



Review Paper

Poly (Ether Ether Ketone) Based Anion Exchange Membrane for Solid Alkaline Fuel Cell: A Review

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Highlights

- Poly ether ether ketone based anion exchange membrane is a promising electrolyte for solid alkaline fuel cell.
- Poly ether ether ketone polymer is a thermoplastic material that having excellent mechanical and thermal stability properties.
- There are three well-known cationic functionalized groups attach on PEEK backbone which are quaternary ammonium, quaternary phosphonium and imidazole group.

Abstract

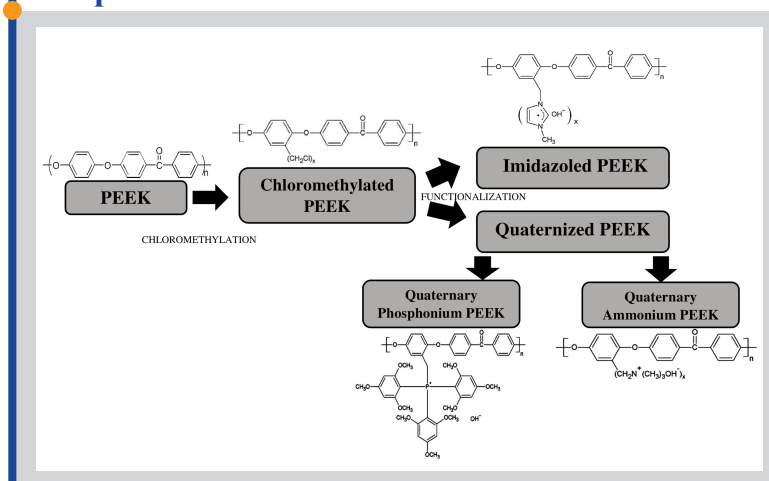
Solid alkaline fuel cell is employed by polymer anion exchange membrane (AEM) that is permeable to hydroxide ion. A number of polymers have been proposed for AEM which include polysulfone (PSF), poly (phenylene oxide) (PPO), and poly (ether ether ketone) (PEEK). The purpose of this paper was to conduct a critical review on the development of PEEK polymer as AEM, particularly in terms of the fabrication methods, cationic functionalized group reagent, and the effect of filler addition on membrane properties. PEEK is a thermoplastics polymer that possesses superior mechanical, thermal, and chemical stability. The basic development of PEEK-based AEM involves the process of attaching the cationic functionalized group, namely quaternary ammonium (QA), quaternary phosphonium (QP), and imidazolium (Im) groups onto the PEEK backbone. Up to the recent time, the chloromethylation-functionalization and acid-base blending methods are among the commonly used fabrication methods in developing PEEK-based AEM. The increase in the degree of functionalization (DF) caused the basic PEEK-AEM, namely QA-PEEK, QP-PEEK, and Im-PEEK to exhibit high hydroxide conductivity apart from the degradation in alkaline stability, mechanical property, and dimensional stability. The modification of the membranes performed through the addition of filler or ionic-crosslink between acid and base may improve the anion conduction pathway, alkaline stability, mechanical property and water retention property of the membrane due to the increase of the DF.

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Graphical abstract



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1. Introduction

Fuel cells are described as electrochemical device that is capable of converting the chemical energy stored in fuels into direct current (DC) electricity for stationary, portable, and traction applications. The fuel cells were introduced by Sir William Robert Grove in 1839 which can be further categorized into several types depending on their employed electrolyte and fed fuel [1-2]. The main types of fuel cells are proton exchange membrane fuel cells (PEMFC), alkaline fuel cells (AFC), solid alkaline fuel cells (SAFC), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs). The alkaline fuel cell (AFC) was first introduced by F.T. Bacon during the 1930s, whereby it has been widely used in Space Shuttle and Apollo (space program) since 1960s [3]. The AFC offers several advantages such as faster reaction rates at cathode that can lead to high performance and higher energy efficiency as well as can be used as a variety of catalysts [4]. Moreover, it is employed by liquid electrolyte that is mainly based on potassium hydroxide (KOH) which is dependent on the operating temperature. On a more important note, the concentrated (85 wt.%) KOH is used as electrolyte when AFC operates at high temperature (250 °C). On the other hand, less concentrated (35-50 wt.%) KOH is more preferable at low temperature (<120 °C) [3].

The use of liquid alkaline electrolyte leads to gas crossover and carbonation environment in AFC [5]. Meanwhile, the presence of carbon dioxide in gas streams tends to cause electrolyte poisoning, in which potassium hydroxide (KOH) is converted to potassium carbonate (K_2CO_3). In this case, the ionic conductivity of AFC tends to be reduced because potassium carbonate blocks the cathode pore. The problem may become significantly worse when liquid alkaline electrolyte is used with methanol fuel in AFC, similar to the findings provided by Murray and Grimes in their study which showed that the performance was steadily decreased over 70 hours at 60 °C and 94 hours at 30 °C at 0.3 V, due to anode degradation [6]. In the same study, the AFC was fed by methanol fuel, while the electrolyte is based on aqueous KOH (6 mol dm^{-3}). Apart from that, other fuels that can be used for AFC include hydrogen, propanol, ethanol, sodium borohydride, and ethylene glycol. In regard to this matter, several researchers have created solid polymeric-based membrane that is known as solid alkaline fuel cell which is normally fueled with hydrogen/oxygen due to the fact that liquid KOH can lead to electrolyte poisoning. The SAFC was developed in early 2000 with the operating temperature between 60 to 90°C which can be used for powering purposes of the portable application of 100 mW to 100 kW [7]. The electrolyte of SAFC is based on polymer anion exchange membrane (AEM), thus allowing only anion to pass through it. Meanwhile, the AEM consists of positive charge ion that permits only negative charge ion to crossover the membrane and at the same time repels the positive charge ion. In regard to this, the application of solid anion exchange membrane provides more advantages compared to liquid AEM which include the prevention of formation of carbonate precipitates, reduction of fuel crossover, improvement in reaction kinetics, and fuel flexibility [8-10]. On a more important note, the SAFC fed by pure H_2/O_2 fuels is more capable of eliminating the presence of CO_2 compared to methanol. Moreover, solid alkaline fuel cell (SAFC) possesses nearly similar operation principle and behavior to those of AFC instead of employing solid polymer electrolyte for membrane. Figure 1 illustrates the operation principle of SAFC. As shown in the figure, it can be observed that the reactant gases are fed on cell which refers to hydrogen fuel on the anode side as well as oxygen fuel on the cathode side. Meanwhile, the oxygen reduction reaction on the cathode side of SAFC is performed by reducing the O_2 into OH^- with the presence of H_2O . Next, the OH^- flows through the anion exchange membrane from cathode to anode and reacts with the H^+ to produce H_2O . In addition, the production of water per electron in SAFC is twice than in PEMFC [10]. On another note, the electrons form and

flow through the external circuit to the cathode during the hydrogen oxidation reaction process, then reacts with O_2 to produce OH^- . Equations (1-3) represent the electrochemical reaction involves in the SAFC.

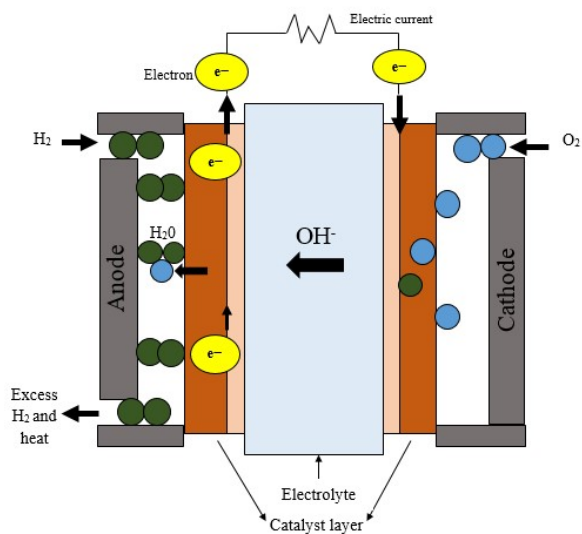
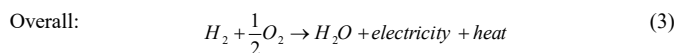
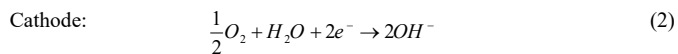
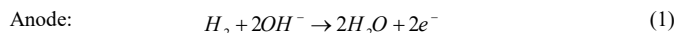


Fig. 1. Schematic diagram representation of working principle in SAFC.



Up to now, several types of solid AEM from polymer materials for SAFC have been developed by researchers in order to replace the KOH solution. In regard to this matter, the polymer materials that have been commonly used to develop AEM are poly (phenylene oxide) [11], polypropylene [12], poly(fluorenyl ether ketone sulfone) [13-14], poly(arylene ether sulfone) [14], and poly(arylene ether ketone) [15-16]. In this case, AEM can be prepared by introducing cationic functional group such as quaternary ammonium, quaternary phosphonium, imidazolium, and guanidium onto the polymer backbone. Ideally, the developed AEM should be able to fulfil several membrane characteristics which include impermeable to reactant gases and electron, high mechanical strength, thermal stability and chemical stability, high anion conductivity, low swelling ratio, and low cost for the purpose of optimizing their performance, durability, and cost-efficiency. However, it should be clearly noted that fulfilling some of the AEM properties are regarded good enough considering that it is difficult to achieve all of the membrane properties. A considerable amount of studies showed that the AEM based on poly ether ether ketone (PEEK) is considered as a good candidate

for SAFC electrolyte among other AEM materials due to their acceptable electrochemical performance and appropriate membrane properties [16]. In addition, the PEEK is described as a semi-crystalline thermoplastics that can be classified into five families, namely poly ether ketone (PEK), poly ether ether ketone (PEEK), poly ether ketone ketone (PEKK), poly ether ether ketone ketone (PEEKK), and poly ether ketone ether ketone ketone (PEKEKK) which are mainly dependent on the ratio and sequence of ether to ketones [17]. Nevertheless, PEEK is the most widely used ion-exchange membrane due to its excellent mechanical property, good thermal stability, and high thermal stability. PEEK was introduced for the first time by Victrex Company, followed by Imperial Chemical Industries in the early 1980s and made to be commercially available. The chemical structure of PEEK is shown in Figure 2, while Table 1 displays the basic properties of the commercial PEEK.

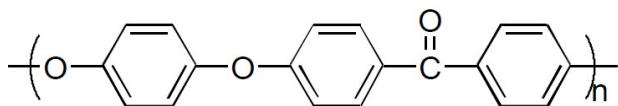


Fig. 2. Chemical structure of PEEK.

Table 1
Properties of commercial PEEK from Victrex Company [18].

Properties	Value
Molecular weight (g/mol)	39200
Glass transition temperature (°C)	143
Density (g/cm ³)	1.30
Melting temperature (°C)	343
Solvent resistance	Soluble in (H ₂ SO ₄ , CH ₃ SO ₃ H) Insoluble in (DMF, DMAc, NMP, DMSO)

1.1. Scope of the Review

The objective of this review is to highlight the development of the quaternized PEEK and imidazolized PEEK membrane for SAFC application. Generally, the membrane characteristics are dependent on numerous variables which include polymer chemical structure, membrane thickness, casted solvent, molecular weight, water uptake, and others. On another note, a brief description on the effect of cationic functionalized group, type of filler, and fabrication methods on membrane properties are briefly discussed in the following section.

2. Fabrication Methods of PEEK Based AEM

Polymer materials such as PSF, PPO, and PEEK are required to be modified and altered into ion-exchange membrane which can be produced by attaching the polymer backbone with quaternary ammonium cations, quaternary phosphonium cations, and imidazole cations. More importantly, the fabrication methods that have received a great deal of attention in developing PEEK-AEM are chloromethylation-functionalization and acid-base blending [19, 20], owing to their wide availability that will be further discussed in the following section.

2.1. Chloromethylation-functionalization Method

Chloromethylation-functionalization is one of the modification techniques that is deemed suitable in preparing PEEK as an anion conducting membrane. In regard to this matter, the appropriate degree of functionalization plays an important role in producing the required functionalize membrane properties for fuel cell application. Moreover, the degree of functionalization represents the functionalized groups concentration in the matrix of polymer. On another note, the cation functionalize group in hydroxide alkaline membrane or AEM is mainly responsible in changing the pristine polymer such as PEEK and PSF into alkaline nature. Next, a well-connected hydrophilic domain is formed in the PEEK matrix through functionalization process which is responsible for the hydroxide ion (OH⁻)

and water transport. Commonly, the PEEK-based AEM will be functionalized with cationic group such as quaternary ammonium [21], quaternary phosphonium [21], or imidazolium [20-23] after the chloromethylated process. The commercial PEEK (i.e. Victrex Company) needs to be dissolved in acid prior to the process of being further chloromethylated with chloromethylating agent because PEEK is generally known to have poor solubility in organic solvent such as the chlorinated hydrocarbons. There are several types of acids that can be used to dissolve PEEK which include sulfuric acid (concentrated/fuming), sulfur trioxide, or chlorosulfonic acid. However, it is important to note that the PEEK is not suitable to be dissolved in chlorosulfonic acid and fuming acid because they may cause PEEK degradation, thus further explains the preferred choice of concentrated acid [22]. PEEK is highly soluble in concentrated H₂SO₄ which makes it possible to be processed as AEM. In the study conducted by Yan et al. [19], the PEEK managed to be successfully chloromethylated for the first time in concentrated H₂SO₄. The chloromethylation of PEEK in H₂SO₄ needs to be carefully performed in order to control the degree of sulfonation and further complete the replacement of anion conducting groups (SO₃H) with cation conducting groups (CH₂Cl) to avoid zwitterionic properties [23].

The chloromethylation of polymer can be performed using the following two techniques: (1) radiation-grafting chloromethyl-containing vinyl benzyl chloride (VBC) monomer onto fluorinated polymers such as poly(ethylene-co-tetrafluoroethylene) (ETFE) [24], poly(hexafluoropropylene-co-tetrafluoroethylene) (HTFE) [25], and poly(vinylidene fluoride) (PVDF) [26], or (2) direct chloromethylation onto polymer matrix. However, direct chloromethylation is more preferable among researchers due to its simpler procedure, easy to be conducted, and better flexibility compared to radiation-grafting. Chloromethylating agent such as chloromethyl methyl ether (C₂H₅ClO), chloromethyl octyl ethers (C₈H₁₇ClO) and bis(chloromethyl) ether (CH₂Cl)₂O are required in the chloromethylating process for the purpose of introducing chloromethyl group onto PEEK matrix. However, it is highly recommended for researchers to take a serious safety precaution because the chloromethylating agent is classified as hazardous and carcinogenic chemicals considering that it can potentially cause respiratory cancers as a result of chronic exposure. Chloromethyl methyl ether has been listed as one of the most hazardous substances by the Occupational Safety and Health Administration. In regard to this matter, Jasti et al. [23] has introduced a safer method for chloromethylating PEEK through the in-situ technique using paraformaldehyde, trimethylchlorosilane, and lewis acid catalyst due to the toxicity of the chloromethylating agent. Moreover, the degree of sulfonation (DS) and chloromethylation (DC) of PEEK can be controlled by varying the temperature, reaction time, acid concentration, and PEEK content [27, 28]. Commonly, a low degree of sulfonation at 10% and below is preferred in the preparation of AEM based on PEEK for the purpose of allowing a better electrophilic substitution between sulfonic acid groups and chloromethylated groups. In addition, the sulfonic acid groups are fully replaced with functional group at this DS. However, Han et al. [27] claimed that the presence of some sulfonic group in QPEEK caused by the increase of sulfonation degree may enhance the membrane properties, especially the dimensional and chemical stability. On another note, the phenomenon of electron-attracting of the neighbouring carbonyl group tends to cause low electron density of the other two aromatic rings in the polymer repeat unit, which further leads to the substitution of one sulfonic acid group per repeat unit. The replacement of SO₃H group with CHCl₂ of PEEK occurs at the aromatic ring which is flanked by two ether links due to the higher electron density of the ring [28]. The degree of sulfonation, degree of chloromethylated, and attachment of cationic group onto PEEK backbone can be determined through nuclear magnetic resonance (NMR) spectroscopy and fourier transform infrared spectroscopy (FTIR). The chemical structure of the chloromethylated PEEK (CMPEEK) is presented in Figure 3.

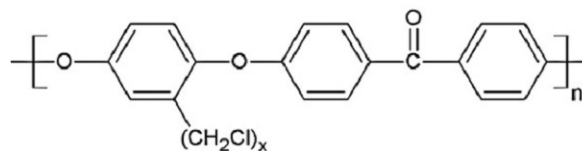


Fig. 3. Chemical structure of CMPEEK.

2.2. Blending Method

There are two well-known AEM based on PEEK polymer which are (1)

acid-base blending membrane and (2) composite membrane based on filler. In this matter, the blending process is regarded as the simplest method to fabricate polymer/inorganic nanocomposites through the direct mixing of the filler/polymer into the other polymer. In addition, there are two methods that can be employed to mix them, namely melt blending or solution blending. Nevertheless, this method is problematic due to the agglomeration of the filler that can be overcome by the modification of the surface of the inorganic particles [29]. However, there are several benefits of acid-base blending from electrostatic interaction in AEM which include the enhancement on intermolecular forces of polymer chains, improvement on membrane stabilities, and the induction of the optimum orientation of water networks through electrostatic attractions within the anion and cation pairs that facilitate the formation of hydrogen-bonding networks in ensuring better mobility of hydroxide ion.

3. Cationic Functionalized Group for PEEK Membrane

Generally, the two well-known types of AEM-PEEK are quaternized PEEK (QPEEK) and imidazole PEEK (imPEEK). In this case, QPEEK occurs when the quaternized group exists in the PEEK matrix, while imPEEK consists of imidazolium group. The QPEEK and imPEEK display interesting membrane behaviour in terms of water uptake, swelling ratio, ion exchange capacity, hydroxide conductivity, mechanical strength, and chemical stability which only requires a simple synthesizing method. In addition, there are several steps in synthesizing the membranes which include the chloromethylation process for the purpose of introducing chloromethyl group onto PEEK matrix, followed by electrophilic-substitution reaction that requires the conversion of the chloromethyl group into quaternize or imidazole group. Figure 4 summarizes the AEM based on chloromethylated PEEK that will be further described in the review. Finally, the Cl^- ion is substituted into OH^- by immersing the membrane in potassium hydroxide (KOH) or sodium hydroxide (NaOH) solution. The quaternize or imidazole groups aggregate for the purpose of producing a hydrophilic domain. Meanwhile, the anionic charge carriers form within inner space, charge layers resulted from dissociation of the alkaline functional groups, and the anion conductivity facilitated by water dynamics occur in hydrated membrane environments [30].

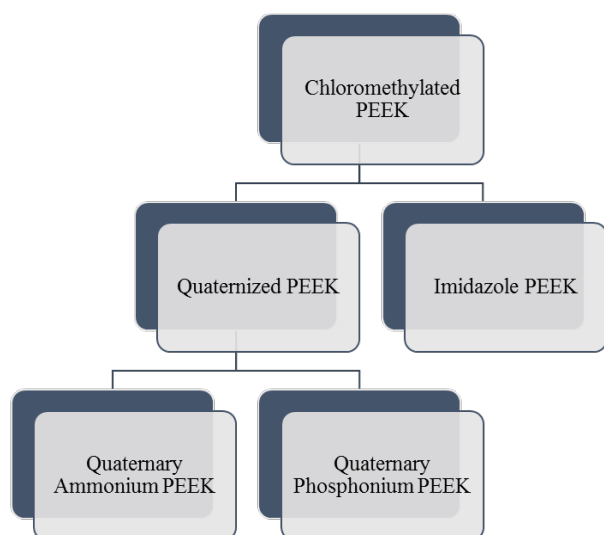


Fig. 4. General AEM based on PEEK.

4. Degree of Chloromethylation

Generally, it is widely known that the pristine PEEK is insoluble in all solvents; however, the presence of the chloromethylated group has caused them to be excellently soluble in high-boiling-point solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and 1-methyl-2-pyrrolidone (NMP). Moreover, the excellent

solubility of CMPEEK in the solvents makes it possible to develop a high-performance AEMs. The DC may affect several important membrane characteristics including the ion exchange capacity (IEC), swelling ratio (SD), water uptake (WU), and hydroxide conductivity (σ) because they are not strictly dependent on the PEEK chloromethylation procedure. On a similar note, the most important parameter of the QAPEEK membranes electrochemical performances refers to the hydroxide conductivity due to its significant dependency on DC and membrane humidity as well as other indicator such as water uptake, temperature, and others. Commonly, there are three states of water that are present in membrane matrix, namely free water, freezing bound water, and non-freezing water [31]. The free water has the same temperature and enthalpy as the bulk water, while the freezing bound water is weakly bound with ionic groups or polar of polymer which can change the temperature and melting enthalpy. On the other hand, there is a strong interaction for the non-freezing water with the ionic groups or polar as well as the absence of phase transition.

The DC of PEEK should be controlled between 35-75 % in order to achieve appropriate water uptake, moderate swelling degree, and acceptable hydroxide conductivity for fuel cell application. In addition, it is also important to control the degree of chloromethylation of PEEK for the purpose of obtaining a targeted ion exchange capacity (IEC) and sustaining its mechanical, thermal, and chemical stability for quaternization method. Meanwhile, the IEC also has a strong relationship with the hydroxide conductivity, water uptake, and swelling ratio of AEM. On another note, the DC of PEEK increases with the increase of chloromethylation time. Fortunately, the IEC of CMPEEK also increases with the DC of PEEK at 38 to 76% of DC, the IEC gradually increase from 0.43 to 1.35 mmol g^{-1} in Yan et al. [19]. The higher DC of CMPEEK will lead to a better hydrophilicity and provides more chance to react with quaternize or imidazole reagent [32, 33]. The degree of chloromethylation of PEEK can be obtained from HNMR analysis based on Equation (4) and Figure 5 [19].

$$DC = \frac{2A(H_d)}{A(H_c)} \quad (4)$$

where $A(H_d)$ represents the integral area of the H_d peak ($-\text{CH}_2\text{Cl}$), and $A(H_c)$ is one of the H_c peak.

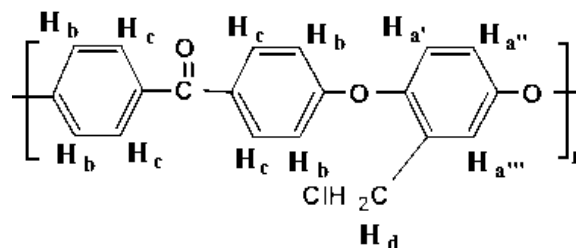


Fig. 5. Aromatic anion nomenclature for a generic chloromethylated PEEK repeat unit.

5. Quaternized PEEK Membrane

Quaternizing is one of the promising methods that can be employed to introduce the functional groups onto polymer matrix for AEM of SAFC. In this method, the chloromethylated PEEK will be substituted with quaternary ammonium and quaternary phosphonium. Most of the current research on the development of AEM mainly focused on the quaternize group because it requires simpler synthesis method with acceptable membrane properties [32]. The nucleophilic-substitution reaction takes place during the replacement of the chloromethyl group with either tertiary-amine or tertiary-phosphine molecules. Commonly, the quaternary amine PEEK chloride can be obtained by immersing CMPEEK membrane into trimethylamine aqueous solution at specific temperature and time, followed by the dipping in NaOH solution in order to produce quaternize amine PEEK hydroxide for fuel cell application. Meanwhile, the procedure for the quaternary phosphonium PEEK hydroxide membrane is similar to QAPEEK, except that it uses phosphonium reagent. The degree of quaternization (DQ) increases with the increase of DC of CMPEEK as shown in Figure 6 based on data obtained from Yan et al. [19]. However, the DQ of PEEK at high DC (98%) cannot be obtained due to excessive swelling faced by the membrane as a result of high water uptake that leads to the loss of membrane morphology during quaternization process.

5.1. Quaternary Ammonium PEEK

Yan et al. [19] is the first team that succeeded to synthesize PEEK in sulfuric acid prior to the chloromethylated process that is performed using chloromethylating agent. The idea to dissolve PEEK in concentrated H_2SO_4 was obtained from the work of Lee et al. [33] that managed to successfully synthesize poly(phthalazinone ether sulfone ketone) in concentrated sulfuric acid without using chlorinated hydrocarbon from the previously used method. In the past studies, only a few researchers showed interest in synthesizing PEEK as AEM due to their poor solubility in organic solvent which makes it impossible to be prepared as membrane. Next, two years later, Jasti et al. [23] conducted an experiment to synthesize PEEK using non-hazardous material or known as "Green method" that is believed to be safer to human health. In their study, the partial sulfonation of PEEK solution was chloromethylated in the mixture of paraformaldehyde, trimethylchlorosilane, and Lewis acid instead of using chloromethyl agents such as chloro methyl methyl ether and chloro methyl dioctyl ether. Overall, it can be concluded that both of the studies have managed to confirm the absence of sulfonic acid group that is attached to the PEEK backbone after the chloromethylation process due to the adoption of low DS ($\leq 10\%$). Figure 7 shows the chemical structure of QAPEEK.

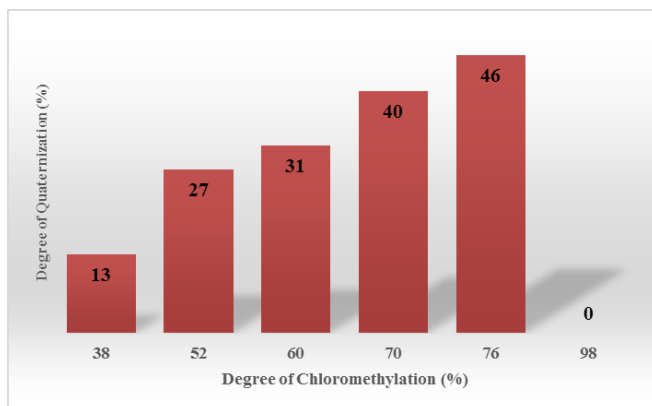


Fig. 6. Degree of chloromethylation (DC) and degree of quaternization (DQ) of PEEK [19].

The IEC of the QAPEEK is dependent on the DC of CMPEEK as well as the time of the chloromethylation reaction. Jasti et al. [23] reported that the IECs of their QAPEEK membrane tends to increase with DC (35%: 0.70 mmol g^{-1} ; 48%: 0.81 mmol g^{-1} ; 75%: 1.15 mmol g^{-1}), thus resulting in the increase of hydrophilic groups in the PEEK matrix. Theoretically, IEC represents the number of exchangeable functional group per unit dry weight of membrane [34, 35]. In addition, the chloromethylation of PEEK polymer

improves its hydrophilicity, which turns water absorption into one of the function of DC. On a similar note, the density of the quaternary ammonium groups is high at high DC and may implicate clustering or agglomeration. The clustered ionomers absorb more water molecules (H_2O) which promotes the increase of water uptake, thus suggesting the presence of ion-rich regions where hydroxide mobility is particularly fast [31, 36]. The water uptake of QAPEEK membrane increases with DC and temperature due to the enhanced hydrophilicity behavior that is caused by the existence of more ionic groups in PEEK matrix. The temperature provides more effect on the water uptake of QAPEEK membranes with higher DC or IEC compared to lower DC. Specifically, the water uptake represents an amount of water absorb or taken up by membranes when immersed in liquid water [37]. Meanwhile, the swelling ratio is used for expressing the membrane swelling degree occur due to change in dimension when soaked in water [38].

Yan et al. [19] stated that their QAPEEK membrane at 76% of DC facing morphological loss, in which the membrane turns into gel at the temperature of 60°C due to the excessive water uptake. Gopi and Bhat [36] reported that the number of bound water are high compared to free water with the increase of DC in membrane matrix due to the presence of hydrophilic groups. Hence, it is important to obtain high bound water in membrane matrix in order to have an optimal hydroxide conductivity at elevated temperature. Similar influence is found on swelling ratio, where their values tend to increase with the increase of IEC, DC, and temperature as presented in Figure 8. As a result, the mechanical strength of QAPEEK membrane is reduced with the increase of swelling ratio due to the dimensional changes. On another note, the chemical stability of functionalize AEM is one of the bigger issues considering that the pristine polymer backbone will face degradation when being attached with cationic functional group. The AEM based on the PEEK is known to be more chemically stable than polysulfone (PSF) due to its structure that has two ethers bond with active electron-donating behavior where the attachment of cationic group occurs. The chemical stability between QAPEEK and QAPSF are performed by immersing the membranes in 1 mol L^{-1} KOH solution at 80°C for 30 days, thus resulting to weight loss of about 6 wt% for QAPEEK and $\geq 40 \text{ wt\%}$ for QAPSF [27]. Apart from that, a test was also conducted for pristine PEEK and PSF with similar result showing high weight loss for PSF compared to PEEK [27].

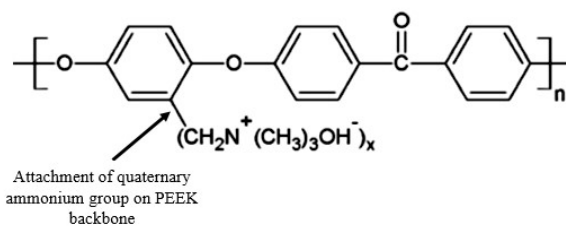


Fig. 7. Chemical structure of QAPEEK [32].

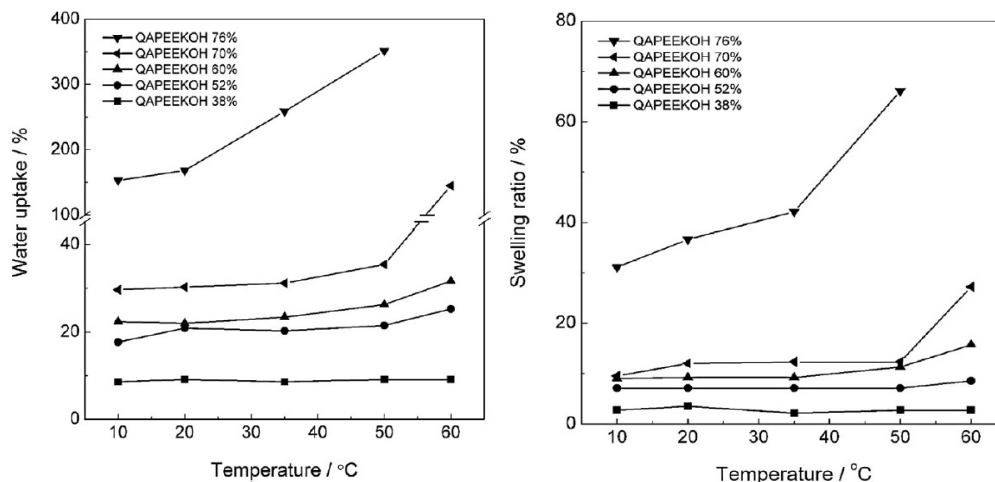


Fig. 8. Graphs of water uptake and swelling degree at different temperature of QAPEEK membrane [19].

It is important to note that the crystallinity of QAPEEK decreases as DC increases, thus making them more hydrophilic and more absorbent to water with better hydroxide mobility via grotthus mechanism. The Grotthus mechanism or ion hopping is one of the ionic transport mechanism in hydrated polymeric matrices that involve the movement of ions in a sequence steps in order to form or break the hydrogen bonding of water molecules which resulted to ionic conduction [39]. Other than that, the increase in DC also increases their solubility in organic solvents. Hence, the chloromethylation status of QAPEEK tends to increase their conductivity by the construction of H₂O mediated pathways for OH⁻ ions as well as the increase number of anion sites. The QAPEEK at DC: 76% exhibits hydroxide conductivity of 17 mS cm⁻¹ compared to DC: 38% with only 5.6 mS cm⁻¹ [19]. Similar result for QAPEEK membrane was also found in the study conducted by Jasti et al. [23] which states that hydroxide conductivity is high at DC: 75% = 20 mS cm⁻¹ compared to DC: 35% = 16 mS cm⁻¹. Nevertheless, the important parameters that need to be considered in the preparation of AEM based on Quaternary Ammonium group for PEEK backbone are: (1) degree of sulfonation for PEEK which determines their solubility in organic solvents and cross-linking degree of the QAPEEK, and (2) degree of chloromethylation which determines the presence of chloromethyl group to be substituted later with quaternary ammonium group that will affect the final IEC and ionic conductivity.

5.2. Ionic-crosslinked Quaternized Ammonium PEEK

Ionic-crosslink QAPEEK membrane consists of sulfonic acid and quaternary ammonium group in the PEEK backbone. In their study, Han et al. [27] prepared ionic-crosslink QAPEEK membrane by increasing the DS of PEEK around 40 to 67% compared to the previous studies that adopted low DS ($\leq 10\%$) in determining the effect of sulfonic acid group existence in PEEK backbone towards the membrane properties. More importantly, this resulted in the crosslink reaction between sulfonic acid group and quaternary ammonium (QA) group after the casting process with the QA as the major functional group as illustrated in Figure 9. Nevertheless, it is undeniable that there is a sulfonic acid (SA) group in the membrane but it still in alkaline nature because the amount of QA groups is greater than SA group. The DC of ionic-crosslink membrane is determined based on the degree of functionalization of residual sulfonic acid groups in CMPEEK based on the fact that they managed to preserve the DS value of PEEK at 40% higher than the previous study. Meanwhile, the DC: 25.3% of ionic-crosslink membrane represents 25.3% of quaternary ammonium groups that have been consumed by the sulfonic acid group in creating ionic cross-linking as well as excessive quaternary ammonium groups that are free and contribute to hydroxide conduction which are deemed different from QAPEEK membrane.

The IEC increases with the DF (16.5 % = 0.46 mmol g⁻¹; 25.3 % = 0.70 mmol g⁻¹; 32.7 % = 0.90 mmol g⁻¹) [27]. In regard to this matter, the increase in the sulfonation degree has provided beneficial influence on QAPEEK membrane which include the increase in hydroxide conductivity, but the swelling ratio remains with temperature. Swelling ratio can be defined as the change of dimension of polymer [40]. As discussed earlier, sufficient IEC is required to achieve high hydroxide conductivity; however, the membrane usually suffers excessive water uptake and swelling rate at high IEC. Hence,

the aim of the study conducted by Han et al. [27] was to overcome this situation by crosslinking the cationic and anionic group for the purpose of reducing the swelling and water uptake at high DC in order to allow better hydroxide conductivity and mechanical stability, especially when they are operating at high-temperature. Moreover, their developed QAPEEK have anti-swelling behavior and cannot be dissolved in conventional solvents. The swelling degree of QAPEEK changes with the increase in the operating temperature with ionic conductivity. In most cases, the SD of membrane increases with operating temperature, thus resulting in dimensional change, reduce membrane and electrodes contact, loss in membrane mechanical stability, and increased gas reactant crossover [41]. According to Kim et al. [42] and Vishal et al. [40], a highly cross-linked polymer membrane exhibits low degree of swelling. The crosslink QAPEEK membrane is very strong and does not break despite being immersed in hot water. The special property makes it very suitable to be used as electrolyte for fuel cell, especially when operating at high-temperature. Apart from that, the ionic-crosslink QAPEEK membrane provides better thermal stability where it degrades at 215 °C (onset decomposition temperatures: T_{OD}) compared to QAPS and QAPEEK employed in the study of Yan et al. [19] (T_{OD}: 148 °C) and Jasti et al. [23] (T_{OD}: ≤ 100 °C) [43].

The ionic-crosslink QAPEEK membrane shows more high hydroxide conductivity 25 mS cm⁻¹ [27] compared to QAPEEK membrane with only 12 mS cm⁻¹ [19] and 14.63 mS cm⁻¹ [23] at 30 °C.

5.3. QA-P(ES1-co-ES2) Blend with Quaternary Ammonium PEEK

The recent novel and promising AEM based QAPEEK is developed by crosslinking it with P(ES1-co-ES2), which is a well-designed polysulfone with dense phenyl groups surrounding its backbone [44, 45]. The QA-P(ES1-co-ES2) was added to QAPEEK with N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA) in order to form the blend membrane. The QA-P(ES1-co-ES2) crosslinking reagent acts as a "hydroxide ion wires" in blend membranes with the purpose of forming efficient and excellent active ion sites to ensure a better transfer of ion. In addition, the QA-P(ES1-co-ES2) has a strong covalent interaction due to the presence of TMHDA that enhances the membrane physical stability in terms of anti-swelling, elongation, and tensile strength. Other than that, the existence of long aliphatic chain in TMHDA tend to cause steric hindrance that will enhance the chemical stability of membrane. Moreover, the blend membrane has excellent well-defined microphase separation structure with improved connectivity of the hydrophobic and hydrophilic domains. On another note, the QAPEEK-QA-P(ES1-co-ES2) membrane exhibits less swelling degree compared to QAPEEK above 50 °C and remains stable in hot water at 90 °C unlike QAPEEK that partially dissolves above 70 °C [46]. The QAPEEK loses about ~76% of hydroxide conductivity when it is immersed in 2M aqueous NaOH at 80 °C for 144 h, while the QAPEEK/QA-P(ES1-co-ES2) membrane only loses 25–60% which further indicates that the blend membrane has improved the chemical stability compared to the control membrane [46]. A possible reason for this may be the presence of long chain of quaternary TMHDA in QAPEEK-QA-P(ES1-co-ES2) that induces higher steric hindrance for reaction compared to the short methyl groups of quaternary TMA [47, 48].

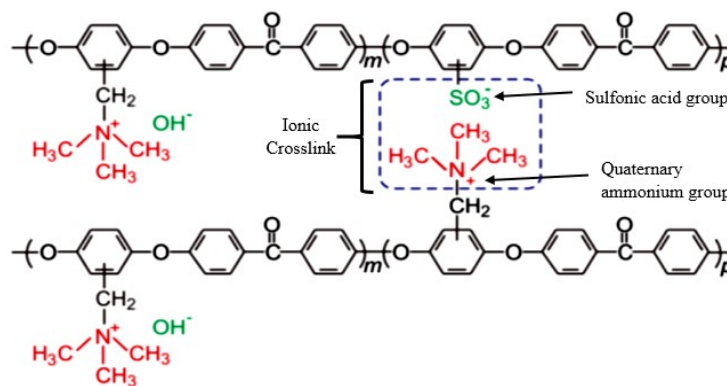


Fig. 9. Chemical structure of ionic-crosslink QAPEEK membrane [27].

The QAPEEK-QA-P(ES1-co-ES2) exhibits superior hydroxide conductivity 40 mS cm^{-1} compared to the QAPEEK which only exhibits about 11.3 mS cm^{-1} at 30°C [46]. The higher hydroxide conductivity of blend membrane is believed to be the result of adding densely QA-P(ES1-co-ES2) for the purpose of improving the connectivity of the ion sites, which further facilitates the vehicular diffusion of anion across the membranes. Furthermore, the short distance between the functional channels permits the first solvent coordination shells of neighboring QA groups to overlap well, thus allowing the Grotthuss hopping as well as the rendering of enough migration freedom for anion [49]. In single fuel cell testing, the QAPEEK/QA-P(ES1-co-ES2) obtains 137.2 mW cm^{-2} of peak power density, which is 181% higher than QAPEEK membrane.

5.4. Gemini Quaternary Ammonium PEEK

Gemini quaternary ammonium (GQA) cation groups is attached to the PEEK polymer backbone for the purpose of improving the hydroxide conductivity of the membranes with moderate swelling ratio ($\leq 40\%$ at $25\text{--}70^\circ \text{C}$) [50]. The suspected reason for the low swelling rate of GQA-PEEK compared to QAPEEK is believed to be caused by the presence of flexible spacers in the Gemini grafting structure. Moreover, that can also reduce the repulsion of grafting QA groups which then minimizes the extension of the backbone enlargement and improves the enlargement and aggregation of hydrophobic domain. The chemical structure of the proposed material looks like an arrangement of two ionic head groups joined through a spacer in the pattern of Gemini surfactants [51], thus further dominating strong surface activity and self-aggregation ability. In addition, the existence of a flexible spacer can prevent the repulsion of QA groups and speed up the aggregation of ion clusters, thus providing excellent interconnected and broad ionic sites for fast water diffusion and ions conduction through the membranes [52]. Similar to other AEMs, it should be noted that GQA-PEEK does not dissolve in DMF, DMSO, and other organic solvents. The hydroxide conductivity of GQA-PEEK membranes are temperatures dependent where it relatively increases with each other. Hence, this indicates that the water motion through GQA-PEEK membrane is promoted by the thermal activation, whereby the migration of hydroxide ion in the membrane occurs via the hopping action between the coordination sites [53]. Therefore, the hydroxide conductivity of GQA-PEEK (10 mS cm^{-1}) is higher than the QAPEEK membrane (8.7 mS cm^{-1}) at 25°C because this membrane exhibits peak power density of about 72 mW cm^{-2} [50].

5.5. Quaternized Phosphonium PEEK

The AEM based on quaternary phosphonium poly ether ether ketone (QPPEEK) can be synthesized through the phosphorization reaction using phosphonating agent such as tris(2,4,6-trimethoxyphenyl) (TMMP). However, the purity of TMMP should be carefully checked prior to their use considering that it plays an important role in the final result of QPPEEK membrane. The functionalized group from quaternary phosphonium (QP) cation possesses the ability to form both physical crosslinking [54] and chemical crosslinking [55] that can improve the membrane properties. Similar to QAPEEK membrane, the pristine PEEK is required to be dissolved in concentrated H_2SO_4 before being further chloromethylated, while chloromethyl group will be replaced with phosphonium group through

Menshutkin reaction. Figure 10 shows the attachment of quaternary phosphonium group onto the PEEK backbone.

The QPPEEK possesses the same solubility as other quaternary phosphonium based membrane such as QP-polysulfone [35] and QP-poly(2,6-dimethyl-1,4-phenyl oxide) [31] that are known to be highly soluble in high-boiling-point solvents: DMF, DMAc, DMSO and NMP. The solubility of the developed polymer in solvents is necessary in ensuring that the membranes are high-quality, flexible, robust, and uniform. Apart from that, the membranes based on QP is also soluble in low-boiling-point water-miscible solvents such as ethanol, methanol, n-propanol, and aqueous solution. Their solubility in the lower alcohols makes it possible to prepare ionomers in electrodes which is significantly required to ensure the high performance alkaline fuel cell. According to Wang et al. [5], the QPPEEK has better hydroxide conductivity, thermal stability, and alkaline stability compared to QAPEEK. In addition, the better chemical stability of QPPEEK membrane compared to QAPEEK is due to the TMMP cationic groups that provide high electron-donor behavior and large steric effect, which is capable of protecting the quaternary phosphonium group from hydroxide ion attack [56, 57]. The water absorption by QPPEEK membrane at high DC: 108% and 126% is highly dependent on the temperature, whereby the water uptake and swelling degree tend to increase with the cell operating temperature as shown in Figure 11. The reason of water uptake being affected by the temperature at high DC can be explained based on the improved plasticization of the absorbed H_2O as well as the relaxation effect of the polymer chain at high temperature. Apart from that, the grotthuss mechanism is dependent on the presence of water in the membrane to hop the hydroxide ion from one water molecule to the next via hydrogen bonding. Hence, higher water uptake will produce better hydroxide conductivity due to the improved anion-hopping activity.

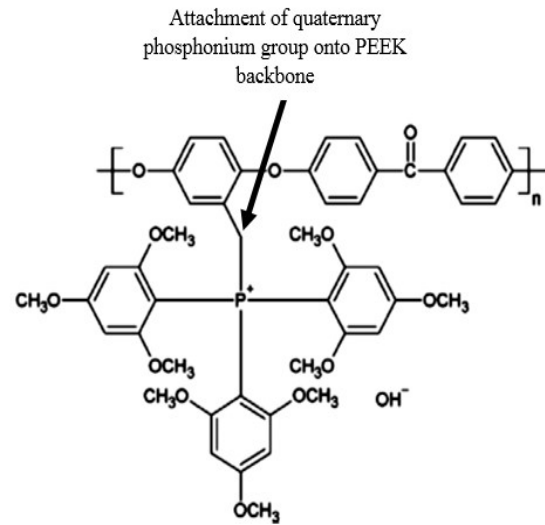


Fig. 10. Chemical structure of QPPEEK using TMMP phosphonium agent [56].

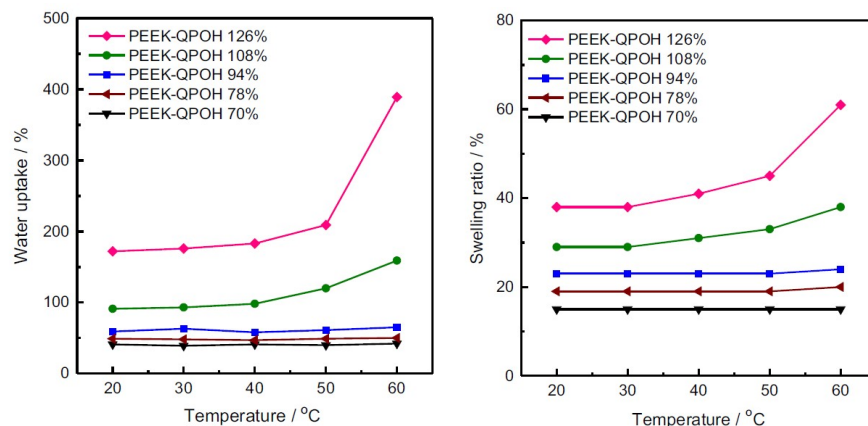


Fig. 11. Graphs of water uptake and swelling degree at different temperature of QPPEEK membrane [56].

The better water uptake at high DC observed in the QPPEEK membrane is resulted from larger ionic clusters and continuous hydrophilic channels. In addition, the PEEK with QP group absorbs more water molecule compared to QAPEEK due to the difference in the basicity of cationic group based on water absorption (λ) or average numbers of absorbed H_2O per functional group result. For example, the λ of QPPEEK at 126% DC is six times higher than QAPEEK at 70% DC with similar IEC of $\sim 1.20 \text{ mmol g}^{-1}$ (λ : QPPEEK = 80, QAPEEK = 14) [46, 58]. The finding shows that the QP functional group has high basicity than QA group for PEEK polymer membrane. However, one of the limitations of the QPPEEK membrane refers to their vulnerability of suffering to dimensional change that can cause high swelling ratio when operating at high temperature and IEC. The possible reason that leads to the excessive swelling ratio of QPPEEK membrane is its superior capability in absorbing water at high temperature.

Meanwhile, the IEC of QPPEEK is dependent on the chloromethylation of PEEK, where the IEC value increases with DC (70% = 0.89 mmol g^{-1} ; 78% = 0.95 mmol g^{-1} ; 94% = 1.06 mmol g^{-1} ; 108% = 1.12 mmol g^{-1} ; 126% = 1.19 mmol g^{-1}) [56]. The QPPEEK also exhibits high thermal stability with onset decomposition temperature (T_{OD} : 170°C) [56] compared to QAPEEK (T_{OD} : 148°C) [55], thus further indicating that the QP functional group intrinsically possesses better thermal stability than QA group. Generally, the onset decomposition temperature refers to the thermal stability of the polymer membrane that can be obtained through thermogravimetric analysis. Most often than note, the typical operating temperature of solid alkaline fuel cell is around 60°C to 90°C which is considered fair enough for AEM based on PEEK of quaternary ammonium or quaternary phosphonium group to act as electrolyte for SAFC.

The QPPEEK membrane (89 mS cm^{-1} at 20°C) [21] exhibits high hydroxide conductivity than QAPEEK (13 mS cm^{-1} at 20°C) [19] at very close IEC (1.19 vs. 1.18 mmol g^{-1}). This finding supports the high basicity of QP group compared to QA group. In addition, the increase in the operating temperature tends to increase the QPPEEK membrane hydroxide conductivity as follows: (i) DC: 108% = 45 mS cm^{-1} at 20°C , 51 mS cm^{-1} at 30°C , 56 mS cm^{-1} at 40°C , 64 mS cm^{-1} at 50°C , 71 mS cm^{-1} at 60°C , and (ii) DC: 126% = 61 mS cm^{-1} at 20°C , 65 mS cm^{-1} at 30°C , 72 mS cm^{-1} at 40°C , 80 mS cm^{-1} at 50°C , 89 mS cm^{-1} at 60°C , which is resulted from the high water absorption that facilitates the anion transport. The QPPEEK membrane faces serious swelling condition despite having high hydroxide conductivity at high DC, which then leads to low mechanical strength as the temperature increases that will degrade the performance and cause the splitting of the membrane if being continuously operated for long hours. Hence, the modification on QPPEEK membrane needs to be proposed considering that it is one of the potential polymers AEM for SAFC.

6. Imidazolium PEEK Membrane

Another potential AEM based on PEEK backbone is through the introduction of imidazole group. The imidazole group is one of the suitable functionalized group for poly-aromatic polymer due to its stability that can be enhanced by the steric hindrance effect [20]. The imidazole agents include 1-methylimidazole, 2-ethyl imidazole, 1-butyl-2-methylimidazole, and 1, 2-

dimethylimidazole. Apart from that, the imPEEK can be synthesized through a chloromethylation-Menshutkin reaction. Moreover, the PEEK needs to be chloromethylated as part of the procedure in quaternize PEEK before being functionalized with imidazole group. Figure 12 shows the chemical structure of imPEEK. The IEC of ImPEEK is found to increase with DC (60%: 1.56 mmol g^{-1} ; 68% = 1.73 mmol g^{-1} ; 74% = 1.91 mmol g^{-1} ; 80% = 2.03 mmol g^{-1}), which is similar to QAPEEK and QPPEEK. The ImPEEK at 80% of DC has greater intensity of the ionomer peak compared to ImPEEK with 74% of DC due to the fact that ImPEEK 80% has more ordering of the hydrophilic domains at higher IEC [59]. On a more important note, the ImPEEK is shown to have excellent solubility in aqueous solutions of acetone and tetrahydrofuran but insoluble in ethanol, methanol, and their aqueous solutions, which makes it suitable to be prepared as AEM.

The water uptake of ImPEEK membrane increases with IEC, which explains higher amount of water being absorbed by the membrane when DC increases due to the increase of hydrophilic domain in PEEK backbone (see Figure 13). The water uptake of 80% imPEEK is more affected by the high temperature (60°C) compared to 60% imPEEK due to the different amount of imidazole group in PEEK matrix. The 80% imPEEK (swelling ratio: $> 40\%$) can be observed to be facing more dimensional change as shown by the swelling ratio result compared to other DC (swelling ratio: $< 30\%$). However, the swelling ratio lower than 50% for ImPEEK is still considered acceptable even though the DC is 80% considering that its mechanical strength is suitable for AEM. Moreover, it should be noted that swelling is limited by the energy solvation balance of the ionic groups as well as the energy to enlarge the polymer backbone. The durability of fuel cell is dependent on the mechanical properties of the membrane due to the fact that variations in humidity and temperature can result in cyclic stresses and strains (mechanical loading) when they are operated. The tensile strength of ImPSF (4 MPa) is high than ImPEEK (18 MPa) which shows that the ImPSF has better mechanical strength. On the other hand, the ImPEEK obtain T_{OD} : 193°C of onset decomposition temperature for thermal stability is regarded as sufficient for operation in SAFC.

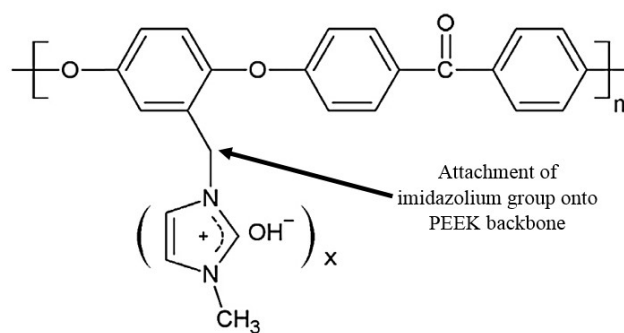


Fig. 12. Chemical structure of ImPEEK [59].

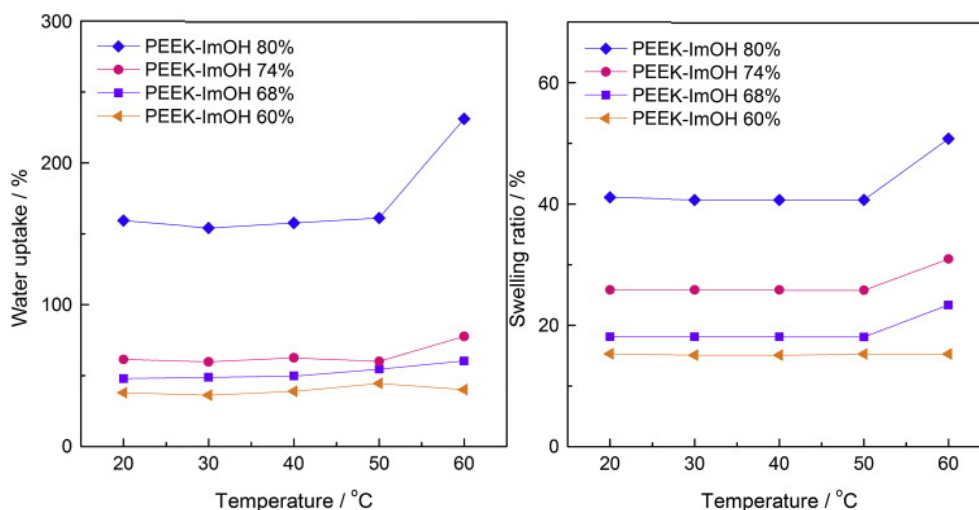


Fig. 13. Graphs of water uptake and swelling degree at different temperature of ImPEEK membrane [59].

The highest hydroxide conductivity of ImPEEK membrane is observed at the highest IEC (2.03 mmol g^{-1} ; 52 mS cm^{-1} , vs. 1.56 mmol g^{-1} ; 15 mS cm^{-1}) due to the high amount of imidazole moiety in the PEEK membrane for high IEC which tends to increase the hydrophilicity of the membrane with the purpose of allowing better anion transportation. Apart from that, the increase of temperature also increases the hydroxide conductivity of ImPEEK membrane, especially for high DC 80% (77 mS cm^{-1} at 60°C , vs. 45 mS cm^{-1} at 20°C) because more water molecule is absorbed when the temperature exceeds 50°C . The electroosmotic drag rate also increases with the increase of temperature, which results in more water to be transported from cathode to anode by carrying together the hydroxide ion in order to increase of hydroxide conductivity. Furthermore, the hydroxide conductivity of ImPEEK (52 mS cm^{-1}) is higher than the 76% QAPEEK membrane (17 mS cm^{-1}) and other imidazolium-functionalized membranes ($10\text{--}42 \text{ mS cm}^{-1}$) [60-70].

6.1. Ionic-crosslinked ImPEEK

To date, the well-known ionic-crosslinked ImPEEK is based on polymer blending between basic ImPEEK with acidic sPEEK. The main purpose of developing this membrane was to improve its alkaline stability and hydroxide conductivity through the employment of sPEEK as cross-linking agent. This blended membrane is prepared via in-situ Menshutkin/crosslinking to avoid flocculation [71]. The membrane based on acid-base blending is able to form excellent electrostatic interaction within the membranes, thus producing more compact polymer chain packing, improving the membrane stabilities, and increasing the hydroxide conductivity. The alkaline stability test shows that the ImPEEK/sPEEK has a good stability than ImPEEK with 94% DC (ImPEEK-94) despite being immersed in hot-aqueous alkali for two hours. The hydroxide conductivity of control ImPEEK-94 membrane degrades to 58% due to the reduction of imidazolium groups. The residual hydroxide conductivity ratios of ImPEEK/sPEEK membrane are higher than that of ImPEEK-94 membrane, which further increases when the sPEEK content and DS of sPEEK increases. This condition implies that the crosslinking is favorable to the ImPEEK/sPEEK stability which may be contributed by the increase in the activation energy of decomposition. The blended ImPEEK with 178% DC (ImPEEK-178/sPEEK) exhibits the highest hydroxide conductivity 31.59 S cm^{-1} compared to ImPEEK-94 membrane (26 mS cm^{-1}) at 30°C [72]. Apart from that, another benefit obtained from the ionic crosslinking membrane refers to the improvement of the stability of high DC of ImPEEK, which normally faces worse swelling rate and loss of morphology. This blended membrane is suitable to be used for low cell operating temperature which starts to decompose at about 190°C .

6.2. Long-spacer-chain ImPEEK

The imPEEK based on chloromethylation-functionalization method can easily be attacked by OH^- ion on the ring opening of C2 position in imidazolium cation that will reduce the membrane stability [73-75]. A possible explanation of this situation may be the benzyl group linking to the imidazolium group tends to lead to the attacking of hydroxide ion by $\text{S}_\text{N}2$. Hence, the stability degradation may also be caused by the deposition of imidazole via a $\text{S}_\text{N}2$ nucleophilic substitution process of OH^- attack on the methylene-carbon that is linked between imidazolium ring and benzene ring. Therefore, the alternative that can be employed in overcoming imPEEK stability is by introducing long alkyl spacer between the imidazole group and benzene ring on the PEEK chain or known as PEEK-AeImBr membrane which has the ability to reduce $\text{S}_\text{N}2$ nucleophilic substitution OH^- attack, thus increasing the alkaline stability as proven in the study of Yan et al. [18]. The PEEK-AeImBr is obtained through the reaction between CMPEEK and 1-Aminoethyl-2, 3-dimethylimidazolium bromide. It was found that PEEK-AeImBr is able to maintain better alkali stability at 60°C compared to imPEEK, which remains to be flexible and robust after being dipped in 1 M KOH. The ImPEEK with long alkyl spacer has appropriate water uptake ($\leq 209\%$) that is important for anion mobility and able to maintain its morphology even at 60°C . More importantly, the hydroxide conductivity of PEEK-AeImBr is still maintained despite being immersed in 1 M KOH at 60°C for 2 hours 52 minutes. However, the conductivity of imPEEK without long spacer chains is dropped at those test rate. The hydroxide conductivity of PEEK-AeImBr increases proportional with the temperature. Other than that, PEEK-AeImBr also exhibits high power density (120 mW cm^{-2}) compared to ImPEEK when being tested in H_2/O_2 single cell [76].

6.3. ImPEEK based on O-POSS Filler

The addition of functional filler into a polymer membrane is one of the

promising approaches in the process of tuning the microphase separation nature of ion exchange membranes [77-84]. The filler nanoparticles that consist of high-density tends to alter the hydrophilic conductive groups, thus producing strong attraction to the hydrophilic pendant chains and strong repulsion to the hydrophobic backbones of polymer, which is shown to behave as 'seeds' that guide the microphase aggregation process at the filler/polymer interface and sequentially generate well-defined channels to facilitate ion mobility. Li et al. [85] introduced a novel filler for imPEEK based on octaphenyl polyhedral oligomeric silsesquioxane (O-POSS). The O-POSS is a type of hybrid material that is composed of inorganic cage-like Si-O cores which is surrounded by 8 phenyl groups. On a more important note, the unique features provide beneficial influence on membrane characteristics as follows: (1) O-POSS particles exhibit precise tuning of the nanoscale (small) ion channels that results in the reduction of gas-crossover, (2) O-POSS increases the amount of ion channels formation at the polymer/filler interface, and (3) O-POSS existence minimizes the aggregation or sedimentation during casting process [86]. The presence of pristine O-POSS and functionalized O-POSS by imidazole group in imPEEK is investigated in order to determine their compatibility state. The incorporation of pristine O-POSS in ImPEEK membrane reduces the homogeneity of membranes, thus leading to the formation of defects. The presence of imidazolium groups in O-POSS (Im-O-POSS) also increases its compatibility with ImPEEK and appears to be very homogenous without any defects. The ImPEEK composited with Im-O-POSS consists of enhanced microphase separation structures which is responsible in forming the hydrophilic clusters in order to facilitate the mobility of hydroxide ion inside the membrane. The hydroxide conductivity shows that the ImPEEK composited with Im-O-POSS (44.11 mS cm^{-1}) produces high hydroxide conductivity compared to the control ImPEEK (30.66 mS cm^{-1}) membranes and ImPEEK composited with pristine O-POSS (ImPEEK-O-POSS) (24.00 mS cm^{-1}). The ImPEEK-O-POSS membrane exhibits the lowest hydroxide conductivity compared to the others because the corresponding O-POSS species does not contain any conductive groups, thus leading to poor hydroxide ion to pass the membrane. Apart from that, Im-O-POSS/ImPEEK also faces worse swelling when the temperature increases as a result of the incorporation of incompatible O-POSS species that distorts the hydrophobic phase of the membranes and badly affecting their physical stability. Meanwhile, the increase in the Im-O-POSS content from 10% (36 mS cm^{-1}) to 20% (44 mS cm^{-1}) improves the membrane homogeneity as well as hydroxide conductivity where the ion clusters tend to adhere to each other in order to produce continuous pathways.

7. Conclusions

Anion exchange membrane is the heart of solid alkaline fuel cell; however, its development for commercialization is deemed to be limited due to the lower hydroxide conductivity than proton conductivity as a result of low inherent anion mobility as well as poor alkaline stability in alkaline condition. The poly ether ether ketone is one of the potential polyaromatic polymers for AEM that has been successfully developed as proton conducting which involves low production cost but with superior properties in terms of mechanical, chemical, and thermal stability. The AEM based on PEEK backbone can be prepared by attaching the cationic functionalized group such as quaternary ammonium, quaternary phosphonium, and imidazole group. Each of the membrane development are shares the same purpose which is to improve the membrane properties and performance in terms of the alkaline stability, mechanical stability, thermal stability, water uptake, and hydroxide conductivity. In this study, PEEK was functionalized with quaternary ammonium group through simple direct nucleophilic-substitution method at the beginning of development stage. Commercialized pristine PEEK had to be dissolved in concentrated acid before undergoing further process because it is not soluble in organic acid. Several researchers managed to prove that the presence of sulfonic group provides beneficial influence in AEM despite the commonly used method which is to control the sulfonation degree of PEEK at low level to be less than 10% in order to avoid the zwitterion effect. The ionic-crosslink between cationic and anionic functionalized group in membrane provides better alkaline stability and mechanical stability.

The PEEK with attachment of quaternary ammonium, quaternary phosphonium, and imidazole have different mechanical, chemical, and transport properties owing to the differences in the basicity of the cationic functionalize groups and microstructure. The current review has paid attention on the recent studies conducted to investigate the experimental result of various PEEK modification procedure such as the direct nucleophilic-substitution reaction of functionalized group, monomer modification, acid-base blend, and anionic-cationic crosslink. The acid-base blend and anionic-cationic crosslink methods have managed to reduce the hydrophobic/hydrophilic region separation and gas reactant crossover in

membranes, thus allowing better SAFC performance. In a nutshell, each of the cationic functionalized group that is attached to the PEEK backbone provides different benefit and drawbacks on the membrane characteristics and performance. The limitation of the existing PEEK-AEM publication report refers to the restricted focus given in evaluating the physicochemical properties without considering the working performance in SAFC. Therefore, it is recommended for future works to test their developed PEEK-AEM in SAFC single-cell operation in terms of I-V polarization curve to evaluate the performance.

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Abbreviations

AEM	Anion exchange membrane
AFC	Alkaline fuel cells
CMPEEK	Chloromethylated poly ether ether ketone
DC	Degree of chloromethylation
DF	Degree of functionalization
DMAC	Dimethyl acetamide
DMSO	Dimethyl sulfoxide
DMF	Dimethyl formamide
DQ	Degree of quaternization
DS	Degree of sulfonation
ETFE	Ethylene-co-tetrafluoroethylene
FTIR	Fourier transform infrared resonance
GQA	Gemini quaternary ammonium
HTFE	Hexafluoropropylene-co-tetrafluoroethylene
IEC	Ion exchange capacity
Im	Imidazolium
KOH	Potassium hydroxide
MCFC	Molten carbonate fuel cells (MCFC)
NMP	1-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
O-POSS	Octaphenyl polyhedral silsesquioxane
PAFC	Phosphoric acid fuel cells
PEEK	Poly (ether ether ketone)
PEEKK	Poly (ether ether ketone ketone)
PEK	Poly (ether ketone)
PEKEKK	Poly (ether ketone ether ketone ketone)
PEKK	Poly (ether ketone ketone)
PEMFC	Proton exchange membrane fuel cells
PSF	Polysulfone
PPO	Poly (phenylene oxide)
PVDF	Poly(vinylidene fluoride)
QA	Quaternary ammonium
QAPSF	Quaternary ammonium polysulphone
QP	Quaternary phosphonium
QPEEK	Quaternized poly (ether ether ketone)
SA	Sulfonic acid
SAFC	Solid alkaline fuel cells
SD	Swelling degree
SOFC	Solid oxide fuel cell
TMHDA	N,N,N',N',-tetramethyl-1,6-hexanediamine
TMMP	Tris(2,4,6-trimethoxyphenyl)
T _{OD}	Onset decomposition temperature
VBC	Vinyl benzyl chloride
WU	Water uptake

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