased with increase in sPOSS content in the hybrid membranes. More specifically, the proton conductivity of the PVA/sPOSS hybrid membranes increased with sPOSS content, reaching 0.042 S/cm when the sPOSS content is 50 wt% in the hybrid, more than double that of Nafion 117. Furthermore, the methanol permeability of the membranes decreased with increasing sPOSS content, reaching a value about one order of magnitude lower than Nafion 117 for the hybrid containing sPOSS 50 wt%. TGA analysis revealed that the hybrid membranes showed improved thermal stability as compared to pristine PVA, especially for the intermediate sPOSS level in the hybrid.

Collectively, our results indicate that crosslinked PVA/sPOSS hybrid membranes offer great potential for use as PEMs in DMFC applications.

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