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FABRICATION AND EFFECT OF SULFONATED POLY (ETHER ETHER KETONE) WITH CLOISITE15A® NANOCLAYS FOR MICROBIAL FUEL CELL APPLICATION

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Abstract

Ion exchange membranes have been used in microbial fuel cell (MFC) because it can prevent high oxygen permeability and the migration of substrate instead of protons from one chamber to another. Despite all these advantages the usage of this type of membrane suffers several operational problems such as high dissolve oxygen permeability, adverse deformation and proton conductivity which can affect the MFC performance. In order to overcome this problem, new membrane for microbial fuel cell system was fabricated using sulfonated polyether ether ketone (SPEEK) and Cloisite 15A®. The membranes were characterized based on their electrochemical and physical properties. The characteristics of the SPEEK nanocomposite membranes were then compared with the unmodified SPEEK membrane and the commercially available Nafion117 membrane. Based on the result, SPEEK/Cloisite 15A® contributed high energy generated across the load compare to SPEEK without additive and Nafion 117. The incorporation of Cloisite 15A® improved the water uptake from 56 to 78.2 wt% and reduced the dissolve oxygen permeability of the membrane from 1.5 to 0.7 cm/s but the tensile strength behaviour was reduced from 11.2 to 7.5 MPa.

Keywords: *Cloisite 15A®, sulfonated poly (ether ether ketone) (SPEEK), ion exchange membrane, microbial fuel cell (MFC)*

1.0 Introduction

MFC is a system that utilises microorganism activity to generate power. Numerous studies have been conducted in order to optimise the MFC performance based on possible factors that contribute such as type of microorganism, electrode, electron acceptor, design and membrane [1-4]. In this system, membrane plays a role as a separator between anode and cathode chamber and also as an ion exchange medium.

Previous studies with different types of membranes have been conducted in order to figure out the most outstanding power generation in MFC system such as anion exchange membrane (AEM), cation exchange membrane (CEM), bipolar membrane (BPM) and charge mosaic membrane (CMM) [5-14]. Most of the studies focused on the performance in term of dissolves oxygen permeability and migration of protons because, ideally, the proton conductive membrane must be able to inhibit the oxygen to migrate and allow high proton conductivity [15].

The coulombic efficiencies (CEs) of MFC can be affected when oxygen replaces the cathode as a terminal electron acceptor. Besides, the exposure of microbe to oxygen as a terminal electron acceptor may lead to an adjustment of the enzymatic machinery of the microbial cells. The consequence of this adjustment can increase the redox potential within a single biological catalytic entity hence reduces the power generation. Previous application of MFC normally used the Nafion membrane as a separator. However, there are some drawbacks associates with Nafion such as high cost of material and high dissolve oxygen permeability.

In response to above mentioned problem, this studied was carried out using SPEEK as a membrane based that possesses not only good electrochemical performance but inexpensive material and lower oxygen permeability. SPEEK is a hydrophilic polymer produced from the sulfonation reaction. SPEEK exhibited many essential properties as an ideal proton exchange membrane in fuel cell application such as good thermal stability, chemical inertness, good mechanical properties, low cost and adequate conductivity depending on the degree of sulfonation (DS) [16-17].

Different kinds of modification in SPEEK polymer matrix had been made in order to improve the proton conductivity performance. Numerous modification of SPEEK polymer can be generally achieved by addition of organic-inorganic component and by cross linking different polymers [18]. Cloisite is one of the materials that have been used to modify perflourinated inomer membrane (PFI) like Nafion and non-flourinated membrane such as SPEEK and have been proved to give a significant effect on the properties of membrane such as mechanical strength, water uptake and proton conductivity [19-20]. Apart from that, the compatibilizer which is 2,4,6-triaminopyrimidine (TAP) was added to enhance the interaction and dispersion of cloisite with SPEEK polymer [22]. Therefore, the main purpose of this study is to prepare SPEEK membrane incorporated with Cloisite 15A® and TAP for MFC application.

2.0 Methodology

For membrane preparation, fine powder PEEK polymer was obtained from Victrex US Inc. Ltd. Sulfuric acid H_2SO_4 (95-97%) and N,N-dimethylacetamide (DMAc) were supplied by Merck KGaA. Cloisite 15A® and 2,4,6-triaminopyrimidine (TAP) were purchased from Southern Clay Products, Inc. and Sigma-Aldrich Inc. respectively. Reference membrane (Nafion 117) was purchased from DuPont. For MFC setup, *Saccharomyces cerevisiae* was obtained from AB Mauri Malaysia Sdn. Bhd. Methylene blue and potassium permanganate were obtained from Sigma–Aldrich Inc. in powder form. Both Sodiumhydrogenphosphate and D-glucose were were supplied by Merck KGaA.

2.1 Preparation and Characterization of SPEEK

Sulfonation process was started by mixing the concentrated sulphuric acid (95-97%) with polyether ether ketone (PEEK) polymer powder in a round bottom flask. The solution was stirred 1 hour to get the homogenous solution. The mixture was then heated up to 60 °C for 3 hours. During this process, the colour of solution changed from light brown to dark brown indicated the progress of sulfonation reaction. The changes of functional group were characterized by using the nuclear magnetic resonance (^{1}H NMR).

The degree of sulfonation (DS) of SPEEK was confirmed by using ^{1}H NMR spectroscopy method (Bruker Avance 300 NMR). The resonance frequency of this instrument was adjusted at 400 MHz at room temperature. Prior to analysis, the dried purified SPEEK sample was prepared 3 wt% and dissolved in deutrated dimethyl sulfoxide (DMSO-*d6*).

2.2 Membrane Preparation

Nanocomposite was prepared by mixing 0.25 g of Cloisite15A® clays and 0.5 g of 2,4,6-triaminopyrimidine (TAP) with 15 mL N,N-dimethylacetamide (DMAc) in different bottle respectively and vigorously stirred for 24h at room temperature. To prepare polymer solution, 10 wt% of SPEEK was dissolve in 60 mL DMAc and stirred for 12h. Then, the prepared Cloisite and TAP solution were added to this solution and once again vigorously stirred for 24 h.

A pneumatic casting machine was used to cast the polymer solution onto a glass plate. The membrane was kept in an oven at 60 °C for 6 hr and further dried for the next 12 hr at 100°C to evaporate the residual solvent. The membrane was removed from the oven and allowed to cool to room temperature before it was immersed in deionized water overnight so it would peel off from glass surface and remove residual solvent. For pre treatment, the prepared membrane was immersed into 1M sulfuric acid H_2SO_4 solution overnight at room temperature. Finally, the membrane was rinsed several time with deionized water to remove the excess acid then blotted with absorbent paper.

2.3 Membrane Characterization

2.3.1 Water Uptake

This analysis was carried out to measure the ability of membrane to absorb water. This measurement was conducted by following the procedure of Ismail [17]. First, the membrane sample was dried at 60°C for 48h and the weight was measured (W_d). The membrane was then kept in distilled water at room temperature overnight and the weight once again being measured (W_w). The calculation of water uptake was carried out using equation 1.

$$\text{Water uptake \%} = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

where W_w is weight of membrane in wet condition while W_d is weight of membrane in dried condition.

2.3.2 Dissolve Oxygen Permeability

All figures must carry numbers in the text (e.g. Fig. 1) and captions.

The dissolved oxygen (Do) measurement was done using un-inoculated MFC system constructed for the membrane test. The method of this analysis was followed the procedure of Kim [29]. First and foremost, the desired membrane was fitted between two chambers of un-inoculated MFC. Both of the chambers were then filled with distilled water and then dissolved oxygen probe was inserted inside cathode chamber. The condition in anode chamber was kept free from dissolve oxygen by purged the nitrogen gas until the reading of Do concentration is zero. Finally, the Do concentration of cathode chamber over time (C_2) was taken. The mass transfer coefficient was calculated from the equation 2.

$$K_O = -\frac{V}{At} \ln\left[\frac{C_{1,0} - C_2}{C_{1,0}}\right] \quad (2)$$

where V is volume of water, A is the surface area of membrane fitted between two chambers, $C_{1.0}$ is the Do in water at anode chamber and C_2 is the measured Do in the cathode chamber at time t. The rate of oxygen diffusion (Do $cm^2\ s^{-1}$) for each prepared membrane and Nafion 117 was calculated using equation 3.

$$D_o = K_o L_t \quad (3)$$

2.3.3 Mechanical Strength

The tensile strength of each membrane was measured using mechanical testing instrument, MTS (LRX 5kN, Llyod instruments). Prior to test, 5 samples from each types of membrane were cut into dumbbell shape with gauge length and the width were 15 mm and 4 mm respectively. The membranes thicknesses were also being measured before the test. Then, the membrane was fitted between the grips of the instrument and run at rate of speed 5 mm min^{-1}.

2.4 Membrane Morphology Structure

The morphology of the prepared membrane was investigated using a field emission scanning electron microscope (FESEM). The FESEM (JSM-6701F) is a useful technique to determine the membrane structures. The samples were prepared by immersed it under the liquid nitrogen to freeze and dry the membrane so that the clean break can be done. The samples are taken out and mounted on sample stubs using double surface scotch tape. Then, cross-sectional fractures of the membranes were vacuum sputtered with a thin layer of gold. Various images of cross-sectional of the membranes were taken and analyzed.

2.5 Electrochemical Measurement

The MFC was of semi-circle construction cylinder divided into anode and cathode chamber. The anode solution consisted of methylene blue, D-glucose, yeast and phosphate buffer solution (PBS). Meanwhile, the cathode solution consisted of potassium permanganate and phosphate buffer solution (PBS). The PBS for each compartment was made by dissolving inorganic salts (NaH_2PO_4 - 8.16 g/L; $Na_2H_2PO_4$ – 6.58 g/L) in distilled water. The pH of PBS was adjusted to 7 by adding 1M of sodium hydroxide (NaOH). For the anode solution, 50 mM of methylene blue and 1 % (wt/v) of glucose-D were added into the buffer solution. On the other hand, the cathode buffer solution was added with 50 mM potassium permanganate ($KMnO_4$) solution. The inoculum was prepared by dissolving 2g *Saccharomyces cerevisiae* (baker yeast) into 100 mL of phosphate buffer solution.

For the measurement, MFC was first run under open circuit voltage (OCV) until the voltage was stabilized at room temperature. Then, the polarization curves were obtained by applying a various external resistance (2 MΩ - 1 kΩ) loaded across the MFC with each resistance being connected until the maximum sustainable voltage was achieved. The voltages were recorded using a digital multimeter (Fluke 259). Current was calculated from I=E/R, where I represent the current, E is the measured voltage across the resistor and R the external resistance while power was calculated using P=IE. Both current and power density was normalized by the projected cathode surface area.

3.0 Results and Discussions

3.1 Nuclear Magnetic Resonance

In ^1H NMR spectrum, the intensity of H_G confirmed the presence of sulfonic acid group (SO_3H) in SPEEK polymer. The nomenclature of the characteristic proton in the aromatic ring in the SPEEK repeat unit is illustrated in Fig. 1. Based on this spectrum, the presence of sulfonic acid group causes 0.25 ppm down-field chemical shift of the hydrogen H_G compared with H_E and H_F in the ring and created a distinct resonance signal for protons at the G position [17]. Peak at 7.25 ppm in this spectrum represents the H_E protons in the PEEK repeat unit. Normally, when the sulfonation reaction occurred, the introduction of sulfonic functional group to the aromatic ring will cause the proton (H^+) differentiate into 3 resonance signals which are H_G (peak at ~ 7.5 ppm),

H_E (peak at ~ 7.22 ppm) and the H_F (peak at ~ 7.12 ppm). The DS at reaction temperature 60 °C was found to be 76 %.

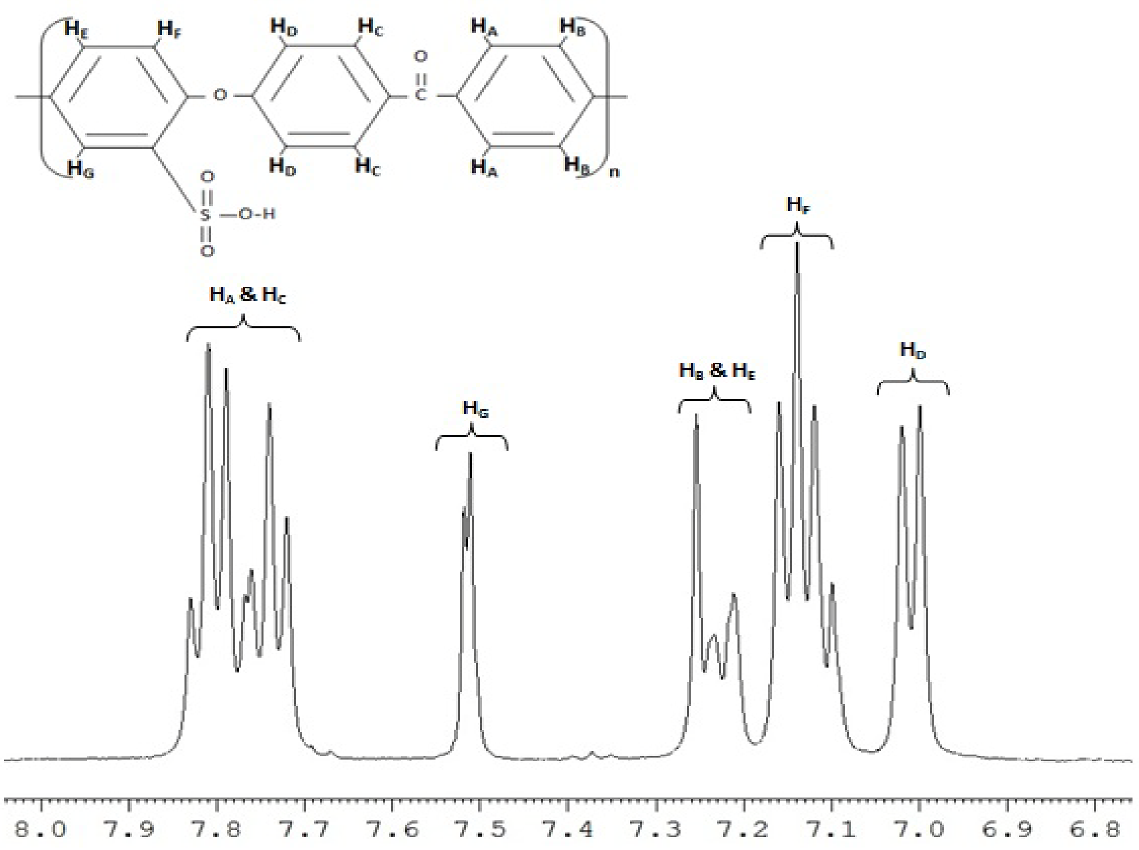


Figure 1: ^{1}H NMR spectrum of SPEEK

3.2 Water Uptake

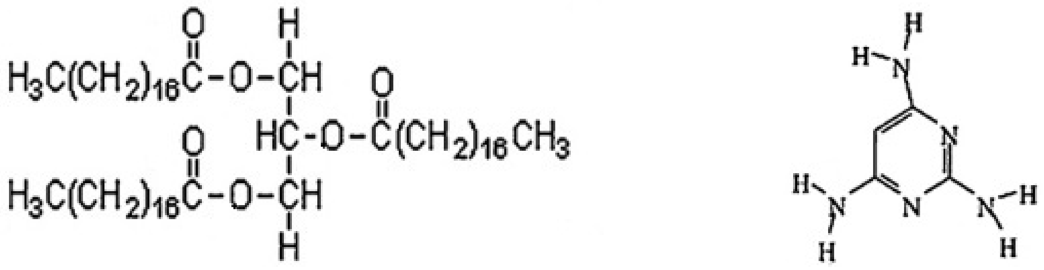
Water plays an important role for proton conductivity membrane. Adequate water adsorption will exhibit good proton conductivity for membrane [17]. Water uptake rate also plays an essential role in the membrane characteristic and related to the basic membrane properties. The amount of water absorbed by the membrane can provide the pathway for proton conductivity across it. Water involve in modifying the mechanical properties by influence the inomer microstructure, creating clusters and altering channel sizes. However, an excess of water uptake would affect the mechanical behaviour of the membrane.

Table 1: Water uptake of the membranes

Membrane	Water uptake (wt%)
Nafion 117	16
SPEEK	56
SPEEK/Cl/TAP	78.2

The water uptake measurement for prepared membrane were analysed at room temperature. Based on Table 2, it is shown that when the Cloisite 15A® and TAP was incorporated into SPEEK membrane, the water uptake increased from 56 to 78.2 wt%. Previous research reported that the incorporation of Cloisite 15A® can successfully improve the water uptake of the SPEEK membrane because of the hydrophilicity properties in that material as well as TAP. Both of these

Cloisite 15A® and TAP material have this characteristic due to the existing stronger hydrogen bond created by hydrophilic groups OH and NH_2 in the chemical structure [19]. Between these materials, the main contributor for high water uptake is Cloisite 15A® [20]. Juhana claimed that SPEEK incorporated with Cloisite15A® show better wettability (34 wt%) compare with TAP (29 wt%). This might be due to the oxygen molecule in the Cloisite 15A® (Figure 2) that has more and higher affinities for electron or polarity and expect to form more hydrogen bond compare to the nitrogen in the TAP [21].



Cloisite15A

2,4,6-triaminopyrimidine (TAP)

Figure 2: The chemical structure of Cloisite 15A and TAP

3.3 Dissolve Oxygen Permeability

The details of oxygen transfer rate (K_O) and diffusivities of oxygen (D_O) are listed in Table 2. From the experimental data, the highest K_O (2.4 x 10^{-3} cm/s) was provided by Nafion 117 and the lowest K_O (0.7 x 10^{-3} cm/s) was recorded by SPEEK/Cloisite 15A® membrane. The K_O of SPEEK was reduced by 53.3 % (from 0.7 x 10^{-3} to 1.5 x 10^{-3} cm/s) when Cloisite 15A® was introduced in the matrix membrane. Generally, the Cloisite 15A® plays a role as a filler. When it was introduced within the SPEEK matrix (Figure 3), the size of voids started to decrease and tend to increase the resistance toward oxygen that can freely pass through. When the stabilizer was added, it can finely dispersed the Cloisite 15A® in the SPEEK causing the arrangement of solid Cloisite 15A® to become closer and less aggregate, thus limiting the oxygen transfer. The high value of K_O explains that the membrane will have higher potential of allowing oxygen to pass through it. Nafion was known to exhibit high oxygen transfer and the results had been reported previously [8].

Table 2: Oxygen-transfer properties of the membranes

Membrane	Permeability rate of dissolve oxygen, K_O (x 10^{-3} cm s^{-1})	Oxygen diffusion coefficient, D_O (x 10^{-5} cm^2 s^{-1})
Nafion 117	2.4	1.9
SPEEK	1.5	1.0
SPEEK/Cl/TAP	0.7	0.6

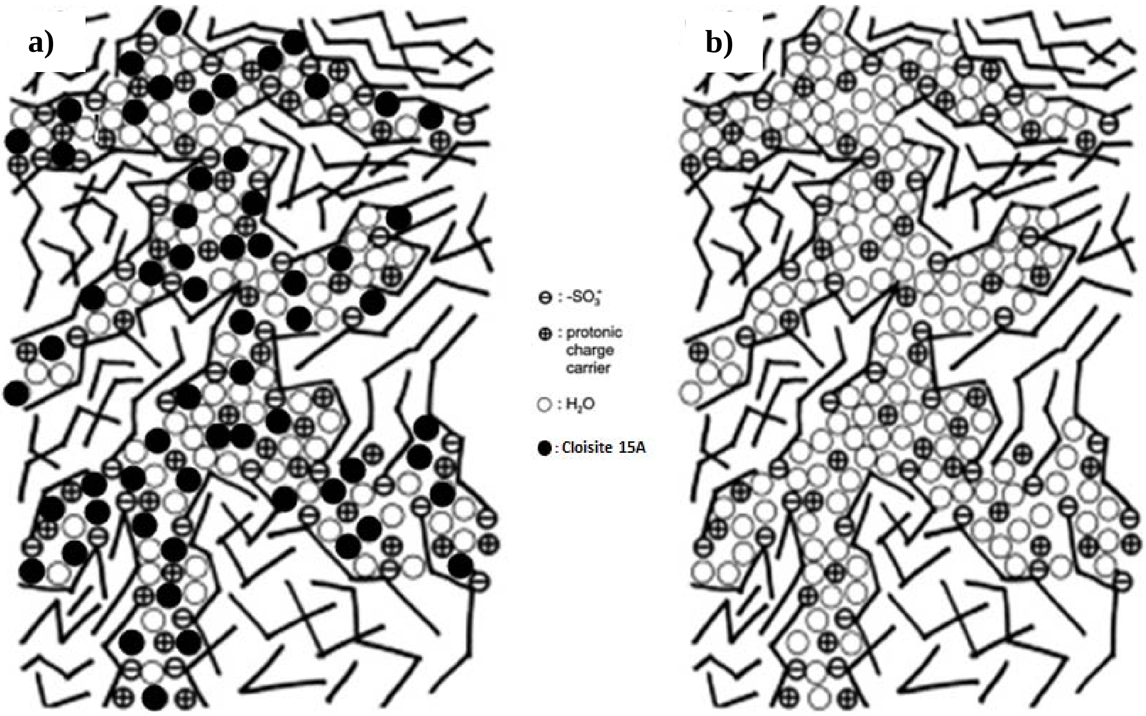


Figure 3: The comparison between (a) SPEEK/Cl/TAP and (b) SPEEK structure and the mechanism of proton transport (modified from Kreuer, 2001) [24].

3.4 Mechanical Strength

Table 3 shows the result of tensile strength tested on each membrane. From the result, pure SPEEK has the highest (11.2 Mpa) mechanical strength compare to the other prepared membrane and Nafion 117. This might be due to the SPEEK structure that has more branches compares to the Nafion 117 (Figure 4) [28]. The increasing of branch might cause the bonding of atom within the membrane become stronger and decrease the flexibility of it. Ironically, there is no significant improvement in the tensile strength when the Cloisite 15A$^{®}$ was load in the SPEEK matrix. The mechanical strength of the SPEEK membrane reduces from 11.2 to 7.5 MPa but nevertheless it is still higher 71 % than that of Nafion 117. The resulting lower tensile strength of SPEEK membrane incorporated with an additive might due to the reduction in the polymer rigidity. The additional of solid material inside the membrane disturb the periodic arrangement of SPEEK atom. Furthermore, it was observed during the experiments that SPEEK with additive membrane shown increase deformity of membrane compared to original SPEEK.

Table 3: Mechanical strength of the membranes

Membrane	Tensile strength (MPa)
Nafion 117	2.2
SPEEK	11.2
SPEEK/Cl/TAP	7.5

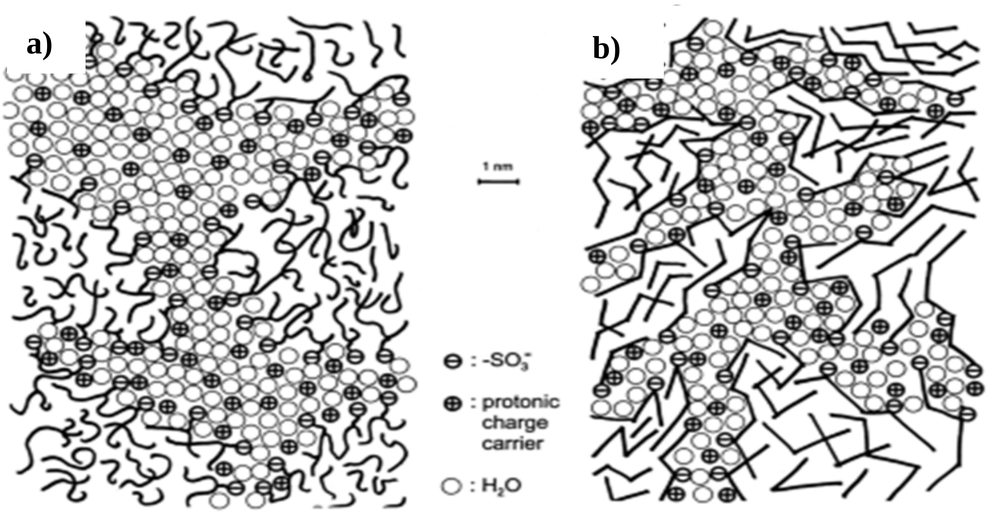


Figure 4: The comparison between (a) Nafion and (b) SPEEK structure and the mechanism of proton transport [28].

3.5 Membrane Morphology

Figure 5a, 5b and 5c shows surface image of SPEEK, SPEEK/Cl/TAP and Nafion117 membranes respectively at magnification 25 KX. Based on these images, the short crack on the surface of SPEEK/Cl/TAP and Nafion117 membranes is higher compare to the SPEEK. This crack indicated the number pores within the membrane. Compare to SPEEK membrane, the crack for SPEEK/Cl/TAP is short and uniformly distribute. This might be due to the role of Cloisite load in the membrane that can create a lot of small pores and uniformly filled by adding the TAP compatibilizer. TAP also might be a reasoned for the smooth surface of SPEEK/Cl/TAP membrane compare to the SPEEK.

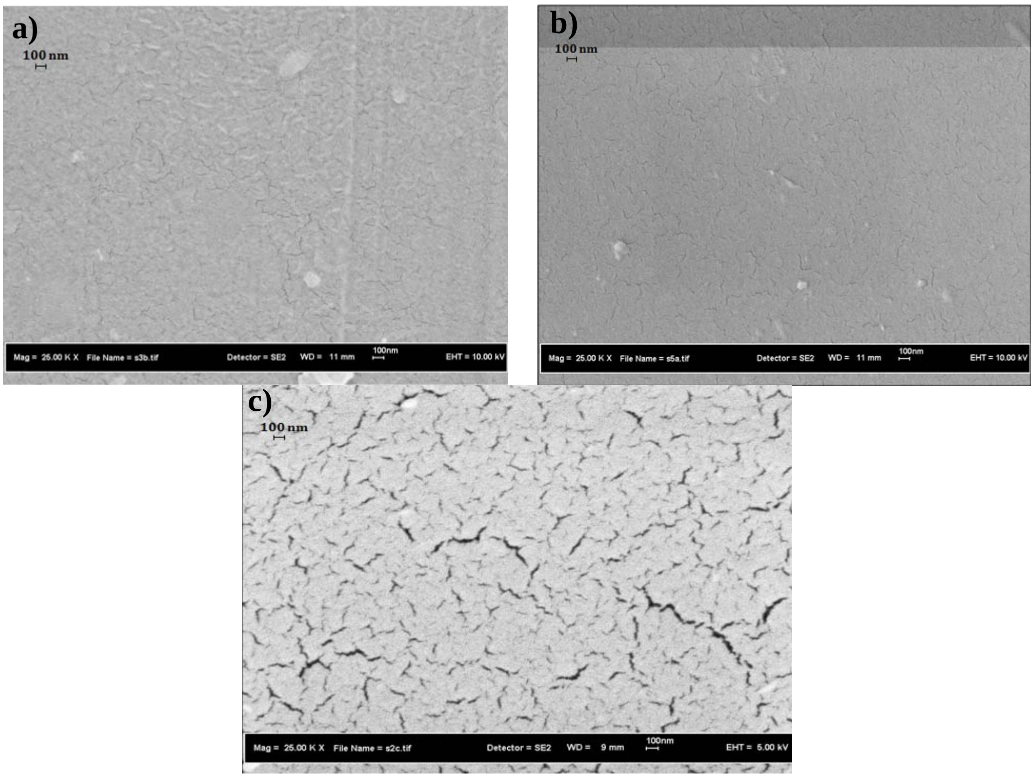


Figure 5 : The surface image of membrane at magnification 25 KX where (a) SPEEK, (b) SPEEK/Cloisite 15A® and (c) Nafion117

The cross-sectional and surface of membrane images of prepared membranes were investigated by using field electric scanning electron microscopy (FESEM). Figure 6a, 6b and 6c shows micrograph of cross-section for SPEEK, SPEEK/Cl/TAP and Nafion117 membranes respectively at low magnification (2.5 KX) and high magnification (25 KX). Based on these images, SPEEK and SPEEK/Cl/TAP membrane proved to have a dense and homogenous structure similar to the Nafion membrane. The images also show that, the number of pores for Nafion is quit high compared to the prepared membranes. At high magnification, the cross section of SPEEK/Cl/TAP membrane quite rough compare to the SPEEK. This roughness was signified the finely dispersed of the Cloisite 15A® in the SPEEK matrix [23-24]. This proved that TAP successfully plays a role as a compatibilizer in the membrane.

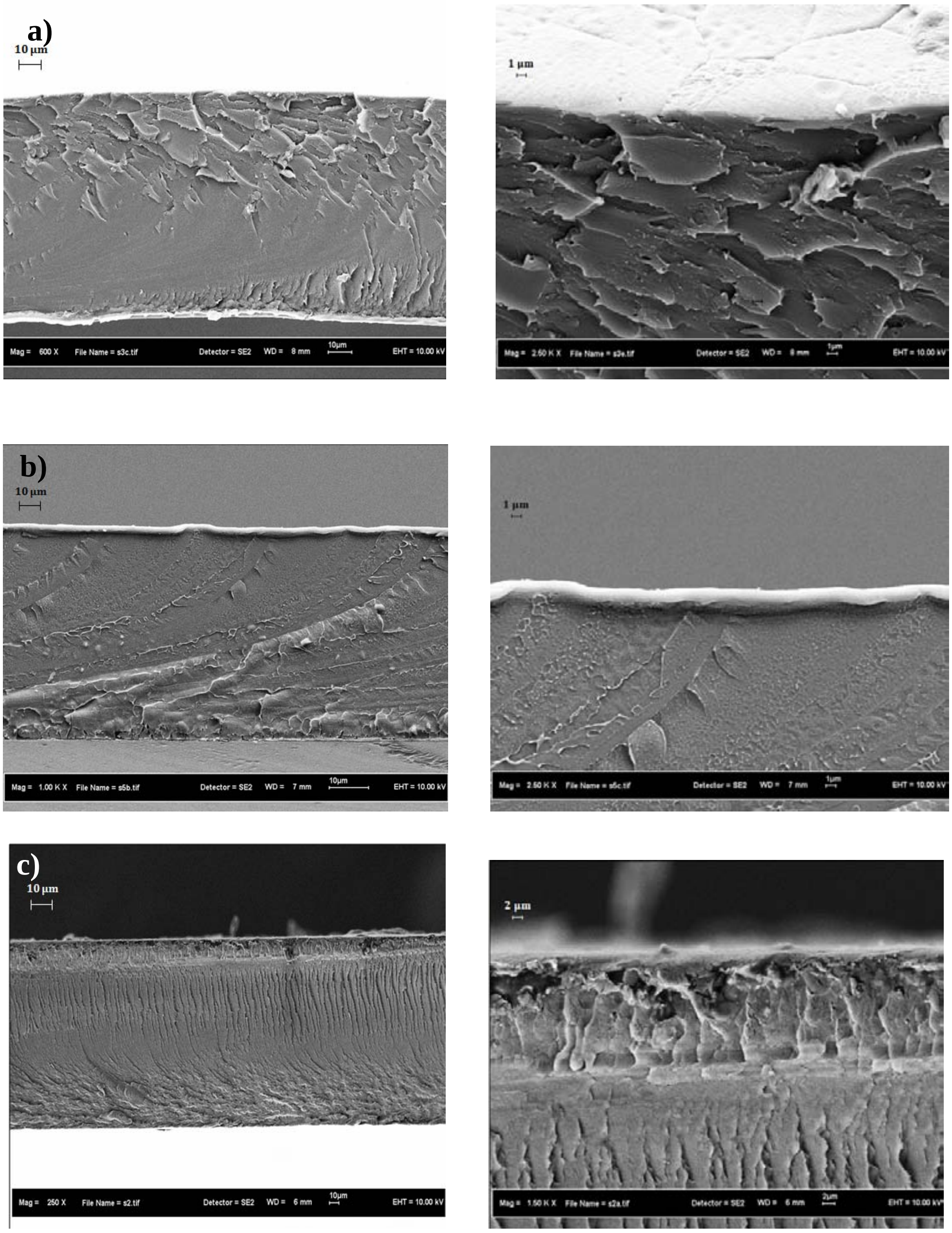


Figure 6 : The cross-section of membrane (a) SPEEK,(b) SPEEK/Cloisite 15A® and (c) Nafion117

3.6 Electrochemical Measurement

The optimum performance can be achieved when appropriate amount of Cloisite is added into the matrix of membrane. However, inappropriate amount of Cloisite 15A$^{®}$ incorporated within SPEEK membrane can give adverse effect on proton conductivity and water uptake [25]. The maximum amount of Cloisite for the optimum performance in MFC for this study was prepared by following the previous research which is 0.25 wt% [20].

Figure 7 shows the cell voltages and power densities as a function of current density for the MFC by using SPEEK/Cloisite 15A$^{®}$ membrane followed by pure SPEEK and Nafion117 as a comparison. Based on the result, it show that when the cloisite was load in the SPEEK membrane, the power density increase from 17.5 to 19.3 mW/m^2. Higher electrochemical performance of this membrane might be due to the conductivity of Cloisite 15A$^{®}$ [21].

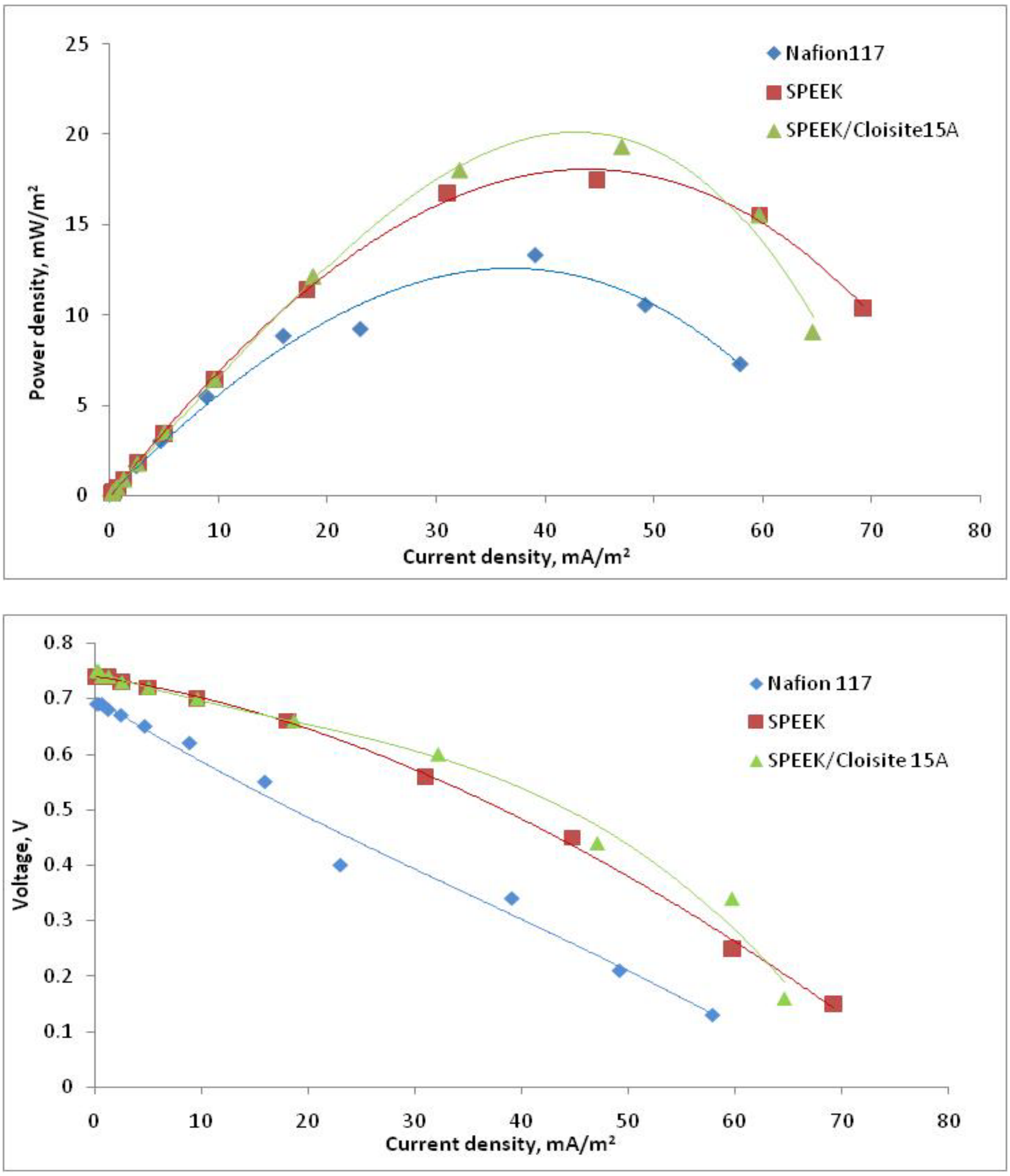


Figure 7 : Polarization curves of membranes

For further explanation, the mechanism of proton transfer is discussed. Generally, there are two main factors that can give a significant effect on proton conduction. First is vehicular mechanism and second, Grotthus mechanism. For vehicular mechanism, water plays a role as a vehicle by carrying the protons from anode to cathode. As for Grotthus mechanism, the proton was transfer from anode to cathode by hopping from stationary water molecule to another and transport along hydrogen-bonded ionic channels [26]. For this membrane, the mechanism that might be a main contributor for high electrochemical is through proton hopping along hydrogen-bonded. As mentioned before, the Cloisite and TAP can enhance the hydrogen bond in the SPEEK membrane. Besides, another factor that contribute to the performance of proton conductivity is the uniformly dispersion or less agglomeration of Cloisite 15A® particles within the membrane causing a lot of ions freely passed through the membrane with less resistance [27].

4.0 Conclusion

SPEEK membrane modified with Cloisite 15A® and TAP were successfully prepared and used in MFC system. Based on the experimental results and analyses, the following conclusions were derived.

- The SPEEK incorporated with Cloisite 15A® and TAP exhibited excellent power generation performance compared to the SPEEK membrane without additive and Nafion117.
- Permeability of dissolve oxygen from cathode chamber to anode was decreased using the membrane with both additives.
- The mechanical strength for SPEEK is not improved through the additional of Cloisite 15A® and TAP.

Based on the result and conclusions, the performance of the SPEEK membrane in MFC can be improved if the membrane with high proton conductivity, low oxygen permeability and good mechanical strength is figured out. For that, SPEEK with medium degree of sulfonation might be a solution because when the DS is decrease the mechanical behaviour will increase. As for high proton conductivity and low oxygen permeability, these properties might be improved by adding sufficient amount of Cloisite 15A® and TAP.

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References

[1] B. H. Kim, I. S. Chang, and G. M. Gadd, “Challenges in microbial fuel cell development and operation,” Application of Microbiology and Biotechnology, vol. 76, pp. 485–494, 2007.
[2] B. E. Logan, B. Hemelers, R. Rozandel, U. Schroder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, and K. Rabaey, “Microbial fuel cells methodology and technology,” Environmantal science and technology, vol. 40 (17), 2006
[3] D. R. Lovely, “Microbial fuel cell: novel microbial physiologies and engineering approaches,” Current opinion in biotechnology, vol. 17, pp. 327–332, 2006
[4] B. E. Logan, and J. M. Regan, “Microbial fuel cell – challenges and application,” Environmental science & technology, vol. 40, pp. 5172-5180, 2006
[5] B. Min, S. Cheng, and B. E. Logan, “Electricity generation using membrane and salt bridge microbial fuel cells,” Water research, vol. 39, pp. 1675–1686, 2005
[6] R. A. Rozendal, H. V. M. Hamelers, and C. J. N. Buisman, “Effects of membrane cation transport on pH and microbial fuel cell performance,” Environment science and technology, vol. 40, pp. 5206-5211, 2006

[7] R. A. Rozendal, T. H. J. A. Sleutels, H. V. M. Hamelers, and C. J. N. Buisman, “Effect of the type of ion exchange membrane on performance, ion transport, and pH in biocatalyzed electrolysis of wastewater,” Water science & technology, vol. 57, pp. 1757-1762, 2008

[8] O, Lefebvre, Y. Shen, Z. Tan, A. Uzabiaga, I. S. Chang, and H. Y. Ng, “A comparison of membranes and enrichment strategies for microbial fuel cells,” Bioresource technology, vol. 102, pp. 6291–6294, 2011

[9] W. W. Li, G. P. Sheng, X. W. Liu, and H. Q. Yu, “Recent advances in the separators for microbial fuel cells,” Bioresource technology, vol. 102, pp. 244–252, 2011

[10] E. Ji, H. Moon, J. Piao, P. T. Ha, J. An, D. Kim, J. J. Woo, Y. Lee, S. H. Moon, B. E. Rittmann, and S. I, Chang, “Interface resistance of anion exchange membranes in microbial fuel cells with low ionic strength,” Biosensors and Bioelectronics, vol. 26, pp. 3266-3271, 2011

[11] T. Xu, “Ion exchange membranes: state of their development and perspective,” Journal of Membrane Science, vol. 263(1–2), pp. 1–29, 2005

[12] T. Saito, M. D. Merrill, V. J. Watson, B. E. Logan, and M. A. Hickner, “Investigation of ionic polymer cathode binders for microbial fuel cells,” Electrochimica Acta, vol. 55, pp. 3398–3403, 2010

[13] A. T. Heijne, H. V. M. Hamelers, V. D. Wilde, R. A. Rozendal, and C. J. N. Buisman, “A bipolar membrane combined with ferric iron reduction as an efficient cathode system in microbial fuel cells,” Environmental Science and Technology, vol. 40, pp. 5200-5205, 2006

[14] X. Zhang, S. Cheng, X. Wang, X. Huang, and B. E. Logan, “Separator characteristics for increasing performance of microbial fuel cells,” Environmental Science and Technology, vol. 43, pp. 8456–8461, 2009

[15] F. Harnisch, and U. Schrçder, “Selectivity versus mobility: separation of anode and cathode in microbial bioelectrochemical systems,” ChemSusChem, vol. 2, pp. 921 – 926, 2009

[16] M. H. D. Othman, A. F. Ismail, and A. Mustafa, “Proton conducting membrane from sulfonated poly (ether ether ketone) and boron orthophosphate for direct methanol fuel cell application,” Journal of membrane science, vol. 299, pp. 156-165, 2007

[17] A. F. Ismail, N. H. Othman, and A. Mustafa, “Sulfonated polyether ether ketone composite membrane using tungstosilicic acid supported on silica–aluminium oxide for direct methanol fuel cell (DMFC),” Journal of membrane science, vol. 329, pp. 18–29, 2009

[18] M. L. Vona, D. Marani, C. D’ottavi, M. Trombetta, E. Traversa, and I. Beurroies, “A simple new route to covalent organic/inorganic hybrid proton exchange polymeric membranes,” Chemistry of materials, pp. 69-75, 2006

[19] R. Gosalawit, S. Chirachanchai, S. Shishatskiy, and S. P. Nunes, “Krytox–montmorillonite–Nafion® nanocomposite membrane for effective methanol crossover reduction in DMFCs”, Solid state ionics, vol. 178, pp. 1627–1635, 2007

[20] J. Jaafar, A. F. Ismail, T. Matsuura, K. Nagai, “Performance of SPEEK based polymer–nanoclay inorganic membrane for DMFC”, Journal of membrane science, vol. 382, pp. 202– 211, 2011

[21] J. Jaafar, A. F. Ismail, and T. Matsuura0, “Preparation and barrier properties of SPEEK/Cloisite15A$^{®}$/TAP nanocomposite membrane for DMFC application,” Journal of membrane science, vol. 345, pp. 119-127, 2009

[22] M. Tsapatsis, J. K. Jeong, and S. Nair, “Layered silicate material and applications of layered materials with porous layers,” US Patent 7, 087: 288 B2, 2006

[23] A. Mahreni, A. B. Mohamad, A. A. H. Kadhum, W. R. W. Daud, and S. E. Iyuke, “Nafion/silicon oxide/phosphotungstic acid nanocomposite membrane with enhanced proton conductivity,” Journal of membrane science, vol. 327, pp. 32-40, 011

[24] S. S. Mohtar, A. F. Ismail, and T. Matsuura, “Preparation and characterization of SPEEK/MMT-STA composite membrane for DMFC application,” Journal of membrane science, vol. 371, pp.10–19, 2011

[25] K. S Reolofs, T. Hirth, and T. Schiestel, “Dihydrogenimidazole modified sulfonated poly(ether ether ketone) hybrid materials as electrolyte membranes for direct ethanol fuel cells,” Material of science engineering B, vol. 176, pp. 727-735, 2011

[26] S. Zhou, Q. Wu, and Z. Liu, “Preparation and conductivity of organic undecatungstochromic heteropoly acid hybrid material,” Polymer Bulletin, vol. 56, pp. 95–99, 2006

[27] M. Wang, and S. Dong, “Enhanced electrochemical properties of nanocomposite polymer electrolyte based on copolymer with exfoliated clays,” Journal of power sources, vol. 170, pp. 25–432, 2007

[28] K. D. Kreuer, “On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells,” Journal of membrane science, vol. 185, pp. 29-39, 2001

[29] J. R. Kim, S. Cheng, O. H. Sang-Eun, and B. E. Logan, “Power generation using different cation, anion, and ultrafiltration membranes in microbial fuel cells,” Environmental Science and Technology, vol. 41, pp. 1004–1009, 2007