DEVELOPMENT OF HIGH PERFORMANCE SULFONATED POLY (ETHER ETHER KETONE) BASED COMPOSITE PROTON EXCHANGE MEMBRANES

By

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ABSTRACT

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Chia Min Yan

Increasing demand of energy and the depletion of non-renewable fossil fuels had instigated the search for alternative sources of energy. Direct methanol fuel cell (DMFC) becomes a very interesting research theme, especially its proton exchange membrane. In this study, attempt to replace the costly Nafion based proton exchange membrane with a new material was done. A low cost polymer, poly ether ether ketone (PEEK) was sulfonated into SPEEK. Additives (silicotungstic acid supported on silica, SiO_2-SiWA) were incorporated into the polymer matrix. In order to enhance the stability, performance and homogeneity of the membrane, various modifications, including ultrasonic treatment and addition of coupling agents were tested. From the results, ultrasonic treatment provided extra energy through its cavitation effect, thereby stabilised SiO_2-SiWA in the membrane. It was also found that silica:SiWA weight ratio of 2:1 could improve the immobilisation effect of silica on SiWA. Addition of aminopropyl triethoxysilane (APTES) and carbonyl diimidazole (CDI) as coupling agent and promoter further improved the compatibility between organic polymer and inorganic additives, where it showed higher selectivity (10.6×10^4 S.s/cm^3) than Nafion membrane. This was achieved through the successful bridging of organic SPEEK and inorganic silica by a series of chemical reactions involving APTES and CDI. As APTES and CDI were able to improve the performance of SPEEK/SiO_2-SiWA composite membrane, the composition was tested by using alumina and iron (III) oxide as support for SiWA. However, due to their amphoteric nature and incompatibility with silane coupling agents, there was no positive outcome. In conclusion, a SPEEK/SiO_2-SiWA composite membrane with 10 wt% of silica and 5 wt% of silicotungstic acid provided the best performance, with the utilisation of ultrasonic treatment to improve dispersion and stability. At the same time, APTES and CDI acted as coupling agent and promoter respectively further enhanced the performance of the membrane. This laid a foundation for future research on SPEEK based membrane development as a continuous effort to replace costly Nafion membrane.

LIST OF PUBLICATIONS

Chia, M. Y., Thiam, H. S., Leong, L. K. and Koo, C. H., 2018. Effect of filler content on transport properties of sulfonated poly ether ether ketone (SPEEK) composite proton exchange membranes. *IOP Conference Series: Materials Science and Engineering*, 409, pp. 012003.

Thiam, H. S., Chia, M. Y., Cheah, Q. R., Koo, C. C. H., Lai, S. O. and Chong, K. C., 2017. Proton conductivity and methanol permeability of Nafion-SiO2/SiWA composite membrane. *AIP Conference Proceedings*, 1828, pp. 02007.

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SUBMISSION OF DISSERTATION

It is hereby certified that **CHIA MIN YAN** (ID No: **17UEM00981**) has completed this dissertation entitled "DEVELOPMENT OF HIGH PERFORMANCE SULFONATED POLY (ETHER ETHER KETONE) BASED COMPOSITE PROTON EXCHANGE MEMBRANES" under the supervision of Dr. Thiam Hui San (Supervisor) and Dr. Leong Loong Kong (Co-supervisor) from the Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science.

I understand that University will upload softcopy of dissertation in pdf format into UTAR Institutional Repository, which may be made accessible to UTAR community and public.

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APPROVAL SHEET

This dissertation entitled "**DEVELOPMENT OF HIGH PERFORMANCE SULFONATED POLY (ETHER ETHER KETONE) BASED COMPOSITE PROTON EXCHANGE MEMBRANES"** was prepared by CHIA MIN YAN and submitted as partial fulfilment of the requirements for the degree of Master of Engineering Science at Universiti Tunku Abdul Rahman.

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DECLARATION

I hereby declare that the dissertation is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

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CHAPTER 1

INTRODUCTION

1.1 Proton Exchange Membrane Fuel Cell

Increasing demand of energy due to rapid urbanisation instigated the search for alternative sources of energy. Proton exchange membrane fuel cell (PEMFC) emerges as a hot research topic due to its suitability for stationary and mobile applications. Besides, intensive development and modifications done on PEMFC are also encouraged by its high efficiency and power density (Shahgaldi, Alaefour and Li, 2018). PEMFC is a device that converts chemical energy in hydrogen carrier into electrical energy via a redox reaction. Common hydrogen carriers are hydrogen gas, methanol, and ethanol (Ozden, et al., 2018; Yang, et al., 2018; Yan, et al., 2017). Liquid based hydrogen carriers such as methanol used in direct methanol fuel cell (DMFC) received much attention due to their ease of handling and high portability.

The structure of PEMFC is shown in Figure 1.1. A PEMFC consists of three main components, which are current collector (at anode and cathode), gas diffusion layer (at anode and cathode) and membrane electrode assembly (MEA). The core of a PEMFC is located at the MEA, where it is made up of a proton exchange membrane (PEM) sandwiched between anode and cathode catalyst layers.

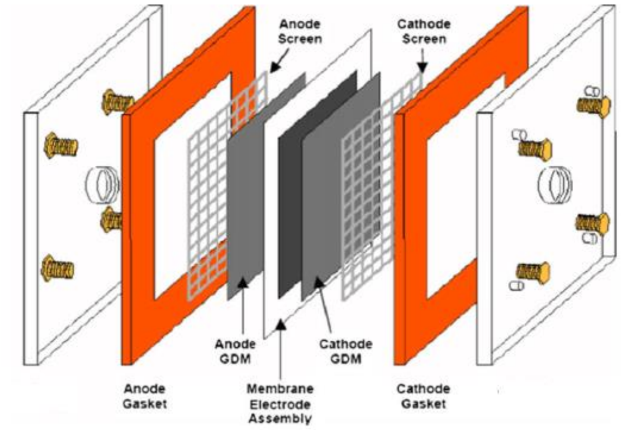


Figure 1.1: Structure of a PEMFC (Martins, et al., 2009)

In order for the PEMFC to work in a more efficient manner, the following characteristics are required:

- Low fuel crossover
- High ionic conductivity
- High mechanical and chemical durability
- High stability and strength
- High operation temperature
- Low cost

1.2 Problem Statement

According to Moreno, et al. (2015), fabrication of MEA, including the PEM as well as the catalyst had made up a major part of PEMFC's production cost. There are two main approaches to increase the cost effectiveness of MEA fabrication, which are

i) development of low cost catalyst, and
ii) development of low cost PEM.

In this study, the second approach was investigated. There are a few aspects to be taken into consideration as follow:

- Performance – the low cost membrane, which used low cost materials such as sulfonated poly ether ether ketone (SPEEK), silica and silicotungstic acid (SiWA) should have at least equal or better performance than conventional Nafion membrane.
- Operating condition – the low cost membrane should be able to withstand harsh operating condition of PEMFC, especially in DMFC.
- Ease of preparation – fabrication of the low cost membrane should be as simple as possible to increase its potential to be commercialised.

1.3 Objectives

The purpose of this research project is to fulfil the following objectives:

- To fabricate and characterise SPEEK/SiO2-SiWA composite proton exchange membrane.
- To study the effects of filler loadings and different preparation routes (ultrasonic treatment and addition of coupling agents) on the performance of SPEEK membrane.
- To investigate the possibility of replacing silica with other inorganic oxides such as alumina and iron (III) oxide as support for silicotungstic acid.

1.4 Organisation of Dissertation

The remaining parts of this dissertation will be divided into four chapters. Chapter 2 will provide a comprehensive literature review to identify the research gap and opportunity so that the problem statement can be answered. In Chapter 3, a detailed outline of the research plan and design of experiment will be presented alongside with the experimental procedures. Findings, results and outcomes of the research will be discussed in Chapter 4 to draw a conclusion for this research. The conclusion will be stated together with recommendations and potential future works in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Nafion Membranes

To date, Nafion based membranes are still the most widely used material for DMFC application. It is recognised as the standard proton exchange membrane due to its excellent thermal, mechanical and chemical stability (Liu, Chen and Li, 2016). Nafion has a molecular structure as shown in Figure 2.1, which consists of a tetrafluoroethylene (Teflon) backbone, perfluorvinyl ether chains and ends with a sulfonic acid functional group.

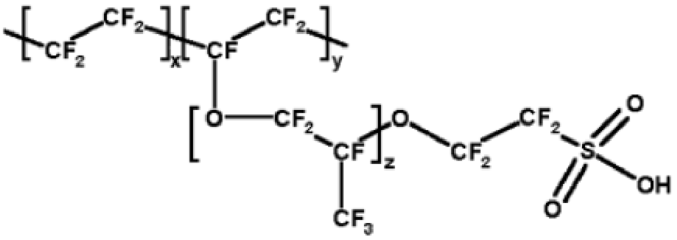


Figure 2.1: Molecular Structure of Nafion (Umirzakov, 2013)

According to Umirzakov (2013), the hydrophobic nature and mechanical stability of the Nafion membrane is attributed to the perfluorinated backbone. Due to the hydrophobic nature of Teflon backbone, it can be well segregated from the hydrophilic sulfonic acid end group when the membrane is hydrated to form ionic clusters. Sulfonic acid groups located adjacent to the hollow part of ionic clusters are responsible to ion conduction because of the resonance stabilised conjugate base. This distributes the negative charges among the oxygen atoms when the sulfonic acid groups lose protons. This property also allows protons to be transported through hydrated ionic clusters. The formation of such cluster is promoted by the extreme difference in polarity of the perfluorinated backbone and the sulfonic acid group (Moilanen, Spry and Fayer, 2008). However, the channels formed are also accessible by methanol and water, which will cause the problems of methanol crossover and cathode flooding.

2.1.1 Proton Transport in Nafion

Proton transport is an important phenomena in DMFC operation. Nafion conducts protons by two main mechanisms, namely vehicle diffusion and Grotthüss mechanism (Moilanen, Spry and Fayer, 2008). In vehicle diffusion, protons travel to the cathode side in the form of hydronium ions (either $H_9O_4^+$ or $H_5O_2^+$) which requires the combination with water. The rate of proton transport is similar to that of diffusion constant of water. On the other hand, instead of moving as a single hydronium ion, the Grotthüss mechanism utilises the hydrogen bonding network formed by water molecules for proton transport. Proton is transported across the membrane through numerous adjacent water molecules which are linked in the hydrogen bonding network. The hydrogen bonding network is greatly influenced by the size and shape of the hydrophilic domains (Moilanen, Spry and Fayer, 2008). In Grotthüss mechanism, the protons (in the form of hydronium ions) “hop” from one hydrated sulfonic group to the next sulfonic group across the membrane. (Kuwertz, et al., 2016).

Transport regime will be dominated by different mechanisms at different hydration levels. At low hydration level, insufficient water to solvate the protons resulting in inability of the formation of bonding network, hence vehicle diffusion will dominate. As the hydration level increases, more proton diffusion will increase although it will not reach the value of water self-diffusion due to the geometrical restrictions of the hydrogen bonding network (Moilanen, Spry and Fayer, 2008). Therefore, it can be concluded that the two most prominent factors that affect the proton conductivity of Nafion will be water uptake and temperature (subsequently affects the water uptake).

Various researches were done to investigate the effect of water uptake on the proton conductivity of Nafion membrane. Wu, et al. (2011) claimed that proton conductivity had positive relationship with water activity within the membrane. Higher water activity resulted in expansion of hydrophilic volume fraction which will form a continuous channel for proton transport. Apart from experimental results, molecular simulations were also done to study how the membrane’s degree of hydration would affect the proton conductivity. It was found that at high degree of hydration, Nafion membrane would exhibit better proton conductivity (Costamagna, Grosso and Di Felice, 2008) and Grotthüss mechanism would dominate the transport (Hwang, et al., 2011).

Literature studies also showed that proton conductivity is influenced by operating temperature. It was reported that proton conductivity would be enhanced at higher temperature and hence DMFC is preferably to be operated at such condition (Jeon, Kim and Kwak, 2012; Boutsika, et al., 2016). The effect of temperature on proton conductivity can be fitted into an Arrhenius plot, and due to this property, higher temperature will be more favourable to overcome the activation energy for proton mobility (Yang, et al., 2016). However, at temperature above 90 ℃, proton conductivity will be better expressed by Vogel-Tamman-Fulcher empirical law instead of Arrhenius' equation (Matos, et al., 2014).

Besides the effect of water uptake and temperature, proton conductivity can also be influenced by pre-treatment method. The concentration and types of acid used for Nafion membrane protonation were found to be decisive in the properties of the membrane. Kuwertz, et al. (2016) proved that Nafion membrane protonated using higher acid concentration would result is higher proton conductivity. Hydrochloric acid showed the best performance in the stated context.

2.1.2 Limitations of Nafion Membrane

Hydrated Nafion membrane will form ionic clusters for proton transport. Unfortunately, the ionic clusters also provide routes for the transport of small methanol molecules from anode to the cathode side of DMFC (Umirzakov, 2013). Methanol will be oxidised at the cathode and produces mixed potential (Berns, et al., 2015). The overall effect is the reduction of the DMFC efficiency where produced electrical energy is lower than theoretical value. This has limited the use of DMFC whereby only low concentration fuel can be used (Li and Faghri, 2013). Methanol permeability of Nafion membrane is around 1.0×10^{-6} cm^2/s to 1.5×10^{-6} cm^2/s at room temperature. (Jeon, Kim and Kwak, 2012; Kim, et al., 2012; Xue and Chan, 2015; Wang, et al., 2017).

Methanol permeability will increase at elevated temperature. This inhibits high temperature operation that favours methanol oxidation reaction at the anode. Several modifications had been done to Nafion membranes in order to improve the methanol rejection ability as shown in Table 2.1.

Nevertheless, addition of additive to reduce the methanol permeability of Nafion membranes will sacrifice its proton conductivity. This is due to the reduction of hydrophilic domain for proton transport (Ke, et al., 2012). Therefore, in order to maintain or improve the proton conductivity of Nafion based composite membranes, additional proton conductive additives (Mahreni, et al., 2009) or modification of additives such as functionalisation and sulfonation (Chien, et al., 2013; Rambabu, Nagaraju and Bhat, 2016) were proposed and investigated.

Low degradation temperature is another drawback of Nafion membranes. Lee, et al. (2012) asserted that the degradation of Nafion polymer will start at 80 ℃. However, operating DMFC at lower temperature will slow down the kinetics of methanol oxidation reaction, thereby promoting the formation of carbon monoxide which is poisonous to the platinum catalyst (Bhure, et al., 2008). Hence, there is a dilemma when choosing the operating temperature of DMFC.

Table 2.1: Performance of Nafion Based Composite Membranes

Membranes	**Methanol Permeability, *P* ($\times 10^{-7}$ cm^2/s)**	**Proton Conductivity, σ (S/cm)**	**Reference**
Nafion	45.0	0.008	(Prapainainar, et al., 2019)
Nafion/Sulfonated SiO_2	7.50	0.110	(Kim, et al., 2012)
Nafion/ETS	7.40	0.008	(Jeon, Kim and Kwak, 2012)
Nafion/Pd-SiO_2	8.36	0.129	(Thiam, et al., 2013)
Nafion/Pillararene	10.00	0.068	(Shen, et al., 2015)
Nafion/Functionalised Fullerene	5.10	0.065	(Rambabu, Nagaraju and Bhat, 2016)
Nafion/NH_4-X Zeolite	2.28	0.087	(Cui, et al., 2015b)
Nafion/Sulfonated GO	0.88	0.036	(Chien, et al., 2013)
Nafion/SiO_2-SiWA	14.10	0.085	(Thiam, et al., 2017)

On top of that, high cost of Nafion membrane (Kraytsberg and Ein-Eli, 2014; Houchins, et al., 2012) has also encouraged researchers to develop low cost PEM that can achieve similar or even better performance than Nafion membrane.

2.2 Alternatives to Nafion Based Membranes

2.2.1 Chitosan Based Membrane

Chitosan is a natural material obtained from the deacetylation of chitin. Its abundance triggers the study into the applicability of this material in various fields including DMFC. The unique chemical properties of chitosan make it to be a potential PEM to be developed (Zargar, Asghari and Dashti, 2015), including:

- Weak base and deprotonated amino group is a strong nucleophile (pK_a 6.3)
- Forms hydrogen bond easily
- Easy chemical modification and cross-linking
- Insoluble in water and organic solvent
- Ion conductor
- Film-forming ability

Chitosan based PEMs were investigated through various studies and their performances were compared to that of Nafion membrane. It was found that although chitosan based PEM has lower methanol permeability, its proton conductivity is also lower as compared to Nafion. This is because the free volume cavities in chitosan is smaller than hydronium ions. As a results, it halts vehicle diffusion of proton and methanol (Ressam, et al., 2017). Thus, attention was given to enhance the proton mobility through Grotthüss mechanism. Modifications performed on chitosan polymer in order to improve its overall performance include incorporating sulfonated graphene oxide (Liu, et al., 2014), adding cross-linked montmorillonite (Purwanto, et al., 2016) or sulfonation chitosan (Wafiroh, Pudjiastuti and Sari, 2016; Shirdast, Sharif and Abdollahi, 2016).

Despite the promising methanol rejection ability and its ease of modification, chitosan polymer is outclassed by Nafion due to its thermal instability (Osifo and Masala, 2012). Therefore, current research on chitosan based PEM is only focussed on low temperature DMFC.

2.2.2 Polybenzimidazole Based Membrane

The main advantage of polybenzimidazole (PBI) based membrane over Nafion is that it can withstand high temperature for better DMFC operation (Li, et al., 2015). It also has better mechanical stability coupled with better oxidative stability, which allow concentrated methanol to be utilised as fuel (Wu, et al., 2014b; Zhao, et al., 2015). Initially, PBI is just used as an additive to improve the properties of base polymer such as Nafion (Ahmad, et al., 2011). This is due to the ion and electric insulator properties of the polymer itself. However, recent studies show that the presence of –NH– and –N= in imidazole rings can be modified in order to change the ionic conductivity of PBI. Table 2.2 summarises some of the studies that use PBI based membrane in fuel cell application.

It can be concluded that although modifications done on PBI polymers can help to improve its proton conductivity, however, the effect of such effort is too insignificant. At low temperature, modified PBI has also very low proton conductivity. Therefore, the future research direction on PBI should be focused on using it as additive to enhance the thermal stability of other PEM.

Table 2.2: Performance of PBI Based Composite Membranes

Membranes	Methanol Permeability, P ($\times 10^{-7}$ cm^2/s)	Proton Conductivity, σ (S/cm)	Reference
PBI	2.53	-	(Chu, et al., 2015)
PBI/Zwitterion Coated GO	0.71	0.016	
PBI/CNT-KOH	0.18	0.035	(Wu, et al., 2014b)
PBI/OMMT	1.00	0.017	(Hasani-Sadrabadi, et al., 2010)

2.2.3 Sulfonated Aromatic Hydrocarbon Based Membrane

It is known that sulfonated aromatic hydrocarbon has better endurance at higher temperature and possess better mechanical stability as compared to the conventional Nafion based membrane (Kraytsberg and Ein-Eli, 2014). Hence, this provide a good starting point for this category of material to be developed into a commercially accepted PEM. There are a few polymers which are studied extensively as a replacement for Nafion membrane, namely poly ether sulfone (PES), poly arylene ether ketone (PAEK) and poly ether ether ketone (PEEK). Sulfonation of such polymers to a certain degree will help to improve their proton conductivity. Above the optimum degree of sulfonation (DS), the hydrophilicity of the polymer would increase and results in excessive swelling as well as mechanical degradation. In the following subsections, a few examples of sulfonated aromatic hydrocarbon based membrane will be discussed.

2.2.3.1 Sulfonated Poly Ether Sulfone

Sulfonated poly ether sulfone (SPES) is given attention due to its excellent film forming properties, low cost, easy preparation and good mechanical, chemical as well as thermal stability (Wen, et al., 2012). The molecular structure of SPES is shown in Figure 2.2.

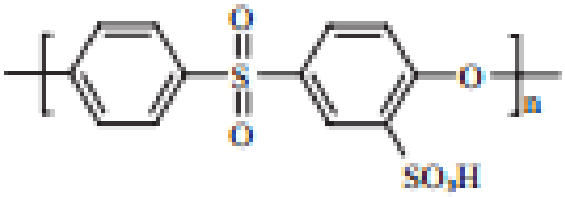


Figure 2.2: Molecular Structure of SPES (Zeng, et al., 2012)

At ambient condition, SPES has proton conductivity of 10 times lower than Nafion while its methanol permeability is about half of Nafion's. SPES can endure harsher temperature than Nafion. Due to this property, there are still efforts to modify SPES polymer although it has extremely low proton conductivity. Table 2.3 summarise the improvement done on SPES based membrane from literature studies.

Based on previous works, although SPES shows promising potential in reducing fuel wastage in DMFC by having lower methanol permeability, however its low conductivity inhibits its chances to be commercialised. Proton conductivity can be elevated at high temperature.

Table 2.3: Performance of SPES Based Composite Membranes

Membranes	Methanol Permeability, *P* ($\times 10^{-7}$ cm^2/s)	Proton Conductivity, σ (S/cm)	Reference
SPES	5.64	0.008	(Miao, et al., 2016)
SPES/Ga_2O_3	5.06	0.004	
SPES/STA	2.50	0.014	(Muthumeenal, John Rethinam and Nagendran, 2016)
SPES/STA-Ppy	1.21	0.009	
SPES/TPA	2.60	0.007	
SPES/TPA-Ppy	1.05	0.006	
SPES/PWA-SiO_2	1.52	0.034	(Chen, et al., 2012)
SPES/Sulfonated GO	1.56	0.006	(Gahlot, et al., 2014)
SPES/PWA-Alginate	2.55	0.030	(Wen, et al., 2012)
SPES/GO	0.49	0.004	(Muthumeenal, et al., 2017)

2.2.3.2 Sulfonated Poly Arylene Ether Ketone

Similar to SPES, sulfonated poly arylene ether ketone (SPAEK) has good thermal and mechanical stability. Moreover, it has better resilience in oxidative and hydrolytic environment after sulfonation (Xiang, et al., 2016). Figure 2.3 depicts the molecular structure of SPAEK.

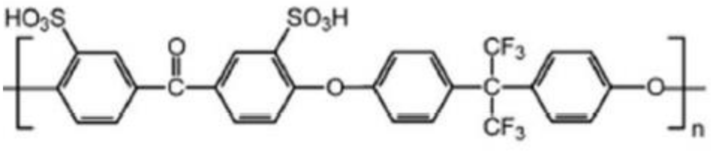


Figure 2.3: Molecular Structure of SPAEK (Kraytsberg and Ein-Eli, 2014)

Proton conductivity and methanol permeability of SPAEK membrane are higher at elevated DS (Xiang, et al., 2016). Two major modifications were commonly done on SPAEK membrane, namely incorporation of additives and cross-linking. Incorporation of additives aims to improve the proton conductivity of SPAEK membranes by using lower DS. On the other hand, cross-linking is used to control the swelling and avoid the dissolution of highly sulfonated polymer (Lin, Zhao and Na, 2010). Literature studies on composite SPAEK membranes are tabulated in Table 2.4.

Table 2.4: Performance of SPAEK Based Composite Membranes

Membranes	**Methanol Permeability, *P* ($\times 10^{-7}$ cm^2/s)**	**Proton Conductivity, σ (S/cm)**	**Reference**
SPAEK	2.66	0.012	(Zhu, et al., 2012)
SPAEK/PAM	0.49	0.004	
SPAEK/PAM-POSS	0.73	0.014	
SPAEK/PANI-PWA	0.46	0.093	(Zhao, et al., 2010)

Generally, proton conductivity of SPAEK based membranes are higher than that of SPES while maintaining good methanol rejection ability. This results in good proton conductivity to methanol permeability selectivity. Research direction on this material is now directed towards using cross-linker to enhance the mechanical stability of this material at high DS whilst lowering the methanol permeability.

2.2.3.3 Sulfonated Poly Ether Ether Ketone

Sulfonated poly ether ether ketone (SPEEK) based membranes are in the limelight of researchers in recent years not only due to their outstanding thermo-chemical properties and lower cost, but most importantly their high proton conductivity which is comparable to Nafion membrane (Intaraprasit and Kongkachuichay, 2011). Furthermore, it is claimed that SPEEK based membrane are durable under fuel cell operating condition with more than 3000 hours of life time (Iulianelli and Basile, 2012). Despite of these advantages, SPEEK based membranes also have low stability at high DS. Figure 2.4 shows the molecular structure of SPEEK polymer.

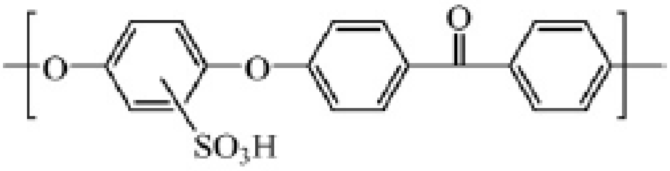


Figure 2.4: Molecular Structure of SPEEK (Colicchio, et al., 2009)

By taking selectivity of membranes into consideration. SPEEK based membranes appear to be the most suitable candidates to be studied as a replacement for Nafion. Therefore, SPEEK polymer will be studied in a more detailed manner in this project.

2.3 Sulfonated Poly Ether Ether Ketone

2.3.1 Sulfonation of PEEK

Sulfonation of PEEK takes place via arylsulfonation which is reversible. Hence, the concentration and amount of sulfonating agent (sulphuric acid) has to be sufficiently high in order to nullify the possibility of desulfonation. Previous works had assumed that the electrophilic substitution occurred during sulfonation is categorised as first type substitution whereby the sulfonic acid group will attach to the aromatic ring without neighbouring carboxyl group due to the higher electron density (as shown in Figure 2.4).

Sulfonic acid group will only be substituted to the remaining two aromatic rings when the first ring is saturated and this is known as second type substitution (Huang, et al., 2001). Determination of DS can be done through several different methods, which are titration method, proton nuclear magnetic resonance or thermogravimetric analysis (TGA) (Banerjee and Kar, 2017; Parnian, Rowshanzamir and Gashoul, 2017).

Before the sulfonation process takes place, PEEK will be dried in order to remove the moisture content. The presence of water in PEEK might dilute the sulfonating agent and affects the reaction kinetics. During sulfonation, nitrogen gas should be purge in order to maintain an inert environment and prevent water contamination. Huang, et al. (2001) showed that nitrogen purged protected sulfonation process would achieve higher ion exchange capacity (IEC) values and hence higher DS. However, according to Sonpingkam and Pattavarakorn (2014), the effect of nitrogen purging during sulfonation is very insignificant. This is due to the high concentration of sulphuric acid used, coupled with pre-drying of PEEK polymer which make the anticipated dilution of sulphuric acid virtually impossible.

The rate of sulfonation is very dependent on the amount of available PEEK. Results from Lee, et al. (2014), Lee, et al. (2013), da Trindade and Pereira (2017) and Sonpingkam and Pattavarakorn (2014) illustrate this point very well as the latter use higher PEEK to sulphuric acid ratio to achieve higher DS.

Apart from that, previous works also proved that the sulfonation time, especially at elevated temperature plays an important role in manipulating the DS of SPEEK polymer (Gong, et al., 2016; Liu, et al., 2015; Sonpingkam and Pattavarakorn, 2014). This can be easily explained by increasing the duration of reaction, more sulfonic acid group can be substituted into the aromatic rings of PEEK, and hence produces SPEEK with high DS. Moreover, the rate of reaction will be accelerated at higher temperature.

2.3.2 Properties of SPEEK Membrane

Although SPEEK membranes have lower proton conductivity than Nafion based membranes, its performance in terms of methanol permeability, water uptake and thermal stability is good enough for it to become a potential substitution of the expensive Nafion. Figure 2.5 illustrates the difference between internal structures of Nafion and SPEEK which leads to their varying properties.

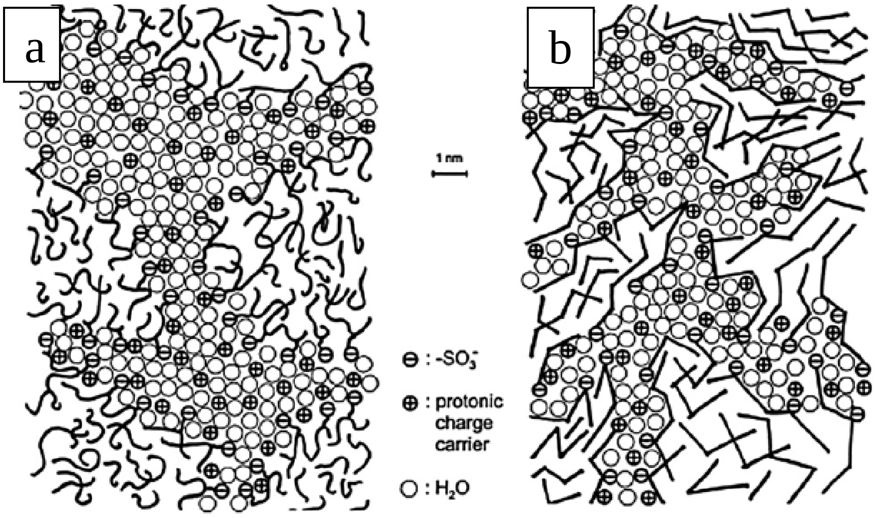


Figure 2.5: Cross-Section Illustrations of (a) Nafion (b) SPEEK (Iulianelli and Basile, 2012)

It can be seen that the channels formed in Nafion is more continuous and well distinguished from the hydrophobic region as compared to SPEEK's. This is because Nafion (perfluorinated sulfonic acid membrane) has a stable perfluorinated backbone (hydrophobic) and sulfonic acid end group (hydrophilic). When the membrane is humidified, water will be captured by the sulfonic acid end group and forms continuous ionic clusters. On the other hand, SPEEK has a less flexible hydrocarbon backbone. This results in difficult separation of hydrophobic and hydrophilic region when the membrane is hydrated. As a consequence, the channels formed in SPEEK membrane is highly branched with numerous dead ends.

By understanding the microstructure properties of Nafion and SPEEK membranes, other characteristics of these two membranes can be deduced. Due the less continuous channels formed in SPEEK, proton cannot be transported easily by vehicle diffusion across the membrane which ends up in low proton conductivity. Moreover, the highly branch ionic channels results in higher interface between hydrophilic and hydrophobic region and this increases the distance between neighbouring sulfonic acid groups (Iulianelli and Basile, 2012). This increases the difficulty for proton transport through hopping mechanism and contributes to the low proton conductivity of SPEEK membrane (Xie, et al., 2015). Nevertheless, highly branched ionic channels of SPEEK can help to block the permeation of methanol molecules across the membrane (Iulianelli and Basile, 2012).

As stated earlier, the difference in hydrophilicity between the hydrophilic and hydrophobic ends of SPEEK membrane is smaller than that of Nafion. This enables the hydrophilic region of the SPEEK to expand into the hydrophobic region. On contrary, the relatively more stable Nafion, the hydration is only limited in the hydrophilic domain (Mayahi, et al., 2013). As a result, the water uptake of SPEEK will be higher than Nafion.

The stability of the membrane is maintained by the presence of hydrophobic backbone. In order to increase the water uptake of SPEEK, more sulfonic acid groups have to be attached to the hydrocarbon backbone (Higher DS). This will reduce the hydrophobic domain through second type substitution (Huang, et al., 2001) and results in undesired deterioration of mechanical stability. Therefore, it is more favourable for the membrane to be used at low humidity level and high temperature. Researchers are seeking to increase the proton conductivity by introducing more ion exchange sites.

In order for the membrane to be used at high temperature, the thermal stability of the membrane is an imperative factor. The works of Parnian, Rowshanzamir and Gashoul (2017) as well as Banerjee and Kar (2017) showed that polymeric backbone of SPEEK had better thermal stability than Nafion due to the presence of aromatic chains. However, the increase in DS will result in the deterioration of thermal stability due to the abundance of sulfonic acid group which can be degraded at lower temperature. Besides, it was also reported that the glass transition temperature ($T_{g)}$ of SPEEK membranes was higher than that of Nafion membranes (Rowshanzamir, et al., 2015). Sulfonic acid pendant groups increased the bulkiness of the polymer and hence restricted its segmental mobility. It is harder to alter the bulky microstructure of SPEEK polymer and only elevated temperature can affect the membrane’s performance by changing its structure.

2.3.3 Modifications of SPEEK Membrane

Several attempts had been done in order to improve the performance of SPEEK membranes, either by adding organic, inorganic additives or fabricating polymeric blend membranes with other polymers.

2.3.3.1 Organic Modifications

Organic additives are generally carbon based materials which can help to improve the performance of SPEEK membrane. From literature studies as presented in Table 2.5, the most commonly used organic additive is graphene oxide (GO) (Jiang, Zhao and Manthiram, 2013; Yin, et al., 2016; Heo, Im and Kim, 2013; Dai, et al., 2014; He, et al., 2014). This is due to the property of GO which has unique two dimensional layered structure with ample functional groups to promote separation of hydrophilic and hydrophobic domains within the polymer. Hydrophilic nature of GO can also help to improve water retention in SPEEK for vehicle diffusion while GO itself also provides another transport pathway for proton. Furthermore, the strong interfacial interaction between GO and SPEEK helped to improve the mechanical properties of the composite membrane.

Addition of only GO itself cannot improve the performance of SPEEK membrane by much. Hence, modification or functionalisation was done on GO in order for it to become a more effective additive. Jiang, Zhao and Manthiram (2013) studied the effect of 3-mercaptopropyl trimethoxysilane (MPTS) modification on GO additive. The results showed that presence of modified GO successfully reduce the dimension of ionic clusters and sulfonic acid groups on GO which provided alternative paths for proton transport, thereby improving the selectivity of SPEEK membrane.

Another interesting material to be studied is carbon based nanoparticles such as carbon nanotube (CNT) and carbon nanofiber (CNF). Their characteristic dimension with unique aspect ratio provide good mechanical strength to improve the performance of SPEEK membrane. Moreover, both CNT and CNF are good electrical conductors which are very suitable to be used in fuel cell industry. However, poor dispersion and leachability remain as the major problems of the application of this class of additive (Gong, et al., 2016; Liu, et al., 2017b).

In addition, biological compounds are another class of organic materials that are used in modification of SPEEK membranes. This will be a great effort in promoting green chemistry and engineering. The attempts of incorporating adenosine triphosphate (ATP) (Yin, et al., 2015a), histidine (Yin, et al., 2016) and dopamine (He, et al., 2014) as part of additive had showed promising outcomes and this may be the research direction in the future.

Table 2.5: SPEEK Composite Membranes with Organic Additives

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/BPO_4-CNT	0 – 5	Optimum loading = 2 % Proton conductivity at room temperature = 0.0418 S/cm Maximum power density in H_2/O_2 cell = 340 mW/cm^2 at 80 ℃ and 100 % RH	(Gong, et al., 2016)
SPEEK/g-C_3N_4	0 – 2.5	Optimum loading = 0.5 % Proton conductivity at room temperature = 0.0786 S/cm Methanol permeability = 5.035×10^{-7} cm^2/s Improved methanol mechanical stability, methanol resistance and proton conductivity Thermal stability is maintained Maximum power density H_2/O_2 cell = 266.24 mW/cm^2 at 45 ℃	(Gang, et al., 2016)
SPEEK/cSMM	4	Optimum DS = 60 % Proton conductivity at room temperature = 0.0203 S/cm Methanol permeability = 1.59×10^{-9} cm^2/s Slight reduction in thermal stability Performance strongly affected by DS of SPEEK polymer	(Mayahi, et al., 2013)
SPEEK/SSi-GO	0 – 8	Optimum loading = 5 % Proton conductivity at 65 ℃ = 0.16 S/cm Methanol permeability at 65 ℃ = 8.3×10^{-7} cm^2/s Better performance than Nafion 112	(Jiang, Zhao and Manthiram, 2013)

Table 2.5 (continued)

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/GO-histidine	0 – 6	Optimum loading = 4 % Proton conductivity at room temperature (100% RH) = 0.0694 S/cm Methanol permeability (2 M methanol) = 1.35×10^{-7} cm^{2}/s Improve thermal and mechanical stability as well as proton conductivity	(Yin, et al., 2016)
SPEEK/SGO	0 – 10	Optimum loading = 7 % Proton conductivity at 80 ℃ = 0.0078 S/cm Methanol permeability at 80 ℃ = 3.33×10^{-7} cm^{2}/s Improved proton conductivity, methanol resistance and mechanical stability Thermal stability is maintained	(Heo, Im and Kim, 2013)
SPEEK/ATP	0 – 20	Improved thermal stability Enhanced proton transport by Grotthüss mechanism	(Yin, et al., 2015a)
SPEEK/IMCs-PMAA	0 – 20	Enhanced proton conductivity by vehicle diffusion and Grotthüss mechanism Improved proton conductivity at low humidity Improved methanol resistance	(Yang, et al., 2015)
SPEEK/GO	0 – 5	Highest proton conductivity achieved at 1 % loading (0.0153 S/cm) Improved thermal and mechanical stability	(Dai, et al., 2014)
SPEEK/DGO	0 – 10	Enhanced proton conductivity by Grotthüss mechanism Improved mechanical and thermal stability	(He, et al., 2014)

Table 2.5 (continued)

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/IMCs SPEEK/IMCs-HPW	0 – 15	Improved proton conductivity, methanol resistance and dimensional stability Enhanced water uptake and retention properties Addition of HPW increase proton conductivity and methanol permeability	(Wu, et al., 2014a)
SPEEK/SiO_2-CNT	0 – 10	Improved methanol resistance at the expense of proton conductivity	(Cui, et al., 2015a)
SPEEK/ENR-50	0 – 2.5	Optimum loading = 0.5 % Improved methanol resistance Reduced mechanical strength ENR did not help to enhance proton conductivity High amount of additives caused agglomeration	(Wan Mohd Noral Azman, et al., 2017)

2.3.3.2 Inorganic Modifications

Inorganic materials are also often introduced into SPEEK polymer to improvise the membrane properties in a more economic and safe manner (Iulianelli and Basile, 2012). Table 2.6 lists the recent studies on the modification of SPEEK polymer using inorganic materials' addition.

The most common inorganic modification of SPEEK membrane is the introduction of inorganic oxide such as silica (SiO_2), titania (TiO_2) and zirconia (ZrO_2). This is due to their hygroscopic property that can boost the water retention capacity of composite membrane especially at high temperature (Ismail, Othman and Mustafa, 2009). However, proton conductivity of membrane with such modification would be sacrificed as the fillers itself has low conductivity and their presence would dilute the proton transport site (Xu, et al., 2011). Therefore, recent researches focus on modification of the filler itself before incorporating it into the polymer matrix. One of the simplest modification is sulfonation (Xu, et al., 2011) or acid functionalisation (Wu, et al., 2015) of inorganic oxides to increase the proton transport sites.

Besides, some researchers also tried to combine organic and inorganic modifications to improve the membrane's performance. This was done through the alteration of additive by organic modification which was discussed in the works of Yin, et al. (2015b) as well as Gosalawit, Figoli and Chirachanchai (2010). The noble proton conductivity provided by organic portion of the additive (amino acid groups or carboxyl group) coupled with the methanol rejection of the inorganic fraction would help to boost the overall selectivity of SPEEK composite membrane.

Recent works claimed that the presence of continuous channels is vital for proton transport. Hence, halloysite nanotube (HNT), a two layered aluminosilicate clay was introduced to modify the internal structure of SPEEK membrane. It has good thermal and mechanical properties as well as high surface area covered by functional groups to improve its hydrophilicity. Further tweaks done on HNT such as coating of dopamine and sulfonation (Liu, et al., 2016; Zhang, et al., 2013) yielded improved performance, where higher proton conductivity was achieved at lower humidity level.

In summary, adding inorganic fillers normally aims to improved thermal, mechanical, methanol rejection and water retention capacity of SPEEK membrane. As this will result in degradation of proton conductivity, functionalisation of the additive becomes essential to achieve good selectivity of SPEEK composite membrane.

Table 2.6: SPEEK Composite Membranes with Inorganic Additives

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/Phosphosilicate	20 – 40	Optimum loading = 30 % Maximum power density in H_2/O_2 cell = 449.9 mW/cm^2 at 60 °C Proton conductivity at room temperature and 95 % RH = 0.0251 S/cm Proton conductivity very dependent on humidity (vehicle diffusion) Improved proton conductivity, mechanical, thermal and dimensional stability	(Xie, et al., 2015)
SPEEK/TC SPEEK/TNC	0 – 25	Optimum loading = 15 % for both fillers Proton conductivity at room temperature = 0.0624 S/cm (TC) and 0.0470 S/cm (TNC) Methanol permeability (2 M methanol) = 5.82×10^{-7} cm^2/s (TC) and 5.32×10^{-7} cm^2/s (TC) Selectivity of TC filler is better than TNC	(Yin, et al., 2015b)
SPEEK/TOL SPEEK/TOLP	0 – 8	Optimum loading = 6 % (TOLP) Proton conductivity at 65 °C and 100 % RH = 0.334 S/cm Methanol permeability = 5.4×10^{-7} cm^2/s Improved proton conductivity, methanol resistance, thermal and mechanical stability Selectivity of TOLP filler is better than TOL	(Wu, et al., 2015)
SPEEK/TiO_2-SO_3H	0 – 15	Improved proton conductivity, methanol resistance and dimensional stability	(Xu, et al., 2011)

Table 2.6 (continued)

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/Ferrierite Zeolite	0 – 20	Improved methanol resistance at the expense of proton conductivity	(Auimviriyavat, Changkhamchom and Sirivat, 2011)
SPEEK/MBS	0 – 20	Optimum loading = 10 % Proton conductivity at 40 ℃ and 95 % RH = 0.019 S/cm Methanol permeability = 4×10^{-7} cm^2/s Improved methanol resistance, thermal stability and water retention capacity Maintain good proton conductivity at low humidity and high temperature	(Xie, Cho and Kim, 2011)
SPEEK/OMB	0 – 20	Optimum loading = 15 % Proton conductivity at 80 ℃ = 0.079 S/cm Methanol permeability = 4.6×10^{-7} cm^2/s Maximum power density in DMFC = 56 mW/cm^2	(Cho, Luu and Kim, 2010)
SPEEK/OMMT	0 – 5	Maximum proton conductivity achieved by 3 % loading at 90 ℃ (0.056 S/cm) Improved proton conductivity, methanol resistance and thermal stability	(Gosalawit, Figoli and Chirachanchai, 2010)
SPEEK/AFT	0 – 10	Optimum loading = 7.5 % Proton conductivity at room temperature = 0.066 S/cm Maximum power density in H_2/O_2 cell = 230 mW/cm^2 at 80 ℃ and 90 % RH	(Salarizadeh, Javanbakht and Pourmahdian, 2017)

Table 2.6 (continued)

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/TiO_2	0 – 12	Improved conductivity and swelling resistance	(Dutra, Santos and Gomes, 2014)
SPEEK/MMT-STA	0 – 50	Improved proton conductivity and methanol resistance MMT stabilised STA to prevent leaching	(Mohtar, Ismail and Matsuura, 2011)
SPEEK/ZrO_2	0 – 10	Improved proton conductivity above 80 ℃ Improved thermal and mechanical stability Enhanced oxidative and hydrolytic stability	(Gashoul, Parnian and Rowshanzamir, 2017)
SPEEK/AIT	0 – 3	Highest proton conductivity achieved at 2 % loading (0.12 S/cm at 80 ℃) Maximum power density in H_2O_2 cell = 204 mW/cm^2 at 80 ℃ and 90 % RH Improved proton conductivity, oxidative stability, mechanical and thermal stability	(Salarizadeh, et al., 2016)
SPEEK/HNT SPEEK/SHNT SPEEK/DHNT	0 – 15	Good interfacial compatibility and enhance phase separation with bigger hydrophilic domain in SPEEK/SHNT Enhanced proton conductivity especially at low RH	(Liu, et al., 2016)
SPEEK/IT	0 – 2	Highest proton conductivity achieved at 1 % loading (0.048 S/cm at room temperature) Maximum power density in H2/O_2 cell = 143 mW/cm^2 at 80 ℃ Improved mechanical stability Effect of loading on thermal properties is insignificant High loading is not possible due to agglomeration of filler	(Salarizadeh, Javanbakht and Pourmahdian, 2015)

Table 2.6 (continued)

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/DHNT	0 – 25	Reduction in water uptake and membrane swelling Hinder proton transport by vehicle diffusion but enhance Grotthüss mechanism Overall improvement in proton conductivity	(Zhang, et al., 2013)
SPEEK/TiO_2 SPEEK/TiO_2-RSO_3H	0 – 10	Improved methanol resistance Regained proton conductivity lost by adding ceramic oxide through functionalisation of TiO_2 (introducing propylsulfonic acid group) Reduce water self-diffusion due to higher reticulation of polymer matrix that increased the tortuosity of transport pathway (favoured Grotthüss mechanism) Smaller ionic channels formed with better selectivity of water diffusion than methanol diffusion	(de Bonis, et al., 2016)
SPEEK/$SrZrO_3$ SPEEK/s$SrZrO_3$ SPEEK/$SrZrO_3$-TiO_2 SPEEK/s$SrZrO_3$-TiO_2	0 – 4	Addition of hollow cuboid and core shell $SrZrO_3$/$SrZrO_3$-TiO_2 formed by hydrothermal and chemical bath techniques Improved thermal and oxidative stability More ion exchange sites available in perovskite oxide resulted in higher proton conductivity Sulfonation and TiO_2 increase conductivity due to increase in hydrophilicity Methanol permeability reduced by addition of nano-fillers Highest proton conductivity achieved by 3 % SPEEK/s$SrZrO_3$-TiO_2 (0.12 S/cm at 80 °C and 100 % RH) Corresponding methanol permeability = $9.03 \times 10-7$ cm^2/s	(Gnana kumar and Manthiram, 2017)

Table 2.6 (continued)

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/TiNF	0 – 1.5	Improved thermal stability Improved proton conductivity Improved methanol resistance Improved tensile strength Optimum loading = 1 wt% Proton conductivity at room temperature = 0.0376 S/cm Methanol permeability (1 M methanol) = 2.1 $\times 10^{-7}$ cm^2/s Maximum current density = 423.6 mA/cm^2 Maximum power density = 57.1 mW/cm^2	(Dong, et al., 2017a)
SPEEK/CeO_2	0 – 10	Improved oxidative stability Improved durability Optimum loading = 5 wt% Performance similar to pristine SPEEK membrane but have more superior durability	(Parnian, et al., 2018)

2.3.3.3 Polymeric Blend Membranes

Unlike Nafion, SPEEK rarely combines with other polymers to form polymeric blend membrane. The purpose of adding polymer additive is to enhance the mechanical strength of PEM but at the same time its proton conductivity is sacrificed. Instead of fabricating polymeric blend membrane, foreign polymers are preferred to be coated on the surface of SPEEK membrane as methanol barrier, proton conductivity enhancer and as a protective layer (Xi, Dai and Yu, 2015; Baicea, et al., 2013; Ren, et al., 2014). Table 2.7 lists some of the polymeric blend membrane based on SPEEK and their performances.

Various methods were used to fabricate SPEEK based polymeric blend membrane. Coating of polymer additive on the surface of pristine SPEEK membrane can be done by immersing the membrane into a solution of polymer additive. The thickness of coating layer could be controlled by varying the immersion time (Xi, Dai and Yu, 2015). Besides, Baicea, et al. (2013) demonstrated an alternative method for coating of polymer additive. In this work, aniline was sprayed on the surface of pristine SPEEK membrane. In-situ polymerisation was induced by dipping the membrane into iron (III) chloride solution and concentrated hydrochloric acid. In the same work, polyaniline (PANI) was also coated by first immersing pristine SPEEK membrane into hydrochloric acid solution, followed by the introduction of p-phenylenediamine by dipping the pre-treated membrane into it. Potassium persulphate and hydrochloric acid were added to initiate the polymerisation of p-phenylenediamine into PANI.

Table 2.7: Polymeric Blend SPEEK Based Membranes

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/Poly(AA-co-4vlm)	50	Improved ion exchange capacity, hydrophilicity and surface smoothness of membrane Reduced proton conductivity	(Jithunsa, et al., 2011)
SPEEK/HP SPEEK/HPS SPEEK/HPSS	0 – 15	SPEEK/HPSS achieved better proton conductivity and water retention capacity Highest proton conductivity achieved at 15 % HPSS composition (0.33 S/cm at 75 ℃ and 100 % RH) Improved methanol resistance	(Zhang, et al., 2015b)
SPEEK/PVdF	0 – 30	Reduction in proton conductivity Improved mechanical stability	(Li, et al., 2013)
SPEEK/POP	0 – 3	Improved mechanical and thermal stability Improved methanol resistance Reduction in proton conductivity	(Peera, et al., 2013)
SPEEK/PVdF-co-HFP SPEEK-SPVdF-co-HFP	0 – 25	Selectivity of SPVdF additive is better than PVdF Optimum loading = 20 wt% Proton conductivity at room temperature = 0.033 S/cm Methanol permeability = 2.11×10^{-7} cm^2/s Maximum power density in DMFC = 43.02 mW/cm^2 Maximum current density = 215.3 mA/cm^2 Improved methanol resistance Reduction in proton conductivity Improved mechanical and oxidative stability	(Bagheri, et al., 2016)

Table 2.7 (continued)

Membrane	Additive Loading (wt%)	Remarks	Reference
SPEEK/BPPO	0 – 40	Improved methanol resistance Optimum loading = 20 wt% Maximum power density in DMFC = 23.9 mW/cm^2 at 60 °C and 10 M methanol concentration (four times higher when compared to 30 °C) A membrane suitable for high temperature and methanol concentration operation	(Liu, et al., 2017c)
SPEEK/PPy	0 – 15	Improved thermal and dimensional stability Improved methanol resistance Reduced proton conductivity	(Mahanwar and Bhattad, 2019)

2.3.4 Fabrication of SPEEK Based Membrane

2.3.4.1 Fabrication Methods

The most common method to fabricate membrane is the solution casting method. SPEEK polymer is dissolved in various kinds of solvent such as DMAc, NMP, DMF and DMSO and is casted by using casting knife on glass plate or glass dish. Different polymer concentration is used to alter the viscosity of the polymer solution, thereby changing the properties of membrane.

Besides the conventional solution casting method, a new approach known as electrospinning process is introduced for SPEEK membrane fabrication. This process produces nanofibers (aligned or random orientation) from concentrated polymer solution. The simplicity, straightforwardness and cost effectiveness of this process attract the attention of researchers to study on the properties of electrospun SPEEK membrane (Hasbullah, Sekak and Ibrahim, 2016). In addition, formation of uniform ionic alignment and tortuous pathway helps to boost the proton conductivity and methanol resistance of the membrane (Junoh, et al., 2015). Organisation of hydrophilic and hydrophobic region can be controlled and designed through the modification of electrospun material, volume fraction of the nanofibers and the experimental parameters such as applied voltage, distance, flow rate and frequency (Sood, et al., 2016). This was illustrated by Sadrjahani, Gharehaghaji and Javanbakht (2017) who claimed that SPEEK nanofiber would have higher conductivity when the orientation was aligned due to the ordered proton transport pathway available.

Aligned nanofiber also possessed more amorphous region, thus allowed higher water uptake to promote proton mobility.

Another method to fabricate SPEEK membrane is the phase inversion method. Exchange of solvent assists in the formation of porous membrane. By using phase inversion method, additive would attach on the pore surface to ensure high accessibility (Narayanaswamy Venkatesan and Dharmalingam, 2017). Several techniques were employed in phase inversion method. In the work of Baicea, et al. (2011), SPEEK was fabricated by casting the PEEK-sulphuric acid solution on a glass plate followed by immersion in water for solvent substitution. On the other hand, Narayanaswamy Venkatesan and Dharmalingam (2017) dissolved solid PEEK in NMP and 35 % hydrochloric acid was used to precipitate the membrane.

2.3.4.2 Effects of Casting Solvent

The common solvents used for the fabrication of SPEEK membrane include DMAc, DMF, NMP and DMSO. Utilisation of different solvent would result in different membrane properties due to the nature of the solvent itself and the interaction of solvent with polymer. Jun, Choi and Kim (2012) claimed that DMAc and DMF interacted strongly with sulfonic acid group of SPEEK, thereby reducing the hydrophilicity of the membranes. This also resulted in the lower proton conductivity of the casted membranes as compared to the membranes formed using NMP and DMSO as solvent. However, stronger interaction between solvent and polymer can improve the membrane’s breaking strength as confirmed by Xi, et al. (2015). Luu, et al. (2009) compared SPEEK membranes fabricated using DMAc and NMP solvents. The work asserted that DMAc casted membrane had more compact structure (thinner with smaller ionic clusters) which resulted in lower proton conductivity and methanol permeability. However, when the membranes are tested in DMFC, DMAc casted membrane yielded better performance due to its excellent dimensional stability which helped to avoid swelling unlike NMP casted membrane.

Different solvent has different volatility and under the same drying condition, the residual solvent within the polymer will show variation. Liu, et al. (2017a) studied the role of solvent as well as the amount of residual solvent on the structure and performance of SPEEK membrane. It was reported that apart from solvents’ boiling point, SPEEK with higher DS would retain more solvent as explained by the interaction of solvent with sulfonic acid groups.

Amount of residual solvent within the membrane also has immediate effect on the properties of the membrane. Higher amount of solvent, which is hydrophilic in nature will increase the size of ionic clusters, thus provides possibility on the enhancement of proton conductivity (Liu, et al., 2017a). Besides, water uptake of SPEEK membrane also increase with the amount of residual solvent. This is due to the fact that more residual solvent will lead to larger hydrophilic domain to bind with more water. Proton conductivity of SPEEK membrane will increase with water uptake until a certain point where hydrophilic region is too large for effective proton transport. High amount of water actually dilutes the concentration of ion exchange sites.

2.3.4.3 Incorporation of Additives

Additives are incorporated into SPEEK membranes using numerous methods, depending on the properties of the additives as well as the purpose of adding them. Most commonly used approaches include direct dispersion of solid nanoparticles in the polymer solution, in situ sol-gel process and surface modification by layer(s) of coating on the membrane.

Direct dispersion of solid nanoparticles is popular among researchers due to the ease of membrane preparation. This method is normally applied when the additives (commercial or synthesised) are inorganic oxides or nano-sized organic compounds such as CNT and GO. Solid additive is either added directly into the polymer-solvent solution for stirring (Gong, et al., 2016; Liu, et al., 2017b) or dispersed in solvent prior mixing with the polymer (Xu, et al., 2011; Gashoul, Parnian and Rowshanzamir, 2017).

In situ sol-gel reaction is utilised in two ways to fabricate composite membranes. Precursor of inorganic oxides such as tetraethyl orthosilicate (TEOS) and tetrabutyl titanate (TBT) are mixed with water and alcohol for hydrolysis and condensation reaction. The reacted mixture is added into the polymer solution which is subsequently casted (Yin, et al., 2015b; Wu, et al., 2015). Alternatively, a pristine membrane can be fabricated without incorporation of any additives. Then, the membrane is swelled in methanol solution followed by soaking in precursor-water solution to allow in situ sol-gel reaction (Ke, et al., 2012; Wang, et al., 2014; Huang, Yu and Lin, 2017). This method is further applied in the incorporation of ionic liquid as presented by the work of Zhang, et al. (2015a).

Surface modification is usually applied when layer(s) of additive polymer is coated on the membrane surface. This technique serves to protect the membrane from harsh operating environment, to act as a blocking agent (Xi, Dai and Yu, 2015) and to enhance the performance of the base membrane (Baicea, et al., 2013). Some researchers applied this technique into the preparation of layer-by-layer membrane where regular packing of polymer is made possible without compromising the mobility of proton through the membrane (Meemuk and Chirachanchai, 2016). However, unevenness of coating applied will reduce the effect of coating and this remains to be one of the challenges that has to be overcome (Ren, et al., 2014).

2.4 Electrochemical Degradation of Proton Exchange Membrane

2.4.1 Mechanism of Electrochemical Degradation

Electrochemical stability is an important consideration to be taken into account when designing a promising PEM. Parnian, Rowshanzamir and Gashoul (2017) explained that free radicals formed in the operation of DMFC could attack the polymeric backbone of the membrane which leads to degradation of polymer and loss of membrane’s performance and integrity.

Since the membrane is located within the MEA in DMFC, it will be in contact with both the anode and cathode sides. Zhang and Mukerjee (2006) proposed two plausible mechanisms to produce free radicals in hydrogen fuel cell at anode and cathode, initiated by hydrogen and oxygen, respectively. The reactions occur at the anode and cathode are as shown in Equation 2.1 to Equation 2.8:

At anode (“M” for metal):

$$H_2 \rightarrow 2H\bullet \tag{2.1}$$

$$H\bullet + O_2 \rightarrow HOO\bullet \tag{2.2}$$

$$HOO\bullet + H^+ \rightarrow H_2O_2 \tag{2.3}$$

$$M^{2+} + H_2O_2 \rightarrow M^{3+} + \bullet OH + OH^- \tag{2.4}$$

$$M^{3+} + H_2O_2 \rightarrow M^{2+} + \bullet OOH + H^+ \tag{2.5}$$

At cathode (“M” for metal):

$$O_2 + H^+ + 2e^- \rightarrow H_2O_2 \tag{2.6}$$

$$M^{2+} + H_2O_2 \rightarrow M^{3+} + \bullet OH + OH^- \tag{2.7}$$

$$M^{3+} + H_2O_2 \rightarrow M^{2+} + \bullet OOH + H^+ \tag{2.8}$$

The presence of free radicals will attack the polymeric backbone of PEM. Chen and Fuller (2009) further divided the degradation into two main types, namely main chain unzipping process and side chain scission process. Available free radicals will attack any terminal bond with hydrogen atom in the polymeric backbone. For polymers with aromatic ring backbone, carbon ortho to alkyl substitution is the most vulnerable point. This is due to the blocked para position and also the presence of sulfonic acid group which is usually substituted at meta direction. This also explains the inversed relationship between DS and oxidative stability of a polymer (Parnian, Rowshanzamir and Gashoul, 2017). In SPEEK polymer, the circumstance is more complex where electrophilic nature of free radicals' attack could happen at the α-carbon of aromatic group, ether links or branching points. The situation could be worsen at low humidity and temperature above 90 °C (Rowshanzamir, Peighambardoust and Amirkhanlou, 2013). The overall degradation process can be summarised in Equation 2.9 to Equation 2.13 ("P" for polymer):

$$PH + HO\bullet \rightarrow P\bullet + H_2O \tag{2.9}$$

$$P\bullet + O_2 \rightarrow PO_2\bullet \tag{2.10}$$

$$PO_2\bullet + PH \rightarrow POOH + P\bullet \tag{2.11}$$

$$PH + \bullet OOH \rightarrow P\bullet + H_2O_2 \tag{2.12}$$

$$PH + \bullet OOH \rightarrow P\bullet + \bullet OOH + H\bullet \tag{2.13}$$

Measurement of oxidative degradation of PEM is usually conducted using ex-situ Fenton test (Rowshanzamir, Peighambardoust and Amirkhanlou, 2013; Parnian, Rowshanzamir and Gashoul, 2017; Taghizadeh and Vatanparast, 2016). This method mimics the oxidative environment of DMFC by allowing the redox reaction between the low concentration of iron (II) ions (reducing agent) and hydrogen peroxide (oxidising agent). Formation of free radicals at the end of reaction will degrade the membrane. Some literatures used Fenton's reagent without iron (II) ions to slow down the formation of free radicals, thus making it more suitable for membrane which is more susceptible to radicals' attack (Fu, et al., 2008; Liu, et al., 2010). Residual weight of the membrane is used as a parameter to estimate the stability of the membrane in oxidative environment.

2.4.2 Mitigation of Electrochemical Degradation

Efforts were done in order to improve the electrochemical or oxidative stability of PEM for DMFC. He, et al. (2016) attempted to incorporate aliphatic sulphide structure into PBI based membrane through poly-condensation process. According to the authors, sulphide can act as an antioxidant for a specific period of time to improve the durability of the membrane. The confirmation was done using Fenton’s test complemented with FTIR analysis. The authors proposed a mechanism for such antioxidative ability. The presence of oxidative radicals converted sulphide into sulfoxide. The quenching of oxidative radicals prevented the immediate destruction of base polymeric backbone being attacked for limited period. In the said study, imidazole ring was reported lost from the FTIR spectrum, suggesting that the polymeric backbone started to degrade after the complete transformation of all sulphide into sulfoxide groups.

Another simpler approach is to incorporate inorganic oxides, which are believed to be a scavenger to oxidative radicals. Rowshanzamir, Peighambardoust and Amirkhanlou (2013) added caesium salt of PWA with platinum catalyst into SPEEK membrane for hydrogen fuel cell application. It was asserted that the presence of such catalyst could capture hydrogen peroxide and hydrogen, subsequently converting them into water to prevent the formation of oxidative radicals. The idea was supported by results from ex-situ Fenton’s test and in-situ open circuit voltage, where different catalyst loading will affect the durability of membrane. Nevertheless, the electrochemical stability of SPEEK composite membrane was still incomparable with Nafion 117 membrane.

In another study, zirconia was used to decompose hydrogen peroxide to avoid the formation of free radicals. Increasing amount of zirconia was proved to be feasible where the degradation time of composite membrane was increased (Gashoul, Parnian and Rowshanzamir, 2017; Taghizadeh and Vatanparast, 2016).

Moreover, ceria was also employed to reduce the concentration of hydroxyl radicals by reducing it into hydrogen and water with available protons (Schlick, et al., 2016). The effects of nanoparticles concentration and size were investigated. It was found that at equal concentration, the activity of smaller nanoparticles was lower. This was explained by the ineffective dispersion and agglomeration of small nanoparticles which resulted in the ineffective contact of hydroxyl radicals with ceria. This also suggested that the conversion of hydroxyl radicals into water was a diffusion-limited process. Although ceria showed promising reduction in hydroxyl radicals, oxidised ceria with higher oxidation state could convert hydrogen peroxide into hydroperoxyl radicals which might also degrade the polymer (Schlick, et al., 2016).

Feasibility of silica nanoparticles as an antioxidant was also investigated by several researchers (Ren, et al., 2013; Chakrabarty, Singh and Shahi, 2012; Zhang, et al., 2010). It was reported that hydrophilic domains of polymer became compact due to cross-linking of silica with the polymer. This prevented the free radicals from penetrating into the siloxane containing polymer within their short lifetime. Higher amount of silica could increase the degradation time of polymer. However, a loading of exceeding the optimum value would result in aggregation of nanoparticles which might reduce the effectiveness to resist oxidative degradation.

2.5 Heteropoly Acids

Heteropoly acids (HPA) are inorganic crystals which show high thermal stability and proton conductivity. When in hydrated condition, HPA usually has two different structures, namely Keggin unit (primary structure) and Bravais lattices (secondary structure) as shown in Figure 2.6. The Keggin unit is a tetrahedral structure of oxygen atoms surrounded by 12 oxygen atoms. These oxygen atoms are bound with tungsten or molybdenum in octahedral position. Keggin units are arranged in lattices to form the secondary structure through the formation of water bridges (Tian and Savadogo, 2005). The most common types of HPA are phosphotungstic acid (PWA), silicotungstic acid (SiWA) and phosphomolybdic acid (PMA).

Incorporation of HPA is found to be useful in improving proton conductivity as well as thermal stability of PEM. It is crucial when addition of inorganic oxides deteriorates the proton conductivity of composite membrane.

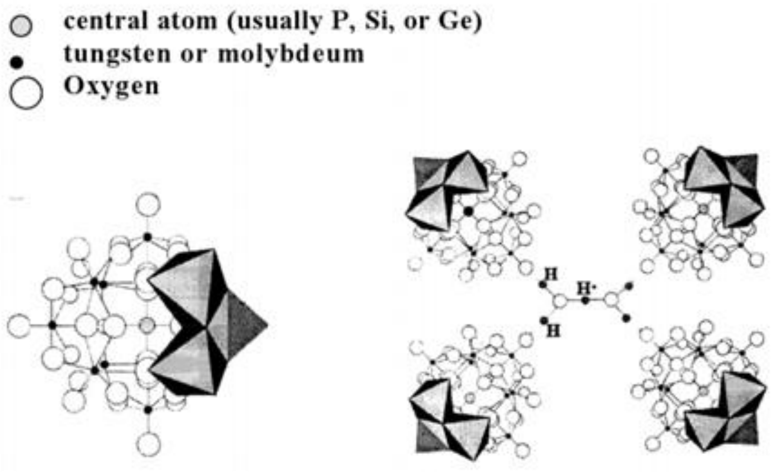


Figure 2.6: Primary (left) and Secondary Structure (right) of HPA (Tian and Savadogo, 2005)

Numerous studies had been done to investigate the doping effect of HPA in SPEEK membrane. Narayanaswamy Venkatesan and Dharmalingam (2017) concluded that the optimum loading of SiWA in SPEEK membrane is 7.5 wt% where the said membrane achieved highest water uptake and proton conductivity. SiWA was also proven to have better ability in enhancing proton conductivity and bound water of PEM as compared to PWA (Gao and Lian, 2010). Performances of PWA, SiWA and PMA were compared and it was found that SPEEK/sulfosuccinic acid membrane doped with SiWA achieved the highest water sorption, proton conductivity, thermal stability and tensile strength and hence the best DMFC performance. However, doped SiWA experienced high level of undesirable leaching (Bhat, et al., 2010).

In view of such circumstance, Bhat, et al. (2010) attempted to improve the stability of HPA by partially substituting the protons of HPA with caesium ions. The stability of PWA and SiWA was improved dramatically. Oh, et al. (2010) investigated on caesium salt of HPA and they had confirmed the enhancement in additive stability and proton conductivity with slight compromise in thermal stability. Caesium salt of SiWA doped SPEEK membrane had slightly higher power density (247 mW/cm^2) as compared to the PWA caesium salt (245 mW/cm^2). Osipov, et al. (2017) also proved that Nafion membrane with caesium salt of SiWA had higher proton conductivity than that of PWA as well as rubidium salt of SiWA. Similar study also reported by using caesium salt of PWA as a support for platinum catalyst in order to reduce the reactant gas crossover in PEMFC while maintaining high proton conductivity. Stability of supported PWA in the form of caesium salt was once again proven using hydrolytic stability test, where the percent weight loss was almost negligible as compared to SPEEK/PWA composite membrane (Peighambardoust, et al., 2011). Aluminium salt of PWA was also used as an initiative to stabilise the additives within the polymer matrix and was proven to be successful (Banerjee and Kar, 2016).

However, preparation of HPA salt requires complex chemical reactions which is less practical in nature. Therefore, alternative method to immobilise HPA is preferred such as the utilisation of supports. Organic and inorganic compounds were used as supports for HPA besides playing their respective role in reducing methanol permeability and improving proton conductivity (Lee, et al., 2014; Ismail, Othman and Mustafa, 2009; Zhang, Jiang and Liu, 2011; Mohtar, Ismail and Matsuura, 2011). These efforts not only helped to solve the leaching issue of HPA, at the same time, HPA can be used to regain the proton conductivity lost when incorporating the additives.

In addition, organic materials such as graphitic carbon nitride (g-C_3N_4) nanosheet and carbon nanotubes (Dong, et al., 2017b; Li, et al., 2017) were also used as a support to anchor highly unstable HPA. Weight loss due to leaching was greatly reduced in conjunction with the improvement in proton conductivity and methanol resistance. SPEEK and HPA can bind g-C_3N_4 through hydrogen bonding and the acid-base interaction promoted dissociation of sulfonic acid group while reducing the distance for proton transport effectively (Dong, et al., 2017b).

Self-anchoring is another methodology used to stabilise HPA in the polymer matrix. Wu, et al. (2016) performed the anchoring of PWA into chitosan membrane with sub-microspheres formed by dispersing polyethylene glycol-block-polypropylene glycol-block-polyethylene glycol into the polymer solution. Removal of the soft template would allow PWA to occupy the sub-microspheres and interact with the neighbouring amino functional groups. Another approach was done by Xu, et al. (2016) using polyvinylpyrrolidone which contains N-heterocycles to entrap PWA in PES membrane. This was to provide similar environment as in chitosan polymer with the availability of amino groups for anchoring PWA. Both works reported that the stability of the composite membrane was good and self-anchoring could reduce the leaching of PWA.

Recently, Gong, et al. (2017) had employed a method known as polydopamine-assisted coating method, where PWA was sandwiched between polydopamine and chitosan polymer for stabilisation. It was believed that the charge interaction between PWA and chitosan would helped to hold the super acid at the membrane surface as methanol barrier and proton conductivity booster.

Despite the vast amount of studies done on the effect of HPA doping, most works were focused on the use of PWA instead of the more conductive SiWA. This could be attributed to the comparatively less stable SiWA within the polymer matrix which increases the difficulty in fabricating a durable membrane for harsh conditions.

2.6 Silica

As stated in the previous subsection, inorganic oxides are good support to be used in the stabilisation of HPA within the polymer matrix. In particular, silica is one of the most used inorganic oxide for such application (Ismail, Othman and Mustafa, 2009; Zhang, Jiang and Liu, 2011). According to Bhure, et al. (2008), HPA was attached or immobilised on the surface of silica by electrostatic force and evenly distributed. Besides HPA, silica was also used to immobilise ionic liquids which are also very prone to leaching (Li, et al., 2016; Peng, et al., 2016). Therefore, utilisation of silica to entrap proton conductive HPA appears to be an economic and practical approach to boost the performance of SPEEK membrane.

Besides acting as a support for HPA, silica can also play its role in improving the properties of SPEEK membrane. Hygroscopic silica can increase the water uptake of SPEEK membrane. Furthermore, it can also help to retain substantial amount of water at high temperature and low humidity (Slade, et al., 2010). It is believed that this ability can help to increase the proton conductivity of SPEEK for high temperature DMFC application where moisture content in the membrane becomes a critical factor. Besides, since silica is hydrophilic in nature, it will occupy the hydrophilic domain of SPEEK polymer matrix, thereby increasing the tortuosity of methanol transport pathway and reduce membrane’s methanol permeability (Tripathi and Shahi, 2009; Vijayalekshmi and Khastgir, 2017).

In a study done by Li, et al. (2014), mesoporous silica was incorporated into SPEEK membrane by direct dispersion of nanoparticles. It was found that thermal stability of the membrane increased as the loading of additive increased. However, strong interaction between additive and sulfonic acid group of SPEEK reduce the hydrophilic domain of the polymer and hence decrease water uptake and proton conductivity. In view of the downsides of silica incorporation, Unnikrishnan, Mohanty and Nayak (2013) made a comparison between SPEEK/silica membrane and SPEEK/sulfonated silica membrane. Silica was sulfonated in order to compensate the lost proton transport sites during the addition of additive. Their results claimed that composite membrane with sulfonated silica exhibited better water uptake at high temperature. At the same time, SPEEK/sulfonated silica membrane also showed lower affinity towards methanol.

Sivasankaran and Sangeetha (2015) investigated the influence of sulfonated silica content in SPEEK membrane for microbial fuel cell application. It was reported that although the water uptake of the composite membrane did not vary much from SPEEK/silica membrane, however the membrane did achieved lower internal resistance and higher IEC. Beside direct sulfonation of silica nanoparticles, co-condensation method was also used to attach sulfonic acid group on silica surface (Rangasamy, et al., 2014). This was done by first coating silane coupling agent, (3-mercaptopropyl)trimethoxysilane (MPTS) on the surface of fuming silica followed by suspending silica in sulphuric acid. The results showed that membrane incorporated with sulfonated silica from co-condensation had better resistance to swelling. Mechanical and thermal stabilities were also improved due to the better coordination of sulfonic acid group on the silica nanoparticles. The authors also claimed that by using this method, sulfonated silica will have high retention of sulphur and further heat treatment would oxidise the sulphur and prevent leaching of silica.

Apart from sulfonation of silica, other approaches were also adopted to improve the performance of SPEEK/silica composite membrane. Wang, et al. (2015) attempted to modify silica with polydopamine before incorporation into SPEEK polymer. Silica nanoparticles were produced from TEOS precursor and were dispersed in dopamine solution. Addition of dopamine modified silica into SPEEK also strengthened the interaction between additive and sulfonic acid group of polymer, leading to moderate swelling and water uptake. Formation of acid-base pairs within the composite membrane resulted in strong hydrogen bonding. This increased the mechanical strength as compared to SPEEK/silica membrane besides providing additional pathways for proton transport.

Silica is also used in the form of microsphere instead of nanoparticle. This was done by Zhao, et al. (2013) where phosphorylated silica microspheres with different coupling agents were compared. In fact, silica submicrosphere could also improve the proton conductivity of pristine SPEEK membrane extensively due to the presence of phosphonic acid functional group. The results of this work inferred that the role played by silica in improving proton conductivity can be magnified by using it as a support or complement for other proton conductive materials.

2.7 Coupling Agent

Nanoparticles (usually inorganic oxides) incorporated into SPEEK membrane have small size which leads to large overall surface area. This will cause the nanoparticles to be unstable due to the reactivity of their surfaces. Consequently, leaching or agglomeration will occur and reduce the performance of the membrane. To control such situation, physical or chemical modifications can be performed on the nanoparticles. It was claimed that chemical modification (using coupling agent) is better than physical modification (using surfactant) as the latter tends to be thermally and solvolytically unstable due to the utilisation of weak Van der Waals force and hydrogen bonding in this approach (Mallakpour and Madani, 2015).

Coupling agent is a compound that is used to hold two non-homogenous phase or dissimilar materials by forming stable bonds in between them. Hence, besides increasing the stability of the additive within SPEEK membrane, coupling agent also plays role to improve the compatibility of the organic membrane and inorganic additives (Zhao, et al., 2013). Generally, coupling agents can be classified into four main categories, namely silanes, carboxylic acids, polymers and organophosphorus molecules (Mallakpour and Madani, 2015).

Among these four, silane coupling agent is the most common coupling agent used to modify inorganic additives. Silane coupling agent basically has four ends with two functionalities. One end has functional organic while the other three are hydrolysable functional groups. The functional organic is responsible for enhancing the compatibility of the two phases (organic and inorganic) within the polymer matrix while the hydrolysable functional groups will form linkages with the inorganic additives. The application of silane coupling can be done before or after the formation of nanoparticles, which is also known as in situ modification and post-modification respectively (Mallakpour and Madani, 2015). The most commonly used silane coupling agents are MPTS, APTES and γ-glycidoxypropyl trimethoxysilane (GMPTS).

Prapainainar, et al. (2016) investigated the effect of different silane coupling agents on the properties of Nafion/mordenite composite membrane using post-modification for direct ethanol fuel cell (DEFC). It was found that silane coupling agents containing sulfhydryl group (MPTES and MPTS), which can be converted into sulfonic acid group exhibited higher degree of improvement in proton conductivity. To reduce ethanol permeability, dispersion of additive is an important factor. The authors claimed that silane coupling agents with sulfhydryl groups (more reaction sites with Nafion), higher number of alkoxy silane (more reaction sites with mordenite) and ethoxy functional organic group (easy hydrolysis) were more favourable to improve dispersion and compatibility of mordenite within polymer matrix, thereby reducing ethanol permeability.

In order to prove the roles played by silane coupling agent in SPEEK composite membrane, Salarizadeh, Javanbakht and Pourmahdian (2017) compared the performance of pristine SPEEK membrane, SPEEK/TiO_2 membrane and SPEEK/APTES-TiO_2 membrane. It was reported that the composite membrane with modified nanoparticles showed better water uptake and lower degree of swelling, plausibly due to the functionalisation and better distribution of additives. Furthermore, thermal conductivity of SPEEK/APTES-TiO_2 membrane was slightly improved alongside with achievement of optimum proton conductivity and power density at 7.5 wt% loading.

2.8 Conclusion

Based on the literature review, it is believed that the low cost SPEEK polymer has the greatest potential to be developed into a substitute for commercial Nafion membrane. This is attributed to its good mechanical and thermal stability as well as the low methanol permeability. Mechanical integrity will be compromised at high DS. Hence, SPEEK polymer should be sulfonated until moderately low DS is achieved. In view of the low proton conductivity, HPA can be incorporated to improve the proton mobility through the membrane. There is a research gap where highly proton conductive SiWA has the potential to enhance the performance of SPEEK membrane. In order to tackle the leaching problem of SiWA, silica can be used as a support to immobilise SiWA within the polymer matrix, thereby improving the durability of the membrane. Not only that, silica can also plays a role in methanol blocking. Solid oxide is deemed to have anti-oxidative ability and thus the addition of silica is an initiative to increase the life-span of SPEEK composite membrane. Considering the plausible incompatibility of organic phase (polymer) and inorganic phase (inorganic additives), coupling agents are used as a solution to phase heterogeneity, such as weak interaction. Hence, composite membranes based on SPEEK polymer containing silica and SiWA of different loadings will be fabricated and characterised in this research. Effects of coupling agents will also be studied after the optimisation of additives' loadings.

CHAPTER 3

METHODOLOGY

3.1 Materials and Equipment

Table 3.1 and Table 3.2 summarise the materials and equipment used throughout the research period.

Table 3.1: Materials and Correspondent Suppliers

Materials	Specifications	Suppliers
Poly Ether Ether Ketone (PEEK)	-	Aldrich Chemistry
Tetraethyl Orthosilicate (TEOS)	-	Merck
Silicotungstic Acid (SiWA)	-	Aldrich Chemistry
N-Methyl-2-Pyrrolidone	≥ 99.0 %	R & M Chemicals
3-Aminopropyl Triethoxysilane (APTES)	≥ 98.0 %	Merck
1, 1’-Carbonyldiimidazole (CDI)	≥ 97.0 %	Merck
Sulphuric Acid	95 % - 97 %	Merck
Methanol	≥ 99 %	Merck
Hydrogen Peroxide	30 vol%	HmbG Chemicals
Iron (II) Sulphate Heptahydrate	-	Aldrich Chemistry
Aluminium Nitrate Nanohydrate	-	Merck
Iron (III) Nitrate Nanohydrate	-	Merck

Table 3.2: Equipment and Correspondent Model Number

Equipment	Model Number
Scanning Electron Microscope	Hitachi S-3400N
Energy Dispersive X-Ray Spectroscopy	Ametek
Thermogravimetric Analysis	Perkin Elmer STA8000
Gas Chromatogram	Perkin Elmer Clarus 500
Potentionstat	Zive SP1

3.2 Preparation of SPEEK Polymer

PEEK was dried in oven overnight to remove all the moisture content. 1 g of PEEK was dissolved in 35 mL of concentrated sulphuric acid for 6 hours at 55 °C. The solution was then quenched in excess of ice-cold water and was left overnight. Solid SPEEK was recovered and washed with deionised water until the washing water becomes neutral (pH 6 – 8). Finally, solid SPEEK was dried in oven until constant weight was achieved. DS of the prepared SPEEK was determined by back titration method. 2 M sodium chloride solution was used to extract H^+ ions from SPEEK and 0.01 M sodium hydroxide solution was used for titration purpose. Phenolphthalein was used as an acid-base indicator. The DS of the produced SPEEK was in range of between 55 % and 60 %.

3.3 Preparation of Inorganic Additives

3.3.1 Preparation of SiO_2-SiWA

TEOS was used as precursor to synthesis silica. SiO_2-SiWA additive was prepared by the following steps. First, 5 wt%, 10 wt% or 20 wt% of SiWA was dissolved in deionised water. Next, common solvent (ethanol in this case) was added to form a homogenous solution. TEOS was then added such that the molar ratio of TEOS to both water and ethanol remained at 1:4. Finally, the solution was ultrasonicated for 30 minutes at room temperature.

3.3.2 Preparation of Al_2O_3-SiWA

Aluminium nitrate nanohydrate was used as a precursor to synthesis alumina. Al_2O_3-SiWA additive was prepared by the following steps. First, 5 wt% of SiWA was mixed with aluminium nitrate nanohydrate. The mixture was then dissolved in excess NMP solution. The final solution was ultrasonicated for 30 minutes under room temperature.

3.3.3 Preparation of Fe_2O_3-SiWA

Iron (III) nitrate nanohydrate was used as precursor to synthesis alumina. Fe_2O_3-SiWA additive was prepared by the following steps. First, 5 wt% of SiWA was mixed with iron (III) nitrate nanohydrate. The mixture was then dissolved in excess NMP solution. The final solution was ultrasonicated for 30 minutes under room temperature.

3.4 Fabrication of Membranes

Solid SPEEK was dissolved in NMP solvent to form a 5 wt% polymer solution. The polymer solution was then added into the prepared additive solution and was ultrasonicated for 30 minutes at room temperature. After that, the polymer solution was casted to a petri dish and dried at 80 ℃ for 24 hours in the oven.

For composite membrane with coupling agents, prior to the addition of the additives, coupling agents such as APTES and CDI were added to the polymer solution. The molar ratio of the coupling agents to sulfonic acid group of SPEEK was remained at 1:4. The solution were stirred at 60 °C for 2 hours. If both coupling agents were used together, CDI was added first followed by APTES. The dried membrane after casting was immersed into a warm water bath to remove from petri dish. Membrane pre-treatment can be done by immersing the membrane in 1 M sulphuric acid for 24 hours at room temperature. Figure 3.1 depicts the flowchart of membrane fabrication steps in detail.

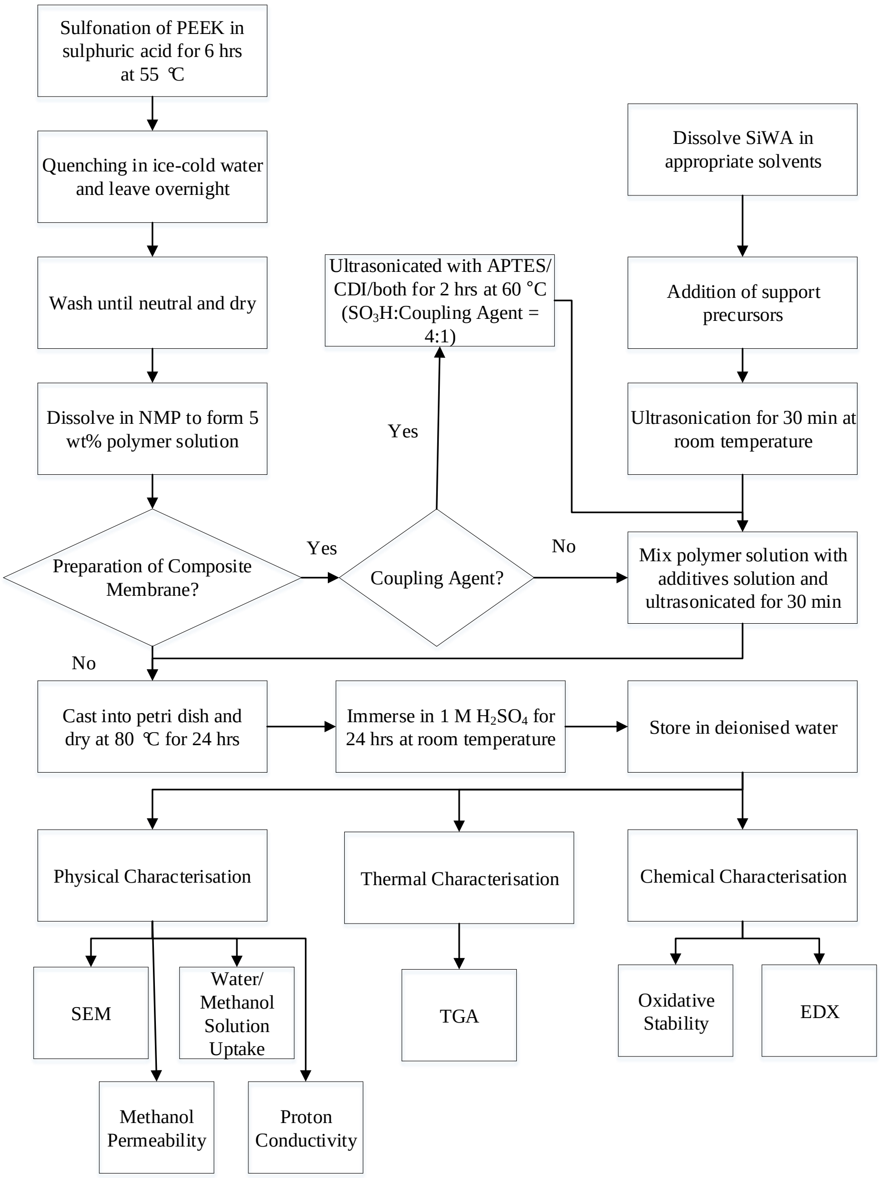


Figure 3.1: Research Phase Methodology

3.5 Membrane Characterisation

3.5.1 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

The surface morphology of SPEEK composite membrane was studied using scanning electron microscopy (SEM) instrument (Hitachi S-3400N). A thin layer of gold was coated on the membrane surface before it was fixed on a copper stub for micrographs imaging. The applied voltage and magnification was set at 20 kV and 5 000 × respectively. Ametek energy dispersive X-ray spectroscopy (EDX) was used to obtain the elemental composition and elemental mappings of the membrane sample.

3.5.2 Water and Methanol Solution Uptake

Membrane sample was immersed in water or 1 M methanol solution for 24 hours. The wet weight of the sample was measured after the surface water on the sample was removed. The membrane sample was then dried in oven until constant dry weight was achieved. Water or methanol solution uptake was calculated using Equation 3.1.

$$\text{Water/Methanol Solution Uptake} = \frac{W_W - W_D}{W_W} \times 100\ \% \qquad (3.1)$$

where:

W_W = wet weight of membrane, g

W_D = wet weight of membrane, g

3.5.3 Methanol Permeability

Methanol permeability of SPEEK composite membrane was determined by diffusion method. The membrane sample was fixed between two compartments containing 1 M methanol solution and deionised water respectively. Samples from water compartment were collected at suitable intervals. The apparatus setup was shown in Figure 3.2.

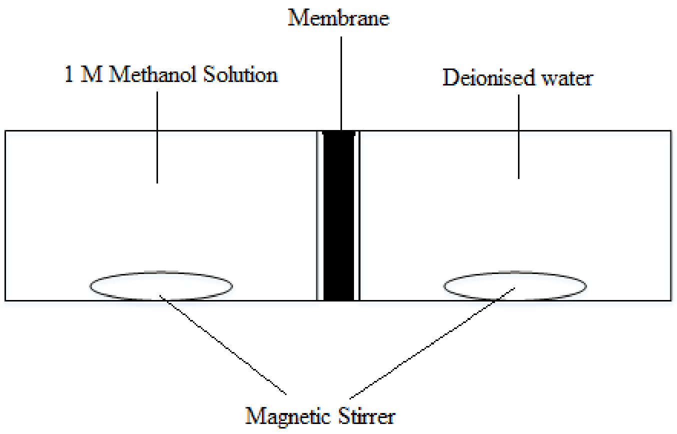


Figure 3.2: Apparatus Setup for Methanol Diffusion Test

Methanol concentration of the water sample was examined using gas chromatography (Perkin Elmer Clarus 500). Methanol permeability can be calculated using Equation 3.2.

$$P_M = \frac{SVt}{C_{Mo}A} \tag{3.2}$$

where:

P_M = methanol permeability, cm^2/s

S = rate of change of methanol concentration in deionised water compartment, M/s

V = volume of compartment, cm^3

t = thickness of membrane, cm

C_{M0} = initial methanol concentration in methanol compartment, M

A = effective diffusion area, cm^2

3.5.4 Proton Conductivity

Proton conductivity of SPEEK composite membrane was determined using in-plane conductivity method. A membrane sample with the dimension of 2.5 cm × 0.5 cm was placed on a four-probed conductivity cell and connected to Zive SP1 potentiostat. Current sweep from 3 mA to -3 mA with scan rate of 0.28 mA/s was used to plot a graph of voltage against current, and the resistance of the membrane could be obtained from the graph's gradient. Conductivity of the membrane sample was calculated using Equation 3.3:

$$\sigma = \frac{L}{Rwt} \tag{3.3}$$

where:

σ = proton conductivity, S/cm

L = distance between two inner electrodes, cm

R = resistance, S^{-1}

w = width of the membrane, cm

t = thickness of the membrane, cm

A membrane with good performance shall have high proton conductivity while blocking the diffusion of methanol fuel. Therefore, ratio of proton conductivity to methanol permeability (stated as "selectivity" in upcoming discussion.) was calculated as a metric to compare the overall performance of membrane.

3.5.5 Thermogravimetric Analysis

10 mg of SPEEK composite membrane sample was cut into small pieces. The small pieces were then placed in a heat-resistant crucible followed by insertion into the thermal analyser (Perkin Elmer STA8000). 20 mL/min flow of inert nitrogen gas was set, and the thermal analysis was done from 35 °C to 700 °C with a ramp of 10 °C/min. Residual weight of the membrane sample was recorded.

3.5.6 Oxidative Stability

The oxidative stability of SPEEK composite membrane was tested using Fenton's test. Fenton's reagent was prepared by producing a solution with 3 vol% of hydrogen peroxide and 4 ppm of Fe^{2+} ions. The weight of the dried membrane was measured before immersing it into the Fenton's reagent at 60 °C for 3 hours. The membrane was then dried once again and the change in dried weight of membrane was used to evaluate its degradation oxidative stability as shown in Equation 3.4.

$$\text{Degradation} = \frac{W_i - W_f}{W_i} \times 100\ \% \qquad (3.4)$$

where:

W_i = initial dry weight of membrane, g

W_f = final dry weight of membrane, g

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In Chapter 4, the findings and the results of this study will be discussed in detail. The discussion will include all the results obtained from the characterisation studied as stated in Chapter 3 as well as the explanations based on scientific proof. The discussion will be done in the following order:

- Effect of ultrasonic treatment
- Effect of different silica:SiWA weight ratio
- Effect of various coupling agents
- Alternatives for Silica

4.2 Effect of Ultrasonic Treatment

Good and uniform dispersion of additives within polymer matrix was always a challenge for the researchers worldwide, especially dealing with leaching-prone additives. Hence, part of this study was to investigate ways to enhance the stability of silica and SiWA in SPEEK. In this context, ultrasonic treatment was used.

4.2.1 Distribution and Stabilisation of Inorganic Additives

A SPEEK/SiO_2-SiWA composite membrane with 10 wt% of SiWA supported on 10 wt% of silica was used as the subject to be studied. To evaluate the stability of the inorganic additives in the membrane structure, an elemental analysis was performed and the results are as shown in Table 4.1.

Table 4.1: Elemental Compositions of SPEEK/SiO_2-SiWA under Different Preparation Methods

Membrane Preparation	Sulphuric Acid Treatment	Elemental Compositions (wt%)	
		Si	W
Without ultrasonic treatment	Before	19.66 (±0.03)	7.28 (±0.76)
	After	14.25 (±0.60)	3.51 (±0.07)
With ultrasonic treatment	Before	21.73 (±0.94)	6.51 (±0.01)
	After	21.77 (±0.87)	5.74 (±0.12)

Elemental compositions of silicon (Si) and tungsten (W) before and after 1 M sulphuric acid protonation process were determined. The results showed that silicon and tungsten composition had suffered a significant drop after the activation step when the composite membrane was prepared without ultrasonic treatment. This proved that mechanical stirring was unable to properly incorporate or embed silica and SiWA into the polymer matrix. The weight ratio of Si:W had also experienced a huge change due to the rapid leaching of SiWA (Mahreni, et al., 2009; Wang, Xia and Zhang, 2001).

On the other hand, when the membrane fabrication steps involved ultrasonic treatment, the elemental composition of silicon and tungsten remained almost constant. It is believed that the interaction of silica with the SPEEK polymer was enhanced by the extra energy provided through the cavitation effect of ultrasound. This energy helped to break the Van der Waals forces among the particles, thus prevent plausible agglomeration and hence better dispersion and effective incorporation were achieved.

4.2.2 Summary

It was realised that ultrasonic treatment could be an essential step to prepare SPEEK/SiO_2-SiWA composite membrane. This is because it promotes strong interaction between the polymer and inorganic additives. Therefore, ultrasonic treatment step will be remained throughout the other research phases.

4.3 Effect of Different Silica:SiWA Weight Ratio

Besides the preparation step, the amount of support used to immobilise SiWA is another important factor in developing a high performance SPEEK based PEM. In this subsection, the weight ratio between silica support and SiWA was manipulated to investigate the optimum additives' loading and ratio of silica to SiWA.

4.3.1 Abbreviations and Details of Samples

The abbreviation, compositions and details of all samples used in this subsection are tabulated in Table 4.2. Membrane fabrication steps involved the use of ultrasonic treatment to disperse the inorganic additives.

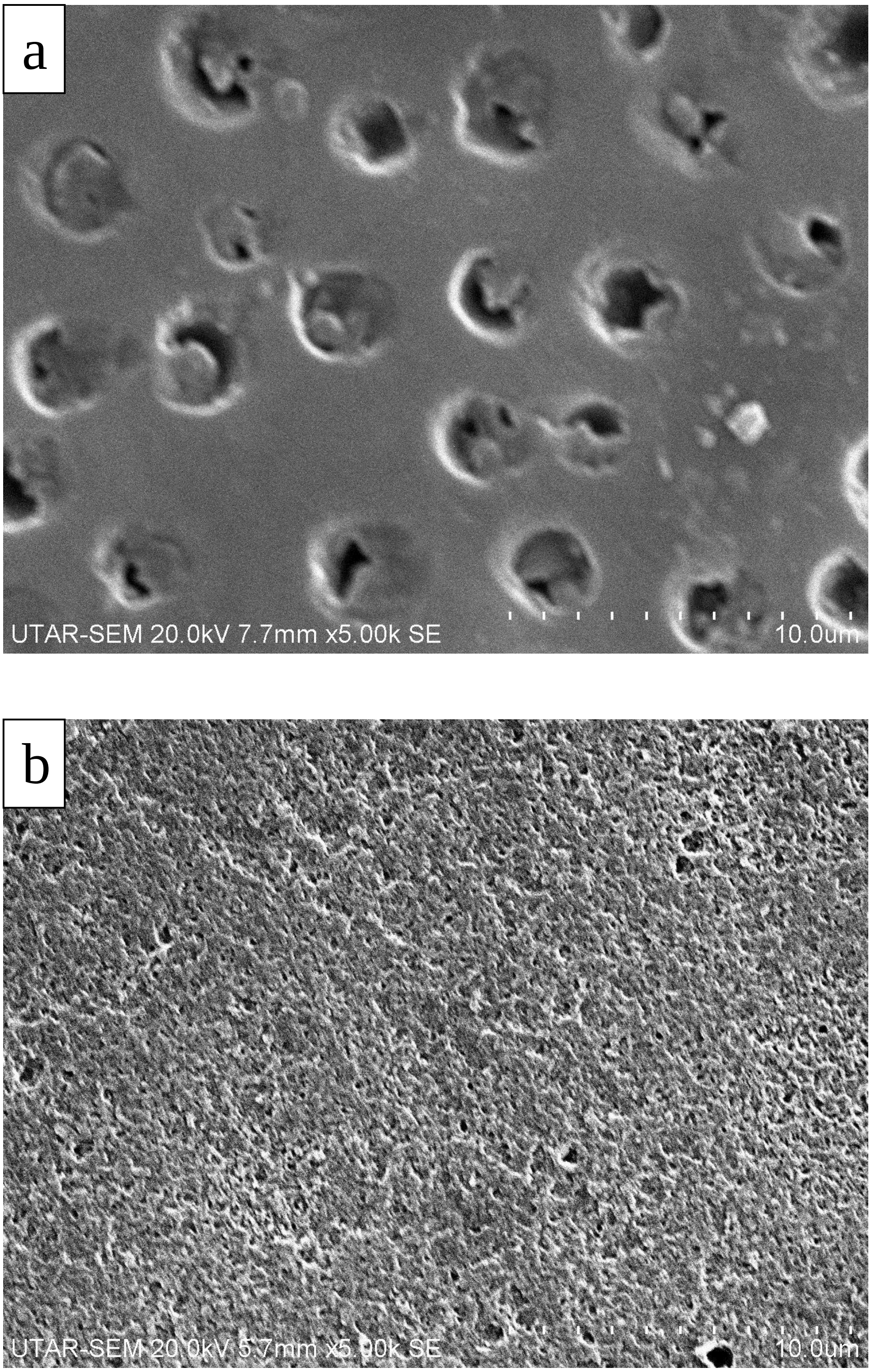
Table 4.2: Abbreviations of SPEEK/SiO_2-SiWA Composite Membrane with Different Compositions

Membrane	Silica Loading (wt%)	SiWA Loading (wt%)	Silica:SiWA Weight Ratio
SPEEK-10-5	10	5	2:1
SPEEK-10-10	10	10	1:1
SPEEK-10-20	10	20	1:2

4.3.2 Surface Morphology

Surface morphologies of the membranes were studied using SEM and the images are shown in Figure 4.1. Since ultrasonic treatment was used during membrane fabrication, the agglomeration of silica would unlikely to occur. The morphology of the membrane was essentially affected by the amount of TEOS added or the silica produced.

From the SEM images, it could be seen that when the loading of SiWA increased, the compactness of the membrane also increased. In Figure 4.1(a), when loading of SiWA was 5 wt%, a membrane with porous structure was seen. The membrane became compact when SiWA content was increased to 10 wt% (Figure 4.1(b)). When the silica content was further increased to 20 wt%, the surface of the membrane became flaky as shown in Figure 4.1(c). It was suggested that amount of SiWA could affect the amount of silica converted from its precursor, TEOS and hence affect the morphology and structure the resultant membrane.


a
UTAR-SEM 20.0kV 7.7mm x5.00k SE
10.0um
b
UTAR-SEM 20.0kV 5.7mm x5.00k SE
10.0um

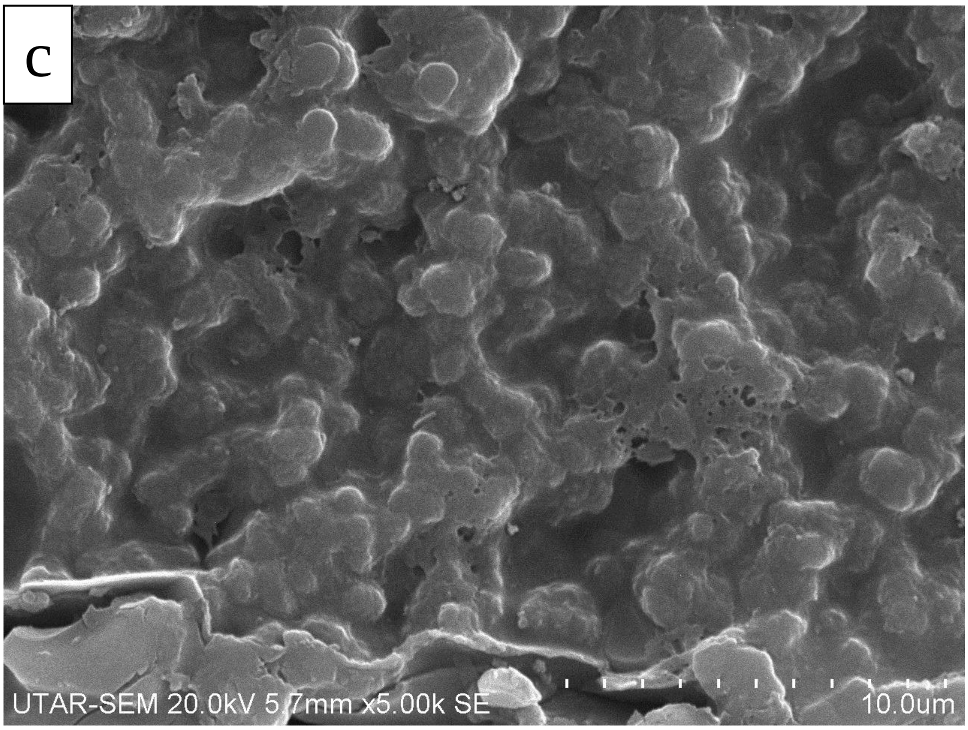


Figure 4.1: Surface Morphology of (a) SPEEK-10-5 (b) SPEEK-10-10 (c) SPEEK-10-20

SiWA is a type of solid acid and a proton donor. It is acidic in nature. Hydrolysis and condensation reactions of TEOS to form silica is faster and more favourable when the reaction condition is acidic (Rahman and Padavettan, 2012). Therefore, when the amount of SiWA was increased, the rate of hydrolysis and condensation reactions of TEOS also increased. This would increase the amount of silica produced. Higher amount of silica produced would make the membrane more compact (SPEEK-10-5), and when there is excess of silica, they will start to accumulate on the surface of the membrane (SPEEK-10-20).

4.3.3 Distribution and Stabilisation of Inorganic Additives

In order to study the effect of different loadings of silica support on the immobilisation of SiWA, an elemental analysis was done. Elemental composition as well as distribution were studied after the membranes were subjected to 1 M sulphuric acid protonation. The elemental compositions of silicon and tungsten are summarised in Table 4.3.

Table 4.3: Elemental Compositions of Silicon and Tungsten of Different SPEEK/SiO2-SiWA Composite Membranes

Membrane	**Elemental Compositions (wt%)**	
	Si	**W**
SPEEK-10-5	9.72 (±0.43)	4.81 (±0.19)
SPEEK-10-10	21.77 (±0.87)	5.74 (±0.12)
SPEEK-10-20	24.21 (±0.93)	0.00 (±0.00)

From Table 4.3, it could be observed that as the weight ratio of silica:SiWA became smaller, elemental composition of silicon increased. This observation is in agreement with the SEM images, where more silica was formed from TEOS precursor under more acidic condition.

In SPEEK-10-5, the weight ratio of Si:W was close to 2 (theoretical value). However, when the loading of SiWA increased, the elemental composition of tungsten was actually decreasing. In fact, there was no any detectable tungsten in SPEEK-10-20. This is because when SiWA loading increased while silica content was kept constant, there was no enough silica to immobilise or support all the available SiWA. Interaction between silica support and SiWA is said to be poor. Although it was claimed that more silica was formed from more acidic condition, but most of the silica only accumulate on the surface. SiWA on the surface of the membrane was directly exposed to external solution, resulting in easier leaching..

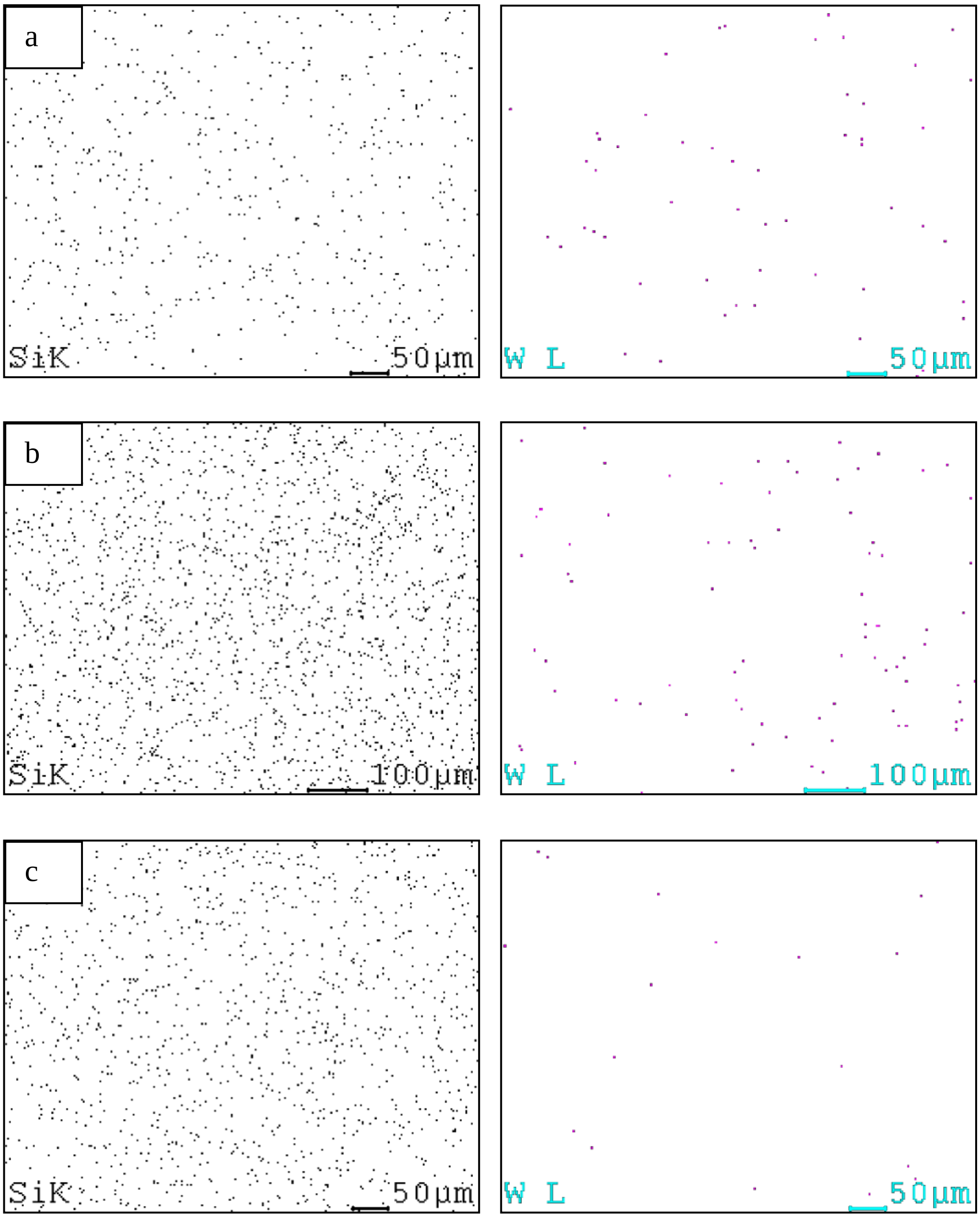


Figure 4.2: Silicon and Tungsten Elemental Mappings of (a) SPEEK-10-5 (b) SPEEK-10-10 (c) SPEEK-10-20

On the other hand, the dispersion of the additives were obtained using elemental mapping, shown in Figure 4.2. From the results, it could be said that the dispersions of the additives were uniform, which was contributed the ultrasonic treatment used in the preparation steps.

4.3.4 Water and Methanol Solution Uptake

Table 4.4 summarises the water and methanol solution uptake of different SPEEK/SiO_2-SiWA composite membranes.

Table 4.4: Water and Methanol Solution Uptake of Different SPEEK/SiO_2-SiWA Composite Membranes

Membrane	Water Uptake (%)	Methanol Uptake (%)
SPEEK-10-5	50.98 (±0.84)	55.74 (±0.79)
SPEEK-10-10	33.33 (±0.62)	35.29 (±0.21)
SPEEK-10-20	50.00 (±1.24)	46.81 (±0.44)

Since the PEM will be used in a DMFC, water and methanol solution uptake become important parameter to determine the degree of swelling as well as dimensional stability of the PEM. From Table 4.4, it could be seen that water uptake and methanol solution uptake decreased as the compactness of the membrane increased. This trend was shown by SPEEK-10-5 and SPEEK-10-10. High compactness and rigid membrane structure prevent water and methanol molecule from being able to occupy spaces in the membrane. In other words, compact membrane has better mechanical integrity which can reduce swelling and expansion. In SPEEK-10-5, due to the porosity of membrane as shown in Figure 4.1(a), it could absorb more water and methanol molecules. Besides, it was noticeable that methanol solution uptake was always slightly higher than water uptake for SPEEK-10-5 and SPEEK-10-10. This was due to the presence of SiWA which had terminal oxygen atoms that can capture polar molecules such as methanol, resulting in higher methanol solution uptake (Kozhevnikov, Sinnema and van Bekkum, 1995).

However, such trend was not observed in SPEEK-10-20. It did not exhibit even lower water and methanol solution uptake when silica content increased. Surprisingly, SPEEK-10-20 also had lower methanol solution uptake than water uptake. The inability of silica to entrap SiWA had caused serious leaching of SiWA. After leaching, voids and small holes were left behind in the membrane internal structure, which in another way increased the membrane porosity, consequently making the membrane to have higher water and methanol solution uptake (Zeng, et al., 2019). The methanol solution uptake of SPEEK-10-20 was lower than its water as there was no SiWA that can capture the polar molecules.

4.3.5 Thermal and Oxidative Stability

One of the purpose of using SiWA as an additive is to enhance the thermal stability of SPEEK membrane. The thermal stability of SPEEK-10-5, SPEEK-10-10 and SPEEK-10-20 were studied using TGA. Rate of degradation and the degradation temperature were observed. Figure 4.3 shows the TGA graph of SPEEK composite membranes as compared to pristine SPEEK membrane.

From Figure 4.3, the degradation temperatures of pristine SPEEK membrane are around 350 ℃ and 420 ℃, which are due to the degradation of sulfonic acid group and hydrocarbon backbone respectively. For SPEEK/SiO_2-SiWA composite membrane (SPEEK-10-5, SPEEK-10-10 and SPEEK-10-20), the first degradation due to the decomposition of sulfonic acid group did not show significant difference. However, the thermal stability of the polymeric backbone was improved, where significant degradation could only be observed at around 500 ℃ (20 %) with lower rate of degradation as compared to pristine SPEEK in other literatures, where more than 20 % of degradation were reported (Dutra, Santos and Gomes, 2014; Lee, et al., 2014). The results justified the role of SiWA in improving the thermal stability of SPEEK based membrane.

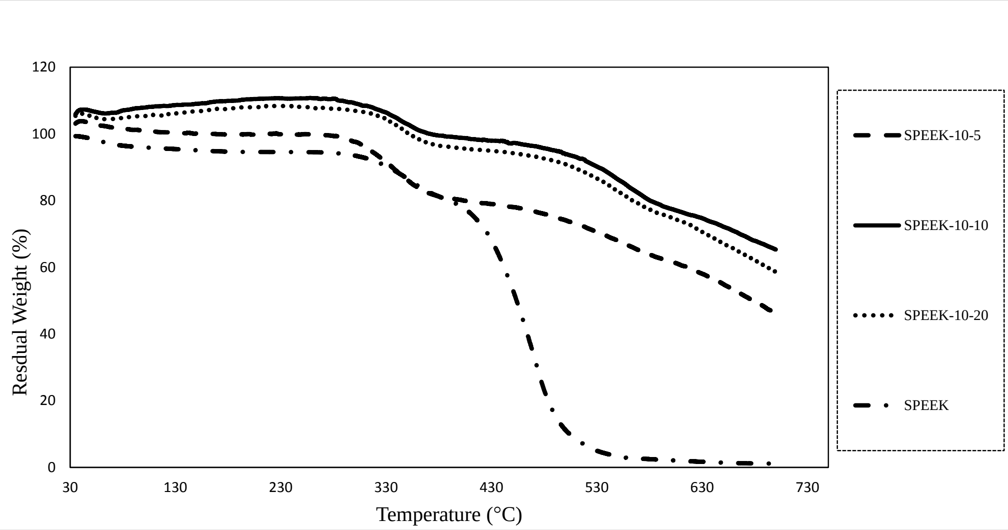


Figure 4.3: TGA of Various SPEEK based Membranes

Silica did not only act as a support of leachable SiWA, it also functioned as an anti-oxidant which helped to maintain the chemical and oxidative stability of SPEEK membrane. Table 4.5 shows the percentage degradation of membranes after Fenton’s test.

Table 4.5: Chemical Degradation of Different SPEEK/SiO$_2$-SiWA Composite Membranes

Membrane	Chemical Degradation (%)
SPEEK	4.70 (± 0.24)
SPEEK-10-5	0.22 (± 0.03)
SPEEK-10-10	2.33 (± 0.11)
SPEEK-10-20	3.33 (± 0.14)

Chemical degradation of SPEEK/SiO$_2$-SiWA composite membranes ranged from 0.22 % to 3.33 %. As compared to the 4.70 % degradation of pristine SPEEK membrane, addition of silica provided minor effect, probably due to the accumulation of silica on the membrane surface instead of being embedded into the polymer matrix. Free radicals could still attack the polymer internally as the membrane swelled.

4.3.6 Methanol Permeability

Table 4.6 shows the methanol permeability of SPEEK/SiO$_2$-SiWA with different silica:SiWA weight ratio. The trend of methanol permeability could match the results of water and methanol solution uptake. SPEEK-10-5, which was quite porous had considerable methanol permeability (7.45×10^{-7} cm^2/s). SPEEK-10-10 had more silica which will increase the tortuosity of transport pathway of methanol across the membrane, which in turn reduced the diffusion of methanol. Furthermore, high mechanical stability of SPEEK-10-10 also prevented the ionic clusters or hydrophilic channels in the membrane structure to expand continuously after hydration. This would also reduce the transport of methanol molecules across it.

In SPEEK-10-20, besides having porous internal structure that increased the methanol permeability, excessive silica was another factor that promoted methanol diffusion. According to Jiang, Kunz and Fenton (2006), instead of only blocking the hydrophilic channels, excessive silica would accumulate in the hydrophobic backbone of SPEEK polymer. Since silica is hygroscopic in nature, presence of silica in hydrophobic domain provided alternative transport pathway for methanol and hence raised its methanol permeability.

Table 4.6: Methanol Permeability of Different SPEEK/SiO_2-SiWA Composite Membranes

Membrane	Methanol Permeability ($\times 10^{-7}$ cm^2/s)
SPEEK-10-5	7.45 ($\pm$0.67)
SPEEK-10-10	5.21 ($\pm$0.70)
SPEEK-10-20	8.72 ($\pm$0.71)

4.3.7 Proton Conductivity

One of the most important parameters of a PEM is its proton conductivity. In this study, proton conductivity of SPEEK/SiO_2-SiWA composite membrane with different additive loadings was tested using in-plane analysis, where the membrane's resistance was measured. Proton conductivity and selectivity were tabulated in Table 4.7.

Table 4.7: Proton Conductivity and Selectivity of Different SPEEK/SiO2-SiWA Composite Membranes

Membrane	Proton Conductivity (S/cm)	Selectivity ($\times 10^4$ $S.s/cm^3$)
SPEEK-10-5	0.0480 ($\pm$0.0057)	6.44
SPEEK-10-10	0.0293 ($\pm$0.0028)	5.63
SPEEK-10-20	0.0291 ($\pm$0.0024)	3.34

SPEEK-10-5 had the highest proton conductivity. This was due to its high porosity which allow more protons to diffuse easily. Besides, high water uptake also increased the size of ionic clusters for proton transport. On top of that, the presence of SiWA also provided extra ion exchange sites for proton to be transported via Grotthüss mechanism (proton hopping mechanism). SPEEK-10-10 had compact structure which restricted its swelling and proton movement. Proton transport of the membrane was dictated mainly by proton hopping mechanism through sulfonic acid group and SiWA (Ismail, Othman and Mustafa, 2009). Although SPEEK-10-20 also had porous structure, however its proton conductivity was considerably low due to the absence of SiWA. This suggested proton conductivity of SPEEK-10-20 was contributed mainly by vehicle diffusion.

By comparing the proton conductivity and methanol permeability, SPEEK-10-5 was reported to have the highest selectivity (6.44×10^4 S.s/cm^3) among the three membranes. This was attributed to its porosity and presence of ample amount of SiWA, which resulted in high proton conductivity and moderately low methanol permeability.

4.3.8 Summary

In this subsection, SPEEK/SiO_2-SiWA composite membranes with different silica:SiWA weight were fabricated. Their properties and performance were evaluated. It was found that SPEEK-10-5, with the silica:SiWA weight ratio of 2:1 had the best performance in terms of selectivity. This proved that silica was an effective support for the leach-prone SiWA, if and only if used in excess. The membrane with this recipe would be modified in the following subsection to further improve its performance.

4.4 Effect of Various Coupling Agents

In this study, inorganic additives were incorporated into organic polymer. The heterogeneity between the two phases could result in incompatibility as well as phase separation. In this subsection, coupling agents which consist of two functionalities (organic and inorganic groups) were used to promote the compatibility of the organic and inorganic constituents in the membrane (Mallakpour and Madani, 2015). Effect of different coupling agents were studied.

4.4.1 Abbreviations and Details of Samples

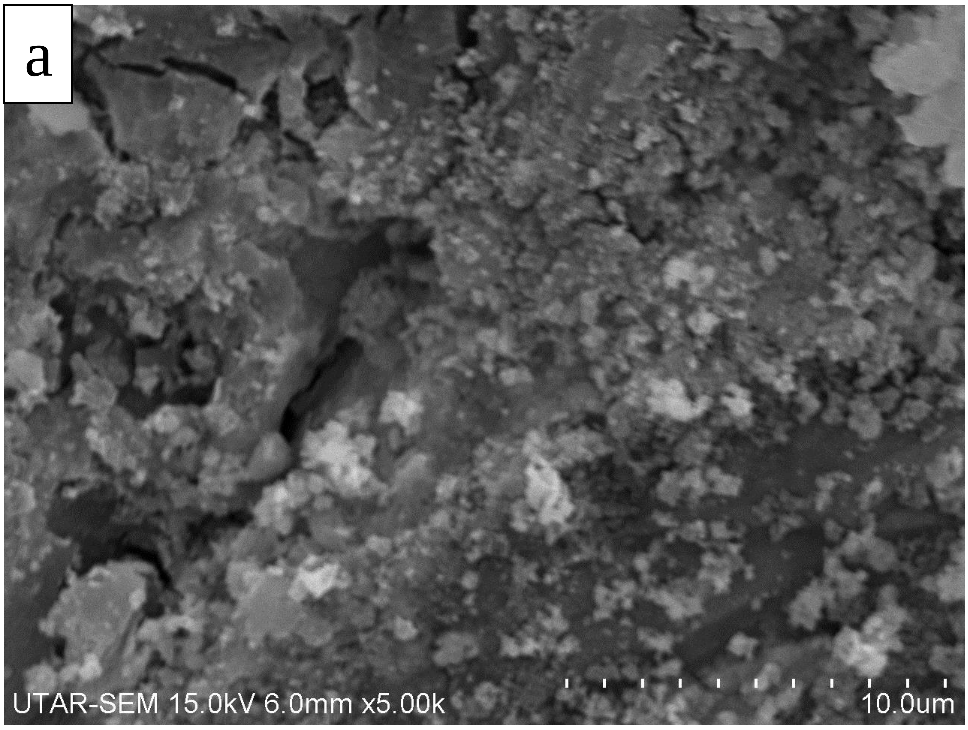
The abbreviation, compositions and details of all samples used in this subsection are tabulated in Table 4.8. Two coupling agents, APTES and CDI were used on SPEEK-10-5 from Section 4.3.

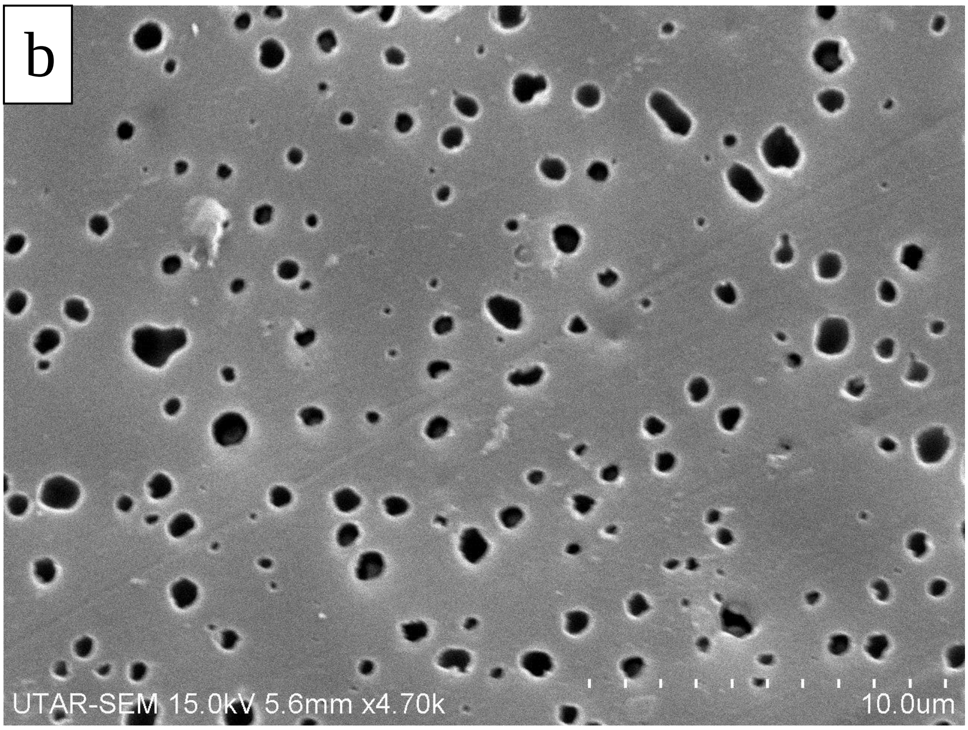
Table 4.8: Abbreviations of SPEEK/SiO_2-SiWA Composite Membrane added with Different Coupling Agents

Membrane	APTES	CDI	Remark
SPEEK-10-5 (A)	✓		All membranes had 10 wt% silica loading and 5 wt% SiWA loading.
SPEEK-10-5 (C)		✓	
SPEEK-10-5 (A + C)	✓	✓	

4.4.2 Surface Morphology

Surface morphologies of the membrane were studied using SEM and the images are as shown in Figure 4.4.





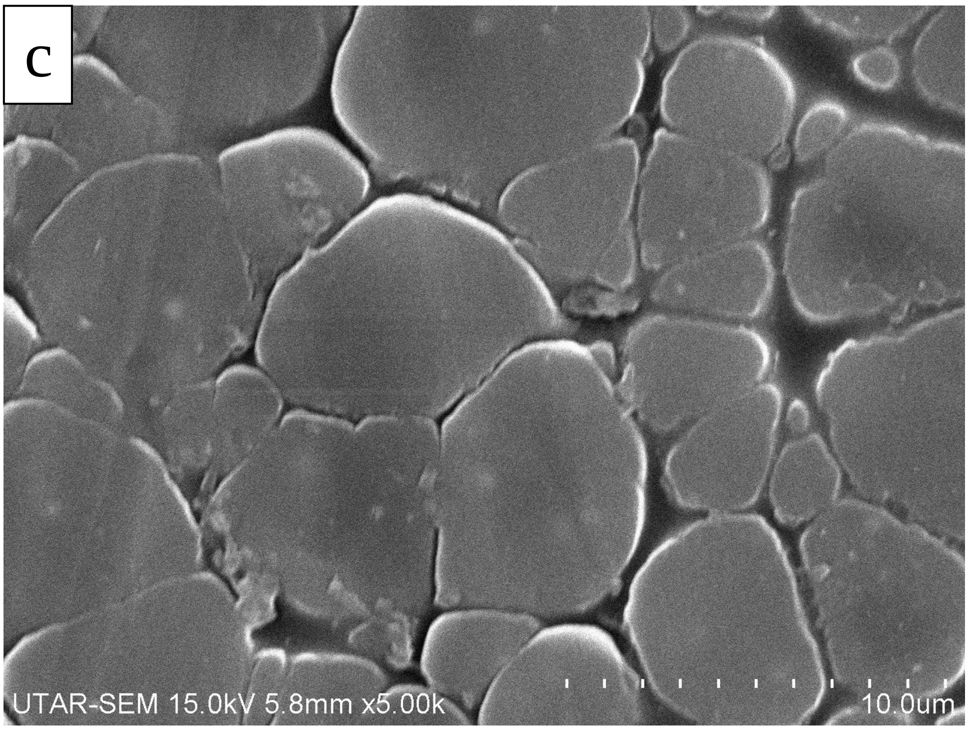


Figure 4.4: SEM Micrographs of (a) SPEEK-10-5 (A) (b) SPEEK-10-5 (C) (c) SPEEK-10-5 (A + C)

SPEEK-10-5 (A) had relatively rough surface as compared to the other two membranes. APTES, besides being a coupling agent, is also another precursor of silica. In this case, adding only APTES into the membrane cast solution increased the amount of organic silica. Excessive silica started to accumulate on the surface of the membrane. On the other hand, inclusion of only CDI did not significantly change the surface structure of the membrane. When compared with the original SPEEK-10-5 (Figure 4.1(a)), SPEEK-10-5 (C) also exhibited similar porous structure. Therefore, it is suggested that instead of being a coupling agent, CDI could probably functioned as a promoter which prepare the SPEEK polymer for further reactions with other chemicals such as APTES.

As for SPEEK-10-5 (A + C), a smooth, homogenous and compact morphology was observed. Although silica was also produced due to the addition of APTES coupling agent, however, the presence of CDI successfully reduced the dissimilarity between the organic and inorganic phases. Instead of accumulating on the membrane surface, all the additives were successfully incorporated into the membrane internal structure. Thus, it could be said that a smooth and compact composite membrane can be produced by using APTES as a silane coupling agent and CDI as a promoter for the coupling agent to work well.

4.4.3 Distribution and Stabilisation of Inorganic Additives

To study the effect of coupling agents on the incorporation of inorganic additives, elemental analysis was performed on SPEEK-10-5 (A), SPEEK-10-5 (C) and SPEEK-10-5 (A + C). The results are summarised in Table 4.9.

Table 4.9: Elemental Compositions of Silicon and Tungsten of SPEEK/SiO_2-SiWA Composite Membranes with Different Coupling Agents

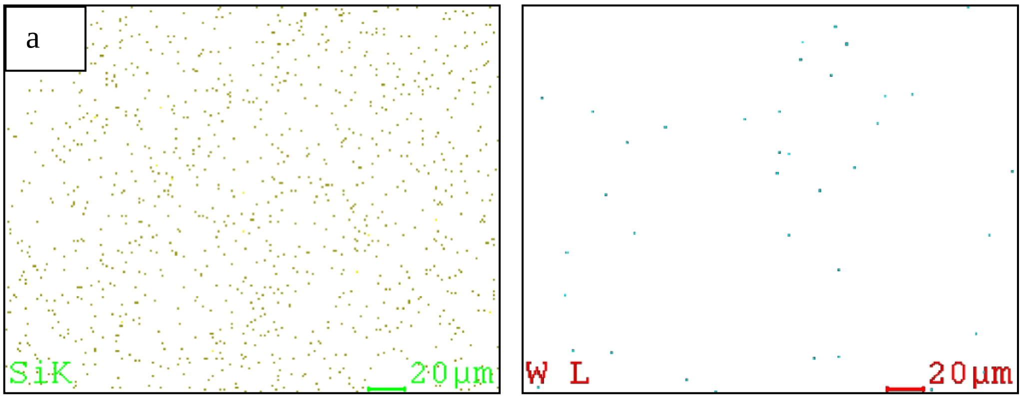
Membrane	**Elemental Compositions (wt%)**	
	Si	**W**
SPEEK-10-5 (A)	5.57 (± 0.42)	2.32 (± 0.45)
SPEEK-10-5 (C)	0.99 (± 0.14)	1.20 (± 0.34)
SPEEK-10-5- (A + C)	4.80 (± 0.24)	3.69 (± 0.19)

The results showed that the elemental compositions of silicon and tungsten for SPEEK/SiO_2-SiWA composite membranes in this subsection were lower than that of SPEEK-10-5 of Section 4.3 (Si – 9.72, W – 4.81).

Nevertheless, the ratio of silicon to tungsten was still remained at two for SPEEK-10-5 (A) and SPEEK-10-5 (A + C). The reduction was mainly due to the incorporation of silica and SiWA into the internal structure of the membrane and cannot be detected by EDX analysis.

However, for SPEEK-10-5 (C), silicon and tungsten compositions dropped significantly. As discussed earlier, addition of CDI prepared the polymer for further reaction (Pokprasert and Chirachanchai, 2017; Lei, et al., 2017). This resulted in less stable membrane properties and loosen the interaction between SPEEK polymer with silica and SiWA additives. After undergoing sulphuric acid protonation, the loosely held additives started to leach out from the membrane, making the membrane to be more porous.

The distribution of silicon and tungsten elements in SPEEK-10-5 (A), SPEEK-10-5 (C) and SPEEK-10-5 (A + C) are as shown in Figure 4.5. Uniform dispersion was observed. Addition of coupling agents did not affect the distribution of additives within the polymer matrix.



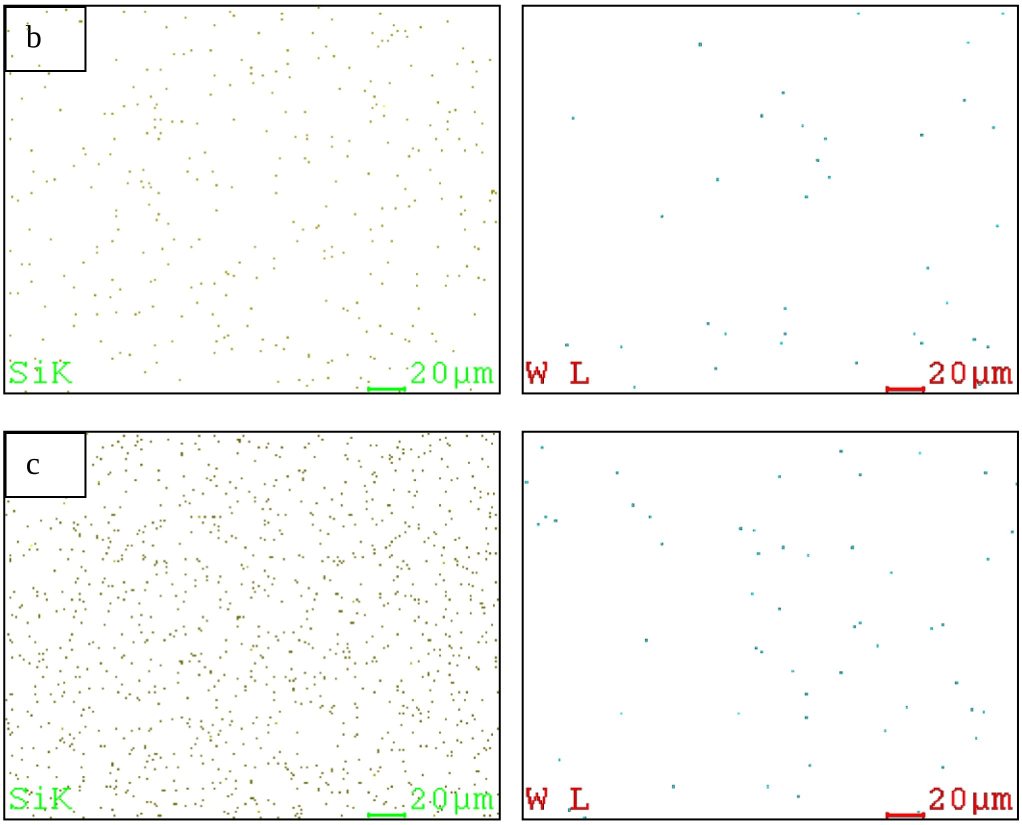
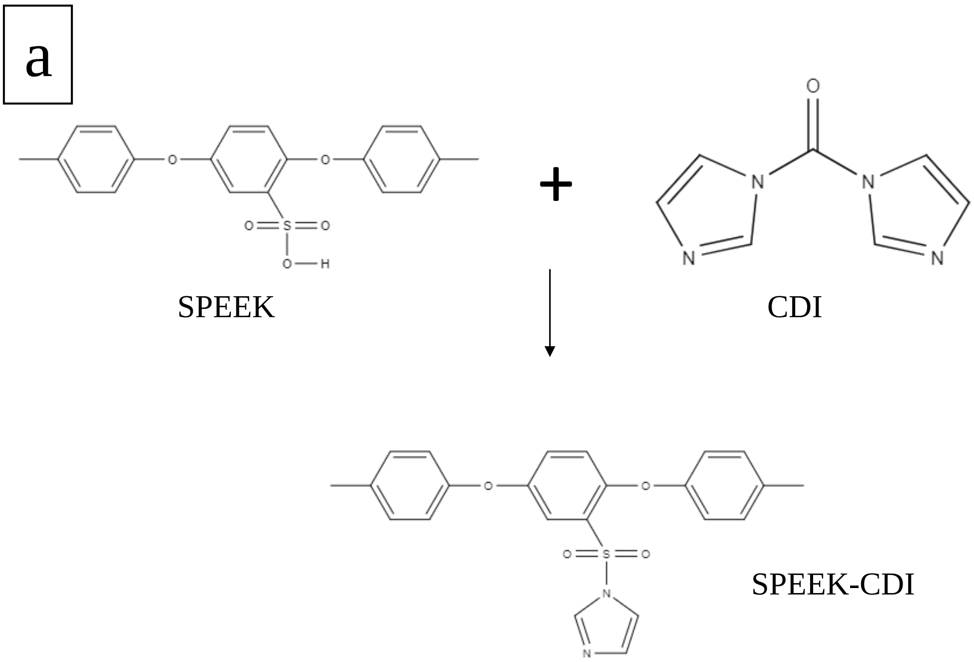
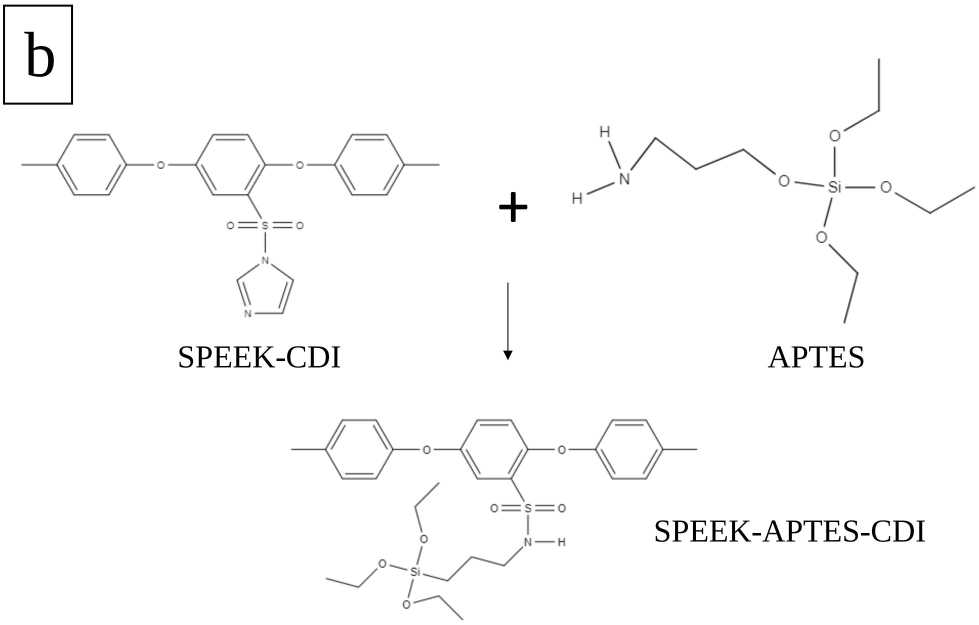


Figure 4.5: Silicon and Tungsten Elemental Mappings of (a) SPEEK-10-5 (A) (b) SPEEK-10-5 (C) (c) SPEEK-10-5 (A + C)

4.4.4 Reaction Mechanism of SPEEK Polymer with Coupling Agents

Addition of both APTES and CDI enhanced the homogeneity and compatibility between organic SPEEK and inorganic silica as well as SiWA. This involved linking the organic composite membrane with the inorganic additives via a coupling agent with multiple functionalities (organic and inorganic in this context). The overall reaction mechanism between SPEEK polymer with the coupling agents were proposed by Elakkiya, et al. (2018) and is illustrated in Figure 4.6.


a
SPEEK
CDI
SPEEK-CDI


b
SPEEK-CDI
APTES
SPEEK-APTES-CDI

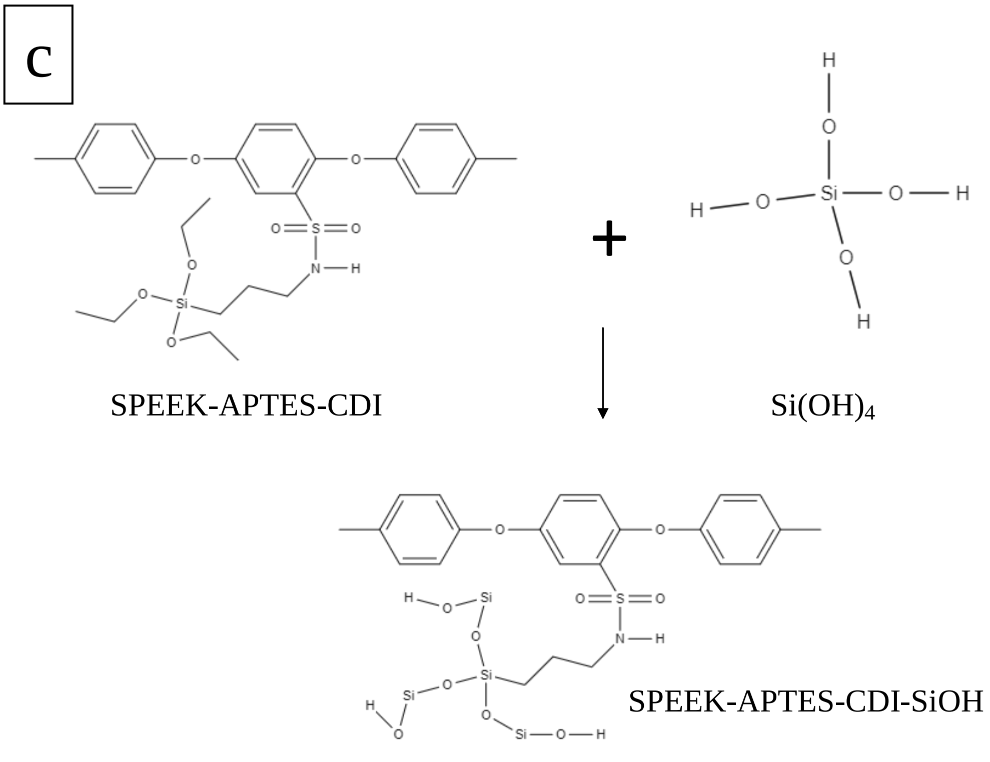


Figure 4.6: Reaction Mechanism between (a) SPEEK and CDI (b) SPEEK-CDI and APTES (c) SPEEK-APTES-CDI and Si(OH)$_4$

Based on the illustration in Figure 4.6, SPEEK polymer will first react with CDI promoter. One of the imidazole groups from CDI displaces hydroxyl group and forms a bond with the SPEEK polymer. Subsequently, addition of APTES leads to the second stage of the reaction, where the whole APTES molecule is linked to the organic polymer to form a –NH bond and displaces the imidazole group. At this point, organic functionality of APTES is connected to the organic polymer, leaving three other inorganic functionalities for further reaction.

Finally. Si(OH)$_4$, which is formed from the hydrolysis of TEOS will replace all the ethyl groups available in APTES, thus completing the whole incorporation process. Condensation and drying will lead to the formation of silica from $Si(OH)_4$.

In SPEEK-10-4 (A), there was no CDI to provide the first nitrogen atom in the polymer, therefore the APTES molecule could not be bonded to the polymer, causing them to accumulate on the membrane surface. In SPEEK-10-5 (C), the absence of stage two of the reaction led to the inability of $Si(OH)_4$ from replacing the ethyl groups, hence incorporation become less successful. In SPEEK-10-5 (A + C), conducive condition for silica incorporation due to the successful linkage between APTES and SPEEK polymer resulted in strong interaction between silica and SPEEK, whereas SiWA could be immobilised through electrostatic interaction with silica.

4.4.5 Water and Methanol Solution Uptake

Water and methanol solution uptake of SPEEK-10-5 (A), SPEEK-10-5 (C) and SPEEK-10-5 (A + C) are tabulated in Table 4.10.

Table 4.10: Water and Methanol Solution Uptake of Different SPEEK/SiO_2-SiWA Composite Membranes

Membrane	Water Uptake (%)	Methanol Uptake (%)
SPEEK-10-5 (A)	71.70 (±1.73)	44.68 (±1.23)
SPEEK-10-5 (C)	70.18 (±1.56)	69.66 (±1.99)
SPEEK-10-5- (A + C)	34.92 (±0.88)	29.17 (±0.58)

The results show that SPEEK-10-5 (C) had high water and methanol solution uptake due to its porous structure and its tendency on capturing water and methanol molecules. For SPEEK-10-5 (A), high amount of organic silica accumulated on the surface and hydrophobic domain of the membrane. Hygroscopic nature of silica increased the water uptake of the membrane.

As shown by the SEM images (Figure 4.4), SPEEK-10-5 (A + C) had the most compact and homogenous structure. This resulted in its high mechanical integrity. Good dimensional stability and high swelling resistance caused it to achieve the lowest water and methanol solution uptake among the three membranes in this subsection.

4.4.6 Thermal and Oxidative Stability

The thermal and oxidative stability of SPEEK-10-5 (A), SPEEK-10-5 (C) and SPEEK-10-5 (A + C) composite membranes were compared. The comparison of thermal stability and oxidative stability are shown in Figure 4.7 and Table 4.11, respectively.

It can be seen that inclusion of different combinations of coupling agents did not show significant effect to the thermal stability of the membrane. In other words, the thermal stability of SPEEK-10-5 from the previous subsection was remained.

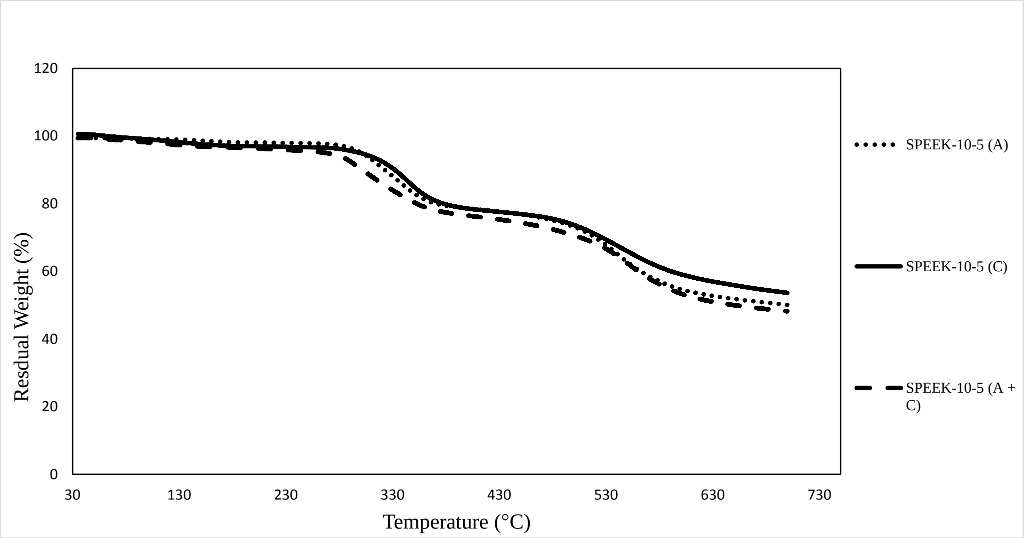


Figure 4.7: TGA of Various SPEEK based Membranes

Table 4.11: Chemical Degradation of SPEEK/SiO$_2$-SiWA Composite Membranes with Different Coupling Agents

Membrane	Chemical Degradation (%)
SPEEK-10-5 (A)	1.74 (±0.06)
SPEEK-10-5 (C)	Dissolved
SPEEK-10-5 (A + C)	0.00 (±0.00)

As for the oxidative stability, SPEEK-10-5 (A), which had higher silica content, exhibited oxidative stability similar to SPEEK-10-5. This again justified the function of silica as an antioxidant. Another positive finding was shown by SPEEK-10-5 (A + C), where initial and final weight of the membrane did not change after Fenton's test. The homogeneity and compatibility between SPEEK and silica resulted in their strong interaction. This improved the performance of silica in protecting the polymer from being attacked by the free radicals and this would possibly increase the durability of the membrane when used in a DMFC.

However, SPEEK-10-5 (C) dissolved in Fenton's solution within 3 hours. Therefore, instead of resisting radicals' attack, SPEEK polymer would react with the free radicals, and this ended up with its accelerated degradation. Furthermore, the situation was worsen by low amount of silica present due to leaching during activation steps, as proved by the EDX results.

4.4.7 Methanol Permeability

Table 4.12 shows the methanol permeability of SPEEK-SiO_2-SiWA composite membrane added with different coupling agents. Among these three membranes, SPEEK-10-5 (C) had the highest methanol permeability (10.00×10^{-7} cm^2/s) due to its high porosity coupled with lacking of silica to block and occupy the hydrophilic channels where methanol diffused through.

SPEEK-10-5 (A) had the second highest methanol permeability (9.53×10^{-7} cm^2/s). Low dimensional stability with high degree of swelling resulted in the increase in size of ionic clusters and hydrophilic channels. Rate of diffusion of methanol across the membrane became easier when the transport pathway became wider.

SPEEK-10-5 (A + C) achieved the lowest methanol permeability (6.55×10^{-7} cm^2/s). Successful linkage between base polymer and inorganic additives formed a compact internal structure as a barrier to block methanol transport. Due to the presence of APTES and its connection with SPEEK polymer, the position of formed silica was more predictable (attached to

APTES as shown in Figure 4.6) and well distributed as compared to random incorporation without silane coupling agent. On top of that, probability that silica to appear in the hydrophobic domain also became lower. When silica only appears at the hydrophilic channels, its can block polar methanol better, resulting in low methanol permeability.

Table 4.12: Methanol Permeability of SPEEK/SiO_2-SiWA Composite Membranes with Different Coupling Agents

Membrane	**Methanol Permeability ($\times 10^{-7}$ cm^2/s)**
SPEEK-10-5 (A)	9.53 ($\pm$0.31)
SPEEK-10-5 (C)	10.00 ($\pm$0.22)
SPEEK-10-5 (A + C)	6.55 ($\pm$0.13)

4.4.8 Proton Conductivity

Proton conductivity of all three membranes in this stage of research was measured and shown in Table 4.13. SPEEK-10-5 (A) and SPEEK-10-5 (C) exhibited high proton conductivity, which was mostly contributed by vehicle diffusion due to their high water uptake. Vehicle diffusion happens when proton combines with water molecule to form hydronium ion and they move across the membrane together. Similar to methanol permeability, swelling of membrane internal structure provided larger pathway for proton transport and this resulted in high proton conductivity.

However, one very interesting finding was the proton conductivity of SPEEK-10-5 (A + C). Although the membrane had low water uptake and rigid membrane structure, the proton conductivity of the membrane could still be maintained at high level. This means that instead of using vehicle diffusion, another proton transport mechanism actually dictated the movement of proton in this membrane. In SPEEK-10-5, Grotthuss mechanism was mainly contributed by two types of ion exchange sites: sulfonic acid group and SiWA. However, in the case of SPEEK-10-5 (A + C), active sites of some sulfonic acid groups were replaced by coupling agents, hence, majority of the proton hopping sites were only SiWA. High proton conductivity in this membrane suggested that due to the presence of coupling agents, SiWA was incorporated well in the polymer matrix and performed excellently. Moreover, uniform distribution of silica due to the presence of APTES lead to the even dispersion of SiWA. This created a more conducive pathway for proton transport.

By calculating the ratio of proton conductivity to methanol permeability, SPEEK-10-5 (A + C) had the highest selectivity. Enhanced compatibility between the organic and inorganic parts of the membrane resulted in better alignment of inorganic silica and SiWA. This situation provided better resistance to methanol transport, at the same time, assisted proton conduction across the membrane.

Table 4.13: Proton Conductivity and Selectivity of Different SPEEK/SiO2-SiWA Composite Membranes

Membrane	**Proton Conductivity (S/cm)**	**Selectivity ($\times 10^4$ S.s/cm^3)**
SPEEK-10-5 (A)	0.0833 (±0.0027)	8.74
SPEEK-10-5 (C)	0.0691 (±0.0033)	6.90
SPEEK-10-5- (A + C)	0.0696 (±0.0045)	10.60

4.4.9 Summary

In this stage of the research, SPEEK-10-5 was modified by the addition of different coupling agents to boost the compatibility between organic SPEEK and inorganic silica as well as SiWA. It was realised that CDI could only perform as a promoter to APTES silane coupling agent. The resultant membrane had smooth, homogenous and compact morphology coupled with good proton conductivity as well as low methanol permeability. SPEEK-10-5 (A + C) had the highest selectivity and the formulation of this membrane was carried forward to the next stage of research.

4.5 Alternatives for Silica

Besides using silica as a support for SiWA, during the research, search for other inorganic oxide as silica's replacement was proposed. As regards the proposal, alumina and iron (III) oxide were tested as alternatives for silica. Both oxides were prepared from their respective nitrate precursors.

4.5.1 Abbreviations and Details of Samples

The abbreviation, compositions and details of all samples used in this subsection are tabulated in Table 4.14. Membrane preparation steps of SPEEK-10-5 (A + C) were remained. The only modification was the use of 10 wt% alumina or 10 wt% iron (III) oxide in place of 10 wt% silica.

Table 4.14: Abbreviations of SPEEK based Composite Membrane with Different Inorganic Oxides

Membrane	Alumina Loading (wt%)	Iron (III) Oxide Loading (wt%)	SiWA Loading (wt%)
SPEEK/Al_2O_3-SiWA	10	0	5
SPEEK/Fe_2O_3-SiWA	0	10	5

4.5.2 Distribution and Stabilisation of Inorganic Additives

Table 4.15 shows the additives' elemental compositions in SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA composite membranes. From the results, it could be seen that alumina and iron (III) oxide experienced more severe leaching as compared to silica although both ultrasonic treatment and addition of APTES as well as CDI were done. Elemental weight composition of aluminium and iron dropped well below their theoretical value and this was accompanied by the reduction in SiWA content. To explain the results, two main reasons are identified.

Firstly, alumina and iron (III) oxide have amphoteric properties in nature (Tchomgui-Kamga, et al., 2010). When the membranes were immersed in 1 M sulphuric acid for 24 hours during the protonation process, alumina and iron (III) oxide behaved like a base. Hence, it was easier for the oxides to react with acid and detached from the polymer matrix and finally leached out of the membrane.

Secondly, incompatibility of coupling agents used resulted in ineffective stabilisation of inorganic additives. In this research, APTES (silane coupling agent) was used as the main coupling agent. Silane coupling agent links the additives through silane bondings which require silicon atoms. In SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA, there was no silicon atom found, therefore inclusion of incompatible coupling agents would not show any significant or positive effects.

Table 4.15: Elemental Compositions of Aluminium, Iron and Tungsten in Different SPEEK Composite Membranes

Membrane	Elemental Compositions (wt%)		
	Al	Fe	W
SPEEK/Al_2O_3-SiWA	2.22 (±0.18)	-	1.45 (±0.29)
SPEEK/Fe_2O_3-SiWA	-	0.32 (±0.06)	1.34 (±0.31)

By analysing the elemental composition of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA, it could be concluded that alumina and iron (III) oxide were not suitable replacement for silica. Nevertheless, the performance of these two composite membranes were also tested and shown in the next subsection.

4.5.3 Water and Methanol Solution Uptake

Water and methanol solution uptake of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA are tabulated in Table 4.16.

Table 4.16: Water and Methanol Solution Uptake of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA

Membrane	Water Uptake (%)	Methanol Uptake (%)
SPEEK/Al_2O_3-SiWA	190.48 (±4.77)	150.33 (±6.19)
SPEEK/Fe_2O_3-SiWA	64.58 (±1.09)	61.90 (±0.99)

Leaching of the additives left voids and holes in the structure of the membrane. This degraded the dimensional stability of the membrane and led to excessive swelling. SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA had extremely high water and methanol solution uptake. In fact, SPEEK/Al_2O_3-SiWA had the highest water and methanol solution uptake, probably due to the coarser size of alumina. Slower formation of alumina resulted in in higher tendency of their agglomeration and formed particles with larger size (Rahman and Padavettan, 2012). Leaching of alumina left bigger holes in the membrane and increased the water and methanol solution uptake.

When compared with SPEEK-10-5 (A + C), SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA had higher water uptake and methanol solution uptake (Table 4.10). The results further supported the effect of membrane compactness on its dimensional stability. SPEEK-10-5 (A + C) which was more rigid exhibited better resistance to swelling by absorbing less water or methanol solution.

4.5.4 Thermal and Oxidative Stability

Figure 4.8 shows the TGA curves for SPEEK/SiO_2-SiWA, SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA. Addition of SiWA and inorganic supports improved the thermal stability of the membrane (Tian and Savadogo, 2005). However, due to the severe leaching, first degradation temperature of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA dropped to

320 ℃. Furthermore, the final residual weight percent for both membranes were lower than composite membranes that used silica and support of SiWA.

Due to the absence of effective antioxidant (silica) (Ren, et al., 2013), the oxidative stability of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA were also lower. This was especially noticeable in SPEEK/Al_2O_3-SiWA, where porous internal structure of the membrane allowed accelerated free radicals attack, thereby increased the degradation rate of the membrane. The results were compared in Table 4.17.

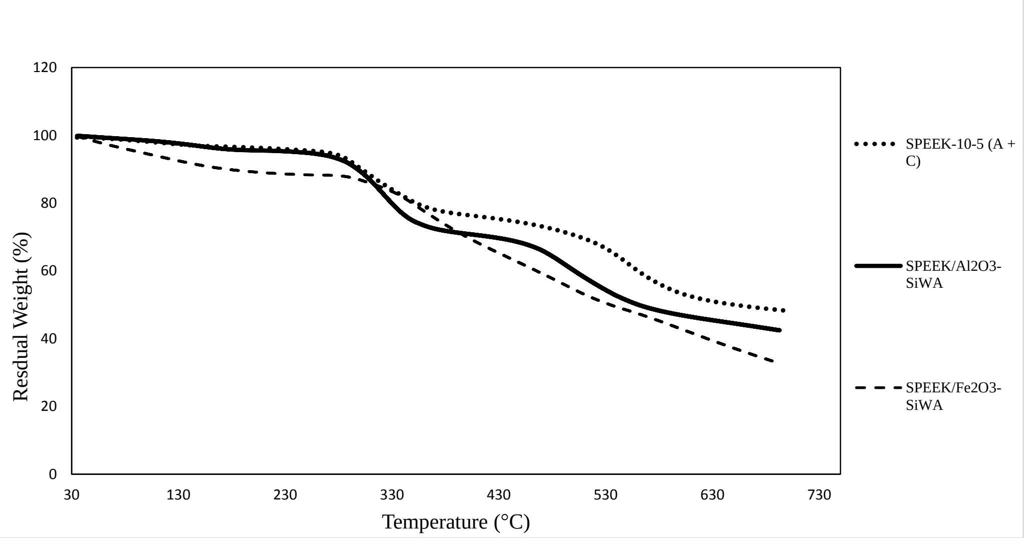


Figure 4.8: TGA of Various SPEEK based Membranes

Table 4.17: Chemical Degradation of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA

Membrane	**Chemical Degradation (%)**
SPEEK/Al_2O_3-SiWA	13.52 (±0.09)
SPEEK/Fe_2O_3-SiWA	3.81 (±0.11)

4.5.5 Methanol Permeability

Table 4.18 compiles the methanol permeability of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA. Methanol permeability has positive relationship with water and methanol solution uptake. This trend was also observed in these two membranes. SPEEK/Al_2O_3-SiWA which had extremely high water and methanol solution uptake also exhibited extremely high methanol permeability. SPEEK/Fe_2O_3-SiWA membrane's methanol permeability was reported to be 8.43×10^{-7} cm^2/s, which was also regarded has high value due to its porosity.

Table 4.18: Methanol Permeability of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA

Membrane	Methanol Permeability ($\times 10^{-7}$ cm^2/s)
SPEEK/Al_2O_3-SiWA	21.30 ($\pm$0.97)
SPEEK/Fe_2O_3-SiWA	8.43 ($\pm$0.93)

4.5.6 Proton Conductivity

Proton conductivity and selectivity of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA are shown in Table 4.19. Porous SPEEK/Al_2O_3-SiWA coupled with high water uptake resulted in its high proton conductivity. Whereas for SPEEK/Fe_2O_3-SiWA, slightly lower water uptake, combined with the consequence of SiWA leaching led to a very low proton conductivity.

As stated earlier, alumina and iron (III) oxide are amphoteric in nature. The inclusion of the inorganic oxides into the polymer matrix neutralised or diluted the sulfonic acid group, which was responsible for proton transport.

This hampered the proton transport capability of the membranes. Proton conductivity test which was done under ambient humidity resulted in low proton conductivity of the membranes. These had subsequently caused the low selectivity of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA.

Table 4.19: Proton Conductivity and Selectivity of SPEEK/Al_2O_3-SiWA and SPEEK/Fe_2O_3-SiWA

Membrane	**Proton Conductivity (S/cm)**	**Selectivity ($\times 10^4$ S.s/cm^3)**
SPEEK/Al_2O_3-SiWA	0.0634 ($\pm$0.0079)	2.97
SPEEK/Fe_2O_3-SiWA	0.0048 ($\pm$0.0005)	0.57

4.5.7 Summary

Alumina and iron (III) oxide were tested to replace silica. However, their amphoteric nature as well as the inability of silane coupling agent to enhance their compatibility with SPEEK polymer caused severe leaching of additives. This had also caused them to have low proton conductivity to methanol permeability selectivity. As a summary, using current formulation for membrane fabrication, alumina and iron (III) oxide were not suitable alternatives for silica.

4.6 Conclusion

SPEEK based composite PEM with varying silica: SiWA weight ratio, coupling agents were fabricated. Attempt to replace silica with alumina and iron (III) oxide was also done. It was reported that SPEEK-10-5 (A + C) had the best performance in terms of selectivity and stability. The performance of SPEEK-10-5 (A + C) was compared with pristine SPEEK membrane and commercial Nafion 117 membrane, and the results are shown in Table 4.20.

Table 4.20: Comparison between Various PEMs

Membrane	**Selectivity ($\times 10^4$ S.s/cm^3)**
SPEEK	1.63
Nafion 117	8.09
SPEEK-10-5 (A + C)	10.60

It was noted that SPEEK-10-5 (A + C) had higher selectivity than Nafion 117 membrane. When compared with pristine SPEEK membrane, the performance of SPEEK-10-5 (A + C) had improved around 10 times. The roles of the additives in improving the properties and performance of the composite membrane were justified.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Development of SPEEK based composite PEM was done in four stages: effect of ultrasonic treatment, effect of different silica:SiWA weight ratio, effect of various coupling agents and alternatives for silica. Best membrane casted from each stage was used in the next stage in as an effort for continuous improvement of PEM's performance.

5.1.1 Effect of Ultrasonic Treatment

SPEEK/SiO_2-SiWA composite membrane with 10 wt% of SiWA supported on 10 wt% of silica was used in this stage. Membrane that was not subjected to ultrasonication suffered serious leaching of silica and SiWA after 1 M sulphuric acid pre-treatment. Conversely, preparation steps that involved ultrasonic treatment produced membrane with better incorporation and dispersion of additives. This was due to the presence of extra energy provided by cavitation of ultrasound, which helped to prevent of agglomeration and enhanced dispersion.

5.1.2 Effect of Different Silica:SiWA Weight Ratio

From the previous stage, silica:SiWA weight ratio was modified from 1:1 to 2:1 and 1:2. It was found that higher composition of SiWA would result in higher rate of hydrolysis and condensation reaction of TEOS. This caused formation of more silica which affected the membranes' morphologies. However, when the loading of SiWA was increased, the insufficient amount of silica to immobilise SiWA causing SPEEK-10-10 and SPEEK-10-20 to experience leaching. SPEEK-10-5 was reported to have the best performance in terms of selectivity (6.44×10^4 S.s/cm^3) and was carried forward to the next stage of research.

5.1.3 Effect of Various Coupling Agents

Attempt to improve the compatibility of organic SPEEK and inorganic silica as well as SiWA was done by the addition of various coupling agents. Coupling agents generally have two functionalities to act as a bridge, linking organic and inorganic constituents of a composite. In this research, APTES and CDI were used as coupling agents. Addition of only APTES or CDI did not improve the performance of the membrane. In the absence of another chemical, APTES only acted as a silica precursor whereas CDI caused SPEEK to be ready for further reactions. However, when the two chemicals were used together, CDI acted as a promoter to link organic functionality of APTES molecules on to the SPEEK polymer backbone. Subsequent substitution of $Si(OH)_4$ into the inorganic parts of APTES completed the linkage between

SPEEK and silica. The membrane formed had smooth, homogenous and compact structure. Thermal and oxidative stability of the membrane were reported to be excellent with the selectivity of 10.60×10^4 S.s/cm^3, which was higher than commercial Nafion 117 membrane. Thermal stability of the composite membrane was improved when compared with the pristine SPEEK membrane. It also exhibited excellent oxidative stability where the SPEEK-10-5 (A + C) was virtually resistant to Fenton's reagent due to the presence of silica.

5.1.4 Alternatives for Silica

This research tried to use alumina and iron (III) oxide, which was prepared from their nitrate salts to replace silica. However, amphoteric nature of alumina and iron (III) oxide as well as their incompatibility with the coupling agents used resulted in the negative findings of the experiment. The leaching of alumina and iron (III) oxide were more severe than silica as they would behave as base and react with sulphuric acid during protonation process. Due to the severe leaching, both membranes exhibited poor performance and were deemed not a suitable replacement for silica.

5.1.5 Summary

SPEEK based composite PEMs were fabricated and characterised. SPEEK-10-5 (A + C) was reported to be the membrane with the best performance, not only in terms of selectivity, but also good membrane structure and outstanding thermal as well as oxidative stability. The fabrication of this membrane involved the use of ultrasonic treatment (stage 1), silica:SiWA weight ratio of 2:1 (stage 2) and the addition of APTES and CDI as coupling agents (stage 3). Search for silica’s alternatives did not have positive feedback as the characteristics and nature of alumina and iron (III) oxide were not a suitable candidate to replace silica under this formulation of cast solution.

5.2 Future Works and Recommendations

A comprehensive study had been done on the development of low cost SPEEK based composite PEM. However, further improvement still could be done on the methodology. For example, in order to accurately determine the compounds and their compositions within the composite membrane, Raman spectroscopy as well as X-ray photoelectron spectroscopy analysis can be carried out on the membrane samples. On top of that, a more complete single cell test and also cyclic test can be done on the membrane to study the performance of the developed membrane in fuel cell operation as well as its durability. Field emission SEM and transmission electron spectroscopy can also be included so that the structure and morphology of the membrane samples can be observed in a more detailed manner, including the structure of nanoparticles if any.

From the foundation laid down by the current work, there are a few new research directions being determined. First, the loadings of the additives can be further tuned to obtain the optimum value. This can be done with the aid of design of experiment software such as Design Expert. Fine tuning can also include the reaction condition, for example pH value and also condition of ultrasonic treatment.

Secondly, trial to scale up the production of SPEEK based composite PEM, with current formulation can be done. Lab scale experiment proved that SPEEK-10-5 (A + C) had the potential to substitute commercial Nafion 117. Scaling up can be one of the most important steps to the commercialisation of SPEEK based membrane, thereby reducing the cost of DMFC fabrication as a whole.

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