Fabrication, Properties, and Performance of Polymer Nanocomposite Ion Exchange Membranes for Fuel Cell Applications: A Review

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ABSTRACT

The membrane in a fuel cell plays an essential role in permeating the ionic charges of positive and negative ions without passing the fuels and electrons through it. The membrane's common materials are perfluorinated polymer, non-fluorinated or hydrocarbon polymer, and natural polymer. The physicochemical properties of the membrane have the most significant influence on the performance of fuel cells in terms of mechanical stability, ionic conductivity, power output, and cell operation longevity. The incorporation of nanoparticles into polymeric-based materials improved the membrane's properties by suppressing fuel crossover, improving water retention, and increasing ionic mobility across the membrane. The effect of incorporating nanoparticles is determined by their type, size, shape, surface acidity, and relationship to the polymer matrix. The blending, sol-gel, and infiltration methods are used to develop the nanocomposite membrane. Compared to a commercial membrane in a fuel cell application, most of these membranes demonstrated superior cell performance. Based on published literature, this review briefly described the design and influence of specific advanced nanomaterials incorporated in polymer matrix toward membrane performance.

Keywords: Nanomaterial, fuel cell, ion exchange membrane, polymer, properties

1.0 INTRODUCTION

Research and development (R&D) of fuel cell applications is continuously conducted and increased from year to year to improve their cell component functions and performances to meet the industry's requirements and demand. According to the ScienceDirect website, by using the keyword 'nanocomposite membrane fuel cell', the number of published papers for these membranes has increased from year to year, as shown in Figure 1. According to the graph, there were 222 published papers in 2010 and 1356 in 2020. There has been a 73.8 percent increase in nanocomposite membrane for fuel cell studies in the last ten years.

The importance of nanocomposite membranes in fuel cell applications has grown over time, as has the need to improve their properties and the availability of modern laboratory equipment that facilitates synthesis and fabrication methods. The fundamental problems in the commercialization of fuel cells are usually inefficient water and thermal management and high fuel crossover, which lead to poor cell

performance [1]–[7]. The fuel cell must achieve excellent performance and durability to efficiently use in electronic devices, electric vehicles, and other applications. The basic working principle of a fuel cell is based on an electrochemical reaction in which fed fuels such as methanol, hydrogen, oxygen, ethanol, and natural gas are oxidized and reduced to produce electricity, water, and heat byproducts [6], [8], [9].
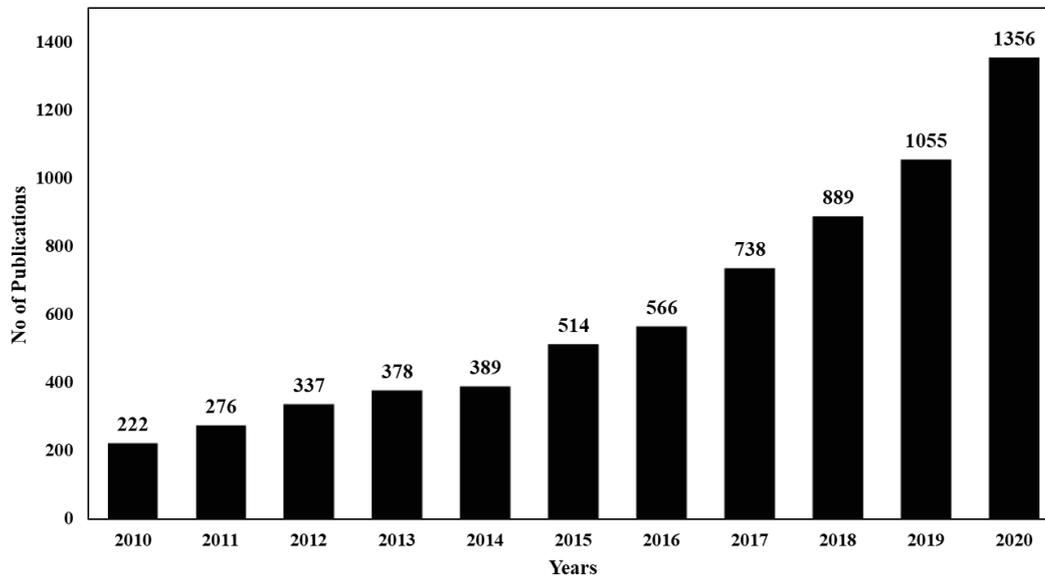

Figure 1 Publish paperwork on polymeric-based nanocomposite membranes for fuel cell applications from the year 2010 to 2020 based on the ScienceDirect website

As shown in Table 1, different types of fuel cells vary in terms of the electrolytes used and the operating conditions. Among the fuel cell types are polymer electrolyte membrane fuel cell (PEMFC), molten carbonate fuel cell (MCFC), alkaline fuel cell (AFC), solid oxide fuel cell (SOFC), and phosphoric acid fuel cell (PAFC). In contrast to other energy generation systems, the fuel cell produces about 40% more electrical energy, while turbine generators provide 30-40%, wind turbines produce 25%, and photovoltaics generate 6-20% of electrical energy [10]–[13]. Besides, the fuel cell offers clean byproducts, fuel flexibility, noise-free operation, off-grid applications, baseload, and modular design. These characteristics enable the fuel cell to be used for portable electronic devices, automotive, minor residential, and off-grid electricity generation in space, marine,

and modular construction. The fuel cell is composed of several parts, including membranes, anode, and cathode flow field plates, catalyst layers, and gas diffusion layer, which each of them serves a specific purpose in a fuel cell.

The membrane/electrolyte is the heart and critical component of a fuel cell responsible for transmitting the ionic charges of positive or negative ions depending on its carrier sites and acting as a separator in the fuel cell for separating cathode and anode reactants. The membrane used in the fuel cell is ion exchangeable and semi-permeable, with ionic head groups attached to polymer matrices that allow ion mobilization. The ion exchange membrane (IEM) is made up of hydrophobic substrates, immobilized ion-functionalized groups (fixed charge ion groups), and movable counter-ions (mobile ions) [5], [14], [15].

Table 1 Major types of fuel cell and their properties [16]

Fuel Cells	PEMFC	AFC	PAFC	MCFC	SOFC
Operating temperature (°C)	40-80	65-220	150-210	600-700	600-1000
Charge carrier	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}
Electrolyte	Hydrated polymeric ion exchange membrane	Potassium hydroxide in asbestos matrix	Liquid phosphoric silicon carbide	Liquid molten carbonate in $LiAlO_2$	Ion conducting ceramics (yttria-stabilized zirconia, gadolinia-doped ceria (GDC), lanthanum gallate
Electrodes	Carbon	Transition metals	Carbon	Nickel and nickel oxide	Perovskite, cermet (perovskite/fluorite and metal cermet)
Fuel	Hydrogen or methanol	Hydrogen or hydrazine	Hydrogen and alcohol	Hydrogen, hydrocarbons	Hydrogen, hydrocarbons
Oxidant	O_2/air	O_2/air	O_2/air	CO_2/O_2/air	O_2/air
Heat quality	-	Very low	Low	High	High
Power density (mW cm^{-2})	350	100-200	200	100	240
Anode reaction	$H_2 \rightarrow 2H^+ + 2e^-$	$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$	$2H_2 \rightarrow 4H^+ + 4e^-$	$H_2O + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$O^{2-} + H_2 \rightarrow H_2O + 2e^-$
Cathode reaction	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$O_2 + 4H^+ + 4e^1 \rightarrow H_2O$	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$
Schematic diagram					

This review is interested in describing the influence of modified polymeric-based electrolytes employed in PEMFC. The identification of either the IEM is proton exchange membrane (PEM) or anion exchange membrane (AEM) is recognized by their fixed charged ions group attached to the polymer backbone, as shown in Figure 2. The PEM is made up of a fixed negative charge ion that only allows positive ions to pass through while repelling negative ions. Meanwhile, the AEM emits negative ions while repelling positive ions. To ensure efficient cell operation in fuel cell applications, the IEM must meet the following criteria [14], [17].

a) Effective ions transfer from one electrode to the other to obtain a high ionic conductivity.

b) The membranes must act as barriers to fuel because their diffusion causes fuel cell to degrade and become less efficient and reduce cell performance.
c) Good water uptake, dimensional change, and mechanical strength are essential for good membrane durability to avoid excessive membrane swelling, loss of contact with electrodes, and performance degradation.
d) Sufficient thermal stability for operating at the desired cell working temperature to avoid membrane degradation.
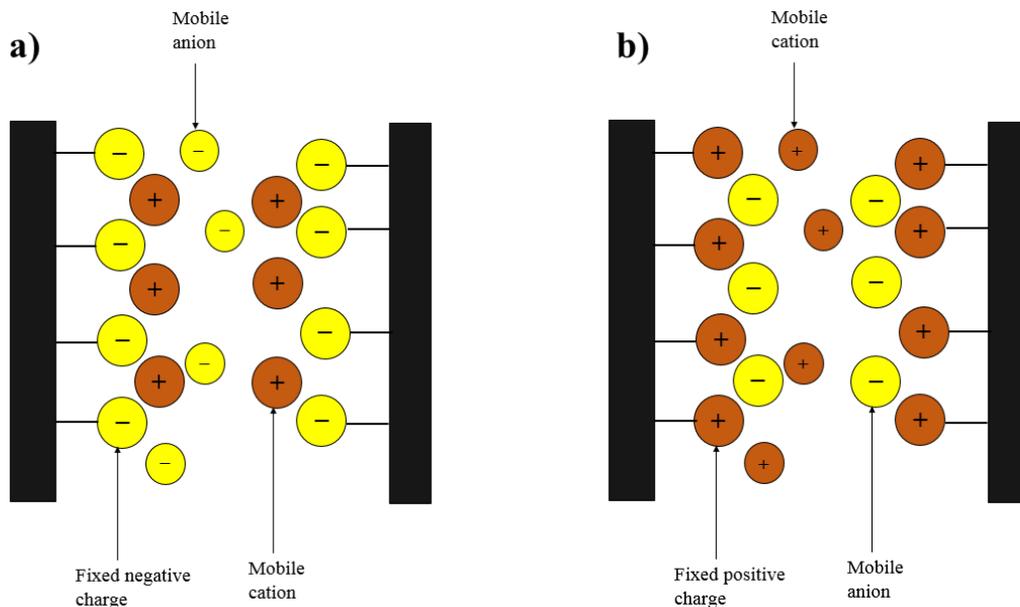e)

Figure 2 Ion exchange membrane: a) PEM electrolyte and b) AEM electrolyte

Polymer is the primary material used in the development of electrolytes for fuel cell applications. There are three main standard polymer classes: perfluorinated polymer, non-fluorinated polymer, and natural polymer. Natural polymers typically exhibit poor conductivity because these polymers contain fewer ionic sites and suffer low mechanical stability. Therefore, most researchers prefer to use perfluorinated polymer and non-fluorinated polymer for synthesizing and fabricating the membrane of fuel cells because of their excellent ionic conductivity and ease of modification [18]–[20]. However, these membranes continue to suffer from several issues, including high fuel crossover, which reduces cell lifetime and performance that is highly dependent on water content and inefficient at high operating temperatures (120 °C). Other than that, the perfluorinated Nafion membrane is expensive, which limits large-scale commercialization.

Meanwhile, the non-perfluorinated sulfonated-based membrane suffers from poor mechanical stability and low ionic conductivity [21]–[24]. Therefore, a modifier is introduced to address these issues. Several types of modifiers have been composited in a polymer-based membrane, such as hydrophobic polymer or nanofiller. A nanofiller or nanoparticle is a material with small particles ranging in size from 1 to 100 nm. This material is widely composited in polymeric-based materials to improve ionic conductivity, thermal stability, dimensional and mechanical stability, oxidative stability, suppresses water retention, and reduces fuel crossover [25]–[31]. The nanocomposite membrane is a polymer composited with nanoparticles. The factors that influence nanocomposite membrane properties are the type of incorporated nanoparticle, their shape, and size, as well as the composition and interactions with the polymer matrix.

The preparation of nanocomposite membranes involves two steps 1) fabrication of polymeric membranes based on non-fluorinated polymers such as poly(arylene ether sulfone) (PAES), poly(ether ether ketone) (PEEK), poly(benzimidazole) (PBI), polyetherimide (PEI), poly(ether sulfone) (PES), and poly(styrene) (PS), 2) preparation of composite membranes through the incorporation of nanoparticles. The purpose of this review is to highlight the advanced nanoparticles that are incorporated into polymer materials and their effects on physicochemical properties and performance. Unlike previous studies that have commonly discussed either one of the electrolytes, this review briefly focused on two of the PEMFC electrolytes, PEM and AEM, to provide a deeper view on the usage of nanoparticles in polymer membranes.

2.0 MATERIAL USED IN NANOCOMPOSITE MEMBRANE AND ITS SYNTHESIZING METHOD

As mentioned earlier, the nanocomposite membrane comprises pristine or modified polymer with inorganic nanoparticles in the membrane matrix. This section discussed the properties of the most common polymer used in nanocomposite membranes and the nanoparticles that are typically incorporated into those polymers. In addition, the method of preparing nanocomposite membranes is described here.

2.1 Type of Polymers used in Preparation of Fuel Cell Electrolytes

2.1.1 *Perfluorinated Polymer*

The most widely used perfluorinated polymer for PEM is Nafion, which Walther Gustav Grot developed for the first time in the late 1960s and commercialized by DuPont Company [32], [33]. Nafion is a random copolymer made up of perfluoro ether side chains terminated with sulfonic acid groups randomly distributed along the semi-crystalline polymer backbone (perfluoroethylene) [34]. Figure 3 depicts the basic chemical structure of the Nafion membrane.
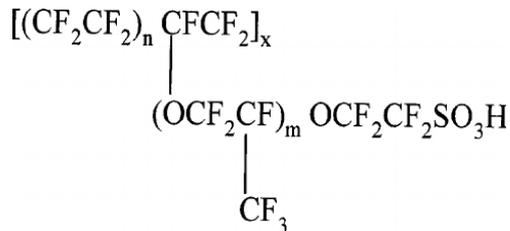
$$[(CF_2CF_2)_n \ CFCF_2]_x$$
$$(OCF_2CF)_m \ OCF_2CF_2SO_3H$$
$$CF_3$$

Figure 3 Chemical structure of Nafion membrane [35]

The commercial Nafion membranes are classified into four types: Nafion 115, Nafion 117, Nafion 211, and Nafion 212. Each of them is given a name based on the number assigned to it. These numbers represent polymer equivalent weights (EW) (first 2-digits) and membrane thickness in 1/1000 inch (mil), which corresponds to 25 μm (3rd digit, or 3rd and 4th digits) [36]. Thus, for example, the Nafion 117 has a thickness of 7 mils (0.012 cm) and a polymer EW of 1100. Polymer EW is a polymer ratio in grams per mole of the material's sulfonic acid groups in acid and dehydrated form [37].

The mechanical and transport properties of the Nafion membrane are strongly affected by the EW of the polymer. This implies that an increase in EW provides a corresponding decrease in sulfonation degree that will significantly improve the mechanical properties and reduce the proton conductivity. Therefore, the Nafion with 1100 g/mol (EW) is commonly preferred for fuel cell applications because of its reasonable balance of mechanical properties and proton conductivity [37]. However, the inability of the Nafion membrane to efficiently operate at temperatures above 120 °C and in low humidity conditions prompted the researcher to incorporate nanoparticles to address the shortcomings mentioned above. Figure 4 depicts various commercial perfluorinated membranes produced by multiple companies.
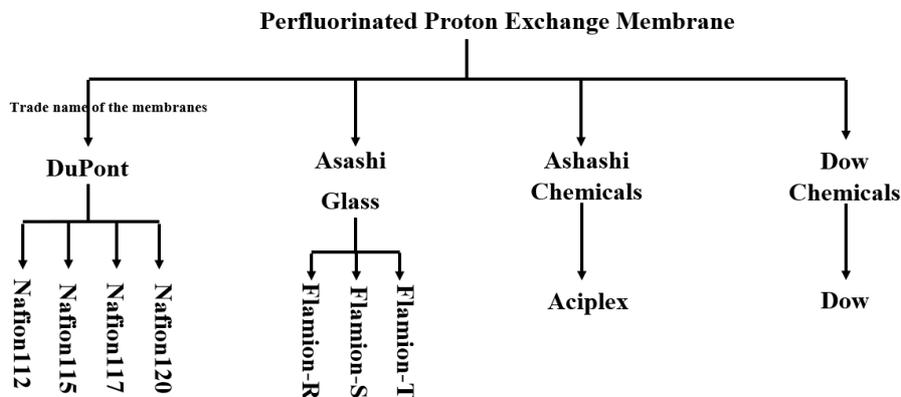

Figure 4 Commercial PEM electrolytes

For AEM-based electrolytes, the Fumatech FAA3 membrane was commonly used. The FAA3 membrane is made from a non-supported or PEEK- or PP-reinforced membrane with many different thicknesses. This membrane is known for having the lowest price compared to other companies and being the most suitable for fuel cell applications. In general, FAA3 is a polyaromatic polymer with ether bonds in the main chain (backbone) and quaternary ammonium groups (functional group) attached to the backbone, giving it alkaline properties that make it suitable for employ in the solid alkaline fuel cell (SAFC). The old FAA3 membrane from 2011 was upgraded to have a slightly crosslinked membrane to improve mechanical stability, and a small amount of trimethylamine was added to prevent gelation. Figure 5 depicts the various types of perfluorinated membrane for AEM produced by various companies (Fumatech: FAA3, Fumapem FAA3; Tokuyama: A201, A901; Ionomer: AF1-HNN, AEMION, Dioxide materials: Sustainion, Orion polymer: TPNI-100).
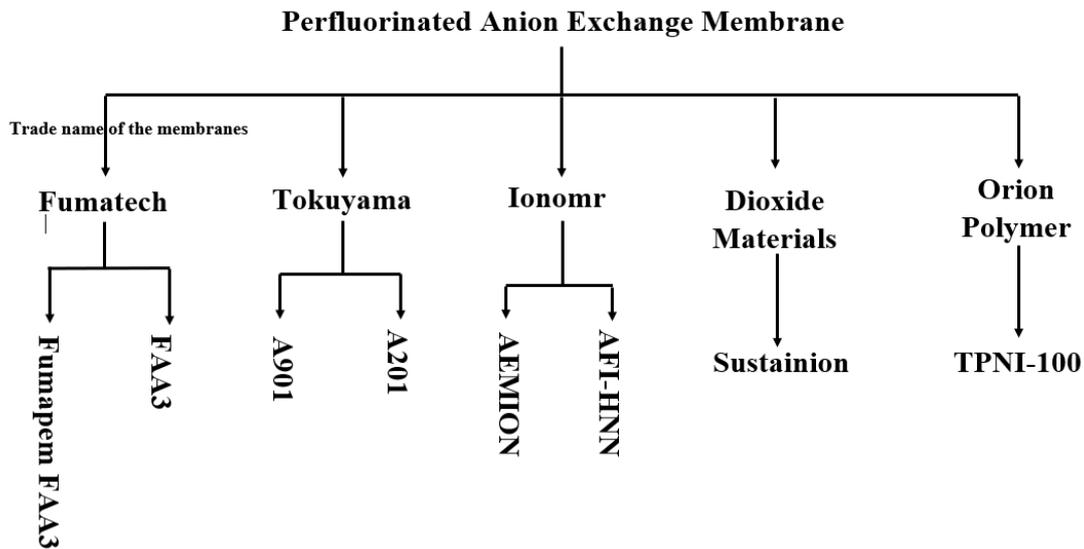
Perfluorinated Anion Exchange Membrane

Trade name of the membranes

Fumatech	Tokuyama	Ionomr	Dioxide Materials	Orion Polymer
Fumapem FAA3 / FAA3	A901 / A201	AEMION / AFL-HNN	Sustainion	TPNI-100

Figure 5 Commercial AEM electrolytes

2.1.2 *Hydrocarbon Polymer*

It is required to modify pristine polymer matrices, such as polyethersulfone (PES), polyetheretherketone (PEEK), polyetherimide (PEI), polyvinylidene fluoride (PVDF), and polyaryletherketone (PAEK), to make it useful as an IEM for fuel cell applications. The pristine polymer is hydrophobic and does not have any charge (neutral). The attachment of an ionic head group to a polymer matrix changes its neutral nature from acidic to alkaline, depending on the type of ionic head group [19], [38]. The PEM electrolyte is typically composed of sulfonic acid, sulfonamides, carboxylic acid, and phosphoric acid groups as functional moieties. The AEM, on the other hand, is created by anchoring quaternary ammonium cations, guanidinium cations, and imidazole cations onto its polymer matrices [39]. Current state-of-the-art PEM and AEM materials are perfluorinated polymers with promising properties such as high ionic conductivity [40]. These membranes are costly and have several drawbacks.

According to research, hydrocarbon-based polymers and natural-based

polymers are more cost-effective and have comparable properties to perfluorinated-based polymers. As a result, the majority of nanocomposite membrane studies employ polymer-based hydrocarbon materials. However, most functional hydrocarbon membranes usually suffer from high swelling when operating at high temperature and hydration levels, contributing to poor membrane chemical and mechanical stability [41]–[44]. Therefore, the modification of hydrocarbon-based membranes is required to improve its ability to withstand various cell operating conditions.
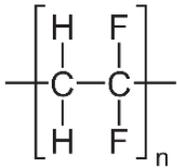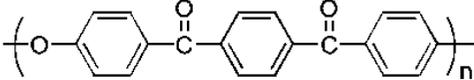
Table 2 summarises the properties of hydrocarbon-based polymers. From the table, it seems that each polymer had different structural, chemical, mechanical, and thermal stability properties. Therefore, the selection of hydrocarbon polymer for fabrication of PEMFC membrane should depend on desired operating cell conditions. For example, polybenzimidazole (PBI) and PEI are widely used for cells that operate above 100 °C [45]–[49]. This is because of their high melting point and glass transition temperature (T_g) that can withstand high operating conditions. Besides, their mechanical
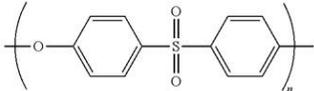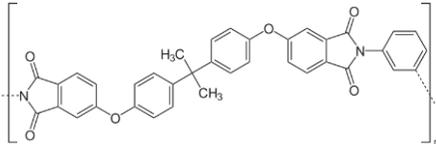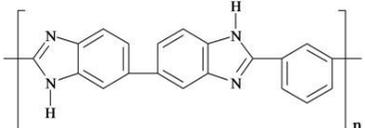
strength is also suitable as electrolytes for high-temperature PEMFC. However, the PBI and PEI based membranes obtained poor conductivity, which led to low cell performance [50], [51]. Thus, advanced modifications are required to enhance its conductivity and the PEMFC performance.

Meanwhile, the PEEK and PES are commonly used as the main membrane matrix for PEMFC operating at < 100 °C. However, most studies found that the maximum operating temperature for membrane-based PEEK and PES polymer is around 90 °C [42], [52]–[54]. When above this temperature, the membrane started to dehydrate, which caused degradation of cell performance. Thus, these membranes should be applied in the mentioned range to avoid membrane damage.

Polyvinylidene fluoride (PVDF) is another polymer had been used in PEMFC applications. The PVDF-based membrane should be operated at low operation conditions because of its low melting point, T_g, and mechanical strength [22], [55]–[57]. However, advanced modifications on these polymers-based membranes can improve their properties.

Table 2 Hydrocarbon polymers that are commonly used in the development of nanocomposite membranes

Polymer and its chemical structure	Properties	Remarks	References
PVDF	• Semi-crystalline thermoplastic • High purity thermoplastic fluoropolymer • Exceptional chemical resistance • Promising mechanical strength • Obtain pyroelectric and piezoelectric properties • Ease processing • Specific gravity: 1.75-1.80 g/cm^3 • Glass transition temperature: -35 °C • Melting point: 154-184 °C • Tensile strength at 23 °C: 36-56 MPa	Suitable as electrolytes for low temperature (> 40 °C) operating condition of fuel cell and operation does not involve temperatures variation.	[55]–[58]
PEEK	• Semi-crystalline thermoplastic • Excellent mechanical and chemical resistance • High-temperature resistance • Good dimensional stability • Specific gravity: 1.32 g/cm^3 • Glass transition temperature: 143 °C • Melting point: 322-346 °C • Tensile strength at 23 °C: 90-100 MPa	Suitable as electrolytes for fuel cell operate at < 100 °C	[42], [52]–[54]

Polymer and its chemical structure	Properties	Remarks	References
PES	• Amorphous and transparent thermoplastic • Good mechanical behavior • Good electrical properties and chemical resistance • High dimensional stability • Specific gravity: 1.37 g/cm^3 • Glass transition temperature: 225 °C • Melting point: 230 °C • Tensile strength at 23 °C: 95.2 MPa	Suitable as electrolytes for fuel cell operate at < 100 °C	[30], [59]–[62]
PEI	• Amorphous and semi-crystalline thermoplastic • High rigidity and strength at high temperatures • Better dimensional stability, heat resistance, and good electrical properties • Good chemical resistance and ductile properties • Good processability • Specific gravity: 1.27 g/cm^3 • Glass transition temperature: 217 °C • Melting point: 354-399 °C • Tensile strength at 23 °C: 85 MPa	Suitable as electrolytes for high temperature (> 100 °C) fuel cell operating conditions.	[49], [63], [64]
PBI	• The best heat resistance and mechanical retention • High compressive and dimensional stability • Excellent electrical insulator • High water absorption • Specific gravity: 1.3 g/cm^3 • Glass transition temperature: 430 °C • Melting point: > 600 °C • Tensile strength at 23 °C: 158.58 MPa	Suitable as electrolytes for high temperature (> 100 °C) fuel cell operating condition.	[46], [65]–[68]

2.2 Type of Nanoparticles use in Preparation of Fuel Cell Electrolytes

In the last few decades, researchers have paid close attention to incorporating nanoparticles into organic polymer membranes (organic-inorganic hybrid membranes or nanocomposite membranes) [69]. This is due to the improved ionic conductivity and membrane stability of such nanocomposite membranes. In addition, it also lowers cost, improves water retention property, and decreases fuel permeation by increasing the meandering of the transport pathway. Furthermore, improvements in the properties of nanocomposite membranes are due to an increase in suspension viscosity and the strong interaction between nanoparticles and polymers [69]–[71]. Inorganic nanoparticles are classified into two types: solid nonporous filler and solid porous filler. Silica (SiO_2) and titanium dioxide are examples of solid nonporous fillers (TiO_2). The solid porous fillers are the zeolites, porous metal oxides, and carbon nanotubes (CNT) [72]–[75]. Table 3 summarises the properties of these inorganic nanoparticles.

Table 3 Common nanoparticle incorporate in polymer matrix for the development of nanocomposite membranes

Nanoparticles	Properties	Remarks	Ref
Silicon dioxide (SiO_2)	• Transparent solid (Amorphous) white/whitish-yellow (powder/sand) • It is easily deposited on various materials • It can be used as a blocking material for ion diffusion of many unwanted impurities • It has high dielectric strength and a relatively wide bandgap, making it an excellent insulator • It has high-temperature stability of up to 1600 °C, making it a useful material for process	• The addition of SiO_2 to polymeric-based membranes had enhanced the water retention and thermal stability characteristics of the membrane at higher temperatures (100 °C). • Enhancement of crystallinity, mechanical strength and cell performance. • Decrement of water uptake capacity, swelling degree, and fuel crossover. • Aggregation between materials occurs at particular SiO_2 contents, leading to a decrement of conductivity and cell performance.	[74], [76], [77]
Titanium dioxide (TiO_2)	• Exists in the form of a white solid inorganic substance • Thermally stable • Non-flammable • Highly resistant to corrosion • Not classified as hazardous substances	• The addition of TiO_2 to polymeric-based membrane enhance thermal stability and reduced water uptake than pristine membrane. • Accelerated decomposition of the membrane at earlier thermogravimetric analysis • Decrement of swelling degree and fuel crossover. • Exhibit higher ionic conductivity and performance	[74], [78]–[80]

Nanoparticles	Properties	Remarks	Ref
		• than a pristine polymer membrane • Aggregation between materials occurs at particular TiO_2 contents, leading to a decrement of conductivity and cell performance.	
Zeolites	• Microporous and aluminosilicate minerals • Durable and resistant to a wide range of environmental conditions • Thermally stable • Resist high pressures • Do not dissolve in water or other inorganic solvents	• Adding zeolites to the polymeric membrane decreases the fuel crossover and good ions pathway. • Higher performance than commercial perfluorinated membrane. • Zeolites-based membrane obtains low tensile strength, which affects cell durability.	[81]– [83]
Graphene oxide (GO)	• Atomically-thin • 2D sheet in a honeycomb structure • High mechanical strength • Electrical conductivity • Molecular barrier abilities	• The addition of GO to the polymeric membrane facilitates ions transport and good water uptake due to its high surface area. • Decrement in fuel crossover. • High mechanical and thermal stability. • Excellent compatibility with almost polymer for membrane fabrication. • Proton conductivity decrease with increasing GO contents.	[84]– [88]
Carbon nanotubes (CNT)	• Tubes made of carbon with diameters typically measured in nanometres • Superior surface area and electrical conductivity • Lighter weight • Perfect hexagonal formation • Promising mechanical, electrical, and chemical features	• The addition of CNT to the polymeric membrane reduces water uptake, swelling degree, and fuel crossover. • Improve mechanical strength, thermal stability, chemical stability, and proton conductivity than pristine polymer membrane.	[44], [89], [90]

3.0 FABRICATION METHODS OF NANOCOMPOSITE MEMBRANES

Many methods have been used to incorporate nanoparticles into a polymer matrix, including the sol-gel method, blending method, and infiltration method (also known as in situ method) [91], [92]. The wide range of approaches and promising outcomes

of these three fabrication methods have piqued the interest of researchers.

3.1 Blending Method

The blending process is the easiest and involves combining nanoparticles directly into a hydrocarbon polymer matrix (Figure 6). This method can be accomplished using either solution or melt blending. However, the main disadvantage of this approach is that the agglomeration of nanoparticles in the polymer matrix causes the polymer to have incompatible properties. Modifying the surface of the particle to increase the degree of compatibility between membrane materials is one approach for overcoming these issues.
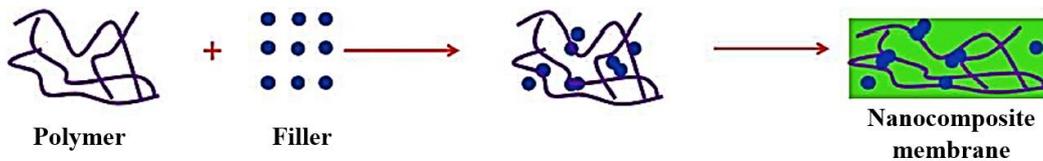

Figure 6 Physical blending method

3.2 Sol-gel Method

The sol-gel method for fabricating nanocomposite membranes was developed in the 1980s (Figure 7). This process involves the hydrolysis and condensation reactions of metal alkoxides, MAn (MA = Ti, Si, VO, Zr, Al, Zn, Ce, Sn, Mo, W, etc., and Y = Me, Et,...) inside a polymer dissolved in aqueous or non-aqueous solutions at low temperatures. The reactions of using this method are described by equations 1 and 2 [84].

$$MA_4 + 4H_2O \rightarrow MA_4 + 4ROH \qquad (1)$$

$$mM(OH)_4 + (MO_2)m \rightarrow 2mH_2O \quad (2)$$
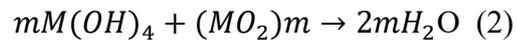
The silicon alkoxides are unaffected by gelation and hydrolysis, which took several days in the presence of water for a reaction to take place. Thus, non-silicate metal alkoxides are conducted without catalysts, whereas silicon alkoxides require acid or base catalysts. Temperature, the form of solvent, tape catalyst, and the molar ratio of water and silane are all factors that affect the kinetic activities and the final properties and structure of the component [93].
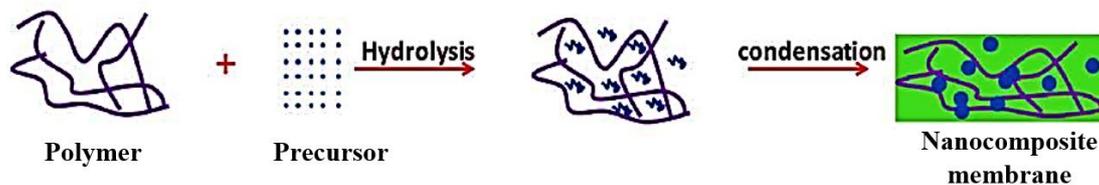
Figure 7 Sol-gel method

3.3 Infiltration Method

Infiltration involves infiltrating precursors of inorganic nanoparticles into a swollen or hydrogel-like polymer matrix to increase the gap or pore volume prior to infiltration. The mixed matrix is then subjected to filler growth, impurity removal, and polymer curing. Through this method, the undesirable agglomeration of nanoparticles can be hindered by controlling the filler size and distributing uniformly into the polymer matrix because of the isolation effect of the polymer network (Figure 8).

Figure 8 Infiltration method

4.0 DIFFERENT TYPES OF NANOCOMPOSITE MEMBRANES

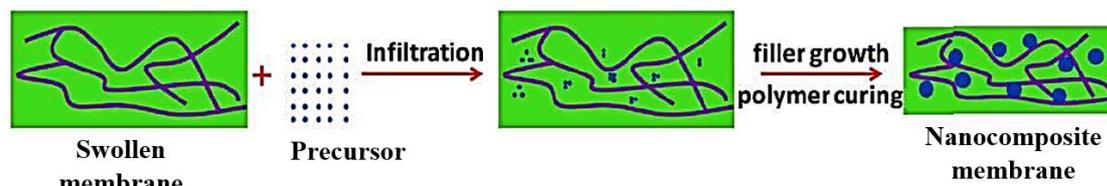In contrast to commercial perfluorinated membranes, much effort has gone into developing nanocomposite membranes based on a deeper understanding of morphology, polymer degradation, transport behavior, and molecular level chemistry. The most recent advancements have focused on introducing new ionomers and hybrid membranes made up of nanoparticles to control properties such as morphology, mechanical and thermal stability, and transport behavior by varying the fabrication approach and molecular design. The following section discussed the most recent fabrication of nanocomposite PEM and AEM based on five years of publications.

4.1 Perfluorinated Nanocomposite Proton Exchange Membrane

Commercial Nafion membranes are the most commonly used electrolyte in PEMFC and DMFC applications. However, its performance is limited when operating at anhydrous and higher temperatures. Thus, the researchers proposed modifying the Nafion membrane by incorporating nanoparticles such as porous silicon aluminium oxide, graphene oxide, titanium dioxide, zirconium oxide, and others to improve its properties. Table 4 summarised the performance of the Nafion-based nanocomposite membrane. The DMFC is a type of fuel

cell that uses methanol and oxygen gases as fuel. The main disadvantage of this fuel cell is its high methanol permeability, which contributes to Pt electrode poisoning and reduces the electrochemical effectiveness of the membrane electrode assembly (MEA). The incorporation of most nanoparticles in Nafion solved the methanol permeability problem, but it decreased proton conductivity, which reduced the DMFC power output. Cui *et al.*, 2018 [86] recently proposed incorporating amorphous porous silicon aluminium oxide (PSAO) particles into Nafion D520 solutions. The Na^+ cations of Na^-_X zeolites with submicron sizes 200–300 nm were replaced with NH_4^+ cations, and the NH_4-X zeolites were thermally converted into PSAO. The PSAO is made up of zeolite cage structures with hydrophilic properties such as –SiOH and –SiOSO$_3$H groups.

They claim that the Nafion/PSAO nanocomposite membrane had higher proton conductivity and power density, but lower methanol permeability than pristine Nafion membranes. The synergistic effect of Nafion, –Si-OH, and –Si–O–SO$_3$H groups and the skeleton framework of the activated nanoparticle could explain the increased proton conductivity by nanocomposite membrane. Meanwhile, the increased methanol permeability was due to the compact matrix membrane structure, the tortuous pathways in the membrane clusters network, and the interaction between methanol and the skeleton framework of the PSAO nanoparticle (Figure 9). The best PSAO loading content in

Nafion was 3.75 wt%, resulting in a peak power density of 217 mW cm^{-2} at 80 °C, which was more than four times higher than pristine Nafion membranes.
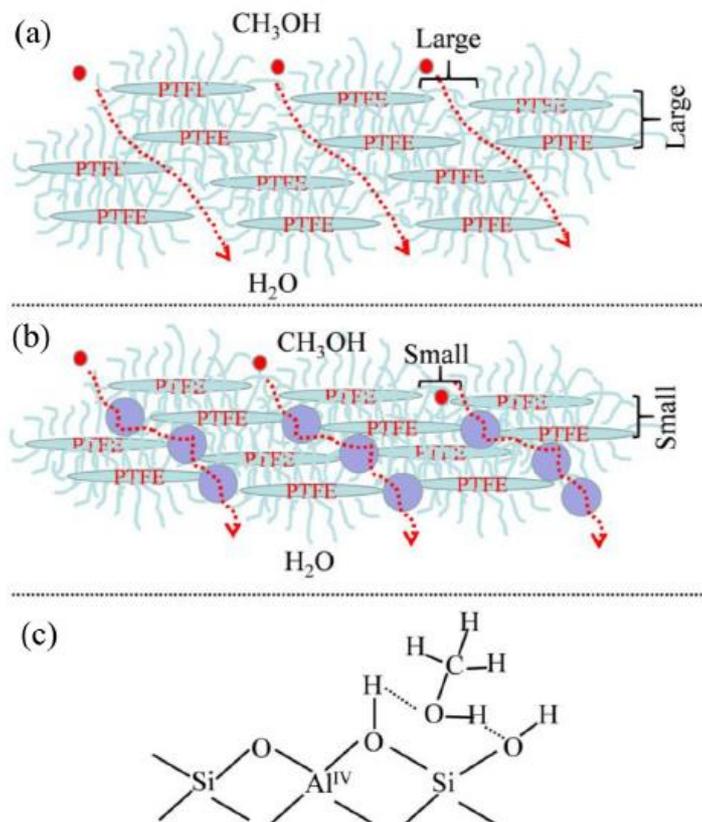

Figure 9 Illustration of methanol permeation by PSAO: (a) methanol permeation in pristine Nafion; (b) methanol permeation in nanocomposite Nafion/PSAO membrane; and (c) the interaction between methanol and PSAO [94]

Table 4 Summary of perfluorinated based nanocomposite PEM properties

Polymer	Modifier	Type of fuel cell	Conductivity or resistance	Power density	Remarks	Ref.
Nafion D520 solution	Porous silicon aluminum oxide (PSAO)	DMFC	30.8 mS cm^{-1}	217 mW cm^{-2} at 80 °C	• PSAO can effectively enhance proton conductivity and restrain methanol penetration. • Highest selectivity was achieved for the membranes with 3.75 wt% PSAO • The peak power density is more than 4 times than that of pure Nafion at 80 °C.	[94]
Nafion 117	Graphene oxide (GO) grafting on the surface of mordenite	DMFC	86.45 mS cm^{-1} at 70 °C	27.5 mW cm^{-2} at 70 °C	• The water uptake, methanol uptake, IEC, methanol permeability, and proton conductivity of all composites membrane was better than that of recast Nafion membrane. • Power density of about 4-fold higher than that of Nafion 117 was obtained.	[95]
Nafion 117	Zirconium Phosphate (ZrP)	DMFC	0.013 S cm^{-1} at 30 °C	209.71 mW cm^{-2}	• Nafion/ZrP nanocomposite membrane obtained low methanol permeability and good proton conductivity, water uptake, ion exchange capacity (IEC), and linear expansion compared to Nafion 117. • The Nafion/5% ZrP membranes exhibited a higher power density than commercial Nafion 117 membranes (126.04 mW cm^{-2}). • However, the proton conductivity of the Nafion/ZrP membrane is lower than Nafion 117 membrane.	[26]
Nafion ionomer dispersion (D1021)	Graphene oxide	PEMFC	Not reported	0.55 W cm^{-2} at 100 °C	• Nafion/GO obtained higher swelling and water uptake and better tensile strength but lower IEC than Nafion.	[96]

Polymer	Modifier	Type of fuel cell	Conductivity or resistance	Power density	Remarks	Ref.
					• Nafion/GO membranes exhibited up to 20% increase in the maximum power density at high temperatures (100 °C).	
Nafion 211	Prism patterned titanium dioxide (TiO_2)	PEMFC	$0.1278 \ \Omega \ cm^2$ at 80 °C	$743 \ mW \ cm^{-2}$ at 80 °C	• The Nafion/prism patterned TiO_2 composite membrane has more proton pathways by enlarging the interfacial surface area between the composite membrane and the catalyst layer and offset the reduced proton conductivity due to the insertion of the inorganic fillers. • The Nafion/prism patterned TiO_2 membrane obtained highly improved performance than the pristine Nafion 211 membrane under elevated temperature and low humidity conditions.	[97]
Nafion 212	Cerium oxide nanotubes (CeNT)	PEMFC	$100 \ mS \ cm^{-1}$ at 80 °C	$902 \ mW \ cm^{-2}$ at 80 °C	• The Nafion-CeNT composite membrane obtained excellent water retention, facile water diffusion, and extremely durable membrane led from efficient free radical scavenging capability. • The Nafion-CeNT composite membrane generates a 1.1 times higher power density than that of Nafion 212.	[98]
Nafion 117	Graphene oxide and dihydrogen phosphate functionalized ionic liquid (GO/IL)	PEMFC	$0.06 \ S \ cm^{-1}$ at 95 °C	$0.02 \ W \ cm^{-2}$ at 110 °C	• The composite membrane achieves 1.3 times higher than of Nafion 117 membrane. • The Nafion/GO/IL membrane produces the best power density, which is 13 times higher than that of the Nafion 117 membrane.	[84]
Nafion 212	Sulfonated silica (SSA)	PEMFC	$230.1 \ mS \ cm^{-1}$ at 80 °C	$454 \ mW \ cm^{-2}$ at 80 °C	• The Nafion/SSA composite membrane produces excellent water uptake, thermal	[99]

Polymer	Modifier	Type of fuel cell	Conductivity or resistance	Power density	Remarks	Ref.
					stability, IEC, and proton conductivity than that Nafion 212 membrane. • The composite membrane showed 2.8 times higher current density and power density than Nafion 212 membrane.	
Nafion dispersion D2020	Graphene oxide (GO)	PEMFC	82.3 mS cm^{-1} at 95 °C	886 mW cm^{-2} at 65 °C	• The nanohybrid of Nafion/GO showed 1.6 folds of proton conductivity and a 35-40% increase in cell performance than Nafion membrane.	[100]
Nafion	Sulfonic acid functionalized multiwalled carbon nanotubes (sMWCNT)	PEMFC	0.023 S cm^{-1}	549 mW cm^{-2} at 60 °C	• The Nafion/sMWCNT membrane positively impacts proton conduction and water diffusion under low relative humidity conditions. • The Nafion/sMWCNT membrane obtained higher power density and current density than that Nafion membrane.	[101]
Nafion 212	In-situ sulfonated silica targeted (s-WR)	PEMFC	0.263 S cm^{-1} at 80 °C	140 mW cm^{-2} at 110 °C	• The Nafion/s-WR membrane showed excellent mechanical, oxidative, and thermal stabilities. • The Nafion/s-WR membrane obtained double proton conductivity and was 65% higher than the Nafion membrane.	[102]
Nafion 212	Silica/phosphotungstic acid (Si/PWA)	PEMFC	0.58 S cm^{-1} at 80 °C	116 mW cm^{-2} at 110 °C	• The Nafion/Si/PWA membrane achieves good mechanical and thermal stability. • The Nafion/Si/PWA membrane obtained 2.4 folds proton conductivity and 41% cell performance higher than Nafion membrane.	[103]

Jang *et al.* [88] developed a novel method for incorporating TiO$_2$ nanoparticles into Nafion ionomer to prevent material agglomeration. In general, Nafion-based nanocomposite membranes prepared using traditional methods (i.e., direct blending) have issued such as a tradeoff between increasing water retention and decreasing the number of proton pathways and particle agglomeration during solvent evaporation.

These agglomerate particles reduced the active surface area for water retention and severely obstructed the proton pathway. The electrospinning method, which creates a foam-like inorganic nanofibrous web, is one of the novel methods for preventing agglomeration. Although the electrospinning method yields promising PEMFC performance and durability even at high temperatures and low relative humidity, it is a time-consuming and challenging process. Thus, Jang and colleagues proposed a simple and straightforward method for developing Nafion/TiO$_2$ membranes using spin-coating and thermal imprinting (Figure 10).
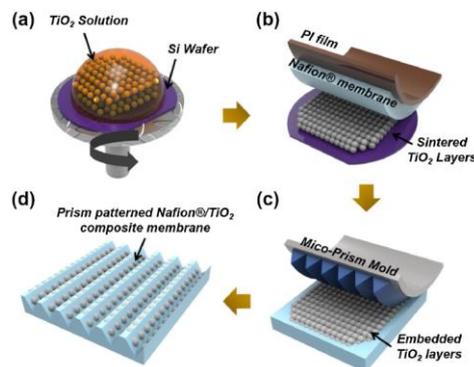

Figure 10 Illustration of preparation prism pattern Nafion/TiO$_2$ nanocomposite membrane (a) Incorporating TiO$_2$ layers on Si wafer through the spin-coating process, (b) transfer the TiO$_2$ layers from Si wafer into Nafion membrane using thermal imprinting process, (c) fabricate prism pattern Nafion/TiO$_2$ membrane via hot-embossing process, and d) produced nanocomposite membrane [97]

As a result, a uniform distribution of TiO$_2$ in the Nafion matrix was obtained, effectively alleviating membrane dehydration at the membrane's forefront. Furthermore, an additional micro-prism patterning process is carried out to improve the proton pathways by increasing the interfacial surface area between the nanocomposite membrane layers and the catalyst layers and widening the gap between the pre-adding nanoparticles. According to them, their novel method has advantages in compatibility, reproducibility, and large-area fabrication. It was discovered that the prism pattern Nafion/TiO$_2$ membrane exhibits 743 mW cm^{-2} at 80 °C, which is greater than the power density of 659 mW cm^{-2} for operating conditions of 80 °C and 100 % relative humidity for Nafion/TiO$_2$ prepared using the traditional approach.

4.2 Hydrocarbon Nanocomposite Proton Exchange membrane

Polybenzimidazole (PBI) is the most studied material as a polymeric membrane in high-temperature PEMFC because of its excellent mechanical, chemical, and thermal stability. Furthermore, the PBI-based membrane is less dependent on water content to

exhibit high power output, making it ideal for use at high operating temperature and low relative humidity. The PBI can operate at temperatures of up to 3% of carbon dioxide and withstand temperatures of up to 185 °C.

In general, the pristine PBI achieves a proton conductivity of 10^{-9} mS/cm, but a modification is needed to improve ionic mobility. Phosphoric acid, sulfuric acid, hydrochloric acid, nitric acid, and perchloric acid are used to prepare acidified PBI membrane. Among these acids, phosphoric acid is the most preferred because it has high thermal stability, a high boiling point, and a high proton conductivity even in its dry form. The proton conductivity of PBI acidified with phosphoric acid is affected by temperature, humidity, and doping level. Even now, increasing proton conductivity remains a challenge to achieve the commercialization of high-temperature PEMFC.

Similar to other polymeric-based membranes, the incorporation of nanoparticles in PBI produces favorable results due to their affinity for intact with water and acid, resulting in a more absorbent and hydrophilic to water membrane. Furthermore, proton conductivity and mechanical strength have improved. Barium Zirconate ($BaZrO_3$) is one of the promising nanoparticles for PBI composites [104]. $BaZrO_3$ has a simple cubic perovskite structure, high chemical stability, and excellent mechanical and structural temperature resistance. In addition, $BaZrO_3$ is one of the best proton conductors with a perovskite structure and low activation energies for ion mobility. The well-balanced geometrical arrangement of basic atoms and their valances could explain why $BaZrO_3$ has a stable structure.

According to Hooshyari *et al.*, [96], among the benefits of incorporating $BaZrO_3$ in PBI are improved phosphoric acid trapping ability, high coordination numbers, low activation enthalpy of proton movement, high lattice constant, specific oxygen site, high conductivity, and high power density at high temperature. Phosphoric acid interacts strongly with relative humidity at high temperatures, which contributes to increased power output. The PBI/$BaZrO_3$ exhibit 125 mS cm^{-1} of proton conductivity and 650 mW cm^{-2} for power density at 180 °C and 5% relative humidity. Table 5 shows the other hydrocarbon-based nanocomposite membranes developed in previous studies.

Table 5 Summary of hydrocarbon-based nanocomposite PEM properties

Polymer	Modifier	Type of fuel cell	Conductivity or resistance	Power density	Remarks	Ref.
Sulfonated poly(ether ether ketone) (sPEEK)	Tin oxide (SnO_2) nanocubes/sulfonated bentonite (sBH)	DMFC	92.01 mS cm^{-1} at 80 °C	118 mW cm^{-2} at 80 °C	• The sPEEK/SnO$_2$/sBH membrane has improved thermal stability, water retention properties, and ionic conductivity. • The sPEEK/SnO$_2$/sBH membrane obtained low methanol permeability and high power density with excellent durability than that pristine sPEEK membrane.	[105]
Sulfonated poly(ether ether ketone) (sPEEK), sulfonated poly(vinilidinfluoride-co-hexaflourpropylen) (sPVDF-co-HFP)	Lanthanum chromite ($LaCrO_3$)	DMFC	75.3 mS cm^{-1} at 20 °C	61.5 mW cm^{-2} at 30 °C	• The sPEEK/sPVDF-co-HFP/LaCrO$_3$ membrane showed desirable proton conductivity, good thermal and mechanical stability, outstanding water and methanol retention, and oxidative stability. • The sPEEK/sPVDF-co-HFP/LaCrO$_3$ membrane obtained a better power density than pristine sPEEK and commercial Nafion membranes.	[106]
Sulfonated poly(phthalazinone ether ketone)/sulfonated poly(vinylidene fluoride-co-hexafluoropropylene) (sPPEK/sPVDF-co-HFP)	Sulfonated tungsten trioxide	DMFC	0.071 S cm^{-1} at room temperature	63.60 mW cm^{-2} at room temperature	• The sPPEK/sPVDF-co-HFP membrane obtained improves thermal and mechanical stability. • The composites membrane showed higher proton conductivity, power density, and excellent selectivity than that pristine Nafion and sPPEK-based membranes.	[107]

Polymer	Modifier	Type of fuel cell	Conductivity or resistance	Power density	Remarks	Ref.
Sulfonated polysulfone (sPSU)	Metal-organic framework and silica (MOF/Si)	PEMFC	17 mS cm^{-1} at 70 °C	40.8 mW cm^{-2} at 80 °C	• The composites membrane showed significantly improved proton conductivity, thermal and mechanical properties. • Good power density for PEMFC application.	[108]
Sulfonated poly(ether ether ketone) (sPEEK)	Phosphosilicate gel	PEMFC	0.017 S cm^{-1} at 70 °C	0.17 W cm^{-2}	• The performance of composite membrane enhances 1.83% from 50 °C to 70 °C operation temperature, improving water uptake and IEC.	[109]
Poly(arylene ether sulfone) (PAES)	Tin(IV) oxide (SnO$_2$)	PEMFC	1.49×10^{-3} S cm^{-1} at 100 °C	Not reported	• The PAES/SnO$_2$ composite membrane showed excellent oxidative stability with 12.3% degradation after undergoing the Fenton reagent test. • The composite membrane also exhibit promising proton conductivity and higher than bare membrane 0.3 mS/cm at 100 °C.	[110]
Polybenzimidazole (PBI)	Barium zirconate (BaZrO$_3$)	PEMFC	125 mS cm^{-1} at 180 °C	0.56 W cm^{-2} at 180 °C	• The PBI/ BaZrO$_3$ composite membrane achieves higher water uptake, acid doping level, and proton conductivity than pristine PBI. • The power density and current density of composite membrane increase from 100 °C to 180 °C operation temperature.	[104]
Sulfonated poly(aryl ether sulfone) (sPAES)	Titanium dioxide/graphitic carbon nitride (TiO$_2$/g-C$_3$N$_4$)	PEMFC	325.3 mS cm^{-1} at 80 °C	525.6 mW cm^{-2} at 180 °C	• The sPAES/TiO$_2$/g-C$_3$N$_4$ composite membrane obtains improved proton conductivity, mechanical, and dimensional stability than that pristine sPAES.	[111]

Polymer	Modifier	Type of fuel cell	Conductivity or resistance	Power density	Remarks	Ref.
					• The sPAES/TiO$_2$/g-C$_3$N$_4$-1.0 composite membrane exhibits high power density and excellent stability than others.	
Sulfonated poly(ether ether ketone) (sPEEK)	Sulfonated polyhedral oligomeric silsesquioxane (POSS-SA)	PEMFC	0.097 S cm^{-1} at 80 °C	0.65 mW cm^{-2} at 80 °C	• The composite membrane obtained higher mechanical stability, proton conductivity, and current density than that pristine sPEEK.	[112]
Sulfonated poly(ether ether ketone) (sPEEK)	Ceria	PEMFC	33 mS cm^{-1} at 80 °C	683 mW cm^{-2} at 80 °C	• The sPEEK/ceria membrane showed higher durability under an accelerated stress test, higher cell performance, and lower gas crossover. • The sPEEK/ceria membrane also obtained improved physical, thermal, and chemical properties than the pristine sPEEK membrane.	[113]
Sulfonated poly(ether ether ketone) (sPEEK)	Sulfated metal oxides (sMO)	PEMFC	37.5 mS cm^{-1} at 120 °C	500 mW cm^{-2} at 120 °C	• The sPEEK/sMO membrane physiochemical characterization and cell performance improved than the pristine sPEEK.	[114]
Poly(vinylidene fluoride-co-hexafluoropropylene) (poly(VDF-co-α)	Thiol functionalized silica	PEMFC	13 mS cm^{-1} at room temperature	Not reported	• The composite membrane obtains comparable water uptake and proton conductivity with commercial Nafion 112 membrane.	[115]
Polybenzimidazole (PBI)	Montmorillonite clay	PEMFC	0.08 S cm^{-1} at 160 °C	Not reported	• The PBI/montmorillonite membrane obtained higher thermal stability and low swelling degree. But the composite membrane exhibit low proton conductivity than pristine PBI.	[116]

The most studied electrolyte in low-temperature PEMFC (40 – 80 °C) is a sulfonated poly(ether ether ketone) (sPEEK) based membrane. The degree of sulfonation has a significant impact on the performance of sPEEK-based membranes (DS). The DS denotes the amount of sulfonic acid group attached to the backbone of the PEEK. The greater the amount of DS, the higher the proton conductivity and power density, but the lower the mechanical strength. The incorporation of nanoparticles is one method for preserving the mechanical stability of high DS sPEEK. Sarirchi *et al.*, [113] used a sPEEK matrix to incorporate sulfated TiO_2 and ZrO_2-TiO_2. Compared to the pristine form, the sulfated form of titania has a higher surface area, increased acidity, and a slower transformation from amorphous to the crystalline state, which is essential for doping sulphate ions.

They also have good acid-base properties and thermomechanical stability. Sulfated TiO_2 is a conductive nanoparticle with high thermomechanical properties of the polymer, whereas sulfated ZrO_2-TiO_2 is a binary metal oxide with superior properties to single oxide. These nanoparticles were developed using the sol-gel method, and the membrane was created using a solution casting technique.

Figure 11 showed the dispersion of TiO_2 and ZrO_2 in the sPEEK matrix where the cross-sectional images (c) and (d) of nanocomposite membranes had layered, relatively firm, flawless, and no phase separation was observed. Figure 10 depicted the dispersion of TiO_2 and ZrO_2 in the sPEEK matrix, with cross-sectional images (c) and (d) of nanocomposite membranes that were layered, relatively firm, flawless, and with no phase separation.
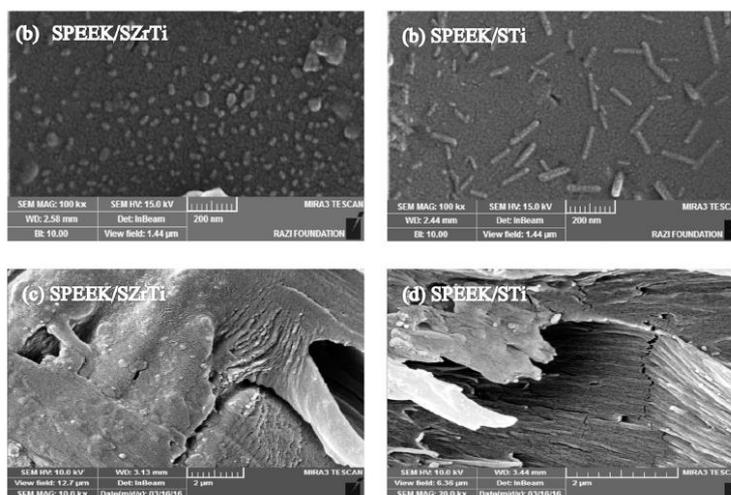

Figure 11 FESEM image of a sPEEK-based nanocomposite membrane [113]

Furthermore, the FESEM images revealed that these nanoparticles are compatible with the sPEEK matrix. This compatibility contributes to polar interaction between acid sites on the surface of sulfated TiO_2 and ZrO_2 and the –SO_3H groups on the sPEEK

matrix, which restricts nanoparticle mobility in the membrane during the development stage. The incorporation of sulfated TiO_2 and ZrO_2 increased the glass transition temperature, which is critical for operating at high temperatures, increased tensile strength

and elastic modules with low elongation at break, and improved power density of 500 mW cm^{-2} at 120 °C and 80 % relative humidity compared to pristine sPEEK membrane.

4.3 Nanocomposite Anion Exchange Membrane

The SAFC comprises a non-precious metal catalyst that allows for a fast oxygen reduction reaction in an alkaline medium while also achieving high energy efficiency. It also has good economics and good performance. The main issue with the SAFC is that the electrolyte, AEM, has a lower anion conductivity than PEM due to its more downward ion mobility, which contributes to anions being bulkier than protons. Aside from that, the functional groups in AEM electrolytes are easily degraded by hydroxide ion attacks, resulting in poor durability and mechanical stability. Thus, developing more advanced AEM electrolytes via block copolymers, chemical crosslinking, polymers with multication side chains, and inorganic nanocomposite membranes is the solution to this problem. As previously stated, various types of inorganic fillers have been introduced into AEM electrolytes to improve ionic mobility, mechanical stability, and durability under alkaline conditions.

Chu et al. [109] formed a random polymer composite of quaternized poly(arylene ether) (QPAE) and quaternary ammonium functionalized graphene oxide (Q-GO). The GO was chosen due to its excellent compatibility with polymers. In general, the GO surface is composed primarily of oxygen groups, which can improve the electrochemical performance of the membrane. Furthermore, the GO is usually distributed uniformly in the polymer matrix due to strong interfacial interactions between the polymer and the GO. It is well known that nanoparticle dispersion in the polymer matrix is related to performance degradation caused by aggregation due to high surface energies between nanomaterials. Thus, it is critical to choose a nanoparticle that can disperse uniformly in the polymer matrix. Aside from using pure GO, adding a functionalizing group to the nanoparticle can improve ionic conductivity, electrochemical performance, and chemical stability.

The efficient functionalization process promotes the formation of interfacial bonds between the GO sheet and the polymer chain, which improves dispersion. According to Chu et al. [109], the Q-GO contains amino silane units and is synthesized using (3-aminopropyl)triethoxysilane (APTS) and (3-bromopropyl)trimethyl ammonium bromide (PTMA) as the primary quaternization reagents. The results demonstrated that the - bonds between the QPAE and Q-GO improve the nanocomposite membrane's mechanical properties and dimensional stability. The nanocomposite membrane is containing 0.7wt.% Q-GO had the highest anion conductivity of 114.2 mS cm^{-1} at 90 °C and peak power density of 135.8 mW cm^{-2} at 70 °C. Figure 12 depicts the migration of ions between pristine and nanocomposite QPAE-based membranes.
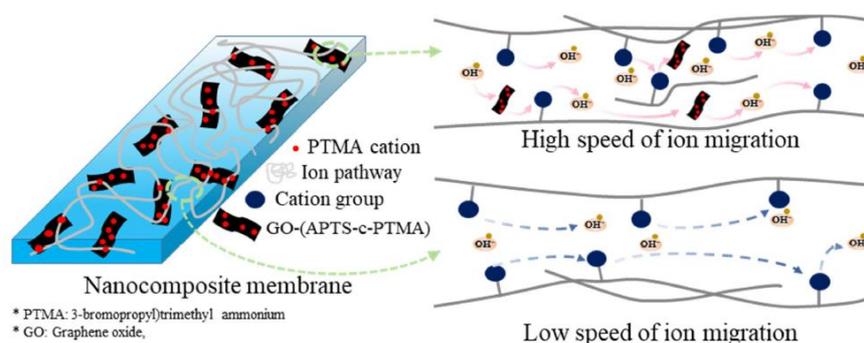
Figure 12 Comparison of ion migration between pristine QPAE and nanocomposite QPAE/Q-GO membranes [109]

Elumalai *et al*. [117] developed a nanocomposite membrane of quaternary ammonium functionalized polysulfone (QPSU) and quaternary ammonium functionalized TNT (QTNT) for SAFC applications. According to them, the PSU was chosen as the base polymer for AEM preparation due to its high mechanical and thermal stability and ease of modification, such as functionalization with Quaternary ammonium groups on its backbone. In this study, ammonium ions are preferred because they are the most stable compared to onium ions such as phosphonium and sulfonium ions. Their research uses TiO_2 as a nanoparticle that has been modified by converting it into 2-dimensional nanostructures of Titanate Nano Tubes (TNT) via the hydrothermal method and functionalized with a quaternary ammonium group (Figure 13). First, TNT has more advantages than TiO_2 because it has a larger surface area (200-300 $m^2 g^{-1}$) and a more significant number of functional groups on the surface. Second, the TNT has a hollow tube morphology that allows it to absorb and retain many water molecules. Quaternizing the TNT resulted in more ion-exchange sites for anion conduction, which improved the AEM's electrochemical performance. They claim that the QPSU/QTNT nanocomposite membrane significantly improved ion exchange capacity, anion conductivity, tensile strength, and water uptake. It was discovered that the QTNT with a 5wt% composition had the highest power density of 285 mW cm^{-2} at 60 °C with an OCV of 0.92 V.
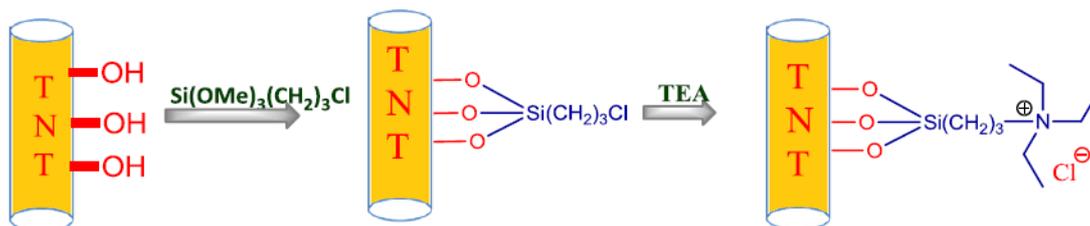

Figure 13 Schematic representation of Quaternary ammonium functionalized TNT [117]

Table 6 Summary of polymeric based nanocomposite AEM properties

Polymer	Modifier	Type of fuel cell	Conductivity or resistance	Power density	Remarks	Ref.
Quaternary aminated poly(arylene ether sulfone) (QPAES)	Titanium dioxide/graphitic carbon nitride (TiO$_2$/g-C$_3$N$_4$)	SAFC	43.8 mS cm^{-1} at 80 °C	64.3 mW cm^{-2} at 80 °C	• The QPAES/ TiO$_2$/g-C$_3$N$_4$ membrane show enhancements in hydroxide conductivity, chemical stability, and fuel cell performance than that pristine QPAES membrane. • The composite membrane also gains larger water uptakes, better hydroxide ion accessibility, and suppressed membrane swelling.	[118]
Quaternized poly(arylene ether) (QPAE)	Quaternary ammonium functionalized graphene oxide (QA-POSS)	SAFC	114.2 mS cm^{-1} at 90 °C	135.8 mW cm^{-2} at 70 °C	• The composite membrane shows the highest hydroxide conductivity, excellent alkaline stability and exhibits long-term chemical stability (>20 days).	[119]
Quaternary ammonium polysulfone (QAPSF)	Quaternary ammonium titanate nanotubes (QATNT)	SAFC	1.95 x 10^{-2} S cm^{-1}	321 mW cm^{-2} at 60 °C	• The composite membrane obtains high IEC, tensile strength, conductivity with minimal water uptake and swelling degree. • The composite membrane shows better electrochemical properties without defects than reported studies.	[120]
Quarternized poly(aryl ether ketone) (QPAEK)	Graphitic carbon nitride (g-C$_3$N$_4$) nanosheets	SAFC	34.5 mS cm^{-1} at 80 °C	49 mW cm^{-2} at 80 °C	• The QPAEK/g-C$_3$N$_4$ membrane exhibits improved ionic conductivity, low methanol permeability, better dimensional stability, and good alkaline resistance compared to the pristine QPAEK membrane. • The power density of QPAEK/g-C$_3$N$_4$ membrane showed 1.5 times higher than control QPAEK membrane.	[121]
Poly(vinyl alcohol) (PVA)	Imidazolium graphene oxides (ImGO)	SAFC	31.6 mS cm^{-1} at 30 °C	Not reported	• The composite membrane achieves good interfacial compatibility and uniform filler dispersion.	[122]

Polymer	Modifier	Type of fuel cell	Conductivity or resistance	Power density	Remarks	Ref.
					• The composite membrane also obtain enhanced thermal/mechanical, anion conductivity, and anti-swelling stabilities than the control membrane.	
Imidized polysulfone (ImPSU)	Quaternized carbon dots (QCDs)	SAFC	109.3 mS cm^{-1} at 80 °C	Not reported	• ImPSU/QCDs membrane showed improved hydroxide conductivity, ion transport channels, and other physicochemical properties than that pure ImPSU membrane.	[123]
Poly(vinyl alcohol), poly(diallydi methylammonium chloride) (PVA/PDDA)	Hydroxylated multiwalled carbon nanotubes (MWCNTs)	SAFC	0.03 S cm^{-1} at room temperature	66.4 mW cm^{-2} at room temperature	• The composite membrane obtains improved oxidative and alkaline stability and decreased water uptake. • The composite membrane also achieve good thermal, mechanical, chemical stability, and swelling property promising power density	[124]
Polybenzimidazole (PBI)	Ionic liquid functionalized graphene oxide (IL-GO)	SAFC	80 mS cm^{-1} at room temperature	Not reported	• The PBI/IL-GO membrane show excellent mechanical stability, good thermal stability, excellent alkaline stability, and high conductivity.	[125]
Quaternized poly(vinyl alcohol) (QPVA)	Chitosan/molybdenum disulfide (CS/MoS$_2$)	Direct methanol alkaline fuel cell	3.153 x 10^{-2} S cm^{-1}	Not reported	• The QPVA/CS/MoS$_2$ membrane improves mechanical and thermal stability and the lowest methanol permeability than that QPVA/CS membrane. • The composite also achieves promising cell performance and higher selectivity of about 4.6 times than pristine QPVA/CS membrane.	[126]
Quaternized poly(phenylene oxide) (QPPO)	1,4-diazabicyclo[2,2,2]octane modified graphene oxide	Urea/O$_2$ fuel cell	90 mS cm^{-1} at 25 °C	5.2 mW cm^{-2} at 60 °C	• The composite membrane show enhanced conductivity with increasing QGO content and promising power density.	[127]

5.0 SUMMARY

The fuel cell has emerged as a potential energy source with green byproducts capable of reducing pollution in our environment. To date, fuel cell research has focused on improving electrochemical performance while also lowering manufacturing costs. The development of advanced materials for the fabrication of fuel cell components has increased from year to year. This review focused briefly on polymeric-based materials combined with nanoparticles to prepare fuel cell electrolyte/membrane. As previously discussed, PEM and AEM are the two main types of fuel cell electrolytes. The Nafion membrane is the best membrane for PEM electrolytes because it has excellent proton conductivity and electrochemical performance. However, the lack of stability at high temperatures and low relative humidity, combined with the high cost, aided in developing hydrocarbon-based polymer membranes. The performance of a hydrocarbon membrane is commonly determined by the amount of functional groups present in its backbone, where a higher amount is provides excellent ion conductivity and power density but lacks mechanical stability. Thus, the incorporation of nanoparticles in Nafion and hydrocarbon-based membranes can solve the problems. According to the literature, many different nanoparticles have been introduced and modified to achieve excellent performance and durable properties. In summary, most of the findings indicated that the nanocomposite membrane outperformed the pristine membrane in terms of properties and performance. However, a few criteria must be considered when preparing the nanocomposite-based membrane, which are the properties of the polymer and nanoparticles themselves, material compatibility, material composition, and synthesis approach. Most previous studies revealed that pristine nanoparticles such as TiO_2, SiO_2, and Zr_2 caused compatibility issues where agglomeration was discovered in membrane structure contribute to different hydrophilicity behavior. The occurrence of agglomeration in the membrane will degrade the performance of the membrane due to the blocking of ions and water pathways. Thus, nanoparticles must be functionalized and advanced modified to increase their hydrophilicity behavior to avoid agglomeration and achieve a more compatible state with a functional polymer membrane. Among nanoparticles, GO with and without modification is widely used in the preparation of nanocomposite membranes because it is most compatible with almost all polymers and has a strong interfacial bonding between the GO and the polymer chain, resulting in better dispersion. Based on this review, it is possible to conclude that the polymer, nanoparticle, and synthesis approaches used influenced nanocomposite membranes properties, and performance for fuel cell applications.

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