Effect of coupling agents on the transport properties of sulfonated poly (ether ether ketone) based composite membrane

Effect of coupling agents on the transport properties of sulfonated poly (ether ether ketone) based composite membrane

Min Yan Chia[1], Hui San Thiam[1], Loong Kong Leong[1], Chai Hoon Koo[2] and Lip Huat Saw[3]

1 Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Bandar Sungai Long, 43000 Kajang, Selangor, Malaysia
2 Department of Civil Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Bandar Sungai Long, 43000 Kajang, Selangor, Malaysia
3 Department of Mechanical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Bandar Sungai Long, 43000 Kajang, Selangor, Malaysia
E-mail: thiamhs@utar.edu.my

Abstract. Development of low cost proton exchange membrane surges as a main research topic in order to replace expensive Nafion in the fuel cell industry. In this study, sulfonated poly (ether ether ketone) (SPEEK) was used as the base polymer for the purpose. Silicotungstic acid supported on silica (SiWA-SiO_2) was incorporated into SPEEK polymer matrix to improve the performance of composite membrane. 3-aminopropyltriethoxysilane (APTES) and carbonyldiimidazole (CDI) were used as coupling agents to increase the compatibility of the organic and inorganic phases in the composite membrane. The reaction mechanisms involve the interaction between imidazole group of CDI with sulfonic acid group of SPEEK polymer followed by substitution using APTES. Finally, inorganic silica will attach to the inorganic functionalities of APTES and complete the organic-inorganic bridge between the two phases. Stabilisation of SiWA-SiO_2 additives in the polymer matrix was greatly improved when APTES and CDI are added. It was found that SPEEK/SiO_2-SiWA exhibited smooth, homogenous and compact membrane structure. This could reduce the permeability of the membrane to methanol. Although the composite membrane had low water uptake, presence of ample amount of SiWA within the polymer matrix helped to enhance the proton conductivity of SPEEK composite membrane. It was reported that the overall selectivity is increased to 10.6×10^4 S.s/cm^3.

1. Introduction

Fuel cells with its high efficiency of energy conversion is targeted as one of the promising candidate to replace fossil fuels in the near future. Direct methanol fuel cell (DMFC) is among the most attractive fuel cell due to its portability [1]. Conventionally, Nafion is used as the industrial PEM due to its high proton conductivity and stable under harsh chemical condition. However, it was claimed that the cost for Nafion production was too high [2]. Low fuel permeability and high proton conductivity of sulfonated poly (ether ether ketone) (SPEEK) is considered as one of the alternative membrane to replace Nafion. The performance of SPEEK membrane is highly dependent on the degree of sulfonation

(DS). Therefore, DS of SPEEK should be controlled at middle range to ensure good stability and low methanol permeability.

Foreign additives such as heteropoly acids are incorporated into the membrane to increase the proton conductivity of PEM [3]. However, heteropoly acids have high water solubility and prone to leaching [4]. The need for an effective method to stabilize silicotungstic acid (SiWA) within the polymer matrix has to be addressed. One of the approaches to immobilise the heteropoly acids is through the utilisation of inorganic supports such as silica [5]. Numerous works are conducted to prove the effectiveness of silica as a support for heteropoly acids, especially phosphotungstic acid (PWA) [6, 7]. Electrostatic interaction between heteropoly acids and inorganic oxides could help to hold the heteropoly acids within the polymer matrix [8]. According to the previous work, silica could be an effective immobilisation route for SiWA when used in excess [9]. However, compatibility of inorganic substance with organic polymer membrane is an issue of concern, where the stabilisation efficiency is very low [10].

In view of above, the objective of this study is to resolve the compatibility issue between organic SPEEK and inorganic additives (SiWA-SiO_2). Coupling agents are used in the process of PEM synthesis to increase the compatibility of organic and inorganic phase. Modification on the SPEEK membrane could enhance the homogeneity of dissimilar materials, and produce more uniform structure. SPEEK composite membranes with 5 wt% SiWA and 10 wt% silica are prepared by solution casting method. At the same time, effects of different coupling agents, namely 3-aminopropyltriethoxysilane (APTES) and carbonyldiimidazole (CDI) on the transport properties of SPEEK based PEM are investigated.

2. Experimental

2.1. Sample Preparation

Poly (ether ether ketone) (PEEK), SiWA crystals, 3-aminopropyltriethoxysilane (APTES) and carbonyldiimidazole (CDI) were purchased from Aldrich. Tetraethylorthosilicate (TEOS), N-methyl-2-pyrrolidone (NMP), ethanol, 97 % sulphuric acid and 99.9 % methanol were purchased from Merck.

Prior to sulfonation, PEEK was dried in an oven overnight to remove moisture. 1 g of PEEK was dissolved in 35 mL of sulphuric acid and was constantly stirred for 6 hours at 55 ℃. The dissolved polymer was quenched in ice water to precipitate out the solid SPEEK polymer. SPEEK polymer was washed with deionised water until it reached neutral pH and dried in the oven. The DS of SPEEK produced ranged from 55 % to 60 %.

5 wt% of SPEEK polymer solution was prepared by dissolving dried SPEEK into NMP solvent. Coupling agent was added where the amount of coupling agent was ¼ of the number of moles of SPEEK. Coupling agents used were APTES, CDI and APTES + CDI. The mixture was then stirred for 2 hours at 60 ℃. To prepare SiWA-SiO_2, SiWA was dissolved in deionised water. Ethanol and TEOS were added into the mixture with the molar ratio of TEOS:ethanol:water = 1:4:4. The mixture was ultrasonicated for 30 minutes before mixing with the polymer solution to form a casting solution. Membrane was formed by drying the casting solution in the oven for 24 hours at 80 ℃. Finally, the membrane was activated in 1 M sulphuric acid for 24 hours at room temperature.

2.2. Characterisations

The surface morphology of the membrane was studied using a Hitachi S-3400N SEM instrument. The distribution of various elements present in the membrane was investigated by elemental mapping technique using Amatek EDX. To investigate the tendency of SPEEK based membrane in absorbing water, the membrane was immersed in deionised water for 24 hours. The membrane was dried in the oven until a constant weight is obtained. Water uptake is calculated by obtaining the percentage difference between a fully hydrated membrane and dried membrane as shown in Equation (1).

$$\text{Water Uptake (\%)} = \frac{W_W - W_D}{W_D} \times 100\% \quad (1)$$

where W_W and W_D are the wet weight and dry weight of the membrane respectively in g.

Methanol permeability was tested using a diffusion cell with two compartments containing 1 M methanol solution and deionised water, respectively. Hydrated SPEEK based membrane was fixed between the compartments and the solutions in both compartments were stirred continuously during the test. Samples from water compartment were collected at specified time intervals to determine the amount of diffused methanol by using gas chromatograph (Perkin Elmer Clarus 500). Methanol permeability is calculated using Equation (2).

$$P = \frac{SVt}{C_0 A} \tag{2}$$

where P is the methanol permeability (cm^2/s), S is the slope of methanol concentration in function of time (M/s), V is the volume of methanol solution (cm^3), t is thickness of membrane (cm), C_0 is the initial concentration of methanol (M) and A is the effective contact area of the membrane (cm^2).

Proton conductivity of SPEEK based composite membrane was measured using Zive SP1 potentiostat. A strip of the membrane was placed in a four-probe conductivity cell and the resistance of the membrane was recorded. Conductivity of the membrane is calculated using Equation (3).

$$\sigma = \frac{L}{Rwt} \tag{3}$$

where σ is proton conductivity of membrane (S/cm), L is the inner distance between electrodes (cm), R is the resistance of membrane (Ω), w and t is the width and thickness of the membrane respectively, in cm.

3. Results and Discussion

3.1. Morphology of Membrane

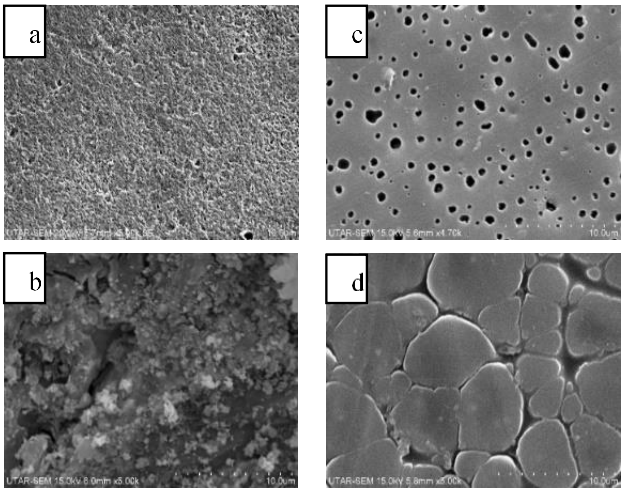

Figure 1. SEM Micrographs of (a) SPEEK/SiO_2-SiWA (b) SPEEK/SiO_2-SiWA-APTES (c) SPEEK/SiO_2-SiWA-CDI (d) SPEEK/SiO_2-SiWA-APTES-CDI

Figure 1 shows the SEM micrographs of SPEEK/SiO_2-SiWA composite membranes with different types of coupling agents. As shown in the figure, incorporation of SiWA-SiO_2 into SPEEK polymer will produce a compact membrane structure. The morphology of the membrane, as illustrated in Figure 1b is very rough when only APTES is added as a coupling agent. Besides being a coupling agent, APTES itself is also another precursor for the formation of organic silica. Therefore, addition of APTES can provide more silica to the membrane, resulting in the rough structure. On the other hand, addition of CDI crosslink agent will reduce the compactness of the membrane (Figure 1c). Pores seen on the surface

of the membrane implies that the internal structure of the membrane is porous. In fact, it is claimed that CDI can only work as an organic bridge between polymers [12]. Successful interaction between SPEEK polymer with inorganic additives (silica and SiWA) in the SPEEK/SiO_2-SiWA-APTES-CDI membrane will produce uniform and compact surface morphology. This can be due to the increased compatibility between organic SPEEK polymer and inorganic silica as well as SiWA.

3.2 Elemental Composition of Membrane

Table 1 compiles the elemental compositions of SPEEK composite membranes in this study. In SPEEK/SiO_2-SiWA, the elemental composition of silicon and tungsten are 9.72 wt% and 4.81 wt%, respectively (Si:W ratio ≈ 2:1). Addition of APTES silane coupling agent into the membrane has significantly increased the carbon content of the composite membrane. This is due to the three ethoxy groups and one propyl group present in APTES. Consequently, the composition of silicon and tungsten were suppressed to 5.57 wt% and 2.32 wt%, respectively (Si:W ratio ≈ 2.4:1). The slight increase in the Si:W ratio is attributed to the increase of organic silica content formed from the hydrolysis of APTES. However, leaching of silica and SiWA is prominent when only CDI is added into the polymer solution. Changes in the membrane structure (more porous) result in higher tendency for the inorganic additives to leach out from the membrane. Moreover, reaction between SPEEK and CDI reduces the attachments sites for silica and SiWA to be incorporated into the membrane. When both APTES and CDI are added into the membrane, the reported elemental composition of silicon and tungsten are 4.80 wt% and 3.69 wt% (Si:W ratio ≈ 1.3:1). This shows that when APTES and CDI present simultaneously, the anchoring effect of SiWA by silica can be stronger due to the higher compatibility between SPEEK polymer, silica and SiWA.

Table 1. Elemental Compositions of SPEEK Based Composite Membranes

Elemental Composition (wt%)	**Membrane**			
	SPEEK/SiO_2-SiWA	**SPEEK/SiO_2-SiWA-APTES**	**SPEEK/SiO_2-SiWA-CDI**	**SPEEK/SiO_2-SiWA-APTES-CDI**
C	38.20	59.76	64.90	59.07
O	19.62	20.45	22.85	22.44
S	27.65	10.71	9.23	9.17
N	0.00	1.18	0.82	0.83
Si	9.72	5.57	0.99	4.80
W	4.81	2.32	1.20	3.69

3.3 Methanol Permeability

Methanol permeability test is used to forecast the performance of PEM. The results are tabulated in Table 2. The control set, SPEEK/SiO_2-SiWA composite membrane had methanol permeability of 7.45 $\times 10^{-7}$ cm^2/s which is lower than that of the pristine SPEEK reported in other literatures [13]. The inclusion of silica into the membrane structure increases the tortuosity of hydrophilic pathway for methanol diffusion. Silica occupies part of the hydrophilic domain, making the ionic clusters to be less continuous for methanol crossover [14].

The effects of adding APTES or CDI during membrane fabrication are studied. When APTES is added, methanol permeability of the composite membrane is increased slightly to 9.53 $\times 10^{-7}$ cm^2/s. The slight increase can be due to the increment in silica content contributed by organic silica formed from APTES. Excessive silica not only occupied the hydrophilic domain, it also accumulates in the hydrophobic region of the polymer matrix. Since silica is hygroscopic in nature, this provides extra hydrophilic pathway for methanol transport [15]. On the other hand, the upsurge of methanol permeability is more obvious in SPEEK/SiO_2-SiWA-CDI composite membrane (1.00 $\times 10^{-6}$ cm^2/s). The sudden increase is mainly caused by the porous structure of the membrane.

Table 2. Comparison of Water Uptake, Methanol Solution Uptake, Proton Conductivity, Methanol Permeability and Selectivity of Different SPEEK/SiO_2-SiWA Composite Membrane

Membrane	**SPEEK/SiO_2-SiWA**	**SPEEK/SiO_2-SiWA-APTES**	**SPEEK/SiO_2-SiWA-CDI**	**SPEEK/SiO_2-SiWA-APTES-CDI**
Water Uptake (%)	50.98	71.70	70.18	34.92
Proton Conductivity (S/cm)	0.0480	0.0833	0.0691	0.0696
Methanol Permeability (cm_2/s)	7.45×10^{-7}	9.53×10^{-7}	1.00×10^{-6}	6.55×10^{-7}
Selectivity S.s/cm^3	6.44×10^4	8.74×10^4	6.90×10^4	1.06×10^5

It is also observed that methanol permeability has reduced when both APTES and CDI were added into the membrane. The successful linkage between SPEEK and silica with the help of APTES and CDI results a more rigid membrane. Formation of alkoxy silane groups provided by APTES and the reaction of CDI with sulfonic acid group produces a good crosslinking between organic and inorganic phase of the composite membrane and decreases the permeability of methanol through the membrane.

3.4 Proton Conductivity

In-plane conductivity test is used to characterise the proton conductivity of the composite membranes. SPEEK/SiO_2-SiWA had proton conductivity of 0.0480 S/cm which is higher than pristine SPEEK membrane [16]. The role of SiWA in increasing proton conductivity is justified. SPEEK/SiO_2-SiWA-APTES has higher proton conductivity of 0.0833 S/cm due to the high water uptake exhibited by the membrane. This will improve vehicle diffusion and proton hopping mechanism as the membrane can be easily hydrated. The proton conductivity of SPEEK/SiO_2-SiWA-CDI is slightly lower (0.0691 S/cm) due to the leaching of silica and SiWA. However, owing to its porous structure and high water uptake, its proton conductivity is still higher than the SPEEK/SiO_2-SiWA. Whereas, SPEEK/SiO_2-SiWA-APTES-CDI has only comparable conductivity with the SPEEK/SiO_2-SiWA-CDI. Although leaching effect is not observed in this membrane, the utilisation of sulfonic acid groups for crosslinking reduced the proton hopping sites. Moreover, lower water uptake and more rigid membrane structure are not favoured for proton transport. Therefore, the proton transport in this membrane is highly dependent on Grotthüss mechanism where the proton will hop across the membrane via limited sulfonic acid groups and proton exchange sites provided by SiWA. In this case, it can be seen that the immobilisation of SiWA by silica is successful by using the crosslinking of silane coupling agent, whereby the proton conductivity can be maintained at comparable level which is 0.0696 S/cm. By combining the results of proton conductivity and methanol permeability, it is found that SPEEK/SiO_2-SiWA-APTES-CDI has the best membrane performance in terms of selectivity (1.06×10^5 S.s/cm^3).

4. Conclusion

SiWA was successfully incorporated into SPEEK membrane using silica as inorganic support. APTES and CDI are used as coupling agents to improve the compatibility of the inorganic phase (SiWA and silica) and organic phase (SPEEK) of the composite membrane. It was found that when only APTES was added, it could only provide extra organic silica to the membrane and increased its water uptake. On the other hand, addition of CDI will deteriorate the membrane performance. Instead of being a coupling agent, CDI was more of a crosslinking agent which prepared SPEEK polymer for further reaction. It did not help to improve the linkage of SPEEK with the inorganic additives. The performance of membrane was improved significantly when both APTES and CDI were added simultaneously into the casting solution. CDI provided a "bridge" between SPEEK and organic part of APTES while APTES completed the linkage with silica. The resulting membrane had a rigid structure. The reported performance parameters of SPEEK/SiO_2-SiWA-APTES-CDI are 6.55×10^{-7} cm^2/s for methanol permeability, 0.0696 S/cm for proton conductivity and 1.06×10^5 S.s/cm^3 for selectivity. Positive findings were obtained from the study where a method to enhance homogeneity of dissimilar materials

was developed. Future studies could be focused on the applicability of the developed method on other materials.

References

[1] Soloveichik GL. Liquid fuel cells. Beilstein J Nanotechnol 2014;5:1399-418.
[2] Ghasemi M, Wan Daud WR, Alam J, Jafari Y, Sedighi M, Aljlil SA, et al. Sulfonated poly ether ether ketone with different degree of sulphonation in microbial fuel cell: Application study and economical analysis. International Journal of Hydrogen Energy 2016;41:4862-71.
[3] Narayanaswamy Venkatesan P, Dharmalingam S. Characterization and performance study of phase inversed Sulfonated Poly Ether Ether Ketone – Silico tungstic composite membrane as an electrolyte for microbial fuel cell applications. Renewable Energy 2017;102:77-86.
[4] Bhat SD, Sahu AK, Jalajakshi A, Pitchumani S, Sridhar P, George C, et al. PVA–SSA–HPA Mixed-Matrix-Membrane Electrolytes for DMFCs. Journal of The Electrochemical Society 2010;157:B1403.
[5] Mohtar SS, Ismail AF, Matsuura T. Preparation and characterization of SPEEK/MMT-STA composite membrane for DMFC application. Journal of Membrane Science 2011;371:10-9.
[6] Shang F, Li L, Zhang Y, Li H. PWA/silica/PFSA composite membrane for direct methanol fuel cells. Journal of Materials Science 2009;44:4383-8.
[7] Chen C-C, Tsi H-Y, Tsen W-C, Chuang F-S, Jang S-C, Shu Y-C, et al. PWA/silica doped sulfonated poly(ether sulfone) composite membranes for direct methanol fuel cells. Journal of Applied Polymer Science 2012;123:1184-92.
[8] Bhure MH, Kumar I, Natu AD, Chikate RC, Rode CV. Phosphotungstic acid on silica with modified acid sites as a solid catalyst for selective cleavage of tert-butyldimethylsilyl ethers. Catalysis Communications 2008;9:1863-8.
[9] Chia MY, Thiam HS, Leong LK, Koo CH. Effect of Filler Content on Transport Properties of Sulfonated Polyether Ether Ketone (SPEEK) Composite Proton Exchange Membranes. IOP Conference Series: Materials Science and Engineering 2018;409:012003.
[10] Zhang G, Zhou Z, Li C, Chu H. Proton conducting composite membranes from sulfonated polyether ether ketone and SiO2. Journal of Wuhan University of Technology-Mater Sci Ed 2009;24:95-9.
[11] Zhao Y, Jiang Z, Lin D, Dong A, Li Z, Wu H. Enhanced proton conductivity of the proton exchange membranes by the phosphorylated silica submicrospheres. Journal of Power Sources 2013;224:28-36.
[12] Pokprasert A, Chirachanchai S. Polymer electrolyte membrane with heterocyclic terminated poly(ethylene glycol) brushes: An approach to decorate proton conductive species on membrane surface. Journal of Membrane Science 2017;524:550-6.
[13] de Bonis C, Simari C, Kosma V, Mecheri B, D'Epifanio A, Allodi V, et al. Enhancement of proton mobility and mitigation of methanol crossover in sPEEK fuel cells by an organically modified titania nanofiller. Journal of Solid State Electrochemistry 2016;20:1585-98.
[14] Tripathi BP, Shahi VK. Surface redox polymerized SPEEK–MO2–PANI (M=Si, Zr and Ti) composite polyelectrolyte membranes impervious to methanol. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2009;340:10-9.
[15] Jiang R, Kunz HR, Fenton JM. Composite silica/Nafion® membranes prepared by tetraethylorthosilicate sol–gel reaction and solution casting for direct methanol fuel cells. Journal of Membrane Science 2006;272:116-24.
[16] Zhang Y, Wang H, Yu W, Shi J, Shi H. Sulfonated poly(ether ether ketone)-based hybrid membranes containing polydopamine-decorated multiwalled carbon nanotubes with acid-base pairs for all vanadium redox flow battery. Journal of Membrane Science 2018.

Acknowledgments

This work was supported by the Universiti Tunku Abdul Rahman (UTAR) through UTAR Research Fund (UTARRF) under project number IPSR/RMC/UTARRF/2016-C1/T8.