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Preparation and Characterization of High Methanol Resistance Sulfonated Poly(ether ether ketone) Membrane for DMFC Application

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ABSTRACT

High methanol resistance sulfonated poly(ether ether ketone) (SPEEK) membranes have been prepared and characterized as a potential proton exchange membrane for direct methanol fuel cell. The sulfonation process was conducted at room temperature to produce SPEEK with 60% degree of sulfonation (DS). The produced membranes were then characterized by evaluating the swelling behavior in terms of water uptake, swelling ratios and methanol sorption as a function of temperature and reaction time. Interestingly, it was observed that the methanol uptake value of SPEEK membrane was lower as compared to the water uptake value as much as 80%. This characteristic showed that SPEEK membrane possesses good resistance towards methanol which is a crucial property requires for direct methanol fuel cell (DMFC) application.

Keywords: SPEEK, swelling behavior, methanol uptake, DMFC

1.0 INTRODUCTION

The employment of liquid methanol in direct methanol fuel cell (DMFC) instead of hydrogen fuel offers several advantages, including easier storage and more straightforward implementation because humidification and thermal management, fuel vaporizer or reformer are no longer needed. However, the DMFC has the disadvantages of the methanol crossover through the commercially used perfluorosulfonic acid membranes such as Nafion (DuPont), Dow (Dow Chemicals) and Flemion (Asahi Glass) [1].

It is accepted that Nafion particularly has a dual structure with a hydrophobic region interspersed with ion-rich hydrophilic domains. The pore sizes of the latter domain are inaccessible by decane (and octane) molecules but accessible by water molecules. It is known that methanol diffuses primarily through the water-rich domains. Thus, the pronounced water-rich domains in Nafion membranes must affect the rate of methanol cross-over which is unessential in DMFC applications [2].

In fact, membranes with high performance, which is described in terms of high proton conductivity and low methanol permeability, are highly crucial as separators and electrolytes in DMFC. DMFC also demands on the material and production costs of proton exchange membranes (PEMs) manufacturing. These circumstances stimulate a research into alternative PEM materials, which can overcome the aforementioned problems that can be produced economically.

Attempts to produce alternative PEM to fulfill DMFC requirements have been carried out on aromatic polymers such as polyethersulfone (PES), poly(ether ether ketone), polyphenylquinoxaline (PPQ) and polybenzimidazole (PBI). Among the aforementioned polymers, PEEK is considered to be the most promising polymer

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owing to good thermal, chemical and mechanical stability, commercially available and very low cost.

In order to reduce the difficulty in processing the aromatic PEEK polymers, more flexible linking groups are often attach between the aromatic rings. Linking groups that impart good flexibility while still maintaining good thermal properties include ketones, sulfones, sulfides, oxides and perfluoroakyl groups [3]. In particular, PEEK doped with strong acid exhibits stable proton conductivity at temperature higher than 100°C. Therefore, sulfonic acid group is the most promising candidate to be linked into the polymer structure via sulfonation process. It is a simple process reaction and required shorter overall reaction time as compared to other processes, hence reduced the membrane production cost [4].

Sulfonating agent is one of the important factors in order to enhance the reactivity of sulfonation process. The sulfonating agents such as concentrated sulfuric acid, chlorosulfonic acid, pure or complex sulfur trioxide, and acetyl sulfide are among those that have been used in sulfonation process. Frequently, researchers employed concentrated sulfuric acid as the sulfonating agent for sulfonated of PEEK [5-8]. This is because sulfuric acid can prevent crosslinking reaction and polymer degradation effect during the sulfonation process with 100% sulfuric acid or chlorosulfonic acid as sulfonating agents. However, the degree of sulfonation (DS) can be controlled by changing reaction time, temperature and acid concentration by diluting strong acid such as fuming sulfuric acid with concentrated sulfuric acid [9,10]. Occasionally, fuming acid or diluted fuming acid with concentrated sulfuric acid were utilized for sulfonated PEEK [11-13].

In order to further develop an understanding on the sulfonated PEEK, therefore the SPEEK membranes have been prepared using a proprietary mixture of fuming sulfuric acid and sulfuric acid as the sulfonating agent. Optimization of the sulfonating agent mixtures represents the most inventive step in developing this SPEEK PEM for DMFC. This step leads to both high ion exchange capacity (IEC) and DS of the membrane within 2 to 3 hours compared 120 hours using conventional methods reported by Zaidi *et al.* [9]. The SPEEK membranes developed were then characterized in terms swelling behaviors by evaluating the water uptake, swelling effect and methanol uptake as a function of temperature and reaction time.

2.0 METHODS/THEORY

2.1 Materials

PEEK polymer was obtained from Victrex US Inc. Ltd. in powder form. Concentrated sulfuric acid (95-98%) and fuming sulfuric acid (15-30%) were provided by Fisher Scientific. Aldrich Chemical Co. Inc. provides the N-methyl pyrrolidone (NMP) as solvent for SPEEK membrane preparation. Nafion 115 (DuPont) was used as a reference material.

2.2 Sulfonation Process

Sulfonation reactions were conducted at room temperature using mixtures of 15-30% fuming sulfuric acid and 95-98% of concentrated sulfuric acid as the sulfonating agent for poly(ether ether ketone) (PEEK). 25 g PEEK and 400 ml (total acid used) of sulfonating agent used was magnetically stirred at room temperature and under nitrogen atmosphere for 6 hour to obtain sulfonated PEEK with 60% DS. The produced sulfonated PEEK polymer was recovered by precipitating the acid polymer solution into a large excess of ice cubes. The resulted sulfonated PEEK polymer was washed thoroughly with distilled water until the pH ~6 to 7. Finally, the SPEEK polymer was dried in the drying oven at 80-100°C for 24 h.

2.3 Membrane Preparation

20 wt.% of SPEEK solution was prepared by dissolving SPEEK polymer in N-Methyl pyrrolidone (NMP) under continuous stirring at room temperature for several hours until the sulfonated PEEK polymer dissolved homogeneously. The SPEEK solution obtained was then degassed in an ultrasonic bath at room temperature in order to eliminate air bubbles. The membranes were

cast onto a glass plate with a thickness in the range of 50 μm to 150 μm. Then, the cast membranes were dried at 60°C for 6 h followed by drying at 100°C for 4 h. After cooling to room temperature, the resultant membranes were peeled from the glass in water and then residual solvent was removed by drying for 3 days in a vacuum oven kept at 120°C. Finally, the membranes were treated with 1 M sulfuric acid solutions for 1 day at room temperature and subsequently rinsed with water several times.

2.4 FTIR

FTIR spectra for SPEEK samples were recorded using Nicolet-Magna 560 IR Spectrometer with powder samples inside a diamond cell and operated at room temperature in the range of 600 to 1800 cm^{-1} wave length.

2.5 Swelling Behavior

The swelling behaviors of the resulting membranes were studied as a function of water and methanol uptakes, respectively. The sulfonated membranes were dried in an oven at 60°C for 48 h, weighed films with diameter ~5.0 cm then soaked in water and methanol overnight at room temperature, blotted dry with absorbent paper to remove any surface moisture, and reweighed. The water uptake experiment was repeated by soaking membranes in water with different temperature in the range of 25-80°C. Water uptake was calculated from

$$\text{water uptake} = \frac{G_w - G_d}{G_d} \times 100\% \quad (1)$$

where G_w is the weight of the wet membranes and G_d the weight of the dry membranes.

3.0 RESULTS AND DISCUSSION

3.1 Sulfonation Reaction Conditions

Previous study by Jaafar *et al.* [14], reported the sulfonation reaction conditions which had been conducted several times by varying the reaction time and acid ratios of sulfonating agent used. From the result it was concluded that the sulfonation process of PEEK membrane with 1:3 (i.e. the ratio of fuming sulfuric acid to sulfuric acid) ratios appears to be the optimum condition. By varying the reaction time at the constant acid ratios, eventually four SPEEK membranes were prepared and characterized. The characterization results showed that SPEEK with 60% DS exhibited the highest overall membrane performance reflected high proton conductivity and low methanol permeability. Therefore, the swelling behaviors characterization on the specific SPEEK membranes with 60% DS has been investigated. Table 1 summarizes the overall membrane performance of sulfonated PEEK membranes sulfonated with different percentages of sulfonic acid.

3.2 FTIR analysis of PEEK and SPEEK

FTIR spectra in Figure 1 indicated the presence of two new absorption peaks at 1026 cm^{-1} and 1083 cm^{-1}, representing the aromatic SO_3H symmetric and asymmetric stretching vibrations, respectively. This was in close agreement with

Table 1 Overall membrane performance of SPEEK and Nafion membranes

Membrane	% SO_3H	Tg (°C)	Water uptake (wt. %)	Proton conductivity, σ (S/cm) ($\times10^{-2}$)	Methanol permeability, P (cm/s) ($\times10^{-7}$)	Overall membrane performance, ($\Phi = \sigma/P$) ($\times10^{3}$)
SPEEK37	37	155	25	0.597	3.45	17.304
SPEEK52	52	175	51	1.07	5.14	20.817
SPEEK60	60	180	82	2.71	7.59	35.704
SPEEK80	80	200	108	3.69	27.3	13.516
Nafion	-	-	18	1.35	63.0	2.143

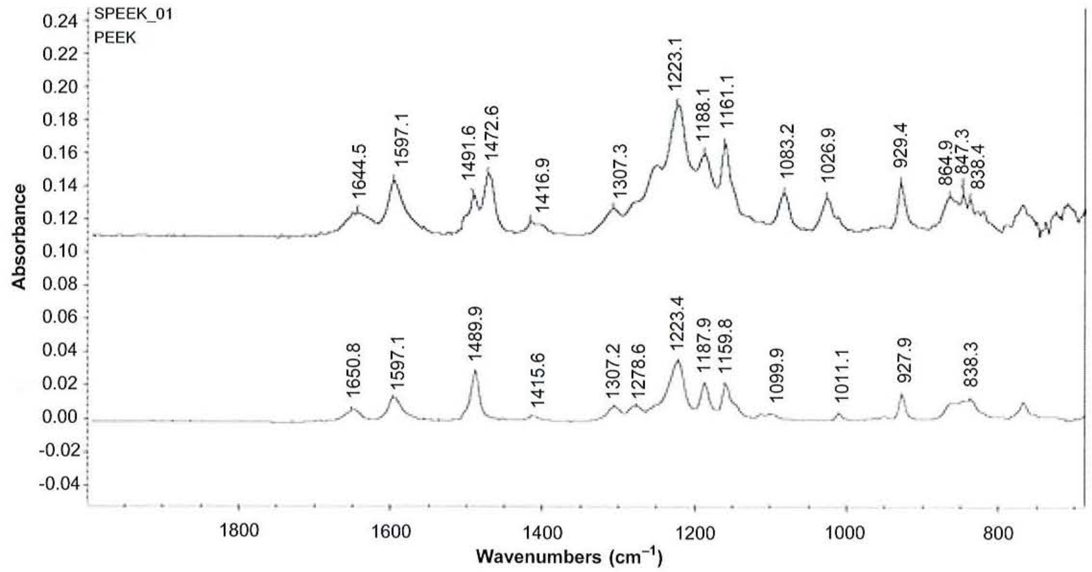

Figure 1 FTIR spectra of PEEK and SPEEK with 60% degree of sulfonation

1020 cm^{-1} and 1080 cm^{-1} as reported by Gao *et al.* [11]. This broadband confirms the presence of sulfonic acid group in the parent PEEK. The peak identified at 1490 cm^{-1} proved the presence of C–C aromatic ring in the PEEK, which referred to the 1,2,4-substitution aromatic ring. This peak was similar to the peak reported by Xing *et al.* [15]. This peak was found to split into two new absorption bands for SPEEK60 at 1472 cm^{-1} and 1491 cm^{-1} that presented the aromatic ring between the ether linkages. The significant shifting feature from peak 1490 cm^{-1} to these two new peaks implied that the sulfonic acid group only attached to the 1,2,4-substitution aromatic ring between the ether linkages ring, which meant only first substitution involved in the reaction. This result was also consistent with the explanation provided by Drioli *et al.* [16] and Wang *et al.* [17]. The peak observed in PEEK and sulfonated PEEK was at 1223 cm^{-1} which referred to the aromatic C–O–C absorption [11].

3.3 Swelling Behavior of SPEEK

Swelling behavior is a property that is important to determine the capability of membranes to absorb water to facilitate penetrates such as ions and methanol to migrate pass through the membranes. There are several PEM properties that are closely related to the hydrophilicity of the membranes includes proton conductivity, mechanical stability and methanol permeability. The loss of water corresponds to a drop of proton conductivity value for almost all PEM. Therefore, high water uptake or high hydrophilic domain in membrane microstructure is crucial in order to produce high proton conductivity. However, excess water uptake can lead to the low dimensional and mechanical property deterioration of membrane due to the soluble nature of membrane in water. Therefore, the water and methanol uptakes capabilities as a function of time were determined. For further understanding of temperature effects on water uptake and swelling ratios of SPEEK membranes, the water uptake and swelling ratios of SPEEK membranes were evaluated as a function of temperature.

The relation between the temperature and water uptake and swelling ratio is illustrates in Figure 2. The result shows that the water uptake raise sharply from room temperature up to 40°C and then increase gradually just after that temperature until 80°C. The changes were due to the increment of intermolecular interaction between the polar groups such as the hydrogen bonding and the sulfonic acid groups via the ionomer effect

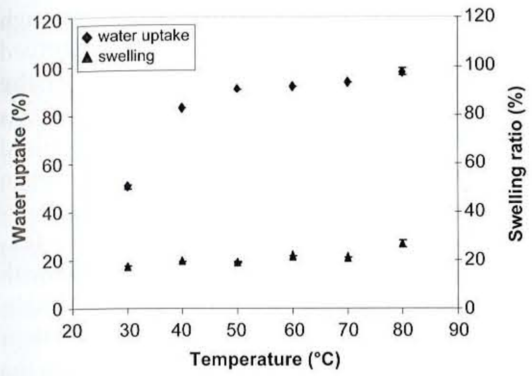

Figure 2 Water uptakes and swelling ratios of SPEEK as a function of temperature

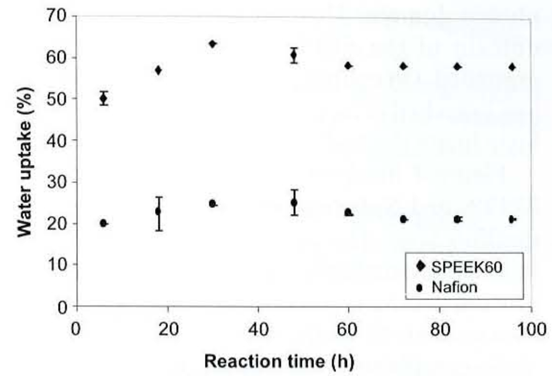

Figure 3 Water uptakes for SPEEK membrane with 60% DS and Nafion membrane as a function of reaction time

and simultaneously, increase the free volume of water absorption [9]. However, after 80°C the membranes tend to dissolve in water. This phenomenon was due to the phase changes from solid to liquid when the energy supplied to the polymer backbone tend to stretch the polymer bonds and finally fractured. A comparable finding was reported by Cai *et al.* [18].

The amount of water uptake is also associated with swelling ratio. The swelling effect is one of the important methods to determine the mechanical stability of SPEEK membranes. Figure 2 also shows the result of the effects of temperature on swelling ratio. The result shows that the swelling ratio was slightly increase from room temperature until 80°C. Similar phenomenon occurred when SPEEK membrane tend to swell just after 80°C [18]. The result also clearly shows that there was a significant difference on water uptake as a function of temperature. On contrary, the SPEEK swelling ratio did not give a significant influence throughout the experiment. It was 70% difference between water uptake value and swelling ratio value when temperature reached 80°C. This phenomenon showed that although the SPEEK membrane absorbed water as much as 100% water uptake at the highest temperature but at the same time it still maintain the shape. This behavior exhibited that the ability of SPEEK membrane to absorb water is superior while maintaining its mechanical stability.

Figure 3 shows the water uptake of SPEEK and Nafion membranes as a function of reaction time. It was observed that both of SPEEK and Nafion membranes had similar trend of curve. Both membranes showed a sharp increment after soaked in water between 6 hours and 30 hours and then decreased gradually and finally remained constant started from 60 hours to 96 hours. This behavior showed that the water uptake increase with increasing reaction time. It was suggested that as the time increased, more water swollen ionic domains produced in the membranes and simultaneously more interconnected to form a network structure developed. The constant water uptake observed for membranes at higher reaction time was due to the diffusion limitation caused by segregation in the ionic domains that showed that the membranes were saturated with water [19].

Figure 3 also shows that the water uptake of SPEEK membranes was outstanding to that of Nafion membrane. The water uptake of SPEEK membranes at constant region showed approximately 65% higher than Nafion membrane. This was due to the microstructure of the polymer which distributed to two domains; hydrophobic domain represented by the polymer backbone and hydrophilic domain represented by the functional group attached to the polymer ring [20]. From the SPEEK membranes point of view, the presence of aromatic group in the SPEEK polymer backbone presented less pronounce of the hydrophobic domain. Hence, hydrated hydrophilic domain of the SPEEK membranes could be expanded. On contrary to the Nafion membrane, less branched of its perfluorinated polymer backbone limits the hydrophilic domain hydration.

Figure 4 illustrates the methanol uptake of SPEEK and Nafion membranes as a function of reaction time. The methanol uptake of Nafion increased dramatically until it reached the highest value at about 40% after soaking in water for 30 hours. After 30 hours, the methanol uptake of Nafion membranes started to decrease constantly until 96 hours. On contrary, the methanol uptake of SPEEK membranes went up slowly and then leveled off at 11% from 72 hours to 96 hours. A significant result was observed that the methanol uptake of Nafion was higher than that of sulfonated PEEK membranes. This was due to the difference in microstructure between Nafion and SPEEK membrane. It was found true by Chang *et al.* [21] and Kreuer [22] as they reported that the Nafion membrane has high hydrophobicity of the perfluorinated backbone and also high hydrophilicity of the sulfonic acid groups. In the presence of water, this character was more pronounced and consequently increased the hydrophobic/hydrophilic domains of Nafion membrane. The hydrophilic domains in the Nafion membrane which were formed by the presence of sulfonic acid group allowed not only proton and water, but also a smaller polar molecule such as methanol to migrate through this domain. However, the less pronounced hydrophilic–hydrophobic separation of the SPEEK membranes produced narrow channels and a highly branched structure hence minimized the amount of methanol permeated through them [22].

The percentage of the solvent uptake (i.e. water and methanol) of SPEEK membranes with reaction time is plotted in Figure 5. Interestingly, it was observed that the methanol uptake values for the SPEEK membranes were lower than the water uptake values as much as 80%. This was due to the degree of polymeric membrane in solvent that was proportional to the hydrogen bonding capability of the solvent. The hydrogen bonding in methanol is not as strong as it is in water. This can be understood based on the fact that the O atom does not have as much partial negative charge in methanol as it does in water because the C atom draws away some of the negative charge. Therefore, the hydrogen atom in methanol does not have as much positive charge as in water. Hence, it may be concluded that the existent of extensive swelling in water is caused by high formation of hydrogen bonding formed which enhanced the facilitation of the water absorption into the membrane. A similar behavior was observed by Ismail *et al.* [23] on the sulfonated polystyrene pore-filled electrolyte membranes by electrons induced grafting.

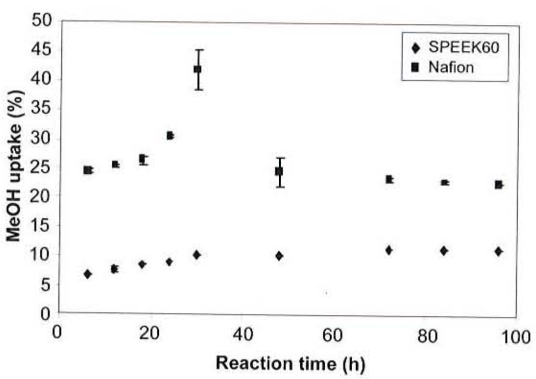

Figure 4 Methanol uptakes for SPEEK with 60% DS and Nafion membrane as a function of reaction time

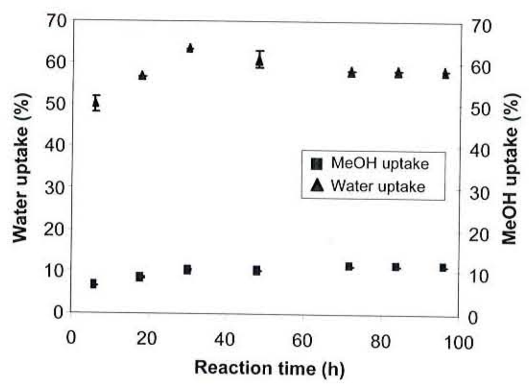

Figure 5 Variation of water uptake and methanol uptake as a function of reaction time for SPEEK membrane with 60% DS

4.0 CONCLUSION

SPEEK membranes with 60% of SO3H content having high methanol barrier were successfully prepared. The water uptake as a function of reaction time of SPEEK membranes was higher than that of Nafion membrane. Result showed that SPEEK membranes exhibited lower methanol uptake as much as 75% as compared to Nafion membrane at the same conditions. Interestingly, the result also showed that SPEEK membranes exhibited lower methanol uptake as compared to water uptake. SPEEK membranes with 60% of DS have performed a high methanol barrier proton exchange membrane for direct methanol fuel cell applications.

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