



## CHAPTER IV

# THERMO AND ELECTROCHEMICAL CHARACTERIZATION OF SULFONATED PEEK-WC MEMBRANES AND KRYTOX-SI-NAFION® COMPOSITE MEMBRANES

### Abstract

Two types of membranes, the sulfonated PEEK-WC (poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxy-phenylene) (SPWC) and Krytox-Si-Nafion® (KSiN) composite membranes are proposed for DMFC applications. The properties based on water uptake, ion exchange capacity, proton conductivity, gas permeability, thermal stability and methanol crossover are summarized. The comparative studies on SPWC and Nafion® 117 membranes clarify us that the amorphous sulfonated PEEK-WC polymer shows thermal and mechanical stability with less methanol flux and gas permeability. The membrane also exhibits the increase in water uptake, ion exchange capacity and proton conductivity as sulfuric acid doping agent concentration was increased. The KSiN is unique in term of its miscible hybrid structure of silica particles modified with Nafion® structured Krytox 157 FSL chain (KSi) and Nafion®. Based on the KSiN membranes with different KSi content, it was found that when KSi content increased, the reduction of gas permeability, methanol crossover and thermal stability are improved. The composite membrane performs the proton conductivity in the wide range of high temperature (60-130 °C).

**Keywords:** Nafion®; Sulfonation of PEEK-WC; Silica; Composite membrane; DMFCs

### 1. Introduction

In recent years, direct methanol fuel cells (DMFCs) have received much attention because of the high power density and energy conversion efficiency without polluting the environment [1]. With the use of methanol as energy resource, DMFCs provide a simple and compact model for mobile and portable power sources [2]. Proton exchange membranes (PEMs) are generally used as an electrolyte to conduct

the protons and prevent internal electric current between anode and cathode in DMFC systems [3].

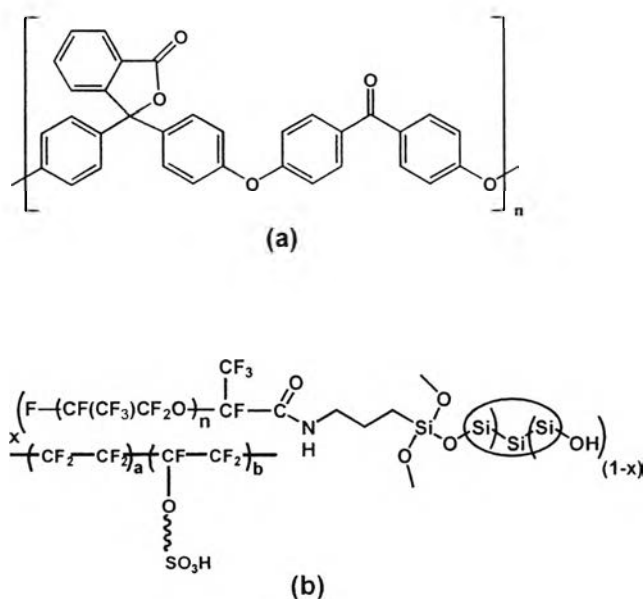
Perfluorosulfonic acid polymer (PFSA) membranes, for example, Nafion<sup>TM</sup> (DuPont), Aciplex<sup>®</sup> (Asahi Chemicals Co.) and Flemion<sup>®</sup> (Asahi Glass Co.) are the available commercial membranes for DMFCs. Based on the high affinity of water and methanol, there is the case that water molecules transporting along the PFSA membranes accompany methanol crossover resulting in depolarization losses at the cathode and conversion losses in term of lost fuel [4, 5]. Thus, the methanol crossover through the membrane is the point to be concerned.

Recent researches have developed novel membranes to conduct protons in DMFCs using two strategies, organic-inorganic composite and new synthetic polymer membranes. Bauer *et al.* [6] showed that the presence of inorganic fillers enhances the membrane mechanical stability decreases the fuel crossover and improves the proton conductivity at low water content. Nafion<sup>®</sup>/zirconium or titanium phosphate [6] and Nafion<sup>®</sup>/Pd nanoparticles [7] composite membranes were reported for the reduction in methanol permeability as compared to unmodified Nafion<sup>®</sup> membrane. Moreover, Gaowen *et al.* [8] exhibited that the sulfonated poly (ether ether ketone) (SPEEK)/organic-montmorillonite (OMMT) composite membrane showed good proton conductivity ( $1.2 \times 10^{-2}$  S/cm) at 90 °C when it was applied to DMFC system. In addition, the methanol crossover of this membrane was lower than that of Nafion<sup>®</sup> and decreased with an increase in OMMT content.

For novel synthetic polymer membranes, polybenzimidazole (PBI) and poly (ether ether ketone) (PEEK) have received much attention due to their mechanical and thermal stability [9, 10]. Zhang *et al.* [11] reported the covalently cross-linked sulfonated PEEK membranes providing good proton conductivity and reduced swelling. Although the methanol crossover is usually increased with temperature, these cross-linked membranes have constant methanol permeation at elevated temperatures up to 130 °C due to the covalent network formed in the membrane structure.

Herein, we focus on the modified PEEK, *i.e.* PEEK-WC (PWC) (Figure 4.1 (a)), which has the Cardo group as pendant groups resulting in more amorphous

phases than PEEK. This favors the solubility in several polar organic solvents such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , DMF, DMA, DMSO and THF as well as the proton conductivity after sulfonation [12]. Previously, there were some reports about the synthesis of SPWC such as the direct reaction of PWC polymer solution with concentrated sulfuric acid (96-98 %) [12, 13] and with chlorosulfonic acid [14]. In those cases, the sulfonation included various consecutive processes and the experiment with the concentrated acid used as sulfonating agent was severe. The aim of the present work is to study both membranes of SPEEK-WC and Krytox-Si-Nafion<sup>®</sup> (KSiN) composite by means of thermochemical characterization, proton conductivity measurements and methanol solution crossover. These studies can be used to be a guideline to develop membrane for DMFC applications in the future work. The simple and mild conditions for sulfonation of SPEEK-WC are also the point of the work. For KSiN (Figure 4.1 (b)), the silica particles modified by Krytox 157 FSL chain are supposed to be miscible with Nafion<sup>®</sup> polymer chain as well as the thermal stability.



**Figure 4.1** PEEK-WC (a) and Krytox-Silica Nafion<sup>®</sup> (b).

## 2. Experimental

### 2.1. Materials

The PWC polymer was supplied by the Chanchung Institute of Applied Chemistry, Academia Sinica, China. Sulfuric acid (96 %) was purchased from Carlo Erba, Italy. Dimethylacetamide was obtained from Lab-scan, Ireland. Five percent weight Nafion<sup>®</sup> in aliphatic alcohol solution was purchased from Aldrich, Germany. Nafion<sup>®</sup> 117 membrane was bought from Ion Power, Inc. (DuPont). (3-Aminopropyl) triethoxysilane was obtained from Fluka, Switzerland. Krytox 157 FSL was provided from DuPont, USA. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride 98 % was purchased from Acros, Belgium. Fumed silica was the product of Degussa, Germany.

### 2.2. Instruments and equipment

The chemical structure was identified by FT-IR using a BRUKER IFS 28 and a Thermo Nicolet Nexus 670. Elemental analysis (EA) was carried out by a PERKIN ELMER 2400 CHN. Proton conductivity was carried out across the membrane using a stainless steel compartment with two electrodes where the membrane was fixed in between during measurement by an IM6 Zahner Electric impedance spectroscopy and a Solartron 1260. Gas permeation was determined using an instrument constructed by GKSS Forschungszentrum, Germany. The gas pressure was measured by an MKS pressure transducer with 0.001 mbar resolution of 13.3 mbar full scale. Thermogravimetric analysis was evaluated by a TGA 2950 DuPont. Glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) were obtained by a Pyris Diamond Differential Scanning Calorimeter (Perkin-Elmer) and a DSC 7 PERKIN ELMER. The concentrations of methanol/water solutions were analyzed by using an Agilent Technologies 6890N Gas Chromatography.

### 2.3. Membrane preparation

#### 2.3.1. SPWC membranes

The PWC polymer solution was prepared by dissolving the purified polymer in dimethylacetamide to obtain 33 wt. % concentration and stirred at room temperature for 24 h. The solution was left at ambient temperature under vacuum for 30 min and cast on the glass plate to obtain the PWC dense membrane. The membranes obtained were dried at 80 °C under vacuum and treated with two

different sulfuric acid concentrations, i.e., 24 and 48 wt. %, for 24 h. After treatment, the membranes were washed by distilled water for several times and dried at 60 °C under vacuum to remove the excess of acid solution. Both sulfonated PWCs (SPWC24 and SPWC48, respectively) membranes had a thickness of around 35 µm.

### 2.3.2. Krytox-Si-Nafion<sup>®</sup> (KSiN) composite membranes

The Krytox-Si-Nafion<sup>®</sup> (KSiN) composite membranes were prepared as reported previously [15]. In brief, the fumed silica was heated at 230 °C in vacuum for 3 h before use. The hydrolyzed (3-aminopropyl) triethoxysilane (0.1427 g) was mixed with the fumed silica (0.5107 g) in 100 ml of 90 % ethanol. The mixture was stirred vigorously at 80 °C for 8 h and washed several times to obtain silica coupled with aminosilane, SiAS. The product was stirred with WSC (0.13 g,  $6.5 \times 10^{-4}$  mol) in aqueous solution at room temperature for 6 h. Krytox 157 FSL (1.625 g) was added with the molar ratio of Krytox: silane: WSC 1:1:1. The mixture was stirred overnight at room temperature to obtain Krytox-Si (KSi). Nafion<sup>®</sup> 5 wt. % in aliphatic alcohol solution was mixed with KSi in DMSO for 2 days and sonicated at ambient temperature for 1 h to obtain KSiN hybrid solutions. The KSiN and Nafion<sup>®</sup> solution were cast onto a Teflon mold and isothermally treated at 160 °C for 3 h to obtain KSiN (KSiN1.5, KSiN2.5 and KSiN5 for 1.5, 2.5 and 5 wt. % of KSi) and the recast Nafion<sup>®</sup> membranes.

### 2.4. FT-IR analysis for SPWC membranes

FT-IR spectra have been obtained on a BRUKER IFS 28 spectrophotometer. The analysis regarded both SPWC24 and SPWC48 and pure PEEK-WC: the presence of the sulfonic group (-SO<sub>3</sub>H) was checked through a direct comparison.

### 2.5. Water uptake

The membrane samples were immersed in distilled water at 60-80 °C for 1-2 days thoroughly wiped off the excess water on the surface and weighed the hydrated membrane. The membranes were dried in vacuum oven at 80 °C for 24 h to obtain the dry weight. The water uptake was evaluated from the weight differences of the hydrated and dried membranes as following equation [16].

$$\text{Water uptake} = \left[ \frac{(\text{wet weight} - \text{dry weight})}{\text{dry weight}} \right] \times 100 \quad (1)$$

The percent weight loss of the water in the membranes was also determined by using the thermogravimetric analysis technique.

## 2.6. Ion exchange capacity (IEC)

SPWC24 and SPWC48 membrane samples have been put in distilled water at 50, 80 and 100°C for 24 h to evaluate the membranes stability. The membranes show to be stable up to 100°C. The membranes were washed with distilled water and dried in oven at 80 °C under vacuum for 24 h. The membranes were weighed in dry state and immersed in saturated NaCl solution at room temperature for 24 h. The solution obtained was titrated with 0.1 N NaOH solution using the phenol red as the endpoint indicator. The IEC was defined as a milliequivalent of exchanged proton per dry polymer weight (meq<sub>H+</sub>/g) [12, 13].

## 2.7. Specific proton conductivity

For SPWC membranes, conductivity measurements were performed on both SPWC24 and SPWC48 in temperature range 40-100 °C at 100 % of relative humidity. Those of KSiN composite membranes were carried out on the fully hydrated membranes obtained from the following procedures. The membranes were soaked in 3 % (v/v) of H<sub>2</sub>O<sub>2</sub> at 80 °C for 1 h, distilled water at 100 °C for 1 h, 1M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 1 h and distilled water at 100 °C for 15 min. The proton conductivity was measured at the range of 20-140 °C [15]. All measurements were performed in the frequency range of 10 Hz-1 MHz.

## 2.8. Gas permeability

All the membranes were equilibrated at 25 and 80 °C under vacuum overnight before measurement. The feed gas pressure was 1 bar and the total permeate volume was 75.5 cm<sup>3</sup>. The permeate pressure was measured. The gas permeation is expressed by the gas permeability coefficient P and calculated as follows [17]:

$$P = \frac{L \times V_p \times V_m}{A \times T \times \Delta P \times R} \left( \frac{dP}{dt} \right) \quad (2)$$

Where  $L$  is the membrane thickness (cm),  $V_p$  is the permeate volume (cm<sup>3</sup>),  $V_m$  is the molar volume of the gas at standard temperature and pressure,  $A$  is the membrane surface area (cm<sup>2</sup>),  $T$  is the absolute temperature (K),  $\Delta P$  is the pressure difference between feed and permeate part (cmHg) and  $dP/dT$  is the changing rate of permeate pressure (cmHg/s).

## 2.9. Thermal properties

The water weight loss of the KSiN composite membranes was determined by the thermogravimetric analysis technique at 80-100 °C with a heating rate of 10 °C/min. Glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) were observed at 90-300 °C with a heating rate of 15 °C/min. All thermal evaluations were accomplished under nitrogen atmosphere. Concerning SPWC membranes, DSC measurements were carried out on a Pyris Diamond Differential Scanning Calorimeter with a heating rate of 15°C/min using samples of about 8 mg.

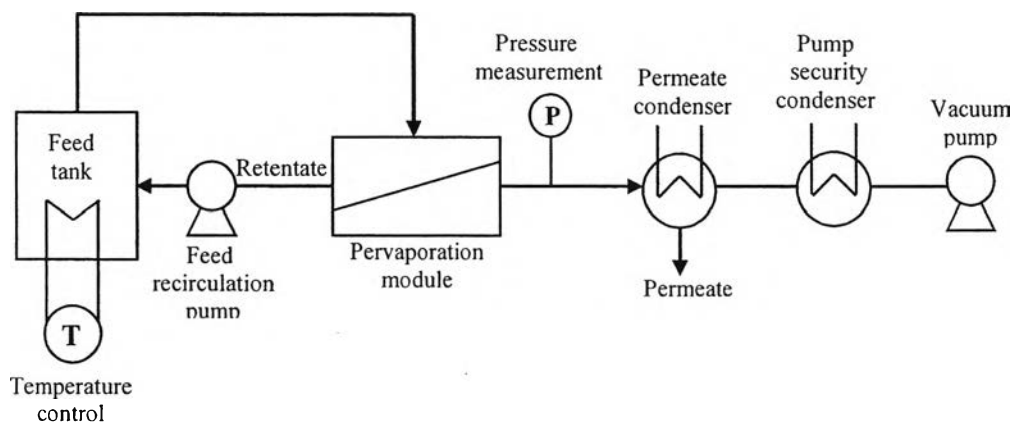
## 2.10. Methanol-water pervaporation

Since the instrument for gas permeation constructed by GKSS (Germany) is only able to quantify the permeation of pure gas and pure vapour, the permeabilities of water/methanol mixtures were measured by using the pervaporation technique, as indicated for example by Ruffmann *et al.* [18] and Nunes *et al.* [19]. Pervaporation was carried out at 25 °C and 60 °C in water containing methanol for 25, 50, 75, and 90 % (v/v). The membrane was assembled in the pervaporation testing unit (Figure 4.2). The pressure of the feed side in the thermostat bath was 1 bar while that of the permeate side was less than 3 mbar. The permeate stream was condensed using the liquid nitrogen bath. The total flux ( $J_{tot}$ ) and methanol flux ( $J_{MeOH}$ ) were evaluated according to the following equations:

$$J_{total} = \frac{W_{perm}}{t \times A} \quad (3)$$

$$J_{MeOH} = \frac{D_{MeOH} \times \%MeOH}{(D_{MeOH} \times \%MeOH) + (D_{water} \times \%water)} \times J_{total} \quad (4)$$

where  $W_{perm}$  is the weight of permeate solution at steady state (g),  $t$  is the permeate time (min),  $A$  is the membrane surface area ( $cm^2$ ) and  $D_{MeOH}$  and  $D_{water}$  are the density of methanol and water ( $g/cm^3$ ), respectively.



**Figure 4.2** Pervaporation plant.

### 2.11. Morphological observation

The morphology of the composite membranes was evaluated by using a JEOL JSM-6400 scanning electron microscope. The membrane was washed thoroughly by 10 % methanol aqueous solution and water for several times before drying in vacuum oven at 40 °C.

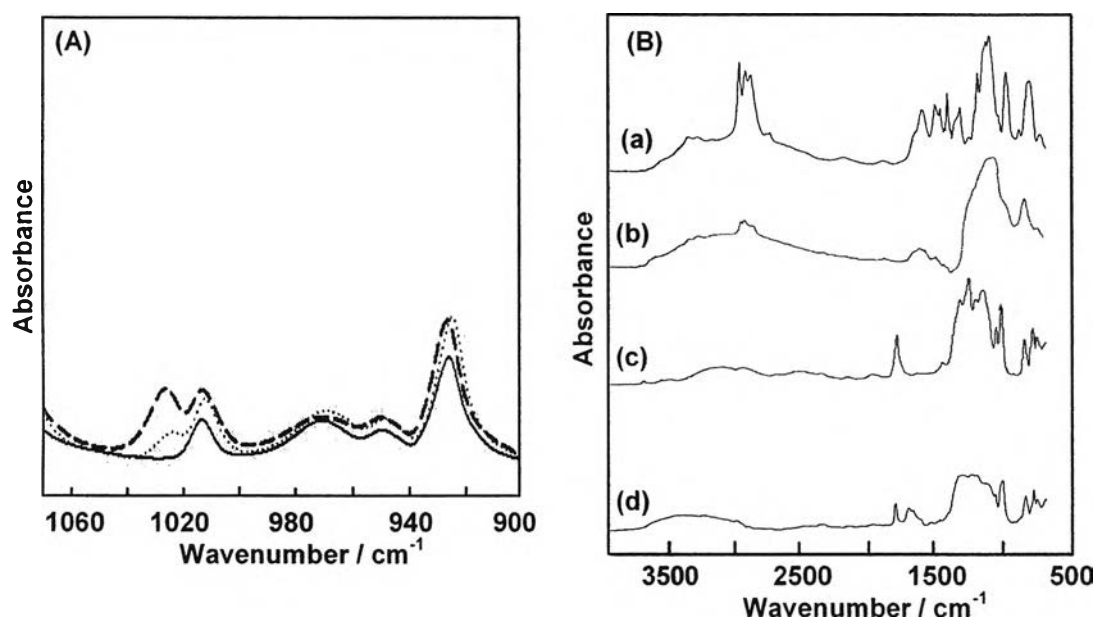
## 3. Results and Discussion

### 3.1. Structural characterization

In order to clarify the presence of sulfonic acid groups in both SPWC24 and SPWC48, the FT-IR spectra of both membranes in the range of 1070-900  $cm^{-1}$  were considered. Figure 4.3 (A) shows the significant characteristic peaks of sulfonic acid group at 1030-1020  $cm^{-1}$  and at 930-920  $cm^{-1}$ . By comparing the peak between 1020-1030  $cm^{-1}$  for both SPWC24 and SPWC48 with respect to pure PWC line, it can be said that they correspond to the symmetric stretching of the sulfonic group ( $-SO_3H$ ) [13, 20]. The second peak, around 920-930  $cm^{-1}$ , could be due to the increasing intensity of the sulfonation level. It could be explained by the electrophilic substitution of a H atom in the PWC aromatic ring with a  $-SO_3H$  group [13, 21]. For what concerns the KSiN, Figure 4.3 (B) shows the OH stretching peak



of HAS at  $3500\text{-}3400\text{ cm}^{-1}$  implying the successful hydrolyzation of (3-aminopropyl) triethoxysilane. For SiAS, the coupling reaction of silica particles and HAS can be confirmed by the strong Si-O-Si peak at  $1150\text{-}1050\text{ cm}^{-1}$ . After conjugation of SiAS and Krytox 157 FSL, the product (KSi) exhibits the characteristic peaks at  $1774\text{ cm}^{-1}$  (C=O of Krytox 157 FSL), at  $1680\text{ cm}^{-1}$  (C=O of amide) and at  $1100\text{-}1040\text{ cm}^{-1}$  (Si-O) meaning for the successful modification of Krytox 157 FSL onto silica surface. The elemental analysis (EA) was also used to evaluate the content of HAS coupled onto silica surface via the data of percent C and N. It was found that one-tenth of HAS was successfully coupled onto the surface of silica particle.



**Figure 4.3** FTIR spectra (A) of PWC ( — ), SPWC24 (.....) and SPWC48 ( - - - ); (B) of hydrolyzed (3-aminopropyl)triethoxysilane (a), SiAS (b), Krytox 157 FSL (c) and KSi (d).

### 3.2. Water uptake

The water uptake, in other words the water retention capacity, is a parameter affecting the proton conductivity [12]. Table 4.1 shows the water content (wt. %) in the SPWC and KSiN. The water uptake of SPWC24 and SPWC48 are 8.3 and 9.4 wt. %, respectively, whereas that of Nafion<sup>®</sup> 117 is 23 wt. %. This implies that the hydrophilicity based on the sulfonic acid groups of the SPWC might be less than that

of Nafion<sup>®</sup> 117 membrane. For KSiN, the water content retained in the KSiN1.5, KSiN2.5 and KSiN5 membranes are 22, 42, and 51.5 wt. %, respectively. Comparing to that of Nafion<sup>®</sup> 117 membrane, the high water retention might come from the silica inorganic content in the membrane [15].

### 3.3. Ion exchange capacity (IEC)

The IEC values, able to influence the SPWCs electrochemical properties were studied and compared to those of Nafion<sup>®</sup> 117. Table 4.1 shows that an increase of doping sulfuric acid concentration leads to the increase in IEC, for example, increasing from 0.169 meq<sub>H+</sub>/g and 0.217 meq<sub>H+</sub>/g for SPWC24 and SPWC48, respectively. With respect to the Nafion<sup>®</sup> 117 (IEC = 0.931 meq<sub>H+</sub>/g), the SPWC membranes show lower IEC. This might be due to the sulfuric acid immersion of PWC membranes generated the sulfonation mainly on the membrane surface.

In the case of KSiN, the IEC values are enhanced to be in the range of 1.48-1.68 meq<sub>H+</sub>/g, 58-80 % higher than that of Nafion<sup>®</sup> 117. Chen *et al.* [22] reported that Nafion<sup>®</sup> composite membrane having higher surface area than unmodified Nafion<sup>®</sup> exhibits the more fractions of proton exchangeable sites (IEC) in the membrane. Besides, the surface of silica consisting of silanol (-Si-OH) and siloxane (-Si-O-Si) has high acidic strength which can function as electron-accepting/donating part [23]. This might lead to the improvement of IEC values after incorporate silica into Nafion<sup>®</sup> for composite membrane preparation.

**Table 4.1** Water uptake and ion exchange capacity (IEC) of the membranes

Membrane	Water uptake (wt. %)	IEC (meq <sub>H+</sub> /g)
SPWC24	8.3 <sup>a</sup>	0.169
SPWC48	9.4 <sup>a</sup>	0.217
KSiN1.5	22 <sup>b</sup>	1.581
KSiN2.5	42 <sup>b</sup>	1.482
KSiN5	51.5 <sup>b</sup>	1.683
Nafion <sup>®</sup> 117	23 <sup>c</sup>	0.931

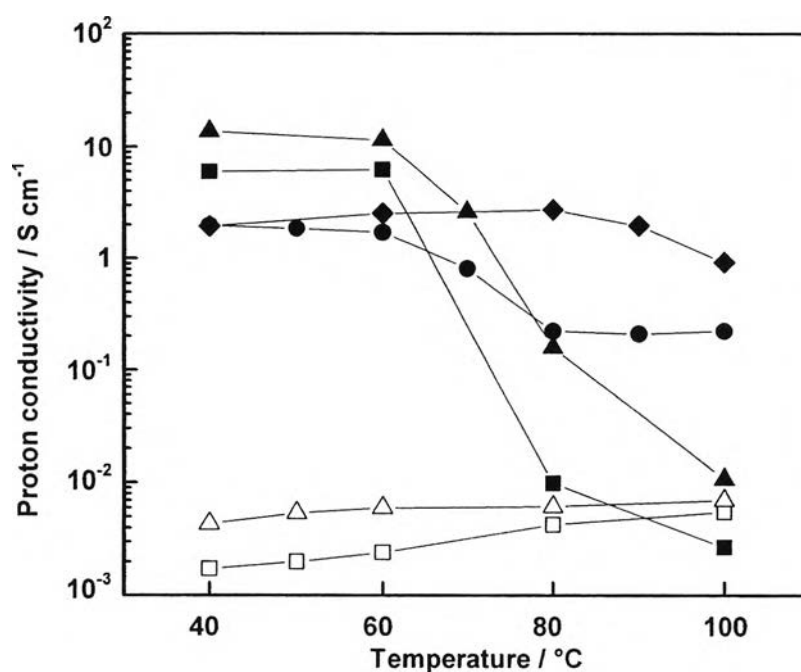
<sup>a</sup> Results obtained from weighing

<sup>b</sup> Result from TGA

<sup>c</sup> From [12].

### 3.4. Proton conductivity

The electrochemical properties of the membranes were studied based on the complex impedances measured by applying alternating current with various frequencies. Figure 4.4 shows the proton conductivity of all membranes at the temperature range of 40-100 °C. By varying temperature, SPWC48 specific conductivity is higher than that of SPWC24 because of its higher sulphuric group concentration. At 100 °C the SPWC48 conductivity is around  $7 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  while for SPWC24 it is  $5.5 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  with 0.5 mS/cm for the experimental error in conductivity measurements. This indicates that the sulfonation time of SPWC membranes plays an important role in enhancing the proton conductivity.



**Figure 4.4** Proton conductivity of the recast Nafion<sup>®</sup> (■), KSiN1.5 (▲), KSiN2.5 (●), KSiN5 (◆), SPWC24 (□) and SPWC48 (△).

The comparison proton conductive studies of the recast Nafion<sup>®</sup> and KSiN composite membranes [15], the proton conductivity of the recast Nafion<sup>®</sup> and KSiN1.5 composite membranes were gradually declined from  $7 \times 10^{-3}$  and  $1 \times 10^{-2}$   $\text{S} \cdot \text{cm}^{-1}$  (60 °C) to be  $2 \times 10^{-6}$  and  $6 \times 10^{-6}$   $\text{S} \cdot \text{cm}^{-1}$  (130 °C) while those of KSiN2.5 and KSiN5 composite membranes were found to be retained at  $2 \times 10^{-4}$  and  $10^{-3} \text{S} \cdot \text{cm}^{-1}$ , respectively, even though the temperature was up to 130 °C and in anhydrous condition. It should be noted that the increase in inorganic content raises the amount of water maintained in the membrane corresponding to the previous results of water uptake of Kim *et al.* [25]. Due to the fact that proton conductivity is strongly dependent on the water content in the membrane [12, 26], the improvement of proton conductivity at temperature above 100°C might be influenced by the silica particles. Taking all conditions in our consideration, the highest proton conductivity obtained was  $10^{-3} \text{S} \cdot \text{cm}^{-1}$  (at 130 °C in anhydrous condition) which can be expected to improve the property of Nafion for the use at high temperature (proton conductivity of the commercial Nafion 117 =  $2.2 \times 10^{-2}$   $\text{S} \cdot \text{cm}^{-1}$  at below 100 °C under 100 % relative humidity [27]).

### 3.5. Gas permeability

The gas permeation is an important parameter for the membrane used in PEMFCs and DMFCs since the low gas feed crossover through the membrane results in the high efficiency of proton conductivity [28]. The permeability of hydrogen and oxygen gas through the hydrated SPWC24 and SPWC48 and Nafion<sup>®</sup>-silica based composite membranes was analyzed at 25 °C and 80 °C as shown in Table 4.2. The gas permeability of pure PWC and Nafion<sup>®</sup> 117 membranes are included for comparison. The gas permeability at both 25 °C and 80 °C is increased with IEC; for example, the hydrogen gas permeability at 25 °C is increased from 6.00 barrers for pure PWC to 8.48 and 35.50 barrers for SPWC24 and SPWC48, respectively. This confirms that more sulfonation leads to higher gas permeability. As mentioned in 3.3, the fact that the sulfonic groups of SPWC are present just on the membrane surface whereas those of Nafion<sup>®</sup> 117 are in polymer bulk, consequently, at 25 and 80 °C both SPWC24 and SPWC48 give the better efficiency to reduce gas permeation than Nafion<sup>®</sup> 117 membranes. Comparing the results at 25 and 80 °C, it should be noted

that the enhancement of gas permeation is discerned at elevated temperatures might be due to polymeric matrix enlargement. The KSiN composite membranes display lower gas permeability at 25 and 80 °C than those of Nafion<sup>®</sup> 117 (Table 4.2). Kumar *et al.* [29] reported that the inorganic content in composite membrane reduced the gas permeability. However, the gas permeation isn't reduced proportionally with the increment of KSi content at both temperatures. This might be due to the fact that the loading content of KSi in each composite membrane limits only for 1.5, 2.5, and 5 wt. % which might not initiate the difference in gas permeation. Similar to SPWCs, the composite membranes also exhibit obviously the increase in gas permeation when increase the temperature. The molecular enlargement of the polymer matrices at higher temperature as well as the water evaporation might be the main factor to initiate the increment of gas permeability.

**Table 4.2** Gas permeability of all membranes

Sample	Gas Permeability (barrers <sup>a</sup> )			
	25°C		80°C	
	H <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>
SPWC24	8.48	0.67	30.50	10.00
SPWC48	35.50	8.24	49.00	13.90
PWC <sup>b</sup>	6.00	0.70	n/a	n/a
KSiN1.5 <sup>c</sup>	5.57	0.70	n/a	n/a
KSiN2.5	5.79	0.58	36.90	12.03
KSiN5	5.34	0.65	36.88	12.63
Recast Nafion <sup>®</sup> <sup>d</sup>	51.00	0.85	150.00	n/a
Nafion <sup>®</sup> 117 <sup>e</sup>	60.00	1.00	180.00	90.00

<sup>a</sup> 1 barrer = 10<sup>-10</sup> cm<sup>3</sup>(STP)•cm/(S•cm<sup>2</sup>•cmHg) [12]

<sup>b</sup> From [34]

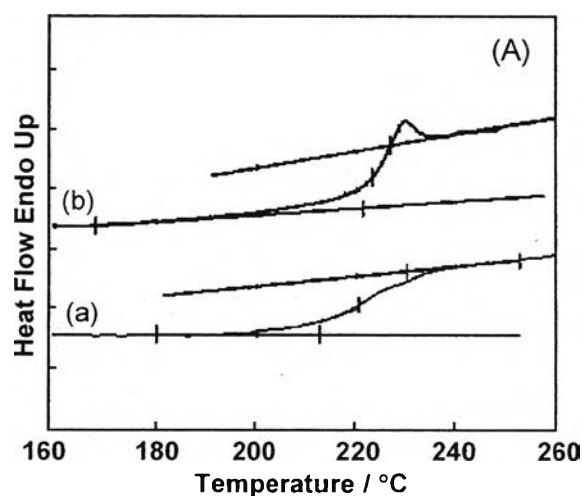
<sup>c</sup> The membrane breaking at 80°C

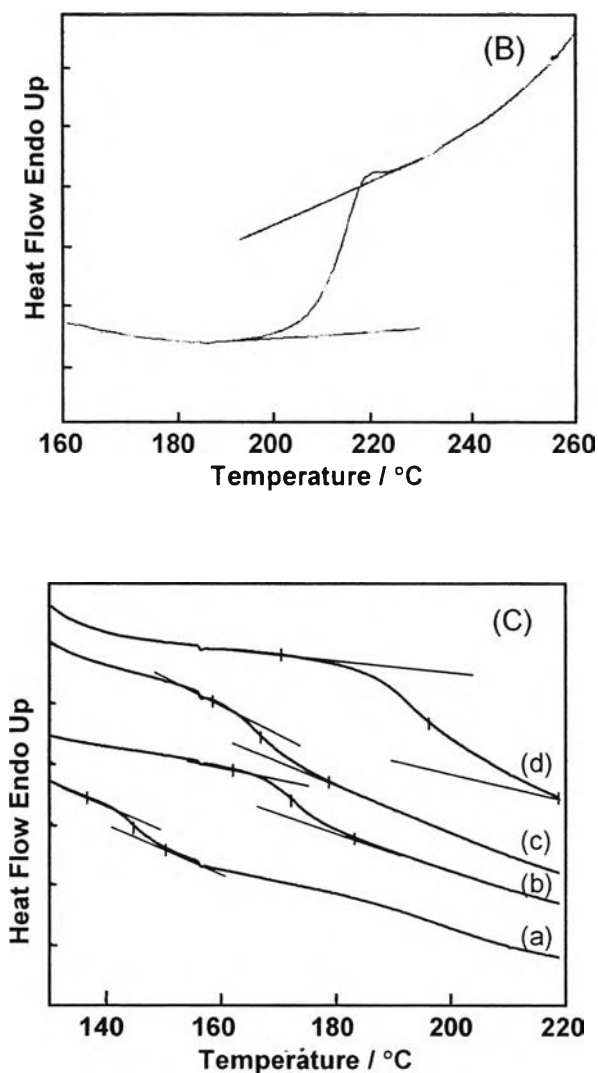
<sup>d</sup> Casting of 5 wt. % Nafion<sup>®</sup> in aliphatic alcohol solution

<sup>e</sup> At 25°C obtained from [35] and at 80°C from [36].

### 3.6. Thermal properties

Previously, Drioli *et al.* [30] reported that PWC showed good results for both thermal and mechanical stability. The PWC has a high glass transition temperature ( $T_g$ ) at 228 °C and degradation temperature ( $T_d$ ) up to 454 °C. Paturzo *et al.* [12] demonstrated that the membrane with high  $T_g$  gives good dimensional stability for fuel cell operation at elevated temperature. Here, the membranes were characterized by DSC in order to evaluate the thermal properties. Figure 4.5 (A) shows the two heating curves of SPWC48 revealing the similar  $T_g$  at around 222 °C stable at fuel cell operative temperature (60-120 °C). Moreover, the melting peak also appears at 230 °C in the second heating run implying that the crystallinity of the membrane is increased after molecular rearrangement during the cooling process. The  $T_g$  value of the SPWC24 is 221 °C (Figure 4.5 (B)), showing also how the thermal properties of the membrane does not change at a lower sulfonation degree. In the cases of KSiN, the  $T_g$  are in the range of 165-190 °C whereas that of the recast Nafion<sup>®</sup> is 145 °C indicating that the higher inorganic content (KSi) incorporated leads to the improvement of  $T_g$  (Figure 4.5 (C)). Merkel *et al.* [31] exhibited that the interactions between the filler surface and polymer chains restrict the chain mobility and as a result, the increase in  $T_g$ . For example, Yim *et al.* [32] presented a direct correlation between polymer-filler interaction and the increase in  $T_g$  for polymer composite with several silica quantities.



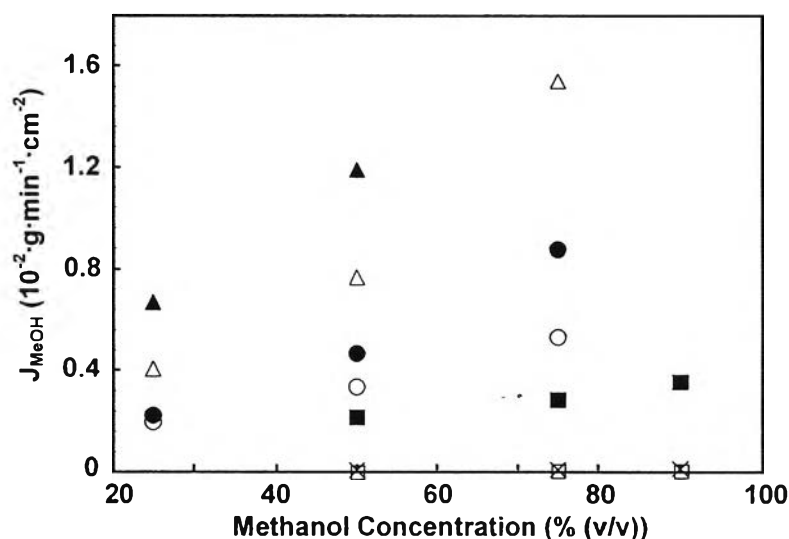


**Figure 4.5** DSC diagram (A) of SPWC48 at first (a) and second heating run (b); (B) of SPWC24; (C) of Nafion<sup>®</sup> (a), KSiN1.5 (b), KSiN2.5 (c) and KSiN5 (d).

### 3.7. Methanol crossover

The pervaporation testing unit based on the percent of methanol passing through the membranes under the different pressure between the feed and permeate phases was applied to evaluate the methanol crossover. The experiments were performed under the several methanol concentrations, i.e., 25, 50, 75, and 90 % (v/v), at 25 °C and 80 °C. Figure 4.6 shows that the permeations are increased with a methanol concentration and/or temperature increase. At 25 °C, the SPWC24 and SPWC48 show a methanol flux in the range, respectively, of  $3.31 \times 10^{-5}$  -  $8.24 \times 10^{-5}$

$\text{g}/\text{min cm}^2$  and  $7.75 \times 10^{-5}$ - $1.38 \times 10^{-4}$   $\text{g}/\text{min cm}^2$ , which are lower than that of Nafion<sup>®</sup> 117 ranging between  $2.17 \times 10^{-3}$ - $3.55 \times 10^{-3}$   $\text{g}/\text{min cm}^2$ . This might be due to the differences in microstructure between the SPWC membranes and Nafion<sup>®</sup> 117. In the presence of water, the sulfonic acid groups in the Nafion<sup>®</sup>'s microstructure might aggregate and form the hydrophilic clusters to generate the polar channels for water and methanol molecules. In contrast, the SPWC membranes with the rigid polyaromatic backbone might not effectively generate the polar channels resulting in the lower methanol crossover as compared to Nafion<sup>®</sup> one [33]. Vice versa, the SPWC48 shows a higher methanol fluxes than the SPWC24 one due to its higher sulfonation degree, which favors a higher methanol cross-over through the membrane.

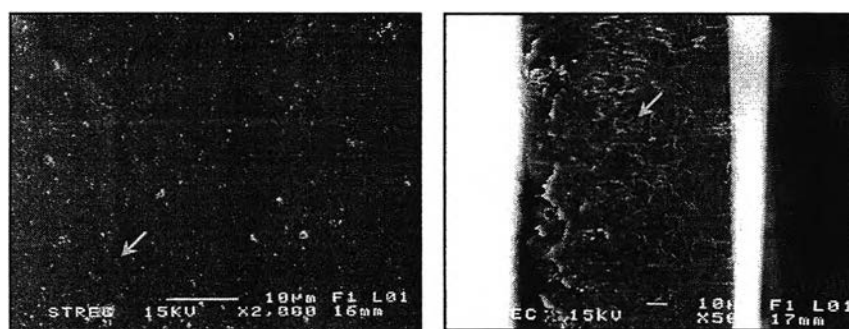


**Figure 4.6** Methanol flux at 25 °C of SPWC48 (×), SPWC24 (□), Nafion<sup>®</sup> 117 (■), KSiN2.5 (●) and KSiN5 (○); at 80 °C of KSiN2.5 (▲) and KSiN5 (△).

For KSiN, the methanol flux is in the range of  $2 \times 10^{-3}$ - $8.5 \times 10^{-3}$   $\text{g}/\text{min cm}^2$  and the increase in KSi content offers the decrease in methanol flux (Figure 4.6). This corresponds to the literatures [6-8] reported that the composite membrane with inorganic content can reduce the methanol permeation. However, compared to the commercial Nafion<sup>®</sup> 117 membrane, KSiN composite membranes have higher



methanol cross over. The results might be due to the defect of the membranes, such as micropores,. Figure 4.7 shows the surface and crosssectional morphologies of KSiN5. The micropores on the surface were in the range 0.25-0.5  $\mu\text{m}$  whereas those in the crosssection were 1-2  $\mu\text{m}$ . In addition, the higher water uptake of KSi comparing to commercial Nafion<sup>®</sup> 117 membrane might be one of the substantial factors to increase methanol permeability [4, 5]. The optimization for KSi inorganic loading content to obtain suitable water uptake for maintaining proton conductivity at elevated temperature as well as high efficiency to transverse methanol crossover is in progress.



**Figure 4.7** SEM micrographs of KSiN5 composite membrane, surface (a) and cross section (b).

#### 4. Conclusions

The PWC membranes were successfully sulfonated by sulfuric acid to obtain SPWC. For Kryrox-Si-Nafion<sup>®</sup> (KSiN) composite membranes, the KSi was obtained by functionalizing a type of fluorocarbon (Krytox 157 FSL) onto silica particles. The KSiN composite membranes were obtained by casting the mixture of KSi and Nafion<sup>®</sup> in aliphatic alcohol solution. The water uptake, ion exchange capacity and proton conductivity of SPWC membranes increased when the concentration of acid groups was increased. The gas permeability and methanol crossover was lower than those of Nafion<sup>®</sup> 117 and increased with acid concentration. For KSiN composite membranes, thermal stability, water uptake and ion exchange capacity were increased when KSi content was increased. The gas permeability was

lower than Nafion<sup>®</sup>117 when the KSi was incorporated. In the case of methanol crossover, although it was higher than the commercial Nafion<sup>®</sup>117, the methanol crossover was decreased when the amount of KSi was increased.

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