

Methanol Permeability and Proton Conductivity of Direct Methanol Fuel Cell Membranes Based on Sulfonated Poly(vinyl alcohol)-Layered Silicate Nanocomposites

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ABSTRACT: Layered silicate nanocomposite membranes to be used as electrolyte polymeric membranes in a direct methanol fuel cell were prepared through the mixing of poly(vinyl alcohol) (PVA) with various amounts (2, 4, and 5% w/w) of sodium montmorillonite layered silicate nanoclay. The proton conductivity of the polymer was induced by the reaction of the polymer with sulfosuccinic acid. After that, a solution of the sulfonated PVA-layered silicate nanocomposite was cast into membranes. The proton conductivity and methanol permeability of the membranes were determined with a four-point probe technique and a gas chromatography technique, respectively. In addition, structures of the nanocomposite membranes were characterized with X-ray diffraction, differential scanning calorimetry, and Fourier transform infrared techniques. The

mechanical properties of the nanocomposite membranes were also determined with a universal testing machine. From the results, it was found that the water uptake, proton conductivity, and methanol permeability of the membranes initially decreased after a 2% (w/w) concentration of the layered silicate was added. Above this nanoclay loading, the water uptake of the membranes increased again. The results were examined in the light of the interaction between the clay and sulfonated polymer, and the steric effect provided the exfoliation of the nanoclay. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 452–458, 2008

Key words: ionomers; membranes; nanocomposites; poly-electrolytes

INTRODUCTION

There has been considerable interest in the development of new electrolyte polymeric membranes to be used as replacements for the commercial Nafion membrane in direct methanol fuel cells (DMFCs). This is because the price of the Nafion membrane is considerable and the methanol resistance of the membrane is rather poor. In this respect, various types of polymeric membranes have been developed, and these can be divided into three main categories, that is, perfluorinated polymeric membranes,¹ partially fluorinated polymeric membranes,² and hydrocarbon polymeric membranes.³ Our current research interest in this field concerns the development of proton-exchange membranes for DMFCs from hydrocarbon polymers such as poly(vinyl alcohol) (PVA). The development of a PVA membrane for DMFC applications is of interest because the polymer is

inexpensive and has been used to separate alcohol from water in a pervaporization process.⁴ Furthermore, proton conductivity in PVA membranes can be induced by modification of the chemical structure of the polymer through sulfonation.⁵ In our earlier studies,^{6,7} however, it was found that the methanol permeability and mechanical properties of sulfonated PVA membranes needed to be improved. This was partly attributed to the quite high water uptake values of sulfonated PVA membranes.

In this respect, we believed that by the addition of some nanofillers such as layered silicates into the membranes, some improvements in the methanol permeability and mechanical properties of the nanocomposite membranes could be expected. In fact, the effects of layered silicate nanoclay on methanol permeability in some other polymeric membranes have been studied. For example, by the addition of only 1% sodium montmorillonite nanoclay to Nafion, it was found that methanol crossover through the membrane decreased.⁸ Similarly, properties of PVA-phosphotungstic acid (PWA) composite membranes filled with sodium montmorillonite (CloisiteNa) were studied.⁹ In this case, PWA, which is a kind of heteropolyacid, was used to induce proton conductivity in PVA membranes. CloisiteNa was also added to enhance the methanol resistance of the mem-

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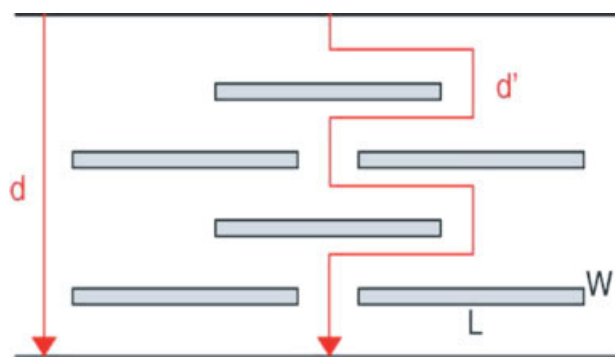


Figure 1 Schematic view of the tortuous pathway. d' is the actual distance that a penetrant must travel, d is the shortest distance that it would have traveled in the absence of the filler, and L and W are the length and thickness of the silicate layers, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

branes. The CloisiteNa nanoclay was mixed with PVA without conversion of the layered silicate into an organic clay because both materials are highly hydrophilic and tend to be compatible. Therefore, an intercalation of the layered silicate in PVA might be expected. The results from that study showed that methanol crossover through the membranes decreased remarkably at the expense of the proton conductivity. The optimum CloisiteNa content corresponding to the maximum proton conductivity/methanol permeability (C/P) ratio for the aforementioned membrane system was 7%. In this respect, an improvement in the methanol resistance of the layered silicate nanocomposite membranes was explained in the light of the formation of a tortuous pathway (Fig. 1), which provided an exfoliation structure of the nanocomposite.

This research work concerns the development of DMFC membranes from PVA-layered silicate nanocomposites. In this study, rather than mixing the polymer with some solid acids, we induced proton conductivity in PVA membranes by modifying the molecular structure of the polymer via sulfonation. The objective of this research work was to investigate the effects of the layered silicate content on the methanol permeability, water uptake, proton conductivity, and mechanical properties of the membranes. Moreover, rather than using fully hydrolyzed PVA (99.5% degree of hydrolysis) to prepare the membranes, this study employed partially hydrolyzed PVA (88% hydrolysis and 12% vinyl acetate). It was believed that by the use of PVA with a lower degree of hydrolysis, the hydrophilicity of the polymer would be reduced, and thus the mechanical properties of the hydrate membrane would be better.

EXPERIMENTAL

Chemicals

Partially hydrolyzed atactic PVA (88% hydrolysis, weight-average molecular weight = 72,000 g/mol) was obtained from Fluka. Sodium montmorillonite nanoclay (CloisiteNa) was supplied by Southern Clay Products (Gonzales, TX). Sulfosuccinic acid (70% solution; Aldrich, Steinheim, Germany), NaOH (analytical-reagent grade; LabScan, Gliwice, Poland), sodium chloride (analytical-reagent grade; Carlo Erba Reagenti, Rodano, Italy), and methanol (analytical-reagent grade; Fisher, Loughborough, UK) were used as received.

Sulfonation of PVA and preparation of the sulfonated PVA membranes

A given amount of layered silicate (CloisiteNa) was dissolved in deionized water and then mixed with an aqueous PVA solution (10% w/w). The CloisiteNa contents used in this study were 2, 4, and 5 wt % with respect to the polymer. The mixture was stirred and refluxed at 90°C for 6 h to obtain a homogeneous solution. Sulfonation of PVA was carried out by the addition of sulfosuccinic acid (20% w/w with respect to PVA) to the solution, and then the mixture was stirred at room temperature for 24 h. Of note, a sulfonated PVA membrane with a higher degree of sulfonation could be prepared by the use of more sulfosuccinic acid, but the obtained polymer would be very brittle and useless for membrane applications. Therefore, partially sulfonated PVA prepared with 20% sulfosuccinic acid was used in this study.

After the sulfonation was carried out for a given time, the solution was cast onto acrylic sheets ($5 \times 5 \text{ cm}^2$) and then dried in a thermostat oven at 60°C for 12 h. Finally, the dried membranes were further heated at 120°C for 1 h to complete the sulfonation and crosslinking reaction. Next, the membranes were peeled off from the acrylic sheets, and then the membranes were rinsed with deionized water to remove some residual acid. Finally, the composite membranes were stored in deionized water before being tested with respect to their ion-exchange capacity (IEC), conductivity, and methanol permeability.

Characterization

Changes in the chemical structure of PVA after the sulfonation were followed with the Fourier transform infrared (FTIR) spectrometer technique with a PerkinElmer (Waltham, MA) Spectrum One instrument. The sample was prepared in the form of a thin film. The spectrum was recorded over wave numbers ranging from 4000 to 650 cm^{-1} .

Intercalation and exfoliation of the nanoclay in the PVA membrane were investigated with an X-ray diffraction (XRD) technique with a D8 Discover diffractometer from Bruker (Madison, WI) Axis. The operation was in the θ - θ geometry. The instrument used radiation from a copper target tube (Cu $K\alpha$ radiation wavelength = 1.541 Å). The XRD data were collected between 2 and 60° in steps of 0.02° with an X-ray generator.

The thermal properties of the membranes were examined with the differential scanning calorimetry (DSC) technique. The DSC experiment was carried out with a Netzsch (Bavaria, Germany) DSC 240F1 instrument under a nitrogen atmosphere at a scanning rate of 10°C/min over temperatures ranging from 10 to 350°C.

Water uptake

Water uptake values of various membranes were measured by the immersion of the membranes in deionized water at 25°C for 24 h. After that, the water-swollen membranes were taken out, wiped with tissue paper, and immediately weighed. The water uptake (W) was then calculated with the following equation:

$$W(\%) = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100 \quad (1)$$

where W_{dry} and W_{wet} are the weights of the dry and water-swollen membranes, respectively.

IEC

IEC of the membrane was measured with a titration technique. About 0.3–0.5 g of the sample was immersed in a 0.1M NaCl solution for 24 h to allow the exchange process between protons and sodium cations. After that, the solution was titrated with an aqueous NaOH solution (0.1M) to determine the amount of HCl generated by the exchange process. From the titration, the IEC value was then calculated with the following equation:

$$\text{IEC} = M_{\text{NaOH}}/W_{\text{dry}} \quad (2)$$

where M_{NaOH} is the molar equivalent (mequiv) of NaOH and W_{dry} is the weight of the dry membrane.

Proton conductivity

Proton conductivities of the composite sulfonated PVA membranes were measured with a four-point probe technique (Fig. 2). The impedance of the membrane was measured with an impedance analyzer (PGSTAT 30, Autolab, Westbury, NY) at a frequency of 10 kHz. The membrane was cut into a 3 × 3 cm² square and immersed in deionized water for 12 h

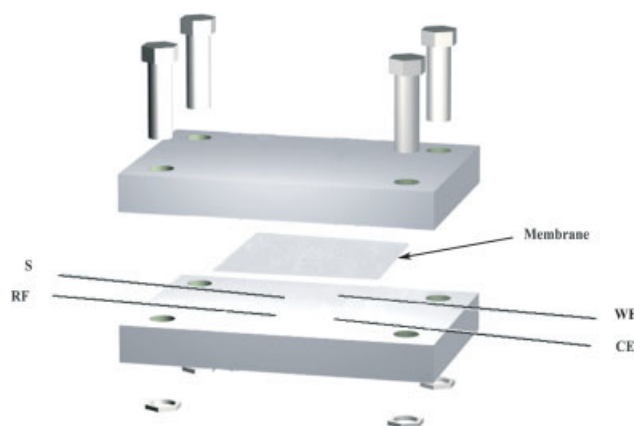


Figure 2 Schematic view of the four-point probe cell used for the measurement of the proton conductivity. WE is the working electrode, CE is the counter electrode, S is the ground, and RF is the reference electrode. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

before the measurement. The hydrated membrane was mounted onto the cell, and an alternating current of 0.35 mA was applied to the cell. The conductance of the sample was obtained from the alternating-current potential difference between the two inner electrodes. The conductivity was calculated with the following equation:

$$\sigma = l/RS \quad (3)$$

where σ is the proton conductivity (S/cm), R is the bulk resistance of the membrane, S is the cross-sectional area of the membrane (cm²), and l is the distance between the counter electrode and the working electrode (cm).

Methanol permeability

Resistance to methanol crossover of the membranes was evaluated by the measurement of the methanol permeability in the membranes with a diffusion cell and a gas chromatography (GC) technique. The membrane was placed between the two compartments in the diffusion cell (Fig. 3) and then clamped. After that, 20 mL of a methanol solution (2M) and 20 mL of deionized water were placed in compartments A and B of the cell, respectively. Both compartments were magnetically stirred at room temperature during the permeation experiments. The concentration of methanol in compartment B was measured as a function of the diffusion time with a GC technique (GC-9A containing a BX-10 column, Shimadzu, Haverhill, MA). The injection temperature, column temperature, and detection temperature used for the GC experiment were 120, 85, and 150°C, respectively. The area under the methanol peak from each GC chromatogram was used in combination

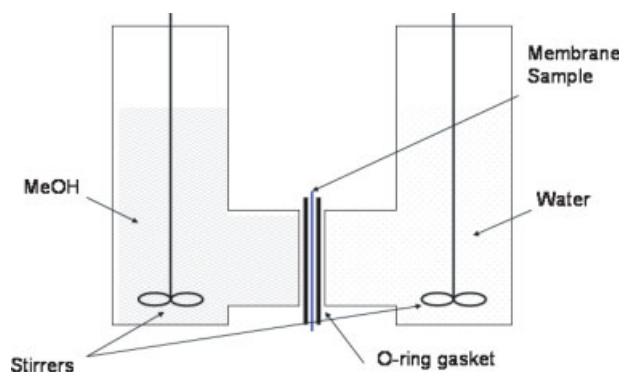


Figure 3 Schematic view of a diffusion cell used for the measurement of methanol permeability in a membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with a calibration curve to determine the methanol concentration. Finally, the methanol permeability was calculated from the slope of the plot between the methanol concentration and diffusion time with the following equation:

$$C_B(t) = A(DK)C_A(t - t_0)/V_B L \quad (4)$$

where C_A and C_B are the concentrations of methanol in compartments A and B, t is diffusion times, t_0 is zero diffusion time (at beginning), and V_A and V_B are the volumes of liquids in compartments A and B, respectively. A and L are the area and thickness of the membrane, and D and K are the methanol diffusivity and partition coefficient, respectively. The product of DK is the membrane permeability.

Tensile testing

Mechanical properties of the various membranes were determined from their tensile properties. Samples for the tensile test were prepared by the membranes being cut into dumbbell-shape specimens in accordance with ASTM D 882-02. The tensile test was performed with a 5-ton tensiometer (universal tensile testing machine, PerkinElmer) at a crosshead speed of 10 mm/min at room temperature (25°C). At least five specimens were tested for each sample, and the average values of the tensile strength and tensile elongation at break were reported.

RESULTS AND DISCUSSION

Characterization

Figure 4 shows overlaid FTIR spectra of the pure PVA membranes both before and after the sulfonation. Some new absorption peaks occurred after the chemical reaction, including the peaks at 1216 and 1034 cm^{-1} . These peaks could be ascribed to the S=O (symmetric stretching) bonds and S=O (asym-

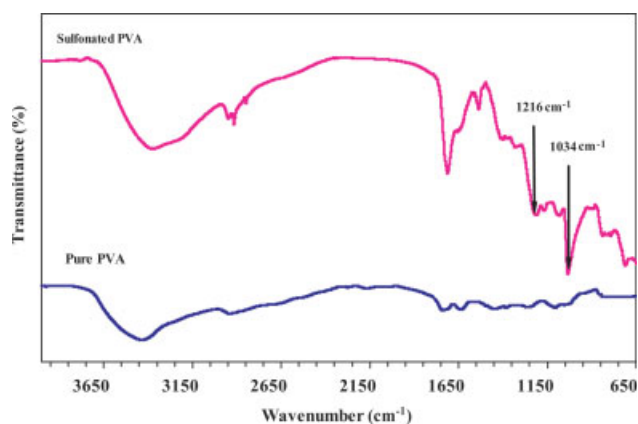


Figure 4 Overlaid FTIR spectra of PVA before and after sulfonation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

metric stretching) bonds, respectively. The results suggest that PVA was sulfonated. Figure 5 shows overlaid XRD patterns of various membranes including the pure PVA, the nanoclay (CloisiteNa), and the nanocomposite membranes with a variety of clay contents (2, 4, and 5% w/w). The XRD pattern of CloisiteNa shows a peak at $2\theta = 7.5^\circ$ corresponding to a basal spacing of 1.18 for the nanoclay.⁹ This peak disappeared after CloisiteNa was mixed with the polymer, regardless of the nanoclay content. These results suggest that the layered silicates are exfoliated in the nanocomposite membrane. In addition, a small peak at $2\theta = 2.92^\circ$, which corresponds to a spacing of about 3.02 nm, can be observed in all XRD patterns of the nanocomposite membranes. This result implies that intercalation also occurred in the composite membranes.

Properties of the membranes

Figure 6 shows the effect of the CloisiteNa content on the water uptake of the sulfonated PVA mem-

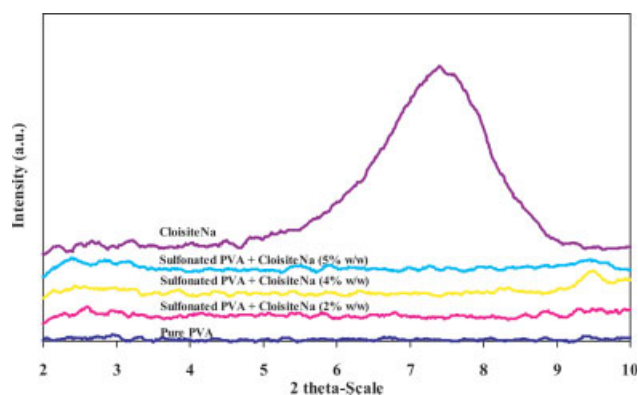


Figure 5 XRD patterns of the sulfonated PVA membranes filled with various contents of CloisiteNa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

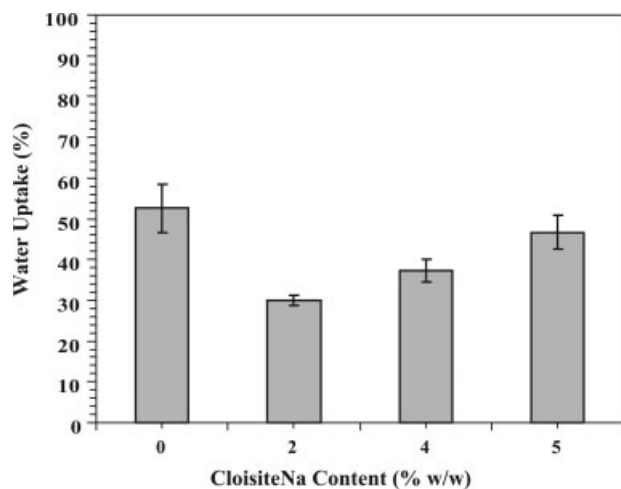


Figure 6 Changes in the water uptake values of the nanocomposite membranes with the CloisiteNa content.

branes. The relationship between the nanoclay content and the water uptake is not a linear function. When 2% (w/w) CloisiteNa clay was added, the water uptake of the membrane initially decreased. A similar effect was also observed in PVA–PVA composite membranes filled with 3–7% CloisiteNa.⁹ We concluded that this effect could be partly attributed to a weaker affinity for water of CloisiteNa versus that of sulfonated PVA. In addition, it was believed that oxygen atoms and hydroxyl groups of the CloisiteNa nanoclay might have been capable of interacting with the hydroxyl-functional groups in the PVA molecules. A similar interaction was observed by Wang et al.¹⁰ for a chitosan–montmorillonite nanocomposite. As a result of the aforementioned polar–polar interaction, the mobility of the sulfonated PVA

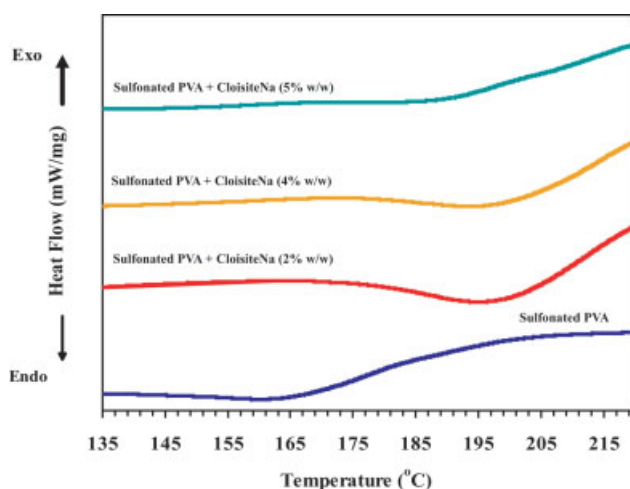


Figure 7 DSC curves of the sulfonated PVA membranes filled with various amounts of CloisiteNa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

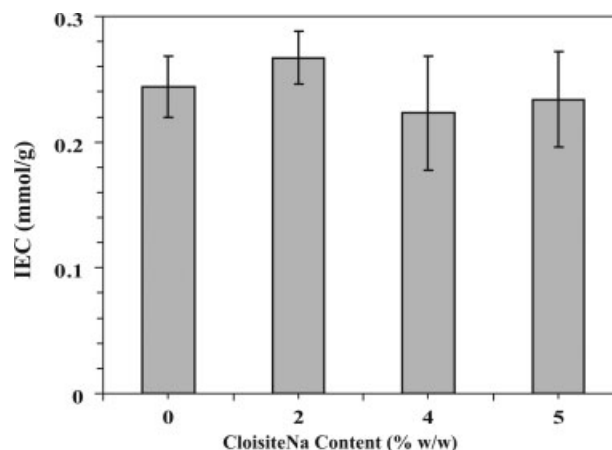


Figure 8 IEC values of the sulfonated PVA membranes filled with various contents of CloisiteNa.

molecules was restricted, and the amount of water uptake within the membrane could be reduced.

In contrast, as the CloisiteNa content was further increased from 2 to 4 and 5% (w/w), the water uptake value tended to increase again. This could be related to the changes in the degree of crystallinity of PVA with the Cloisite content. DSC thermograms of various membranes (Fig. 7) show that the area under an endothermic peak at 195°C, corresponding to the melting transition of the polymer, tended to decrease with the CloisiteNa content. This trend suggests that the degree of crystallinity of PVA decreased with the clay content. A similar effect was also observed by Strawhecker and Manias¹¹ in a study on PVA–montmorillonite nanocomposites.

Figure 8 shows that the IEC values of the nanocomposite membranes hardly changed with the amount of CloisiteNa when standard deviation values were taken into account. This could be due to the fact that the ion-exchange groups are the sulfonic acids that reside in the polymer molecule and remain constant, regardless of the layered silicate nanoclay content. It is noteworthy that the IEC values of these nanocomposite membranes are considerably lower than that of the Nafion membrane reported in the literature (0.91 mmol/g).¹² The differences are attributed to the fact that our PVA membranes were only partially sulfonated as a compromise between the mechanical properties and proton conductivity of the membranes.

Figure 9 shows that the proton conductivity of the sulfonated PVA membranes initially decreased when a 2% (w/w) loading of the CloisiteNa nanoclay was added. Above a 2% (w/w) CloisiteNa loading, the proton conductivity of the membranes did not further decrease but tended to increase with the clay concentration. In this respect, the changes in the proton conductivity of the membranes with the nano-

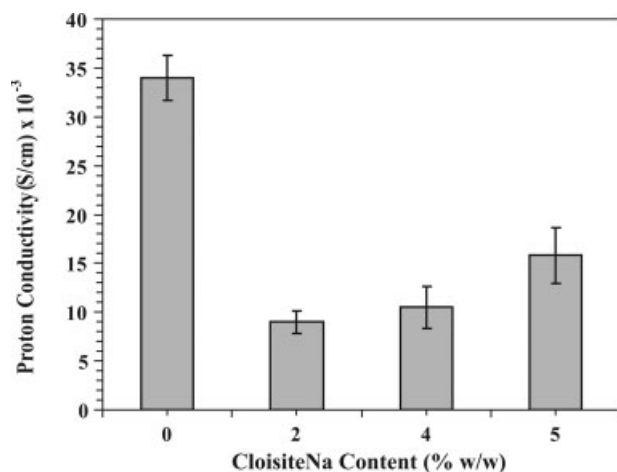


Figure 9 Changes in the proton conductivity values of the nanocomposite membranes with the CloisiteNa content.

clay content could be related to the changes in the water uptake values. This is because the water molecules serve as vehicles, promoting the transportation of protons through the membrane.¹³ Therefore, the higher the water content is, the greater the proton conductivity is of the membrane. It is worth mentioning that proton conductivity values of the aforementioned nanocomposite membranes are comparable to that of the commercial Nafion 115 membrane (10×10^{-3} S/cm) when measured with the same instrument and under the same conditions.

In terms of the methanol resistance of the membranes, it was found that methanol permeability through the nanocomposite membranes rapidly decreased by 1 order of magnitude after a 2% (w/w) concentration of the layered silicate nanoclay (CloisiteNa) was added (Fig. 10). However, when the layered silicate content was further increased above 2% (w/w), the methanol permeability values did not

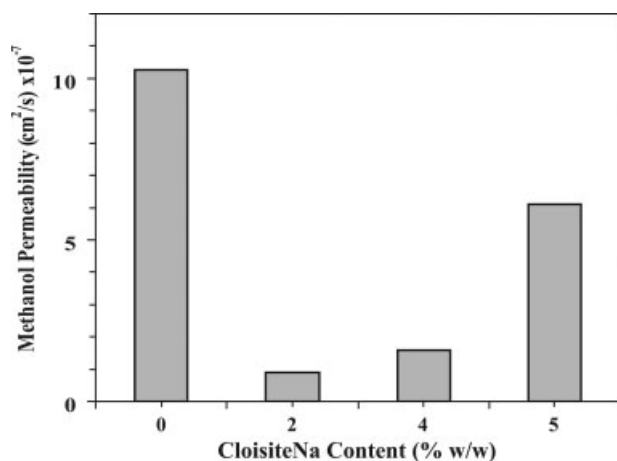


Figure 10 Changes in the methanol permeability values of the nanocomposite membranes with the CloisiteNa content.

decrease but tended to increase. In this respect, the changes in the methanol permeability of the membranes could be attributed to many factors, including the changes in the water uptake of the membranes and a steric effect provided by the layered silicate nanoclay (see Fig. 1). The change in the methanol permeability in the membrane is in good agreement with the changes in the water uptake with the CloisiteNa content (Fig. 6). This is due to the fact that the methanol solution used for the diffusion test is a kind of aqueous solution. Therefore, the higher the water uptake is, the greater the methanol solubility is in the membrane. Consequently, methanol permeability, which is the product of methanol solubility and methanol diffusability, decreased with the CloisiteNa content. Furthermore, the effect of the layered silicate nanoclay on the tortuosity and diffusion path of methanol through the nanocomposite membranes should also be taken into account. In this study, it was possible for the tortuous pathway of methanol diffusion in the membrane to be obtained after 2% (w/w) CloisiteNa was added. As a result, methanol permeability in the membrane decreased. However, as the CloisiteNa content in the membrane was further increased, it could be observed by the naked eye that the nanoclay was agglomerated. Therefore, the layered silicate nanoclay might not be well dispersed in the membrane, and the tortuous pathway might not be evenly dispersed throughout the membrane. In this respect, a further decrease in methanol crossover with the CloisiteNa content should not be expected.

From the aforementioned proton conductivity and methanol permeability values, the C/P ratios of the various nanocomposite membranes were evaluated (Fig. 11). The best membrane with respect to the maximum C/P ratio obtained from this study is that containing 2% (w/w) CloisiteNa nanoclay. The C/P

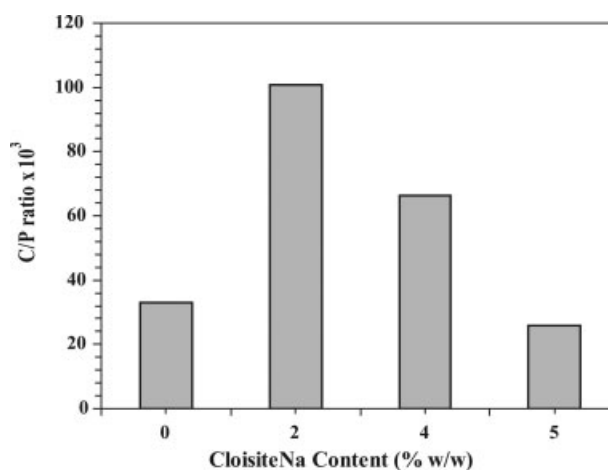


Figure 11 C/P ratios of various nanocomposite membranes.

TABLE I
Mechanical Properties of the Sulfonated PVA Membranes
With and Without CloisiteNa

Sample	Tensile strength (MPa)	Elongation at break (%)
Sulfonated PVA membrane	9.40 (\pm 1.29)	4.95 (\pm 0.49)
Sulfonated PVA + CloisiteNa (2% w/w)	25.63 (\pm 3.53)	13.15 (\pm 0.93)
Sulfonated PVA + CloisiteNa (4% w/w)	19.25 (\pm 2.86)	35.78 (\pm 0.55)

ratio of this membrane (100.79×10^3) is also higher than that of the commercial Nafion 115 membrane (29.49×10^3), whereas the proton conductivity values of the two membranes are comparable. These results suggest that the nanocomposite membrane with 2% (w/w) CloisiteNa might be used as a replacement for the Nafion membrane in DMFC applications.

Finally, the mechanical properties of the aforementioned nanocomposite membranes deserve consideration. Table I compares the tensile properties of the nanocomposite membranes (2 and 4% w/w CloisiteNa) with those of the pure sulfonated PVA membrane. No further attempt was made to determine the mechanical properties of the membrane containing 5% (w/w) nanoclay because of the relatively low *C/P* ratio of the material. From Table I, it was found that the tensile strength of the membrane increased remarkably after the nanoclay was added. This might have been due to a strong interaction between CloisiteNa and the sulfonated PVA, which led to the reinforcing effect. The elongation value of the membranes also increased with the clay content, and that could be related to the decrease in the crystallinity of the polymer with the layered silicate (Fig. 7). Again, from the aforementioned *C/P* ratio and the tensile properties, it seems that the best nanocomposite membrane from this study is that obtained through the mixing of sulfonated PVA with 2% (w/w) sodium montmorillonite nanoclay (CloisiteNa).

CONCLUSIONS

The incorporation of the sodium montmorillonite nanoclay into sulfonated PVA strongly affected the properties of the nanocomposite membranes. The

water uptake, proton conductivity, and methanol permeability of the membranes initially decreased with the nanoclay loading and then increased again upon further addition of the nanoclay. The results might be related to the interaction between sodium montmorillonite and PVA, exfoliation of the nanoclay in the polymer composite, and changes in the degree of crystallinity of the polymer with the nanoclay content. The optimum level of layered silicate sodium montmorillonite at which the maximum *C/P* ratio of the nanocomposite membrane was obtained was 2% (w/w).

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