



Sulfonated poly(ether ether ketone)/clay-SO₃H hybrid proton exchange membranes for direct methanol fuel cells

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ARTICLE INFO

Article history:

Received 26 May 2008

Received in revised form 4 July 2008

Accepted 4 July 2008

Available online 15 July 2008

Keywords:

DMFCs

SPEEK

Hybrid membranes

Clay

Sulfanilic acid

ABSTRACT

A new type of sulfonated clay (clay-SO₃H) was prepared by the ion exchange method with the sulfanilic acid as the surfactant agent. The grafted amount of sulfanilic acid in clay-SO₃H was 51.8 mequiv. (100 g)⁻¹, which was measured by thermogravimetric analysis (TGA). Sulfonated poly(ether ether ketone) (SPEEK)/clay-SO₃H hybrid membranes which composed of SPEEK and different weight contents of clay-SO₃H, were prepared by a solution casting and evaporation method. For comparison, the SPEEK/clay hybrid membranes were produced with the same method. The performances of hybrid membranes for direct methanol fuel cells (DMFCs) in terms of mechanical and thermal properties, water uptake, water retention, methanol permeability and proton conductivity were investigated. The mechanical and thermal properties of the SPEEK membranes had been improved by introduction of clay and clay-SO₃H, obviously. The water desorption coefficients of the SPEEK and hybrid membranes were studied at 80 °C. The results showed that the addition of the inorganic part into SPEEK membrane enhanced the water retention of the membrane. Both methanol permeability and proton conductivity of the hybrid membranes decreased in comparison to the pristine SPEEK membrane. However, it was worth noting that higher selectivity defined as ratio of proton conductivity to methanol permeability of the SPEEK/clay-SO₃H-1 hybrid membrane with 1 wt.% clay-SO₃H was obtained than that of the pristine SPEEK membrane. These results showed that the SPEEK/clay-SO₃H hybrid membrane with 1 wt.% clay-SO₃H had potential usage of a proton exchange membrane (PEM) for DMFCs.

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1. Introduction

Recently, direct methanol fuel cells (DMFCs) with the advantages of compactness, light weight, high power density and low temperature operation have attracted significant attention for the applications of power sources for various portable electronic devices and transportation [1]. However, for commercial feasibility, multiple difficulties of DMFCs should be overcome, such as low methanol oxidation kinetics of the anode catalyst, high methanol crossover through the electrolyte membranes, low electrode performance, etc. [2].

Proton exchange membrane (PEM) which provides ionic pathways for protons and prevents crossover of gases in fuel cells is

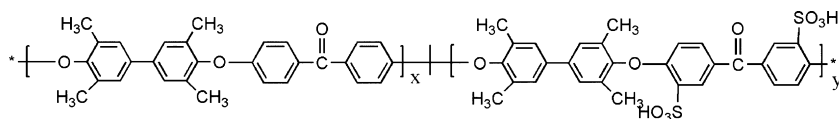
considered as one of the most important components of DMFCs. A series of perfluorinated ionomers such as Nafion[®] with good performances such as excellent chemical and mechanical stabilities, as well as high proton conductivity have been used in fuel cells. However, when methanol diffuses from the anode side to the cathode side of the Nafion[®] membrane, cathode voltage and efficiency of DMFCs will be reduced and the excess thermal load will occur, which hinder Nafion[®] to be used for future DMFC developments [3]. For this, many researches have focused on developing new materials for PEMs based on sulfonated aromatic polymers. Recently, sulfonated poly(aryl ether ketone)s (SPAEEK)s have been developed as alternative PEM materials [4–7]. However, the SPAEEKs with high ion-exchange capacities (IEC) although exhibit high proton conductivity, still have relatively high methanol permeability, high swelling ratio and low mechanical properties at evaluated temperatures, which limit their available usage for DMFCs [4–10].

For last few years, the organic–inorganic hybrid PEMs have been prepared by addition of non-conductive ceramic oxide such

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Scheme 1. The chemical structure of SPEEK.

as silicon oxide, titanium oxide and zirconium oxide, mixed silicon–titanium and silicon–aluminum oxides for improving hydrolysis resistance and reducing methanol crossover of PEMs in DMFCs [11–15]. Among various inorganic compounds, clay (montmorillonite) with the structures of the repeating triple-layer sheets composed of an edge-shared octahedral sheet of alumina sandwiched between two tetrahedral silica sheets with a thickness of 1 nm and a length of 100 nm shows attractive hydrophilic property and good thermal stability at high temperature [16,17]. The clay is also a protonic conductor with the ionic conductivity of $1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature [18]. Jung's groups [19] had reported the clay as the inorganic part to prepare Nafion[®]/clay hybrid membranes to reduce the methanol permeability through the membrane and prevent the loss of the water at high temperature. However, the conductivity of clay is so low that the proton conductivity of the hybrid membranes was markedly lower compared with the pristine Nafion[®] membrane. To solve this problem, Lee et al., Choi et al., Ma et al. and Bébin et al. [20–25], respectively, prepared different types of sulfonated clays (clay-SO₃Hs) to modify Nafion[®] membrane. The resulting hybrid membranes had obtained both lower methanol permeability and higher proton conductivity than those of the pristine Nafion[®] membrane. Therefore, clay-SO₃H can improve the performances of the Nafion[®] membrane, such as methanol resistance, proton conductivity and selectivity. Thus, clay-SO₃H was used to modify SPEEK membranes with high IEC values and the improvement on the performances of the SPEEK membranes by introduction of the sulfonated clay was investigated in this paper.

In this study, we used ion exchange method to prepare a new type of clay-SO₃H. Clay-SO₃H was used for the preparation of SPEEK/clay-SO₃H hybrid membranes in order to minimize the loss of proton conductivity while reducing the methanol permeability of the pristine SPEEK membrane. The SPEEK/clay and SPEEK/clay-SO₃H hybrid membranes with various contents of clay and clay-SO₃H were prepared by a solution casting and evaporation method. The performances of the hybrid membranes such as mechanical and thermal properties, water retention, methanol permeability and proton conductivity were examined and the results were discussed in detail.

2. Experimental

2.1. Materials

SPEEK polymers were prepared by direct aromatic nucleophilic substitution polymerization [4]. The SPEEK in acid form was obtained by heating into a 0.1-M H₂SO₄ solution for 12 h at 100 °C, and then the SPEEK in acid form was washed with deionized water until the pH reached 6–7. The chemical structure of SPEEK was shown in Scheme 1.

Clay (montmorillonite with a cation exchange capacity of 100 mequiv. (100 g)⁻¹) was supported by Zhejiang Fenghong Clay Chemicals Co., Ltd.

2.2. Preparation of clay-SO₃H with ion exchange method

Five grams of clay was added into 500 g of boiling water, mixed, and then heated for 10 min to form the clay suspension. Sulfanilic acid

(Beijing Chemical Works, China) was dissolved in 500 g of water and then a given quantity of hydrochloric acid was added to protonate amine groups. After being vigorously stirred for 1 h at 80–90 °C, the clay suspension was repeatedly washed with deionized water until no chloride ion was detected by AgNO₃ and dried under vacuum.

2.3. Preparation of organic–inorganic hybrid membranes

A desired amount of clay or clay-SO₃H were added to 10 wt.% SPEEK in acid form solution and mechanically mixed for at least 24 h at room temperature until forming high transparent solution. Subsequently, the resulting mixture was poured onto a glass plate. The hybrid membranes (50–150 μm) were prepared and dried at 65 °C for 24 h. In the following sections, hybrid membranes with different weight ratios (1, 3, and 5 wt.%) of clay or clay-SO₃H will be referred as SPEEK/clay-1, SPEEK/clay-3, SPEEK/clay-5, SPEEK/clay-SO₃H-1, SPEEK/clay-SO₃H-3 and SPEEK/clay-SO₃H-5, respectively. The preparation process was shown in Scheme 2.

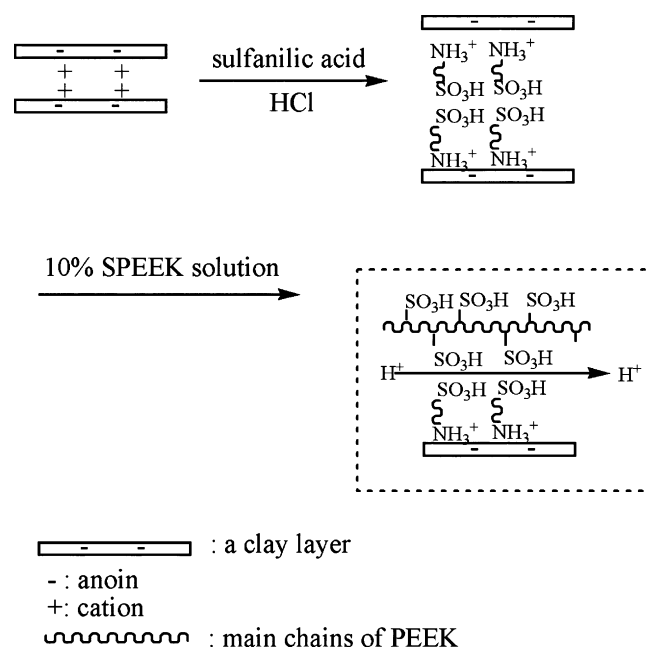
2.4. The analysis of hybrid membranes

2.4.1. FTIR spectroscopy

The FTIR spectroscopy was recorded on the powder samples dispersed in dry KBr in form of disks, using a BRUKER Vector 22 spectrometer at a resolution of 4 cm⁻¹ min⁻¹ from 4000 to 400 cm⁻¹.

2.4.2. Content of grafting sulfanilic acid in clay-SO₃H measurement

To investigate the grafted amount of sulfanilic acid on the surface of the clay, the clay-SO₃H was analyzed by Pyris TGA (PerkinElmer).



Scheme 2. Schematic illustration for the preparation of SPEEK/clay-SO₃H hybrid membranes.

The thermal analyzer was programmed to heat the samples from 80 to 600 °C at the heating rate of 10 °C min⁻¹ under N₂. The content of sulfanilic acid grafting on the surface of the clay was determined using the following equation from the weight loss [26]:

$$\text{graft amount}(\text{mequiv.}(100\text{ g})^{-1}) = \frac{10^3 W_{200-600}}{(100 - W_{200-600})M} \times 100 \quad (1)$$

where $W_{200-600}$ is the weight loss between 200 and 600 °C corresponding to sulfanilic acid degradation, M (g mol⁻¹) is the molecular weight of sulfanilic acid.

2.4.3. Mechanical property

The mechanical property of the dry membrane was measured using SHIMADZU AG-1 1KN at the test speed of 2 mm min⁻¹. The size of specimen is 15 mm × 4 mm. For each test reported, at least three samples were taken and average value was calculated.

2.4.4. Thermal stability

A Pyris TGA (PerkinElmer) was used to study the thermal stability of the hybrid membranes. About 5–10 mg samples of the hybrid membranes were heated to 150 °C and kept at this temperature for 20 min to remove any residual water or solvent under N₂, and then cooled to 80 °C and reheated to 700 °C at the heating rate of 10 °C min⁻¹.

2.4.5. Water uptake (WU)

The water uptake at different temperature was determined by the weight difference between the fully hydrated membrane and dried membrane. The membrane was first equilibrated in water at 25, 40, 60 and 80 °C for about 12 h, and then removed from water quickly, dry-wiped the extra water on the membrane surface and immediately weighed to determine the wet mass (W_{wet}). The dried weight (W_{dry}) of membrane was determined after the membrane was dried at 100 °C for 24 h. The water uptake was calculated by the following formula:

$$\text{water uptake(WU)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

2.4.6. Water desorption measurement

The water desorption measurement was tested by Pyris 1 TGA (PerkinElmer). The temperature was remained at 80 °C and the pressure of the test cell was kept constant. Pyris 1 TGA was used to evaluate the weight changes of samples with time. The plots of M_t/M_∞ versus $t^{1/2}$ initially were linear for Fickian diffusion. Water diffusion coefficient was calculated as follows [27]:

$$\frac{M_t}{M_\infty} = \left(\frac{D_t}{\pi l^2} \right)^{1/2} \quad (3)$$

where D is the water diffusion coefficient. M_t and M_∞ refer to the mass desorbed at time t and infinite time, respectively. M_t/M_∞ is the water desorption, and l is the membrane thickness.

2.4.7. Methanol permeability measurement

Methanol permeability of the membrane was measured using a two-chamber liquid permeability cell. This cell consisted of two reservoirs, which were separated by a vertical membrane after being immersed in 10 M methanol solution for 24 h. Ten molar concentration of methanol solution was placed in one side of the cell and water was placed in the other side. Two magnetic stirrers were used continuously during the measurement. Methanol concentrations in the water cell were periodically estimated using a GC-8A

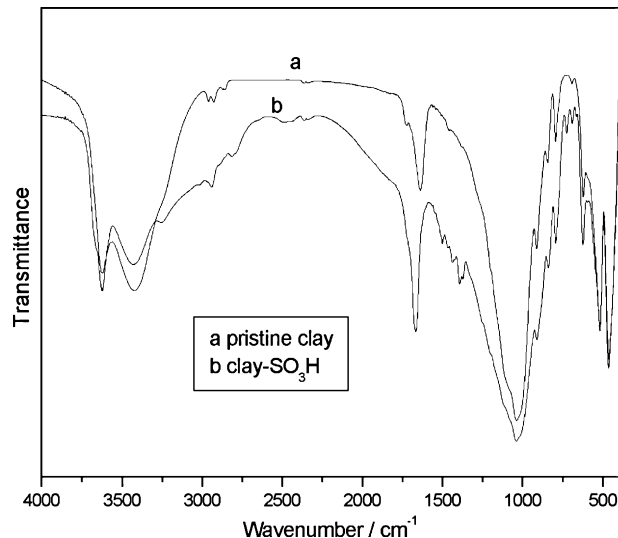


Fig. 1. FTIR spectra of clay and clay-SO₃H.

gas chromatograph (SHIMADZU, Tokyo, Japan). The methanol diffusion coefficient was calculated with equation:

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

where A , L and V_B are the effective area, the thickness of membrane and the volume of permeated reservoirs, respectively. C_A and C_B are the methanol concentration in methanol chamber and water chamber, respectively. DK is the methanol diffusion coefficient.

2.4.8. Proton conductivity

The proton conductivity was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). The membranes were fixed in a measuring cell which was made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops. During the measurement, the measuring cell with the membranes was immersed into water in order to assure the condition of 100% relative humidity at desired temperature after the membranes were full hydrated in water for 24 h. The proton conductivity was calculated using the following equation:

$$\sigma = \frac{L}{RA} \quad (5)$$

where σ is proton conductivity in S cm⁻¹, L is the distance between the two electrodes, R is the resistance of the membrane and A is the cross-sectional area of membrane.

3. Results and discussion

3.1. Analysis of clay-SO₃H

The efficiency of the clay surface modification was confirmed by FTIR as shown in Fig. 1. The FTIR spectrum of the pristine clay displayed typical -OH stretching absorption at 3626 cm⁻¹, and broad bands at 3427 and 1642 cm⁻¹ could be attributed to physisorbed water. The peaks at 1120, 1038 and 915 cm⁻¹ corresponded to Si-O stretching vibrations. The absorption bands between 600 and 400 cm⁻¹ could be associated with Al-O stretching and Si-O bending [28]. For the clay-SO₃H, the new absorption bands at 3247 and 1530 cm⁻¹ (NH₃⁺ stretching), 1500–1300 cm⁻¹ (aromatic C=C

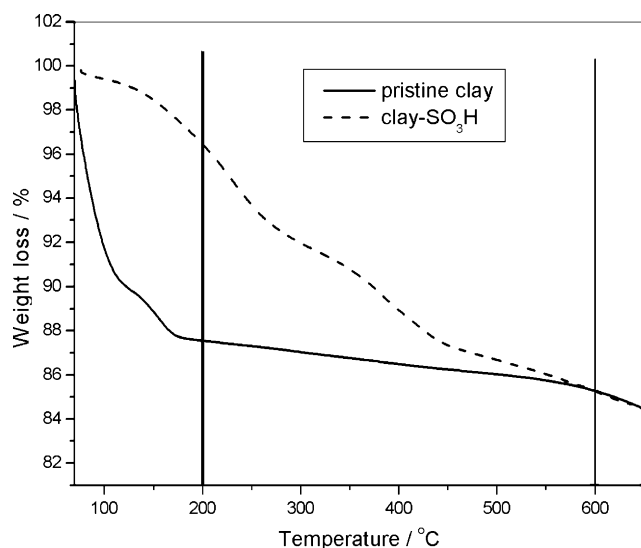


Fig. 2. TGA curves of clay and clay-SO₃H.

stretching) and 691 cm⁻¹ (S–O stretching of sulfonic acid groups) indicated that sulfanilic acid was grafted on the surface of the clay, successfully. The absorbance peaks related to asymmetric and symmetric stretching of SO₃⁻¹ groups, which were expected at 1040 and 1100 cm⁻¹, were not evident as they superimposed onto the intense peaks of Si–O–Si bonds.

TGA was used to determine the grafted amount of sulfanilic acid on the surface of the clay in clay-SO₃H after extensively washing the non-grafted sulfanilic acid. Fig. 2 shows the TGA thermograms before and after organic grafting of the clay. The TGA thermogram of clay-SO₃H exhibited three distinct decomposition regions. The first weight loss between 80 and 200 °C was mainly attributed to the thermal diffusion of water. The second weight loss between 200 and 600 °C represented the thermal decomposition of the organic molecule and was considered for quantitative determination of the sulfanilic acid. The grafted amount determined by TGA analysis was 51.8 mequiv. (100 g)⁻¹ calculated by Eq. (1).

3.2. Analysis of the hybrid membranes

3.2.1. Mechanical and thermal property

Good mechanical and thermal properties are required for PEMs in DMFCs to guarantee a long lifetime of fuel cells. Mechanical properties such as tensile strength, Young's modulus and maximum elongation of the hybrid membranes should be taken into account under operation conditions of DMFCs. The typical mechanical properties of the hybrid membranes were evaluated and the results were listed in Table 1. The Young's moduli for the membranes of SPEEK, SPEEK/clay-1, SPEEK/clay-3, SPEEK/clay-5, SPEEK/clay-SO₃H-1, SPEEK/clay-SO₃H-3 and SPEEK/clay-SO₃H-5 were 0.94, 1.53, 1.20, 1.30, 1.36, 0.98 and 1.20 GPa, respectively. The Young's

moduli of the hybrid membranes were all larger than the pristine SPEEK membranes. Moreover, the Young's moduli of SPEEK/clay systems were larger than those of SPEEK/clay-SO₃H systems with the same contents of clay, which might be because that the sulfanilic acid had somehow lead to void spaces between the clay and the polymer matrix, and these void spaces limited stress transfer to the reinforcing phase of the inorganic clay particles. The tensile strengths of hybrid membranes showed the same tendency with the values from 43 to 64 MPa. The 1 wt.% clay into SPEEK/clay-1 and SPEEK/clay-SO₃H-1 hybrid membranes had been well dispersed, even, formed the exfoliation structures into the SPEEK matrix [29], which caused the highest mechanical properties of all hybrid membranes. It was worth noting that the increase in tensile strength and in Yong modulus was obtained by increasing the clay content from 3 to 5 wt.%, which was consistent with the results in Ref. [29]. It is well known that the inorganic particles are rigid. When the inorganic particles are well dispersed into the organic parts, the rigidity of resulted materials will be improved. The results of the mechanical properties indicated that the hybrid membranes were nice candidates for application of functional PEM materials in DMFCs.

Thermal stabilities of SPEEK and the hybrid membranes were investigated by TGA as shown in Fig. 3. For all the membranes, two distinct weight loss steps were observed. The first weight loss from 300 to 450 °C was attributed to the thermal degradation of sulfonic acid groups. The second weight loss above 450 °C represented the thermal decomposition of the main chains of SPEEK and sulfanilic acid. It was well known that the clay could enhance heat resistance to the hybrid materials, especially at high temperature region. As shown in Table 1, the 5% weight loss temperatures (*T*_{5%}) of the SPEEK was 302 °C and that of the SPEEK/clay-SO₃H-1 hybrid membranes in acid form were up to 308 °C. The results showed that the thermal stabilities had been improved with the increment of clay or clay-SO₃H. At 440 °C, the thermal degradation of the sulfonic acid groups had been approximately complete and the weight loss obtained from TGA at this temperature represented the weight content of the sulfonic acid groups in the SPEEK and hybrid membranes. The char yields of the hybrid membranes at 440 °C were also listed at Table 1. The results showed that the contents of sulfonic acid groups in SPEEK/clay hybrid membranes were decreased with the increasing content of clay. However, the different tendency was obtained in SPEEK/clay-SO₃H hybrid membranes due to the introduction of sulfanilic acid on the surface of the clay. TGA studies revealed that the hybrid membranes had good thermal properties as a result of the incorporation of clay into SPEEK matrix.

3.2.2. Water uptake and water desorption

Water plays an important role in PEMs and directly affects proton transport across their membranes [30]. Generally, it is believed that protons can be transported along with hydrogen-bonded ionic channels and cationic mixtures such as H₃O⁺, H₅O₂⁺, and H₉O₄⁺ in the water [31]. Too low water uptake reduces proton transport, while extreme water uptake causes overmuch swelling and the loss

Table 1
Mechanical and thermal properties of SPEEK and the hybrid membranes

Hybrid membranes	Tensile strength (MPa)	Maximum elongation (%)	Young's modulus (MPa)	<i>T</i> _{5%} (°C)	Char yield at 440 °C (%)
SPEEK	39.7 ± 0.7	15.1 ± 3.8	945.7 ± 70.7	302	79.7
SPEEK/clay-1	63.8 ± 1.9	14.7 ± 0.7	1531.7 ± 50.1	305	82.0
SPEEK/clay-3	53.9 ± 2.5	7.9 ± 1.0	1201.3 ± 35.7	307	82.4
SPEEK/clay-5	56.94 ± 1.02	5.89 ± 0.35	1295.37 ± 41.55	306	83.1
SPEEK/clay-SO ₃ H-1	48.3 ± 1.4	10.7 ± 1.9	1362.2 ± 64.0	308	83.3
SPEEK/clay-SO ₃ H-3	43.3 ± 2.8	9.5 ± 0.5	982.0 ± 24.5	304	83.2
SPEEK/clay-SO ₃ H-5	45.0 ± 1.2	7.7 ± 1.5	1196.0 ± 29.3	304	83.0

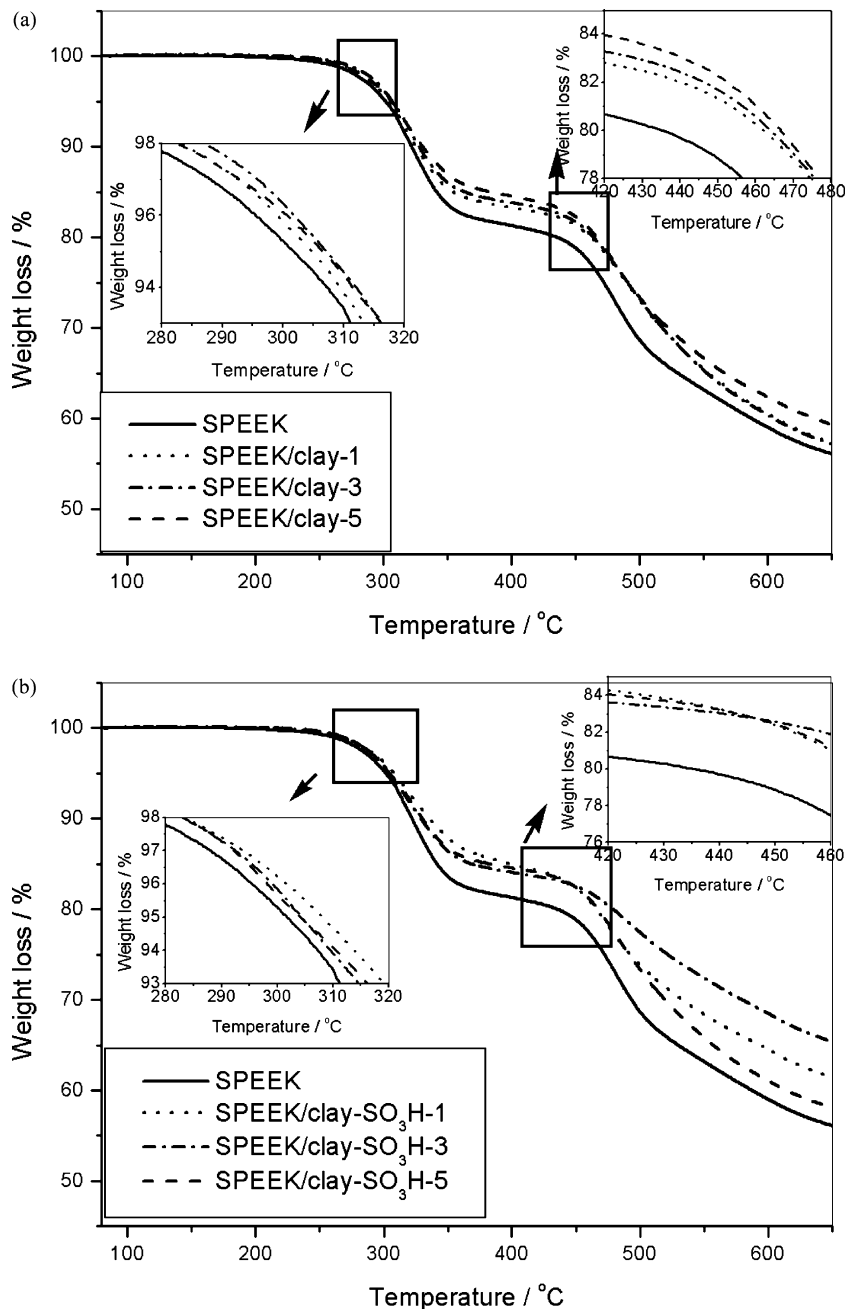


Fig. 3. TGA thermodiagrams of (a) SPEEK/clay and (b) SPEEK/clay-SO₃H hybrid membranes.

of the dimensional stability. The water uptakes of the SPEEK and hybrid membranes at different temperature were shown in Fig. 4 and Table 2. It is well known that the monovalent ions located between the clay layers allow the absorption of polar solvent, like water. Hence, with the increasing content of the hydrophilic clay, the water uptakes of organic-inorganic hybrid membranes would increase. For example, compared with the pristine SPEEK membrane, the water uptakes of the hybrid membranes increased with the addition of clay or clay-SO₃H from 35.24 to 42.20% at 25 °C, and the water uptakes of various membranes at 80 °C also showed the similar tendency, which corresponded to results shown by Bébin et al. [22]. As the increasing of temperature, the polymer chains move and the free volume for water absorption increases. Thus, the water uptakes of all of the hybrid membranes increased with the increase of temperature.

Water retention and diffusion of PEMs have significant effects on their proton conductivity, especially at high temperatures and low relative humidity [32]. To investigate loose and bond water within the hybrid membranes, water diffusion coefficients of the hybrid membranes were analyzed by the velocity of water evaporation in the hydrated membranes at 80 °C. Plots of M_t/M_∞ versus $t^{1/2}$ initially were linear for Fickian diffusion laws [27] and were shown in Fig. 5. The water diffusion coefficients of the SPEEK/clay membranes calculated from the slopes of the lines were 7.53×10^{-5} , 5.47×10^{-5} , and $2.13 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for 1, 3, and 5 wt.% of clay, and those of SPEEK/clay-SO₃H hybrid membranes were 4.02×10^{-5} , 6.06×10^{-5} , and $7.57 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for 1, 3, and 5 wt.% of clay-SO₃H, respectively, which were lower than that of the pristine SPEEK membrane ($8.82 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$). As shown in results, the speed of diffusion of water decreased with the addition of clay. It was considered that the

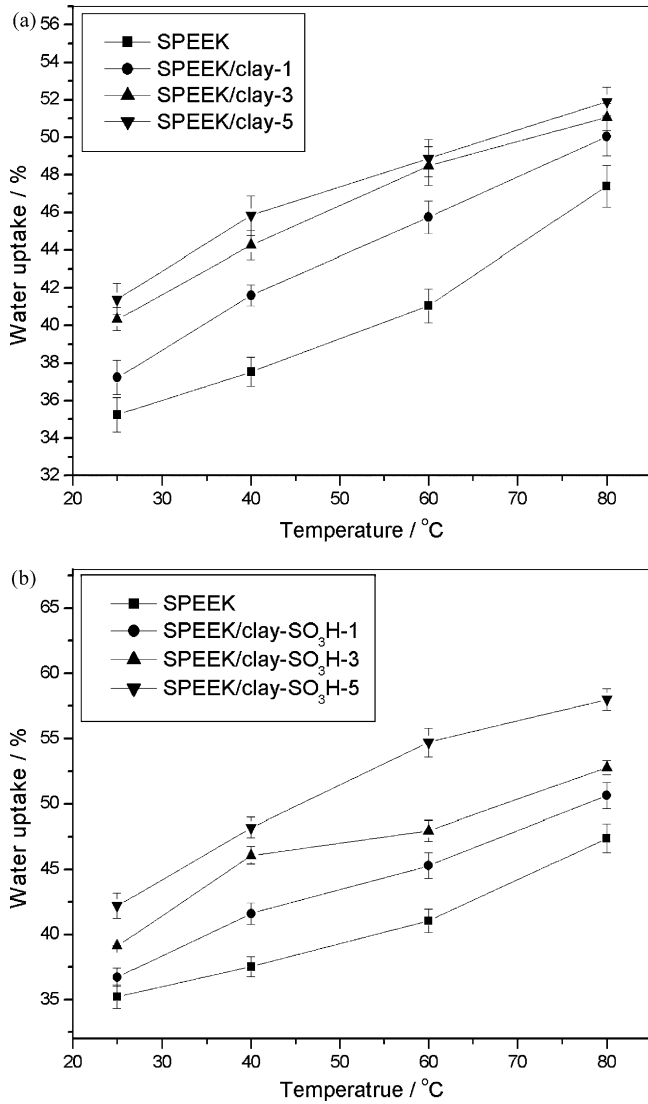


Fig. 4. Water uptakes of (a) SPEEK/clay and (b) SPEEK/clay-SO₃H hybrid membranes at different temperature.

anisotropic clay layers produced a tortuous path through the hybrid membrane and therefore made the loss of the bulk observation of transport of molecules through the hybrid membrane [22]. Namely, the water retention of the hybrid membranes at high temperatures was improved by the introduction of clay.

3.2.3. Methanol permeability, proton conductivity

In DMFCs, the PEMs with low methanol diffusion coefficient are required because methanol diffusion from the anode to the cath-

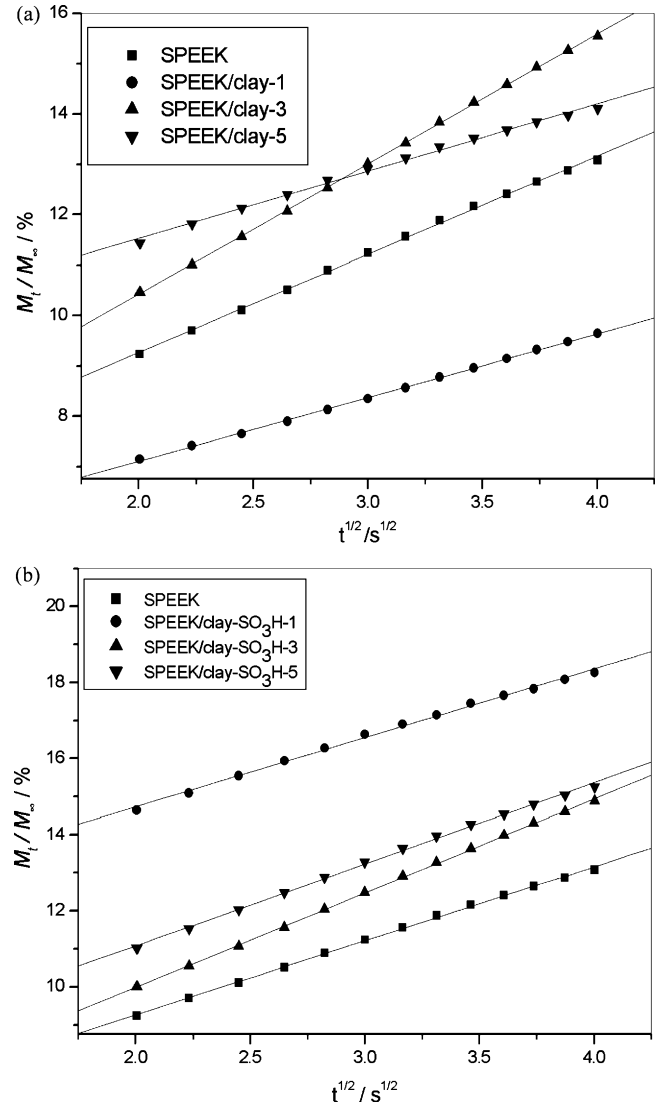


Fig. 5. The plots of M_t/M_∞ vs. $t^{1/2}$ at 80 °C: (a) SPEEK/clay and (b) SPEEK/clay-SO₃H hybrid membranes.

ode leads to lower cell voltage and fuel efficiency. The transport of methanol in membrane requires the connected channels formed by hydrophilic sulfonic acid groups providing with good connectivity [21]. The methanol diffusion coefficients of the SPEEK and hybrid membranes at room temperature were measured and the results were reported in Table 2. The methanol diffusion coefficient of the pristine SPEEK membrane was $1.21 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at room temperature, and those of the SPEEK/clay-SO₃H hybrid membranes with 1, 3, and 5 wt.% of clay-SO₃H were 3.80×10^{-7} , 9.64×10^{-7} , and

Table 2
The properties of SPEEK and the hybrid membranes

Composite membranes	Water uptake (%)		Water diffusion coefficient ($\times 10^{-5}$) (cm ² s ⁻¹)	Methanol diffusion coefficient ($\times 10^{-6}$) (cm ² s ⁻¹)	Proton conductivity (S cm ⁻¹)	
	25 °C	80 °C			25 °C	80 °C
SPEEK	35.24 ± 0.91	47.39 ± 1.10	8.82	1.21	0.0699	0.125
SPEEK/clay-1	37.23 ± 0.92	50.04 ± 1.02	7.53	0.450	0.0510	0.126
SPEEK/clay-3	40.34 ± 0.61	51.08 ± 0.73	5.47	0.342	0.0470	0.155
SPEEK/clay-5	41.40 ± 0.83	51.91 ± 0.77	2.13	0.494	0.0470	0.107
SPEEK/clay-SO ₃ H-1	36.72 ± 0.72	50.63 ± 1.00	4.02	0.379	0.0698	0.166
SPEEK/clay-SO ₃ H-3	39.14 ± 0.38	52.78 ± 0.55	6.06	0.964	0.0595	0.132
SPEEK/clay-SO ₃ H-5	42.20 ± 0.96	58.01 ± 0.82	7.57	1.12	0.0551	0.131

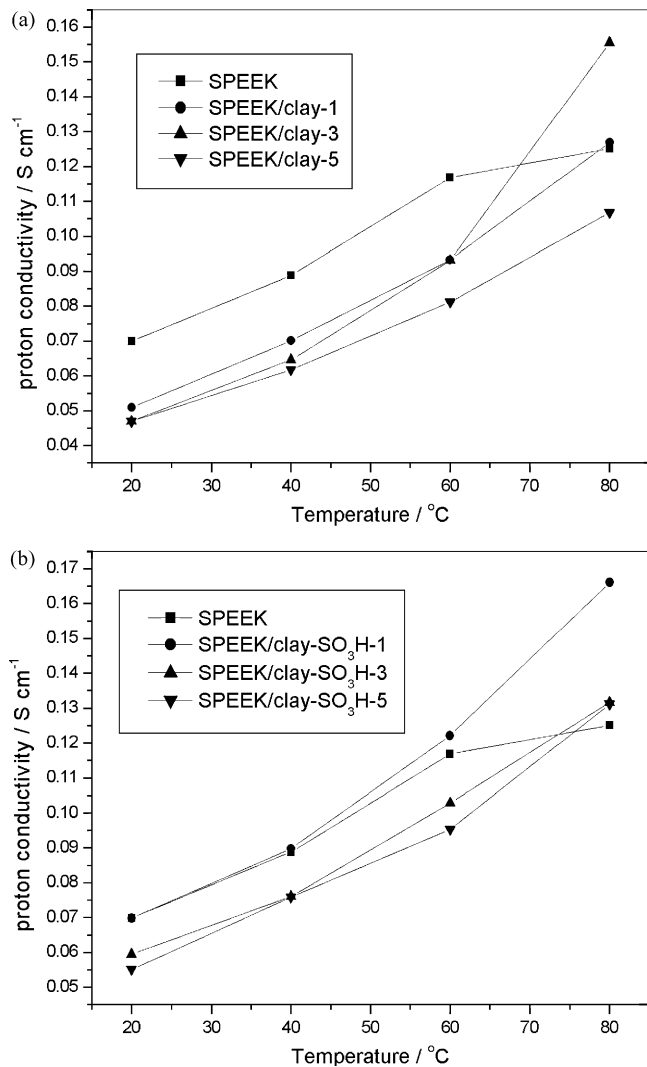


Fig. 6. The proton conductivity of (a) SPEEK/clay and (b) SPEEK/clay-SO₃H hybrid membranes at different temperature.

$1.12 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. The assumption of the destruction by the clay to the connected channels decreased the methanol diffusion coefficients of the hybrid membranes.

The proton conductivities of the SPEEK and hybrid membranes at different temperatures with 100% relative humidity had been shown in Fig. 6 and the relative values were listed in Table 2. The proton transport in membranes requires well-connected channels formed by ion clusters of hydrophilic sulfonic acid groups. Therefore, the content and the diameter of the connected channels have significant effect on the proton transport rate in membranes. When the density of sulfonic acid groups is low, the isolated ionic clusters form in the continuous hydrophobic phase [32]. Since the ionic clusters might be obstructed from the clay with low proton conductivity although the water uptakes of the hybrid membranes increased with the adding of the clay, the proton conductivities of the hybrid membranes decreased with the increment of the clay as can be seen in Fig. 6. Addition of the sulfanilic acid into the clay resulted in an increasing trend of proton conductivities of the SPEEK/clay-SO₃H hybrid membranes in comparison to the SPEEK/clay hybrid membranes. The proton conductivities of the hybrid membranes increased with the increase of the temperature as seen in Fig. 6. All composite membranes showed good proton conductivity more than $10^{-2} \text{ S cm}^{-1}$,

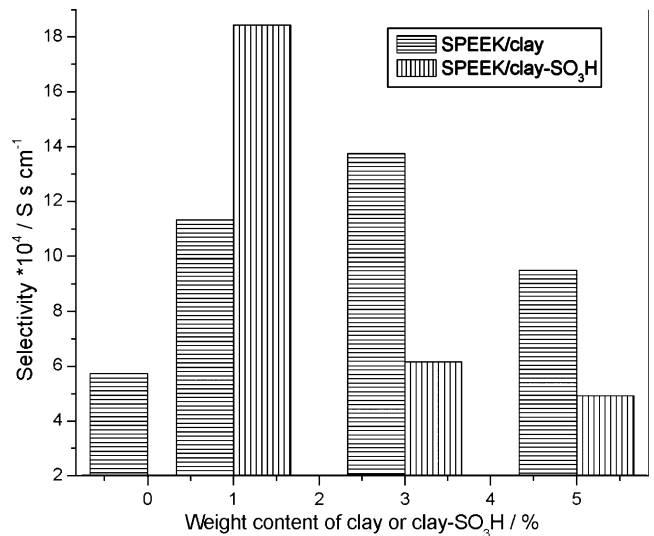


Fig. 7. The selectivity (ratio of proton conductivity to methanol permeability) of SPEEK/clay and SPEEK/clay-SO₃H hybrid membranes at 25 °C.

which was the lowest value of practical interest for PEMs used in DMFCs.

Membranes for the practical usage of PEMs in DMFCs were required to possess high proton conductivity and low methanol permeability. The selectivity means the characteristic factor for evaluating membrane performances of both proton conductivity and methanol permeability. In this case, the selectivity can be used just as a barometer to develop the best proton conductive polymer membranes with reducing methanol permeability. Fig. 7 shows the selectivity defined as the ratio of proton conductivity to methanol permeability of the SPEEK and hybrid membranes. The selectivities of the SPEEK/clay hybrid membranes were improved with the introduction of clay. However, the highest selectivity value was found from the SPEEK/clay-SO₃H hybrid membrane with 1 wt.% clay-SO₃H. The result suggested that the incorporation of 1 wt.% clay-SO₃H into the SPEEK membranes had more impact on the reduction of methanol permeability than proton conductivity, and the hybrid membrane has a potential application for DMFCs.

4. Conclusions

The clay-SO₃H had been prepared from the ion exchange method of surface modification of clay with sulfanilic acid, successfully. The mechanical and thermal properties of the SPEEK membranes were dramatically improved by introduction of clay or clay-SO₃H. The performances of the hybrid membranes for DMFCs such as water uptake, water desorption, methanol permeability, and proton conductivity were investigated. The water uptakes of the hybrid membranes were increased with the increasing content of clay or clay-SO₃H. The water retentions at 80 °C and methanol resistances of the hybrid membranes had been obviously enhanced by adding of clay or clay-SO₃H. The proton conductivities of SPEEK/clay-SO₃H hybrid membranes decreased slightly compared with the pristine SPEEK membrane, however, the higher selectivity of SPEEK/clay-SO₃H-1 hybrid membranes was shown. These results indicated that the SPEEK/clay-SO₃H hybrid membrane which possessed good physical and chemical property was promising to be used as PEMs in DMFCs.

Acknowledgment

The authors thank the China High-Tech Development 863 Program (Grant No. 2007AA03Z218) for financial support of this work.

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