Sulfonated Polyether Ether Ketone Membrane and Its Properties for Direct Methanol Fuel Cells

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Abstract — **A fuel cell, a device transforming directly the chemical energy into electricity through a chemical reaction, is a source of clean energy in the future. Direct Methanol Fuel Cell (DMFC), uses a proton exchange polymer electrolyte which one of the key components developed to realize the commercialization of fuel cells in transportation and portable equipment. Poly Ether Ether Ketone (PEEK) is a thermoplastic material that has a combination of physico-chemical and good mechanical properties. The introduction of sulphonic acid groups into the polymer chain is an easy strategy to improve the properties of PEEK. This research aims to study the effect of time and the temperature of sulfonation in the fabrication of sulfonated PEEK on the membrane characteristics such as water uptake, methanol permeability, Ion Exchange Capacity (IEC), degree of sulfonation and proton conductivity. The results indicated that sPEEK was potential candidate as proton conductive membrane for application of DMFC due to enhancement of proton conductivity although the methanol permeability also increases proportional with IEC or DS.**

Key words – DMFC, fuel cells, sPEEK, sulfonation.

I. INTRODUCTION

Fuel cell acquires a serious attention as an alternative energy source, replacing conventional energy system (fossil), due to its high efficiency, low negative impact to environment, and flexibility in various applications of electricity needs. The technology of Direct Methanol Fuel Cell (DMFC) is similar to the Proton Exchange Membrane Fuel Cell (PEMFC), where methanol substitutes hydrogen to be fed directly into a fuel cell.

Electrolyte membrane is the key component in developing DMFC. Today membrane from ionomer of perfluoronated like Nafion® (DuPont) is used commercially due to its high conductivity. In DMFC application, one of the arising problems is crossover of methanol from anode to cathode causing low cell potential. Other frailty, the perfluoronated membrane is not appropriate if applied at temperatures beyond 100°C. As well, its high cost is another challenge to solve.

Hydrocarbon polymers containing polar groups have high water absorption over a wide range of temperatures. Some examples of developed hydrocarbon polymers are polyethersulfon (PESF) [1, 2, 3], polyether ketone, poly(arilen ether*)*, polyester and polyimide [4]. The sulfonation process of commercial polymer is one of strategies developed to obtain modified polymer acting as a proton exchange membrane [5]. The degrees of hydrophilic, conductivity and mechanical properties of sulfonated membrane depend on the degree of sulfonation (DS) [6]. In addition, previous researchers [7] reported that to reduce the permeability of methanol from anode to cathode, non-fluoronated membranes such as polybenzimidazol (PBI), sulfonated poly(ether ether ketone) (sPEEK), and 2-akrilamindo-2-metil propane sulfonat (AMPS) were developed by adding inorganic components. This approach has been successful in reducing the permeability without decreasing the proton conductivity.

The hydrocarbon polymer material which is potential to develop as a proton exchange membrane is sulfonated polyether ether ketone (sPEEK). The presence of group of sulfonat acid causes sPEEK more hydrophilic because it increases the polymer acidity. The DS is controlled by the temperature and reaction time of sulfonation. This work presents the effects of temperature and reaction time of PEEK sulfonation on the ion exchange capacity (IEC), DS, and other membrane properties including water uptake, methanol permeability, and proton conductivity.

II. EXPERIMENTAL

The materials used in the experimental works include: PEEK kindly provided by the Goodfellow Cambridge Limited, sulfuric acid, methanol, and dimethyl acetamide from Merck.

A. Sulfonation of Poly Ether Ether Ketone

Pellets of PEEK were dried in an oven at 100°C and vacuum condition. These PEEK were then dissolved and reacted with sulfuric acid for certain reaction times and temperatures. The sulfonation times were varied for 1, 1.5 and 2 hours, and at sulfonation temperatures of 30, 60, and 90°C. To stop the reaction, the reaction mixture was poured into icy water and so white deposits were obtained. Then, the deposits were washed several times with deionised water until the pH of waste washing water was neutral. Afterwards, sPEEK was dried in an oven at surrounding temperature for 12 hours, and at 60°C for 12 hours.

B. Membrane Preparation

The sPEEK deposits were dissolved in dimethyl acetamide (DMAc) aided by stirring for 2 hours. Membrane casting was performed by pouring the polymer solution onto a petridish so that a membrane film with a thickness of 100 μm was obtained. The drying of membrane film was carried out in the oven at 50°C for 48 hours.

C. Ion Exchange Capacity (IEC)

IEC represents the number of hydrogen ions that can be transmitted per dry weight of sample. The measurement of IEC applied titration method, by submerging the membrane into the solution of NaOH 1 M for 48 hours, and the solution was then titrated with sulfuric acid 0.01 M using an indicator PP. IEC was calculated using the following equation:

$$N_{\mathrm{sPEEK}} = (V \cdot M)_{\mathrm{NaOH}} - 2(V \cdot M)_{\mathrm{sulfuric\ acid}} \quad (1)$$

$$IEC = \frac{n_{\mathrm{sPEEK}}}{W_{\mathrm{membrane}}} \times 1000\ (\mathrm{meq/g}) \quad (2)$$

DS is defined as the ratio of the number of structural unit containing a sulfonic acid group to the total number of structural unit in sPEEK.

$$DS = \frac{M_P (IEC)}{1000 - (IEC) M_f} \quad (3)$$

where *Mp* is the molecular weight of the PEEK repeat unit (288.3 $g.mole^{-1}$), and *Mf* is the molecular weight of the functional group –SO3H (81 $g.mole^{-1}$).

D. Fourier Tranform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy was used to identify the sulfonat group in the polymeric membrane. In this study, FTIR spectra was given by the spectrometer IR Prestige 21 Shimadzu. The spectra was measured at a wave number range of 400 – 4000 cm^{-1}.

E. X-Ray Diffraction

X-Ray diffraction (XRD) was used to analyse the crystallites structure of membrane. The XRD data were recorded with a Bruker D8 Diffractometer using Cu Kα radiation (λ = 1.54 nm). Radiation was generated at 60 KV and 60 mA. The 2θ angular regions between 10° and 70° were explored at a nominal step size of 0.033° 2θ and time per step of 100 seconds. The scan was carried out in continuous mode.

F. Water Uptake

The membrane water uptake was measured in water at room temperature. It was calculated from the difference in weight between wet and dry samples. The wet weight was determined after immersion of the samples in the water at room temperature for 48 hours. Subsequently, the membrane surfaces were wiped with a tissue paper and weighed immediately. To obtain the dry weight, the samples were heated in an oven at 120 °C for 2 hours.

$$\mathrm{WUT} = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\% \quad (4)$$

where WUT, m_{wet}, and m_{dry} represent *water up take* (wt.%), wet and dry membranes weight, respectively.

G. Methanol Permeability

Methanol permeability was measured with a two-compartment glass cell. One compartment was filled with 100 dm^3 of 3 mol dm^{-3} ethanol solution and the other was filled with 100 dm^3 of deionised water. The membrane was clamped between two compartments. Solutions in each compartment were stirred continuously during measurement. Ethanol concentration in the receiving compartment was measured as a function of time by measuring the refractive index of a 0.5 dm^3 sample from each compartment. The observed refractive index was compared to the corresponding value of the calibration curve.

The time dependence of methanol concentration in the receiving compartment followed Fick's first law, assuming $C_B << C_A$; hence C_A was considered constant.

$$V_B \frac{dC_B(t)}{dt} = \frac{A}{L} DK\, C_A \quad (5)$$

where C_A and C_B are ethanol concentrations in compartment A and B; A and L are the cross section of membrane area and membrane thickness, respectively; and D and K are the ethanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. D was assumed constant throughout the membrane and K was independent of concentration. The product DK is membrane permeability calculated from the slope of C_B with respect to time, $C_B(t)/t$, was as follows:

$$P = \frac{C_B(t)}{t} \frac{V_B\ L}{C_A\ A} \quad (6)$$

H. Proton Conductivity

Proton conductivity was measured using conductivity cell connected to LCR meter, HIOKI 3522-50 LCR HiTESTER. Measurement was carried out in fully humidity condition.

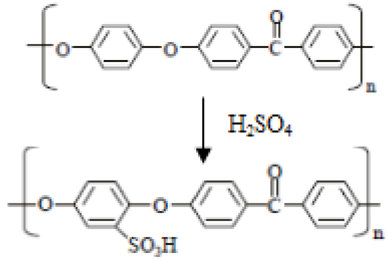
III. Result and Discussion

Polymer sulfonation is one of methods to insert sulfonat acid group into polymer structure. The sulfonation reaction of PEEK to sPEEK is as shown in Equation (7). The presence of sulfonat group in the polymer chain changes the chemical properties of polymer in which the polymer becomes more hydrophilic, and thus facilitates proton transportation through the membrane [9].

A. IEC and DS of sPEEK membrane

The effects of temperature and sulfonation reaction time on IEC are shown in Table 1. Both studied variables control the concentration of sulfonat group in the membrane.

The increase in temperature and sulfonation reaction time results in IEC improvement of the sPEEK membrane produced. The sulfonation time, raised from 1 – 2 hours, causes the increase of IEC from 1.87 to 2.64 meq/g and DS from 63.7 to 96.8%. Contrarily, it was reported that the sulfonation time did not significantly affect the DS at less than 24 hours reaction time [10, 11].



(7)

The increase in temperature from 30 to 60°C at 1 hour reaction time gives membrane with an IEC of 1.87 and 2.3 meq/g, respectively. At higher temperature, 90°C, the produced membrane has an IEC value higher than 2.71 and DS ≅ 100%; however, the membrane is more easily damaged when it is submerged in a solution containing water. This shows that the sulfonat group may also fill up the backbone of carbonyl bond (C=O), hence causing the membrane brittle. Yee et al. [10] reported that at sulfonation temperature higher than 70°C, PEEK was overs-sulfonated even in short reaction periods of 1 h. The produced sPEEK membranes with over-sulfonation deteriorate and swell in water.

TABLE I
TYPE SIZE FOR PAPERS

Temperature (°C)	Sulfonation time (hours)	IEC (meq/g)	DS (%)
30	1.0	1.87	63.8
30	1.5	2.37	84.3
30	2.0	2.64	96.8
60	1.0	2.30	81.4
60	1.5	2.70	100
60	2.0	Dissolved	-
90	1.0	Dissolved	-
90	1.5	Dissolved	-
90	2.0	Dissolved	-

IEC has a correlation with DS; which defined as percentage of repeat PEEK unit that have been sulfonated. A higher DS indicates that more units have been sulfonated.

B. Structure Analysis

The chemical structures of sPEEK were confirmed using FTIR spectroscopy. Fig. 1 illustrates FTIR spectra of sPEEK membranes at some DS. The absorption peak appeared at 1035 cm^{-1} corresponded to the group of S=O. The O=S=O band at 1089 cm^{-1} might be the symmetric streching vibaration peak, however its asymmetric streching vibration peak at 1224 was not observed in samples. The intensity of absorption and clear split at around 1035 cm^{-1} increased with the DS.

The crystallinity of sPEEK membranes was examined using X-ray diffraction technique. The XRD patterns of sPEEK membranes prepared at different temperature and reaction time are shown in Fig. 2 and 3. The diffraction peaks of crystal structure are observed at 2θ = 17, 21, 23 and 30° which correspond to reflection from 100, 111, 200 and 211 planes, respectively. Zaidi [9] found similar result of crystalline peaks at low sulfonated membrane. The broad amorphous scattering background also found at a maximum intensity of 2θ = 20°.

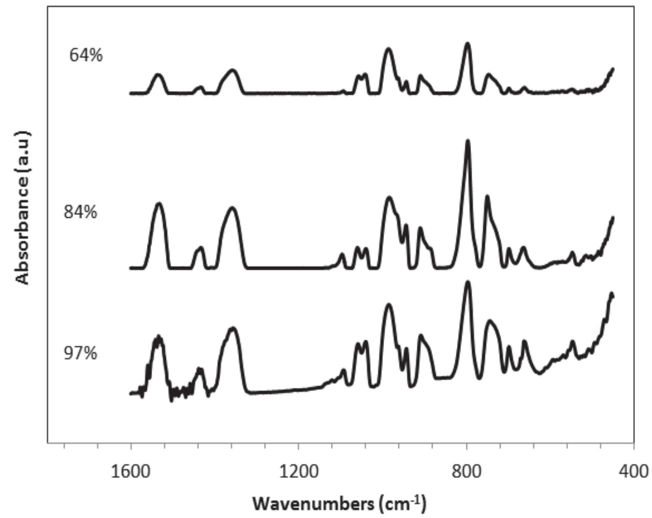


Fig. 1 FTIR spectra of sPEEK at different DS

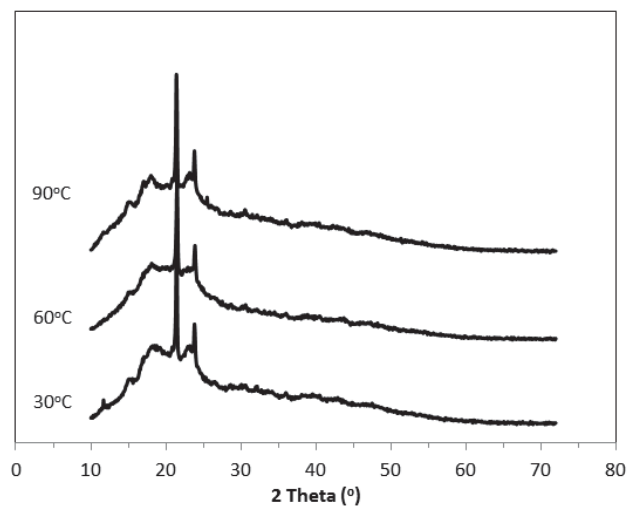


Fig. 2 XRD of sPEEK membranes prepared at different sulfonation temperatures

C. Water Uptake and Methanol Permeability

In general the membrane conductivity in DMFC depends on the number of acid groups and their ability to dissociate in water. The presence of water and acid groups can facilitate proton transport; therefore, water uptake property becomes an important parameter for DMFC membrane. Water uptake and methanol permeability characteristics of sPEEK membrane as a function of IEC are given in Fig. 4. Both water uptake and methanol permeability increase exponentially with increasing IEC.

The ability to absorb water decreases as the membrane IEC is low. The PEEK sulfonation, in fact, increases the hydropilicity of membrane; this may be due to more number of sulfonat groups which are bonded at aromatic chains of PEEK . Li, et. all [8] reported that the water uptake increased linearly with DS, and the sPEEK membrane with DS higher than 40% had water uptake higher than that of Nafion 115 (about 20% w.). Higher water uptake facilitates proton transfer better; however, if the water uptake is too high, it may reduce the mechanical property of membrane so that the membrane becomes brittle. The sulfonation changes the chemical properties of PEEK that the crystallinity decreases and affects the solubility of sPEEK [8].

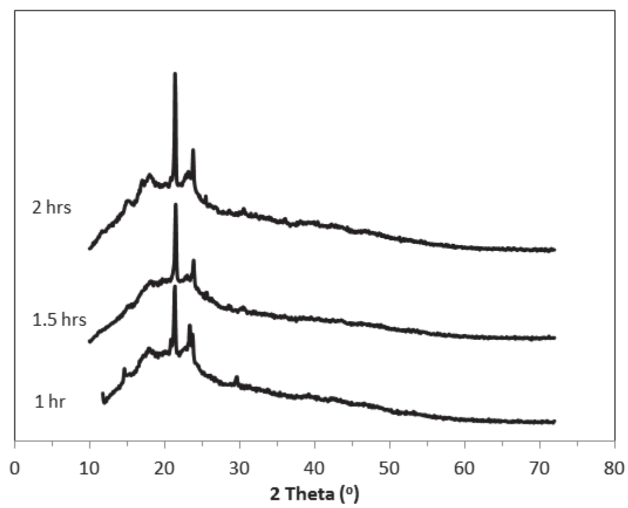


Fig. 3 XRD of sPEEK membranes prepared at different sulfonation time

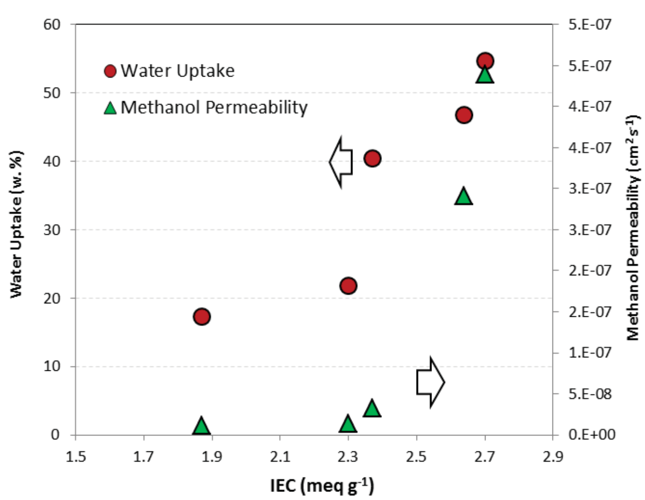


Fig. 4 Water uptake and methanol permeability of sPEEK membranes at various DS

The measurement of methanol permeability is one of important tests for DMFC electrolyte membrane, to know, yaitu untuk mengetahui metanol yang dapat melewati membran. Othman et. al. [9] reported that the methaol permeability increased with the increase of DS. This trend may be caused by the change of membrane solubility. As mentioned in the previous part, the sulfonation process changes the chemical properties of PEEK in which the crystallinity of sPEEK membrane decreases. In sPEEK membrane with a high DS, the crystallinity state turns to amorphous; therefore, the molecular interactions between methanol and water are polar, and thus weaken the chain bonds of amorphous molecules of sPEEK [8, 9].

The methanol permeability through sPEEK is lower than that through Nafion-117 (6,3 x 10^{-6} cm^2/s) [12]. This may be because the molecular structure of PEEK has aromatic basic chains which are more rigid than Nafion of which basic chains are straight. The more rigid chains cause the transfer of water or methanol through the membrane impeded. Due to the methanol's lower permeability, sPEEK is very potential to meet the electrolyte membrane need for DMFC, so that sPEEK has a good prospect in the future.

D. Proton Conductivity

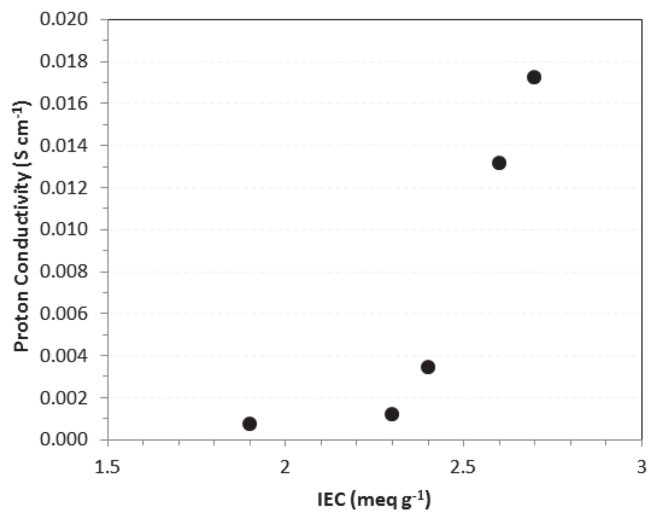


Fig. 5 Proton conductivity of sPEEK varying the IEC

The proton conductivity of sPEEK membranes with various IEC at 100% relative humidity is showed in Fig. 5. It has been observed that the conductivity of sPEEK membranes increased with the IEC. The conductivity increases from 7x10^{-4} S cm^{-1} to 1.7x10^{-2} S cm^{-1} as the IEC increases from 1.9 to 2.7 meq g^{-1}, and thereafter increases sharply above 2.3 meq g^{-1} or the DS of 80%. As expected, the trend of conductivity is confirmed by the water uptake tendency. Conductivity improvement might be caused by the present of more sulfonic acid group in the membranes. By increasing the IEC or DS, the membrane absorbs more water which facilitates proton transport. Therefore sulfonation not only increases the number of protonic sites SO_3H but also provides formation of water-mediated pathways for protons [9].

In comparison with Nafion 117, the proton conductivity of sPEEK is lower than that of Nafion 117 which is 3.4x10^{-2} S cm^{-1}. However, this lower conductivity is still feasible and can be improved for DMFC application due to the lower cost of PEEK material; therefore sPEEK is attractive as an alternative to Nafion® membranes.

IV. CONCLUSIONS

PEEK has been sulfonated using sulphuric acid 98% to produce proton exchange membrane containing SO_3H group. The sulfonation was carried out at various temperatures and reaction times, resulting in different DS. The difference in DS indicated the different number of sulfonat groups in the membrane, and thus water uptake was affected. The addition of number of sulfonat groups increases the membrane capacity in absorbing water, so that its conductivity is expected to increase. As a matter of fact, the increase in number of sulfonat groups also increases the methanol permeability. Therefore, the selection of temperature and reaction time to give membrane with sufficient water uptake and proper methanol permeability is a critical point in the production of sPEEK membrane for DMFC.

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