

## Physico-Chemical Study of Sulfonated Poly(Ether Ether Ketone) Membranes for Direct Methanol Fuel Cell Application

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**ABSTRACT:** Sulfonated poly(ether ether ketone) (SPEEK) membranes have been prepared as a potential polymer electrolyte membrane (PEM) for direct methanol fuel cell (DMFC) application. The SPEEK polymer was dissolved into *N, N*-dimethylacetamide (DMAc) in a subsequent step after sulfonating the raw polymer with concentrated sulfuric acid. The polymer solutions were then cast by pneumatic casting machine. The influence of sulfonation reaction temperature on ion exchange capacity (IEC) and degree of sulfonation (DS) have been investigated. The results showed that the IEC and DS are increased with the temperature. The resulting membranes were then characterized by evaluating their physico-chemical properties such as methanol permeability and proton conductivity as a function of DS. The overall results showed that sulfonation process successfully enhanced the proton conductivity of the membrane and the values were comparable with commercial membrane, Nafion® 117, at room temperature. Although the methanol permeability of membrane also increased after sulfonation process and proportional with DS, the value was still lower than Nafion® 117.

**Keywords:** sulfonated poly(ether ether ketone), direct methanol fuel cell, methanol permeability, proton conductivity

### 1.0 INTRODUCTION

Fuel cells have been gaining much attention as a promising alternative to replace conventional fossil fuel systems due to their high efficiency, low environmental impact and flexible application [1]. In fact, several types of fuel cells have been commercialized, such as proton exchange membrane fuel cell (PEMFC) which utilizes hydrogen as fuel [2]. PEMFC is interesting for automotive and portable applications because of its low operating temperature [3]. However, hydrogen is difficult to store, whether as a compressed gas, as a cryogenic liquid, or in metal hydrides or carbon nanotubes. As a result, effort has been made to utilize hydrogen produced from fuel like methanol, via steam reforming. This is then followed by hydrogen separation using a palladium alloy membrane to remove carbon monoxide. Such processing dramatically increases the weight and complexity of fuel cell system [4].

In order to simplify the system structure, direct methanol fuel cell (DMFC) using methanol as fuel is deemed as a potential option of energy converters, ascribable to the advantage of liquid methanol. In a DMFC, methanol is fed directly to the fuel cell without any fuel processing beforehand. The liquid-feed system does not require any fuel processing equipment and can even be operated at room temperature. These advantages lead to simplicity of operation in DMFC compared to systems using a reformer to produce hydrogen from liquid fuel (i.e. indirect methanol fuel cells) [1]. Therefore, bright prospect of DMFC can

be foreseen in applications like transportation, power generation and most importantly, for portable devices [5].

DMFC technology is similar with that of PEMFC, in which a polymer electrolyte membrane (PEM) is used as the electrolyte. The PEM, one of the essential components in the development of advanced polymer fuel cells, has been studied for decades. Nowadays perfluorinated ionomer (PFI) membranes such as Nafion<sup>®</sup> (DuPont), Aciplex<sup>®</sup> (Asahi Chemical), Flemion<sup>®</sup> (Asahi Glass), and Dow<sup>®</sup> (Dow Chemical) are widely accepted for commercial application. PFI membranes are characterized by their unique chemical structure, as the sulfonic acid group in the fluorinated backbone provides high proton conduction [6] meanwhile the backbone offers excellent mechanical and thermal stability [7]. In term of function, the PFI membranes play role as an ion conductor between anode and cathode, as a separator for the fuel and oxidant, and also as an insulator between the cathode and anode so that electrons flow through an external electronic circuit and not directly through the membrane [8].

Although PFI membranes exhibited very good performance in PEMFC, there is a major problem associated with application in DMFC, i.e. high methanol crossover from anode to cathode side. High methanol crossover results in reduced performance in DMFC by lowering the cell voltage (by several hundreds of mV), even though PEMFC and DMFC have similar theoretical open circuit voltages  $E_o$  [3]. Furthermore, PFI membranes are not suitable to be used at temperature above 100 °C, due to difficulty with water management (difficult humidity control) [9]. Another drawback, which has limited the market penetration of DMFC system, is the cost of PFI membranes.

A number of studies have been done in order to overcome the limitations of PFI membranes. Among several types of polymer membrane, it is evident that sulfonated poly(ether ether ketone) (SPEEK) membrane has the potential to be used as the electrolyte in DMFC [9-17], which due to its high mechanical strength, high thermal stability, cheap, easily to handle, low methanol crossover and also moderate proton conductivity. A raw material for SPEEK membrane is poly(ether ether ketone) (PEEK), a hydrophobic polymer with an aromatic, non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by ether (–O–) and carbonyl (–CO–) linkages. Since PEEK is a hydrophobic polymer and not suitable to fabricate as electrolyte, PEEK has to be modified by the sulfonation process using concentrated sulfuric acid, as shown in Figure 1.

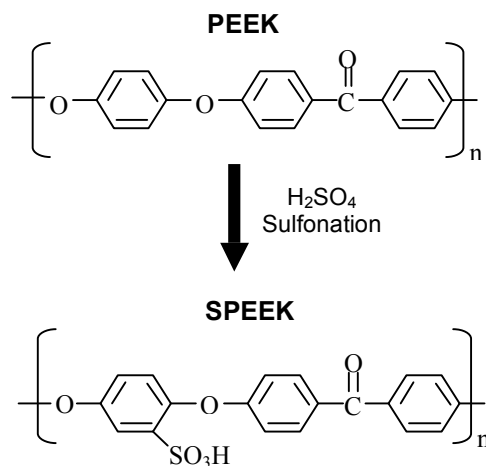


Figure 1: Sulfonation of PEEK

Generally, sulfonation is an electrophilic substitution reaction, which one of hydrogen ion on aromatic rings is substituted by sulfonic acid group ( $-\text{SO}_3\text{H}$ ). The presence of sulfonic acid group make the SPEEK becomes highly hydrophilic, since this functional group increases the acidity of polymer. The enhancement of polymer hydrophilicity has differentiated SPEEK into two environments, the hydrophilic environment (consisting of the polar sulfonic acid groups) and the hydrophobic environment (consisting of the rest of the SPEEK matrix). Apart from that, sulfonation also modifies the chemical character of PEEK, by reducing the crystallinity and consequently affects the polymer solubility. Generally, when the degree of sulfonation (DS) is lower than 30 %, SPEEK is soluble only in strong  $\text{H}_2\text{SO}_4$ ; above 30 % DS, the polymer is soluble in hot dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO); above 40 % they are soluble in the same solvents at room temperature; above 70 % they are soluble in methanol and at 100 % sulfonation in hot water [17].

Different approach has been adopted in this paper, in which the DS of SPEEK was controlled by sulfonation reaction temperature, instead of varying reaction time as have been conducted by most of the previous researches. Apart from carrying out the sulfonation at various temperatures, the effects of SPEEK's DS on polymer properties and membrane performances have also been studied.

## 2.0 EXPERIMENTAL

### 2.1 Sulfonation of Poly(Ether Ether Ketone)

PEEK was sulfonated following the technique described in the literature [17-19]. 5 g of PEEK was dried in a vacuum oven at 100 °C and then dissolved in 95 ml of concentrated (95-98 %) sulfuric acid ( $\text{H}_2\text{SO}_4$ ) at room temperature to suppress the heterogeneous sulfonation. After completing the dissolution of PEEK (~1 h), the polymer solution was brought to the desired temperature ranging from 47 to 63 °C and held for 3 hours. To terminate the sulfonation reaction, the polymer solution was decanted into large excess ice-cold water under continuous stirring and left overnight. The precipitated polymer was washed by using distilled water and repeated until a neutral pH of the polymer was reached. The neutral SPEEK was then dried at 100 °C overnight.

### 2.2 Preparation of SPEEK Membrane

SPEEK polymer was first dissolved in *N,N*-dimethylacetamide (DMAc) to make a 10 wt.% solution and the solution was stirred for 2 to 4 h. After evaporating most of the solvent by heating to temperatures of 100-110 °C, the polymer solution was cast onto a glass plate using a pneumatic casting machine. The cast membrane was dried at 60 °C for 6 h to remove the solvents, and annealed at 100 °C for 12 h. After cooling to room temperature, the resultant membrane was peeled from the glass in deionized water. Finally, the membrane was treated with 1 M sulfuric acid solution for 1 day at room temperature and blotted with absorbent paper. The thickness of a dry membrane is about  $110 \pm 20 \mu\text{m}$ .

## 2.3 Characterization Methods

### 2.3.1 Titration Analysis

The ion exchange capacity (IEC) of the SPEEK, which is defined as the amount of ion exchange (referring to hydrogen ion of sulfonic acid groups) in SPEEK, was determined using the titration method as described by Shao [20]. About 0.5 g of SPEEK-H was immersed into 0.01 M sodium hydroxide (NaOH) solution (200 ml) for three days, which was found to be sufficient to convert SPEEK-H into SPEEK-Na. Dilute sulfuric acid ( $H_2SO_4$ ) (0.003 M) was employed to back-titrate the NaOH solution, which has been partially neutralized by the SPEEK-H sample. Phenolphthalein as the universal indicator was adopted to help determine the neutral point. By measuring the amount of  $H_2SO_4$  consumed in the titration, the molar quantity of the sulfonic acid groups ( $SO_3H$ ) contained in the SPEEK-H sample can be determined by Equation (1) and using this value, the IEC can be estimated by Equation (2).

$$N_{\text{SPEEK-Na}} = (MV)_{\text{NaOH}} - 2(MV)_{\text{Sulfuric acid}} \quad (1)$$

where M and V, respectively the molar concentration and the volume of the solutions used.

$$IEC = \frac{N_{\text{SPEEK-H}}}{W_{\text{Sample}}} \times 1000 \text{ (meq/g)} \quad (2)$$

where,  $W_{\text{Sample}}$  is the weight of the SPEEK-Na sample, and  $N_{\text{SPEEK-H}} = N_{\text{SPEEK-Na}}$ .

SPEEK-Na is a copolymer, consisting of PEEK- $SO_3Na$  unit and PEEK unit. Assuming that  $N_1$  is the molar number of the PEEK- $SO_3Na$  unit in 1 g of SPEEK-Na sample and  $N_2$  is the molar number of the PEEK unit in 1 g of SPEEK-Na sample, then,

$$N_1 = 0.001 \times IEC \quad (3)$$

$$N_2 = \frac{1 - (0.001 \times IEC \times M_{W1})}{M_{W2}} \quad (4)$$

where  $M_{W1}$  and  $M_{W2}$  are the molecular weights of PEEK- $SO_3Na$  unit, and PEEK unit respectively, and  $M_{W1} = 390$ ,  $M_{W2} = 288$ .

Since DS is defined as the ratio of the number of structural unit containing a sulfonic acid group to the total number of structural units in SPEEK), therefore DS can be written as,

$$DS = \frac{N_1}{(N_1 + N_2)} \quad (5)$$

Substituting Equations (3) and (4) into (5) gives

$$DS = \frac{288(IEC)}{1000 - 102(IEC)} \quad (6)$$

The DS can be calculated from IEC using Equation (6). If the DS is assumed to be 100 %, then the IEC of the SPEEK would be 2.56 meq/g, which is the maximum sulfonic acid content that permitted for first type substitution.

### 2.3.2 Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to identify the presence of sulfonic acid group in polymer samples. It was also used to observe the interactions between SPEEK polymer and solvent in the SPEEK membrane. In this study, FTIR spectra were obtained from a Nicolet (Magna-IR 560) spectrometer equipped with attenuated total reflection (ATR) having a Ge spherical crystal. The spectra were measured in transmittance mode over a wave number range of 4000-600 cm<sup>-1</sup>.

### 2.3.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to determine weight loss and hence the thermal degradation of PEEK and SPEEK samples using Mettler Toledo Thermogravimetric Analyzer model TGA/SDTA851e. According to the procedure proposed by Xing *et al.* [20], the samples were preheated under nitrogen from room temperature to 150 °C at 10 °C/min to remove moisture, cooled to 90 °C, then reheated from that temperature to 800 °C at 10 °C/min in air.

### 2.3.4 Differential Scanning Calorimetry

A METTLER TOLEDO DSC 822e differential scanning calorimetry (DSC) was employed to study the glass transition temperature of SPEEK samples. A sample of 10 mg was preheated under nitrogen from room temperature to 160 °C at 10 °C/min to remove moisture, then cooled to 90 °C, and reheated from that temperature to 250 °C at 10 °C/min [20].

### 2.3.5 Scanning Electron Microscopy

The morphologies of the membranes were investigated using scanning electron microscopy (SEM). Specimens for the SEM were prepared by freezing the dry membrane samples in liquid nitrogen up to 10 min and breaking them to produce a cross-section. Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of gold by using an ion sputtering (Biorad Polaron Division) before viewing on the scanning electron microscope (Phillips SEMEDAX; XL 40; PW6822/10) with a potential of 10 kV under magnifications ranging from 500x to 2000x.

### 2.3.6 Water Uptake Measurement

Water uptake, which is used to determine the water content of the membranes, is one of the fundamental measurements for DMFC polymer electrolyte membrane. Firstly, membrane was dried in an oven at 60 °C for 48 h, weighed, soaked in deionized water overnight at room temperature, blotted dry with absorbent paper to remove any surface moisture, and reweighed. Then, water uptake was calculated from the equation below,

$$\text{Water Uptake} = \frac{G_w - G_d}{G_d} \times 100\% \quad (7)$$

where,  $G_w$  is the weight of the wet membrane and  $G_d$  the weight of the dry membrane.

### 2.3.7 Methanol Permeability Measurement

A diaphragm diffusion cell, as schematically illustrated in Figure 2, was used to determine the methanol permeability of the membranes. The apparatus consists of plastic compartments (A and B), separated by the test membrane with an effective area of 6.1575 cm<sup>2</sup>. The compartment A was (V = 50 cm<sup>3</sup>) filled with 1 M methanol and the compartment B was filled with distilled water. The methanol molecules diffuse along the concentration gradient through the membrane into the opposite compartment of the diffusion cell. To determine the methanol permeability of each membrane, liquid samples of 500 µl were taken from the permeate compartment using a syringe for every 30 minutes and the samples were then analyzed with a differential refractometer (WATERS® 410).

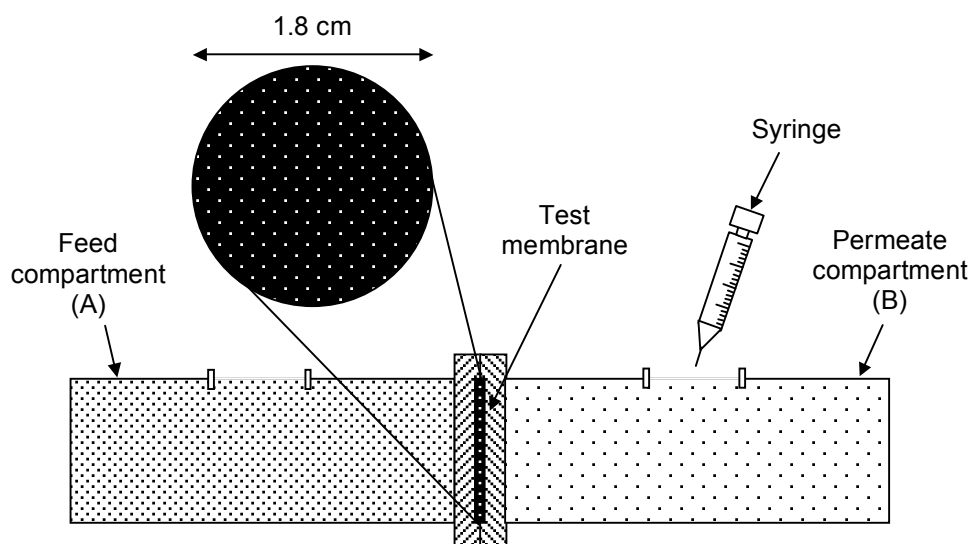


Figure 2: Diaphragm diffusion cell for methanol permeation measurement

Theoretically, methanol diffusion was established across the membrane due to a concentration gradient. The concentration of methanol in the permeate compartment is given by Equation (8), as stated elsewhere [21].

$$\frac{V_B dC_B}{dt} = S \times \frac{DK}{L} C_A \quad (8)$$

where;

$C_B$  = the concentration of methanol in the permeate (water) compartment at time  $t$ ,

$C_A$  = the concentration of methanol in the feed compartment,

$S$  = the membrane cross sectional area,

$L$  = the membrane thickness,

$V_B$  = the volume of the permeate compartment,

$D$  = the methanol diffusivity, and

$K$  = the partition coefficient.

Equation (8) can be solved to give

$$C_B(t) = \frac{S}{V_B} \times \frac{DK}{L} C_A(t-t_0) \quad (9)$$

where  $t_0$  is the time lag, which is explicitly related to the diffusivity ( $t_0 = L^2/6D$ ).

Since the methanol permeability (P) is defined as the product of the diffusivity of methanol through the membrane (D) and the partition coefficient (K), i.e.,  $P = DK$ , Equation (9) can be rewritten as,

$$C_B(t) = \frac{S}{V_B} \times \frac{P}{L} C_A(t-t_0) \quad (10)$$

The permeability was calculated from the linear relationship of concentration change of the concentration of methanol in the compartment B ( $C_B$ ) versus time (t) according to the following equation,

$$P = m \times \frac{V_B}{S} \times \frac{L}{C_A} \quad (11)$$

where m is the slope of the linear plot of  $C_B$  versus t.

### 2.3.8 Proton Conductivity Measurement

The conductivity of the membranes in acid form was measured by AC impedance technique using a Solartron impedance-gain phase analyzer. The impedance spectra were recorded over the frequency range of 10 MHz to 10 Hz with 50-500 mV oscillating voltage. Membrane sample was equilibrated in deionized water for 24 h at room temperature prior to testing. Then, the surface water was removed, and the swollen membrane was rapidly placed between two stainless-steel electrodes in a conductivity cell (this cell is used to host the sample). The water content of the membrane was assumed to remain constant during the short period of time required for the measurement. All impedance measurements were performed at room temperature.

The membrane resistance (R) was obtained from the intercept of the impedance curve with the real-axis at the high-frequency end. Then, proton conductivity of membrane,  $\sigma$  (Siemens per centimeter (S/cm)), was calculated according to Equation (12), where  $\sigma$  is defined as the reciprocal of R.

$$\sigma = \frac{L}{RS} \quad (12)$$

where L and S are the thickness and area of the membrane, respectively.

## 3.0 RESULT AND DISCUSSION

### 3.1 Ion Exchange Capacity and Degree of Sulfonation of SPEEK Polymer

The temperature of the sulfonation reaction is one of the variable parameters that control the concentration of sulfonic acid groups in the polymer, apart from reaction time and type of sulfonating agent. In the present study, the PEEK was sulfonated with sulfuric acid ( $H_2SO_4$ ) for 3 h at the desired temperature ranging from 47 to 63 °C to produce polymers with

various ion exchange capacities (IEC) and degrees of sulfonation (DS). These IEC and DS of SPEEK were then determined by the titration analysis. Figure 3 shows the variation of IEC and DS as a function of reaction temperature for 3 h reaction time.

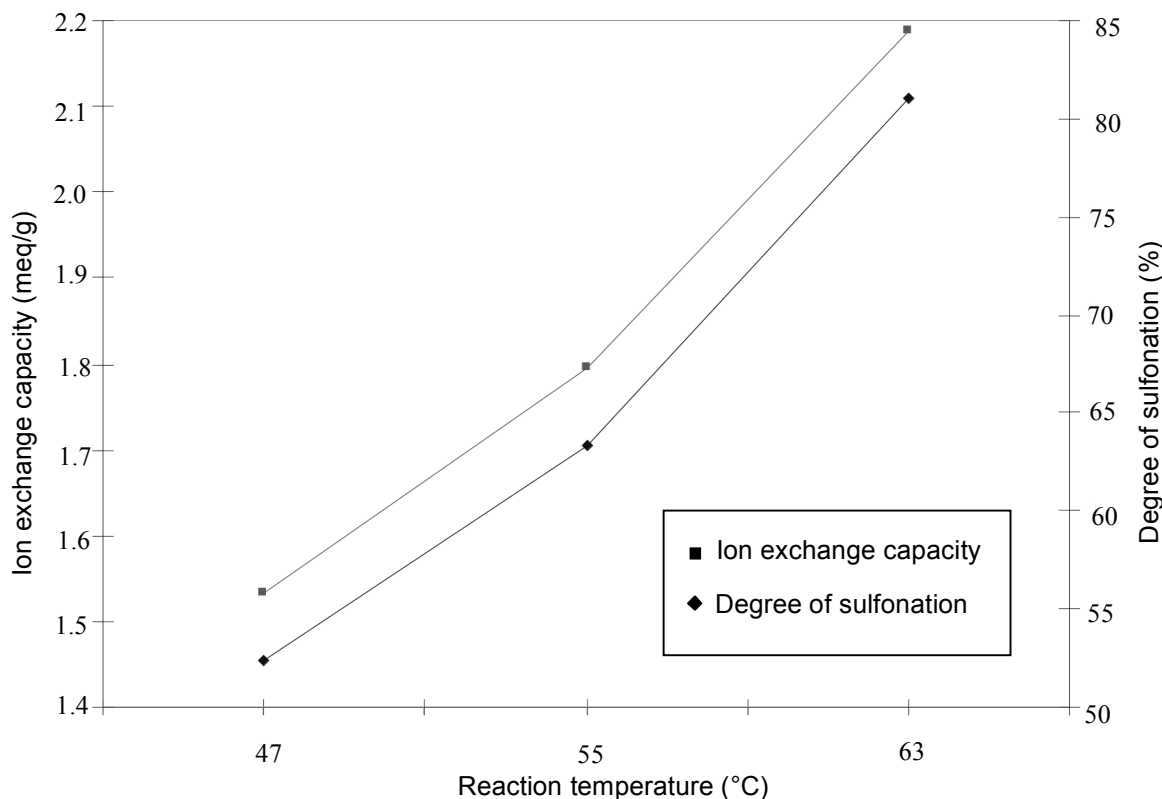


Figure 3: Dependence of IEC and DS on sulfonation reaction temperature

It can be seen that the IEC and DS of SPEEK increased tremendously with the increment of reaction temperature. At the lowest reaction temperature (47 °C), DS above 52 % could be reached (IEC is about 1.53 meq./g). When the sulfonation reaction was conducted at higher reaction temperature which about 55 °C, the IEC increased by 0.26 meq./g and DS jumped to 63 %. While, the sulfonation rate of SPEEK is led to exceed 81 % with IEC 2.19 meq./g at reaction temperature 63 °C. From the result, it can be observed that the sulfonation reaction temperature has a big influence on the DS of polymers and therefore, the second substitution of sulfonic acid groups on polymer could occur if the reaction temperature keeps on increasing. Although the DS of polymer seemed apparently less controllable by varying sulfonation reaction temperature, it is possible to obtain high DS within a shorter time as compared to sulfonation reaction at room temperature. For example, Li *et al.* [17] reported that SPEEK with 85 % DS could be achieved within 120 h at room temperature, as compared to only 3 h at 63 °C reaction temperature to obtain 81 % DS.



### 3.2 Confirmation of the Presence of Sulfonic Acid Group in SPEEK Polymer

In order to identify the presence of sulfonic acid group in polymer samples, Fourier transform infrared (FTIR) spectroscopy was used in the present study. The FTIR spectra of SPEEK with different DS are shown in Figure 4.

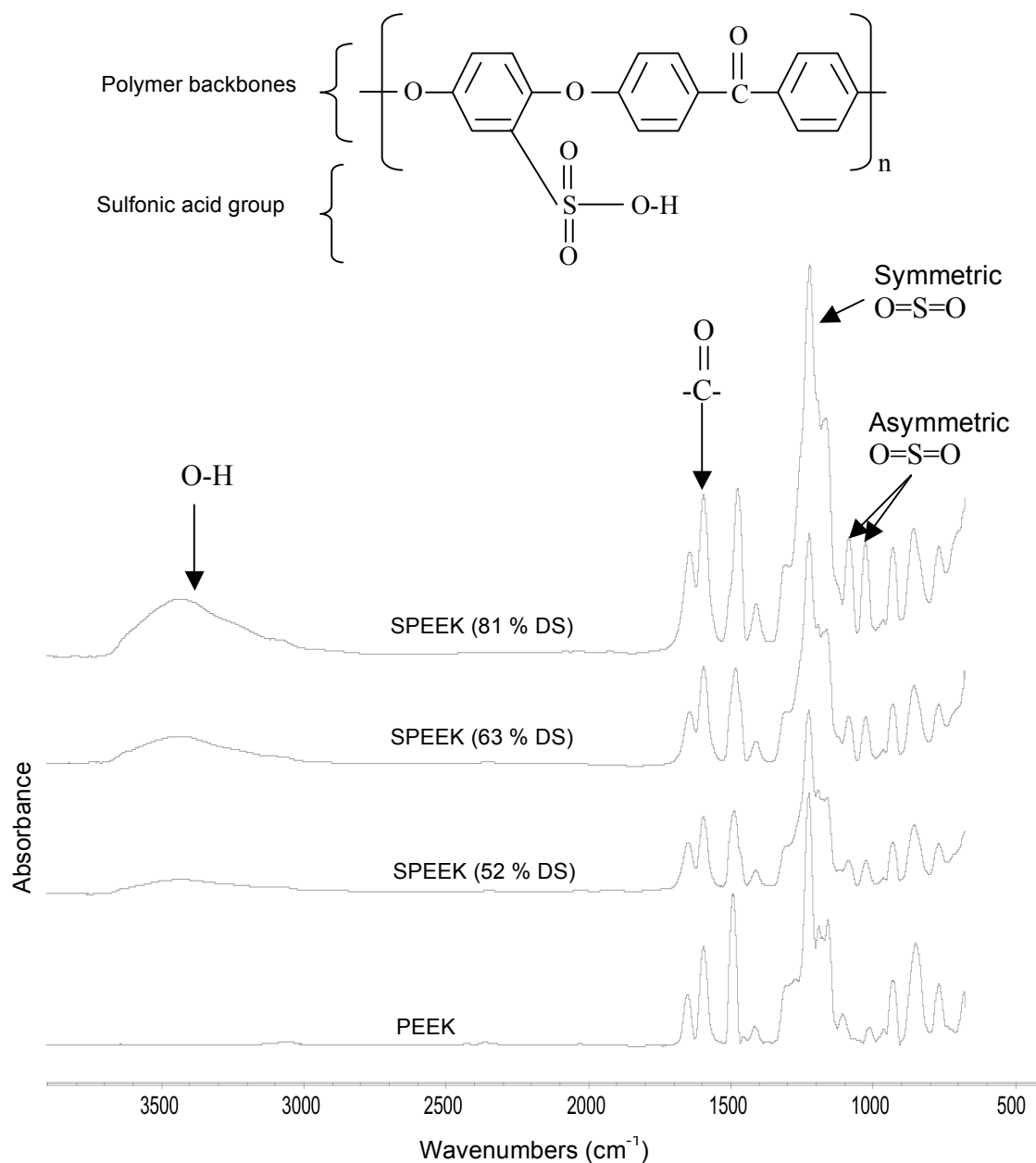


Figure 4: FTIR spectra of PEEK and SPEEK

The presence of sulfonic acid group in SPEEK was confirmed by the strong characteristic peaks at 1255, 1080 and 1020  $\text{cm}^{-1}$ , were assigned to the symmetric and

asymmetric O=S=O stretching vibrations, as their intensities with respect to the backbone carbonyl (C=O) band at  $1651\text{ cm}^{-1}$  increased with DS. These O=S=O stretching vibrations spectrum for unsubstituted PEEK were weak, meanwhile there is no significant difference in the carbonyl band for PEEK compared with SPEEK. Another evidence of the presence of sulfonic acid group is the appearance of the peak at  $3460\text{ cm}^{-1}$  in SPEEK samples, which is assigned to O-H vibration from sulfonic acid group. The spectrum shows that the O-H peak increased with SPEEK DS, thus indicating the polymers with higher DS are more acidic. The same findings were also reported by Xing *et al.* [20].

### 3.3 Thermal Properties of PEEK and SPEEK Polymers

The thermal stability of PEEK and SPEEK were investigated using thermogravimetric analysis (TGA). Table 1 presents the degradation temperature ( $T_d$ ) of PEEK and SPEEK as a function of DS.

Table 1: Degradation and glass transition temperatures of PEEK and SPEEK

Sample type	DS of polymer (%)	Degradation temperature ( $^{\circ}\text{C}$ )		Glass transition temperature ( $^{\circ}\text{C}$ )
		Degradation of sulfonic acid groups	Degradation of polymer backbones	
PEEK	0	-	552	158.77
SPEEK	52	335	530	213.76
SPEEK	63	320	525	230.38
SPEEK	81	285	490	237.97

PEEK demonstrates excellent thermal stability with a single step degradation temperature of polymer chain higher than  $550\text{ }^{\circ}\text{C}$ . On the contrary, SPEEK exhibit two distinct steps degradation, from 285 to  $400\text{ }^{\circ}\text{C}$  and 490 to  $800\text{ }^{\circ}\text{C}$ . The observed weight loss between  $285\text{--}400\text{ }^{\circ}\text{C}$  in SPEEK sample was attributed to the decomposition of sulfonic acid groups. Breakdown of the SPEEK backbone took place at temperatures lower than that of PEEK, due to the catalytic degradation of the polymers backbone caused by sulfonic acid groups. Since no thermal degradation was detected below  $200\text{ }^{\circ}\text{C}$ , SPEEK polymer is still considered as thermally stable membrane for DMFC system because DMFC only operates at temperature below  $150\text{ }^{\circ}\text{C}$ .

Table 1 also shows that the glass transition temperatures ( $T_g$ ) of SPEEK, which displays much higher than that of PEEK and increased with increasing DS. This increment is mainly due to the strong interaction between sulfonic acid groups in SPEEK. The narrow dispersion of  $T_g$  values ( $\sim 30\text{ }^{\circ}\text{C}$  range) may however be attributable to the effective sulfonic acid groups interaction, which could become saturated at a certain DS as  $T_g$  is a parameter reflecting the polymer chain mobility. This effective interaction may not increase with increasing DS above a certain DS value, which would make the chain mobility and therefore,  $T_g$  invariant under these conditions. For example, the effective sulfonic acid groups interaction may assume attained almost the same level in both SPEEK with 63 and 81 % DS as their  $T_g$  was close to each other.

### 3.4 Interactions between Polymer and Solvent in SPEEK Membrane

The interaction between polymer and solvent in SPEEK membrane was observed by using FTIR spectroscopy. FTIR spectra of SPEEK polymer and SPEEK membrane are compared in Figure 5. In agreement with Robertson *et al.* [22], DMAc solvent, which was used to dissolve SPEEK polymer in the present study, exhibits a strong hydrogen-bonding with the sulfonic acid groups of SPEEK membrane (as displayed in Figure 6) at high fabricating temperature ( $>100\text{ }^{\circ}\text{C}$ ). This claim is supported by the peak at  $3460\text{ cm}^{-1}$  in SPEEK polymer spectrum, which was assigned to O-H vibration from sulfonic acid groups, does not appear in the SPEEK membranes spectra. The major drawback of the SPEEK-DMAc interaction is the reduction of the number and/or mobility of protons available for proton transport and dramatically reduces the membrane conductivity. However, by comparing with other solvents such as dimethylformamide (DMF) or *N*-methyl-2-pyrrolidone (NMP), DMAc is the best choice since the DMF also formed a hydrogen bonding with SPEEK even at low fabricating temperature ( $\sim 60\text{ }^{\circ}\text{C}$ ), while NMP has high boiling point ( $202\text{ }^{\circ}\text{C}$ ) and make the solvent difficult to evaporate from the membrane matrix.

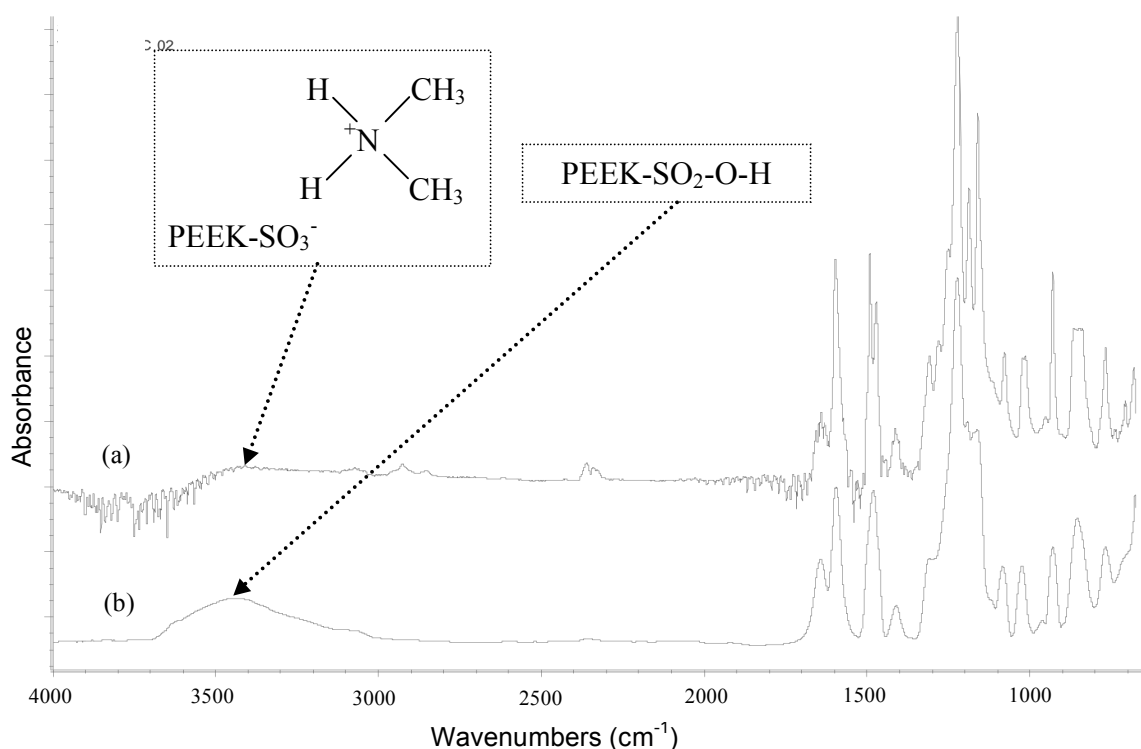


Figure 5: FTIR spectrum of (a) Pure SPEEK (63 % DS) membrane, and (b) SPEEK polymer with 63 % DS

### 3.5 Morphology of SPEEK Membrane

The performance of SPEEK membrane should be closely related to its internal structure, especially its morphology. Figure 6 shows the cross-sectioned scanning electron microscopy (SEM) micrographs of three SPEEK membranes, i.e. 52, 63 and 81 % DS. All micrographs, even up to magnifications of 1000x, did not show any evidence of the presence

of microporous structure. The production of non-porous structure is due to the fabrication technique of the membrane itself. Dry phase inversion technique, which was implemented in this study, involved slow solvent evaporation as the membrane was dried under ambient condition for 24 h and subsequently for another 12 h at 100 °C. Generally, the membrane produced by this technique is in a dense structure due to the slow moving of solvent molecules when it is evaporated from the polymer membrane. DMFC system resumes dense membrane, as porous membrane tends to allow methanol and water to permeate through it.

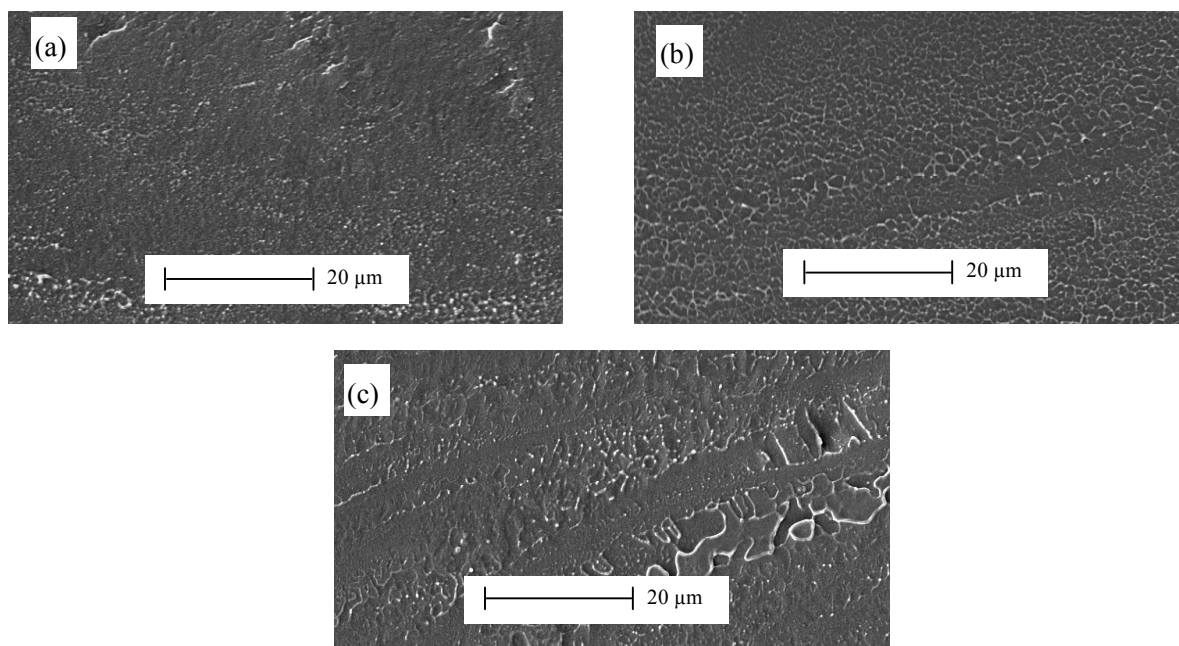


Figure 6: SEM micrographs of cross-sectional cryogenic fracture of SPEEK membranes (Magnification 1000x); (a) 52 % DS, (b) 63 % DS, and (c) 81 % DS

In term of the DS effect, the fracture surface of these pure SPEEK membranes were found almost the same, thus indicating that the DS did not significantly change the morphology of the dry membranes. However, it is expected that the morphology of the hydrated membrane will be different for each membrane as the hydrophilicity of the membrane increases with increasing polymer DS, thus makes the hydrophilicity domain of membrane with higher DS larger than that with lower DS.

### 3.6 Water Uptake of SPEEK Membrane

In general, the ionomeric membrane conductivity in DMFC is strongly dependent on the number of available acid groups and their dissociation capability in water, accompanied by the generation of protons. Since water molecules dissociate acid functionality and facilitate proton transport, the water uptake becomes an important parameter in studying electrolyte membranes for fuel cell application [16, 21, 23]. Therefore, it is crucial to fully understand the relationship between the water uptake and the membrane's DS. Figure 7 shows the water uptake for different DS of SPEEK membrane.

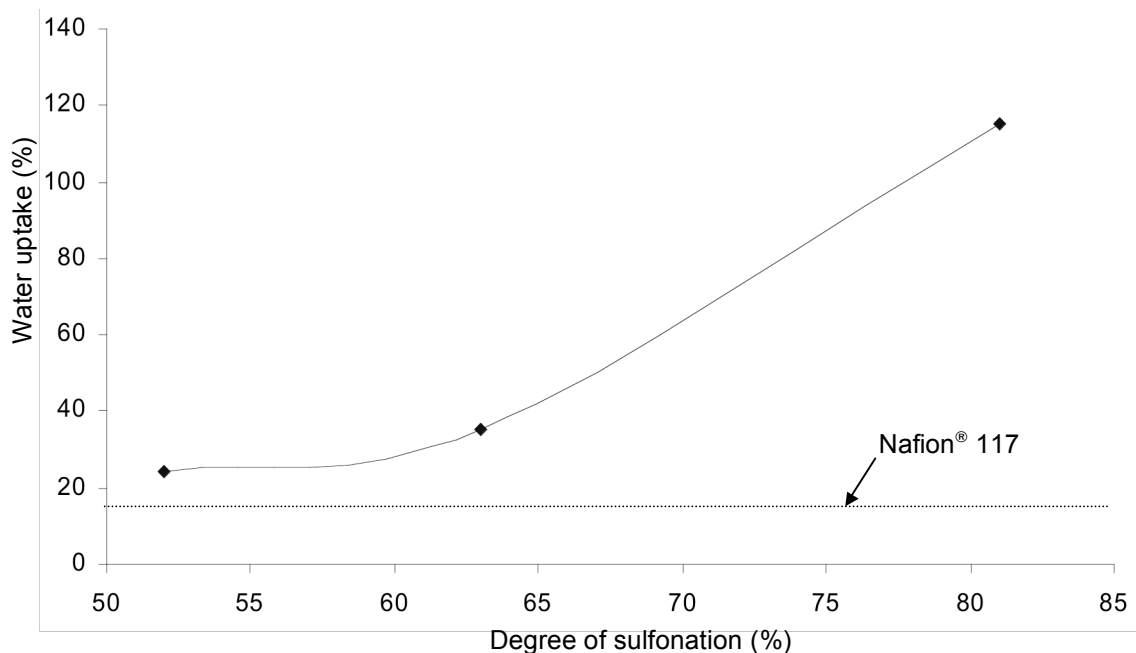


Figure 7: Water uptake of SPEEK membranes as a function of degree of sulfonation

It indicates that the water content of the membranes increased with DS, probably due to the presence of more sulfonic acid groups, resulting increment in hydrophilicity of membrane and thus, increasing the capability to absorb water. The most significant increment was noted for the membrane with 81 % DS, which the water uptake differences of this membrane and the membranes with 63 and 52 % DS are more than 50 %. This observation can be attributed to the stronger interaction between water molecules and sulfonic acid groups. Thus, the additional sulfonic acid groups in the PEEK repeat unit have drastically increased the number of water molecules that can be absorbed by the membrane. In addition, it can be found that the water uptake of SPEEK membranes are higher than that of Nafion<sup>®</sup> 117 and recorded the highest difference at SPEEK 81 % DS membrane, which was almost 100 % water uptake.

### 3.7 Methanol Permeability of SPEEK Membrane

Methanol permeability measurement is one of the fundamental tests of electrolyte membrane for DMFC application, in order to determine methanol crossover through the membrane. The variation of methanol concentration in the permeate compartment with the time for SPEEK membranes with various DS is given in Figure 8, along with that for a Nafion<sup>®</sup> 117 membrane. All membranes, including Nafion<sup>®</sup> 117, report a linear relationship.

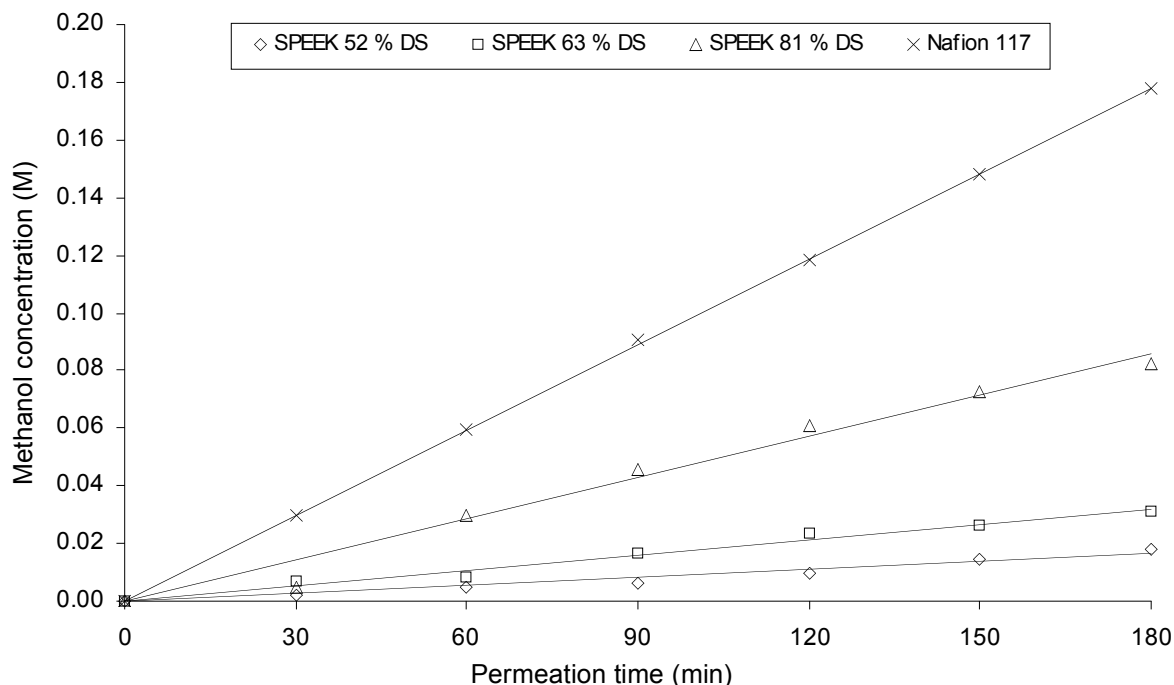


Figure 8: Variation of methanol concentration in water compartment with time for SPEEK membranes with various DS and in Nafion® 117 membrane

The slopes obtained from these linear relationships were used to calculate the methanol permeability according to Equation (11). The results are listed in Table 2. From this table, it can be seen that the methanol permeability of SPEEK membrane increased with the increment of DS, which shows that the trend was probably affected by the polymer membrane solubility. As aforementioned, the sulfonation process modifies the chemical property of PEEK, by reducing the crystallinity and hence affecting the polymer solubility. While DS is high enough, the crystallized population of PEEK can be broken completely and the SPEEK will become amorphous. The main interaction between the amorphous SPEEK molecular chains is resulted from the electrostatic forces between the sulfonic acid groups. The major drawback of this interaction is that the highly polar methanol and water molecules can undermine it. The evidence was reported by Li *et al.* [17], which stated that the SPEEK greater than 70 % DS can dissolve in methanol and at 100% sulfonation dissolve in hot water. It can be the reason for high methanol permeability in the membranes with high DS compared to the membranes with low DS as in the present study.

Table 2: Variation of methanol permeability of SPEEK membranes with DS

Degree of sulfonation (%)	Methanol permeability (cm <sup>2</sup> /s)
52	3.05 x 10 <sup>-7</sup>
63	7.07 x 10 <sup>-7</sup>
81	20.51 x 10 <sup>-7</sup>
Nafion® 117	62.98 x 10 <sup>-7</sup>

The table also stated that the highest methanol permeability of SPEEK membrane was recorded by the membrane with 81 % DS SPEEK at  $20.51 \times 10^{-7} \text{ cm}^2/\text{s}$ , which almost 4-folds and 7-folds compared to membranes with 52 and 63 %, respectively. However, it is important to note that the methanol permeability of the membrane is much lower than that of Nafion<sup>®</sup> 117 membrane ( $62.98 \times 10^{-7} \text{ cm}^2/\text{s}$ ). The different methanol permeation of SPEEK and Nafion<sup>®</sup> membranes can be explained by the difference in their microstructures. In Nafion<sup>®</sup> membrane, because of its high hydrophobicity perfluorinated backbone and its high hydrophilicity of the sulfonic acid groups, it would give rise to the formation of hydrophobic/hydrophilic domains, especially in the presence of water [17]. As shown in Figure 9 (a), the sulfonic acid groups aggregate to form a hydrophilic domain. These hydrophilic domains are interconnected in Nafion<sup>®</sup> membrane. Not only proton and water can transport through these domains, but a smaller polar molecule such as methanol can also permeate through these domains.

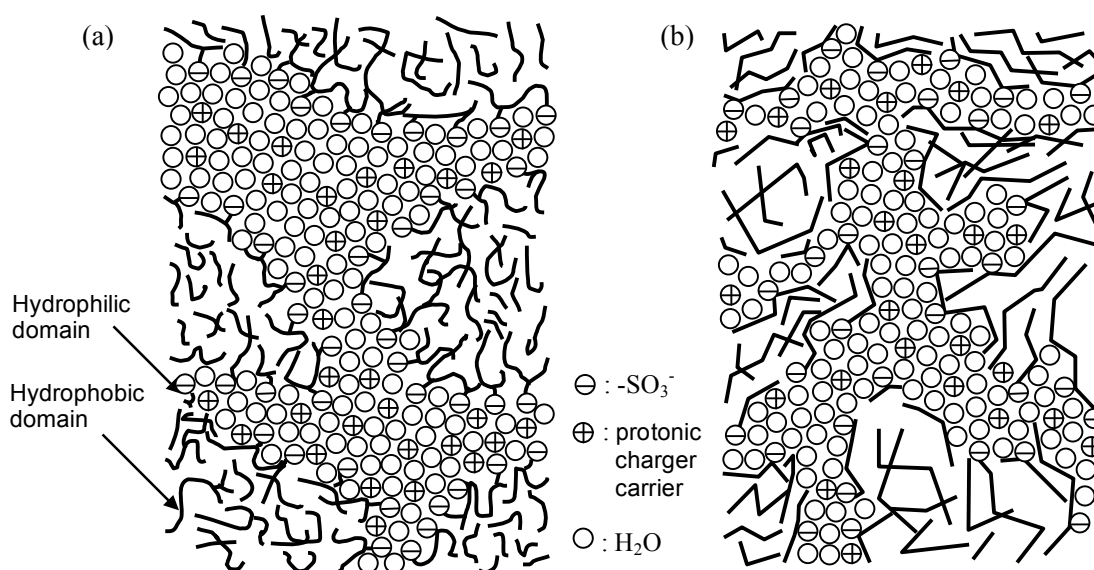


Figure 9: Proposed microstructure for (a) Nafion<sup>®</sup> membrane, and (b) SPEEK membrane (redraw from Kreuer [24])

However, the microstructure of SPEEK membrane was found to be distinctly different from Nafion<sup>®</sup> membrane. By modifying the model as proposed by Kreuer [24], the membrane is less separated due to smaller hydrophobic/hydrophilic difference (i.e. the backbone is less hydrophobic, and the sulfonic acid group is less acidic than Nafion<sup>®</sup> membrane) and more branched with more dead-end “pockets”, as depicted in Figure 9 (b). Owing to this smaller difference and the lesser flexibility of the polymer backbone, the separation into a hydrophilic and a hydrophobic domain is less pronounced, thus making the methanol permeability for SPEEK membrane much lower than that of Nafion<sup>®</sup> membrane.

Since low methanol permeability is one of the paramount requirements for electrolyte membrane in DMFC system, thus the SPEEK membrane may be very attractive for future development of DMFC technology.

### 3.8 Proton Conductivity of SPEEK Membrane

The effect of the DS on the proton conductivity of SPEEK membrane at room temperature is shown in Figure 10. It gives a clear illustration of the fact that the conductivity of membrane proportionally increased with DS. The conductivity increases from  $9.97 \times 10^{-4}$  to  $9.25 \times 10^{-3}$  S/cm as the DS increases from 52 to 81 %. This can be explained by the presence of more ion exchanges (ion hydrogens of sulfonic acid groups) in the higher SPEEK's DS membrane, as revealed in Figure 3. Furthermore, with increasing DS, the polymer becomes more hydrophilic and absorbs more water, which facilitates proton transport. Hence, the sulfonation raises the conductivity of PEEK not only by increasing the number of protons, but also through the formation of water mediated pathways for protons.

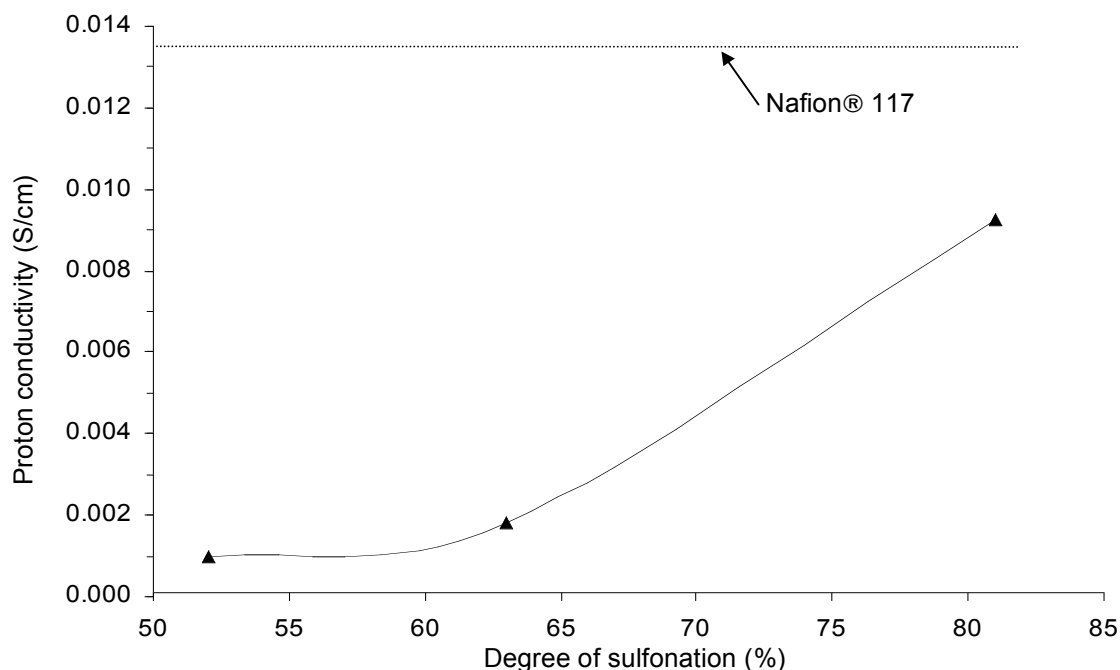


Figure 10: Variation of proton conductivity of SPEEK membrane with DS

As expected, the trend of these results is in agreement with the water uptake results shown in Figure 7, since the proton conductivity as reported by Kreuer [24] relies more heavily on the amount of water. The increment in water uptake is increasing the conductivity value, and the membrane with the highest water uptake possesses the highest proton conductivity. This correlation can be explained by looking into the transportation of protons (hydrogen ions) in hydrophilic domain, which is facilitated by the presence of water molecules.

The proton conductivity of SPEEK membrane is also compared with that of Nafion<sup>®</sup> 117 membrane under the same conditions. The result shows that the SPEEK membrane has lower conductivity than Nafion<sup>®</sup> membrane. However, the increment of DS significantly improved the proton conductivity. In fact, the conductivity of SPEEK membrane with 81 % DS is comparable with Nafion<sup>®</sup> 117 membrane. It is also worth taking note that the dependence of the conductivity on water is more pronounced for SPEEK membrane than for Nafion<sup>®</sup> since



the water uptake of Nafion<sup>®</sup> as shown in Figures 8 is less than SPEEK membrane but it has higher proton conductivity.

#### 4.0 CONCLUSION

SPEEK membranes have been successfully prepared and characterized, specifically for DMFC application. From the results and the preceding discussion, there are several conclusions have been drawn:

1. The DS of SPEEK can be well varied by sulfonation reaction temperature. This technique is possible to obtain the SPEEK of higher DS within a shorter time compared with conducting sulfonation reaction at room temperature.
2. The FTIR analysis of SPEEK confirmed the presence of sulfonic acid groups in polymer. The TGA observed that the increment in sulfonic acid groups content was lowering the temperature degradation of polymers backbone, meanwhile the glass transition temperature of SPEEK, which was measured by DSC, was increased with the DS, probably due to the interaction between sulfonic acid groups in SPEEK.
3. With the increment of DS, the water uptake, methanol permeability and proton conductivity of SPEEK membranes increase at room temperature. Among 52, 63 and 81 % DS, the latter is found to have more remarkable effect on these three measurements due to the presence of high content of sulfonic acid groups and resulted in the high hydrophilic membrane. However, too hydrophilic membrane is not desirable for DMFC electrolyte since it leads to high methanol crossover and thus lowering the overall DMFC performance.
4. In comparison with Nafion<sup>®</sup> 117 membrane, the SPEEK membrane demonstrated better methanol barrier property. The highest proton conductivity value of the membrane achieved was  $9.25 \times 10^{-3}$  S/cm, and this value is comparable with the proton conductivity of Nafion<sup>®</sup> 117 membrane.

#### 5.0 ACKNOWLEDGEMENTS

The authors would like to acknowledge Universiti Teknologi Malaysia for the generous financial support.

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