

Synthesis and Performance of Water-Retention PEMs with Nafion-Intercalating-Montmorillonite Hybrid

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ABSTRACT: A proton exchange membrane modified with montmorillonite (MMT) was prepared by introducing perfluorosulfonylfluoride resin into the interlayer of MMT at high temperature and high pressure. The intercalating structure was analyzed by wide-angle X-ray diffraction (XRD), and the results showed that the polymer was indeed intercalated into the interlayer of the modified montmorillonite (m-MMT) matrix without destroying the microstructure of the matrix by largely increasing the *d*-spacings of m-MMT. SEM analysis on the surface and cross-section of these composite membranes shows that

the MMT nanoparticles are dispersed in the membrane uniformly. This composite membrane reveals excellent water retention and conductance at high temperature. The composite membrane was evaluated in a single cell, and the results show that the performance of composite membrane is higher than that of pure Nafion membrane at high temperature especially without external-humidification. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 529–534, 2008

Key words: montmorillonite; Nafion; intercalated; fuel cell

INTRODUCTION

As one of the key components in fuel cell, proton exchange membrane (PEM, such as Nafion[®]) provides the ionic pathway and acts as the gas separator. The conductivity of the PEMs is much related to the water content in the PEMs, e.g., with the increase of water content from about 0 to 50%, the conductivity of the Nafion membrane have a tremendous increase.¹ Hence, the PEMs have to be swollen and kept humidified since good ionic conductivity is required.^{2,3} To prevent the membrane from dehydration and to keep it in its most conductive state, many researches mixed hydrophilic particles (such as SiO₂, TiO₂, and other silicate particles) into PEM polymer to improve its hydrophilic capacity.^{4–12} The water-retention efficiency of this composite PEMs have been demonstrated especially when such PEM is used in high-temperature fuel cells. However, the water-retention capacity of the hydrophilic particles can not be efficiently achieved because of the random disperse of the particles in the PEM polymer. In this condition, water in the hydrophilic particles can not be transferred to —SO₃— proton exchange channel immediately when the —SO₃— is dehydrated. To supply water to the —SO₃— clusters val-

idly, the —SO₃— functional groups should be contacted directly to the hydrophilic particles.

Montmorillonite (MMT) is a promising choice compared with other hydrophilic particles because of its excellent proton conductivity, which is 10⁻⁴ S/cm at room temperature and have considerable increase when the temperature is raised.¹³ As a multilayered alumino-silicate mineral, MMT can contain 20–25 wt % water in the interface of the multilayer at the condition of 25°C.^{14–16} The structure of MMT is showed in Figure 1. In former reports, side chains of many polymers can insert into the multilayer of the MMT because of the wide *d*-space (the distance of the space) in this mineral. Hence, it is possible to introduce the —SO₃— side chains of the PEM into the multilayer of the MMT and then give the PEMs good water-retention capacity as well as water transferring capacity when the —SO₃— proton exchange groups is dehydrated.

In this article, isopropyl alcohol dispersed MMT/Nafion composite resin was prepared by intercalating Nafion side chains into the multilayer of the MMTs. The resulted resin was constructed to proton exchange membrane and used as water-retention PEMs in fuel cell.

EXPERIMENTAL

Preparation of composite membrane

Materials

Perfluorosulfonate resin solution (DE-520, EW1100) and proton exchange membranes (Nafion211) used

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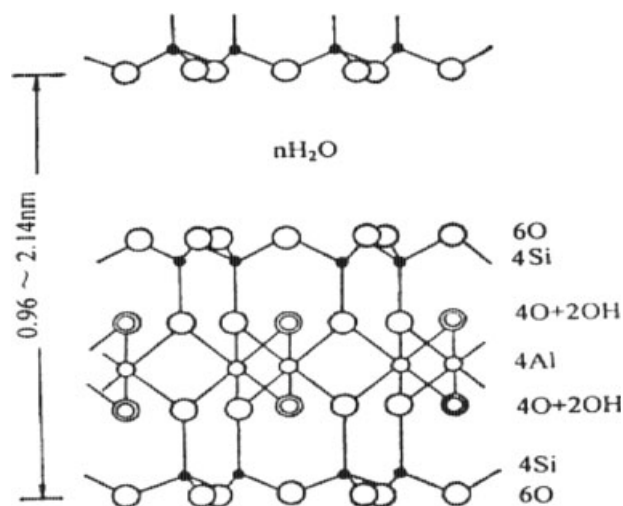


Figure 1 The structure of MMT.

in this study is supplied by DuPont Ind. (Wilmington, DE). The montmorillonite (Na^+ Mont with cation exchange capacity (CEC) of 100 mequiv (96 g^{-1}) is purchased from Southern Clay Product. Dodecylamine (CP) is purchased from Wh Helian.

Preparation of dodecylamine-exchanged montmorillonite

Dodecylamine (9.25 g) (CP) was changed to H^+ -form by mixing it with 50-mL diluent H_2SO_4 (0.5 mol/L) and then stirring for 30 min. Following with adding 20 g MMT (which has been purified and 400-mL deionized water into H^+ -dodecylamine), the mixture had been stirred for 1 h at 80°C . After dried and triturated, the m-MMT was obtained.

Preparation of m-MMT/Nafion composite membrane

The m-MMT was added into 5 wt % Nafion solution (DuPont), the contents of m-MMT in the mixture were varied in 1, 3, 5, 8, and 10 wt %. After mixing, the mixture was put into an autoclave which was supplied 3 MPa N_2 with high speed stir and temperature of 150°C . Four hours later, the mixture was

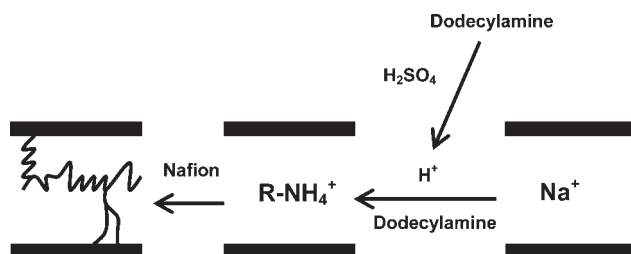


Figure 2 The schematic diagram of preparing the Nafion/m-MMT composite membrane.

poured into a glass dish to form composite membrane with 100°C . Finally, the membrane was converted to H^+ form by immersing it in H_2O_2 at 80°C for 30 min, in deionized water at 80°C for 30 min, in 8 wt % H_2SO_4 solution at 80°C for 30 min. The schematic diagram of preparing the Nafion/m-MMT composite membrane is given in Figure 2.

Characterization methods

Wide-angle X-ray diffraction

X-ray diffractometer (RIGAKU D/MAX-YB) was adopted to measure the change in d -spacing of montmorillonite crystal before and after the intercalation with perfluorosulfonate copolymer resin. $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) was used as an X-ray source at d -generator voltage of 45 kV and current of 100 mA. The 2θ scanning rate was $2^\circ/\text{min}$. The repeat distance in the silicate, d , was calculated using the Bragg's law, $d = \lambda/2 \sin 2\theta$, where 2θ is the position of the (001) peak in the XRD pattern.

Differential scanning calorimetry

Nafion211 membranes and various m-MMT/Nafion composite membranes were tested in N_2 . The temperature ranged from 0 to 600°C .

SEM analysis

Using SEM (HITACHI H-600SEM/EDXPV9100) investigated the morphology of the composite membranes and Nafion211. Both the surfaces and sections were observed. We investigated distribution and size of MMT nanoparticles in composite membranes.

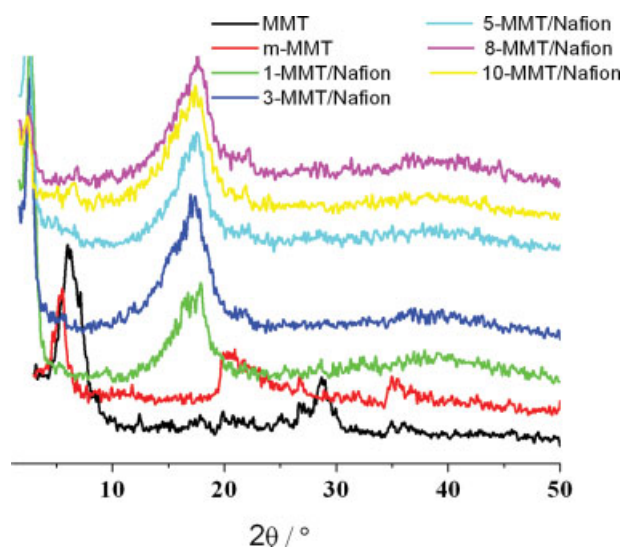


Figure 3 Wide-angle X-ray diffraction (XRD) patterns of (a) MMT, (b) m-MMT, (c-g) m-MMT/Nafion composite membrane with various content of MMT (1, 3, 5, 8, 10 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Interlayer Distance (d_{001}) of MMT, m-MMT, and the Intercalated Composites

	MMT	m-MMT	1% MMT/Nafion	3% MMT/Nafion	5% MMT/Nafion	8% MMT/Nafion	10% MMT/Nafion
d_{001}	14.8286	15.9518	32.9651	32.4804	35.3382	33.7199	36.5062

Performance of hydrophile and water retention

1. Measure m-MMT/Nafion composite membranes and Nafion211 membranes, make sure they are dry, and the weight is W_1 (g). Then put them to a beaker filled with deionized water. Twenty-four hours later, they were fully swollen. Then wipe the water away from their surface. Measure the weights, W_2 .

So the content of water is as follows:

$$\frac{W_2 - W_1}{W_1} \times 100\%$$

2. Both Nafion211 membranes and various m-MMT/Nafion composite membranes were put into a vacuum-dry oven, and kept at the temperature 80°C. Measure the weights every minute. Calculate the content of water in composite membranes while Nafion211 just become dry and using FTIR (60SXB, NICOLET) to analyze these membranes immediately.

Conductivity test

First, the membranes were put into deionized water, then they were put into 1 mol/L H_2SO_4 after 24 h. Thirty minutes later, wipe the water on their surface away. Cut a piece of membrane to make sure that the length is a , the width is b , and the thickness is c . The resistance was tested by using an impedance analyzer (Autolab PG30/FRA, Eco Chemie, The Netherlands) and a four-electrode system.^{17–19} The conductivity (Q) can be calculated by this formula as follows:

$$Q = a/(R*b*c)$$

Measure the conductivity of various m-MMT/Nafion composite membrane and Nafion211 which were dipped in water sufficiently. Then put them under the ultraviolet radiation bulb (75 W) to be roasted. Every 2 min later, measure their conductivities again. The experiment ended when the value did not change, which showed that the membranes have dried.

H₂ crossover of membrane

In this study, the limiting oxidation currents of the crossovered H₂ were measured by using the Autolab

PG30/FRA and a three-electrode system at 80°C. H₂ gas (300 sccm) was fed to the anode side of the cell, while the cathode side was kept in an inert N₂. By applying a dynamic potential from 0 to 0.6 V vs. dynamic hydrogen reference electrode (DHE, RE) at 0.5 mV/s on the cathode side (which was used as the working electrode), the limiting H₂ oxidation current measured voltammetrically was used as an indication of the H₂ crossover. The anode side, where hydrogen evolution took place, served as the counter electrode as well as the DHE reference electrode.

Single cell test

The 40 wt % Pt/Vulcan XC-72 (Pt/C) catalysts, carbon paper, PTFE suspension, and Nafion solution (Dupont) were used for electrode preparation. Pt catalyst loading of the anode and the cathode is 0.2 mg Pt/cm², respectively, and the dry loading of Nafion is 0.4 mg/cm². Two electrodes with effective area 25 cm² were hot-pressed with one piece of PEM to form a MEA. The MEA was mounted on a single cell. Prior to the test in 80°C without humidifier, every cells were activated by performing with humidified reactant gases till stable performance was obtained under the conditions of humidifier temperature TH₂/T_{air} = 60/60°C, cell temperature 60°C, and 0 psi back pressure. Before operation with dry gases, the cells were dried overnight with dry N₂.

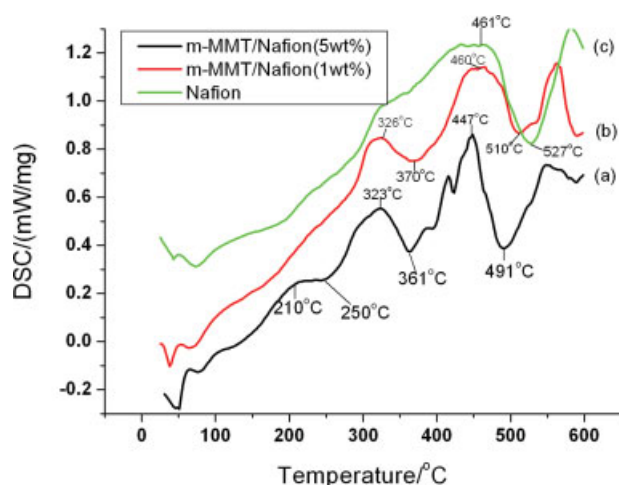


Figure 4 Differential scanning calorimetry diagrams of (a) Nafion; (b) m-MMT/Nafion (1 wt %); (c) m-MMT/Nafion (5 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

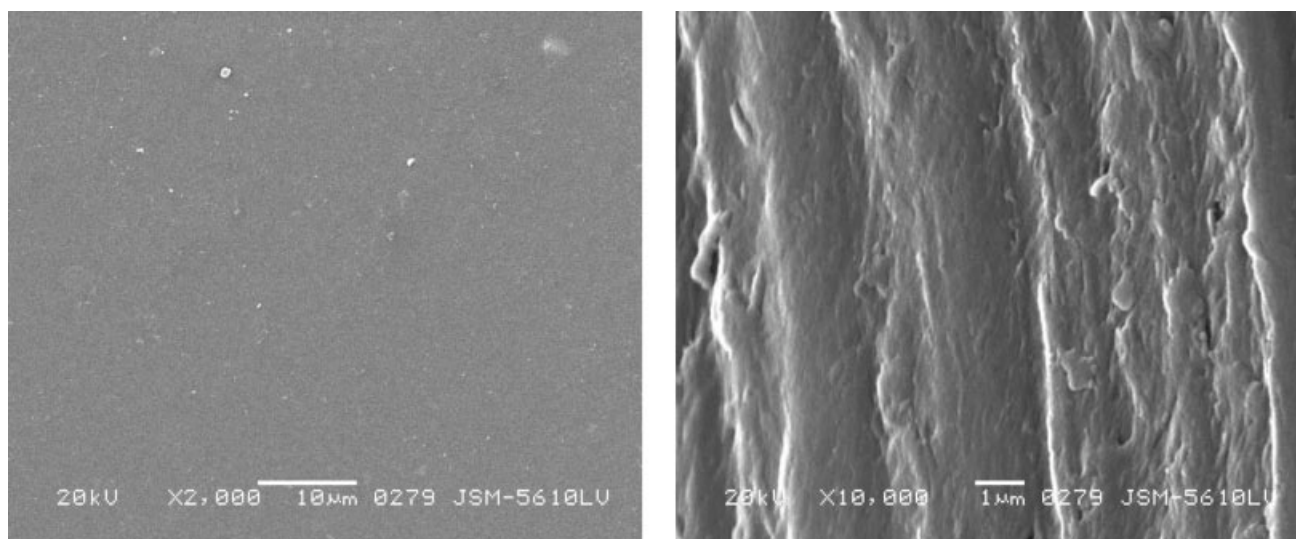


Figure 5 (a) SEM analysis: surface of composite membrane (5 wt %), (b) SEM analysis: section of composite membrane (5 wt %).

Mechanical strength

All the membranes were tested by the Electromechanical Universal Testing Machine (WDW-1C).

RESULTS AND DISCUSSION

The evidence for the intercalation on interlayer of MMT can be obtained from the XRD patterns of the composite. Figure 3 shows XRD patterns of MMT, m-MMT, and various Nafion/m-MMT, respectively. From Bragg's law, the d_{001} value are calculated and summarized in Table I. The d -spacing of (001) plane of m-MMT (15.9518 nm) is larger than MMT (14.8286), and it became larger after polymer molecules' intercalation. It is clear that the polymer ma-

trix is intercalated into interlayer of the m-MMT. But the d -spacings are not increased with the increments of the m-MMT with the polymer.

The thermal stability of the MMT/Nafion composite membranes was studied by differential scanning calorimetry (DSC), and the results are shown in Figure 4. The temperature range from 210 to 250°C in curve (a), which the vitrification process of Nafion. But it is not showed in curve (b) and (c). This is because the polymer molecules were limited by the interlayer of MMT. So this polymer could not show the character of ordinary polymers.²⁰

The exothermic peak in 323°C in curve (a) is the temperature of rearrangement of polymer segments.

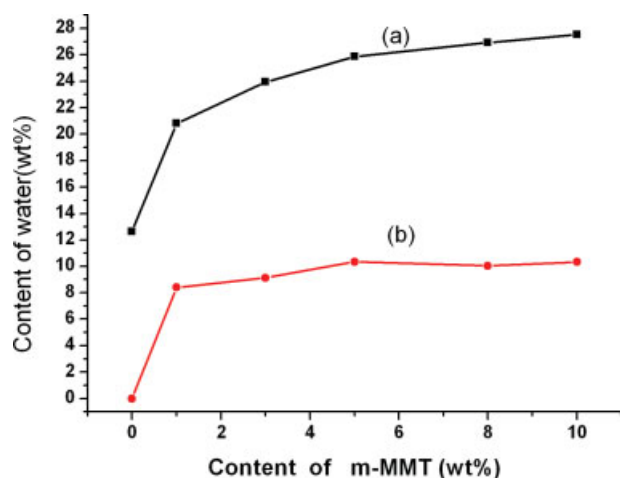


Figure 6 Content of water: (a) 25°C, fully swollen; (b) 80°C, the time Nafion211 just lose water completely. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

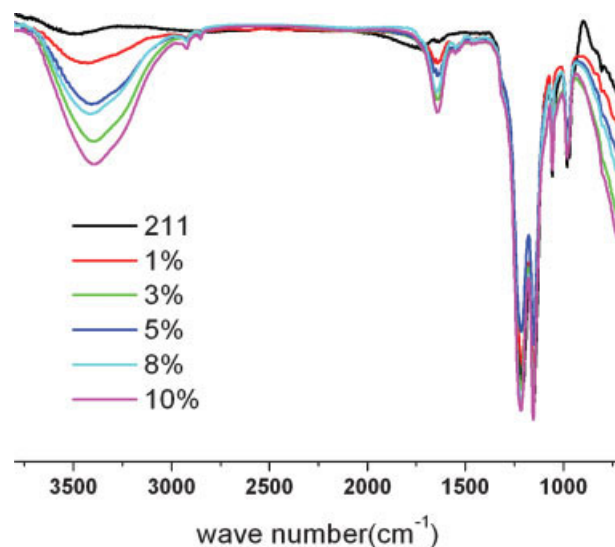


Figure 7 Infrared spectra (FTIR) of composite membrane and Nafion211, when Nafion211 just lose water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Area of —OH Stretching Absorbed Peak in Nafion211 and Composite Membrane when Nafion211 Just Lose Water

	211	1%	3%	5%	8%	10%
Area	199.800	757.315	1719.582	1991.338	3058.680	2636.350

High temperature accelerates the movement of polymer molecules. But when the temperature is over 361°C, the ordered structure was destroyed and represents decalescence. This representative process disappears gradually with increasing content of MMT. It is also the limit of interlayer of MMT.

The exothermic peak in 447°C and decalescence peak in 491°C in curve (a) reflect the temperature of oxidation and decomposition of polymer. These temperature increases as the increasing of the MMT. The reason is the binding force of MMT.

The SEM photograph (Fig. 5) of composite membrane shows that the MMT nanoparticles were dispersed in the membrane uniformly.

The contents of water when all the membranes had been fully swollen are shown in Figure 6(a). The test was done at 25°C. It is clear that the composite membranes can contain more water than Nafion211, and the contents increase if the weights of m-MMT increase. But the increase becomes very slow when the content of m-MMT is over 5 wt %. Figure 6(b) was tested in 80°C when Nafion211 lost water completely. m-MMT/Nafion composite membranes showed an excellence: the capacity of water retention at high temperature.

It is also shown that only a small quantity of m-MMT can improve the capacity of water retention. It also reflected in infrared spectra (Fig. 7). When Nafion211 lost water completely, the composite membranes and Nafion211 were analyzed in FTIR immediately. Those bands at 3500 (—OH stretching) can reflect the content of water correspondingly. The areas of —OH stretching absorbed peak were calculated and summarized in Table II. It is clear that not only the content of water in Nafion211 was improved, but also the capacity of keeping water at high temperature was improved very highly. It is good for the performance in the environment of fuel cell clearly.

Conductivity is a very important performance for proton exchange membrane. But the conductivity of ordinary PEMs depends on the content of water highly that brings much trouble.²¹ On the other hand, the conductivity increases on condition that

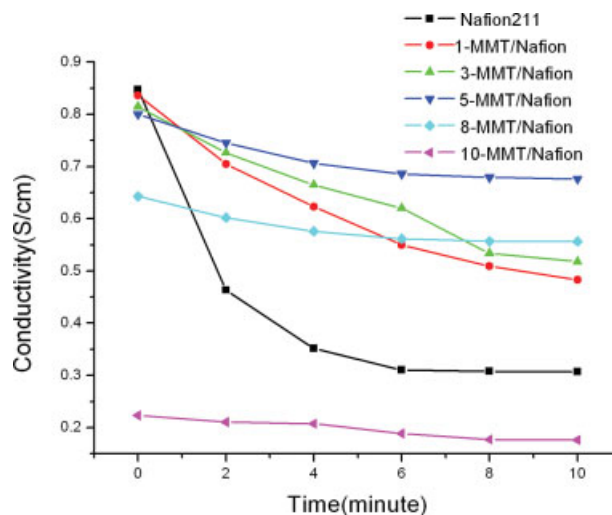


Figure 8 Conductivity of Nafion211 and composite membranes after being roasted by ultraviolet radiation bulb in various minutes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the temperature increases if the content of water is kept enough.²² So these membranes with great capacity of water retention may show a good performance in fuel cell without humidifier at high temperature.

Figure 8 shows the conductivity of Nafion211 and m-MMT/Nafion composite membranes. All the membranes were roasted by ultraviolet radiation bulb. The conductivities were tested every 2 min.

The m-MMT/Nafion composite membrane has showed its advantage of water retention on conductivity at high temperature. It can be concluded that the advantage is clearer if the temperature is higher.

Gas permeation rate is very important to proton exchange membranes, and ordinary composite membranes may have some trouble in this test. Our nanoparticle intercalated composites membrane represents a quite low-gas pervasion rate for fuel cell which is shown in Table III. Though it is higher than pure perfluorosulfonate membrane, it is enough for use in fuel cell.

Figure 9 shows the performance of Nafion211 and 3 wt % MMT/Nafion compositemembrane at 80°C without external-humidification. The composite membranes represented a better performance. There is also some drawback found in the mechanical strength testing. The strength was lower than Nafion211 as shown in Figure 10. But it is still enough for fuel cell.

TABLE III
H₂ Crossover

	Nafion211	1%	3%	5%	8%	10%
Current density (mA/cm ²)	0.9783	3.2764	5.0826	5.5873	6.7672	9.0651

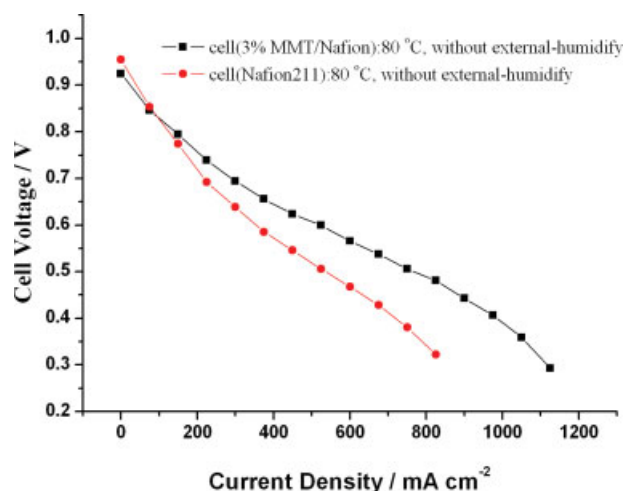


Figure 9 Performance of Nafion211 and 3 wt % MMT/Nafion composite membrane under the conditions of: cell temperature 80°C, without external-humidification. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSION

In this work, a novel fabrication method of water-retention PEMs was developed by intercalating Nafion side chains into the multilayer of the MMTs, and then constructed this composition to proton exchange membrane. XRD and DSC analysis showed that the side chain of Nafion polymer had been intercalated into the interlayer of m-MMT. The *d*-spacing had been enlarged from 14.8286 nm to more than 32 nm. The intercalated membranes show excellent water retention performance. The content of water in composite membranes was more than twice over that in Nafion211 at 25°C. Especially the content of water in composted membranes decreased very slowly when Nafion211 was just dehydrated at 80°C. This advantage was proved in the conductivity test at high temperature and single cell test at 80°C without external-humidification.

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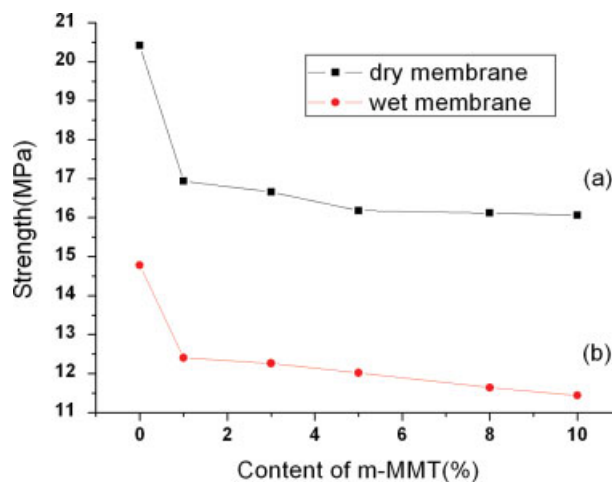


Figure 10 Mechanical strength of membranes with different content of m-MMT: (a) dry membrane, (b) wet membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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