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A New Frontier Towards Development of Efficient SPEEK Polymer Membranes for PEM Fuel Cells Applications: A Review

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Abstract

Proton exchange membrane fuel cells (PEMFCs) have gained popularity over the last decade as a potential clean energy source for electric vehicles and portable electronic devices. Nafion is commonly used as a membrane material but suffers from high methanol crossover and cost. These drawbacks negatively influence the widespread commercial application of PEMFCs. Currently, the focus is on developing high-performance, low-cost PEMs to replace Nafion membranes. Sulfonated poly-ether-ketone-ether (SPEEK) has been identified as a promising alternative PEM in fuel cell applications due to its advantageous properties, such as low cost, mechanical and chemical stability, and ease of preparation and operation. The main purpose of this review is to demonstrate the benefits of SPEEK-based composite membranes over Nafion® by mixing the SPEEK material with fluorinated polymers, hydrocarbon polymers, carbon-based materials, metal oxide materials, etc. The ion-exchange capacity and proton conductivity of SPEEK polymer with different fillers are highlighted. SPEEK-based composite membranes are far more suitable for PEMFC and DMFC applications because SPEEK polymer is produced in an environmentally friendly manner. This critical review guides researchers in developing processes to maximise the SPEEK-based membrane's properties for fuel cell applications.

Keywords: Polymers, Composite membranes, SPEEK-based membranes, PEM Fuel Cells

1. Introduction

For decades, fossil fuels have been considered the main sources of the increased pollution levels in the environment due to the emission of toxic greenhouse gases such as COx, NOx, and SOx upon their combustion [1-3]. Furthermore, there are growing concerns about the long-term viability of fossil fuels which are expected to run out sooner rather than later. As a result, sustainable, renewable, and environmentally friendly fuels will emerge sooner or later.

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To address these issues, extensive research and development are being conducted to identify alternative sources of electricity that are efficient, renewable, and environmentally friendly. Fuel cells are one of many technologies that will enable future sustainable hydrogen, carbon-free cycles, and a circular economy [4, 5]. Over the last two decades, fuel cell applications have grown in popularity as engines, stationary and portable power sources. [6, 7]. Mohammed et al.,[8] described a fuel cell as an electrochemical device that converts chemical energy of a fuel (the reactant) such as methanol, ethanol or ethylene glycol into electrical energy without any fuel combustion. The fuel is directly oxidised, producing electricity, heat, and water vapour. The electrochemical reactions within the fuel cell are explained as follows: When hydrogen passes through the anode, it is converted into hydrogen ions, and electrons are released, which travel through an external circuit before reaching the cathode to produce electrical current. [9]. The membrane electrode assembly (MEA) is the primary component of the fuel cell, consisting of a gas diffusion layer, catalyst, and electrolyte (membrane). The protons migrate through the electrolyte to the cathode, where they unite with oxygen and the electrons to produce water and heat. Fuel cell technologies are characterized by the nature of electrolyte they use. The electrolyte is one of the important part of the fuel cells as it defines the properties and the operating conditions of the fuel cell [10, 11]. There are six distinct types of fuel cells namely, (i) Alkaline Fuel Cell (AFC), (ii)Direct Methanol Fuel Cell (DMFC), (iii) Molten Carbonate Fuel Cell (MCFC), (iv) Phosphoric Acid Fuel Cell (PAFC), (v) Proton Exchange Membrane Fuel Cell (PEMFC) and (vi)) Solid Oxide Fuel Cell (SOFC), each operating at different reaction conditions and use different electrolytes. Out of the six fuel cells, two fuel cells (i.e. hydrogen Fuel Cell (H_2-FC) and direct methanol fuel cell (DMFC)) use polymeric membrane as an electrolyte, while others are based on the electrochemical principles. The components, fuel types and performance characteristics of the types various of Fuel Cells are presented in Figure 1.

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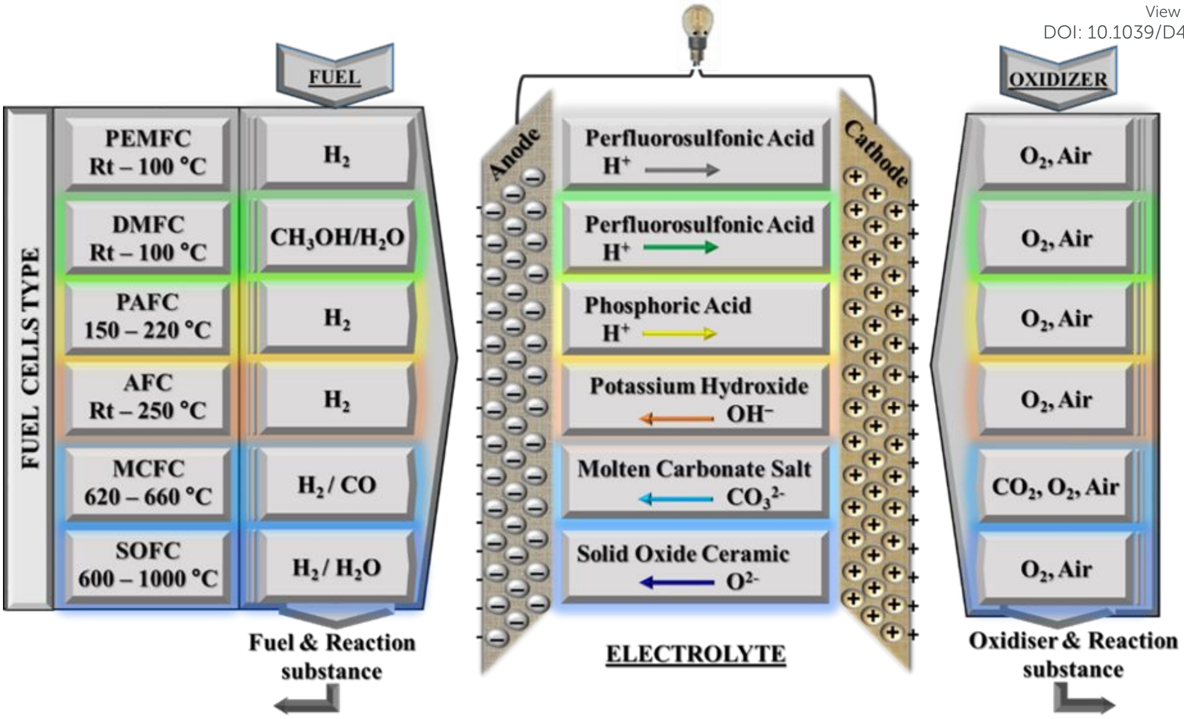

Figure 1. Schematic representation of different types of Fuel Cells and their properties

Among the fuel cells listed above, proton exchange membrane fuel cell (PEMFC) technology is a major area of global research interest [12]. Their high energy density and efficiency, along with their potential for low emissions, make them a promising clean energy technology. The proton exchange membrane (PEM) acts as a barrier to the fuel gas between the electrodes, transferring protons from the anode to the cathode of the PEMFC. The reactions that occur in the PEMFC are as follows.

Anode side: $2H_2 \rightarrow 4H^+ + 4e^-$ (1)

Cathode side: $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$ (2)

Overall cell reaction: $2H_2 + O_2 \rightarrow 2H_2O + Heat + Electrical\ energy$ (3)

For the anodic reaction, hydrogen flows through the gas diffusion layer before dissociating into two electrons and two protons in the catalyst layer (equation 1). The two protons pass through the PEM to reach the catalyst layer at the cathode, and the two electrons pass through the external circuit to the cathode [13, 14]. Similar to the anodic reaction, which results in the production of heat and water, the cathodic reaction occurs when air enters the catalyst layer through the gas diffusion layer and

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reacts with the two electrons and two protons (equation 2). The most common membranes used in PEM fuel cells are fluorinated membranes. The perfluorosulfonic acid (PFSA) polymers known as Nafion membranes are the most common type. Sulfonated polymers, such as Nafion, with perfluorinated backbones and sulfonated side-chains, are the most widely used membrane for PEM cells because they function well at temperatures below 100 °C. Perfluoroether in Nafion is responsible for chemical stability, while sulfonated sidechains aggregate and facilitate hydration [15]. Due to its high ionic conductivity (approximately 0.1 S/cm when fully hydrated), as well as its thermal and chemical stability, Nafion membrane has been chosen as a standard for polymeric electrolyte fuel cells [16]. However, Nafion membranes have several drawbacks, including a decrease in ionic conductivity and low humidity at high temperatures, which makes commercialization difficult. For these reasons, other proton conducting membranes with either partially fluorinated or hydrocarbon-based polymers containing ionic transfer sites have been developed to improve fuel cell performance. The chemical structure of Nafion is shown in Figure 2.

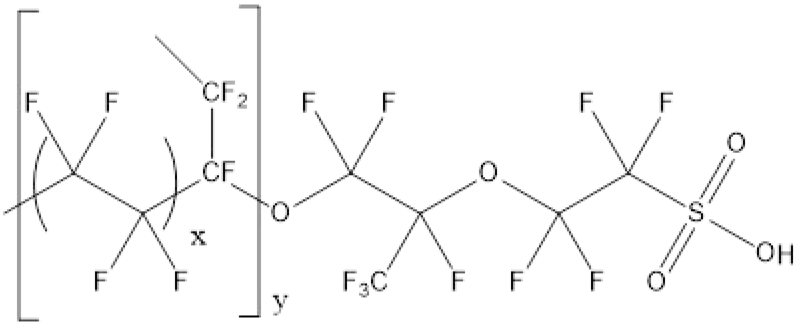

Figure 2. Chemical structure of Nafion.

In this context, many studies have been conducted to develop PEM with improved performance characteristics such as low cost, ease of synthesis, good thermal and mechanical stability, and eco-friendliness. Partially fluorinated PEM can be created by synthesizing block copolymers, one of which is a fluoropolymer. Partially fluorinated membranes, like fluorinated membranes, have demonstrated high proton conductivity. However, it is costly and cannot be referred to as low cost due to the use of expensive

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fluorinated materials. Furthermore, commercialization of these materials has been hampered by high costs and a scarcity of trifluorostyrene monomer [16].

Non-fluorinated membranes are made from polymer materials with aromatic structures and functional groups in either the polymeric backbone or side groups are being used in the proton exchange membranes (PEMs) in place of perfluorinated membranes.

One major advantage of hydrocarbon membranes is that it's simple to design the polymeric structure to have the right characteristics for fuel cell applications [17]. Various types of monomers are used to control the reaction conditions when preparing hydrocarbon membranes with excellent properties. Moreover, the cost of the monomers used in the production of hydrocarbon-based polymers is comparatively lower than that of fluorinated membranes, which is a major benefit for commercialization [15, 18]. In general, hydrocarbon-based polymers have polar groups and a carbon backbone, and they have high water uptake over a wide temperature range. Despite having increased proton conductivity and poor dimensional stability in membranes, water channel formation occurs [19]. Rigid sites, such as aromatic structures, are incorporated directly into the polymer backbone to improve membrane stability and properties. The aromatic rings provide rigidity, which leads to thermal and mechanical stability. As a result, a variety of hydrocarbon-based polymers, including, poly-ether ketones (PEK), poly(arylene ethers), polyether ether ketone (PEEK), polyesters, and polyimides (PI), have been actively researched and developed for use in fuel cell applications [20-23]. With a wide variety of alternative aromatic polymers to choose from, polyether ether ketone (PEEK) appears to have the best potential as a PEM for fuel cell application. PEEKs are semicrystalline thermoplastic polymers with ether and ketone chemical properties. This polymer has a well-balanced blend of excellent mechanical properties, low cost and superior thermo-oxidative stability [22]. PEEK polymer has an aromatic, nonfluorinated backbone with 1,4-disubstituted phenyl groups separated by ether (—O—) and carbonyl (—C=O) linkages (as shown on Figure 3 below), making it a high-performance thermostable engineering polymer [24].

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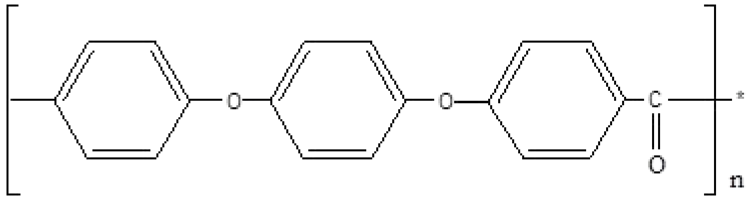

Figure 3. General structure of PEEK [24].

This polymer's inherent hydrophobicity is typically overcome through chemical modification of the polymer chains. Sulfonic acid functionalities are easily incorporated onto the aromatic backbone of PEEK. Sulfonated poly(ether ether ketone) (SPEEK) is a semi-crystalline, amorphous polymer that exhibits high chemical and thermal stabilities due to the presence of aromatic rings [25]. It is made by polymerizing different monomers using the following synthesis techniques: (i) displacement reaction; (ii) nickel-catalyzed coupling polymerization; (iv) ring-opening polymerization involving monomers with sulfonic acid groups; and (iii) Friedel-craft acylation [26]. The degree of sulfonation (DS) has a strong influence on the properties of SPEEK, which can be controlled by adjusting the reaction conditions (reaction temperature, acid concentration, and sulfonation time). The SPEEK demonstrated desirable chemical durability at low DS, with greater dimensional, mechanical, and thermal stability than Nafion but lower water uptake and proton conductivity [27]. At higher DS, membrane swelling in aqueous solutions promotes the formation of interconnected channels of hydrophilic clusters. This resulted in high proton conductivity similar to Nafion, but with undesirable mechanical properties, excessive dimensional swelling, fuel permeability, and consequently low durability. Many studies have been conducted to develop modified SPEEK membranes in order to improve fuel cell performance [28, 29].

The intensive research activities in the development of modified SPEEK membranes, particularly for fuel cell applications, are critical for evaluating progress in this specific research field. With considerable efforts made to enhance SPEEK membranes, this review concentrates on the development of PEMs based on sulfonated poly(ether ether ketone) (SPEEK) polymers. The physicochemical properties and characteristics of pure sulfonated polyether ether ketone membranes (SPEEK) are discussed. The article also discusses strategies for improving the performance of the SPEEK matrix membrane. The results for various types of modified SPEEK membranes are

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summarised and analysed. This paper concludes with the challenges and opportunities encountered during the development of SPEEK-based membranes for fuel cell applications.

2. Mechanism of proton conduction in PEM

Proton conduction is the most important factor to consider when assessing membranes for possible fuel cell applications. In PEMFC operation, the membrane must ensure the systematic movement of water and ions, rejection of electrons, and dissociation of reactant gases. Sufficient hydration levels of PEM are critical for maintaining high proton conductivity during fuel cell operation. Two major mechanisms can hydrate proton transfer at the molecular level: electro-osmotic drag (vehicle) and proton hopping (Grotthuss) [30].A schematic design of the Grotthus and vehicular mechanisms is shown in Figure 4.

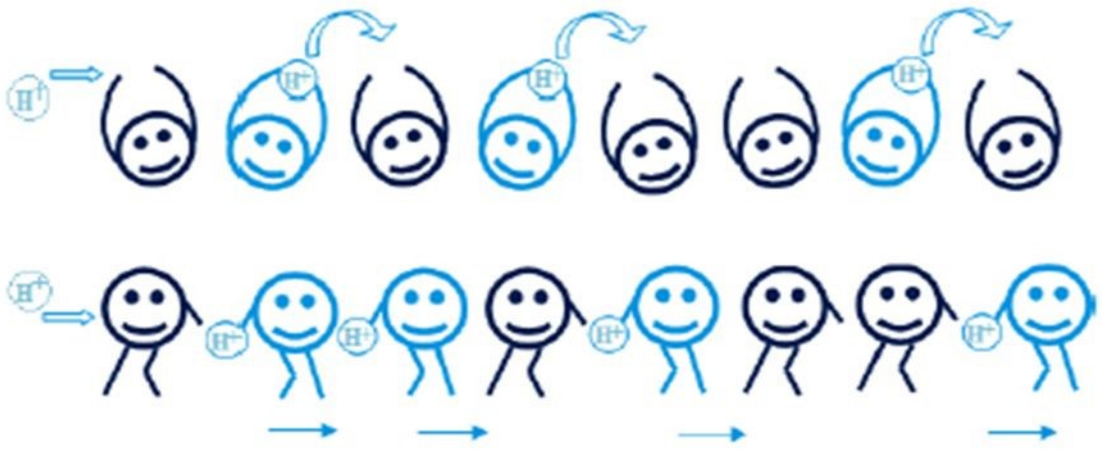

Figure 4. A schematic representation of the Grotthus and vehicular mechanisms [31] .

In the proton hopping (Grotthus) mechanism, protons move from one hydrolyzed ion (SO_3^-, H_3O^+) to another via polymeric matrices. The activation energy required for proton conductivity to occur for this proton hopping mechanism is 0.1- 0.4 eV. Protons are drawn from the hydronium ions by more adjacent water molecules, and the cycle is repeated. In this mechanism, the ion area forms a specific hydrophilic cluster that expands with water. As a result, protons will undergo percolation mechanisms. The

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Grotthus mechanism contributes to the conductivity of a perfluorinated sulfonic acid membrane like Nafion [32].

The ion exchange capacity (IEC) value affects Grotthus-type transfer because it represents the number of ionizable groups loaded into the fuel cell membrane. Electro-osmotic drag (vehicle) in the membrane transports hydrogen ions (H3O$^+$) throughout the aqueous medium. As a result, water and methanol molecules act as proton transporters in the polymeric membrane. The activation energy is required to initiate proton conductivity Eact > 0.5 eV [33]. In this mechanism, hydrated protons (hydronium ions) permeate an aqueous medium due to electrochemical differences. Protons bind to vehicles such as water or methanol before diffusing into the medium to form cationic complexes such as H_3O^+, $H_5O_2^+$, $H_9O_4^+$, and $CH_3OH_2^+$. The presence of free volumes in the polymeric chain of proton exchange membranes is critical to the vehicular mechanism. Water aids proton conductivity in PEM by influencing size, stability, production, clusters and ion route connection. In aqueous conditions, as cluster size increases, proton conductivity increases in proportion to humidity. The proton conductivity of polymeric membranes at high temperatures and low relative humidity could be enhanced by choosing inorganic additives using this mechanism [34].

3. Sulfonation of PEEK

Poly (ether ether ketone) polymers are chemically resistant, thermally and mechanically stable. However, due to their completely hydrophobic segments, they cannot be used directly in fuel cell applications [29]. As a result, adding a sulfonic acid group to PEEK polymer improves its hydrophilicity, solubility in polar solvents, and ion exchange capacity. At different degrees of sulfonation, the sulfonated form (SPEEK) is soluble in different solvents. The solubility of the SPEEK membrane is reported as follows: A sulfonation degree (DS) of about 30% makes it soluble only in hot DMF, DMAc, DMSO, and NMP; a DS of 40–70% makes it soluble at room temperature in DMF, DMAc, DMSO, and NMP; a DS of above 70% makes it soluble in methanol; and a DS of 100% makes it soluble in hot water [35]. Three synthetic methods can be used to prepare sulfonated poly(ether ether ketone):

(a) Direct sulfonated monomer copolymerization reactions with suitable monomers.

(b) Direct post-polymerization sulfonation reactions with poly(ether ether ketone).

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(c) Sulfonation reactions of poly(ether ether ketone)s to introduce the sulfonate group pendant into the polymer chains.

3.1 Direct sulfonated monomer copolymerization reactions with suitable monomers.

A specific sulfonated dihalogenated diaryl ketone monomer or sulfonated bisphenol derivative can be directly copolymerized with a suitable dihalogenated diaryl ether monomer unit to produce random (statistical) sulfonated poly(ether ether ketone) [36]. Through careful control of the reaction stoichiometry, the sulfonate group can be introduced regiospecifically along the polymer backbone. This is achieved through the step-growth copolymerization reaction utilising sulfonated monomers [37]. Electrophilic aromatic substitution reactions with various sulfonating agents can be used to produce sulfonated dihalogenated diaryl ketone or bisphenol monomer derivatives [38]. Nguyen et al. [39] synthesised a sulfonated di-halogenated diaryl ketone monomer by treating 4,4'-difluorobenzophenone with 25.3% fuming sulfuric acid, resulting in 100% yield and high purity disodium-3,3'-disulfate-4,4'-difluorobenzophenone (Figure 5).

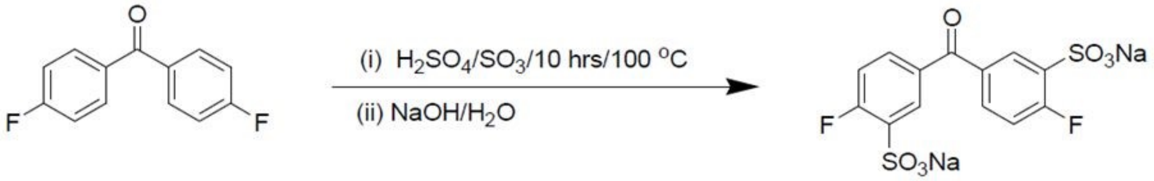

Figure 5. The reaction formula of a sulfonated di-halogenated diaryl ketone monomer [39].

A series of sulfonated poly(ether ether ketone) were produced by the base-catalysed nucleophilic aromatic polycondensation reaction of 4,4'-difluorobenzophenone and pure sulfonated monomer,disodium-3,3'-disulfate-4,4'-difluorobenzophenone with hexa-fluoro isopropylidene diphenol (Figure 6) [40]. High molecular weight polymers

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that exhibit thermal stability up to 260 °C were produced. The resulting sulfonated poly(ether ether ketone)s were used as proton exchange membranes in fuel cells.

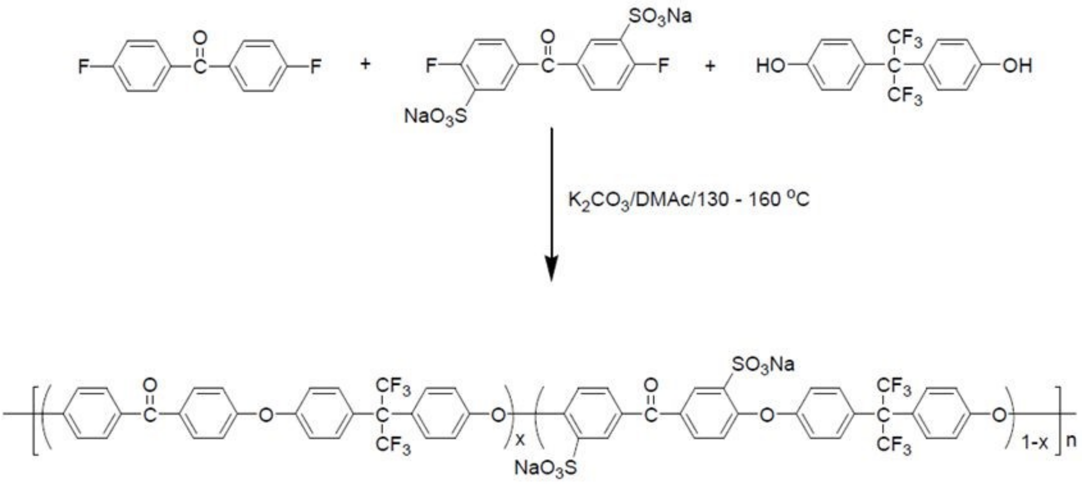

Figure 6. Reaction mechanism for preparation of Sulfonated poly (ether ether ketone) by the base catalyzed nucleophilic aromatic polycondensation [40].

3.2 Direct post-polymerization sulfonation reactions with poly(ether ether ketone)

Poly(ether ether ketone)s are highly effective polymers that are insoluble in the vast majority of organic solvents. Incorporating the sulfonic acid group along the polymer backbone of poly(ether ether ketone) reduces crystallinity and increases polymer solubility [41]. Direct sulfonation of poly(ether ether ketone)s using different sulfonating agents is not region-specific due to the lack of control over the degree and site of sulfonation during the sulfonation process [41]. Furthermore, polymer degradation and numerous side reactions have been observed. The electrophilic substitution reaction mechanism is used in the sulfonation of poly(ether ether ketone)s by sulfonating agents such as Sulfuric acid (H_2SO_4) as shown in figure 7. The ether linkage activates the polymer chain's phenyl rings for electrophilic substitution reactions, and the sulfonating group is introduced into the polymer chain's hydroquinone segment [42, 43]. One sulfonic acid group is typically added per unit because the carbonyl group attracts electrons, which lowers the electron density of the other aromatic rings [41, 44]. However, disulfonation reactions are possible at higher temperatures or for longer reaction time. Sulfonation reactions with poly(ether ether ketone)s are typically carried out in the presence of sulfonating agents like chlorosulfonic acid or sulfuric acid [45].

The reaction time, temperature, and acid concentration all influence sulfonation with sulfuric acid. In order to create polymers with different levels of sulfonation, Daud et al ,.[46] prepared sulfonated poly(ether ether ketone) from Victrex and 95-97% concentrated sulfuric acid and chlorosulfuric at room temperature acid to avoid PEEK polymer degradation and cross-linking reactions .The reaction was performed over a range of reaction times and degree of sulfonation of 80% was reported. In another study, Muthu Lakshmi et al., [47] investigated the effect of temperature and reaction duration on the degree of sulphonation of Gatone, as well as the characteristics of sulphonated polymers. Sulphonation was performed at 35-50 °C for 3-5 hours. The degree of sulphonation was between 50-80%. The sulfonated poly (ether ether ketone) derivatives were used in fuel cell and electrodialysis processes as electrochemical device.

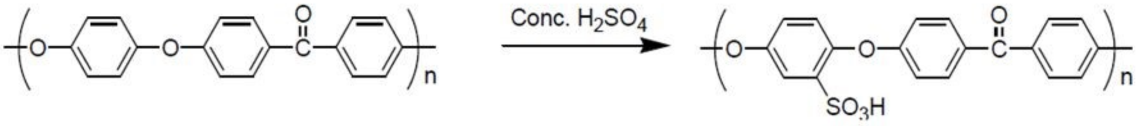

Figure 7. Sulfonation reactions of Gatone poly (ether ether ketone) [47]

To make it easier to incorporate the sulfonic acid group pendant into the polymer chain, standard organic reactions are commonly used to functionalize poly(ether ether ketone)s. Reactive sites in the polymer chain can be added either directly along the polymer backbone or by incorporating a suitable functional group pendant to the chain prior to the polymer precursor's sulfonation functionalization reaction.

Xu et al., [42] used dihydroxy functionalized poly(ether ether ketones) as substrates to synthesise a series of new sulfonated poly(ether ether ketones). The base catalyzed nucleophilic aromatic substitution polymerization method was used to create the corresponding dihydroxynaphthalene based poly (ether ether ketone) derivative. Sulfonated poly(ether ether ketone) was produced by the base-catalyzed nucleophilic reaction of dihydroxynaphthalene-based poly(ether ether ketone) with 1,4-butane sulfone (Figure 8). The resulting sulfonated poly (ether ether ketone) derivative exhibited high proton conductivity in DMFC applications.

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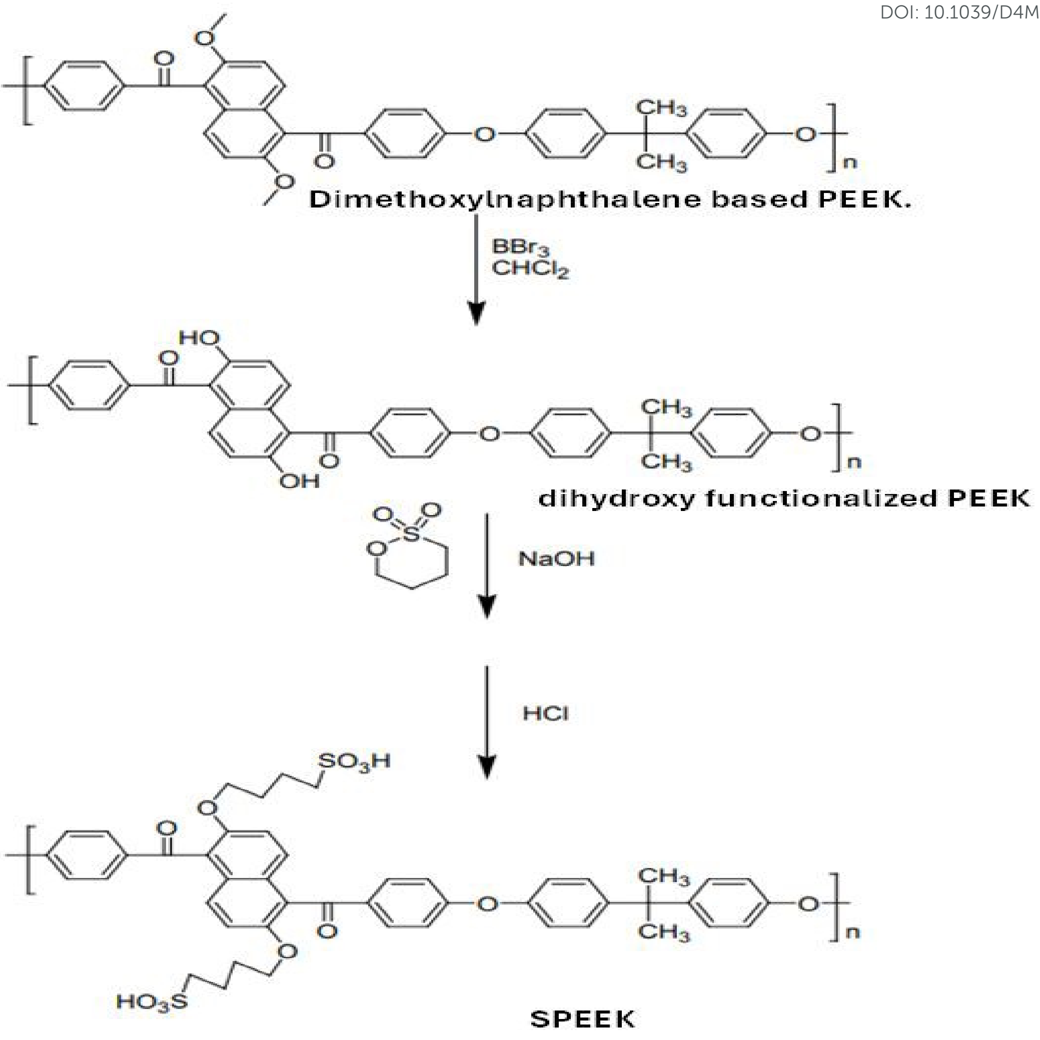

Figure 8. Nucleophilic reaction of dihydroxynaphthalene-based poly(ether ether ketone) with 1,4-butane sulfone [42]

Another synthetic method for creating sulfonated poly(ether ether ketone)s with the sulfonic acid group pendant to the polymer chain was created by Tsai et al., [48]. In order to produce pristine sulfonated poly(ether ether ketone), poly(ether ether ketone) was first treated with concentrated sulfuric acid. This was done by treating the resulting sulfonated poly (ether ether ketone) with 1,1'-carbonyl-diimidazole (CDI). Novel main-chain and side-chain sulfonated poly(ether ether ketone) with enhanced nano-phase separation morphology were formed after reaction with 2-aminoethanesulfonic acid (see figure 9). The addition of the new sulfonated group pendant to the polymer chain

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resulted in well-defined nano-phase separation morphology and improved the properties of the proton exchange membrane in DMFC applications.

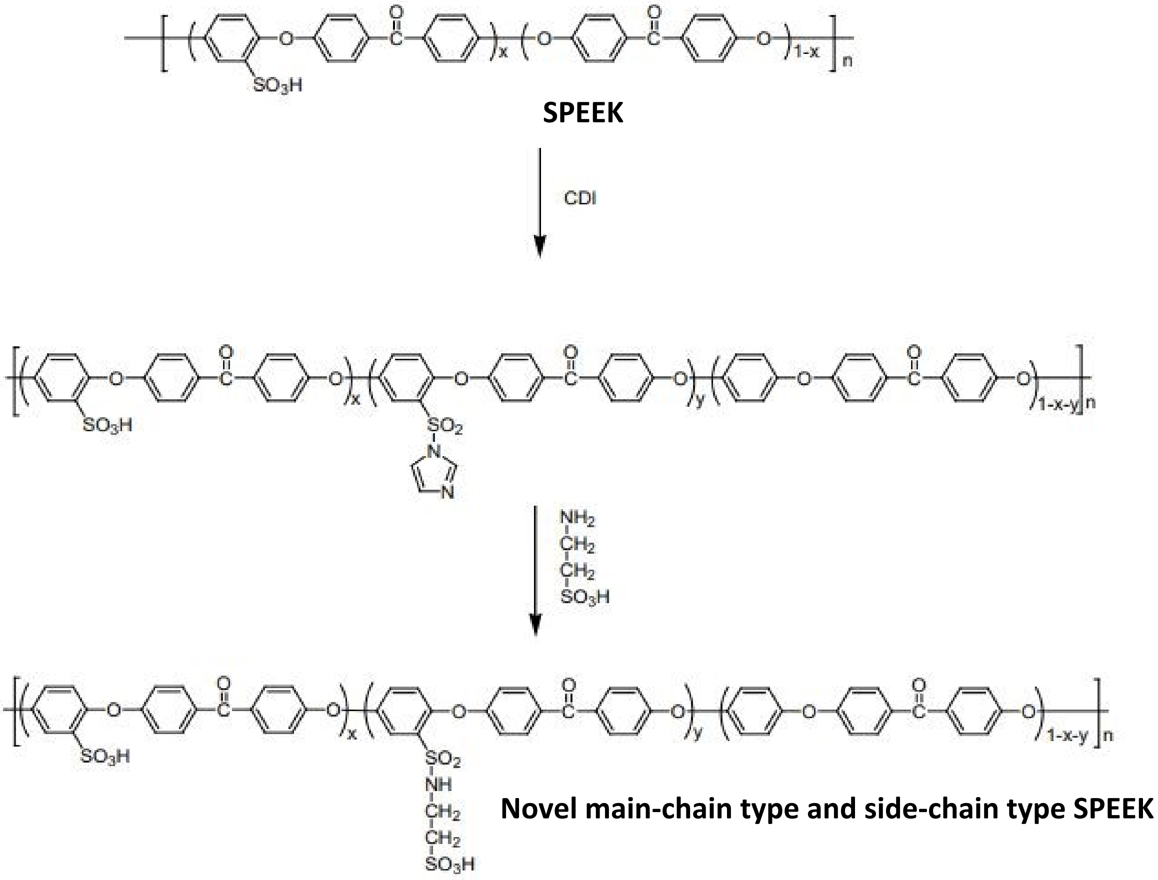

Figure 9. Sulfonated poly(ether ether ketone) synthesis route using 1,1'-carbonyl- diimidazole (CDI) [48]

The sulfonic acid group can also be added to the poly(ether ether ketone) chain by the thiol-ene reaction, which involves the following steps:

(i) The synthesis of a poly(ether ether ketone) precursor derivative with an unsaturation site attached to the polymer chain.

(ii) The pendant site of unsaturation reacts with a mercapto compound containing a sulfonate group using the classic thiol-ene reaction.

Li et al., [49] employed the thiol-ene method to synthesise poly(aryl ether ketone) ionomers with pendant sulfonic acid groups to the polymer backbone, as illustrated in figure 10. Quantitative yields of sulfonated poly(ether ether ketone) were obtained by treating the propenyl derivative of poly(ether ether ketone) with sodium 3-mercapto-1-propane sulfonate and AIBN in NMP/DMSO. Sulfonated poly(ether ether ketone)s were utilised as polymeric membrane substrates for fuel cell technology.

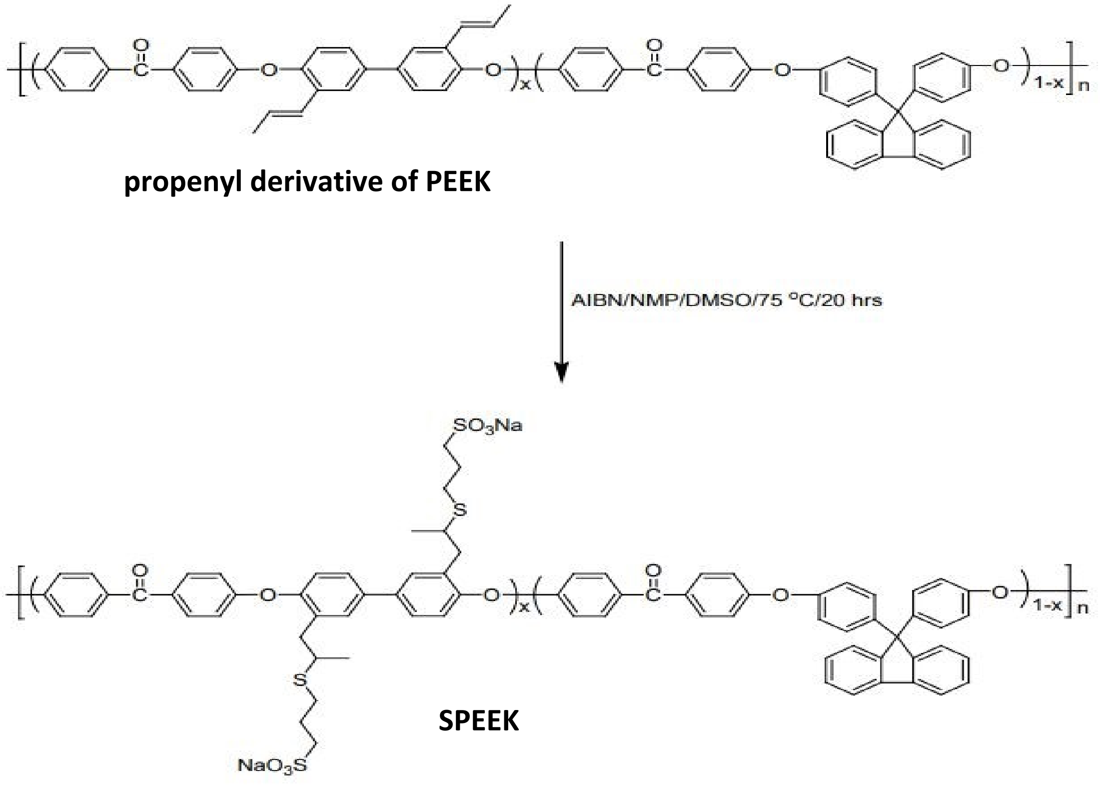

Figure 10: synthesis of Sulfonated poly(ether ether ketone) using the Thiol-ene method [49]

4. SPEEK modification methods

SPEEK polymer sulfonation is highly dependent on reaction conditions such as reaction time, temperature, and inert atmosphere. If the conditions are not properly maintained, the degree of sulfonation (DS) will either increase or decrease. The higher the DS of the SPEEK material, the more it swells at high temperatures before dissolving in water. Higher DS has always been associated with superior ion exchange capacity (IEC) and proton conductivity. Consequently, a range of modification

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techniques, including blending and cross-linking, have been researched to create effective SPEEK membranes [50].

4.1 Membrane crosslinking

4.1.1 Electron beam (EB) radiation

Radiation-induced crosslinking using electron beam (EB) is now extensively used for processing polymer materials due to its inherent advantages over UV and thermal curing methods. A radiation cross-linking strategy is a simple and efficient way to reduce methanol permeability and improve membrane thermal and dimensional stability, as well as mechanical properties, while maintaining proton conductivity [50].

Xiang et al [51] used a combination of cross-linking agents comprising trimethylolpropane triacrylate (TMPTA), polyester acrylate, 2-(2-ethoxy-ethoxy)ethyl acrylate (EOEOA), and 1,6-hexandiol diacrylate (HDDA) to introduce EB cross-linking in the SPEEK structure . When different EB irradiation samples dosed at 6 kGy min^{-1} were used, the degree of cross-linking and the density of the structure were directly influenced by the exposure dose. Higher EB irradiation doses resulted in greater thermomechanical and dimensional stability. They discovered that cross-linked polymer membranes have greater cluster transition temperature than Nafion® 117 membrane, implying that cross-linked membranes may be more beneficial in high temperature fuel cells than Nafion® 117 membrane. SAXS revealed Ionic sites were not deactivated by the cross-linking reaction, but rather increased proton conductivity, especially at higher temperatures (90 °C). Moreover, greater proton conductivity and dimensional stability at 80 °C and fully humidified conditions allowed for the achievement of the maximum power density of 0.225 W.cm-2 at a higher EB irradiation dosage (200 kGy). Xiaomin et al [52] synthesised 1,6-bis (4-vinylphenyl) hexane (BVPH), an unhydrolyzable cross-linker, to cross-link SPEEK membranes by EB irradiation at room temperature in order to address challenges with dimensional stability, mechanical strength, and methanol crossover. A higher degree of cross-linking was achieved by adding the cross-linking agent (BVPH) at varying content ranges of 5-15 wt% at a constant irradiation dose of 350 kGy and dose rate of 6 kGy min^{-1}. Cross-linked membranes containing 15% BVHP outperformed pristine SPEEK membranes in terms of dimensional and chemical stability, as well as mechanical strength. Additionally, SPEEK containing 15% BVPH showed enhanced oxidative resistance and tensile strength of 93 MPa (dry) and 38 h (3% H_2O_2, 2 ppm $Fe^{2+,}$ 80

°C). However, due to increased hydrophobicity and decreased water sorption and active ionic sites, the proton conductivity of cross-linked SPEEK was slightly reduced.

4.1.2 UV radiation

Prior to Hayes publishing a patent claiming that UV crosslinking increases the environmental stability and lowers the gas permeability of polyimide materials, the crosslinking of polymer materials by ultraviolet (UV) irradiation has been studied for a long time but received little attention in the PEM research field [53]. Several polymer membranes cross-linked by UV irradiation have since been studied in an effort to improve the properties of the membrane.

Although there are many photo initiators and crosslinking agents on the market, they can be highly unstable or very costly [54]. Chemical crosslinking can decrease the efficiency of polymer chain packing, leading to an increase in gas permeability and potential modifications in the properties of membranes [55]. Consequently, most researchers have focused their attention on adding the photo initiator and/or suitable crosslinking sites to the polymer backbone. The UV-crosslinked hybrid SPEEK membrane, which is combined with biodegradable polymer, reduces the polymer chains' elasticity by forming a denser network. Ramly et al., [56] studied SPEEK with methylcellulose (MC) and UV radiation, using benzoin ethyl ether (BEE) as a photo initiator. Increased hydrophilicity was achieved through radiation-induced demethylation, chain cleavage, acid group formation, and carbonyl in MC. After the non-crosslinked membrane was crosslinked with BEE under UV light for 30 minutes, the proton conductivity at 30 °C increased from 0.004 S cm^{-1} to 0.008 S cm^{-1}. The UV membrane improved dimensional stability after crosslinking because of its denser structure. Teruel-Juanes et al., [57] carried out the crosslinking reaction first by UV irradiating polystyrene-ethylene-butylene block copolymers (SEBS) with DVB, as opposed to first performing the sulfonation and then the crosslinking. This was followed by a post-sulfonation of the hardened membranes in trimethylsilyl chlorosulfonate solutions in 1,2-dichloroethane (DCE). The dielectric relaxation spectrum (Figure 11) revealed two main relaxations that corresponded to the glass transitions of the ethylene-butylene (EB) and styrene (S) blocks, as well as sub-Tg intramolecular non-cooperative dielectric relaxation. In addition to having an impact on the fragilities of both styrene (S) and ethylene-butylene (EB) blocks, the photo-crosslinking and post-sulfonation processes also have an effect on the entire dielectric

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relaxation spectrum. They concluded that the behaviour of the membranes can be estimated and reengineered based on modifications to the desired cell performance thanks to a correlation found between relaxation processes and membrane performance in H_2/O_2-PEM single cells.

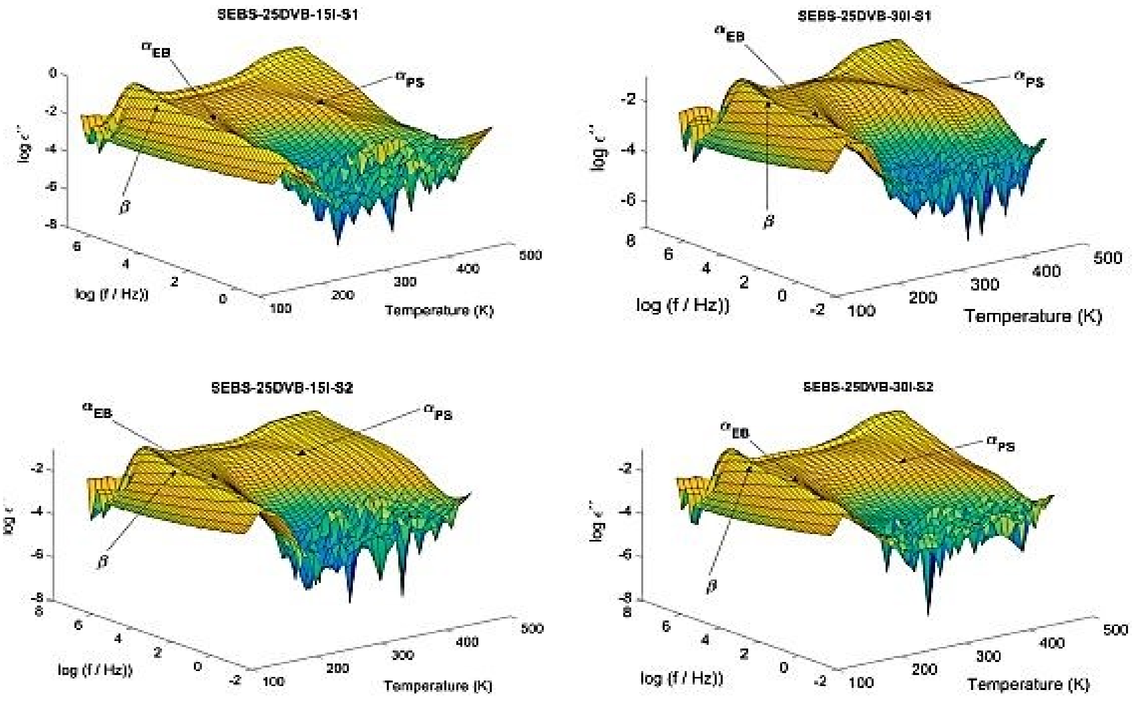

Figure 11: Dielectric relaxation spectrum [57].

4.1.3 Chemical cross-linking

Crosslinking of polymers can also be initiated by adding chemical additives during the membrane casting process. A wide range of unique additives, such as sulfonic acid groups and "free" hydrocarbon locations on the polymer chain, are identified in the literature, each with a unique crosslinking mechanism.

Polyatomic alcohols such as glycerol, ethylene glycol, and meso-erythrite can be used as crosslinking agents to increase or maintain the SPEEK membrane's flexibility (Figure 12). This is due to the fact that sulfone bond created by thermal crosslinking between two sulfonic acid groups are less flexible than the sulfonic ester bond created by condensation with polyatomic alcohol. Conductivity is enhanced by the flexibility of the macromolecular chains, which enable them to align into hydrophilic and hydrophobic domains [58]. Kumari et al., [59] reported on the effect of polyatomic alcohol linker length. They used ethylene glycol (PEG) with different molecular weights

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(MW/Da: 200 to 10000) and measured the effect of the molecular weight on the membrane's final properties. The authors reported that PEG 400 could form many small hydrophilic and hydrophobic clusters, which were more feasible than larger clusters formed by PEG with a MW less than 600. They made this discovery using atomic force microscopy (AFM) and small-angle X-ray scatting (SAXS). The results also demonstrated that there was an optimal linker length for stacking macromolecular chains into hydrophobic and hydrophilic domains.

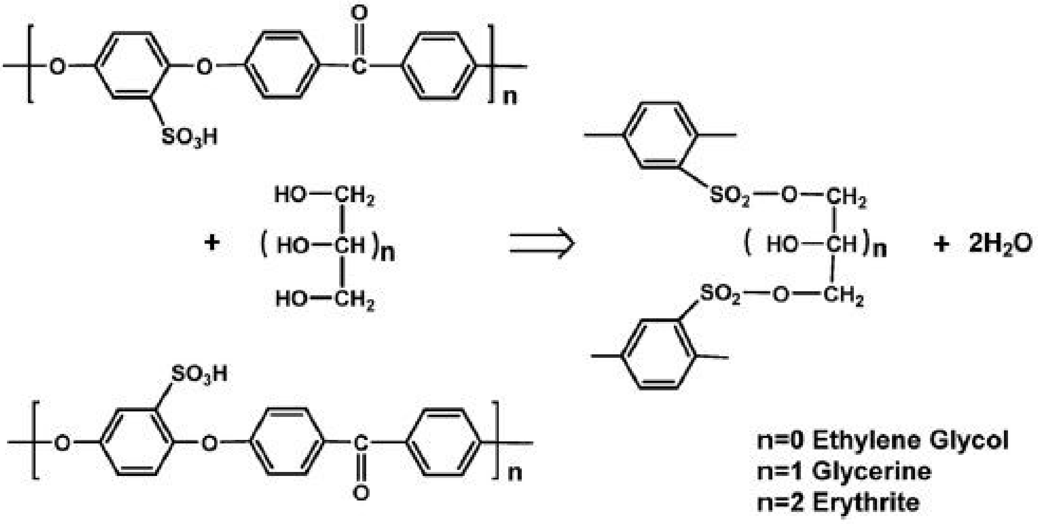

Figure 12: Reaction scheme of SPEEK cross-linked with polyatomic alcohol [42]

The diol crosslinking agents' flexibility was also examined by Gupta et al in a different study [60]. To crosslink the SPEEK membrane, cyclohexane di-methanol (CDM) was utilised as the stiff crosslinking reagent and PEG (MW 200) as the flexible crosslinking reagent. According to their report, the ideal ratio of polymer to crosslinker was determined to be 3:1 after conducting conductivity and water uptake experiments with various crosslinking agent ratios. Moreover, membranes crosslinked with the stiff CDM exhibited inferior properties in comparison to those crosslinked with the flexible crosslinker PEG. Therefore, the crosslinkers' flexibility is another factor to consider when crosslinking SAP.

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4.2 SPEEK blend polymer membrane

Blending is a simple method for defining and adjusting phase separation in the microstructure of homopolymers, provided the second polymer is completely compatible with the primary polymer [61]. Hydrogen bonds and ionic interactions, which are the most common physical interactions between polymers, can be used to reinforce blend membranes.

4.2.1 Acid-base polymer blend

An acid-base blend membrane is formed when benzimidazole side groups are introduced to the polysulfone backbone and blended with SPEEK [62]. The benzimidazole group uses basic nitrogen as a medium to transfer protons between the sulfonic acid groups of SPEEK, supporting both the hopping-type and vehicle-type mechanisms. The blend membrane outperforms the Nafion® and pristine SPEEK membranes in PEMFC between 60 and 100 °C [63]. Numerous researchers selected Poly(amide imide) (PAI) to blend with SPEEK due to the effectiveness of sulfonated polyimides in preventing methanol diffusion. The addition of PAI to the membrane structure reduces the swelling ratio and methanol permeability while increasing mechanical, thermal, and oxidative properties. As expected, as the PAI content was increased, a decrease in proton conductivity was observed. To improve mechanical properties, Raja et al.,[64] loaded $BaCeO_3$ nanoparticles in the SPEEK/poly (amide-imide) (PAI) matrices. The addition of $BaCeO_3$ nanoparticles improved conductivity, ion exchange, and water uptake (WU) properties while maintaining controlled stability due to the good interfacial interaction between nanoparticles and polymer. The polymer was reported to have stronger methanol barrier properties, making them suitable for DMFC.

4.2.2 Acid-acid polymer blend

Introducing hydrogen bonds between polymer chains in a blend PEM is an appealing approach to reduce methanol permeability and improve the durability of DMFC. Fully aromatic polyamide (fa-PA) was blended with 76% sulfonation degree into SPEEK by Li et al [65]. There are plenty of electronegative sites, such as carbonyl, amine, and sulfonate groups, which can form dense morphology, to establish H-bonds between polymer chains, as shown in Figure 13a. In comparison to pristine SPEEK, the fa-PASP-20 (20 weight percent fully aromatic polyamide) showed improved mechanical strength and swelling behaviour at 25 °C. Furthermore, in an aqueous methanol solution (2 M) at room temperature, faPASP-20 demonstrated relatively low methanol permeability of

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1.29×10^{-7} cm^2 /s, while SPEEK's values were 3.06×10^{-7} cm^2 /s. The open circuit voltage (OCV) values for fa-PASP-20 and Nafion® 117 as a function of methanol concentration are shown in Figure 13b, indicating that the blend PEM has good methanol resistance even at high concentrations.

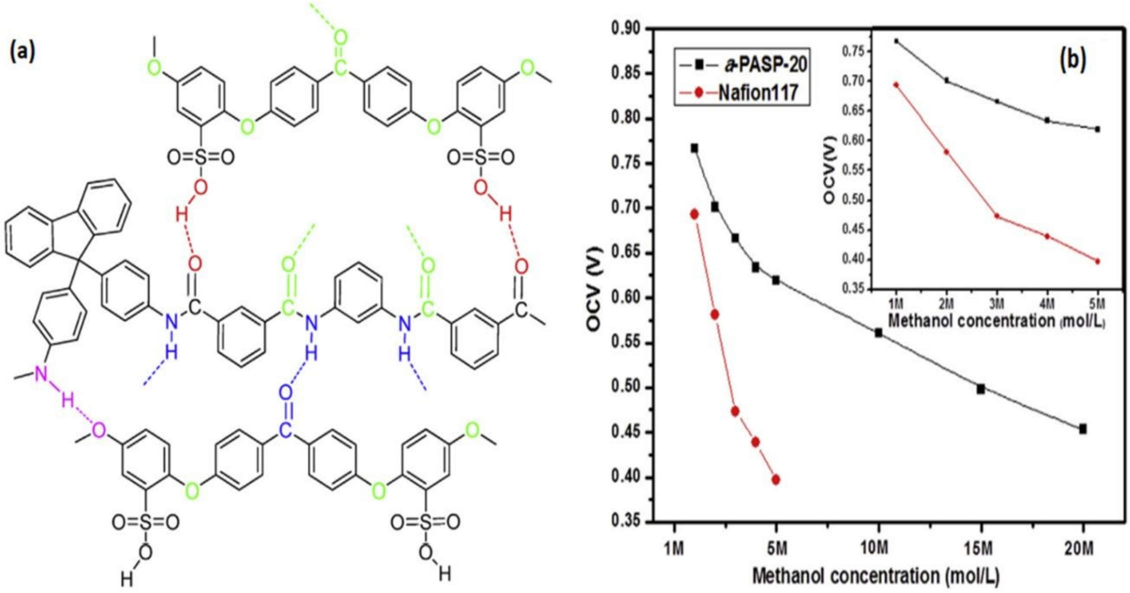

Figure 13: Expected hydrogen bonding between the blend of sulfonated poly (ether ether ketone) with fully aromatic polyamide (fa-PA), and (b) OCV of fa-PASP-20 blend and Nafion® 117 membranes at different methanol concentrations [65].

Haragirimana et al., [66] created a synergistic effect in SPEEK and SPAES by using acid-acid blending and sulfone bridges between sulfonic acid groups and electron-rich phenyl units. In their study, they fabricated a series of PEEK/SPAES polymer blends through a three-component system. Ductile and dense membranes were successfully fabricated through simple solution mixing and casting due to the excellent compatibility and fine dispersion of both copolymers inside the membrane. The incorporation of SPAES into SPEEK had a significant positive effect on the control of membrane water-swelling behaviour and oxidative stability, particularly at high temperatures. This resulted from the interfacial interactions (π-π interactions) and strong hydrogen bond formation between the SPAES and SPEEK chains.

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4.2.3 Blending with Perfluorosulfonic acid (PFSA) membrane.

PEMs can be made from PFSA polymers blended with SPEEK. The SPEEK nanofiber mat was first electrospun, followed by impregnation with PFSA polymers [67]. Dimensional stability and mechanical properties improved, but proton conductivity decreased when compared to the pristine membrane. Fluoropolymers, such as poly(-vinylidene fluoride) (PVDF) or poly(vinylidene fluoride-cohexafluoropropylene) (PVDF-HFP), can simply be blended with SPAEKs or SPAESs to create composite membranes [68]. The addition of PVDF or PVDFHFP decreased proton conductivity while improving water uptake, swelling ratio, and methanol barrier properties.

In another fascinating study, Nayak et al.,[69] combined non-fluorinated blend membranes and SPEEK with fluorinated blend membranes. Sulfonated poly (ether-ether-ketone)/poly (vinylidene fluorideco-hexafluoro propylene)/Silica (SPEEK/PVdF-HFP/SiO_2) composite proton exchange membranes were developed for fuel cell applications. The SiO_2 (7.5 wt.%) polymer membrane of SPEEK (80 wt.%) / PVdF-HFP (20 wt.%) demonstrated the highest proton conductivity value of 8×10^{-2} $S.cm^{-1}$. Additionally, a maximum power density of 1.5 $mW.m^{-2}$ was reported. According to this study, a different PEM may be possible if SiO_2 is added to polymer composite membranes.

A high ionic conduction sulfonated poly(ether ether ketone)/poly(vinylidene fluoride) (SPEEK/PVDF) blend membrane doped with boron phosphate (BP) was developed by Cali et al. [70]. SPEEK/ PVDF/10BP had the highest current density (0.4 $A.cm^{-2}$) and power density (0.242 $W.cm^{-2}$) at 0.6 V. The proton conductivity of the SPEEK/PVDF/10BP sample was measured at 80 °C to be 39 $mS.cm^{-1}$. The addition of both the boron phosphate and the SPEEK/PVDF mix membrane resulted in promising results for future fuel cell operations.

4.2.4 Blending with non-fluorinated membrane

Wang et al. reported the preparation of PVA-SSA/SPEEK composite membranes from sulfosuccinic acid crosslinked with polyvinyl alcohol (PVA-SSA) [71]. In comparison to the pristine membrane, the blended polymers ion exchange capacity (IEC) and water uptake (WU) were found to be lower, despite their high tensile strength PVA-SSA reaction may be hindered by low DS and PVA crosslinking when SPEEK is present. The presence of SPEEK in the blend, as well as the crosslinking of PVA with SSA, appear to result in greater thermal stability. When hydrated, PVA-SSA/SPEEK

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(70:30) was found to have a proton conductivity of 0.070 S.cm^{-1}. A blend of SPEEK and sulfonated poly (phthalazinone ether sulfone ketone) (SPPESK) was developed by Liu et al., [72]. Excellent water absorption and a low swelling ratio are features of the reported SPPESK/SPEEK membrane. At 80 °C, the blend membrane's proton conductivity was reported to be 0.212 S.cm^{1}.

4.3 The modification of SPEEK membranes with other polymers

In most polymers, carbon atoms are covalently bound to other elements like hydrogen, oxygen, or nitrogen. These organic molecules can be thought of as polymers. Hence, combining a polymer with SPEEK can result in the formation of acid-base interactions or hydrogen bonds between polymer chains, which can drastically alter the mixture's characteristics. SPEEK combined with other polymers is a technique commonly utilized in composite membranes manufacture, offering excellent proton conductivity and acceptable mechanical qualities. Blends of SPEEK with various polymers, including polyacrylonitrile (PAN) [73], polybenzimidazole (PBI) [74], poly(ether sulfone) (PES) [75], polyimide (PI) [76], polyphenylene oxide (PPO) [77], polytetrafluorethylene (PTFE) [78], vinylidene fluoride [79], polyvinylpyrrolidone (PVP) [80] and poly(tungstophosphoric acid (TPA) [81]. According to Peng et al., the performance of SPEEK membrane can be enhanced by altering its microstructure using either dibutyl phthalate (DBP) porogen or Nafion resin, which is applied as a layer over polypropylene (PP). It has been reported that a modified membrane structure consisting of the SPEEK membrane coated with polydopamine (PDA) layers improves mechanical strength and selectivity. All of these methods improve performance and point to the use of composite SPEEK membranes in PEMFC applications.

Recently, phosphonate membranes have received increased attention as potential replacement for PEMFC applications. Phosphorylated polysulfone (PPSU-As) in the acid form with degrees of phosphonation (DP) of 0.4, 0.75, and 0.96 was successfully prepared and blended by Abu-Thabit et al., [82] using SPEEK with a DS of 0.75 . The phosphoryl group (-PO3H2) could form strong hydrogen bonds with acidic SPEEK polymers, reducing swelling while sacrificing minimal proton conductivity. When compared to pure SPEEK, the blend SPEEK/PPSU membrane demonstrated lower methanol permeability, increased mechanical strength, and water uptake without sacrificing proton conductivity. The blend membrane (30PPSU-A-0.96) performed

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better in terms of proton conductivity than the pristine SPEEK membrane. The maximum proton conductivity of 0.124 S.cm^{-1} was reached at 120 °C, where this performance was sustained. Sultan et al., [83] created a novel hybrid membrane poly (trimellitic anhydride chloride-co-4,4'-methylenedianiline) (SPEEK/PTCMA) with PTCMA loadings ranging from 10% to 50% with a DS of 53%. SPEEK/PTCMA (50 wt.%) exhibited lower water uptake of 11% at room temperature, because of the acid-base interaction of amine and sulfonated groups. At 90 °C, the composite membrane SPEEK/PTCMA (20 wt.%) demonstrated higher proton conductivity of 0.004 S.cm $^{-1}$. The addition of PTCMA improved proton conductivity because the nitrogen atom of PTCMA can be protonated and contribute to proton transfer. Overall, the findings demonstrated that the proton conductivity value decreased as the PTCMA content increased. In turn, this lowers the amount of sulfonic acid groups in the composites, increasing their crystallinity and thereby decreasing water uptake a crucial stage in proton transfer.

Han et al., [84] ., created SPEEK/PBI composite membranes by dissolving the two polymers in DMAc before casting the membrane . The interaction of the -NH groups in PBI and the -SO_3 groups in SPEEK results in the formation of a three-dimensional network polymer structure that is advantageous for proton transport. The PEM demonstrated excellent proton conductivity performance, with a value of 0.14 S cm^{-1} at 80 °C, comparable to Nafion 117 (0.142 S cm^{-1}). The permeability of methanol is also as low as 2.38 x 10^{-8} cm^2. s^{-1}, which is much lower than that of Nafion. Aside from mechanical properties, thermal stability is also important. Such a polymer membrane design is successful and close to being used in DMFCs. Wei et al., [76] proposed a PI/SPEEK/PI nanofiber composite membrane with a sandwich structure and simple fabrication processes. The formation of an acid-rich layer and the solid support of PI nanofibers on the SPEEK matrix resulted in significantly improved proton performance. Due to the acid-base interaction between tertiary amide groups and sulfonated groups, the novel hybrid membranes PI/SPEEK with PI loadings of 3% and PI/SPEEK/PI with PI loadings of 1.5% had lower methanol permeability than SPEEK membranes. The sandwiched membranes demonstrated excellent conductivity of 0.178 S.cm^{-1} at 60 °C, which is noticeably higher than that of neat SPEEK membrane. The fuel cell's performance can reach 0.152 W.cm $^{-2}$. The swelling ratio and water uptake of the PI/SPEEK nanofiber composite membrane are 24.3% and 50.8%,

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respectively, at 60 °C and 100% RH, demonstrating the sandwiched PEM's excellent dimensional stability. The excellent results of the polymers indicate that the PI/SPEEK membrane is a promising candidate for commercial PEM with balanced proton conductivity, stability, and durability. The sandwich-structure membrane concept can also be applied in other areas such as vanadium redox flow battery, gas separation membrane, and so on.

Another promising membrane with strong chemical resistance and high hydrophilicity is chitosan. The combination of SPEEK and the natural polymer chitosan was suggested by Hidayati et al. [85]. Chitosan with low methanol permeability and good conductivity has been treated with SPEEK to eliminate hydroxyl and amine groups. The SPEEK/Chitosan composite membrane showed enhanced methanol permeability of 2.46 x 10^{-6} $cm^2.s^{-1}$ at room temperature when compared to pristine chitosan. SPEEK/Chitosan IEC values are higher, resulting in high proton conductivity. It was reported that SPEEK/Chitosan produced contrasting results for DMFC, implying that more research is needed.

5. Modification of SPEEK membranes with inorganic materials

SPEEK polymer modification with inorganic materials such as silica, clays, metal oxides, HPA, carbon nanotubes, and others has recently been investigated in fuel cell applications. The incorporation of inorganic substances into PEMs is known to improve proton conductivity, mechanical strength, and composite membrane durability [86]. While simultaneously enhancing the mechanical and thermal stabilities of the composites, Inorganic elements can reduce methanol crossover and excessive water swelling [87]. The various types of additives in SPEEK, such as graphene, silica, metal oxides, Heteropolyacids (HPAs), carbon nanotubes, Metal organic framework (MOFs) and clay will be thoroughly discussed in these subtopics. The influence of different additives on the SPEEK matrix; and its impact on the SPEEK performance with focus on fuel cells are shown in Table 1.

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TABLE 1: THE INFLUENCE OF DIFFERENT ADDITIVES ON THE SPEEK POLYMER MATRIX

Additive Type	Temperature (°C)	IEC (meq g $^{-1}$)	Water Uptake (%)	Proton conductivity (S cm^{-1})	Power density (mW cm^{-2})	Ref
SiO_2@CNT	25	-	43	4.1x10^{-2}	-	[88]
SWCNT-fly ash	90	1.59	27.3	3.4x10^{-2}	672	[89]
SsCNT-5	90	2.19	43.85	4.31x10^{-2}	-	[90]
CCNF	80	-	32.3	5.6x10^{-2}	-	[91]
β-CD-DHNTS/HPW	-	1.04	30	9.0x10^{-2}	-	[92]
Cs-HPAs	80	-	40	2.25x10^{-3}	247	[93]
Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	60	1.96	46	6.82x10^{-2}	-	[94]
PEOS/PWA/SiO_2	100	-	-	6.25x10^{-3}	25	[95]
Cs-TPA	80	1.5	37	1.3x10^{-1}	-	[96]
Pd-GO-L-Tyr	-	2.05	50.6	2.56x10^{-3}	-	[109]
PANI-GO	-	1.83	40	8.4x10^{-3}	13.51	[97]
SPBI/PrSGO	90	2.02	-	1.7x10^{-1}	820	[98]
SPVdF-HFP-SiO_2	90	1.83	36.5	7.9x10^{-2}	110	[99]
HPW@KMSNs	60	-	31.5	2.43x10^{-1}	-	[100]
PVA/TEOS	80	2.02	76	8.1x10^{-2}	336	[101]
IL/SHMO	200	-	-	4.6x10^{-3}	-	[88]
Bentonite/clesite30	80	-	18.4	1.24x10-^{5}	-	[102]
fGO/halloysite	-	0.35		4.7x10^{-4}	72.2	[103]
SiO_2-montmorillonite	100	-	25	1.58x10^{-1}		[104]
$BaZro_3$	90	1.96	41.5	3.12x10^{-1}	183	[105]
Al-$CeZrO_4$/HPW	80	1.65	8.1	1.3x10^{-3}	1001	[106]
NBO	90	1.80	38.4	2.9x10^{-2}	601	[107]
ZCO	90	1.46	20.3	2.0x10^{-2}	-	[108]
HPW@ML	60	1.54	50	1.36x10^{-1}	-	[109]
MOF-C-SO_3H	80	1.63	28.7	1.1x10^{-1}	82	[110]
Co-MOF-74/[IM_2][H_2PO_4]	120	6.5	90	2.6x10-^{2}	-	[111]
Cu-MOF	80	2.46	36.7	7.1x10^{-2}	-	[112]
ZIF-8/CNT	120	1.48	40.2	5.0x10^{-2}	-	[113]
ZIF-67	120	0.3	40	1.4x10^{-2}	28	[114]

5.1 Carbon nanotubes as fillers for SPEEK membrane

CNTs are one-dimensional tubular-like hexagonal graphene sheets formed by sp^2 bonds between carbon atoms. CNTs have extremely high mechanical properties due to this bonding structure, which is stronger than the sp^3 bonds found in diamond. CNTs can be single-walled (SWCNT) or multiwalled (MWCNT), with diameters ranging from 1 nm to more than 100 nm, as shown in Figure 14. The rolling-up direction of the graphene sheet has a significant impact on the CNT's electrical conductivity. This is due to the fact that the chirality vector describes the hexagonal carbon atom lattice. However, due to their higher surface defects and lower electrical conductivity,

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MWCNTs are preferred over SWCNTs for use in PEMs [115]. Due to their stiffness, low density, high aspect ratio, and optical qualities, as well as their exceptional tensile strength of roughly 63 GPa, which is 50 times stronger than steel, carbon nanotubes (CNTs) have received a lot of attention as a reinforcing material for polymers [116].

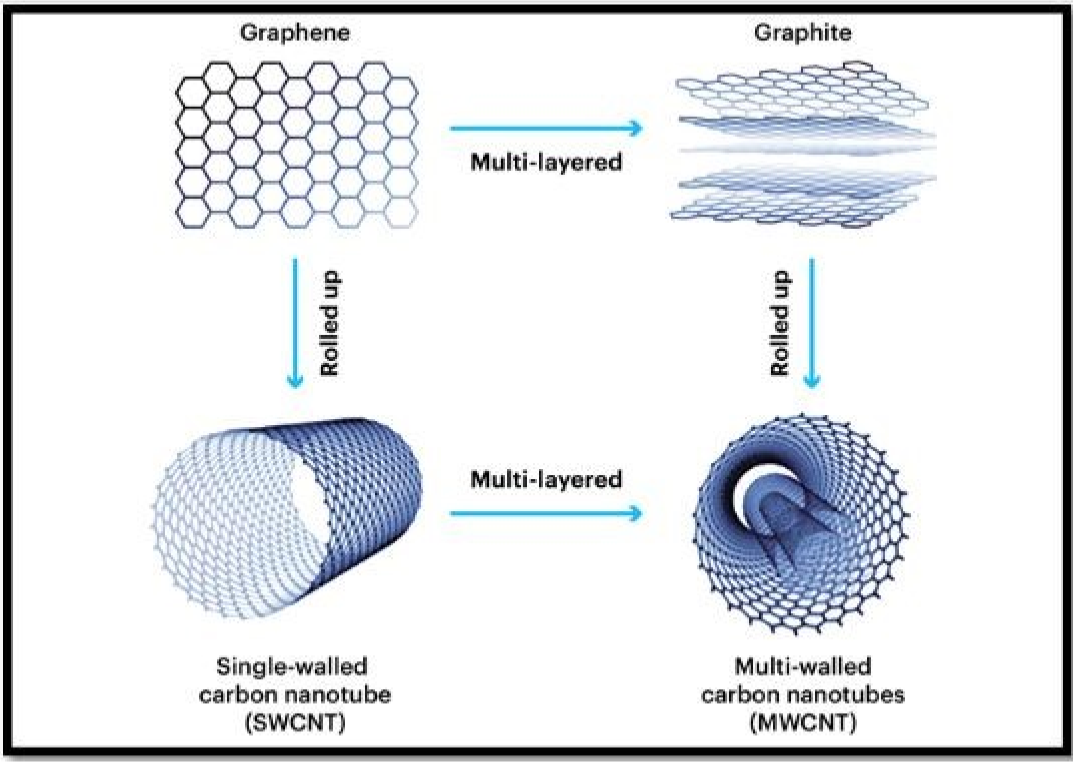

Figure 14: Single walled and multiwalled carbon nanotubes [116].

Carbon nanotubes (CNTs) are a cutting-edge nanomaterial for the production of exceptional polymer composites. Recently, SPEEK has employed CNTs as fillers to address DS-dependent issues. Nonetheless, CNTs have a negative impact on proton conductivity because they are an electron conductor rather than a proton conductor, which may pose a significant risk of short-circuiting on PEMs in fuel cells. Cui et al., [88] successfully prepared silica-coated CNTs (SiO_2@CNTs) by a simple sol-gel method, and subsequently applied as a novel additive to SPEEK-based composite membranes, which are enhanced by silica's exceptional water retention and electronic shield properties. Not only did the hydrophilic and insulated silica coating on the CNTs' surface prevent short circuiting, but it also enhanced the CNTs' interfacial contact with the SPEEK matrix, promoting the CNTs' uniform dispersion. Moreover, the methanol permeability of the SPEEK/SiO2@CNT composite membrane with a SiO_2@CNT loading of 5% was nearly one order of magnitude lower at 4.22×10^{-8} $cm^2.s^{-1}$ as compared to the pure SPEEK membrane (3.42 x 10^{-7}cm^2.s^{-1}). At room temperature, the proton conductivity remained greater than 10^{-2} S.cm ^{1}. The obtained results demonstrate that SPEEK/SiO$_2$@CNT membranes can be used as high-performance PEMs in direct methanol fuel cells. Sivasubramanian et al., [89] successfully synthesised Sulfonated poly (ether ether ketone) (SPEEK)-based polymer nanocomposite membranes comprising single-walled carbon nanotubes (SWCNTs) and fly ash as inorganic fillers using the solution casting method. The degree of sulfonation in poly (ether ether ketone) was evaluated using proton nuclear magnetic resonance spectroscopy and found to be 64%. They investigated and analyzed the produced membranes' physicochemical characteristics and potential for fuel cell applications. At 90°C, the SP-CNT-FA-8 membrane had the maximum proton conductivity (3.4 x 10^{-2} S cm^{-1}), whereas the pristine membrane had a conductivity of 3.1 x 10^{-2} S cm^{-1}. Apart from their favourable proton conductivity, it was also reported that the electrolyte membranes demonstrated remarkable thermal and mechanical stability. These findings suggest that the composite membranes utilizing SPEEK, SWCNT, and fly ash could be promising electrolyte membrane options for fuel cell applications.

Gahlot et al., [90] used solution casting to create functionalized carbon nanotubes (f-CNT) that are aligned electrically with SPEEK. The CNTs were functionalized via carboxylation and sulfonation. During the membrane's drying process, the CNTs were aligned using a constant electric field of 500 V.cm $^{-1}$. To determine whether they have the potential for direct methanol fuel cell application, the proton conductivity and methanol crossover resistance were assessed at temperatures s ranging from 30 °C to 90 °C. According to the findings, addition of aligned carbon nanotubes (CNTs) reduces the permeability of methanol while increasing the ion-exchange capacity, water retention, and proton conductivity. The highest proton conductivity (4.31 x 10^{-2} S.cm^{-1}) was observed in the SsCNT-5 nanohybrid PEM, which exhibited a higher resistance to methanol crossover. As the concentration of s-CNTs in the SPEEK matrix increased, so did the storage modulus (Figure 15). The S-sCNT-5 membrane had the highest modulus value of 2503 MPa, which is nearly 2.4 times higher than the SPEEK membrane. The increase in storage modulus of S-sCNT membranes indicates strong bonding due to the presence of a common sulfonic acid group in CNT and

PEEK, as well as the effect of electric field on CNT alignment in the SPEEK matrix. The electrically aligned functionalized CNT/SPEEK membranes outperformed the randomly aligned composite membranes.

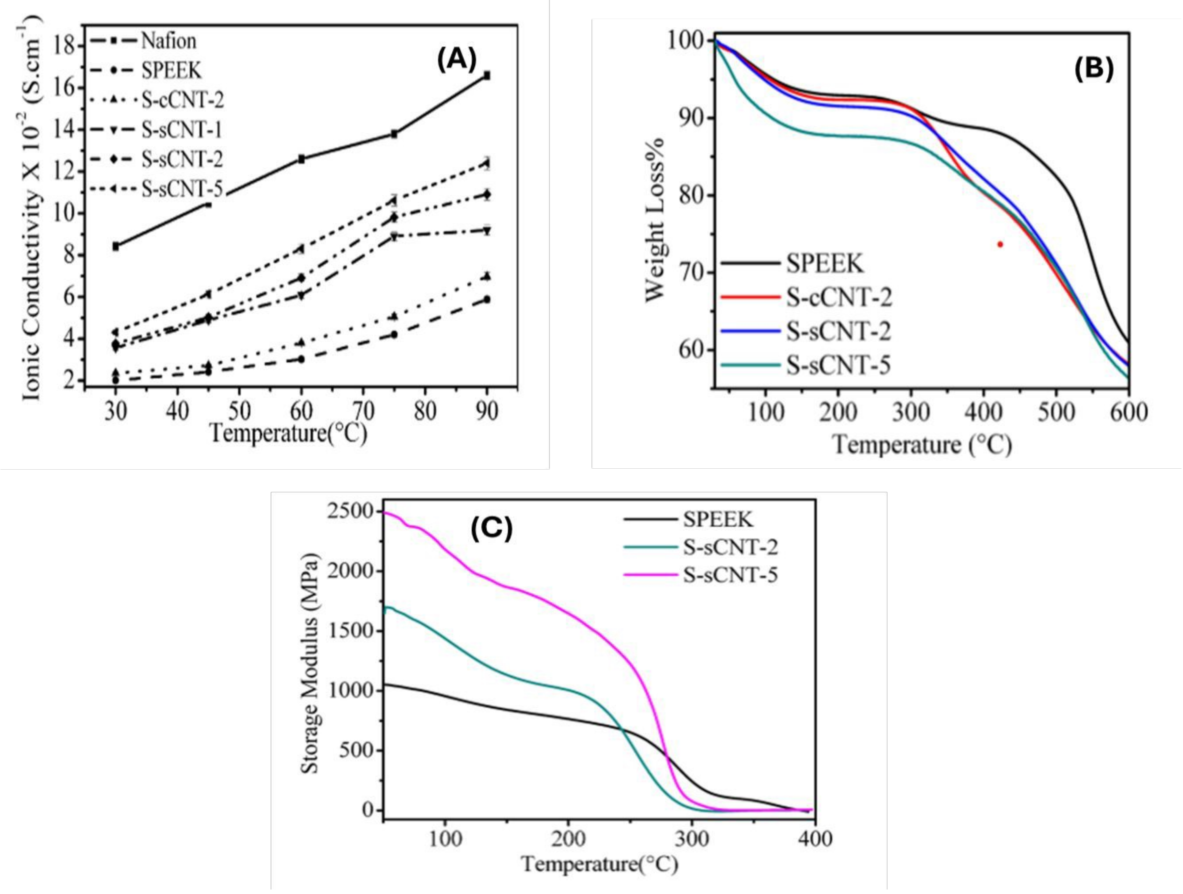

Figure 15: (a) Proton conductivity vs temperature (b) TGA thermographs and (c) DMA of SPEEK, S-sCNT-2, and S-sCNT-5 membranes[90].

Zhao Guodong et al., [91] prepared a composite membrane for use in PEMs by incorporating continuous carbon nanofibers (CCNFs) into SPEEK. The (CCNFs) were evenly distributed in an electrolyte polymer membrane after being easily blended into SPEEK matrix. The characterization of the composite membranes shows that all dense composite membranes have low methanol permeability, good proton conductivity, high mechanical performance, and excellent water swelling. The composite membrane containing 0.51 weight percent (wt%) CCNFs was fully hydrated and had a proton conductivity of 0.056 S.cm^{-1} at room temperature. Moreover, 1.5 times the relative selectivity of a pure SPEEK membrane was observed in the hybrid membrane containing 2.52 weight percent CCNFs. These results showed that

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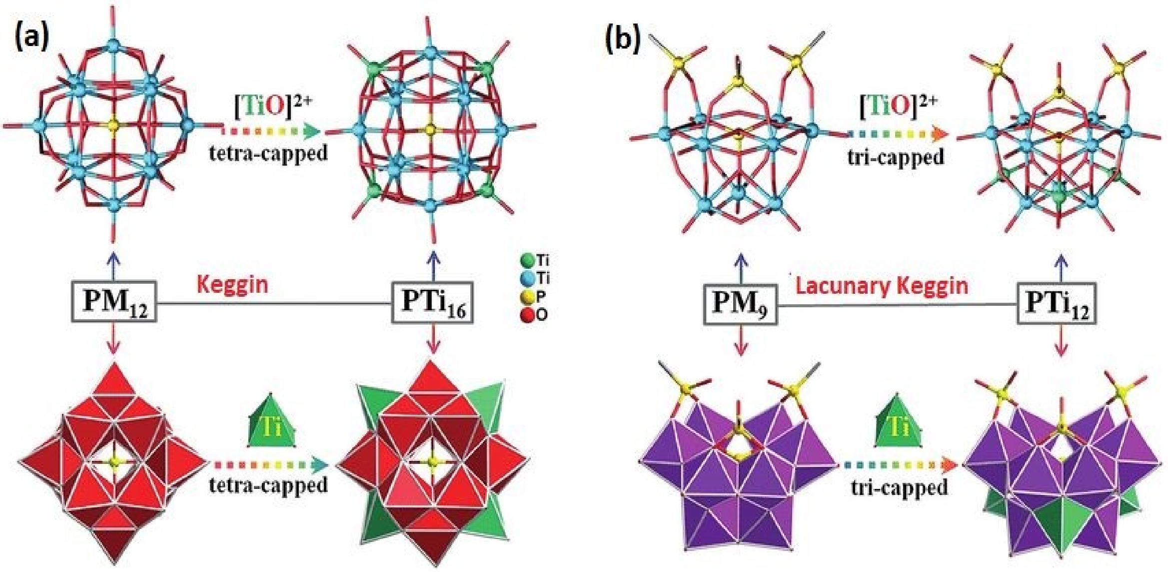
polyelectrolyte membranes for fuel cells with CCNF support (SPEEK) are a promising option.

5.2 Heteropolyacids (HPAs) as fillers for SPEEK membrane

The HPAs are highly conductive and thermally stable crystalline inorganic materials. HPAs salts are composed of MOx polyhedral, where M represents polyatoms such as Tungsten (W), Molybdenum (Mo), Niobium (Nb), Tantalum (Ta), and Vanadium (V), and x represents heteroatoms such as Silicon (Si), Phosphorus (P), Iron (Fe), and Cobalt (Co) through an oxygen atom coordination bridge [117]. They are typically distinguished by Wells-Dawson, Keggin, or lacunar structural configurations (Figure 16). Different salts with different structures and properties can be formed by changing the central metal ion and addenda atoms. HPAs are soluble in polar solvents, where they form the Keggin structure ($XM_{12}O_{40}$), which is a heteropolyacid anion structure with a condensation ratio of 1:12. The high acidity of HPAs is attributed to the polyanion's large size, which results in a low delocalized charge density. Chemical analysis, ion selective membranes, sensors, chemical cleaners, catalysts, and additives in fuel cell component materials are just a few of the applications for HPAs. Phosphotungstic acid (PWA) is one of the most promising inorganic additives for PEM composites due to its high proton conductivity and excellent thermal stability.



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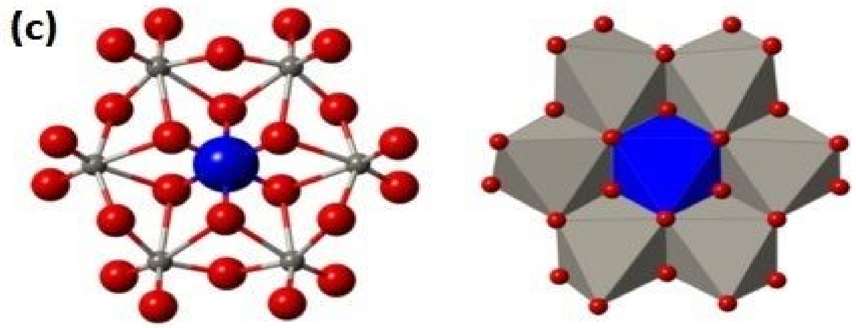

Figure 16: Structures of (a) Keggin,(b)Lacunary Kegging[118] and Wells-Dowson[119].

HPA can be partially replaced with cesium (CsHPA) to increase its surface acidity [120]. This substitution can maximise contact with the polymer matrix by decreasing the solubility of salt in water while increasing its surface area. Silica-based salts enhance the mechanical properties of the membrane while also improving its conductivity. Metal oxides (silica, titania), functional metal oxides [121], clay [122], aluminium phosphate (ALP) [123] and zeolites [124] have been used to modify the SPEEK membrane as a water retainer.

He et al., [92] successfully incorporated -cyclodextrin (-CD) onto halloysite nanotubes (HNTs) using polydopamine coating to make water-insoluble -CD-DHNTs, and subsequently SPEEK/-CD-DHNTs/HPW composite membranes were fabricated by traditional solution casting. It is reported that both HPW and β-CD-DHNTs were well dispersed in the SPEEK matrix because of the hydrogen bonding complexation between $[PW_{12}O_{40}]^{3-}$ and β-CD. The SPEEK/β-CD-DHNTs/HPW composite membranes proton conductivity increased with the increase of HPW content (0.090 S cm^{-1}), reaching the maximum of ~120% increase relative to that of the SPEEK membrane. Cs-HPAs, were added to the SPEEK matrix by Oh et al., [93] to create composite membranes. The greatest power density values (245 and 247 mW/cm^{2}) and enhanced conductivity of approximately 2.25 x 10^{-3} S cm^{-1} at 80 °C under 80% RH were demonstrated by these membranes. By embedding $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ on Pt in a SPEEK matrix, Zhang et al., [125]and Peighambardoust et al., [94] obtained nearly identical results. At 60 °C and 100% relative humidity, Zhang et al., obtained a proton conductivity of 5.3 x 10^{-2} S cm$^{-1,}$ while Peighambardoust et al. obtained approximately

6.82×10^{-2} S $cm^{-1,}$ which is thought to be higher than Nafion 117. Colicchio et al., [95] also investigated SPEEK, polyethoxysiloxane (PEOS), and PWA ($H_3PW_{12}O_{40}$) with 20% silica (SiO_2). According to the findings, this combination's proton conductivity is twice as high as pure SPEEK's at 90% relative humidity and 100 °C. Overall, the HPA-modified SPEEK membranes showed higher stability and increased proton conductivity values (6.25×10^{-3} $S.cm^{-1}$) when compared to the low values produced by a plain SPEEK membrane (2.21×10^{-3} $S.cm^{-1}$). Therefore, the HPA/SPEEK composite membranes are good candidates to replace Nafion-based membranes in PEM fuel cells due to their better proton conductivity and long-term stability.

Dogan et al., [96] created cesium salt of tungstophosphoric acid (Cs-TPA) particles by combining aqueous solutions of tungstophosphoric acid and cesium hydroxide, as well as Cs-TPA particles and sulfonated (polyether ether ketone). They investigated the effects of Cs-TPA on SPEEK membranes in terms of SPEEK sulfonation degrees and Cs-TPA content. The composite membranes' performance was measured in terms of water uptake, ion exchange capacity, proton conductivity, chemical stability, hydrolytic stability, thermal stability, and methanol permeability. It was discovered that the Cs-TPA particles aggregated as the degree of sulfonation of SPEEK increased from 60 to 70%. SPEEK (DS: 60%)/Cs-TPA membrane with 10% Cs-TPA concentration reduced methanol permeability to 4.7×10^{-7} $cm^2.s^{-1}$. At 80 °C and 100% RH, the membrane attained an acceptable proton conductivity of 1.3×10^{-1} S cm^{-1}. They also discovered that weight loss at 900 °C increased with the inclusion of inorganic particles, as expected. The addition of Cs-TPA particles to the SPEEK/Cs-TPA based composite membranes increased their hydrolytic stability. The authors also discovered that SPEEK60/Cs-TPA composite membranes were more hydrolytically stable than SPEEK70/Cs-TPA composite membranes. SPEEK60 composite membranes had reduced permeability values for methanol, water vapor, and hydrogen compared to Nafion®.

5.3 Graphene as fillers for SPEEK membrane

Graphene, a two-dimensional sheet of carbon, has astounded the world with its fascinating unique chemical, physical, and thermal properties, opening the door to numerous applications [115]. Due to its large surface area, which is highly valued in

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energy storage systems, graphene is primarily used as an electrode material in various electrochemical applications. Graphene is a carbon allotrope with a honeycomb lattice of sp^2-hybridized two-dimensional monolayers [126]. In comparison to graphite and carbon nanotubes (CNTs), graphene has a larger surface area (2629 m^2/g) than CNTs (1315 m^2/g), and is regarded as a fundamental building block for graphitic materials [127]. Graphene also has excellent electronic properties, exhibiting half integral quantum Hall effect even at room temperature [128, 129]. Graphene was extracted from graphite using a simple scotch tape method, and it was awarded the Nobel Prize in 2010 for its discovery [130]. Since then, many scientists have shifted their research focus to it, particularly in the areas of synthesis, functionalization, and application in various electrochemical devices such as fuel cells, solar cells, batteries, and ultra-capacitors.

Das et al., [131] synthesised solution-cast palladium graphite oxide-grafted amino acid nanocomposites (Pd-GO-L-Tyr) in sulfonated poly(ether ether ketone) (SPEEK). The composite membrane exhibited enhanced proton conductivity when compared to the pristine SPEEK membrane, owing to its increased hydrophilicity, surface wettability, and ion exchange capacity, which are attributed to the increased presence of hydroxy and carboxyl groups. The SPEEK/Pd-GO-L-Tyr membrane's high proton conductivity (2.56 $mS.cm^{-1}$) and low methanol crossover resulted in significantly higher selectivity (5.57 × 10 $S\ cm^{-3}\ s$) compared to the SPEEK membrane (4.8 × 10^2 $S\ cm^{-3}\ s^{-1}$) and Nafion-117 membranes (2.78 × 10^3 $S\ cm^{-3}\ s^{-1}$). Incorporating Pd-GO-L-Tyr into the SPEEK membrane matrix creates a physical barrier to prevent methanol crossover. With the above-mentioned factors, the authors concluded that composite membranes (Pd-GO-L-Tyr-SPEEK) are better candidates for DMFC applications, compared to the standard Nafion®117 membranes. Yogarathinam et al., [97] synthesised conductive polyaniline decorated graphene oxide (PANI-GO) and graphene oxide (GO), which they added to a sulfonated poly(ether ether ketone) (SPEEK) nanocomposite membrane to decrease methanol crossover. Surface morphology and crystallinity analysis verified the formation of PANI coated GO nanostructures (Figure 17). The analysis of membrane topography and morphology verified that PANI-GO and GO were evenly distributed across the surface of the SPEEK membrane. With a water uptake of 40% and an ion exchange capacity of 1.74 meq g^{-1}, the 0.1 wt.% PANI-GO modified SPEEK nanocomposite membrane demonstrated the highest performance.

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The nanocomposite membranes' oxidative stability was also improved. The modified SPEEK membrane with 0.1 wt.% PANI-GO had a lower methanol permeability of 4.33 x 10^{-7} $cm^2.S^{-1}$. The presence of acidic and hydrophilic groups in PANI and GO increased the proton conductivity of the PANI-GO modified SPEEK membrane. The selectivity of the PANI-GO modified SPEEK membrane was 1.94 x 10^4 S cm^{-3} s^{-1}. PANI-GO modified SPEEK membrane was discovered to be a potential material for DMFC applications.

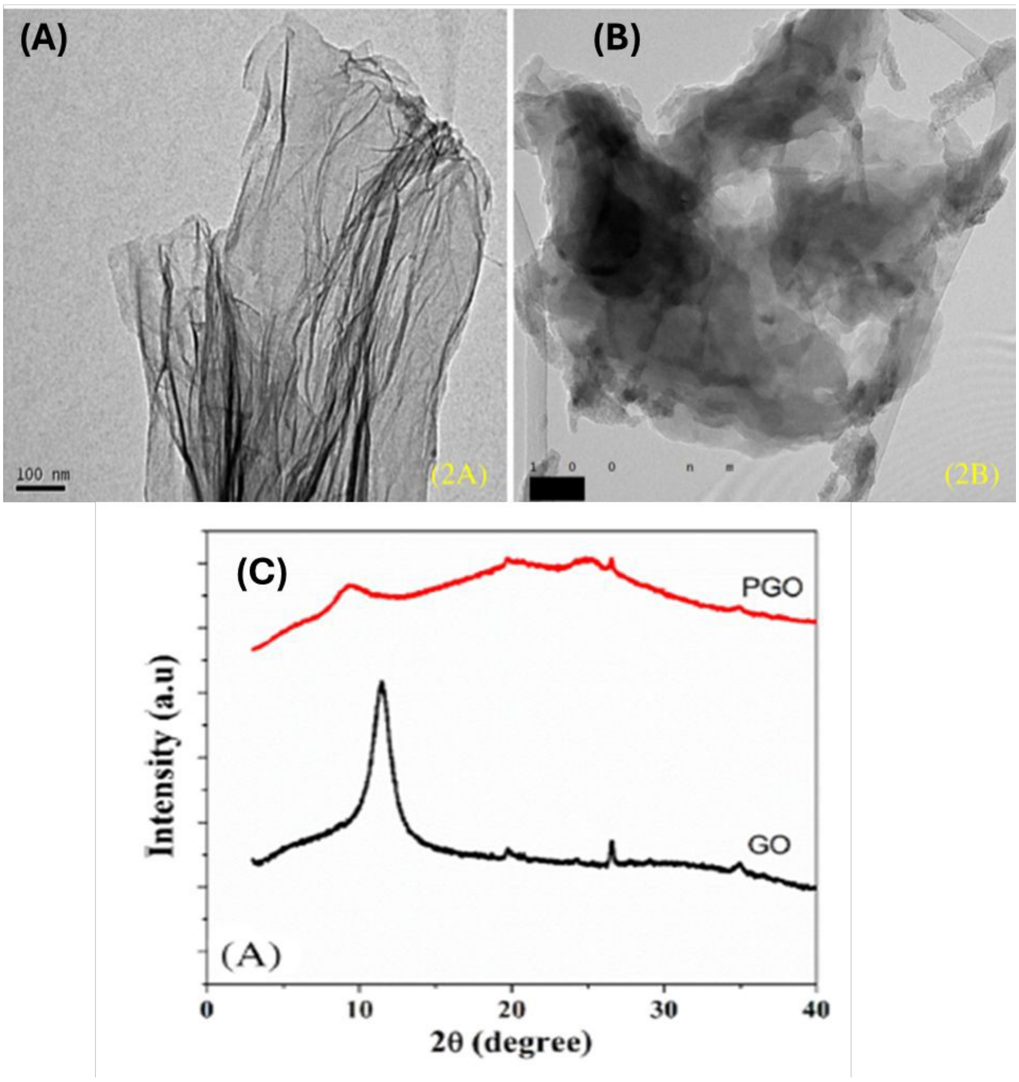

Figure 17: (A) Transmission electron microscopy (TEM) morphology of GO, (B) TEM morphology of PANI-GO nanocomposites and (C) X-ray diffractometer (XRD) patterns of GO and PANI-GO nanocomposites [97].

Maiti et al., [98] investigated a novel strategy for the advancement of proton exchange membranes by incorporating propylsulfonic acid-functionalized graphene oxide in crosslinked acid-base polymer blends and explored its fuel cells applications. The molecular dynamics (MD) simulations were conducted at different PrSGO loadings for the SPEEK/SPBI, XSPEEK/SPBI, and cross-linked SPEEK/SPBI composite systems. After increasing the loading percentage of SPBI and PrSGO filler in the polymer matrix and cross-linking the polymer composites, the glass transition temperature (T_g) was increased. It was also reported that the mechanical, chemical, and thermal stability of the XSPEEK/SPBI/PrSGO nanocomposite membranes increased significantly with an increase in PrSGO loading, owing to the strong interfacial interaction between PrSGO and the XSPEEK/SPBI matrix. The proton conductivity of the XSPEEK/SPBI/PrSGO nanocomposite membrane improved significantly up to 0.17 S.cm^{-1} at 4 weight percent PrSGO loading at 100% relative humidity (RH) and 90°C. Furthermore, at 100% RH, 80 °C, the XSPEEK/SPBI/PrSGO nanocomposite membrane demonstrated excellent fuel cell (FC) performance with a maximum power density of 0.82 W.cm ^{2}. Due to the hygroscopic nature of PRs GO, the authors observed a higher number of sulfonic acid groups and excellent interaction between the acid functionalized fillers and the cross-linked SPEEK/SPBI-based matrix. The membranes' overall performance and other critical characteristics, including their proton conductivity, were enhanced by the addition of PrSGO nanofillers to the polymer matrix.

5.4 Silica as fillers for SPEEK membrane

The extensive research on silica-based nanoparticles is due to their lower cost, good mechanical, and water retention properties. However, due to their poor organic compatibility and non-conductive properties, SiO_2 particles aggregate in the polymeric matrix and reduce the conductivity of PEMs [132]. Higher silica loading in the membrane results in a significant dilution effect for the membrane's ion exchangeable groups [133]. As a result, as pure silica content increases, the membrane's ion exchange capacity decreases [134]. However, numerous studies have been conducted to improve membrane IEC by functionalizing silica filler with sulfonic group derivatives. Optimal silica loading improves membrane strength [135]. Higher silica content in the matrix, on the other hand, is detrimental to the mechanical properties of the polymer due to increased filler-filler interaction compared to filler-polymer interaction, which destroys membrane homogeneity and causes the membrane to

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become brittle. As a result, a perfect combination of inorganic material and membrane can result in nanocomposites with improved mechanical properties [136].

Martina et al., [99] used the solvent cast method to create Sulfonated silica (S-SiO_2) nanoparticles incorporated into a blend of sulfonated poly (vinylidene fluoride-co-hexafluoropropylene) (SPVdF-HFP) and sulfonated poly (ether ether ketone) (SPEEK). They claimed that incorporating S-SiO_2 into SPEEK improved the polymer's water uptake, IEC, and mechanical properties. At 90 °C and 100% RH, sulfonated silica with an 80 wt% SPEEK-20 wt% SPVdF-HFP nanocomposite membrane demonstrated maximum proton conductivity and current density of 7.9 $x10^{-2}$ $S.cm^{-1}$ and 354 mA cm^{-2}, respectively. The enhanced proton conductivity is attributed to the presence of S-SiO_2. The hydrophilic nature promotes the ion channels and swells the membrane which results in enhanced proton conductivity.

Meng et al., [100] investigated how amino-modified mesoporous silica nanospheres affected the properties of SPEEK/phosphotungstic acid (HPW). They state that while immobilising acids is an issue, adding acid proton carriers to a polymer matrix is an effective method for increasing proton conductivity. They discovered that adding HPW and aminated mesoporous silica nanoparticles (K-MSNs) to SPEEK enhanced dimensional stability and proton conductivity. At temperature of 60 °C and 1 wt.% K-MSNs loading, the composite membrane's proton conductivity was 243 mS/cm, indicating that SPEEK/HPW/K-MSNs composite membranes have significant potential in methanol fuel cells application. Sahin et al. produced a blending polymer consisting of SPEEK, PVA, and tetraethyl orthosilicate (TEOS) [101]. The author demonstrated how adding PVA could increase the number of modifiable groups, which would enhance proton transport and improve oxidative and hydrolytic stability when TEOS is added. This finding was supported by the author's results, which showed that the SPEEK/PVA/TEOS blend outperformed the other samples (pure SPEEK, PVA, and SPEEK/PVA composite) in terms of oxidative and hydrolytic stability. The addition of TEOS increased hydrolytic stability while reducing the amount of –OH groups, which in turn improved water resistivity. Additionally, the membrane shows better cell performance values when compared to Nafion 117. The outcomes demonstrate how promising these membranes are as PEMFC application candidates.

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In another study, Li et al., [88] successfully synthesised composite membrane by dispersing ionic liquid (IL) in sulfonated hollow mesoporous organosilica (sHMO) into the SPEEK polymer backbone. The comparison study of various SPEEK/IL/sHMO-x (where x represents: 2.5, 5.0, 7.5 and 10 wt%) composite membranes and SPEEK/IL/HMO was conducted. The authors reported that SPEEK/IL-30/sHMO-7.5 membrane had a conductivity of 1.13 mS.cm^{-1} at 200 °C, which is twice that of the SPEEK/IL-30/HMO-7.5 (0.60 mS cm^{-1}) at same conditions. The improvement of the conductivity can be attributed to the addition of sHMO might have facilitated the formation of continuous network or continuous pathway with IL. The organosilica sphere's surface exhibits a strong interaction between the hydroxyl group and IL, leading to significant IL retention. The IL loss study revealed that adding organosilica sphere significantly reduced the membrane's IL loss. The anhydrous membrane is expected to be useful in PEMFCs at medium temperature conditions.

5.5 Clay as fillers for SPEEK membrane

Clay is a common nanofiller used in many different applications. Natural and synthetic clays include talc, mica, layered double hydroxide (LDH), laponite (LAP), SAP, and montmorillonite (MMT). The structures of laponite clay, layered double hydroxide, and montmorillonite are depicted in Figure 18. Compared to mica and talc, MMT, which has the chemical formula $(Na,Ca)_{0.33}(AlMg)_2(Si_4O_{10})(OH)_2nH_2O$, has drawn a lot of attention and is used as a nanofiller in many applications, including fuel cells. MMT is a cation clay with a 2:1 crystal structure made up of one layer of octahedral aluminium hydroxide or magnesium hydroxide sheets and two interconnected tetrahedral silicon oxide sheets. LDH consists of a positively charged metal hydroxide brucite-type sheet with various anions and water inside galleries to counterbalance the charge [137]. Apart from LDH, LAP is also a component of a synthetic clay that belongs to the 2:1 phyllosilicate structural group. The structure and composition of LAP, which has the chemical formula $Na_{0.7}(Si_8Mg5.5Li_{0.3})O_{20}(OH)_4$ are similar to those of natural clay hectorite minerals [138]. LAP is made up of octahedral magnesium oxide and two parallel sheets of tetrahedral silica, resulting in two-dimensional layers. A single LAP layer is 25 nm in diameter and 1 nm thick, with positive charges on the edges and negative charges on the faces. Clay is readily available in nature and easily synthesised. It has high ion-exchange capacity, chemical stability, and rheological

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properties. Clay's thin platelet structure contributes to its high aspect ratio [139]. Due to its morphology, size, structure, and ionic nature, clay nanofiller performs exceptionally well as an electrolyte, particularly in fuel cell composite membranes.

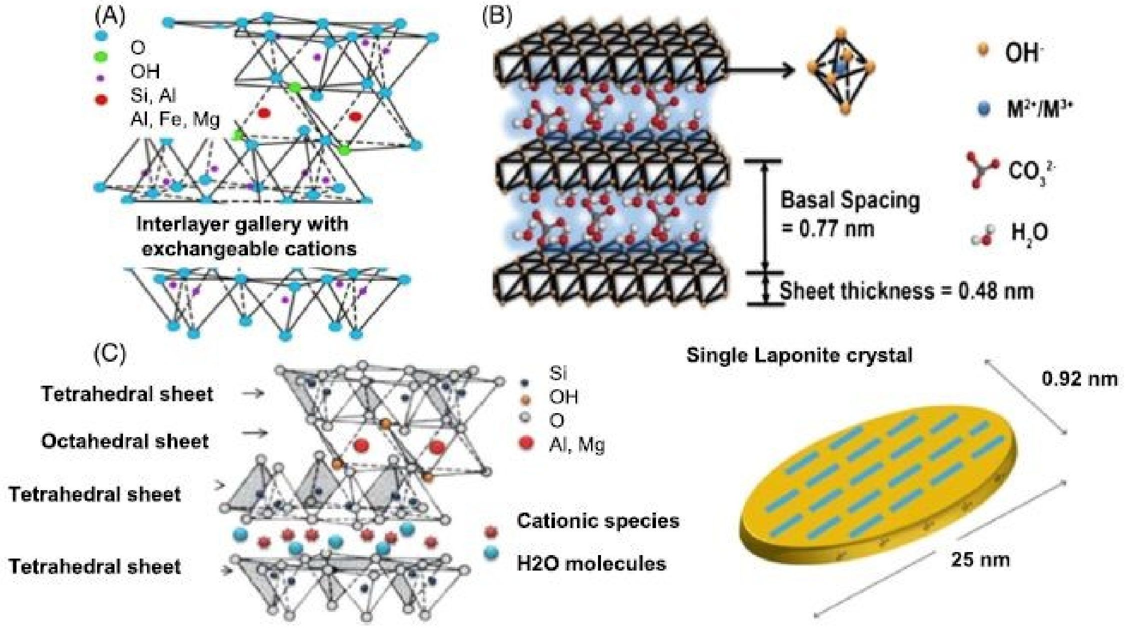

Figure 18: Structures of (A) montmorillonite (MMT), (B) layered double hydroxides (LDH), and (C) laponite (LAP) clays with single laponite crystal [140]

He et al., [141] compare the performance of unmodified clays (Na^+ montmorillonite) (IC) with that of organ modified clays (I.44P (Na^+ montmorillonite modified by I.24TL (Na^+montmorillonite modified by $HOOC(CH_2)17NH_3^+$)(HC) and ($CH_3(CH_2)17N(CH_3)_2^+$) (OC). When loading less than 10 wt% of HC, SPEEK/HC membrane outperforms all other types of SPEEK/clay composite membranes in terms of overall performance and achieves higher selectivity than pure SPEEK membrane. These SPEEK/HC composite membranes have been reported to have increased methanol permeability and proton conductivity. Combining the HC carboxylic acid group increased HC bonding between membrane ion groups and dispersibility due to higher proton conductivity without compromising membrane stability. For SPEEK/IC and SPEEK/OC hybrid membranes, proton conductivity simultaneously decreases with increasing filler content.

Kumar et al., [102] created sulfonated polyether ether ketone (SPEEK) composites with of bentonite and cloisite 30B nanoclays. The enhanced glass transition temperature and altered membrane morphology in the pristine SPEEK membrane (Figure 19) indicated the presence of nanoclays. In comparison to the pristine membrane, the addition of 0.5 weight percent of bentonite and cloisite to SPEEK decreased proton conductivity and water uptake. According to the author, this could be due to blocked ionic micro-structure channels caused by nano clay particles, which reduce ion exchange carriers. The addition of cloisite and bentonite to SPEEK polymer matrices limits the available nanometric channels for the migration of polar molecules such as hydrogen ions and water. Cloisite and bentonite layers' increased rigidity complicates proton transport, which accounts for the decrease in conductivity. Gokulakrishnan et al., [103] synthesised membranes of functionalized graphene oxide (f-GO) nanocomposites at different concentrations and halloysite nano clay using dry phase inversion. The study discovered that the sulfonic acid group in SPEEK and silane functionalization of GO increased the ion exchange capacity from 0.22 to 0.35 meq/g, which improved proton conductivity. In comparison to the pure SPEEK membrane, which had proton conductivity of 0.31 mS cm^{-1} and power density of 28 mW cm^{-2}, the composite membrane, which contained 3 wt.% halloysite nano clay and 2 wt.% f-GO, maintained values of 0.47 mS cm^{-1} and 72.2 mW cm^{-2}. The 2 wt.% f-GO and 3 wt.% SPEEK membranes with halloysite incorporation showed improved proton conductivity; these membranes are crucial for direct methanol fuel cell (DMFC) applications.

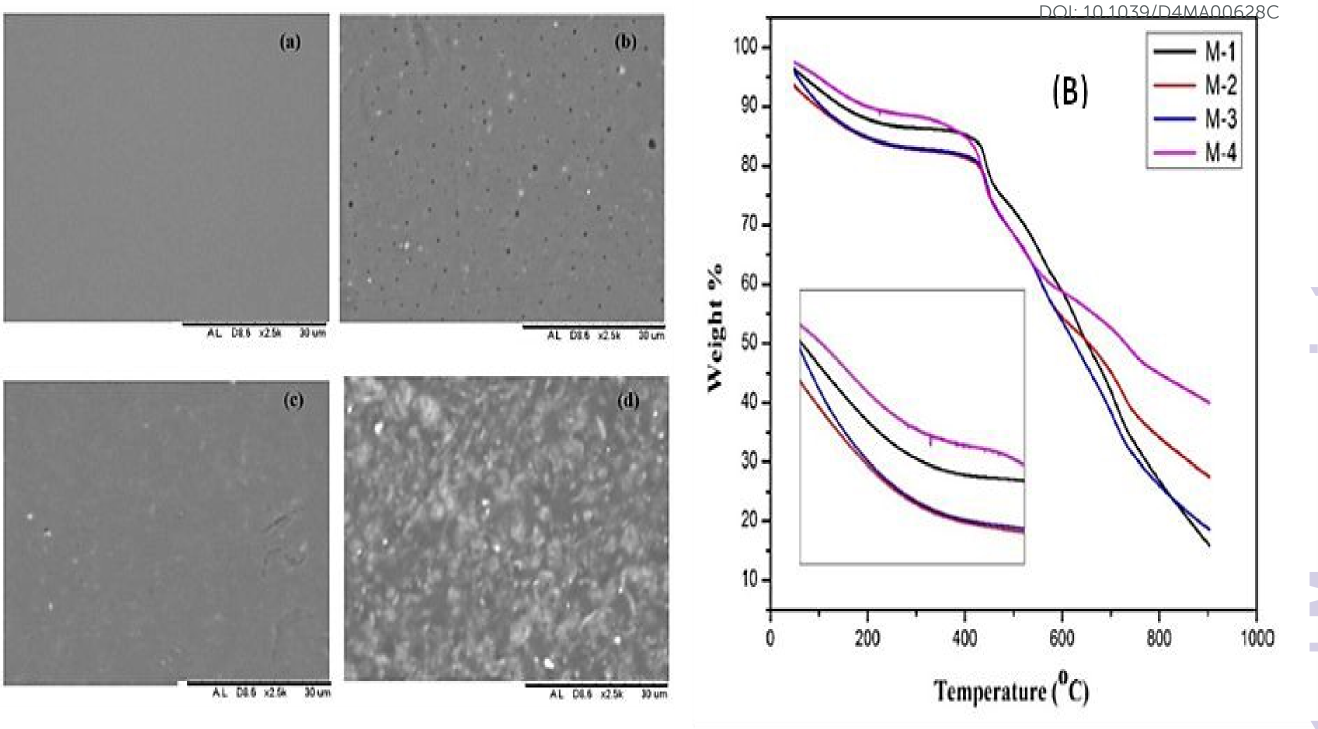

Figure 19: SEM images of various membranes: (**a**) SPEEK, (**b**) SPEEK/bentonite, (**c**) SPEEK/cloisite and (**d**)SPEEK/bentonite/cloisite, **(B)** TGA thermograms of SPEEK (M-1), SPEEK/cloisite (M-2), SPEEK/bentonite(M-3) and SPEEK/cloisite/bentonite (M-4) [102].

To create composite membranes with different nanofiller contents, Charradi et al., [104] used a porous SiO_2-montmorillonite heterostructured material packed with delaminated clay particles and a synthetic Mg-Al layered double hydroxide (LDH) exchanged with sulphate anions. The addition of Mg-Al LDH and SiO_2-motmorillonite fillers to the SPEEK appears to improve water retention and thermal stability of the resulting composite electrolyte membranes. At 120°C and 100% relative humidity, Si-motmorillonite exhibited a higher proton conductivity (0.158 $S.cm^{-1}$) than both Mg-Al LDH and neat SPEEK (0.070 and 0.023 $S.cm^{-1}$, respectively). This could improve the performance of fuel cell membranes at high temperatures.

5.6 Metal Oxide as fillers for SPEEK membrane

Interfacial interactions between membranes and catalysts, which constitute MEA components, are critical to the proper operation of fuel cells. This interfacial interaction is closely related to the catalyst and membrane structures, as well as the method used

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to prepare MEA [142]. Metal oxides are classified into several types, including ZrO_2, SiO_2, Al_2O_3, and TiO_2, each with its own set of properties. The conductivity of the membrane protons is typically increased when a metal oxide is added as an additive in composite polymers for a variety of reasons, such as the following:

1. Defects in the interface that arise when metal oxides occupy the polymer chamber and distance charge sheets are present.

2. Metal oxides nanofillers are the predominant material in amorphous conditions because they promote proton transport and increase the free volume within the polymer matrix.

3. Increased ion dissociation in the polymer electrolyte membrane.

However, the PEM water intake and conductivity are affected by the properties and reactions of metal oxides such as strontium cerate, silica, titania, zeolite and zirconia. Because of their large aspect ratio and surface area, metal oxide nanofibers are superior to other additives for composite materials. The addition of Fe_3O_4 to PEEK, SPEEK, SPES and Nafion improved proton conductivity by promoting precise water hopping mechanisms. Furthermore, molybdenum oxide (MoO_3) has good conductivity and physicochemical properties, making it suitable for use in energy-related fields.

Alumina, or aluminium oxide, is a common nanofiller in composites. Alumina has the chemical formulaAl_2O_3 and can be found in a variety of minerals, including bauxite, diaspore ($Al_2O_3H_2O$) and gibbsite ($Al_2O_{33}H_2O$) [143, 144]. Alumina can exist in various crystalline structures, but $Al2O_3$ is the most thermodynamically stable. Its large surface area and high catalytic activity make it a good nanofiller. One of the metal oxide types that is frequently utilised as a nanofiller in fuel cells is silicon oxide, or silica (SiO_2). Sol gel, microemulsion, fuming, and precipitation are a few of the techniques used to create nanoparticle silica. The hydrophilic characteristics of this metal oxide have been attributed to the development of siloxane and silanol groups on the SiO_2 surface, which is a 3D network in structure. Surface-modified SiO_2, which comes in a range of sizes (mesopores, spheres, fibres, and rods) has been employed as a nanofiller in fuel cell membranes. The common techniques for producing the silica/polymer composite are sol-gel, in situ polymerization, and straightforward blending. The most popular technique is simple blending because it is easy to control the parameters (sonicating time and temperature) needed to create high homogeneity of the polymer composite [145].

Selvakumar et al., [105] created sulfonation PEEK membranes using the solvent casting technique of bariun zirconate ($BaZrO_3$). The polymer electrolyte's proton conductivity was significantly enhanced at a high weight ratio of 6 wt.% $BaZrO_3$ filler, with 3.12 × 10^{-1} $S.cm^{-1}$ at 90 °C. They found that the values of proton conductivity rise with increasing temperature. Proton conduction occurs because $BaZrO_3$ nanoparticles can dissolve protons from water in wet environments. The composite membrane exhibited current density of 280 mA cm^{-2} and power density of 183 mW cm^{-2}. The author concluded that the 94 wt% SPEEK 6 wt% $BaZrO_3$ polymer composite membrane is a viable option for PEM fuel cell applications. Wang et al. have effectively synthesised a sulfonated poly (ether ether ketone) (SPEEK) nanocomposite membrane through the integration of phosphotungstic acid (HPW) and aluminium doped cerium-based oxides (Al-$CeZrO_4$) into the SPEEK matrix [106]. The addition of Al-$CeZrO_4$ improved the chemical stability of SPEEK membrane while maintaining conductivity, and the addition of HPW increased proton conduction via acid-base interactions. Comparing the SPEEK/Al-$CeZrO_4$ nanocomposite membrane to the SPEEK/HPW nanocomposite membrane, there was a 15.5% increase in proton conductivity. Therefore, it is believed that Al-$CeZrO_4$/HPW is a useful inorganic nanofiller for enhancing the chemical stability and proton conductivity of SPEEK membranes, and more research should be done on the hybrid composite membrane.

Gandhimathi et al., [107] developed sulfonation PEEK membranes by casting niobium oxide in a solvent. At a high weight ratio of 10% NBO filler, the polymer electrolyte's proton conductivity was dramatically increased to 2.9 × 10^{-2} $S.cm^{-1}$ at 90 °C, compared to 1.8 × 10^{-2} S.cm-1 for pure SPEEK membrane. The thermal stability of the composite membranes was also significantly enhanced by the impregnation of NBO. It was reported that SP-NBO-10 nanocomposite membrane achieved a maximum power density of 601 mW cm^{-2}, while the pristine membrane could only achieve a maximum of 497 mW cm^{-2}. The increase in the trend of current density and power density of the composite membrane may be induced by the vehicular proton transport mechanism involved in sulfonic acid-based ionomeric membrane that leads to adsorption and retention of more water molecules. Based on the electrochemical results the author concluded that the SP-NBO-10 polymer composite membrane is a feasible material for PEM fuel cell applications. Prathap et al., [108] successfully created a new set of polymer composite membranes employing a linear sulfonated poly(ether ether ketone) (SPEEK) polymer and zinc cobalt oxide (ZCO) as an inorganic filler, which were tested for fuel cell applications. SPEEK was created by directly sulfonating PEEK with concentrated sulfuric acid, then loading sufficient amounts of ZCO into it to form polymer composites. Proton nuclear magnetic resonance investigations demonstrated a 55% sulfonation of SPEEK, whereas XRD and morphological examinations confirmed the successful integration of inorganic fillers into the polymer matrix, as illustrated in Figure 20. Additionally, the authors stated that at 30°C, the pristine SPEEK membrane had a proton conductivity of 9 x 10^{-3} S cm^{-1}, while the composite membranes loaded with 2.5 to 10 wt% of ZCO showed values in the range of 1.2 x 10^{-2}– 2 x 10^{-2} S cm^{-1}. The membranes' measured ion exchange capacities fell between 1.26 and 1.46 meq g^{-1}. The composite membranes demonstrated remarkable thermal stability up to 370°C. Thus, the membranes created in this study have the potential to considerably contribute to the creation of new proton conducting SP-ZCO composite membranes for use in PEM fuel cells.

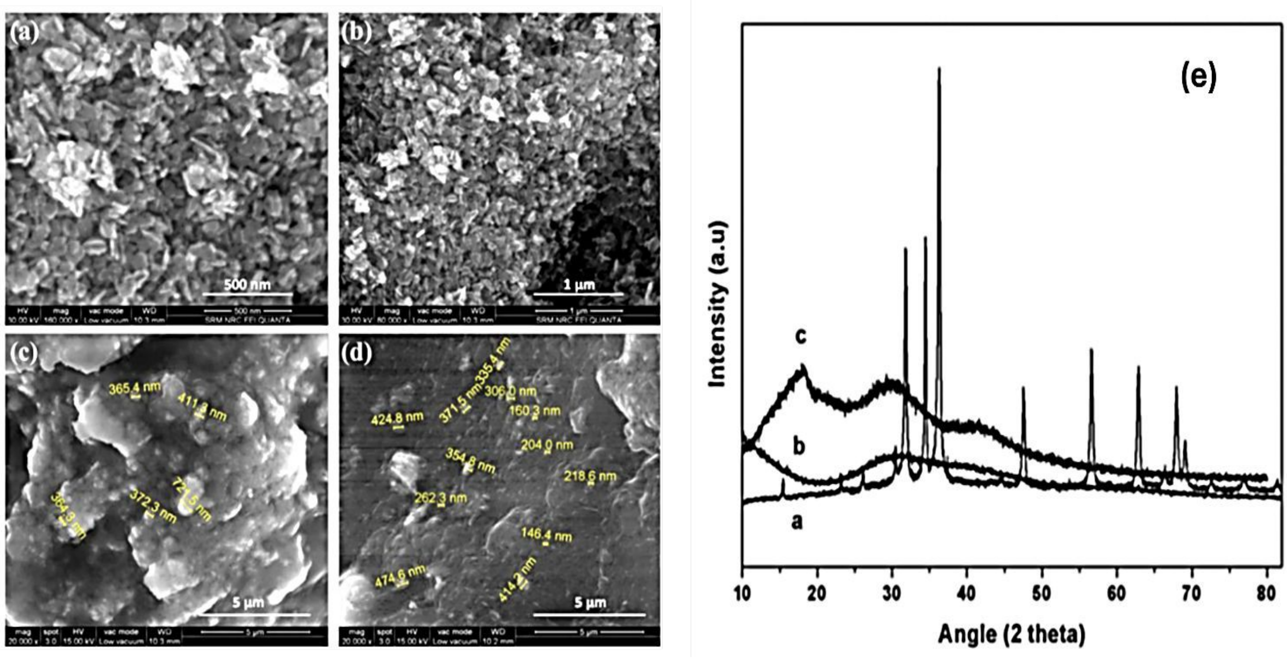

Figure 20: FESEM images of (a), (b) ZCO, (c) SP-ZCO-5, and (d) SP-ZCO-10, (e) XRD spectra of SPEEK and SP-SZO nanocomposites.

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5.7 Metal-organic frameworks (MOFs) as fillers for SPEEK membrane

Metal-organic frameworks (MOFs) are highly porous materials with tunable pore size and chemical functionality. They are created by unifying metal ions or their clusters with various organic linkers. Compared to other additives, MOFs' organic linkers provide higher loading because of their improved compatibility with the organic polymers [146, 147]. The effective manipulation of MOFs' composition and pore size can be achieved through the appropriate choice of precursors, adjustment of synthesis conditions (reagent molar ratio, temperature, etc.), or post synthetic chemical modifications. The tunable functionality of MOFs, combined with their high porosity and surface area, makes them appealing for applications involving interactions with guest species [148]. Zeolite imidazolate frameworks, or ZIFs, are a significant subclass of metal-organic frameworks (MOFs) that offer high surface area and thermal stability due to their structural similarities to zeolite and the structural diversity that MOFs provide through properties like pore size tunability and chemical functionality [149]. For small molecules like hydrogen, the tiny pores at the entrance provide a molecular sieving effect, and the large internal cavities encourage quick diffusion [150, 151]. Several ZIF-polymer composite membranes containing ZIF-7, ZIF-8, ZIF-22, ZIF-90, ZIF-100, and other components have been proven to significantly improve hydrogen separation, but ZIF-8 has been successfully commercialised and widely used due to its higher stability and better resistance to acid and alkaline environments [152]. MOFs are increasingly being used in electrochemical systems for clean energy applications, such as solar cells, fuel cells, hydrogen production and storage, supercapacitors, and lithium-ion batteries. Over the last decade, the chemistry of MOF compounds has received a lot of attention for its use in many fields of material chemistry, including gas storage and separation [153], biomedical applications [154], catalysis [155], and electro-optical devices [156].

Zhang et al., [109] developed a (SPEEK/HPW@MIL) membrane by combining amino-modified MIL-101 (Cr) with HPW to form nano-hybrid membranes for PEMFC applications. HPW was anchored using hydrogen bonds to reduce leakage and improve overall compatibility. The SPEEK/HPW@MIL composite membrane's proton conductivity increased by 26% due to the effective anchoring effect of MIL-101(Cr)-NH2 on HPW and the hydrogen bond network with HPW and SPEEK. Huang et al.

created sulfonated spindle-like carbon derived from metal-organic framework, MOF-C-SO_3H, has been employed as a filler for the SPEEK membrane [110]. The obtained MOF-C-SO_3H@SPEEK membrane exhibits improved properties as a PEM for DMFCs when 3 wt.% MOF-C-SO_3H is added. They also found that the MOF-C-SO_3H@SPEEK membrane had higher proton conductivity and significantly lower methanol permeability than Nafion 115. According to their findings, the MOF-C-SO_3H@SPEEK membrane's high performance was due in large part to its specific porous and sulfonated carbon structures. The effective dispersion of MOF-C-SO_3H in the SPEEK matrix decreased the membrane's methanol permeability and swelling ratio while simultaneously enhancing proton transport and improving the membrane's proton conductivity. The authors reported a maximum power density of 83.91 mW cm $^{-2}$, approximately 50% higher than that of Nafion 115. The superior stability of the MOF-C-SO_3H@SPEEK membrane in contrast to Nafion 115 implies that it is a viable proton exchange membrane for fuel cells.

In another study, Sun et al., [111] used the solution casting method to incorporate Co-MOF-74/phosphate-4-phenylimidazole into SPEEK ternary composite membranes (Co-MOF-74/[IM_2][H_2PO_4]/SPEEK). A minor agglomeration on the surface of the Co-MOF-74/[IM_2][H_2PO_4]/ SPEEK. A ternary composite membrane with increased Co-MOF-74 contents and a gear-like structure was observed in the cross section of the prepared composite membrane using SEM. By means of hydrogen bonding, the metal organic framework (MOF) encapsulates the ionic liquid (IL) and reducing its loss, consequently enhancing the proton conductivity of the Co-MOF-74/[IM_2] [H_2PO_4]/SPEEK membrane. The authors found that using 2.5 wt.% Co-MOF-74/[IM_2] [H_2PO_4/SPEEK resulted in a 25.96 mS·cm^{-1} increase in proton conductivity at 120 °C, as well as a decrease in IL loss rate. Additionally, it was proposed that the Co-MOF-74/[IM_2] [H_2PO_4]/SPEEK ternary composite membrane could be used at temperatures up to 320 °C. These suggest that encapsulating IL in the MOF enhances the SPEEK membrane's thermal stability in addition to increasing its proton conductivity.

Aparna et al., [112] have also fabricated Cu-MOF anchored SPEEK and SPEEK/PI composites membranes for PEMFC applications. This membrane displayed high mechanical, thermal and physiochemical properties. Cu-MOF loading at 3 wt.% resulted in maximum proton conductivity of 0.0711 S cm^{-1} IEC value of 2.35 meq g^{-1} with a water uptake of 38.18 %. The experimental results of the prepared membranes revealed that they function as an efficient proton exchange membrane (PEM) for PEMFCs. Sun et al., successfully synthesizes a novel two-dimensional (2D) zeolite structure ZIF8/CNT hybrid crosslinked networks (ZCN) by in-situ growth procedure as shown in Figure 21 [113]. The introduction of ZCN and SPEEK significantly improved the proton conductivity and inhibited methanol permeability. The proton conductivity of SPEEK@ZCN composite membrane was reaching 50.24 mS cm^{-1} at 120 °C and 30% RH, which was 11.2 times that of the recast SPEEK membrane 4.50 mS cm^{-1} under the same conditions. Furthermore, it was discovered that the membrane's proton conductivity was greatly enhanced by the addition of two-dimensional fillers.

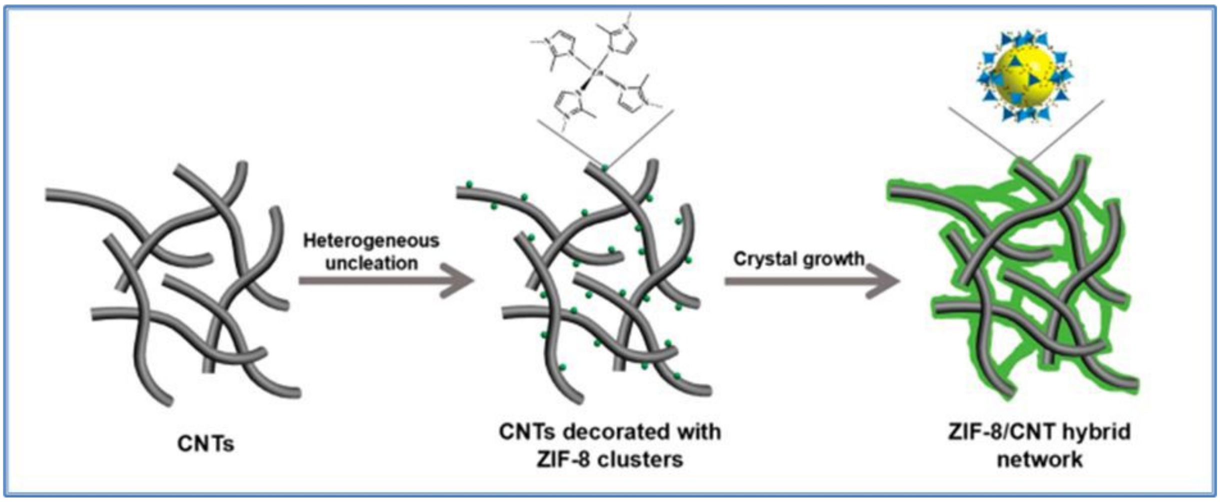

Figure 21: Schematic illustration of the synthesis process of ZCN through in situ growth procedure [113]

Barjola et al., [114] prepared nanocomposite membranes by mixing of 1, 3, and 5 wt% (SPEEK-Z1, SPEEK-Z3, and SPEEK-Z5) cobalt-based zeolitic imidazolate framework (ZIF-67) with a sulfonated poly(ether ether ketone) (SPEEK) by casting method. Thermal stability and proton conductivity were greatly enhanced by the addition of 1wt% ZIF-67 to SPEEK. The proton conductivity of 0.014 S cm^{-1} for SPEEK-Z1 composite membrane was reported. The authors believe that a proper optimisation process is still necessary, even though the Polymer Electrolyte Membrane Fuel Cells (PEMFC) performance experiments showed promising results for these membranes working at intermediate temperatures above 100 °C.

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6. Conclusion and future perspectives

Without a doubt, the growing fuel cell market will provide a powerful driving force for increased research into non-fluorinated PEMs, which are less expensive and perform better than expensive Nafion® membranes. Polymers based on sulfonated poly (ether ether) ketone have the potential to be used as fuel cell electrolyte membranes. This review article examined the most current advancements in the design of various SPEEK-based electrolyte membranes for PEMFC and DMFC applications. Nevertheless, there are still certain issues with using SPEEK membranes in practical applications.: 1) SPEEKs could not achieve the excellent performance of the C-F chemical bond of PFSA membranes without any modification; 2) excessive overall swelling and low thermal stability are always caused by the higher DS of SPEEK for higher proton conductivity; 3) cross-linked SPEEK membranes formed by covalent bonds may improve dimension and chemical stability, but they will also reduce proton conductivity. Other polymers and fillers should and have been introduced into the fabrication of SPEEK membranes. As a result, one of the primary goals of future research will be to design and prepare the SPEEK membrane with proper structure in the presence of other polymers and fillers. When compared to Nafion® membranes, SPEEK's organic-inorganic composite membranes offer the best chances of superior performance. The addition of inorganic fillers may improve membrane mechanical and electrical properties, making them more suitable for fuel cell applications. However, there are still some issues that require further investigation:

a) More hopping sites should be produced by the composite process to encourage the tendency of the proton conduction mechanisms towards the hopping mechanism, which will help to increase the methanol permeability and proton conductivity even at higher temperatures (preferably 120 °C).
b) To strengthen the bond between filler and polymer, it's crucial to choose the right inorganic filler and modify their interface.
c) To understand the morphology and structure of PEMs, it is important to perform dynamic simulations using mathematics and computer software. This allows for the design of modifications to SPEEK and inorganic fillers, as well as optimisation of polymer and filler combinations.

The SPEEK composite membrane has significant advantages, including low methanol crossover and high proton exchange. Proton conductivity of almost all SPEEK-related composite materials was on the order of 10^{-2} S cm^{-1}, which was adequate for them to be utilised as a membrane in a hydrogen-oxygen fuel cell. The impact of various metal oxides on the SPEEK matrix was also covered in this review, which concludes that SPEEK-based membranes are among the best polymer electrolytes for proton exchange in fuel cells. More investigation is needed to use the right inorganic particles and focus on the increase in affinity towards water-containing membranes, which increases proton conductivity. Regarding PEM development in the future, it is unrealistic to think that a single type of PEM will be able to satisfy all the needs for a larger range of applications, including stationary, mobile, and automotive fuel cell applications. Research priorities will vary depending on the application goals, but it is more important for specialists in various fields to collaborate, including physics, electrochemistry, polymers, composite materials, and simulation. As a result, we hope that this review will give a general overview of the developments surrounding SPEEK-based PEMs and offer some suggestions for the creation of high-performing non-fluorinated PEMs in the future.

CRediT authorship contribution statement

Mayetu Segale: Conceptualization, Writing - original draft, Writing - review & editing. **Tumelo Seadira**: Conceptualization, Supervision, review & editing. **Rudzani Sigwadi:** Conceptualization, Supervision, review & editing. **Touhami Mokrani**: Supervision, Writing - review & editing. **Gabriel Summers**: Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.