SYNTHESIS, CHARACTERIZATION OF SEPIOLITE AND KAOLINITE ADDED, THERMALLY CROSSLINKED SULFONATED POLY (ETHER ETHER KETONE) INORGANIC-ORGANIC COMPOSITE MEMBRANES FOR PROTON EXCHANGE MEMBRANE FUEL CELL APPLICATIONS

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ABSTRACT

Proton conductive membrane is considered as the heart of proton exchange membrane fuel cells (PEMFC) and it has a significant effect on the fuel cell performance. The aim of this study is to increase the proton conductivity of the sulfonated poly ether ether ketone (SPEEK) membrane by adding sepiolite and kaolinite additives to its structure, enhance its thermal stability and improve the pem fuel cell performance. As a result of this study; ion exchange capacity of the synthesized sepiolite and kaolinite added SPEEK membranes are ranging between 0.05 and 0.18 meq/g. The highest water uptake capacity was calculated as 16% (SPEEK). The proton conductivity of the SPEEK membrane was found to increase from 0.172 S/cm to 0.568 S/cm by adding %9 (w/w) of kaolinite. A current density and cell potential values of 141 $mA.cm^{-2}$ and 0.0846 mW/cm^2 were obtained respectively at 0.6 V for SPEEK/S9 membrane, whereas 600 $mA.cm^{-2}$ and 0.348 mW/cm^2 values were obtained for Nafion 117 commercial membrane under the same conditions.

1. INTRODUCTION

Fossil fuels such as; coal, oil and natural gas have been consumed to produce energy for a long time. Since lack of these fossil resources, limited accessibility for most of the countries and especially detrimental effects on human life and ecology, studies focused on renewable energy sources. As one of the promising renewable energy sources, hydrogen can be used as a secondary energy resource for fuel cell applications and their most wide application is used for PEMFC due to their low emission and high energy density [1].

Fuel cells convert chemical energy directly to the electrical energy at different operating temperatures. Their high energy conversion, low operation pressure, rapid response to the disturbances and quick start-up capability make them promising candidates for alternative energy technology. However, their high production cost and necessity of pure hydrogen utilisation need to be developed [1].

PEM Fuel Cells use proton conductive membranes as an electrolyte which is considered as the heart of this type of fuel cells by the most of the scientists. The membrane is located between the two electrically conductive, porous electrodes and it is impermeable to gases. Electrochemical reactions occur at the surface of the catalyst in between the electrolyte and the electrode. While the hydrogen side is negative, anode side, the oxygen side of the fuel cell is positive and it is called the cathode. Protons and electrons forming as a result of splitting of hydrogen that is fed on the anode side of the membrane are transferred into the separate ways of the membrane. Protons travel through the membrane, whereas the electrons travel through the current collectors, outside of the circuit, and they come back to the cathode side of the membrane. The oxygen that is fed on the cathode side of membrane meets with the proton that conducted by the membrane. As a result, the water and the heat are produced as by product by electrochemical reaction.

In order to obtain a good performance from a fuel cell, its membrane has to be thermally, mechanically and chemically stable, has to have high proton conductivity, ion exchange capacity, water uptake and low swelling. There are different types of membranes that used for PEMFC's such as; sulfonated aromatic hydrocarbon polymer membranes, inorganic–organic composite membranes, blend polymer membranes, acid–base polymer membranes [15]. As a perfluoro sulphonic acid membrane, Nafion is one of the most used membranes for fuel cell applications. Since its low proton conductivity at high temperatures and its high-cost, studies have been focused on the development of Nafion composite materials [16]. Besides, studies to develop a new polymer as an alternative to Nafion, have been carried out. Synthesis of sulfonated aromatic hydrocarbon polymers such as sulfonated polysulfone [17], sulfonated poly (arylene ether sulfone) [18-19] and sulfonated poly(ether ketone) [20-21] can be given as an example to these studies.

In this study; poly-ether-ether-ketone polymer which involved in sulfonated aromatic hydrocarbon polymer membranes were studied due to its high proton conductivity, good mechanical properties, high-temperature stability, flexibility to modify OH^- groups in its polymer chain and low cost as compared to commercial Nafion membranes. The sepiolite and kaolinite clays have the ability to adsorb certain cations and anions without a change in their basic structure. Also, their ability to improve proton conductivity and thermal stability of SPEEK membrane make them great candidates as additives for PEM fuel cell membranes. For the purpose of improving the stability of SPEEK membrane, thermal crosslinking was applied and the thermal stability was enhanced by adding sepiolite and kaolinite clays in different ratios (w/w). Due to the fact that there are only a few studies in order to use clays or zeolites as additives, this study brings light to understand the effects of clays on SPEEK membrane and it is a good breakthrough in order to enhance the SPEEK membrane properties for the usage in PEMFC applications. Characterization methods such as FT-IR analysis, water uptake capacities, swelling, ion exchange capacity, proton conductivity, mechanical and thermal stability tests were carried out. Moreover, the fuel cell performance parameters of the synthesized membranes were determined in a fuel cell test station.

1.1. Experimental Section

1.1.1. Materials

Membrane matrix was made of PEEK (Sigma-Aldrich 99%, M_w:20800) and dimethylacetamide (Sigma-Aldrich 99%) was used as a solvent. An aqueous solution of sulphuric acid (Sigma Aldrich 99.8%) was used to sulfonate the PEEK membrane as active group source. The sepiolite ($H_8Mg_2O_{10}Si_3$, %13 MgO, M_w: 300.919 g/mol) and the kaolinite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$,$M_w$:294.19)is purchased from Sigma-Aldrich.

1.1.2. Sulfonation of PEEK Polymer

The polymer was dissolved in preheated H_2SO_4 (1/20 w/v) solution by continuous mixing for 5 hours at 65 °C using Multimatic-5N magnetic stirrer. After 5 hours, dark-viscous solution's reaction was stopped by using an ice-cold water bath. The precipitate that occurred was washed and filtered until the excess acid is removed. Finally, washed polymer dried at 50 °C, for 4 h.

1.1.3. Sepiolite and Kaolinite Containing SPEEK Membrane Preparation

The dried SPEEK containing sepiolite or kaolinite in different ratios were poured into preheated DMAC solution and this solution was mixed for 3 h at 50°C. Then the obtained viscous solution was poured into petri dishes by drop casting method and then dried under vacuum for 3 days.

1.1.4. Thermal Crosslinking of Membrane

Kaolinite and sepiolite added membranes sandwiched between glass plates and left in the incubator for 3 hours at 120 °C.

1.2. Characterization Methods

1.2.1. Proton Conductivity

For the measurement, 4 probes technique at 10Mv Ac stimulating current and in 100 Hz - 106 Hz frequency range was used. The measurements were conducted with 100% humidity at different temperatures ranging between 25 °C and 80 °C with equipped a heating system and a temperature controller. The conductivity was calculated by using equation (1);

$$\sigma = L/RA \quad (1)$$

1.2.2. Ion Exchange Capacity

Ion exchange capacity (IEC) of membranes was determined by using classic titration method. Membranes were held in 2 M of NaCl solution for 48h at room temperature. This H^+ ion containing solution is titrated with 0.01 M NaOH by using Shott-TA500 plus model computer titrator having a sensitivity of 0.01 mL. The ion exchange capacity equation was calculated from equation 2:

IEC = (Consumed ml NaOH x molarity NaOH)/(weight of dried membrane) (2)

1.2.3. Water Uptake and Swelling Ratio

Prepared dry membranes were weighted and their thickness value was measured at different points. The measured membranes were immersed in deionized water for 24 h at room temperature. After 24 h, membranes were weighted and measured again. In order to measure the thickness of the membrane Sheen Thickness Measurement Device was used.

Calculations of water uptake and swelling ratio were shown below from equation (3) and (4):

W.U. (%) = (Wwet-Wdry)/Wdry x100 (3)

S. R. (%) = (Twet-Tdry)/Tdry x100 (4)

1.2.4. FT-IR Analysis

Jasco FT-IR instrument was used and absorbance vs wave length data was obtained in the range of 4000-400 cm^{-1} wave length.

1.2.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of membranes was carried out by using Setaram TGA + DSC analyser. TGA measurements were carried out at a heating rate of 10 °C/min and 120-800 °C temperature range.

1.2.6. Membrane Electrode Assembly (MEA) and Performance Tests

Protonation was carried out by immersing the synthesized membranes in to continuously stirred 0.5 M H_2SO_4 solution at 60 °C for 1 hour and then soaking in distilled water at 60 °C for 1 h. The catalyst solution was prepared with a mixture of VULCAN XC-72, 5% Nafion and isopropanol/distile water solution in 7/1 ratio. The prepared mixture was homogenized in an ultrasonic homogenizer for 2 h. The catalyst ink was loaded onto the anode and the cathode side of the gas diffusion layer (GDL) until the desired catalyst loading (0.4 mg Pt/cm^2) was achieved. GDLs were dried in an oven at 50 °C for 1h after the catalyst loading process. The prepared GDLs were hot pressed to the membrane at 90 °C for 3 min. The fuel cell performance experiments were carried out in a stoichiometric H_2-dry air atmosphere at 80 °C in Fideris single cell test station.

1.2.7. Mechanical Properties

The mechanical strength of membranes was measured by using Shimadzu AG-11KN model mechanical resistivity test equipment at 2 $mm.min^{-1}$ drawing rate.

2. RESULTS

2.1.1. Structural Properties of Synthesised Membranes

FT-IR spectrums of sepiolite and kaolinite added membranes are given in Figure 1 and Figure 2.

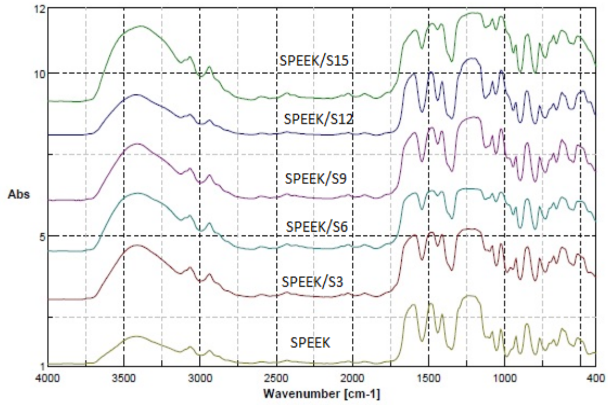

Fig. 1. FT-IR Spectrums of sepiolite added SPEEK membranes

The characteristic sulfonation peaks are at a wave length of 1025 and 1079 cm^{-1}. The peak at 1079 cm^{-1} can be assigned to the O=S=O linkage in sulfonic acid and the peak at 1025 cm^{-1} corresponds asymmetric/symmetric of S=O in the sulfonation group. The peaks at 1488 cm^{-1} can be assigned to C-C bonding vibration. C=C and C=O stretching vibration peaks are at 1596.77 cm^{-1}. A broadband around 3417 cm^{-1} shows the O-H vibration and interaction with water molecules.

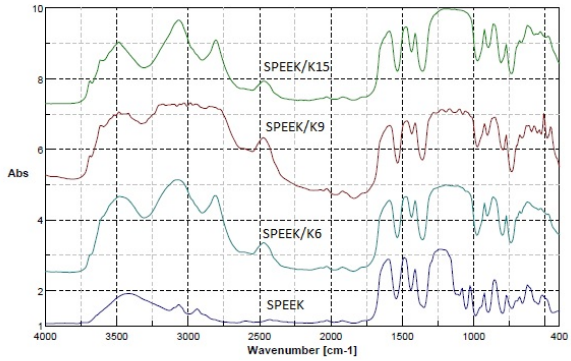

Fig 2. FT-IR spectrums of kaolinite added SPEEK membranes

Si-OH peak can be seen at 925 cm^{-1} wavenumber. The characteristic peaks shown for SPEEK and silica can be found in the literature [2-3]. The small bands at 3695 cm^{-1} and 3620 cm^{-1} are inner hydroxyls of kaolinite in the matrix respectively [22].

2.1.2. IEC, Water Uptake and Swelling Ratio

Ion exchange capacity of the membrane is a measure of its ionic conductivity. While ion exchange capacity increases, density of ionisable hydrophilic groups in the membrane can attach more to structure and it causes the increasing ionic conductivity. The uncrosslinked sulfonated membranes that show high swelling block the mobility of the protons and negatively affect the proton conductivity. Since protons are facilitated by water in the membrane structure, high water uptake can increase the proton conductivity.

Table 1. IEC, water uptake capacity and swelling ratio of membranes

Polymer	IEC (meq/g)		Water Uptake (%)	Swelling Ratio (%)	
	25^{ob}	25^{oc}	25°C^{c}	25^{ob}	25^{oc}
SPEEK	0,11	0,12	16,03	7,04	8,47
SPEEK/S9	0,09	0,06	8,89	18,32	3,93
SPEEK/K9	0,02	0,02	3,98	2,25	2,54
NAFION	0,09	0,09	38	0	0

Consequently, swelling and water uptake properties are important measurements for the proton conductivity and PEMFC performance [4].

Before thermal treatment, ion exchange capacities of sepiolite added SPEEK membranes (from 3% to 15% w/w) were determined as between 0.05 and 0.18 meq/g and kaolinite added SPEEK membrane’s (from 6% to 15% w/w) ion exchange capacities were determined as between 0.02 and 0.04 meq/g. After thermal treatment, ion exchange capacities of sepiolite added SPEEK membranes have decreased. This decrease can be explained by the temperature effect on the SPEEK membrane. Compounds that inside of the SPEEK polymer tend to link more with each other at high temperatures and consequently molecular space in polymer decreases and hence ion exchange starts to decrease. Di Vona et. al., studied the temperature and thermal treatment effects on SPEEK proton conducting membranes and the authors found that increasing thermal cross-linking hour leads to decrease in ion exchange capacity of SPEEK membranes with the same degree of sulfonation [5]. After thermal crosslinking, ion exchange capacity of the sepiolite added SPEEK membranes was relatively proportional to swelling ratio which is expected since these two parameters effect with each other due to water relation. The molecular passage that needed for ion’s exchange has decreased after thermal crosslinking, due to the fact that the crosslinking causes the membrane's structure become more rigid and strict. Synthesized sepiolite added and unloaded SPEEK membranes have higher ion exchange capacity than commercial Nafion membrane. On the other hand, kaolinite added SPEEK/K9 have lower ion exchange capacity than commercial Nafion membrane. The SPEEK membrane that has a high water uptake is more likely to swell more due to the water that transferred into the membrane’s structure. However, swelling is not desired for membranes because of the fact that the more membrane swells the path taken by proton becomes longer and consequently diffusional resistance increases. Therefore, swelling ratio of the kaolinite added SPEEK membrane is directly proportional to ion exchange capacity and the water uptake which is expected due to the kaolinite chemical structure's characteristic swelling property. The swelling ratio of the sepiolite added SPEEK membranes decreased dramatically after thermal treatment which means thermal crosslinking was applied successfully. The reason for increasing swelling ratio of the SPEEK/S9 membrane can be explained by the hydrophilic character of sepiolite. Beaugel et. al., prepared Nafion-sepiolite composite membrane with sulfo-fluorinated sepiolite and their swelling ratios are ranging between 5% and 7% which have similar results with compared to our thermally treated sepiolite added SPEEK membranes. Although, authors found the increasing swelling ratio with increasing sepiolite additive [6]. Swelling ratios for kaolinite added SPEEK membranes are ranging between 2.25% and 7.5% which thermal treatment didn't affect much their swelling ratios. The water uptake capacity and the ion exchange capacity of the synthesized membranes and commercial Nafion membrane have given in Fig.3. and Fig.4.

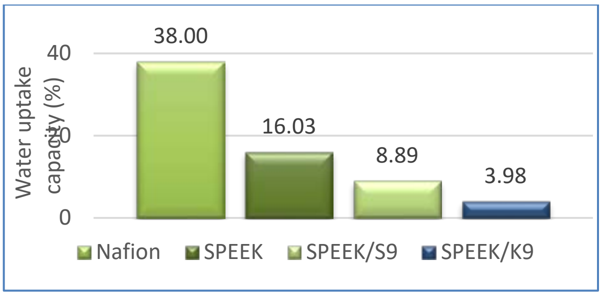

Figure 3. The water uptake capacity of th membranes

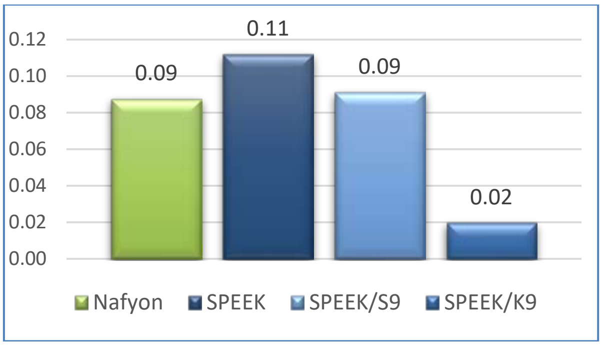

Figure 4. The ion-exchange capacity of synthesized membranes

SPEEK/S9 membrane had shown higher ion exchange capacity than SPEEK/K9 membrane since its water uptake capacity is higher than SPEEK/K9 membrane.

2.1.3. Proton Conductivity

The proton conductivity results of the synthesized membranes are given in Table 2. The proton conductivity of the sepiolite and kaolinite added SPEEK membranes increases with increasing temperature which implies that proton conductivity of SPEEK polymer at high temperatures can be enhanced by adding sepiolite and kaolinite. Wang et. al., synthesised SPEEK membrane by introducing n-BuOH and they found proton conductivity of 0.314 S cm-1 at 80 °C [7]. The highest proton conductivity obtained in this study belongs to SPEEK/K9 membrane as 0.213 $S.cm^{-1}$ at 25 °C and 1.156 S cm^{-1} at 60 °C. The later one is the highest value reported in the literature up to now by using SPEEK membrane at intermediate temperatures in PEM fuel cell systems.

Table 2. Proton conductivity results of synthesized membranes

Polymer	**Proton Conductivity $S.cm^{-1}$**			
	25 °C	40 °C	60°C	80°C
SPEEK	0,063	0,114	0,204	0,172
SPEEK/S3	0,058	0,061	0,107	0,167
SPEEK/S6	0,075	0,084	0,147	0,156
SPEEK/S9	0,091	0,109	0,262	0,329
SPEEK/S12	0,086	0,071	0,100	0,199
SPEEK/S15	0,085	0,087	0,123	0,097

SPEEK/K6	0,073	0,164	1,079	0,531
SPEEK/K9	0,213	0,831	1,156	0,568
SPEEK/K15	0,216	0,529	0,256	0,212
NAFION 117	0,03	0,031	0,031	0,019

For sepiolite added SPEEK membranes, the highest proton conductivity value was obtained for 9 % sepiolite loaded SPEEK membrane as 0.33 $S.cm^{-1}$ at 80°C. On the other hand, a further increase in sepiolite content, the proton conductivity of the SPEEK membrane starts to decrease and it reaches the lowest value of 0.097 $S.cm^{-1}$ for SPEEK/S15 membrane. Also, SPEEK/S15 membrane has one of the lowest values of ion exchange capacity (0.03 meq/g) and water uptake (2.6%) amongst the SPEEK membranes. Therefore the obtained results support each other. The kaolinite addition significantly improved the ionic conductivity of the SPEEK membrane and increased the proton conductivity up to 9% (w/w). Further increase in kaolinite amount in the membrane causes to limit the conductivity of the SPEEK membrane because of its hydrophilic character leads to increase in the swelling of the membrane and consequently increases the resistivity to the diffusion of protons. The proton conductivity of SPEEK/K9 membrane started to increase dramatically after room temperature ($\sigma_{speek/K9}$ = 0.831 $S.cm^{-1}$ at 40 °C). The proton conductivity of the same membrane started to decrease after 60 °C from 1.156 $S.cm^{-1}$ to 0.568 $S.cm^{-1}$ at 80 °C. Despite their decreasing proton conductivity at high temperatures still, its conductivity is above the average values of reported results in the literature and it is a good development to improve the proton conductivity of SPEEK membrane at 80 °C. The proton conductivity values of the commercial Nafion 117 membrane is too low in every temperature up to 80 °C when compared to synthesized membranes in this study. These results show that the synthesized sepiolite and kaolinite added and unloaded SPEEK membranes have better proton conductivity than the Nafion 117 commercial membrane.

2.1.4. Thermal and Mechanical Properties of Membranes

Thermal gravimetric analysis (TGA) spectrums of SPEEK, SPEEK/K6, SPEEK/K9 and SPEEK/S12 membranes were analysed to understand the effects of the different additive's on thermal behaviour of the SPEEK membrane and obtained results are given in Figure 5. For SPEEK/K6 membrane, 5% weight loss occurred at 243 ºC and 5% weight loss occurred at around 206 ºC for SPEEK, SPEEK/K9 SPEEK/S12 membranes. According to thermal gravimetric analysis, kaolinite and sepiolite added SPEEK membranes are more thermally stable than SPEEK membrane which means sepiolite and kaolinite addition have successfully increased the thermal stability of SPEEK membrane. In fact, the amount of sepiolite or kaolinite additive in the membrane increases, membranes become thermally more stable. The first weight loss is related to the loss of absorbed water. The second degradation step belongs to decomposition of the sulfonic acid group in the membrane [8]. This result also confirms the results obtained by Banerjee and Kar (2015). Authors also increased the thermal stability, water retention and ionic conductivity of the SPEEK membrane by adding polypyrrole/aluminium phosphate to SPEEK nano composite membrane in their study [9]. Authors observed that thermal degradation of SPEEK membrane occurs by two steps weight loss process. They explained the TGA curves as; first weight loss occurred at around 310 ºC due to the loss of sulfonic acid side groups and second weight loss occurred at 480 ºC due to the main chain degradation. In this literature, after the main chain degradation for sepiolite and kaolinite added SPEEK membrane, there is still almost 50-60 % of the membrane left at around 800 ºC which can be explained by the existing kaolinite and sepiolite additives in the membrane. Peighambardoust et. al., studied the self-humidifying nanocomposite SPEEK proton exchange membranes and they observed that SPEEK polymer's thermal stability is higher than Nafion 117 membrane [10].

The mechanical properties of synthesized membranes are given in Table 3. Tensile strength values of the synthesized membranes are ranging between 32.8 and 40.3 MPa and elongation at break values are ranging between 26.8 and 42.8 %. The highest tensile strength value belongs to SPEEK membrane. According to the results, when sepiolite or kaolinite additive in the membrane increases the mechanic stability of the SPEEK membrane decreases due to the clay molecules settle into the SPEEK membrane's molecular chain structure and it leads to weakening of the molecular bond. Still, even for sepiolite or kaolinite added SPEEK membranes elongation at break values are above the average [11-12].

Table 3. Tensile strengths and elongation break of the composite membranes

Membrane	Tensile strength (MPa)	Elongation at break (%)
SPEEK	40.3	42.8
SPEEK/S9	37.5	36.0
SPEEK/K6	34.2	29.6
SPEEK/K9	33.6	24.6
SPEEK/K15	32.8	26.8

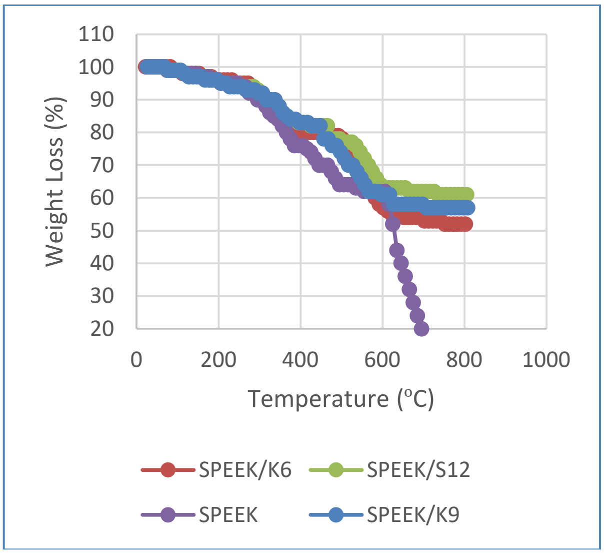

Figure 5. Thermal stabilities of SPEEK/K6, SPEEK/K9, SPEEK/S12 and SPEEK coded membranes.

2.1.5. Fuel cell Performance Tests

Fuel cell performance tests were conducted with a flow rate of 0.4 L/min H_2 and dry air and values were measured at 100% relative humidity. The temperature of the fuel cell was set to 80 °C which is the same temperature of the humidification system.

SPEEK/K6 and SPEEK/S9 labelled membranes were chosen according to their high proton conductivity at 80 °C for fuel cell performance tests and these results were compared to fuel cell performance test of Nafion commercial membrane. In order to prepare the MEA, the same method was used for commercial Nafion membrane. Cell potential and power density data are given as a function of current density in Fig. 6. In these experiments, the current density of the SPEEK/S9 membrane starts to increase with decreasing potential value. A current density and cell potential values of 141 mA.cm^{-2} and 0.0846 mW/cm^2 were obtained respectively at 0.6 V for SPEEK/S9 membrane, where as 600 mA.cm^{-2} and 0.348 mW/cm^2 values were obtained for Nafion membrane under the same conditions. According to the results, the current density of the commercial Nafion is higher than SPEEK/S9 membrane's current density under the same conditions which means there are deviations on the potential-current density curve of the SPEEK/S9 membrane that indicating over potentials. The ohmic resistance of the fuel cell might be the first reason for over potential occurrence. Electrodes and bipolar plates have a resistivity of electrons that flow from anode to cathode and flow of ions through the electrolyte and this resistivity increases the ohmic loss of the fuel cell. The concentration overpotantial within the SPEEK/S9 membrane is another reason for poor fuel cell performance of it compared with Nafion commercial membrane. There are a few reasons for concentration polarization occurrence:

a) Slow diffusion of reactants and products,
b) High voltage or low current density,
c) Dissolution of products out of the system,
d) Poor ionic conductivity.

The concentration of hydrogen and oxygen that fed to the anode and cathode side starts to fall during the fuel cell performance and this decreasing concentration causes a decrease in partial pressure. Thus, reduction of gas pressure decreases the cell voltage and therefore concentration losses occur. Consequently, concentration polarizations occurred for commercial Nafion membrane and synthesized membranes due to the instant voltage drop that was shown in Figure 5. On the other hand, the proton conductivity mechanism is also related to the thickness of the membrane. As the thickness of the membrane increases the path that protons need to transfer becomes longer and hence resistance to proton diffusion increases that leads to poor fuel cell performance. Differences between the thickness and conditioning time of the membranes must also be considered as a reason of fuel cell performance differences [13].

A current density and cell potential value of SPEEK/K6 membrane are obtained as 60 $mA.cm^{-2}$ and 0.036 mW/cm^2 respectively, at 0.6 V which means the ohmic resistance of the SPEEK/K6 membrane is higher than SPEEK/S9 membrane. This difference may be explained by the differences between the ionic conductivities of the synthesized membranes. Fuel cell performance of the SPEEK/S9 membrane is better than SPEEK/K6 membrane since the ion exchange capacity of the SPEEK/K6 membrane is lower than SPEEK/S9.

In performance experiments, activation polarizations observed for all tested membranes including Nafion membrane. This over potential formation is due to the electrochemical reaction activation loss on the catalytic surface. The most of the reason that activation polarization occurrence is related to the catalyst effectiveness in the MEA [14]. Despite the fact that the platinum catalyst is commercial, activation loss issue in fuel cell performances is considerably common. Peighambardoust et al., synthesized the self-humidifying nanocomposite SPEEK membrane with supported Pt catalyst and they compared the fuel cell performance results with Nafion commercial membrane. They found that the SPEEK membrane, with 65.12% of degree of sulfonation with dry and fully humidified reactants, exhibited a poor performance when compared to Nafion-117 membrane. The current density of the SPEEK membrane is lower than 100 $mA.cm^{-2}$ where the values of Nafion membrane obtained as between 100 and 140 $mA.cm^{-2}$ at 0.6 V. Although, they managed to achieve higher performance than Nafion-117 membrane with a composite of SPEEK membrane [10].

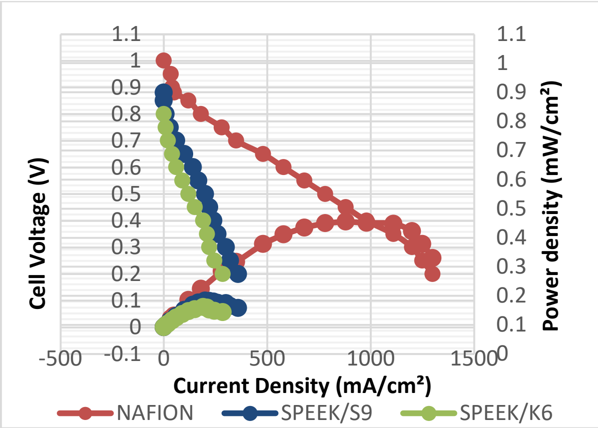

Figure 6. Fuel cell performance plot of SPEEK/S9, SPEEK/K6 and NAFION membrane

3. CONCLUSIONS

Sepiolite and kaolinite added sulfonated PEEK proton conducting membrane for intermediate temperature PEM fuel cells was successfully synthesized and characterization tests namely water uptake, swelling, ion exchange capacity, proton conductivity, thermal and mechanical properties determination were carried out.

Sepiolite, kaolinite structures and functional groups in the SPEEK membranes were confirmed by using FT-IR analysis.

The proton conductivity of the SPEEK membrane was improved by adding sepiolite and kaolinite clays and the highest proton conductivity values are found as 1.156 $S.cm^{-1}$ for SPEEK/K9 membrane at 60 °C and 0.329 $S.\ cm^{-1}$ for SPEEK/S9 membrane at 80 °C.

It was observed that further 9% (w/w) of sepiolite or kaolinite addition leads to decreasing proton conductivity of the SPEEK membrane.

Kaolinite and sepiolite added SPEEK membranes showed lower IEC and water uptake than SPEEK membrane after thermal crosslinking. After thermal treatment, all of the SPEEK membranes showed lower swelling ratio which showed the significance of thermal crosslinking.

The swelling ratio of the sepiolite added SPEEK membranes decreased with increasing sepiolite addition.

Thermal gravimetric analysis showed that sepiolite and kaolinite addition successfully increased the thermal stability of SPEEK membrane.

Results of characterization of the sepiolite added SPEEK membranes showed that SPEEK/S3, SPEEK/S6 and SPEEK/S12 membranes demonstrated a major impact in order to have higher ion exchange capacity and lower swelling ratio.

On the other hand, SPEEK/K9 membrane and SPEEK/S9 membrane demonstrated a big breakthrough that implies high proton conductivity. SPEEK/K9 has the highest proton conductivity among the values reported in the literature until now.

Fuel cell performance test of SPEEK/S9 and SPEEK/K6 membranes was conducted and these results were compared to the commercial Nafion-117 membrane. For SPEEK/S9 membrane, a current density and cell potential values of 141 $mA.cm^{-2}$ and 0.0846 mW/cm^2 obtained at 0.6 V, where those of Nafion membrane are obtained as 600 $mA.cm^{-2}$ and 0.348 mW/cm^2 under the same conditions. It was concluded that fuel cell performance of the SPEEK membrane, with different additives of sepiolite and kaolinite, still needs to be improved in another research.

As a result, all these tests showed that the sepiolite and kaolinite added SPEEK membranes are promising candidates as an alternative to the Nafion and widely used commercial membranes.

Acknowledgements

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Nomenclature

σ, proton conductivity of the membrane
L, distance between the electrodes
R, resistance of the membranes
A, membrane area
n_{SO3-}, number of moles of SO3-
m_{dry}, mass of dry polymer
W_{dry}, weight of dry membranes
T_{dry}, thickness of dry membranes
W_{wet}, weight of wet membranes
T_{wet}, thickness of wet membranes

Abbreviations

PEEK, Poly ether ether ketone
SPEEK, Sulfonated poly ether ether ketone
PEMFC, Proton exchange membrane fuel cell
EIS, Electrochemical Impedance Spectroscopy
PBI, Polybenzimidazole
DMAC, Dimethylacetamide
IEC, Ion exchange capacity
TGA, Thermal gravimetric analysis
W.U., Water uptake
W.S., Water swelling
SPEEK/S3, 3% (w/w) sepiolite added SPEEK membrane
SPEEK/S6, 6% (w/w) sepiolite added SPEEK membrane
SPEEK/S9, 9% (w/w) sepiolite added SPEEK membrane
SPEEK/S12, 12% (w/w) sepiolite added SPEEK membrane
SPEEK/S15, 15% (w/w) sepiolite added SPEEK membrane
SPEEK/K6, 6% (w/w) kaolinite added SPEEK membrane
SPEEK/K9, 9% (w/w) kaolinite added SPEEK membrane
SPEEK/K15, 15% (w/w) kaolinite added SPEEK membrane

Footnotes of Table 1

b, Before thermal crosslinking

c, After thermal crosslinking

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