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Effect of Filler Content on Transport Properties of Sulfonated Polyether Ether Ketone (SPEEK) Composite Proton Exchange Membranes

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Abstract. Proton exchange membrane for direct methanol fuel cell was developed by the incorporation of silicotungstic acid supported on silica (SiO_2-SiWA) into SPEEK polymer. The properties of composite membranes with various silica/SiWA ratios were investigated and compared in this study. It was found that high silica to SiWA weight ratio (2:1) resulted in porous membrane with high proton conductivity and moderate methanol permeability. Reduction in the aforementioned ratio to 1:1 resulted in a more compact structure with better thermal stability, however, leaching of SiWA from the membrane occurred due to insufficient support. SPEEK membrane incorporated with 10 wt% SiO_2 and 5 wt% SiWA showed the highest selectivity of 6.44×10^4 S.s/cm^3 and performed better than that of the pure SPEEK membrane. These results suggested that these membranes have potential to be considered for DMFCs applications.

1. Introduction

The high energy conversion efficiency of fuel cell results in its emergence as one of the potent power sources. According to Kolli and co-workers [1], proton exchange membrane fuel cell (PEMFC) is the most widely used fuel cell technology due to its high power density at low volume and weight. Conventional PEMFC which uses hydrogen as fuel presented some problems related to the portability and physical properties of hydrogen fuel. This has sparked the researches on liquid organic hydrogen carrier such as direct methanol fuel cell (DMFC) [2].

At present, Nafion membrane is considered as the standard in DMFC industry due to its good thermal, chemical and mechanical properties. However, high methanol permeability of Nafion membrane and its low resistance towards high temperature operation have restricted its commercialization [3]. Modifications were done to improve the performance of Nafion membrane in DMFC by incorporating foreign materials [4]. Nevertheless, high cost of Nafion germinates the initiative to discover new DMFC membrane materials. In terms of proton conductivity to methanol permeability selectivity, sulfonated poly ether ether ketone (SPEEK) membrane is regarded as the best

candidate to replace Nafion membrane due to its low methanol permeability and comparable proton conductivity with Nafion [5].

In this study, silicotungstic acid (SiWA), a crystalline material with high proton conductivity and thermal stability is incorporated into SPEEK polymer to enhance the membrane's performance. In fact, SiWA is reported to have the best proton conductivity enhancement among other heteropoly acids (HPA) [6]. However, SiWA is very soluble in water and prone to leaching. Therefore, silica is used as an inorganic support to immobilise SiWA while improving the thermal property and methanol rejection ability of SPEEK composite membrane [7]. Solution casting method is used to prepare the SPEEK composite membrane. In this method, mixing of additives into polymer solution can be achieved by ultrasonic treatment [8]. It is believed that under ultrasonic treatment, multiple effects such as dispersion and crushing can be obtained from cavitation which involves rapid formation, growth and collapse of microbubbles. This can help to ensure better dispersion and stabilisation of inorganic nanoparticles in the polymer matrix [9].

2. Experimental

2.1. Materials

Poly ether ether ketone (PEEK), SiWA and N-methyl-2-pyrolidone (NMP) were received from Sigma Aldrich. 95 – 98 % sulphuric acid (H_2SO_4), tetraethyl orthosilicate (TEOS, > 90 %), methanol (> 99.9 %) and ethanol (95 %) were obtained from Merck. All chemicals were used without further purification.

2.2. Synthesis of SPEEK and preparation SPEEK/SiO_2-SiWA Composite Membrane

1 g of PEEK was dissolved in 35 mL concentrated H_2SO_4. The reaction lasted for 48 hours at room temperature. Then the polymer-acid solution was quenched into ice-cold water to obtain solid SPEEK polymer and the precipitated polymer was left overnight. SPEEK polymer was washed with excess deionised water until the washing water becomes neutral (above pH 6.0) and dried in oven before use. DS of the synthesised SPEEK polymer was determined by titration method using 2 M sodium chloride solution. The DS of SPEEK polymer used in this study ranged from 55 % to 60 %.

SPEEK polymer was dissolved completely in NMP to form a 5 wt% polymer solution. SiWA was dissolved in deionised water and ethanol to form a homogeneous solution. Then, TEOS was added where TEOS:water:ethanol molar ratio was kept at 1:4:4. The solution was ultrasonicated for 30 minutes at room temperature. Polymer solution was added to the inorganic additive solution and ultrasonicated for 30 minutes at room temperature. The final solution was casted to a petri dish and dried in oven for 24 hours at 80 °C. The membrane was then peeled off and activated by immersing it in 1 M H_2SO_4 solution at room temperature for 24 hours. Finally, the membrane was washed several times and stored in deionised water for at least 24 hours before use. The membranes were labelled in SPEEK-X-Y where X and Y indicating the weight percentage of silica and SiWA, respectively.

2.3. Characterization

The composition of synthesised composite membranes was confirmed using energy dispersive X-ray spectroscopy (EDX, Amatek). Surface morphologies of the membranes were studied using scanning electron microscopy (SEM, Hitachi S-3400N). Water uptake and methanol uptake were measured by first immersing the membrane in water or 1 M methanol solution for 24 hours and then drying it to a constant weight. The percentage of the weight difference between wet and dry membranes to the dry weight was used as an indicator of water uptake (or methanol uptake).

Methanol permeability of the membranes was determined using diffusion method. A diffusion cell with two compartments was used where one compartment contained 1 M methanol solution and the other compartment contained deionised water. The membrane was fixed in between two compartments and the solution in each compartment was stirred constantly to ensure homogeneity. At suitable intervals, samples were collected from water compartment and methanol concentration of the sample

was determined using gas chromatography. Equation (2) was used to calculate the methanol permeability (P_M):

$$P_M\,(\mathrm{cm^2/s}) = (S \times V_B \times t)/(A \times C_{M0}) \qquad (2)$$

where S (M/s) is the slope of methanol concentration as a function of time, V_B ($\mathrm{cm^3}$) is the volume of deionised water, t (cm) is the membrane thickness, A ($\mathrm{cm^2}$) the effective contact area and C_{M0} (M) is the initial methanol concentration

Proton conductivity was measured using a four-electrode conductivity cell connected to a potentiostat (Zive SP1). In-plane conductivity (σ) of the membrane was calculated using Equation (3):

$$\sigma\,(\mathrm{S/cm}) = L/Rwt \qquad (3)$$

where L (cm) is the distance between two inner electrodes, R (Ω) is the membrane resistivity while w and t are the width and thickness, in cm of the membrane, respectively.

3. Results and Discussion

3.1. Membrane Morphology

Fig 1 depicts the surface morphology of different SPEEK/SiO_2-SiWA composite membranes. SPEEK-10-5 had the largest pore size and the size reduced subsequently with the increment of SiWA loading. SiWA was acidic in nature and different amount of SiWA added in fact provided different hydrolysis/condensation reaction conditions for TEOS precursor. Studies had showed that the acid catalysed hydrolysis/condensation reaction of TEOS precursor occurred much faster than neutral and basic reaction conditions [10]. However, this rapid reaction also led to the formation of agglomerated silica particles within the polymer matrix.

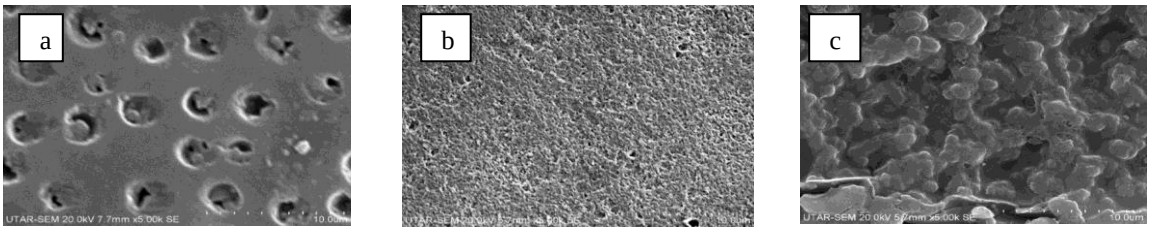

Figure 1: Surface Morphology of (a) SPEEK-10-5 (b) SPEEK-10-10 (c) SPEEK-10-20

In this study, agglomeration of silica particles was less of a problem due to the application of ultrasound during the reaction. Therefore, the amount of reacted TEOS was the key factor which would affect the surface morphology. From the presented SEM micrographs, the mentioned reducing pore size could be due to the increasing amount of silica produced from TEOS precursor. As shown Fig. 1a, there was some particles filling or clogging in the pores. More silica produced would enhance the blocking effect and hence resulted in a more compact morphology as shown in Fig. 1b for SPEEK-10-10 and Fig. 1(c) for SPEEK-10-20. Note that in SPEEK-10-20, there was no visible pores from the captured image due to the complete coverage of the silica on the surface of the membrane sample which led to the flaky morphology as shown.

EDX analysis results of the SPEEK/SiO_2-SiWA composite membranes were tabulated in Table I. From the results, it could be observed that as the ratio of silica to SiWA became smaller (from 10:5 to 10:20), the ability of SiWA to be incorporated into the polymer matrix (represented by weight composition of tungsten) became weaker. In SPEEK-10-5, the elemental weight ratio of silicon to tungsten was about 2, which was quite close to the theoretical value. However, in SPEEK-10-10, although there was an increase in tungsten loading, the ratio between silicon and tungsten could not match the theoretical 1:1. This effect became worse when the SiWA weight composition was raised to 20 %, where the amount of tungsten present in the membrane sample was too low to be detected. This

was also accompanied by the increase in silicon elemental composition resulted from the decrease of another component in the sample. The reason for such phenomena could be due to the insufficient amount of silica available to secure all the added SiWA. Silica loading should be in excess of SiWA in order to immobilise high amount of the leach-prone additive successfully.

Table 1. Elemental Composition Of SPEEK/Sio2-Siwa Composite Membranes

Membrane	**Elemental Compositions (wt%)**	
	Si	***W***
SPEEK-10-5	9.72	4.81
SPEEK-10-10	21.77	5.74
SPEEK-10-20	24.21	0.00

3.2. Water and Methanol Solution Uptake

Water uptake and 1 M methanol solution uptake of SPEEK/SiO_2-SiWA composite membranes with different compositions were presented in Table II. Both results showed similar trend, where the water/methanol solution uptake experienced a drop from SPEEK-10-5 to SPEEK-10-10 before gaining some increment in SPEEK-10-20. Such trend could be explained by the microstructure of the membrane resulted from different membrane composition. In SPEEK-10-5, low level of silica and SiWA resulted in relatively porous and loose-packed structure. This would ease the swelling and thus water/methanol solution uptake ability of the membrane itself. As SiWA has terminal oxygen atoms which could form bonds with polar molecules such as methanol, successful incorporation of SiWA into SPEEK polymer matrix would also increase the methanol uptake of the composite membrane.

Table 2. Comparison Of Water Uptake, Methanol Uptake, Methanol Permeability, Proton Conductivity And Selectivity Of Different SPEEK/SiO_2-SiWA Composite Membranes

Membrane	Water Uptake (%)	Methanol Uptake (%)	Methanol Permeability ($\times 10^{-7}$ cm^2/s)	Proton Conductivity (S/cm)	Selectivity ($\times 10^4$ $S.s/cm^3$)
SPEEK-10-5	50.98	55.74	7.45	0.0480	6.44
SPEEK-10-10	33.33	35.29	5.21	0.0293	5.63
SPEEK-10-20	50.00	46.81	8.72	0.0291	3.34

As for SPEEK-10-10, there were significant reductions in both water and methanol solution uptake. Such phenomena could be attributed to the compact structure of the membrane as shown in Fig. 1b. The compact structure allowed reasonable water and methanol solution uptake by the hydrophilic domain of the polymer matrix. At the same time, the expansion of hydrophilic region was greatly restricted by the presence of silica which provided better mechanical integrity to the membrane. However, the trend did not persist when higher SiWA loading was added to the membrane. In SPEEK-10-20, the water and methanol solution uptake increased once again. As stated earlier, inability of silica to entrap all added SiWA had caused the latter additive to leach from the polymer matrix. Although the SEM image showed that the surface of the membrane did not have visible pores, however, it was believed that the internal structure of the membrane was relatively porous after the leaching of SiWA. The location where SiWA was originally being situated now became a void area which could be utilised by the hydrophilic domain for its expansion. It was also at this loading where methanol solution uptake was less than water uptake. The very low loading of SiWA within the SPEEK polymer matrix reduced the ability of the membrane to capture polar methanol and hence causing some depression in the methanol solution uptake.

3.3. Methanol Permeability

Methanol permeability of different SPEEK/SiO_2-SiWA membranes were also reported in Table II. The trend of methanol permeability was similar to that of water and methanol solution uptake. For SPEEK-10-5, the methanol permeability was 7.45×10^{-7} cm^2/s, which was considerably lower than that of conventional Nafion membrane, which was 1.23×10^{-6} cm^2/s [11]. This successfully showed that SPEEK based composite membrane had better methanol rejection capability as compared to Nafion. Incorporated silica particles blocked the pores available for methanol transport, as shown by the SEM image in Fig. 1. When the amount of SiWA was increased to 10 wt%, incorporation of silica in the SPEEK polymer matrix at a more acidic condition had caused more silica occupying hydrophilic domain of the composite membrane, specifically the ionic clusters and resulted a remarkable drop in methanol permeability.

Moving on to SPEEK-10-20, there was an increase in methanol permeability when compared to other SPEEK composite membranes. Such increment was due to the leaching of SiWA which created voids within the membrane's internal structure. This allowed methanol molecules to pass through the membrane more easily, thereby deteriorating its methanol rejection ability. Furthermore, silica content in SPEEK-10-20 was higher when compared with SPEEK-10-5 and SPEEK-10-10 as shown by the results of EDX analysis (Table I). In this case, there was a possibility that high silica content would not only present in the hydrophilic region, instead, it might appear in the hydrophobic backbone as well [12]. As silica was hygroscopic in nature, this would provide extra hydrophilic pathway which would be used by methanol for diffusion. By combining the two effects above, the SPEEK-10-20 experienced a significant increase in methanol permeability which might affect its overall performance.

3.4. Proton Conductivity

Proton conductivity values of different SPEEK/SiO_2-SiWA composite membranes were tabulated in Table II. SPEEK-10-5 had the highest proton conductivity of 0.048 S/cm, while SPEEK-10-10 and SPEEK-10-20 had similar proton conductivity which were 0.0293 S/cm and 0.0291 S/cm, respectively. Incorporation of SiWA in SPEEK especially in SPEEK-10-5 managed to improve the proton conductivity of the SPEEK membrane, which is 0.011 S/cm according to previous study [13]. This was because of the extra proton exchange sites available after the modification. At the same time, lower silica content and larger pore size allowed easy transportation of proton by vehicle diffusion or Grotthüss mechanism. The high proton conductivity was also aided by sufficient water uptake of the membrane. In SPEEK-10-10, higher amount of silica incorporated produced a relatively compact structure. This was proved by the low water and methanol solution uptake. The compact structure reduced the passing of proton through the membrane by the formation of smaller ionic clusters. However, SPEEK-10-20 which had a more porous membrane structure attained similar proton conductivity as SPEEK-10-10. It was because of the loss of SiWA through leaching reduced the membrane's capability to conduct proton. This result also justified the importance of SiWA in promoting and enhancing the transport of proton through SPEEK composite membrane.

By considering both proton conductivity and methanol permeability, selectivity of the membrane could be deduced and shown in Table II. SPEEK-10-5 (with reasonable amount of incorporated silica and SiWA) had the highest selectivity, with the reported value of 6.44×10^4 $S.s/cm^3$. It was followed by SPEEK-10-10 and SPEEK-10-20 with the values of 5.63×10^4 $S.s/cm^3$ and 3.34×10^4 $S.s/cm^3$ respectively. For summary, the outcome of this study was satisfactory with the realization of incorporation of silica and SiWA into SPEEK polymer to enhance its properties.

4. Conclusion

SiWA was successfully incorporated into SPEEK polymer by using silica as support to fabricate SPEEK/SiO_2-SiWA composite membrane. Effect of inorganic additive loadings and their interaction were deduced from SEM images and EDX analysis. High TEOS to SiWA ratio (SPEEK-10-5) would result in porous structure, while low TEOS to SiWA ratio (SPEEK-10-20) would cause leaching of SiWA alongside with the increase in compactness of membrane by formation of more silica. SPEEK-

10-5 had the highest selectivity because of its high proton conductivity coupled with moderate methanol permeability. The results showed that the proton conductivity of the composite membrane dropped with the increase in SiWA loading due to the increase in membrane's compactness (SPEEK-10-10) and leaching of SiWA (SPEEK-10-20). Similar reason was also used to explain the decrease in methanol permeability in SPEEK-10-10 and the increment of the same metric in SPEEK-10-20. Further works are in progress to use the SPEEK-10-5 composite membrane in membrane electrode assembly (MEA) for DMFC performance evaluation.

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References

[1] A. Kolli, A. Gaillard, A. De Bernardinis, O. Bethoux, D. Hissel, and Z. Khatir, "A review on DC/DC converter architectures for power fuel cell applications," Energy Conversion and Management, vol. 105, Nov. 2015, pp. 716-730, doi: 10.1016/j.enconman.2015.07.060.

[2] G. L. Soloveichik, "Liquid fuel cells," Beilstein Journal of Nanotechnology, vol. 5, Aug. 2014, pp. 1399-1418, doi: 10.3762/bjnano.5.153.

[3] H. S. Thiam, M. Y. Chia, Q. R. Cheah, C. C. H. Koo, S. O. Lai, and K. C. Chong, "Proton conductivity and methanol permeability of Nafion-SiO_2/SiWA composite membranes," Proc. AIP International Symposium on Green and Sustainable Technology (ISGST 17), AIP Conference Proceedings, Apr. 2017, pp. 020007, doi: 10.1063/1.4979378.

[4] H. S. Thiam, W. R. W. Daud, S. K. Kamarudin, A. B. Mohammad, A. A. H. Kadhum, K. S. Loh, et al., "Overview on nanostructured membrane in fuel cell applications," International Journal of Hydrogen Energy, vol. 36, Feb. 2011, pp. 3187-3205, doi: 10.1016/j.ijhydene.2010.11.062.

[5] N. Intaraprasit and P. Kongkachuichay, "Preparation and properties of sulfonated poly(ether ether ketone)/Analcime composite membrane for a proton exchange membrane fuel cell (PEMFC)," Journal of the Taiwan Institute of Chemical Engineers, vol. 42, Jan. 2011, pp. 190-195, doi: 10.1016/j.jtice.2010.05.002.

[6] K.-M. Lee, J.-Y. Woo, B.-C. Jee, Y.-K. Hwang, C.-h. Yun, S.-B. Moon, et al., "Effect of cross-linking agent and heteropolyacid (HPA) contents on physicochemical characteristics of covalently cross-linked sulfonated poly(ether ether ketone)/HPAs composite membranes for water electrolysis," Journal of Industrial and Engineering Chemistry, vol. 17, Jul. 2011, pp. 657-666, doi: 10.1016/j.jiec.2011.02.017.

[7] Z. Li, W. Dai, L. Yu, J. Xi, X. Qiu, and L. Chen, "Sulfonated poly(ether ether ketone)/mesoporous silica hybrid membrane for high performance vanadium redox flow battery," Journal of Power Sources, vol. 257, Jul. 2014, pp. 221-229, doi: 10.1016/j.jpowsour.2014.01.127.

[8] J. Wang, H. Bai, H. Zhang, L. Zhao, H. Chen, and Y. Li, "Anhydrous proton exchange membrane of sulfonated poly(ether ether ketone) enabled by polydopamine-modified silica nanoparticles," Electrochimica Acta, vol. 152, Jan. 2015, pp. 443-455, doi: 10.1016/j.electacta.2014.11.165.

[9] Q. Wang, H. Xia, and C. Zhang, "Preparation of polymer/inorganic nanoparticles composites through ultrasonic irradiation," Journal of Applied Polymer Science, vol. 80, Mar. 2001, pp. 1478-1488, doi: 10.1002/app.1239.

[10] A. H. E. Yousif, O. Y. O. Alhussein, and M. S. A. Eltoum, "Characterization of hydrolyzed products of tetra ethoxy silane prepared by sol-gel method," International Journal of Multidisciplinary Science and Engineering, vol. 6, Jan. 2015, pp. 19-22.

[11] H. S. Thiam, W. R. W. Daud, S. K. Kamarudin, A. B. Mohamad, A. A. H. Kadhum, K. S. Loh, et al., "Nafion/Pd–SiO2 nanofiber composite membranes for direct methanol fuel cell

applications," International Journal of Hydrogen Energy, vol. 38, Jul. 2013, pp. 9474-9483, doi: 10.1016/j.ijhydene.2012.11.141.

[12] R. Jiang, H. R. Kunz, and J. M. Fenton, "Composite silica/Nafion® membranes prepared by tetraethylorthosilicate sol–gel reaction and solution casting for direct methanol fuel cells," Journal of Membrane Science, vol. 272, Mar. 2016, pp. 116-124, doi: 10.1016/j.memsci.2005.07.026.

[13] H. Zhang, T. Zhang, J. Wang, F. Pei, F. He, and J. Liu, "Enhanced proton conductivity of sulfonated poly(ether ether ketone) membrane embedded by dopamine-modified nanotubes for proton exchange membrane fuel cell," Fuel Cells, vol. 13, Oct. 2013, pp. 1155-1165, doi: 10.1002/fuce.201300130.