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Effect of Temperature on Sulfonated Poly (Ether Ether Ketone) Blended with Charged Surface Modifying Macromolecule Membrane for DMFCs

A. Mayahi[1], J. Jaafar[2], M. N. A. Mohd Norddin[3*] & H. Hassan[4]

[1,2&3]Advanced Membrane Technology Research Center (AMTEC), Universiti Technologi Malaysia, 81310 Johor Bahrou, Johor, Malaysia
[4]Department of Chemical Engineering, Universiti Teknologi Malaysia, , 81310 Johor Bahru, Johor, Malaysia

ABSTRACT

The purpose of this research was to determine the behavior of modified sulfonated poly (ether ether ketone) (SPEEK) with degree of sulfonation (DS) 68% blended by charged surface modifying macromolecule (cSMM) at different operating temperatures (room to 80°C) for direct methanol fuel cell application. The fabricated SPEEK (68)/cSMM membrane was compared with SPEEK (68) and Nafion112 membranes in terms of water uptake, proton conductivity, and methanol permeability at relatively high temperatures. The water uptake of SPEEK (68)/cSMM was higher than that of SPEEK (68) and Nafion112 over the temperature ranges studied; however it was dissolved at 80°C. Proton conductivity of SPEEK (68)/cSMM showed improvement compared to SPEEK (68) at temperature range, but still lower than Nafion112, moreover methanol permeability behavior of fabricated membrane was lower at high temperatures as compared to that of SPEEK and Nafion112 and better overall performance was allocated to the fabricated membrane at 60°C.These results indicate that SPEEK (68)/cSMM membrane is promising to be used as a proton exchange membrane in direct methanol fuel cell.

Keywords: Direct methanol fuel cell, proton exchange membrane, charged surface modifying macromolecule, different operating temperatures

1.0 INTRODUCTION

Energy crisis and environment pollution have promoted researchers to find alternative energies instead of fossil fuels. Fuel cell is an alternative energy which has attracted a great deal of attention nowadays[1]. Direct methanol fuel cell (DMFC) is a type of fuel cell which has been studied widely to be used in the notebook computers, cell phones and other electronic devices due to its convenient fuel supply and quick start time[2, 3]. Proton exchange membranes (PEMs) are the heart of fuel cells which should have some criteria to be commercialized: high proton conductivity, low methanol permeability and good mechanical and chemical stabilities[4]. Nafion is considered as the most commercialized PEM in fuel cell industry due to its excellent chemical and electrochemical properties and its high proton conductivity when it is hydrated, however its downsides such as high cost, and high methanol permeability especially at high temperatures have stimulated researchers to consider other possible alternatives[5-9]. Sulfonated poly (ether ether ketone) (SPEEK), Poly (ether sulfone) (PES), and polybenzimide (PBI) are non-fluorinated polymers which possess outstanding criteria such as superior chemical stability, high thermo-oxidative resistance, cheaper prices compare to Nafion and well-behaved mechanical properties[4]. The major issue of SPEEK membrane is beside water uptake

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* *Corresponding to:* M. N. A. Mohd Norddin (email: anam@petroleum.utm.my)

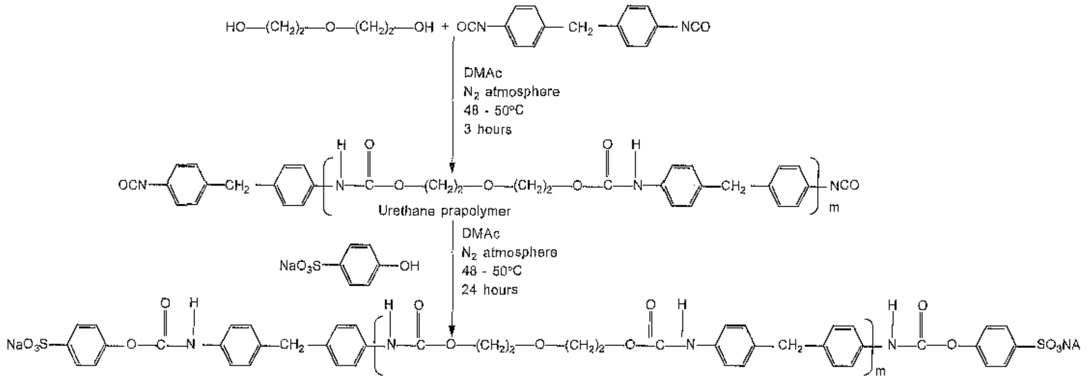

Figure 1 Schematic presentation of the synthesis reaction of cSMM

increment at high temperatures methanol permeability also increases which declines the DMFC performance due to the presence of methanol in the cathode side, however recently DMFC operation at high temperatures has attracted attention due to better proton conductivity, better kinetics of methanol oxidation and improvement of the electrodes tolerance to carbon monoxide[10]. Hence many studies have been carried out to tackle this issue: crosslinking[1], blending with other polymers[11], adding nanoclay to the base polymer[12], applying inorganic fillers like BPO_4, SiO_2, TiO_2 and ZrO_2 into SPEEK membrane[13-15]and surface modifying macromolecule (SMM) approach. SMM is a simple blending method which has the concept of polymer segregation in polymer science elsewhere[16-18].cSMM is a modified structure of the SMM which possesses sulfonic acid groups. The synthesis of cSMM is shown in Figure 1.

In this study the behavior of SPEEK (68)/ cSMM on water uptake, methanol permeability, and proton conductivity was studied at different temperatures. The membrane also was compared with SPEEK (68) and Nafion112 at relatively high temperatures.

2.0 EXPERIMENTAL

2.1 Materials

Materials which were used in this study are as follows; PEEK in powder form (<80 mm) was obtained from Victrex Inc., USA. The weight average molecular weight of poly (ether ether ketone) was 3.92×10^4 and its density was$1.29 \times 10^6 \frac{g}{cm^3}$. The sulfonation agent is concentrated sulfuric acid (95-97%) obtained from Merck Co. and it was used as received without further purification. 1-Methyl2-pyrolidinone (NMP, anhydrous 99.5%) and Methanol, 99.9% were bought also from Merck Co. Nafion112 was bought from Dupont de Nemours Co. and cSMM was used as it received.

2.2 Synthesis of Sulfonated Poly (Ether Ether Ketone)

PEEK was sulfonated by following technique which is described in [19, 20]. 5 grams of PEEK was dried in a vacuum oven at 100°C for 24 hrs. and then it was dissolved in 95 ml of concentrated sulfuric acid (95-97%) at room temperature to suppress the heterogeneous sulfonation. After completing the dissolution of PEEK (about 1 h), the polymer solution was brought to the desired temperature 65 and it was hold for 3 h to obtain the desired degree of sulfonation (DS). In order to terminate the reaction, the polymer solution was poured into excess ice-cold deionized water under continuous stirring for one night to remove the residual acid. The polymer was washed repeatedly with deionized water till a neutral PH is reached. Then it was dried by air circulation oven at 60°C overnight [21].

2.3 Characterization of Sulfonated Poly (Ether Ether Ketone)

A crucial characterization of SPEEK was on the sulfonation degree (DS). It was measured by Hydrogen Nuclear Magnetic Resonance (^{1}H NMR) (Bruker, USA) at a resonance frequency of 400.13 MHz and at room temperature [19, 20].

2.4 Preparation of Membranes

10 gram of SPEEK was dissolved in 90 gram NMP to make a 10 wt% of original SPEEK solution. The blend solution was prepared by mixing 0.416 g of cSMM and 10 gram of SPEEK, to make 4 wt% of cSMM in total solid. Both are stirred for 24 h, before the mixtures were cast onto a glass plate using a pneumatic casting machine. The membrane was dried at 100°C for 24 h in a vacuum oven. After cooling to room temperature, the membrane was converted into the H^+ form by immersing it into a 1 M sulfuric acid solution for 24 hrs at the room temperature and blotted dry with absorbent paper before it was air dried [21].

2.5 Characterization of Membrane

2.5.1 Methanol Permeability Measurement at Different Temperatures

Diaphragm diffusion was used to determine the methanol permeability of the fabricated membrane at different temperature. The apparatus was made of two identical compartments (A and B) which were separated by an effective area of 5.067 cm^2. Compartment A (V = 150 cm^3) was filled with 1 M methanol, while compartment B (V = 150 cm^3) was filled with deionized water. The methanol molecules diffused along the concentration gradiant through the membrane into the opposite compartment. It should be expressed that during the experiment magnetic stirrer was used in each compartments to ensure uniformity. Liquid samples (500 μl) were taken every 30 min to measure methanol concentration changes in compartment B by a digital refractometer (Perkin Elmer, USA). Before testing all membranes were hydrated in de-ionized water for at least 24 h and the thicknesses in hydrated form were from 54 to 72 μm. it should be mentioned that methanol diffusion was induced by a concentration gradient across the membrane. Hence, the change of methanol concentration in the diffusion reservoir expressed with below equation, the diffusion coefficient was obtained by following equation [22]:

$$C_B(t) = \frac{A}{V_B}\frac{DK}{L}C_A(t - t_0) \qquad (1)$$

Where C_B is the methanol concentration in diffusion reservoir $\left(\frac{\text{mol}}{\text{L}}\right)$ at time t, C_A is the methanol concentration in feed $\left(\frac{\text{mol}}{\text{L}}\right)$ compartment, A is the effective area of membrane (cm^2), L is the thickness of membrane (cm), and V_B is the volume of diffusion reservoir (cm^3). The time lag, t_0 is explicitly related to the diffusivity $\left(t_0 = \frac{L^2}{6D}\right)$.

Methanol permeability (τ) is defined as the product of the diffusivity of methanol (D) and the partition coefficient (K); $\tau = DK$. τ is calculated from the linear interpolation of C_B versus t and the slope of the graph (m) by equation (2):

$$\frac{C_B(t)}{t - t_0} = m \qquad (2)$$

As a consequence equation (3) can be rearranged to calculate the methanol permeability $\left(\frac{\text{cm}^2}{\text{s}}\right)$ as expressed below:

$$t = m\frac{V_B}{A}\frac{L}{C_A} \qquad (3)$$

The Figure 2 shows the apparatus which was used to measure methanol permeability. To control the temperature two digital thermometers were attached to the heater and put in each compartment.

2.5.2 Proton Conductivity Measurement at Different Temperatures

The proton conductivity of the membrane was measured by AC impedance technique using a Solarton 1260 impedance-gain phase analyzer. The impedance spectra recorded over the frequency range of 0.1 Hz to 10 MHz with 50

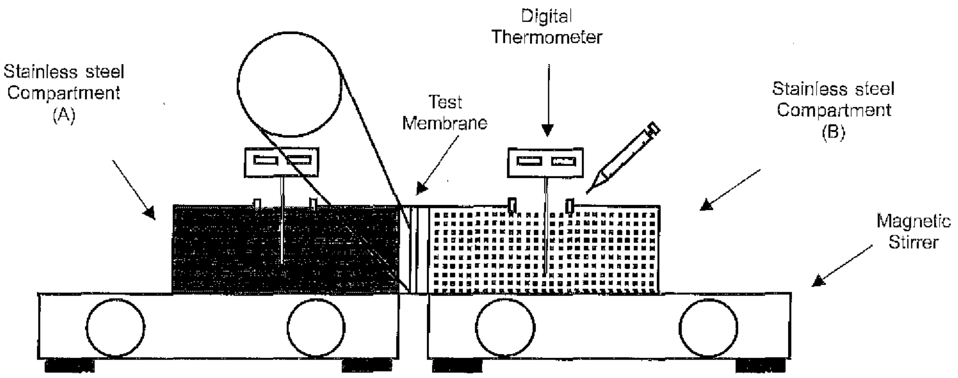

Figure 2 Methanol permeability measurement apparatus

to 500 mV oscillating voltage in 100% RH and different temperatures (room to 80°C). Membrane samples with thicknesses between 57 to 74 μm equilibrated in deionized water for 24 hrs before being tested. Then, the membranes were placed between two stainless-steel electrodes which had 2.011 cm^2 face areas, and then these stainless-steel electrodes and membrane were put in a conductive cell (this cell was used to host the sample tightly). The membrane resistance (Ω) obtained from the intercept of the impedance curve with the real-axis at the high-frequency end. Finally proton conductivity of membranes were calculated according to below equation [23]:

$$\sigma = \frac{L}{\Omega S} \tag{4}$$

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

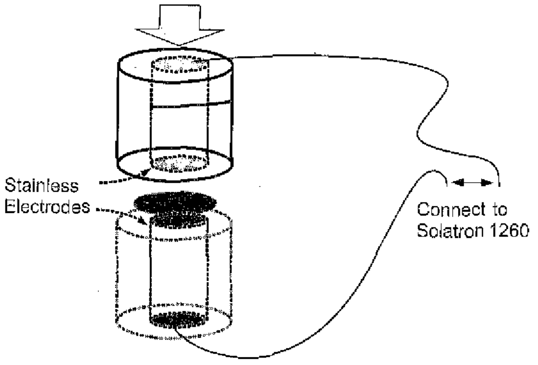

Figure 3 Proton conductivity measurement apparatus

2.5.3 *Water Uptake Measurement at Different Temperatures*

The membranes were dried in an oven at 60°C for 48 hrs and weighted (W_{dry}) and then immersed in deionized water at desired temperature. After taking out the membranes the surface water was removed by absorbent paper and membranes were weighted quickly (W_{wet}). Finally, % of water uptake calculated from below equation (5)

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{5}$$

Where W_{wet} and W_{dry} where the weight of the wet and the dry membrane, respectively [21].

2.5.4 *Overall Membrane Characteristic*

The overall membrane characteristic can be determined using the following expression (6) [22]:

$$\Phi = \frac{\sigma}{P} \tag{6}$$

Where Φ is a parameter that evaluate the overall membrane characteristic in terms of the proton conductivity, σ to the methanol permeability, P.

3.0 RESULTS AND DISCUSSION

3.1 Degree of Sulfonation of Sulfonated Poly (Ether Ether Ketone)

The degree of sulfonation of the freshly produced SPEEK was determined by H NMR analysis. In

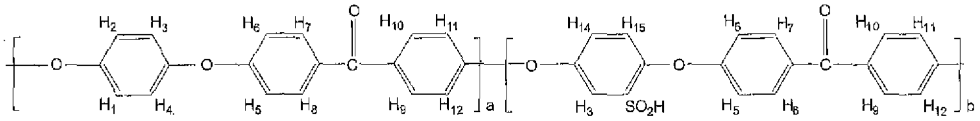

Figure 4 Classification of the aromatic protons SPEEK repeat unit

H NMR spectra it can be seen obviously that presence of sulfonic acid group causes 0.25 downfield signal of $H_{13,}$ compared with H_{14} and H_{15} in the hydroquinone ring, resulting in a distinct signal for protons at the 13 position.

The classification of the aromatic protons for the SPEEK repeat unit is according to Figure 4.

The intensity of H_{13} is equivalent to the SO_3H group content. The H NMR signal for SO_3H is difficult to be recorded directly due to the fact that the proton is able to change its position [24]. The DS can be calculated by below equation

$$\frac{DS}{S-2DS} = \frac{A_1}{A_2} \ (0 < DS < 1) \qquad (7)$$

Where S is the total number of hydrogen atoms for repeat unit of the polymer before sulfonation which is 12 for PEEK, A_1 is the peak area of the H_{13} signal for SPEEK and A_2 is the sum of the peak areas of all the signals H_{13} for SPEEK. Finally DS should be multiplied by 100 to be expressed by percentage.

The result of the H NMR for SPEEK is presented in Figure 5. From the Figure 5 the H1, H_2, H_3 and H_4 of non-sulfonated repeat units show their characteristic singlet almost at 7.25 ppm. The sulfonation process happening at the position where the sulfonic functional group is introduced to the aromatic ring causes this type of protons to differentiate into three categories; H_{13} (the singlet at almost 7.5 ppm), H_{14} (the doublet at almost 7.22 ppm) and H_{15} (the doublets at almost 7.12 ppm). According to the equation 7 and results which are tabulated in Figure 4, the DS was found to be 68.

3.2 Water Uptake Study at Different Temperatures

In this study water uptake of all membranes was carried out from room temperature to 80°C and the results are summarized in Table 1. From the Table 1, it can be observed that firstly, the water uptake of all membranes increased when temperature increased;this is most likely because of ionic cluster formation. When the temperature is high the sulfonic groups will readily form ion domains, which are hydrophilic and are responsible for the majority of the water uptake [25].

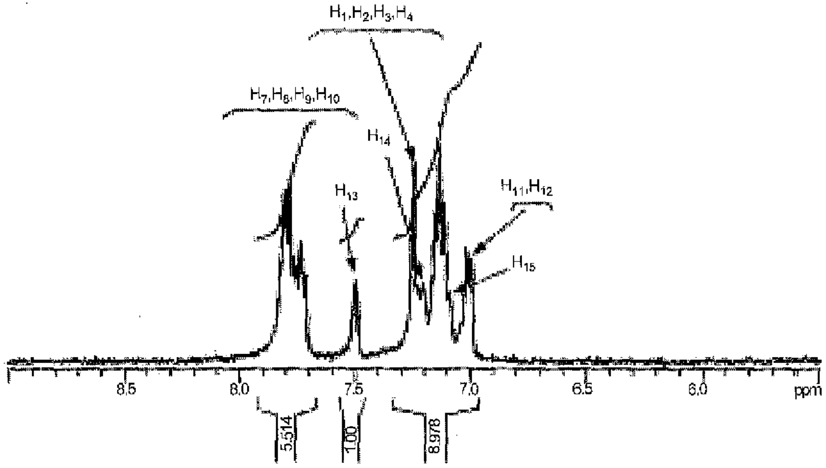

Figure 5 H NMR spectra of sulfonation at 60°C

Table 1 Water uptake of all SPEEK (68) and SPEEK (68)/cSMM membranes

Sample	**Water uptake %**					
	25°C	**40°C**	**50°C**	**60°C**	**70°C**	**80°C**
1. SPEEK (68)	31.87	34.73	38.6	45.5	79.35	137.42
2. SPEEK (68)/cSMM	32.57	37.37	41.8	50.19	101.59	dissolved
3. Nafion112	8.49	10.01	10.96	12.21	13.81	15.58

Secondly the water uptake of SPEEK (68) and SPEEK (68)/cSMM membranes were considerably more than that of Nafion112 at each individual temperature, this may be due to the microstructure of the polymers which is distributed in two domains; in SPEEK membrane the hydrophobic/hydrophilic domain difference is smaller than that of Nafion due to its backbone which is less hydrophobic when its sulfonic acid functional group is less hydrophilic as compared to Nafion [26]. This causes hydrated hydrophilic domain of the SPEEK membranes can be expanded, but in Nafion less branched of its perfluorinated polymer backbone limits the hydrophilic domain hydration [23].

The final trend according to the data is that the SPEEK (68)/cSMM blend membranes showed more water uptake as compared to SPEEK (68) and Nafion 112 at each individual temperature, the reason is due to cSMM which provides more sulfonic acid groups and makes the membrane surface more hydrophilic as compared to the SPEEK (68) and Nafion112 [21].

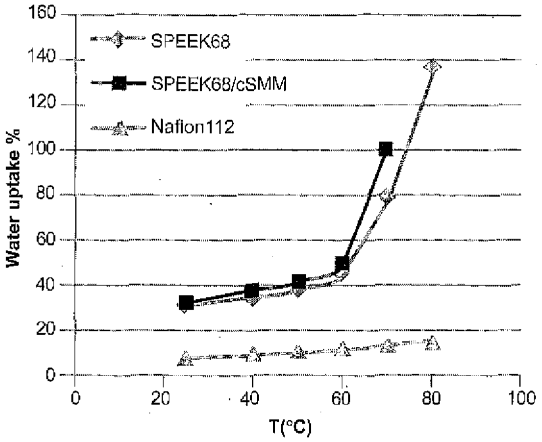

Figure 6 Water uptake of SPEEK68, SPEEK (68)/cSMM andNafion112 membranes at different temperatures

According to the data from the Table 1 water uptake of the SPEEK (68) and SPEEK (68)/cSMM membranes increased significantly at high temperatures. The highest amount of water uptake at each individual temperature was allocated to the SPEEK (68)/cSMM before 80°C (101.29% at 70°C), on contrary the lowest one was for Nafion112.

For showing the effect of temperature on water uptake of all membranes better, the water uptake of membranes were plotted versus temperature, as shown in Figure. 6.

3.3 Proton Conductivity Study at Different Temperatures

Proton conductivity of SPEEK (68), SPEEK (68)/cSMM membranes and Nafion112 was carried out at different temperatures. According to the results which are tabulated in Table 2 the proton conductivity changes with temperatures is as follows. First of all proton conductivity of all membranes increased as the temperature increased, the reason is when temperature increment occurs, consequently rate of proton migration increases, moreover in case of SPEEK (68) and SPEEK (68)/cSMM membranes the dissociation of the sulfonic acid groups increases considerably at high temperatures, however in Nafion112 case the dissociation reaches almost 100% at room temperature so the increment of proton conductivity mostly is because of proton mobility rate increment for Nafion112 [11]. Secondly the highest amount of proton conductivity at each individual temperature was for Nafion112 despite of its lower water uptake. The reason is due to the differences between Nafion112 and SPEEK membranes structure. In

Table 2 Proton conductivity of SPEEK (68) and SPEEK (68)/cSMM membranes from room to 80°C

Sample	Proton conductivity (S/cm)					
	25°C	40°C	50°C	60°C	70°C	80°C
1. SPEEK (68)	0.02307	0.02992	0.03716	0.04707	0.05695	0.06304
2. SPEEK (68)/cSMM	0.03675	0.04449	0.04762	0.05731	0.0638	-
3. Nafion112	0.07086	0.07267	0.0766	0.08098	0.09143	0.09773

SPEEK membrane the hydrophobic/hydrophilic domain difference is smaller than that of Nafion112 and because of this reason SPEEK possesses narrower channels with dead end and highly branched structure [26], subsequently lower proton conductivity compare to Nafion112.

Secondly between SPEEK and SPEEK/cSMM membranes at same DS and at each individual temperature the SPEEK/cSMM membrane showed higher proton conductivity, the reason is due to the cSMM which provides more sulfonic acid groups and makes the membrane more hydrophilic and more water uptaeke compare to the SPEEK [21] and finally according to the Table 2 which has been tabulated below the proton conductivity of SPEEK (68)/cSMMdecreased at 80°C, The reason is due to dissolution and loss of mechanical stability of the membrane at high temperatures [11]. Figure 7 depicts proton conductivity changes over the temperatures clearly.

3.4 Methanol Permeability Study at Different Operating Temperatures

In this study methanol permeability of all membranes was carried out from room temperature to 80°C and the results are summarized in Figure 7. From the Figure 8 some observation can be described about the trend of the methanol permeability with the elevated temperature. First of all methanol permeability of all membranes increased when temperature increment occurred, the reason is faster molecular movement due to heat increment and consequently increasing rate of methanol permeability. Secondly according to the Figure 7 the highest methanol permeability was for Nafion112 (1.77×10^{-6} and $5.52 \times 10^{-6} \frac{cm^2}{s}$ at room temperature and 80°C, respectively). The reason is due to the Nafion112 and SPEEK structural differences; in Nafion112 case channels are wider so it is easier

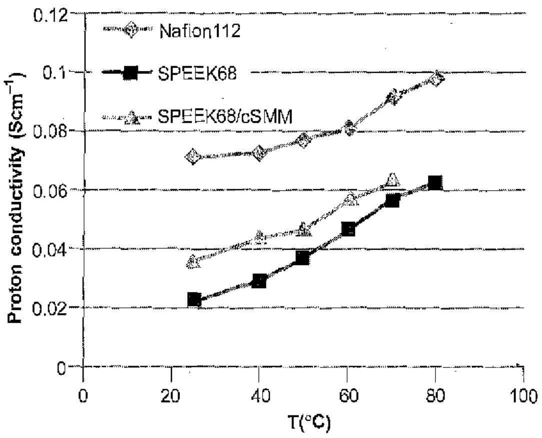

Figure 7 Proton conductivity of SPEEK (68), SPEEK (68)/cSMM, and Nafion112 at different temperatures

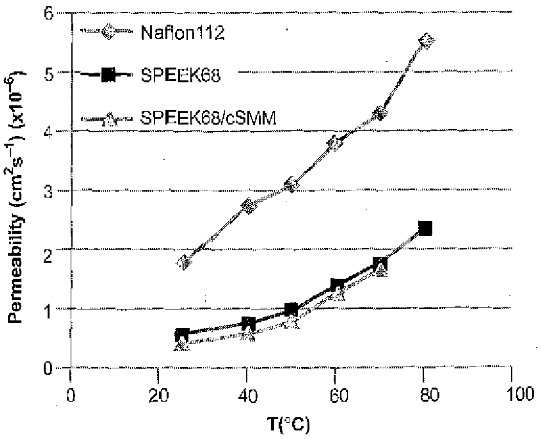

Figure 8 Methanol Permeability versus temperature for SPEEK (68) and SPEEK (68)/cSMM membranes

for methanol to pass through these channels [23]. Thirdly it can be seen from the Figure 7 that methanol permeability of SPEEK (68)/cSMM membrane was lower in comparison with SPEEK (68) membrane. The reason is methanol permeability mostly occurs via free water inside the interconnected membrane structure channels and trivially via non-freezing bound water associated with the ionic sites, since the addition of cSMM reduces the free water content, probably due to the reduction in the size of the interconnected channels, decreased in methanol permeability seems natural [21].

3.5 Overall Membranes Characteristics

The overall performance for membranes was calculated at 60°C. According to the Figure 9 which is illustrated, SPEEK (68)/cSMM membrane showed higher overall performance (4.51×10^4) at 60°C, while the lowest one was allocated to Nafion112 (2.12×10^4). Decrement in methanol permeability and at the same time increment in proton conductivity causes cell efficiency and power density to increase[4], so the blended membrane has potential to be used in DMFC instead of Nafion112 due to its higher overall performance.

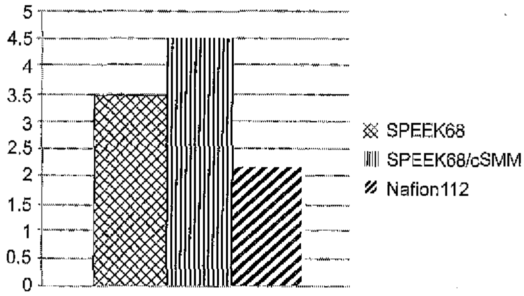

Figure 9 Overall performance of SPEEK (68), SPEEK (68)/cSMM, and Nafion112 membranes at 60°C

4.0 CONCLUSION

SPEEK (68)/cSMM membrane showed better behavior compared to other membranes over the temperature range before 80°C. Water uptake of the blended membrane showed improvement compared to SPEEK (68) and Nafion112. Furthermore proton conductivity also was higher as compared to SPEEK (68), but still lower than that of Nafion112. Moreover methanol permeability of SPEEK (68)/cSMM was lower than SPEEK (68) and Nafion112 and finally the highest overall performance at 60°C also was allocated to SPEEK (68)/cSMM. These results indicate that SPEEK (68)/cSMM membrane is promising to be used as a proton exchange membrane in direct methanol fuel cell.

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