

CHAPTER VI
SULFONATED MONTMORILLONITE/SULFONATED POLY(ETHER
ETEHR KETONE) (SMMT/SPEEK) NANOCOMPOSITE MEMBRANE FOR
DIRECT METHANOL FUEL CELLS (DMFCs)

Abstract

A nanocomposite membrane of sulfonated montmorillonite/sulfonated poly(ether ether ketone) (SMMT/SPEEK) is proposed for direct methanol fuel cells. The SMMT is clay modified with silane of which the structure consists of a sulfonic acid group for proton conductivity improvement. The micro- and nano-scaled morphology of the membranes performs the increase in inorganic aggregation with SMMT loading content as confirmed by SEM and AFM. The membrane stability, i.e., the swelling ratio in water and in methanol aqueous solution as well as the mechanical stability is increased with the SMMT loading content whereas thermal stability doesn't improve significantly. The methanol permeability reduction reveals as high as 53 % when the SMMT loading content reaches 5 wt. %. A comparative study of the SPEEK nanocomposite membranes with SMMT and with pristine MMT showing that a four-fold increase in proton conductivity is obtained after sulfonation is a potential proton exchange membrane. The DMFC single cell tests inform us that all composite membranes give the significant performance revealed by the plot of current density-voltage and power density.

Keywords: SPEEK; Montmorillnite; Composite membrane; Proton exchange membrane; DMFCs

1. Introduction

Nowadays, direct methanol fuel cell (DMFC) is attractive for several applications especially portable devices since its liquid-feed system operating without fuel processing unit provides a practical fuel and a compact cell design. Apart from that, DMFCs offer many advantages, such as high power density, low or zero emission, low temperature and pressure operation and reliability [1-3]. Yet, one of the main drawbacks for the development of DMFCs is the lack of suitable proton

exchange membrane. Up to the present, Perfluorinated membranes, Nafion[®] and Flemion[®], have been broadly used as membranes in DMFCs regarding to their high proton conductivity below 100 °C and good chemical stability [4]; however, their high methanol permeability and excessive swelling in alcohol environment cause overpotential at cathode resulting in the lowering of cell performance and mechanical strength [5-8]. The perfluorinated membranes are expensive and not environmentally friendly especially in the mass-produced system. The desired membranes, therefore, possess not only high proton conductivity but also low methanol crossover as well as good mechanical, thermal and chemical stability during DMFC operation including the low price.

Due to the drawbacks of perfluorinated membranes, many researches have focused on alternative membranes based on fluorine free hydrocarbon ionomer, e.g., polyethersulfone [9, 10], polyvinylalcohol [11], polyimide [12] and polyphosphazene [13]. Among them, sulfonated aromatic poly(ether ether ketone) (SPEEK) is a promising candidate for its good thermal stability and mechanical strength [14, 15]. The proton conductivity of SPEEK depends on the sulfonation degree controlled by reaction time and temperature of sulfonation process [6]. Although SPEEK exhibits various advantages to be used in proton exchange membrane fuel cells, high sulfonation degree resulting in the relatively high methanol permeability has limited its applications [16].

Recently, a series of organic-inorganic composite membranes using SPEEK as a polymer matrix have been investigated for DMFCs, for example, the composite membrane of SPEEK with: (i) heteropolyacid [11, 17]; (ii) zirconium phosphate [3]; (iii) silicon oxide (SiO₂), titanium oxide (TiO₂) and zirconium oxide (ZrO₂) [2, 9]; and (iv) layered silicate materials [7]. Sodium-Montmorillonite (Na⁺-MMT), a type of layered silicate composed of the silica tetrahedral and alumina octahedral sheets, is a well known inorganic material which can considerably improve the membrane properties. The montmorillonite embedded in the polymer matrix is expected for reducing methanol permeability, preventing extreme swelling at high operation temperature, increasing mechanical strength and maintaining the humidity in the membrane under various cell conditions [7, 18]. However, the drawback of proton conductivity reduction in the composite membrane with montmorillonite loading

content is the point to overcome, for example Gaowen et al. [4] reported a twice decrease in proton conductivity when 10 % of organic modified MMT was incorporated into SPEEK polymer matrix and also revealed from other research works [7, 19, 20].

In this study, we consider the functionalization of montmorillonite (MMT) with silane coupling agent of which the structure is further modified with 4-sulfophthalic acid (Scheme 6.1). Based on this approach, it can be expected that the modified clay provides not only the proton conductivity but also the improvement of the methanol permeability retardation, mechanical and thermal stabilities as well as the stability in methanol aqueous solution. The present work, thus, demonstrates the design, synthesis, and characterization of the SMMT/SPEEK nanocomposite membrane including the performance on DMFC system.

2. Experimental

2.1 Materials

Poly(ether ether ketone) (PEEK) powder was purchased from Victrex, England. Sulfuric acid 95-97 % was bought from Merck KGaA, Germany. Nafion[®] 117 membrane was purchased from Ion Power, Inc., USA. (3-Aminopropyl)triethoxysilane was purchased from Fluka, Switzerland. 4-Sulfophthalic acid 50 % in water was the product of Acros Organics, USA. Water conjugating agent (WSC), 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide hydrochloric 98 %, was purchased from Acros, Belgium. Dimethylformamide (DMF) was bought from Merck KGaA, Germany. Sodium-montmorillonite (Na⁺-MMT) namely Cloisite Na⁺ was the product of Southern Clay Product, Inc., USA. All chemicals were used without further purification.

2.2. Composite membrane preparation

2.2.1. Sulfonated PEEK (SPEEK)

PEEK powder was dried in vacuum oven at 70 °C for 24 h before use. The dried polymer (16 g) was dissolved in concentrated (95-97 %) sulfuric acid (H₂SO₄) (800 ml) and vigorously stirred at 50 °C for 3, 4 and 5 h to give SPEEK3, SPEEK4 and SPEEK5, respectively. The solution was precipitated in an excess of ice-cold water. The suspension was continuously stirred for another hour before filtering and

washing several times with distilled water until neutral. The precipitate was dried in vacuum at 70 °C for 12 h to obtain sulfonated PEEK (SPEEK).

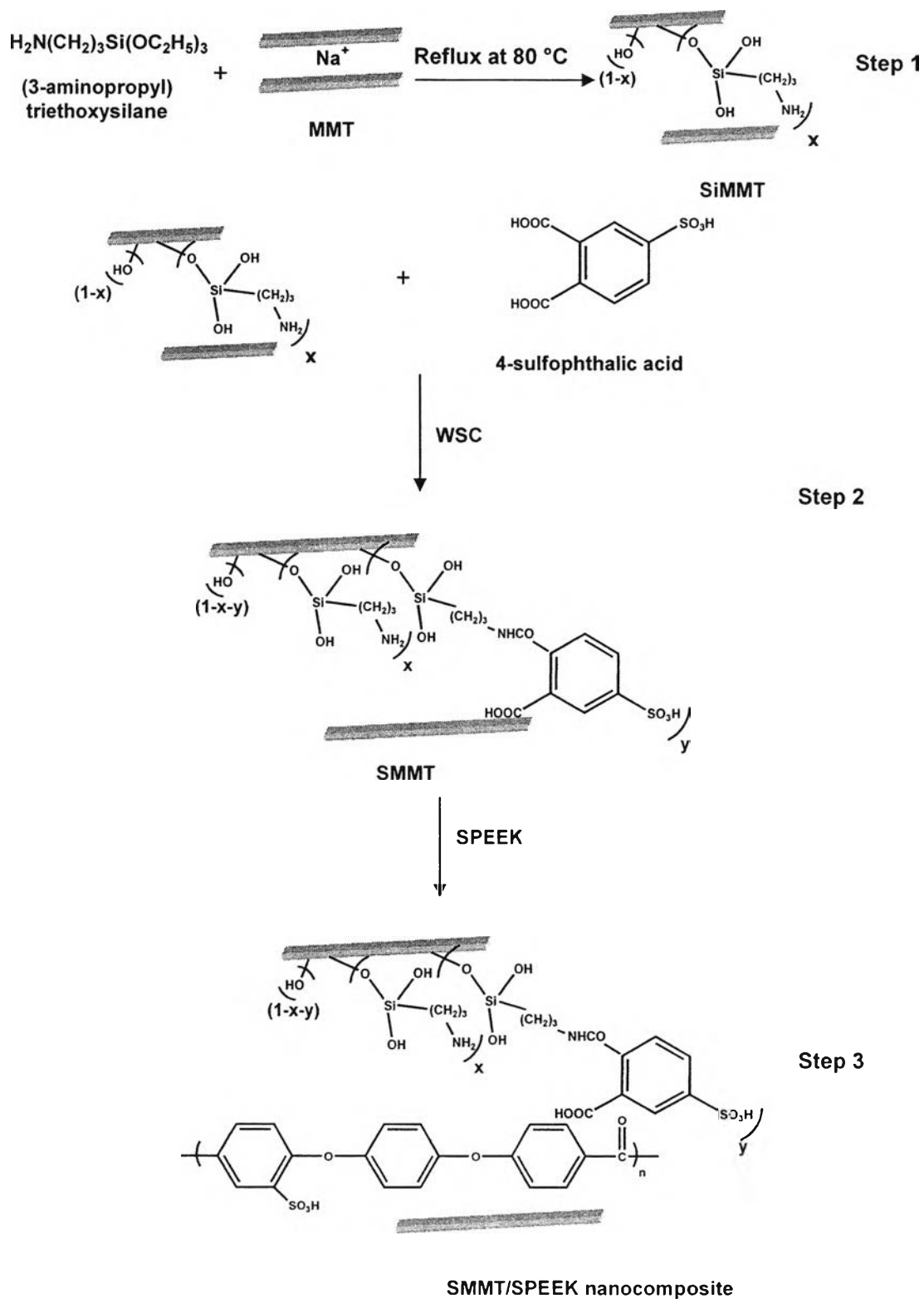
2.2.2. Sulfonated MMT (SMMT)

Na⁺-montmorillonite (MMT) (2.01 g) was suspended into 75 % ethanol solution (800 ml) and vigorously stirred at room temperature for 3 h. In this suspension the (3-aminopropyl)triethoxysilane (γ -APS) (2.4 ml) was dropped into and the mixture was refluxed at 80 °C for 24 h. The suspension was filtered and washed several times with distilled water to obtain the SiMMT (Scheme 6.1, Step 1). The SiMMT was dispersed in distilled water and mixed with WSC (2.51 g, 1.30×10^{-2} mol) and 4-sulfophthalic acid (5.37 ml, 1.09×10^{-2} mol). The mixture was stirred vigorously at room temperature for 24 h. The product was filtered, washed several times with distilled water and dried in vacuum at 60 °C for overnight to obtain the SMMT (Scheme 6.1, Step 2).

2.2.3. Composite membrane preparation

SPEEK4 in dimethylformamide (DMF) (10 wt. %, 15 ml) was mixed with various SMMT content, i.e., 1, 3 and 5 wt. %, and vigorously stirred at room temperature for 4 days followed by sonicating at ambient for 1 h to obtain SMMT/SPEEK hybrid solutions (Scheme 6.1, Step 3). In similar, MMT/SPEEK membranes were prepared from the solutions of SPEEK and by using MMT at 1, 3 and 5 wt. % in DMF. All hybrid solutions (15 ml) were cast on the glass plate and isothermally heated at 60 °C for overnight and dried in vacuum at 70 °C for 12 h to obtain the composite membranes. The SPEEK membrane was prepared as a reference membrane using SPEEK polymer solution (10 wt. %, 15 ml). All membranes had an average thickness 100 μ m.

Scheme 6.1 SMMT/SPEEK nanocomposite preparation



2.3. Structural characterization

Fourier transform infrared (FT-IR) spectra were identified by a Bruker Equinox 55. Elemental analysis (EA) was carried out by a Thermo Finnigan-CE Instruments Model Flash EA 1112 CHNS series.

An amount of aminosilane and 4-sulfophthalic acid modified onto the MMT layers defined as subscript x and y in the tentative structure of the product from Scheme 6.1 (Step 2) was calculated by the following equations:

$$N(\%) = \left(\frac{14x + 14y}{164x + 45(1 - x - y) + 392y} \right) \times 100 \quad (1)$$

$$S(\%) = \left(\frac{32y}{164x + 45(1 - x - y) + 392y} \right) \times 100 \quad (2)$$

FT-IR (film, cm^{-1}) for SPEEK: 3406 (OH), 1645 (C=O), and 1080 (S=O).

Anal. Calcd. for SPEEK3 (-OC₆H₃(SO₃H)-O-C₆H₄-CO-C₆H₄-) (%): C, 61.69; H, 3.26; and S, 8.70. Found (%): C, 62.27; H, 4.31; and S, 4.75.

Anal. Calcd. for SPEEK4 (-OC₆H₃(SO₃H)-O-C₆H₄-CO-C₆H₄-) (%): C, 61.69; H, 3.26; and S, 8.70. Found (%): C, 61.08; H, 4.19; and S, 5.18.

Anal. Calcd. for SPEEK5 (-OC₆H₃(SO₃H)-O-C₆H₄-CO-C₆H₄-) (%): C, 61.69; H, 3.26; and S, 8.70. Found (%): C, 62.18; H, 3.90; and S, 6.10.

FT-IR (KBr, cm^{-1}) for SiMMT: 3625 (free OH) and 3425 (hydrogen-bonded OH), 3300 (NH₂), 2930 and 2860 (CH₂) and 1632 (NH₂).

FT-IR (KBr, cm^{-1}) for SMMT: 3625 (free OH) and 3425 (hydrogen-bonded OH), 3300 (NH₂), 3067 (=CH benzene ring), 2932 and 2865 (CH₂), 1706 (C=O carboxylic acid), 1634 (C=O amide I) and 1559 (NH₂ and C-N amide II).

Anal. Calcd. for SMMT ((SO₃H)(COOH)C₆H₃-NHCO-(CH₂)₃Si(OH)₂-O-MMT) (%): C, 27.95; H, 4.16; N, 4.66; and S, 5.32. Found (%): C, 9.53; H, 2.65; N, 2.37; and S, 1.37.

2.4. Interlayer distance of modified MMT

The interlayer distance of MMT after modification was confirmed by a Seifert3003 X-ray diffractometer (40 kV, 30 mA) with Ni-filtered Cu K α radiation ($\lambda=1.54056$ Å), from 2° to 30° 2 θ . For 2°-15° 2 θ , the scanning rate was 12 °/min with the scanning step of 0.02 °/step whereas for 15°-30° 2 θ , it was 0.3 °/min and 0.05 °/step for the scanning rate and step, respectively.

2.5. Membrane morphology

The cross sectional morphology of the membranes was observed by an LEO 1550 VP scanning electron microscope (SEM) and a multi mode scanning probe Veeco Digital atomic force microscope (AFM). The observations were carried out in air at ambient temperature using tapping mode probes with constant amplitude. The tapping mode etched phosphorous (n) doped silicon probe (square pyramid shape with 40 N/m spring constant, curvature nominal radius < 10 nm) with a resonance frequency ~ 300 kHz was chosen. Phase images were recorded simultaneously at the resonance frequency of the cantilever with a scan rate of 2 Hz and resolution of 512 samples per line. The scanning was done at 3 different positions for each sample.

2.6. Stability of the membranes in water and in methanol aqueous solution

The SPEEK and its composite membranes were cut into a round-shape with 1.2 cm membrane diameter. All membranes were immersed in 1.5 M methanol aqueous solution and in distilled water for 48 h at room temperature. The membranes were wiped thoroughly before measuring the weight. The dry membranes were obtained from drying in vacuum for 24 h at 70 °C. The swelling ratio was evaluated from the weight differences between wet (W_w) and dry (W_d) membranes (Eq. 3). The linear expansion rate was determined by the membrane diameter before (L_0) and after (L_1) soaking in 1.5 M methanol aqueous solution for 1 h at 65 °C (Eq. 4) [21].

$$\text{Swelling ratio (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (3)$$

$$\text{Linear expansion rate (\%)} = \frac{L_1 - L_0}{L_0} \times 100 \quad (4)$$

2.7. Thermal stability

Thermogravimetric analysis was carried out by using a TG209 NETZSCH from room temperature (25 °C) to 700 °C. Differential scanning calorimetry was performed by a DSC204 NETZSCH at the temperature range of 25 °C to 300 °C. Both thermal evaluations were operated with the heating rate of 10 °C/min under nitrogen atmosphere.

2.8. Mechanical stability

The membranes were cut into 35 mm × 15 mm. Mechanical stability of the membrane was measured using a Zwick/Roell Z020, Germany at the speed of 10 mm/min.

2.9. Methanol permeability

The methanol permeability through the membrane was determined by pervaporation measurement [22]. In brief, the membranes were immersed in 1.5 M methanol aqueous solution for 24 h at room temperature. The measurements were carried out at 55 °C using a Millipore cell with 47 mm membrane diameter. Methanol aqueous solution (1.5 M) was circulated in the feed side, at the same time, it was evacuated at the permeate side. The permeated vapor was collected under the liquid nitrogen every single hour. The permeate was weighed and analyzed by using a Hewlett Packard 5890A gas chromatography. The methanol permeability was estimated by the following equations based on the total (J_{tot}) and methanol (J_{MeOH}) fluxes.

$$J_{\text{tot}} = \frac{W_{\text{perm}} \times L}{t \times A} \quad (5)$$

$$J_{\text{MeOH}} = \frac{J_{\text{tot}} \times C_{\text{MeOH}}}{100} \quad (6)$$

where W_{perm} is the weight of permeate (g), t is the permeation time (min), L , A and C_{MeOH} are the thickness (m), surface area (m^2) of the membrane, and the methanol concentration in the permeate (wt. %), respectively.

2.10. Electrochemical performance

All membranes (SPEEK, its composite membranes and Nafion[®] 117) were pretreated by immersing in 1 M H₂SO₄ solution for various durations of time, i.e., 12, 24, 36 and 48 h followed by treating in distilled water for 48 h at room temperature.

2.10.1. Proton conductivity

The proton conductivity was measured by using an IM6 Zahner Elektrik and evaluated by an in-house electrochemical impedance software. The proton conductivities of the membranes with and without acid treatment were evaluated. The measurements were carried out using a four-stack membrane with a cumulative thickness of 400 μm in the frequency range of 10-10⁶ Hz at 40-100 °C under 100 % relative humidity. The relative humidity was controlled by a sealed-off stainless steel impedance cell consisting of two cylindrical compartments connected by a tube. One compartment was filled with water while the other was fixed with the membrane. The proton conductivity was obtained by the impedance value at phase angle zero [23].

2.10.2. Membrane electrode assembly (MEA) fabrication and DMFC single cell test

The membranes were pretreated in 1.5 M methanol aqueous solution at 65 °C for 1 h and in distilled water at the same temperature for 30 min. The membrane electrode assemblies (MEAs) were prepared by hot pressing, without any additional optimizations. The pretreated membrane was compressed in between the two E-TEK electrodes (50 mm \times 50 mm) at 80 °C for 30 sec followed by under the pressure (2 tons) at 80 °C for 30 sec. The anode and cathode electrodes were loaded on a Vulcan XC-72 with 3.0 mg/cm² of 60 % Pt:Ru alloy (1:1) and 4.0 mg/cm² of 100 % Pt black, respectively. The membrane performance was evaluated in a direct methanol fuel cell test station with cathode gas flow unit from an Electrochem, Inc. (CompuCell-GT) and anode flow controller from Bronkhorst HI-TEC. The feed concentration at anode was fixed at 1.5 M methanol aqueous solution with the flow rate of 5 ml/min. The fresh air pressure at cathode was 2 bars at operating temperature of 60 °C. An Advance Optima-Uras14 carbon dioxide sensor connected to an Easy Line-IR detector constructed by ABB Automation Products (Germany) was mounted at the cathode to estimate the methanol crossover during the measurement. The methanol permeability at a constant current of 1 A was calculated as the following equation:

$$P = \frac{F_{\text{cat}} \times C_{\text{CO}_2}}{V_{\text{STP}} \times A \times 100} \quad (7)$$

where P is the methanol permeability ($\text{mol min}^{-1} \text{cm}^{-2}$), F_{cat} is the air flow rate at cathode (L min^{-1}), C_{CO_2} is the CO_2 concentration (% (v/v)), V_{STP} is the molar volume of gas at STP (22.4 L mol^{-1}) and A is the membrane surface area (25 cm^2).

3. Results and Discussion

3.1. Sulfonation of PEEK and MMT

3.1.1. Sulfonated PEEK (SPEEK)

Figure 6.1 (a) shows the characteristic peaks of PEEK, i.e., C=O (1658 cm^{-1}), =CH (1599 and 1493 cm^{-1}) and C-O-C (1224 cm^{-1}). After treating with sulfuric acid, the product obtained, SPEEK, shows the OH peaks at 3406 cm^{-1} , C=O peak at 1645 cm^{-1} and S=O peak at 1080 cm^{-1} (Figure 6.1 (b)). This confirms the successful sulfonation of PEEK polymer backbone.

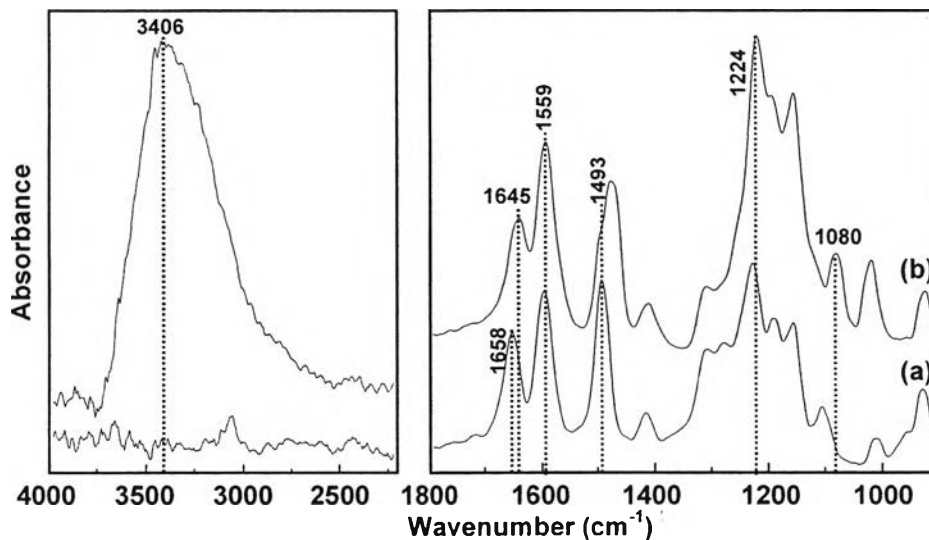


Figure 6.1 FT-IR spectra of PEEK (a) and SPEEK (b).

The degree of sulfonation of SPEEK was determined by estimating the sulfur/carbon ratio obtained from elemental analysis results [24]. Table 6.1 shows that the degree of sulfonation (DS) increases with reaction time. According to the

fact that the more DS the higher proton conductivity, hence, it can be expected that the most favorable polymer for proton exchange membrane (PEM) is SPEEK5. Table 6.1 also shows the solubility of SPEEK5 suggests the instability of this polymer in the DMFC required condition considering the stability in methanol aqueous solution as well as the DS value, SPEEK4 is considered to be a preferable membrane.

Table 6.1 Degree of sulfonation (DS) and solubility behavior in 1.5 M methanol aqueous solution at 50 °C of SPEEK

Polymer	Reaction temperature (°C)	Reaction time (h)	DS (%)	Solubility behavior
SPEEK3	50	3	54.5	-
SPEEK4	50	4	60.6	-
SPEEK5	50	5	70.1	+

(+) soluble; (-) insoluble.

3.1.2. Sulfonated MMT (SMMT)

After the MMT suspension was treated with hydrolyzed γ -APS to obtain SiMMT, the new peaks of free and hydrogen-bonded OH groups (3625 and 3425 cm^{-1}), NH_2 (3300 cm^{-1}) and CH_2 (2932 and 2865 cm^{-1}) are identified (Figure 6.2 (a) and (b)). This confirms the silylation of γ -APS onto MMT layers (Step 1, Scheme 6.1). Figure 6.2 (c) shows the characteristic peaks of 4-sulfophthalic acid of $\text{C}=\text{O}$ at 1706 cm^{-1} and $=\text{CH}$ of benzene ring at 1600 and 1570 cm^{-1} . When SiMMT was further reacted with 4-sulfophthalic acid, the product obtained (SMMT) shows the peaks at 1706 cm^{-1} ($\text{C}=\text{O}$ acid), 1634 cm^{-1} ($\text{C}=\text{O}$ amide I) and 1559 cm^{-1} (amide II) with other characteristic peaks similar to those of SiMMT (Figure 6.2 (d)). This assures the presence of 4-sulfophthalic acid on the MMT layers via chemical bonding with SiMMT (Step 2, Scheme 6.1). Moreover, the amount of aminosilane and 4-sulfophthalic acid developed onto MMT layers was quantitatively analyzed by elemental analysis based on the content x and y of SMMT as shown in Scheme 6.1 [25]. From EA results, the percentages of N and S were 2.72 and 1.37, respectively.

The x and y indicated in Scheme 6.1 were calculated (Eq. (1) and (2)) to obtain 0.1 and 0.03, respectively. This means that the OH groups on the MMT layers for 10 % and 3 % for silylated and sulfonated, respectively.

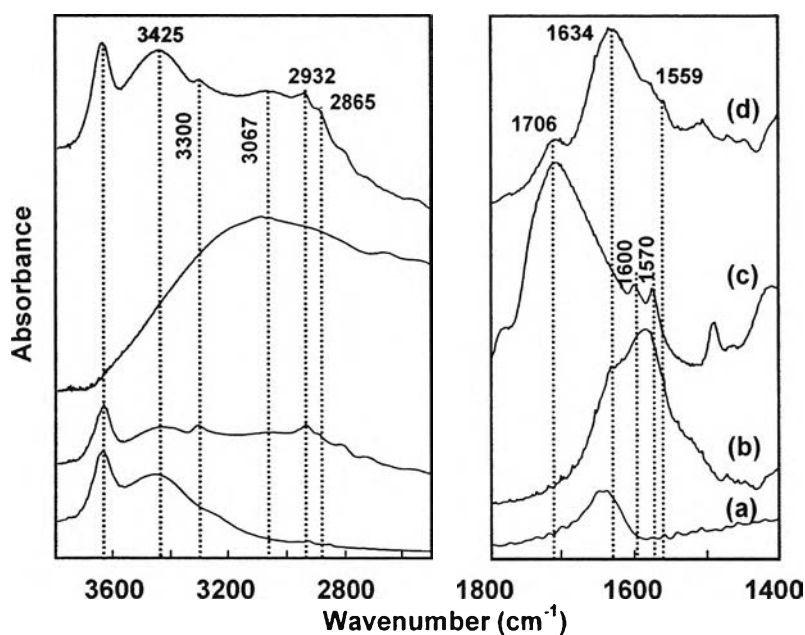


Figure 6.2 FTIR spectra of MMT (a), SiMMT (b), 4-sulfophthalic acid (c) and SMMT (d).

3.2. Interlayer distance of modified MMT

The interlayer distance of MMT was evaluated by XRD. The pristine MMT presents the diffraction peak of the basal spacing (d_{001}) at $7.29^\circ 2\theta$ or $d=12.1$ Å (Figure 6.3 (a)). After the MMT was silylated, the diffraction peak (d_{001}) is shifted to the lower 2θ angle at $4.29^\circ 2\theta$, $d=20.6$ Å (Figure 6.3 (b)). This suggests that the aminosilane was intercalated into the MMT layers. When 4-sulfophthalic acid was introduced into SiMMT to obtain SMMT, the diffraction peak (d_{001}) appears at the lower 2θ angle, i.e., $3.53^\circ 2\theta$, $d=25$ Å (Figure 6.3 (c)). As the results are relevant to those of FTIR spectra (Figure 6.2), we propose the structure of SMMT as in Scheme 6.1.

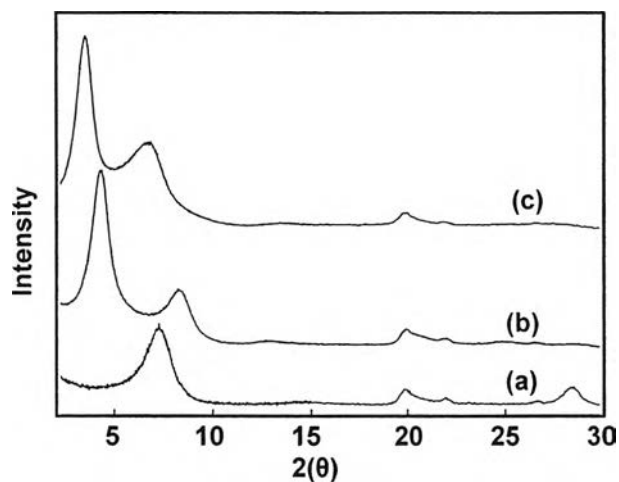
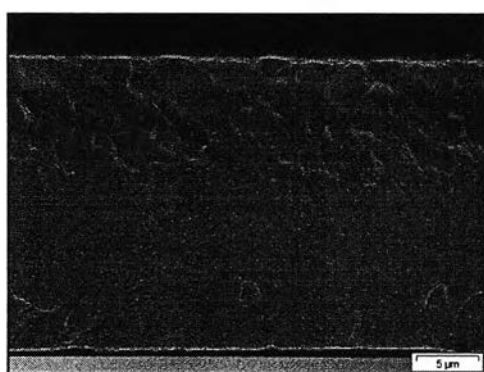


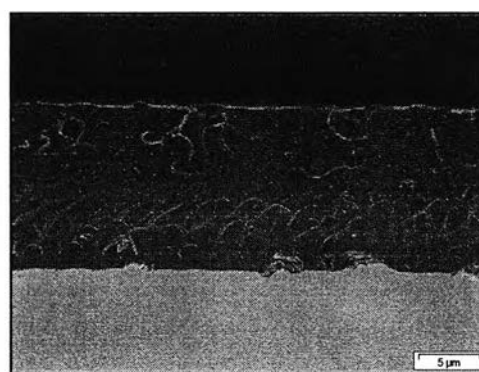
Figure 6.3 X-ray diffraction patterns of MMT (a), SiMMT (b) and SMMT (c).

3.3. Membrane morphology

The microscale morphology and the layer silicate filler (SMMT) dispersion on the composite membranes were observed via the cross-sectional images obtained from SEM. Figure 6.4 (a) shows the smooth cross sectional area of the SPEEK membrane. When the SMMT is incorporated into the SPEEK polymer matrix, the filler aggregation is observed (Figure 6.4 (b)-(d)). The SMMT aggregation was found to increase as the loading content increased.



(a)



(b)

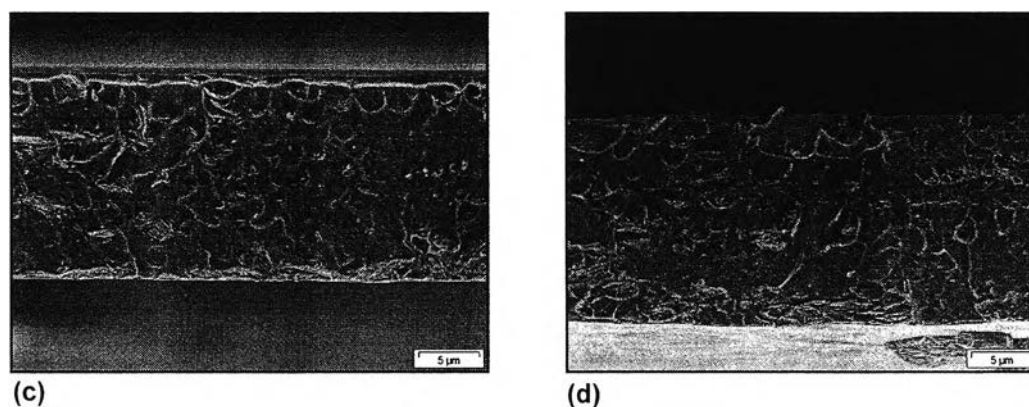


Figure 6.4 SEM cross-sectional images of SPEEK (a) and its composite membranes containing 1 wt. % (b), 3 wt. % (c) and 5 wt. % (d) of SMMT.

In order to further investigate the morphology and the filler dispersion of the composite membranes in nanolevel, the observation by atomic force microscopy (AFM) was carried out. As mechanical properties, such as hardness and modulus, of the hard inorganic and soft polymeric domains in the composite membranes are quite different, we traced those domains by force differences in the tapping mode. The bright and dark regions in the images obtained from the phase contrast mode reflect the differences in domain hardness. Figure 6.5 shows that the nanoclay layers (SMMT) disperse in the SPEEK polymer matrix as seen in the bright region on the smooth dark region. From Figure 6.5 (a)-(b), the size of the bright domains increases with the SMMT loading content. This implies the increase in SMMT loading content leads to an increase in inorganic aggregation. This result is relevant to those of SEM images.

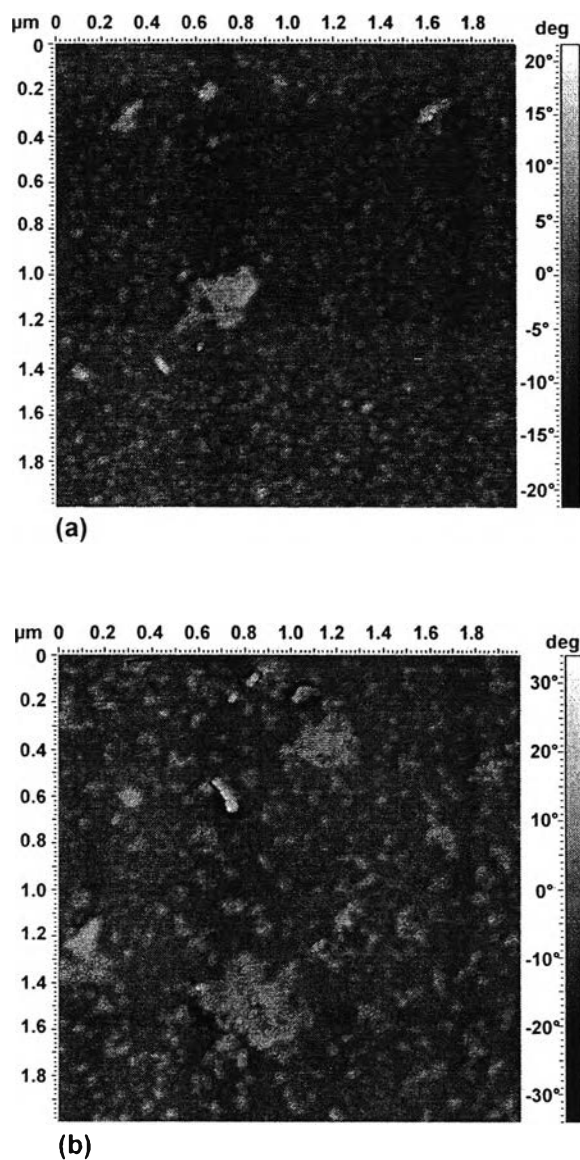


Figure 6.5 AFM images (phase contrast mode) of the SPEEK composite membranes containing 3 wt. % (a) and 5 wt. % (b) of SMMT.

3.4. Swelling behavior in water and in methanol aqueous solution

The membrane stability based on the swelling ratio in water and in methanol aqueous solution at room temperature of SPEEK and its composite membranes were studied. Table 6.2 shows that when SMMT loading content increases from 0 to 5 wt.%, the swelling ratio at room temperature in water and in methanol aqueous solution decrease from 28 to 10 % and 30 to 22 %, respectively. The decrease of swelling ratio of the membranes might be due to the significantly

silicate-layered aggregation as a consequence of the increase in SMMT loading content as could be observed by SEM and AFM images (section 3.3). This inorganic aggregation results in the weakening of hydrogen bond between water or methanol molecules and the hydrophilic groups (OH and NH₂) on the SMMT layers. Besides, it also might be due to the fact that the clay layers embedded fix the polymer chain movement resulting in tightly chain packing as observed from the increase in T_g with the SMMT loading content and the decrease in membrane capacity for water.

3.5. Thermal and mechanical stabilities

The thermal stability of the composite membranes based on the degradation (T_d) and glass transition (T_g) temperatures was evaluated. Table 6.2 shows that the SPEEK and its composite membranes have two degradations steps. Based on the reports of Li et al. [14] and Vetter et al. [24], we interpreted that one at 311-327 °C (T_{d1}) might attribute to the decomposition of sulfonic acid groups of SPEEK whereas the other at 462-466 °C (T_{d2}) might from the main polymer chain (Table 6.2). The composite membranes show the higher degradation temperature than that of SPEEK. For T_g , the SPEEK membrane shows at 149 °C while that of composite membranes are in the range of 176-182 °C (Table 6.2). Moreover, the mechanical stability of the membranes was evaluated via the measurement of the strength at break, which increases from 38.6 to 51.2 MPa when the SMMT loading content are 0-3 wt. % and remarkably decreases to 23.6 MPa at 5 wt. % SMMT (Table 6.2). The decrease in mechanical stabilities of 5 wt. % SMMT/SPEEK composite membranes might be due to the significant aggregation of SMMT layered silicate as revealed in SEM and AFM images (section 3.3). The more aggregation leads to the lower organic (SPEEK)-inorganic (SMMT) interaction resulting in the fact that the SMMT works as the defect rather than the helpful filler. As corresponding to the composite membranes of Nafion/MMT reported by Jung et al. [26], the thermal and mechanical resistant of those composite membranes decreased when the MMT loading content were 5 and 7 wt. % comparing to those with 3 wt. %. However, it should be noted that the thermal stability (T_d and T_g) is not improved significantly, i.e., only some small numbers of degree Celsius increasing are observed with the

increase in SMMT loading content 0-3 wt. % although the mechanical strength is increased remarkably.

Table 6.2 Swelling ratio at room temperature (25 °C), degradation (T_d) and glass transition (T_g) temperatures and strength at break (σ_Y) of the SPEEK membrane containing the different SMMT loading contents

SMMT content (wt.%)	Swelling ratio at 25 °C (%)		T_{d1} (°C)	T_{d2} (°C)	T_g (°C)	σ_Y (MPa)
	Water	1.5 M methanol aqueous solution				
0	28	30	312	463	149	38.6
1	15	24	323	466	178	44.7
3	13	23	327	466	182	51.2
5	10	22	326	464	176	23.6

3.6. Methanol permeability

One of the most important factors influencing the performance of DMFC system is the methanol permeability of the membrane. The methanol-water pervaporation tests at 55 °C were performed to estimate the methanol permeability in term of methanol flux (J_{MeOH}). The methanol flux of SPEEK is $3.8 \times 10^{-10} \text{ kg s}^{-1} \text{ m}^{-1}$ while those of the composite membranes are decreased to 2.8×10^{-10} , 2.5×10^{-10} and $1.8 \times 10^{-10} \text{ kg s}^{-1} \text{ m}^{-1}$ for 1, 3 and 5 wt.% of SMMT loading content, respectively (Figure 6.6). In other words, the methanol flux of the membranes is decreased with the SMMT loading content. The composite membrane with 5 wt. % of SMMT performs a significant reduction of the methanol permeability (more than 50 %). This might be due to the role of the clay in preventing the methanol through the membrane as in the case reported by Chang et al. [7]. For comparative information, the methanol permeability of Nafion[®] 117 membrane was also studied. The methanol flux of Nafion[®] 117 membrane was in the range of two orders of magnitude higher than that of SPEEK, i.e., the methanol flux of Nafion[®] 117 membrane was $1.2 \times 10^{-8} \text{ kg s}^{-1} \text{ m}^{-1}$. The relative high methanol permeability of Nafion[®] 117 membrane as compared to SPEEK membrane might be possibly due to

the wide channels for methanol permeability based on the inconspicuous phases between hydrophilic and hydrophobic part in Nafion[®] 117 membrane [27].

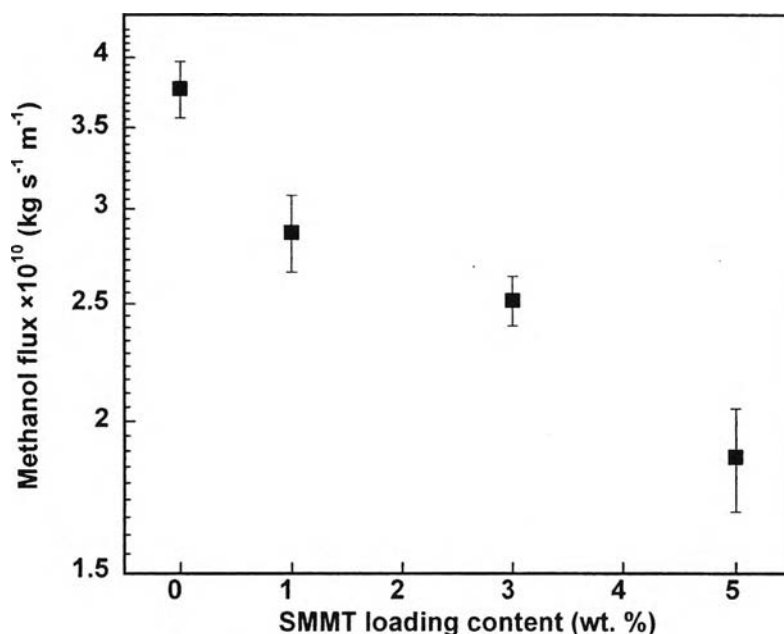


Figure 6.6 Methanol flux of the SPEEK membranes containing the different SMMT loading content.

3.7. Electrochemical properties

3.7.1. Proton conductivity

The electrochemical property based on the ability to conduct proton of the membrane was studied by using AC impedance spectroscopy with various frequencies ($10\text{-}10^6$ Hz) and temperatures ($40\text{-}100$ °C). Figure 6.7 shows an increase in the proton conductivity with the temperature for all membranes. Nafion[®] 117 membrane exhibits the highest proton conductivity at all temperatures, for example 120 mS cm^{-1} at 100 °C. The proton conductivity at 100 °C of SPEEK is 90 mS cm^{-1} while those of the composite membranes containing 1, 3 and 5 wt.% of SMMT are 105, 100 and 30 mS cm^{-1} , respectively. The higher proton conductivity of the composite membranes containing 1 and 3 wt. % of SMMT as compared to that of SPEEK might result from the better ability to retain water (proton carrier) at high temperature (100 °C) due to the hydrogen bond with the hydrophilic groups of the composite membrane (OH, NH_2 and SO_3H) even though the swelling ratio at

room temperature of the composite membranes are lower than that of SPEEK as mentioned in section 3.4. However, the proton conductivity (at 100 °C) of the composite membrane is gradually declined when the SMMT loading content reaches 5 wt. %. The aggregation of SMMT as shown in SEM and AFM images (section 3.3) might hinder proton transferring in the membrane as reported by Gaowen et al. [4] and Kim et al. [8]. Here, it should be noted that the proton conductivity of the composite membranes could be improved when the MMT layers were sulfonated.

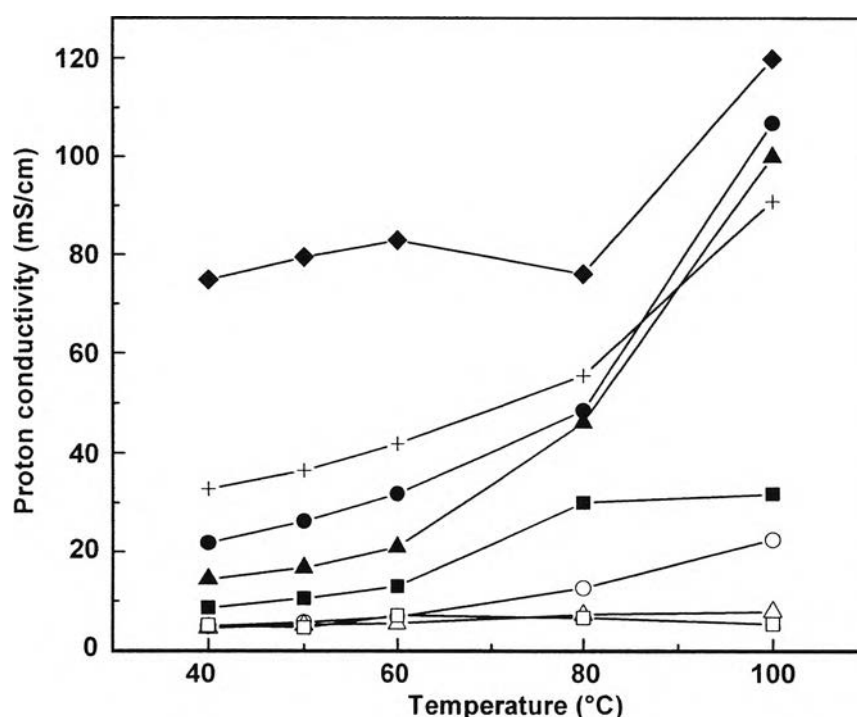


Figure 6.7 Proton conductivity of Nafion[®] 117 (◆), SPEEK (+), and the SPEEK composite membranes containing SMMT (filled symbol) and MMT (blank symbol) for 1 wt. % (●), 3 wt. % (▲) and 5 wt. % (■).

3.7.2. DMFC single cell performance

In order to obtain the best performance in DMFC system, the acid treatment with 1 M H₂SO₄ at room temperature was performed for various durations of time, i.e., 12, 24, 36 and 48 h. For SPEEK composite membranes, this treatment ensures us that the original Na⁺ ions in the MMT layers were replaced with acidic protons and in consequence, the proton conductivity can be improved by increasing

the sulfonation degree. However, at the same time the mechanical stability of the membrane of the membrane electrode assemblies (MEA) used in the DMFC test has to be concerned. Before the DMFC single cell is assembled, the MEAs have to be checked if both electrodes are contacted each other, which implies the break of the membrane in between, showing zero MEA resistant. The membrane stability after acid treatment evaluated by the ability to prepare membrane electrode assembly (MEA) without any defect was also quantitatively determined by the linear expansion rate. Table 6.3 shows that the linear expansion rate of the membranes increases with the acid treatment time. Based on the preliminarily experiments, it was found that the MEAs could not be done when the linear expansion rate more than 100 %. Therefore, the acid treatments for 12, 24, 36 and 48 h were performed on SPEEK and the composite membranes containing 1, 3 and 5 wt.% of SMMT, respectively, denoted as SPEEK (12 h), 1 wt.% (24 h), 3 wt.% (36 h) and 5 wt.% (48 h), respectively. For Nafion[®] 117 membrane, the acid treatment for 48 h showing the stability with the linear expansion rate of 48 % was chosen and defined as Nafion[®] (48 h).

Table 6.3 Linear expansion rate in 1.5 M methanol aqueous solution at 65 °C of the acid-treated membranes

Acid treatment time (h)	Linear expansion rate (%) of the SPEEK membrane with various SMMT loading contents (wt. %)			
	0	1	3	5
12	67	17	8	8
24	105	42	33	17
36	139	100	43	17
48	233	150	117	25

Figure 6.8 shows that the current density generated from the MEAs of Nafion[®] 117 (48 h), SPEEK (12 h), 1 wt.% (24 h), 3 wt.% (36 h) and 5 wt.% (48 h) membranes at the constant voltage of 0.2 V are 51, 76, 103, 96 and 94 mA cm⁻², respectively with the maximum power density of 10, 15, 21, 19 and 18 mW cm⁻²,

respectively. The acid-treated composite membranes present the significant DMFC performance compared to that of SPEEK and Nafion[®] 117 (48 h) membrane at the same DMFC test condition; however, the performance of the acid-treated composite membranes is decreased with the SMMT loading content.

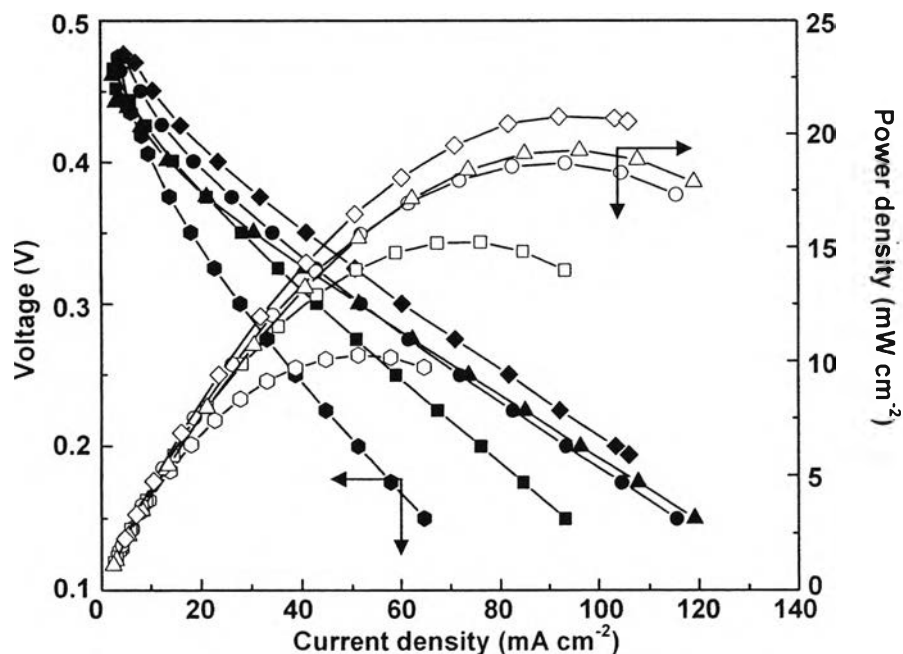


Figure 6.8 Current density-voltage (filled symbol) and power density curves (blank symbol) of the DMFC single test cell at 60 °C of Nafion[®] 117 (48 h) (●), SPEEK (12 h) (■) and the composite membranes of 1 wt.% (24 h) (◆), 3 wt. % (36 h) (▲) and 5 wt. % (48 h) (●).

Since the DMFC performance depends not only on the proton conductivity but also on the ability to prevent the methanol permeability of the membranes, the proton conductivity at 60 °C (operating temperature of the DMFC single cell test) and the methanol permeability at the constant current of 1 A estimated from the CO₂ concentration at the cathode were considered. It was assumed that all CO₂ at the cathode was from the total conversion of methanol crossing through the membranes. Here, the membrane selectivity defined as the ratio of proton conductivity at 60 °C (σ) to the methanol permeability (P). The higher membrane selectivity results in the better membrane performance [19]. From

Figure 6.9, the selectivity of all acid-treated composite membranes is higher than that of Nafion[®] 117 (48 h) and SPEEK (12 h) membranes. The acid-treated composite membrane of 1 wt.% (24 h) presents the best selectivity while those of the 3 wt.% (36 h) and 5 wt.% (48 h) composite membranes give the same level of selectivity relevant to the DMFC single cell results (current density-voltage and power density).

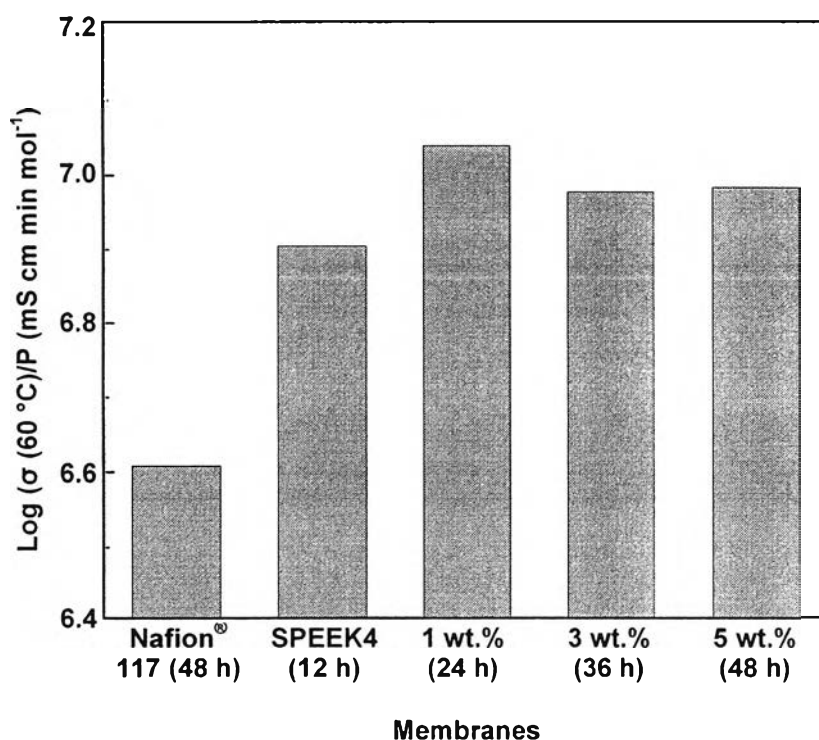


Figure 6.9 Membrane selectivity (the ratio of the proton conductivity (60 °C) to the methanol permeability) of the membranes.

4. Conclusions

(3-Aminopropyl)triethoxysilane was used as a coupling agent to immobilize 4-sulfophthalic acid onto montmorillonite (MMT) layers to obtain sulfonated MMT (SMMT). The functionalization of 4-Sulfophthalic acid was expected to improve the proton conductivity of the composite membrane based on its structure consisting of a sulfonic acid group. The composite membrane was obtained from casting the hybrid solution of SMMT/SPEEK. The inorganic aggregation in the polymer matrix increased with SMMT loading content was

observed by SEM and AFM, respectively. The stability in water and in methanol aqueous solution as well as the mechanical stability was enhanced with SMMT loading content whereas thermal stability improvement did not exist significantly. The methanol permeability was more than 50 % reduction when the SMMT loading content reached 5 wt. %. The comparative study confirmed that the proton conductivity was improved with sulfonation of MMT. The composite membranes showed the significant performance for DMFC test cell as compared to pristine SPEEK and Nafion[®] 117 membranes.

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