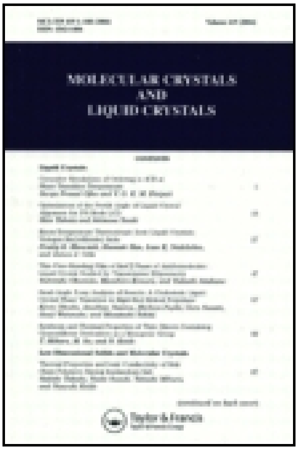

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NANOCOMPOSITE POLYMER MEMBRANE BASED ON CATION EXCHANGE POLYMER AND NANO-DISPERSED CLAY SHEETS

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Nafion/organo-clay nanocomposite membranes were prepared by solution intercalation technique in order to reduce methanol permeability while maintaining essential proton conductivity. Featureless XRD patterns of nanocomposite indicated that organically treated clay particles were completely disordered and exfoliated in continuous Nafion matrix at clay loading less than 10 wt%. TEMicrographs also revealed that nanolayers of clay are well delaminated in Nafion matrix. In addition, thermal degradation and glass transition temperature were slightly shifted to higher temperature due to strong adhesion of Nafion chains on organo-clays. It was observed that methanol permeability of Nafion 117 (~180 μm) was ca. $2.3 \times 10^{-6}\,cm^2/s$ *while that of Nafion/organo-clay nanocomposite membrane (~50 μm) decreased down to* $1.6 \times 10^{-7}\,cm^2/s$ *only by 1 wt% clay loading, without apparent conductivity loss. This improvement might result from greater affinity of nanocomposite membrane for water over methanol.*

Keywords: DMFC; methanol crossover; Nafion®; nanocomposite; organo-clay

1. INTRODUCTION

Direct methanol fuel cell (DMFC) has received much attention as an alternative power source for portable electronics as well as transportation

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application because of their high efficiency, very low emissions, and fast and convenient refueling [1]. There are still two major obstacles to their large-scale commercial use, namely, limited anode catalyst activity and methanol crossover through ionomer membrane [2]. Methanol is much more difficult to be oxidized, compared with pure hydrogen, but the activity of anode catalyst can be promoted partly by use of state-of-the art bimetal catalysts such as Pt–Ru and Pb–Sn [3].

However, perfluorosulfonic acid (PFSA) ionomer membranes, represented by Nafion®, exclusively used in DMFC systems are not sufficient to be an efficient barrier for methanol permeation [4]. The large methanol crossover not only reduces fuel efficiency but also increases the overpotential of cathode, thus drastically lowering cell performances. As a result, most DMFC systems show relatively lower power density than hydrogen fuel cells. It is, therefore, required to find an ionomer membrane with better methanol selectivity. In these respects, a number of reports have been given lately on various composite ionomers that are resistant to methanol permeation.

Pu *et al.* proposed a methanol impermeable composite membrane in which thin palladium (Pd) foil was sandwiched between two layers of Nafion 115 [5]. It was also reported that plasma polymerized barrier or sputtered Pd layer on Nafion membrane decreased its pore diameter and increased the methanol permeation length [6]. Scott *et al.* prepared a composite membrane by radiation-graft copolymerization of ethylene monomers into ETFE [7]. Miyake *et al.* obtained Nafion/SiO_2 hybrid membrane via *in*-situ sol-gel reaction of tetraethylorthosilicate (TEOS) [8]. Other efforts include works on membranes of partially fluorinated polymer, non-fluorinated polymers and their combinations [9–11]. These modified membranes were found to be a good methanol barrier, but they either sacrifice the mechanical strength of the native Nafion film or cause the increase of membrane resistance [12].

To solve the intermixed problems, we prepared a nanocomposite membrane in which organically treated montmorillonite (MMT) clay particles are nano-dispersed in Nafion matrix. It is well known that when the clay particles are completely and individually dispersed (exfoliated and delaminated) in a continuous polymer matrix, their extremely high aspect ratio and huge interfacial area make it possible to improve all aspects of mechanical properties of nanocomposite even at limited loadings of less than 5 wt% clay, compared to the neat polymer resin and conventional phase-separated composite [13]. Furthermore, the impermeable clay layers could mandate a tortuous pathway of gaseous or liquid permeants to transverse the nanocomposite membrane [14].

Considering the difficulties of intercalating polymer chains into clays with a small interlayer distance, many research efforts have been made to hydrophobically modify the clays by inserting long chain surfactants into the galleries of the native clay. Thus, if Nafion/organo-clay nanocomposite presents proper hydrophobic-hydrophilic balance, it is expected to have high selectivity for water over methanol like pervaporation membranes used in ethanol dehydration to break the ethanol-water azeotrope [15]. This paper first reports the characterization of a nanocomposite of Nafion with organically modified montmorillonite (MMT) clay prepared by solution intercalation technique.

2. EXPERIMENTAL

Nafion gels were precipitated from commercial 5 wt% Nafion®/H_2O/prorpanol solution (Solution Technology, E.W. = 1100) by evaporating alcoholic solvents at room temperature under vacuum. After they were dissolved in N,N'-dimethylacetamide (Aldrich) at 80°C, Nafion/dimethylacetamide solution was ultrasonifically mixed with an organo-clay, montmorillonite (Cloisite® 10A). Then Nafion/clay membranes were cast on a glass substrate above 100°C in a drying oven. The recast membranes were boiled in 3% hydrogen peroxide and rinsed with deionised water. Finally, the composite films were boiled in 1 M sulfuric acid, followed by rinsing with deionised water several times in order to remove the excess of acid.

X-ray diffraction study were carried out with a Rigaku Rad-C 4037Al diffractometer in symmetrical reflection geometry using CuKα emission ($\lambda = 1.5406$ Å). Transmission Electron Microscopy (TEM) was obtained with JEM-100CX2 TEM using an acceleration voltage of 100 KV. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere from 30 to 700°C at a heating rate of 20°C/min by using a Perkin-Elmer TGA7. Glass transition behavior of composite samples was also monitored by dynamic mechanical analysis (DMA, TA Instruments Q800) under dynamic strain of 0.1% in a temperature range of 25–140°C at a frequency of 1 Hz and heating rate of 2°C/min.

The proton conductivity measurement (Zahner IM6 impedance analyzer) was conducted by a coaxial probe method [16]. Samples were stored in distilled water for adsorbing waters, and then wiped quickly and insert into a cell that allowed the coaxial probe to be pressed against one side of the fully hydrated membrane. Water content of the membrane is assumed to remain saturated during measurement over the frequency range 100 kHz to 10 MHz. The methanol permeability was measured by using the difference in reflective index (RI) between methanol and distilled water [17]. Each side of sample membrane was exposed to distilled water and 10 wt% methanol, respectively and R.I. meter detected the amount of methanol molecules at water compartment with time, as methanol penetrating across the membrane.

3. RESULTS AND DISCUSSION

XRD was used to identify intercalated structure of Nafion/organo-clay nanocomposite membranes. The intercalation of the polymer chains usually increases the interlayer spacing, compared with that of the pristine organo-clay. As far as exfoliated structure is concerned, no more diffraction peaks are visible in the XRD patterns either because of too large spacing between the layers or because the nanocomposite does not present ordering any [13]. Figure 1 shows XRD patterns of Nafion/organo-clay membranes at different clay loading. Even though montmorillonite clays displayed characteristic peak at $2\theta = 7°$, both recast Nafion membrane and Nafion/organo-clay nanocomposites showed featureless diffraction patterns in the region from $2\theta = 2$ to 10° until clay loading reached 20 wt%. This strongly implies that the entropy loss associated with polymer confinement that ordinarily inhibits intercalation was compensated by entropy gains associated with the layer separation [18], and organo-clay fillers were disordered and exfoliated in continuous Nafion matrix.

As given in Figure 2, 20 wt% Nafion/organo-clay nanocomposite showed the dark lines indicative of semi-exfoliated hybrids where small stacks of intercalated clay layers were embedded within a polymer matrix. When the filler content was around 10 wt%, there was no agglomerated clay tactoids because nanolayers of clay are well dispersed and delaminated in ionomer matrix and further exfoliation occurred. Accordingly, the size of

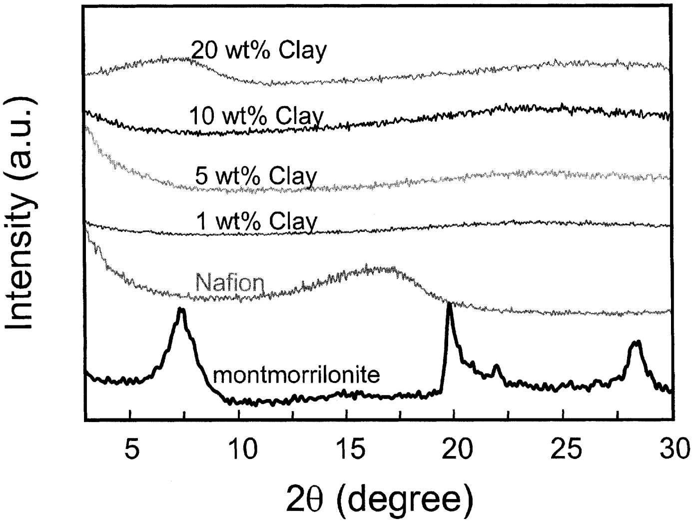

FIGURE 1 XRD patterns of Nafion/organo-clay nanocomposites.

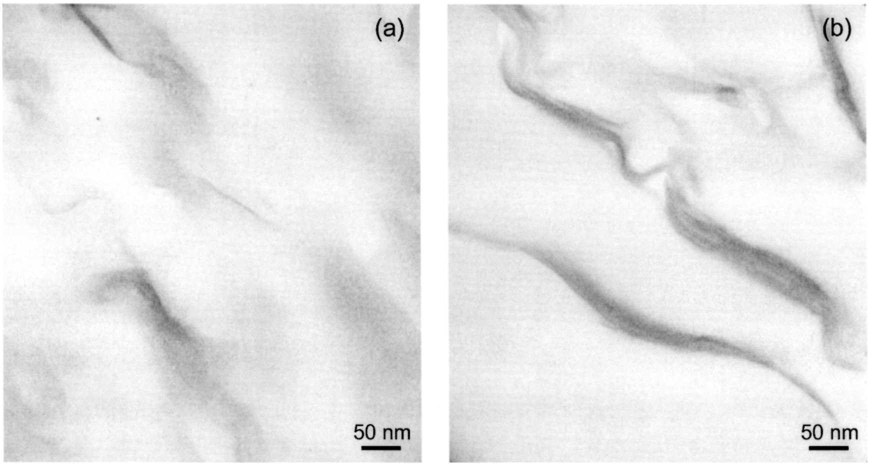

FIGURE 2 TEMicrographs of Nafion/clay nanocomposite: (a) 10 wt% clay and (b) 20 wt% clay.

clay-derived particles is almost an order of magnitude smaller than 20 wt% Nafion/organo-clay. The exfoliation of clay in Nafion resin might be attributed to the strong interaction between hydrophobic Nafion backbone and organophilic clay particles.

Figure 3(a) displays TGA thermograms of Nafion/organo-clay nanocomposite at different clay loading. Unmodified Nafion resin showed a nominal weight loss in the 300–350°C regions, which is suggested to be associated with the loss of sulfuric acid moeity [19], and the following weight loss was influenced by the decomposition of fluorocarbon backbone of Nafion along with -SO_3H groups. For nanocomposite samples, all profiles showed a shift toward higher temperature, and the onset of degradation temperature was slightly improved by about 20°C at a filler concentration 5 wt%. It is usually well accepted that the improved thermal stability for polymer-layered silicates is mainly due to the formation of char that hinders the out-diffusion of the volatile decomposition product, as a direct result of the decrease in permeability, usually observed in exfoliated nanocomposite systems [20]. Figure 3(b) illustrates the loss factor (tan δ) for Nafion/organo-clay nanocomposites with temperature. The intense peak at 107°C for neat Nafion film corresponds to main glass transition owing to mobilization of amorphous domains while the glass transition temperature (T_g) of Nafion/organo-clay nanocomposite was shifted to higher temperature. This might be related to strong adhesion between two components.

Figure 4 shows the changes in methanol permeability of Nafion/organo-clay nanocomposites at different loading. The methanol concentration of

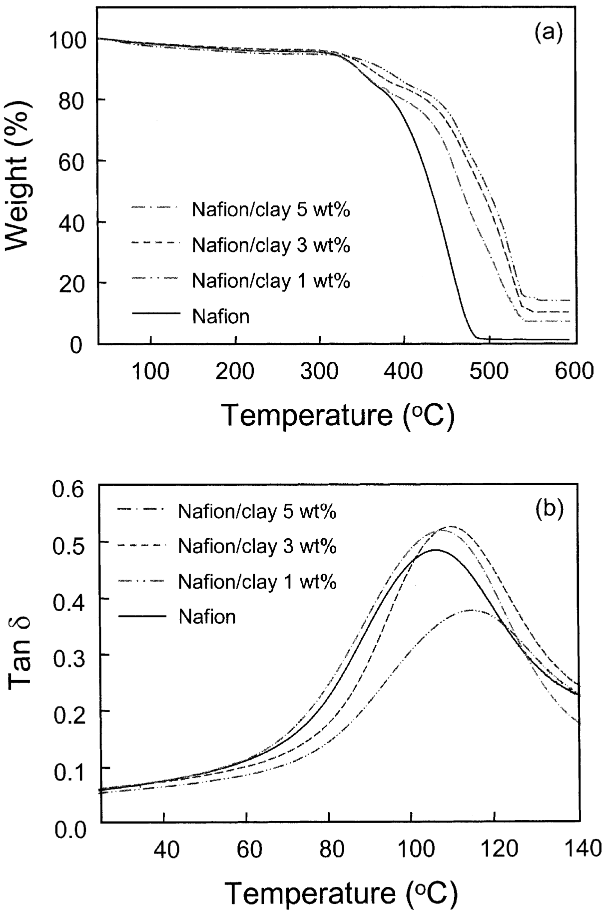

FIGURE 3 Thermal analysis of Nafion/organo-clay nanocomposites at different clay loading: (a) TGA and (b) DMA.

pure water side was monitored with time and the permeability was calculated from the slope of the concentration vs. time curves, i.e. methanol flux. As shown in Figure 4, the methanol permeability of recast Nafion 117 was about $2.3 \times 10^{-6}\,\mathrm{cm^2/s}$ and it is in good agreement with the literatures [21]. On the other hand, the methanol crossover in Nafion/organo-clay nanocomposite significantly decreased by only 1 wt% organoclay fillers, which amounted to more than 90% reduction. It seems that the impermeable clay layers mandate a tortuous zigzag diffusion pathway for methanol to transverse the membrane. It can be noted that the methanol flux through Nafion/organo-clay nanocomposites became much less sensitive to film thickness.

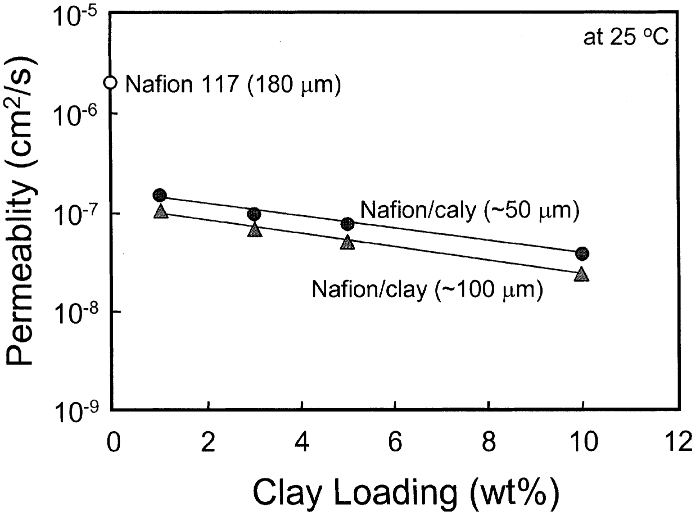

FIGURE 4 Methanol permeability of Nafion/organo-clay nanocomposite membranes.

Figure 5 shows the proton conductivities of Nafion/organo-clay nanocomposite membranes. The proton conductivity was estimated by impedance spectra using coaxial probe method. The coaxial probe is defined that when the thickness of membrane (h) is small compared to the gap size

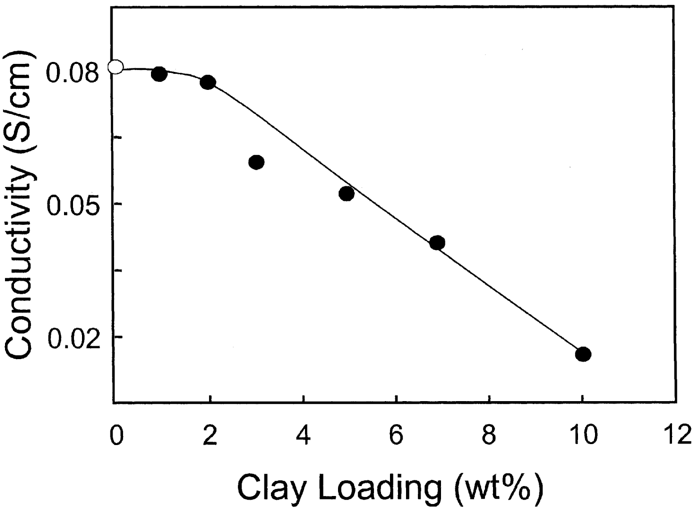

FIGURE 5 Proton conductivity of Nafion/organo-clay nanocomposite membranes.

$(b - a)$ as well as the skin depth (δ), the current distribution across the membrane can be considered to be uniform and the membrane characterized by a surface resistivity (R_s) is defined by $R_s = 1/\sigma h$. The value of R_s was determined from high frequency intercept on the real axis in complex impedance spectra. Then, the measured resistance, R_T, is obtained by carrying out the integration [16]:

$$R_T = \int_a^b \frac{R_s}{2\pi r} dr = \frac{R_s}{2\pi} \ln(b/a)$$

The conductivity of the membrane is related to the measured resistance by the following expression:

$$\sigma = \frac{1}{2\pi R_T h} \ln(b/a)$$

All sample membranes were equilibrated with water at ambient temperature for three days prior to conductivity measurement. As shown in Figure 5, the proton conductivity of unmodified Nafion 117 membrane reached about 0.082 S/cm at room temperature. For Nafion/organo-clay nanocomposite membranes, the conductivity was almost similar to neat Nafion below clay loading of 2 wt% and then decreased gradually with the increase in hydrophobic filler content. However, 2 wt% organo-clay is good enough to minimize methanol permeation in Nafion/organo-clay nanocomposite even at limited thickness, and exfoliated organo-clays generally provide the composite structure with mechanical integrity and dimensional stability. Thus, if the composition is optimized below 2 wt% in the near future, it is possible to obtain the best compromise between proton conductivity and methanol barrrier property.

4. CONCLUSIONS

Nafion/organo-clay nanocomposite membranes were prepared by simple solution intercalation. The exfoliation of organo-clay was captured in featureless X-ray diffraction patterns. TEM study also confirmed that organo-clay were nano-dispersed in continuous Nafion matrix upto 10 wt% clay loading. TGA thermograms showed that the thermal stability of nanocomposites was improved by about 20°C when the clay loading was 5 wt%. In addition, the strong adhesion between Nafion matrix and clay fillers resulted in Tg shift toward higher temperature (~8°C).

Methanol crossover through Nafion/organo-clay nanocomposite membranes significantly decreased by only 1 wt% organoclay fillers, and it became much less sensitive to film thickness compared with neat Nafion membrane because the impermeable clay layers mandated a tortuous zigzag diffusion pathway for a permeant to transverse the nanocomposite. When clay loading was less than 2 wt%, the proton conductivity of Nafion/organo-clay nanocomposites was found to be comparable to Nafion resin itself. Consequently, their good hydrophobic-hydrophilic balance is thought to be highly desirable for DMFC application.

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