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Polymer Electrolyte Membranes Fuel Cell: Review of Polymeric Materials

*[1]Idibie C.A., [2]Eyide O., [1]Umudi Q.E., [2]Onwenna D.N., [3]Ahmed M.H., [4]Ukaegbu E.E., [1]Lokwutor R.O.

[1]Department of Chemical Sciences, University of Delta, Agbor, Delta State

[2]Department of Chemical Engineering, University of Delta, Agbor, Delta State

[3]Department of Chemistry, Auchi Polytechnic, Auchi, Edo State, Nigeria

[4]WST ENERGY, Port Harcourt, Rivers State, Nigeria

*Corresponding Author: christopher.idibie@unidel.edu.ng

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ABSTRACT

This review discusses the polymers used in producing polymer electrolyte membranes (PEMs) for fuel cells. Information for this review was found using resources such as Google Scholar, Scopus, ScienceDirect, and Web of science. Information regarding traditional polymers, aromatic homopolymers, random and block copolymers, graft copolymers, cellulose derivatives and composite membranes were searched. It was found that traditional perfluorosulfonic acid membranes have high proton conducting properties but lack in cost effectiveness and lower conductivity when temperatures increase. Aromatic polymers with functional groups and double bonds show great potential. Cellulose and derivatives show benefits including renewable resources, hydrophilic properties, high strength and chemical compatibility but suffer from low ionic conductivity and swelling. Adding cellulose nanocrystals, functional polymers and inorganic fillers can improve the mechanical strength, ionic exchange and proton conductivity. Composite polymers show great potential as a sustainable alternative. Future research should be focused on improving the interactions of the polymers, cellulose and fillers to produce affordable and long lasting membranes with high performance suitable for future fuel cells.

Key words: Conductivity, fuel cell, electrolyte, ion exchange capacity, polymeric materials,

INTRODUCTION

The polymer electrolyte membrane fuel cell (PEMFC) enjoys the consideration of being one of the most promising fuel cell systems, majorly because of its high efficiency and fast start-up [1-4]. These and other advantages such as high power density, portability, rapid response to varying

loads, low operating temperature and almost zero emission, make it to stand out as a viable, environmentally friendly and reliable alternative source of energy to fossil fuel that is finite with attendant environmental pollution problem [2, 5]. Generally, fuel cell (Figure 1) is an electrochemical device that converts chemical energy into electrical energy [2]. It is a method of energy production via electrochemical redox reaction that occurs at both the anode and cathode of the cell. This is unlike battery, because fuel cell is designed to operate with continuous replenishment of the reactants with continuous production of electrical energy from the external supply of the reactants [4,6].

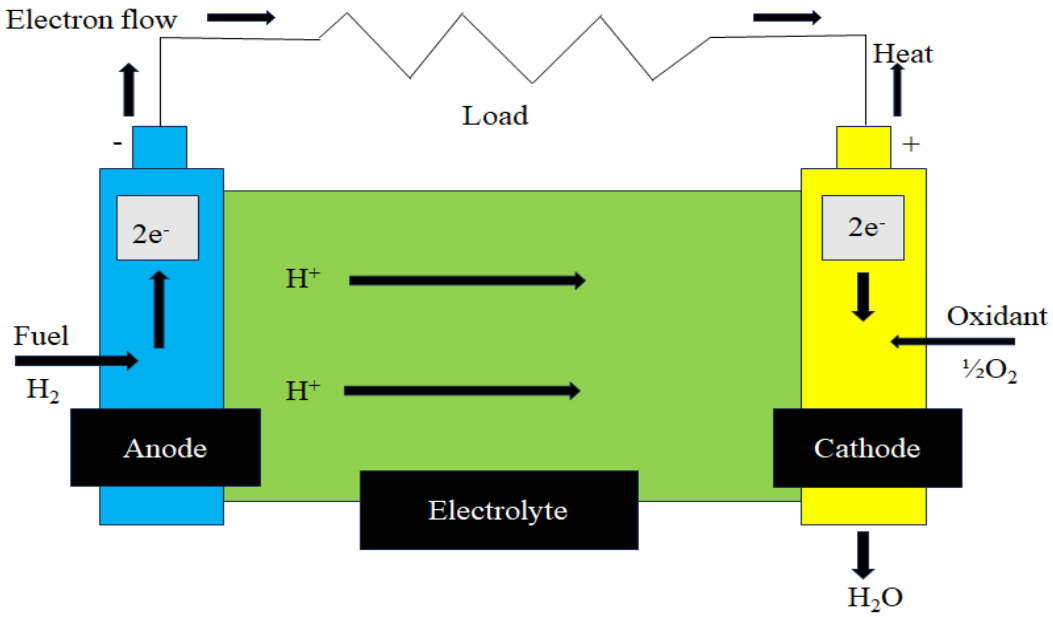

Figure 1: Schematic of polymer electrolyte membrane fuel cell.

The polymer electrolyte membrane (PEM) is a key component in PEMFC, which conducts the transport of protons generated at the anode, and at the same time opposes direct contact between the hydrogen gas (fuel) and the oxygen (oxidant) [2, 7]. The way PEMFC operates is such that hydrogen is oxidised at the anode/electrolyte interface into a hydrogen ion (H^+) and gives up an electron (e^-) [2,8] as shown in Equation (1):

Anode half-cell reaction: $H_2 \rightarrow 2H^+ + 2e^-$ (1)

This can be seen from the fuel cell diagram (Figure 1) where the produced proton moves through the solid electrolyte that is properly hydrated, while the electrons also generated on the other

hand flows through the electrode to the external circuit, to carryout work on the electric load and, which represents the useful output of electrical energy (*E*) from the fuel cell. Both the electron and proton will eventually arrive at the cathode and react with the oxidant supplied from an external gas flow stream and gets reduced to water as shown in equation 2 [2,8]:

Cathode half-cell reaction: $½O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (2)

Both the electric current as well as the mass transfer of the H^+ form a complete circuit, and this reaction is usually associated by waste heat generated due to the electrochemical reactions occurring at both electrodes. However, the overall reaction from the two half-cell reactions is expressed as shown in Equation (3) [2]:

Overall cell reaction: $H_2 + O_2 \rightarrow H_2O + E + \text{Heat}$ (3)

The overall reaction shows that water and heat are the bye-products from the use of PEMFC, and thus justifies PEMFC as a source of green energy since it does not release any pollutant to the environment like its fossil fuel counterpart known with carbonization of the environment with associated environmental and health issues. No doubt, it has been credited as a very promising alternative to fossil fuels in areas of vehicular transportation, electricity for homes and institutions, mobile electronic devices and industrial [9-11]. The ability to capture the heat generated (excess) can be deployed in cogeneration like manner or space water heating application. This is seen as one of the benefits of fuel cell that makes it better than some industrial combustion processes [6,12]. Nevertheless, while the electrolyte plays a key role of selectively allowing only the appropriate ions to pass between the anode and cathode, the two electrodes; positive (cathode) and negative (anode) allow the reactions that produce the electricity.

The aim of this review is to evaluate the properties, performance, limitations, and potential applications of different polymeric materials for developing efficient, durable, and sustainable polymer electrolyte membranes (PEMs) for fuel cell applications. Specifically, the review examines the properties and limitations of conventional PEM materials, evaluates the suitability of homopolymers, random copolymers, block copolymers, and graft copolymers as alternative membrane materials, assesses the potential of cellulose, cellulose derivatives, and

cellulose nanocrystals for PEM development, investigates the effects of polymer–cellulose–inorganic filler combinations on proton conductivity, mechanical stability, and ion-exchange capacity, and identifies existing research gaps and future prospects for developing cost-effective, high-performance, and sustainable composite PEMs.

Polymer electrolyte membrane

PEM is not just the central component but also the heart of fuel cell. There are certain requirements it must satisfy before it can be used as PEM for fuel cell application. They include: high ionic conduction particularly proton conductivity; barrier to passage of electron transport; resistance to fuel crossover especially for fuel cells using methanol as source of fuel; chemical stability against the attack of oxygen, acids and radicals; suitable water uptake; thermal stability in the operating range; and good mechanical properties. However, the current state-of-the-art PEM which is the Dupont Nafion®, is a perfluoronated ionomer (Figure 2) derived from polyethelene. It is known for high proton conductivity ($\sigma \geq 10^{-2}$ S cm^{-1}) and excellent durability under fuel cell operating

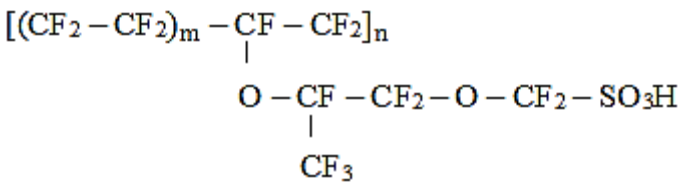

Figure 2: Chemical structure of Nafion.

Conditions [10, 13]. However, large scale application is encumbered, largely due to its very high cost, as well as other negative factors such as high methanol permeation, and dehydration at high temperature (> 80°C), which consequently leads to loss of conductivity [10]. Against these militating disadvantages, efforts have been committed towards getting an alternative PEM. Thus, the quest for the development of an alternate PEM for hydrogen and methanol fuel cells, research in the field of fuel cell is seriously tailored towards the preparation and testing of low methanol crossover and cost effective polymer electrolyte membranes with good conductivity that can benchmark Nafion.

Generally, the solid electrolyte is synthesized from polymeric materials, which are functionalized such that they carry ionisable groups or functional groups like SO_3H (sulphonic

acid) or any salt of alkali cations like SO_3Na, SO_3Li, SO_3K, SO_3Rb etc. One of the processes of functionalization is sulphonation. It is a viable process used simultaneously to render these polymers proton conductive and hydrophilic in nature. Meanwhile, when these ionasable groups or functional groups dissociate to produce two ionic components of their kind [2]. While one of the components (SO_3^-) is retained in the structure, the other component is a mobile or replaceable simple ion (counter ion) such as H^+, Li^+, Na^+, K^+, Rb^+ etc) that is electrostatically related to the fixed ion (Xianguo, 2006). The counter ion usually exchanges freely with ions of same sign from the solution (in the presence of water), hence PEM is referred to as 'ion exchange membrane' [2,8].

The methods of rendering sulphonated hydrocarbon polymers into PEM are; direct polymerization of sulphonated monomers [2,14] and post-sulphonation of prepared polymers using different agents like concentrated chlorosulphonic acid, chlorosulphonate, sulphur trioxide-triethyl, sulphuric acid, fuming sulphuric acid, trimethylsilyl phosphate complex etc. [2,15]. The sulphonic group is ionically bonded to the polymer matrix and as such, cannot be leached out. As the SO_3^- molecules are fixed to the polymer, the protons (H^+) on the acid groups migrate through the membrane when fully hydrated

Polymeric materials

Polymeric materials (PMs) now find a very promising area of application as ion-conductive membranes for batteries or as a proton exchange membrane for fuel cells (PEMFC) [16-17]. They also find application in membrane capacitive deionization and electrodialysis [18]. Aside the major draw backs associated with the Nafion membrane previously highlighted, and since it has been recognized that PEM greatly affects the performance and durability of a device, interest in the role of the electrolyte membrane has been on the increase in the direction of developing low-cost and high-performance PEMs, as alternatives to the very expensive Nafion [18-20]. Homopolymer, random copolymers and block, as well as graft copolymers containing aromatic rings or double bonds, have been recognized as suitable materials for PEMs in fuel cell application [21].

The development of PEMs from polystyrene butadiene rubber via aromatic sulphonation in different acidic media and using composite materials had been carried out [22-24]. The aromatic sulphonation is due to the presence of benzene ring in the styrene, and the

sulphonic group is attached to the ring as a result of electrophilic substitution reaction [23,24]. In this regard, the synthesis of low methanol permeation polymer electrolyte membrane from polystyrene-butadiene rubber was investigated [22], and results showed that the synthesized membrane achieved an ideal and competitive proton conductivity to Nafion in the order of 10^{-2} S cm^{-1}. It also demonstrated lower methanol permeation of 2.13 x 10^{-7} mol/cm^2s than Nafion1 (3.15 x 10^{-6} mol/cm^2s). Besides, the water and solvent uptake of the synthesized membrane were found moderate as compared to that of Nafion. The development of composite proton exchange membrane from polystyrene butadiene rubber and carbon nanoballs for fuel cell application that was carried out by Abdulkareem et al [5], showed that blending of the membrane with carbon nanoballs (CNBs) improved the thermal stability, water uptake retention and proton conductivity of the membrane with about 50 % increase in proton conductivity. Though the proton conductivity of both the unblended and blended polystyrene butadiene rubber achieved the required conductivity of 10^{-2} S cm^{-1} but the blended achieved a higher conductivity. Thus when Nafion 112 produced a maximum power density of 66.9 mW/cm^2, the developed blended membrane produced a maximum power density in the range of 73.7 - 97.1 mW/cm^2 depending on the mass of CNBs used to reinforce the material to be proton conductive. In the same vein, the sulphonation of the blend of polyisoprene and polystyrene (PI/PS) was studied in varying ratios and at constant ratio, where the methanol cross over was found lesser than Nafion as well as demonstrating moderate hydrodynamic properties ideal for ionic transport and idea conductivity (10^{-2} S/cm), having minimal swelling that was also idea for fuel cell application [25].

Conversely, non-aromatic polymeric material in polyisoprene had been studied both solely [26] and composites for PEM application [16,18]. In this light, the properties of polyisoprene elastomer that was functionalized via sulphonation for possible PEM fuel cell had been studied, and the conductivity results though promising (10^{-3} - 10^{-2} S/cm) with varying degrees of sulphonation (DS) and thicknesses (µm), but with the likeliness of suffering from operational failure due to excessive swelling when membranes of very high DS (>50%) are used [26,16]. Against this backdrop, the synthesis of moderate water-uptake and low methanol permeable polymer electrolyte membrane from functionalized polyisoprene impregnated carbon nanotubes, was investigated, and results indicated that aside the conductivity of the developed PEM achieving an increase by 1 order with the membrane impregnated with CNTs from 10^{-3}

S/cm to 10^{-2} S/cm, it was also found out that the water uptake was ideal for PEM in fuel cell application, and very profoundly, the methanol crossover was lesser than that of Nafion with a difference of 0.48 Mol/L [16]. The power densities it generated in another study were 35.83 - 68.67 mW/cm^2 based on different catalyst loadings [26].

Historic insight into electrolyte polymeric materials

Suffice to state that from 2005 to 2025, polymer electrolyte research has evolved through distinct innovation phases, each reflecting advancements in material design, performance optimization, and sustainability. Between 2005 and 2010, studies focused on non-fluorinated synthetic polymers such as sulfonated polyether ether ketone (SPEEK), polybenzimidazole (PBI), and polyvinyl alcohol (PVA)/ montmorillonite (MMT), which offered enhanced thermal stability and cost reduction, providing alternatives to expensive Nafion membranes. Between 2020 to 2022, research advanced into hybrid cellulose membranes such as cellulose-acetate-grafted - vinylbenzyl chloride-trimethylamine (CA-g-VBC-TMA), cellulose nanofiber (CNF), and CNC–Nafion, leading to higher power density and proton conductivity, which reflect better integration between natural and synthetic phases [27,28]. Finally, between 2023 and 2025, the focus tilted towards sustainable and high-stability polymers, emphasizing non-fluorinated AEMs and cellulose composites that exhibit superior durability, environmental compatibility, and long-term performance, and thus aligning with global sustainability goals [29,30].

Perfluorinated polymeric electrolyte membranes

Perfluorinated polymer electrolyte membranes are known to represent the most advanced and widely utilized class of electrolytes due to their exceptional thermal stability, high proton conductivity, and long operational lifetime [30]. No doubt, their success in both fuel cells and electrolysers is primarily attributed to the robustness of the carbon–fluorine bond in the polymer backbone, which imparts excellent chemical resistance and mechanical integrity [31]. These membranes feature hydrophobic backbones combined with hydrophilic sulfonic acid groups, forming efficient proton conduction channels. However, under temperatures above 90 °C, excessive dehydration can disrupt these channels, and thus bring about reduction in conductivity and overall performance.

Other known perfluorinated membranes share a similar structural framework composed of perfluorinated backbones with ionic side chains that facilitate proton transport [32]. Its superior oxidative stability and ionic conductivity established it as the benchmark for electrochemical systems. Early versions of PEM fuel cell demonstrated outstanding lifetimes exceeding 57,000 hours, which underscores their reliability for industrial and defense applications [33,34].

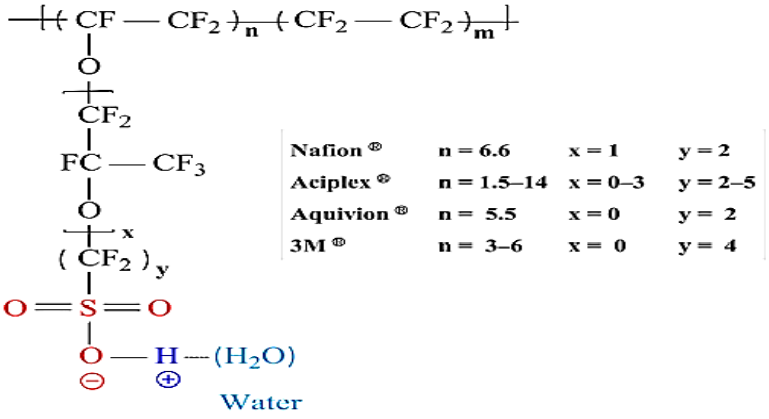

Figure 3: Types and structures of perfluorinated sulfonic acid polymers [35]

Partially fluorinated polymeric electrolyte membranes

Partially fluorinated polymer electrolyte membranes have emerged as promising alternatives to fully fluorinated types due to their enhanced structural robustness and mechanical strength [29]. While these membranes retain moderate proton conductivity, their fabrication cost however, remains relatively high, often comparable to that of perfluorinated membranes. A notable example according to literature is the sulfonated copolymer containing the α,β,β-trifluorostyrene monomer, which provides an effective balance between chemical stability and mechanical durability [36].

Early efforts in developing such membranes gravitated towards the creation of polystyrene-sulfonic acid (PSSA), later modified by substituting tertiary hydrogen atoms with methyl and fluorine groups. This modification was reported to produce sulfonated poly (α,β,β-trifluorostyrene), a material known for greater resilience and extended operational life. Expanding on this design, various fluorine-containing polymers such as tetrafluoroethylene, poly (tetrafluoroethylene-co-perfluoropropylvinylether), and poly (vinylidene fluoride) have been

identified as strong backbone candidates for sulfonic acid ($–SO_3H$) grafting, which further improves both proton conductivity and durability [29,36].

Non-fluorinated polymeric electrolyte membranes

Non-fluorinated PEMs are fluorine-free proton-conducting materials developed as sustainable and cost-effective alternatives to conventional fluorinated systems such as Nafion. They are composed of polymers like polybenzimidazole (PBI), sulfonated polyarylene ethers (SPEEK, SPPSU), polyimides (PI), and polyphosphazenes (PP), which exhibit strong chemical resistance, thermal stability, and mechanical tunability [29,31]. Although these properties can be further improved through sulfonation or other structural modifications that allow better control over proton transport pathways and membrane flexibility.

Although non-fluorinated PEMs are generally less conductive and durable under harsh operational conditions than their perfluorinated counterparts, but they are found to offer significant advantages in low production cost, ease of synthesis, and compatibility with high-temperature operations. These characteristics make them attractive for use in next-generation fuel cells, electrolysers, and other clean energy systems [30, 29].

Among these, PBI stands out for its exceptional chemical and thermal resilience and economic feasibility, though its proton conductivity (0.02–0.06 S cm^{-1}) remains relatively limited [37]. Similarly, SPEEK, SPPSU demonstrate high mechanical strength and chemical stability, and their performance can be improved through sulfonic acid functionalization, which enhances ion transport [38].

PI-based membranes possess excellent thermal resistance and structural stability; however, fabrication challenges, particularly in producing uniform films from solution, have constrained their widespread adoption [39]. On the other hand, PP-based membranes offer moderate proton conductivity and good chemical tunability, allowing easy modification of their backbone. Nevertheless, their insufficient mechanical robustness under long-term operation limits their application in demanding environments [40].

Composite polymeric electrolyte membranes

Composite polymeric electrolyte membranes (CPEMs) have been engineered to improve Direct Methanol Fuel Cell (DMFC) efficiency, particularly at low temperatures. Their development

primarily was aimed at minimizing methanol crossover, maintaining high proton conductivity, and reducing fabrication costs. As highlighted by Gagliardi, et al [31], these membranes are generally grouped into modified perfluorosulfonic acid (PFSA)-based types such as Nafion composites and non-perfluorinated polymer-based CPEMs.

a. Modified Nafion-based composite membranes

Modified Nafion-based composite membranes (MNBCMs) are fabricated by incorporating organic or inorganic fillers to improve proton conduction, mechanical stability, and methanol tolerance ([41,42]. These fillers modify the internal microstructure of Nafion, enhancing the separation between hydrophilic and hydrophobic domains, which is crucial for selective ion transport. Research has expanded across various filler categories such as organic polymers, inorganic oxides, and carbon nanomaterials each contributing unique physical and electrochemical advantages.

b. Organic filler-based Nafion composites (COFBNs)

Organic fillers significantly reinforce polymer electrolyte membranes by enhancing structural strength, dimensional stability, and cost-effectiveness[31] Polytetrafluoroethylene (PTFE), though non-conductive, was found to improve Nafion's durability and corrosion resistance [43,44] Nafion/PTFE composites demonstrated lower methanol diffusion and improved fuel barrier performance compared to pure Nafion [45], while zirconium phosphate (ZrP) addition further reduced methanol permeability, albeit at the expense of proton conductivity [46].

Beyond fluorinated systems, PBI and polyvinyl alcohol (PVA) have emerged as cost-effective, thermally stable alternatives [47,48]. Nafion/PVA composites, due to PVA's hydrophilicity, exhibited superior water retention, methanol resistance, and electrochemical stability, yielding higher open-circuit voltages [49]. Similarly, PBI-modified Nafion membranes, prepared via dip-coating and screen-printing, achieved 42% higher current density and 46% greater power output at 60 °C and 3.2 M methanol feed [50,51].

c. Conductive and sulfonated polymer-modified Nafion

Conductive polymers such as polyaniline (PANI) and polypyrrole (PPy) have been used to suppress methanol crossover while maintaining catalyst stability [52,53]. PANI-based Nafion membranes outperformed PPy systems, particularly at high methanol concentrations [54,55]. In parallel, sulfonated polymers like SPAEK and SPEEK have been integrated into Nafion to

increase proton conductivity and methanol resistance, yielding a 30% improvement in open-circuit voltage and 10% higher maximum power density compared to pristine Nafion [56].

d. Inorganic filler-based composites for DMFCs

Inorganic fillers such as silica, titania, montmorillonite (MMT), and zeolites have been incorporated into Nafion to enhance water retention, mechanical strength, and high-temperature operation. Silica-based composites exhibit reduced methanol permeability but slightly lower proton conductivity due to limited water uptake [57,58]. TiO_2 and SiO_2 composites, however, demonstrate enhanced performance, achieving power densities exceeding 640 W/m² at 80 °C and 1 M methanol [59].

MMT fillers drastically decrease methanol crossover (> 90%) while maintaining acceptable conductivity [60]. Sulfonated MMT variants (MMT–SO_3H) further improved performance, particularly at 5 wt.% filler loading and 2 M methanol concentration [61]. Zeolite-based composites, particularly mordenite (MOR), achieved 1.5 higher conductivity and twice the power density of Nafion 117, owing to their molecular sieving and hydrophilic properties [62]. Incorporating graphene oxide (GO) into MOR composites enhanced filler dispersion and hydrophilicity, though high-temperature dehydration remained a limiting factor [63].

e. Inorganic composite membranes for hydrogen PEM fuel cells (H_2 PEMFCs)

At moderate temperatures (~ 80 °C), water-saturated PEMs facilitate proton transport via both the Grotthuss and diffusion mechanisms. However, at elevated temperatures, dehydration sets in as well as hydrogen crossover, and thus lowering open-circuit voltage [31]. To overcome this, hybrid organic–inorganic Nafion membranes have been developed. Incorporation of metal oxides (e.g., TiO_2, ZrO_2, WO_3) were found to improve thermal stability up to 170 °C [64,65]. Sulfonated ZrO_2 fillers enhanced low-humidity current density and ohmic behavior, reaching 1015 mA cm^{-2} at 0.6 V [65].

TiO_2 nanotube and nanowire composites provided improved hydration and stability up to 130 °C [66,67]. Similarly, porous ZrO_2 nanotubes that was investigated maintained an OCV of 0.92 V after 200 h at 80 °C [68]. For non-fluorinated systems, SPEEK–titania and SPEEK–silica composites achieved conductivities between 4×10^{-2} S cm^{-1} and 8×10^{-2} S cm^{-1} at 90–140 °C [69,70]. PBI-based composites with SiO_2, TiO_2, or ZrP fillers displayed superior acid retention and conductivity, reaching 0.20 S cm^{-1} at 180 °C [71].

Reinforced poly(ether sulfone) (SPES) and poly(aryl ether ketone) (SPAEK) membranes with CeO_2, sulfonated TiO_2–polyaniline, and sulfonated SiO_2 additives further improved oxidative stability and proton transport [72-74], confirming their viability for durable PEMFC operation.

f. Composite electrolytes for polymer electrolyte membrane water electrolysers (PEMWEs)

Composite membranes integrating metal oxides like SiO_2, TiO_2, and WO_3 have been reported to exhibit exceptional performance in Polymer Electrolyte Membrane Water Electrolysers, sustaining operation above 100 °C [75,76]. Their hygroscopic nature enhances water retention and uniform distribution, lowering ohmic resistance and improving overall efficiency [77]. These composites also reduce gas crossover but still face gradual degradation over long-term use.

To further advance electrolyser membranes, short-side-chain Aquivion® PFSA variants were introduced, displaying higher crystallinity and conductivity but limited durability [78]. Reinforcement with SPEEK or electrospun polysulfone (PSU) nanofibers improved mechanical strength without significant voltage loss [79,80]. Meanwhile, graphene-coated composites offered improved conductivity and water adsorption due to graphene–polymer [81]. Alternative polymers such as SPEEK, sulfonated polysulfone (SPSU), and PBI are being actively explored for PEMWE operation. SPEEK–TPA–CeO_2 composites, for instance, achieved 1.82 V cell voltage at 1 A cm^{-2} and 80 °C lower than Nafion 117while maintaining superior mechanical strength and elongation [82]. Despite these advancements, further research on durability and long-term operational stability remains essential for commercialization.

g. Carbon nanomaterial fillers for d**irect methanol fuel cells (DMFCs)**

Graphene oxide (GO) is one of the most extensively studied fillers for Nafion membranes in direct methanol fuel cells (DMFCs) due to its high surface area, mechanical strength, and excellent water retention capacity. The presence of oxygen-rich functional groups such as hydroxyl, epoxide, carbonyl, and carboxyl enhances its hydrophilicity and compatibility with the polymer matrix [83]. Within Nafion, the hydrophobic regions of GO interact with the polymer backbone, while hydrophilic groups associate with ionic clusters, creating strong interfacial adhesion. [84] demonstrated that adding 0.5 wt.% GO reduced methanol permeability by 60%, though excessive loading (2 wt.%) reduced proton conductivity. The optimal concentration (1 wt.%) achieved power densities of 62 mW cm^{-2} at 30 °C and 141 mW cm^{-2} at 70 °C.

At higher methanol concentrations where crossover typically degrades fuel cell efficiency, the benefits of GO become more evident, producing nearly triple the power output compared to pure Nafion membranes. To improve dispersion and proton conduction, [85] developed sulfonated graphene oxide (SGO)/Nafion composites. The sulfonic groups formed interconnected proton pathways and suppressed methanol diffusion, though excessive SGO caused aggregation and conductivity loss. Optimized membranes exhibited higher current and power densities, confirming enhanced reaction kinetics and reduced crossover relative to Nafion 115 [31]. Building on this, [86], introduced a layered Nafion–GO–Nafion configuration, where a single GO film decreased methanol permeability by 68.6% with only a minor (7%) loss in conductivity at 80 °C. This structure enabled efficient operation at elevated methanol concentrations (5–15 M), proving graphene-based fillers can effectively mitigate crossover while maintaining high performance.

h. Carbon nanomaterial fillers for hydrogen PEM fuel cells (H_2 PEMFCs)

In PEMFCs, GO and related carbon nanomaterials are used to enhance proton transport, water retention, and mechanical integrity. Their oxygen-functionalized layered structure facilitates strong polymer–filler interactions, improving both hydration and strength. [87], reported that incorporating 4% GO in Nafion improved ion exchange capacity and produced nearly fourfold higher power density than pristine Nafion. However, excessive filler stiffened the membrane and reduced water uptake.

Surface-functionalized nanofillers, such as sulfonated graphene, was credited to further enhance proton transport under dry conditions [88]. A membrane with 1 % sulfonated graphene was found to achieve 300 mW cm^{-2} at 70 °C and 20 % RH significantly outperforming unmodified graphene composites. Similarly, combined GO with Pt-decorated graphene for self-humidifying fuel cells [89], while later work adding silica [89] improved water retention but highlighted the need for careful optimization to prevent proton-blocking.

Maiti et al. [90], developed GO/ionic liquid composites exhibiting excellent conductivity and thermal stability (up to 230 °C), outperforming Nafion 117 between 70–110 °C. [91], fabricated multilayer GO–Nafion–polyindene composites, which showed better proton transport and thermal endurance, especially in solution-cast films.

Ibrahim et al. [92], showed that thinner GO composite membranes (~30 µm) retained more water and improved conductivity. Similarly, Kumar et al. [93], reported that sulfonated GO/SPEEK membranes delivered 51 % higher power density than pure SPEEK under varied humidity.

Carbon nanotube (CNT) fillers also enhanced durability and conductivity. [94], incorporated sulfonated CNTs into SPEEK, improving both strength and proton transfer. [95], achieved similar effects using GO in PBI membranes, reducing acid leaching and ensuring stable operation at 165 °C.

Further advancements include PBI membranes functionalized with phosphonated GO or phosphonic acid-modified CNTs, which increased conductivity fourfold and improved strength [96,97]. In another approach, Dai et al. [98], utilized carbon dots (2–5 nm) as fillers in PES–PVP membranes, achieving superior anhydrous performance, while Ahmed et al. [99], used sulfonated multi-walled CNTs to reinforce chitosan membranes with minimal loss of water uptake.

Non-perfluorinated polymers composite membranes for **DMFCs**

Non-perfluorinated composite membranes have emerged as efficient and affordable substitutes for conventional perfluorinated membranes used in direct methanol fuel cells, which commonly face challenges such as methanol and ruthenium crossover. Aromatic polymers, particularly poly (ether ether ketone) (PEEK), polyvinyl alcohol (PVA), and poly(arylene ether) derivatives, offer a good balance between structural stability, tunable functionality, and proton conduction [31].Their chemical flexibility and high resistance to oxidation make them suitable for next-generation DMFC applications.

Sulfonated poly(ether ether ketone) (SPEEK) is among the most widely studied non-fluorinated polymers due to its excellent mechanical and thermal strength. The introduction of sulfonic acid groups into the polymer chain was reported to significantly enhance proton conductivity and reduce methanol permeability [100]. However, excessive sulfonation often increases swelling and fuel crossover. To overcome these issues, SPEEK has been combined with organic and inorganic fillers such as phenoxy resin (PR), polyphenylsulfone (PPS), heteropolyacids (HPA), polyaniline (PA), SiO_2, ZrP, zeolite, and polypyrrole, which improved selectivity and dimensional integrity [101,102].

The integration of fillers like MMT and PBI into the SPEEK matrix further enhanced DMFC performance. Gosalawit et al. [103], observed that SPEEK/MMT membranes produced higher current densities and output power than pure SPEEK or Nafion 117, though with lower thermal endurance. Similarly, Pasupathi et al. [104], reported that SPEEK/PBI composites achieved nearly twice the power density of Nafion 117 at 60 °C, maintaining good operational stability under moderate conditions. Nonetheless, degradation occurred at higher temperatures, prompting further efforts to improve high-temperature durability.

A major limitation of sulfonated aromatic polymers is maintaining mechanical and dimensional stability while achieving high proton conductivity. Higher sulfonation improves ionic transport but leads to excessive swelling or dissolution in methanol–water environments [26,105]. Therefore, structural modification through crosslinking or filler incorporation is widely employed to balance conductivity and mechanical strength [106].

Sulfonated poly (arylene ether sulfone) (SPAES) composites have also demonstrated promise in DMFCs. Kim et al. [107], found that incorporating laponite into SPAES reduced methanol crossover by increasing the diffusion path length. However, the gain in barrier properties was offset by slightly reduced conductivity, suggesting a need for microstructural optimization. Similarly, Feng et al. [108], achieved crosslinked SPAES membranes with proton conductivity comparable to Nafion 117 but with lower methanol permeability due to compact hydrophilic domains.

Polyvinyl alcohol (PVA) membranes, known for their chemical robustness and low fuel permeability, represent another non-fluorinated alternative. Despite their inherently poor ionic conductivity, modification with ionic species or fillers such as MMT, SiO_2, or polyrataxane can significantly enhance proton transport [109]. Yang et al. [110], demonstrated that PVA/MMT membranes attained conductivity of 0.0368 S cm^{-1} and superior methanol barrier performance compared to Nafion 117, resulting in higher power density under ambient conditions.

Overall, non-perfluorinated composite membranes incorporating various fillers have shown substantial improvements in DMFC selectivity and efficiency by balancing proton conductivity with methanol impermeability. While non-conductive fillers like PTFE or metal oxides may slightly restrict proton mobility, they increase membrane tortuosity and effectively suppress fuel crossover. Functionalized fillers especially sulfonated variants offer even greater

benefits by providing additional proton pathways. However, long-term durability remains the primary limitation preventing these systems from replacing Nafion in commercial DMFCs. Future efforts should prioritize lifetime testing, degradation analysis, and interfacial stability between composite membranes and catalyst layers to advance their practical deployment.

Overview of anion exchange membranes and cation exchange membrane

In recent years, several types of anion exchange membranes (AEMs) and cation exchange membranes (CEMs) have been engineered to improve the cost-efficiency and electrochemical performance of proton exchange membrane fuel cells (PEMFCs) and alkaline fuel cells (AFCs) [111-113], Increasing attention has been directed toward biopolymer-based membranes, particularly those derived from cellulose, due to their abundance, renewability, and favorable intrinsic characteristics such as hydroxyl functionality and hydrophilicity [114,115].

Recent research (2018–2022) has explored the use of cellulose and its derivatives including cellulose nanofibers, nanocrystals, and bacterial cellulose as sustainable alternatives for polymer membranes. These cellulose-based membranes are often hybridized with materials such as Nafion, poly (aryl ether ketones), ionic liquids, or inorganic fillers, enhancing conductivity and stability. The development trend reveals growing interest in cellulose-reinforced AEMs and CEMs for cleaner, low-cost fuel cell technologies [111,115].

Comparison between cationic and anionic polymeric membranes in fuel cells

The fundamental distinction between cationic and anionic polymeric membranes lies in the type of charge carrier: CEMs conduct protons (H^+) while AEMs transport hydroxide ions (OH^-). This difference influences their electrode reactions, electrolyte function, catalyst composition, and operating medium. Cationic membranes are ideal for acidic systems such as PEMFCs, whereas anionic membranes operate in alkaline conditions, enabling the use of non-precious catalysts and potentially reducing overall system cost. Table 1 presents the comparison between cationic and anionic polymeric membranes in fuel cells.

Table 1: Comparison between cationic and anionic polymeric membranes in fuel cells [30, 116, 117]:

Feature	Cationic PEMFC	Anionic EMFC	References
Type of Fuel Cell	Proton Exchange Membrane Fuel Cell (PEMFC)	Anion Exchange Membrane Fuel Cell (AEMFC)	[116]
Charge Carrier	H^+ (protons)	OH^- (hydroxide ions)	[30]
Direction of Ion Flow	Anode → Cathode	Cathode → Anode	[116]
Electrolyte Function	Conducts protons; blocks electrons and gases	Conducts hydroxide ions; blocks electrons and gases	[117]
Electrode Reactions	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $½O_2 + 2H^+ + 2e^- \rightarrow H_2O$	Anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ Cathode: $½O_2 + H_2O + 2e^- \rightarrow 2OH^-$	[116]
Operating Medium	Acidic	Alkaline	[117]
Polymer Examples	Nafion, SPEEK, PBI	QAPEEK, QPPO, FAA-3	[30]
Functional Group	Sulfonic acid ($-SO_3H$)	Quaternary ammonium ($-NR_3^+$), imidazolium, phosphonium	[116]
Operating Temperature	60–200 °C	40–100 °C	[30]
Catalyst Requirement	Precious metals (Pt-based)	Non-precious metals (Ni, Co, Ag)	[117]
Chemical Stability	Excellent in acidic medium	Moderate; susceptible to OH^- attack	[116]
Fuel Crossover	Low	Low	[117]
Cost	Higher	Lower	[30]
Main Challenges	Cost and hydration management	Long-term chemical stability	[116]
Water Formation Site	Cathode	Anode	[117]
Example Membranes	Nafion®, SPEEK, PBI	Tokuyama A201, FAA-3, QAPEEK	[30]

Cellulose-based materials in membrane development

Cellulose $(C_6H_{10}O_5)_n$, the most abundant natural polysaccharide, consists of β-(1→4)-linked D-glucose units. It exists in both crystalline and amorphous domains, with crystallinity levels between 40–70% depending on its source and extraction method [118]. The crystalline regions contribute to its stability, while amorphous areas are more chemically reactive. Various polymorphic forms (cellulose I, II, III, IV) can interconvert through chemical or thermal modification [119]. Due to their abundance, renewability, and biocompatibility, cellulose and its

derivatives are widely utilized in biomedical, environmental, and electrochemical energy systems [120,121]. However, in membrane science, cellulose-based polymers are increasingly integrated into ion exchange membranes for PEMFCs and AEMFCs, offering a sustainable path toward cost-effective and high-performance energy device.

Modified cellulose offers enhanced ion conductivity, mechanical stability, and environmental compatibility, making it ideal for sustainable energy systems. Incorporating quaternized cellulose nanocrystals (QCNCs) into QPPO matrices significantly enhances the physicochemical performance of AEMs.

Further improvements were achieved by incorporating quaternized cellulose fibers (QCF) and quaternized graphene oxide (QGO) into QPPO matrices [122]. The optimized QPPO: QCF: QGO (100:1:1) composition yielded an ion exchange capacity (IEC) of 2.64 meq g^{-1} and ion conductivity of 114.6 mS cm^{-1} at 25 °C, outperforming the unmodified QPPO membrane due to uniform filler dispersion and interconnected ionic channels.

Sulfonated cellulose nanofibers (SCNF) derived from bamboo have also been successfully integrated into quaternized poly(ether ether ketone) (QAPEEK) matrices to improve AEM performance [123]. Incorporating SCNF reduced swelling degree (SD%) from 20% to 7.5% and enhanced mechanical strength. The optimal 8:1 QAPEEK: SCNF ratio achieved an ion conductivity of 21.4 mS cm^{-1} and IEC of 1.76 mmol g^{-1}, with a power density increase from 760 mW cm^{-2} to 930 mW cm^{-2} compared to pure QAPEEK membranes.

Similarly, Samaniego et al. [124], prepared cellulose acetate (CA)–based AEMs through radiation grafting with vinyl benzyl chloride (VBC) followed by trimethylamine (TMA) functionalization. The CA-g-VBC-TMA membranes achieved an ion conductivity of 16.3 mS cm^{-1}, demonstrating cellulose acetate's viability as a cost-effective AEM substrate.

TEMPO-mediated oxidation is commonly employed to convert cellulose pulp into carboxylated cellulose nanofibers (CNFs), followed by mechanical fibrillation to produce thin, uniform membranes [125]. The electrochemical performance of these membranes depends on factors such as relative humidity (55–95%), membrane thickness, counter ion type (H^+ or Na^+), and surface charge density (600–1550 μmol g^{-1}). At relative humidity levels above 75 %, well-defined water channels form, enabling high proton conductivity (>1 mS cm^{-1} at 30 °C). CNF membranes exhibit superior mechanical strength compared to Nafion® and allow thinner

fabrication with minimal hydrogen crossover, maintaining high open-circuit voltages similar to commercial PEMs [125].

Further functionalization of cellulose can significantly improve its ionic conductivity [126], synthesized nitro-oxidized carboxy cellulose nanofibers (NOCNFs) from jute, forming two types of nano-paper membranes: one with carboxylate groups and the other with carboxylic acid groups. The latter demonstrated higher proton conductivity (14.6 mS cm^{-1} at 80 °C, 100% RH) and superior fuel cell power density (19.1 mW cm^{-2}) due to its denser structure, greater acidity, and hydrogen-bonded network.

Introducing heterocyclic groups onto cellulose enhances proton transport through hydrogen-bonded networks and acid-base interactions. [127], functionalized cellulose microfibers with imidazole, achieving conductivity of 2.7×10^{-4} S m^{-1} at 150 °C four orders of magnitude higher than pure cellulose. Proton conduction was governed by imidazole dissociation and hydrogen bond rearrangement. Similarly, Lindner et al [128] doped nanocrystalline cellulose with 1H-1,2,3-triazole (Tri), forming transparent polymer films that reached 4×10^{-4} S m^{-1} at 135 °C. Triazole reorientation facilitated proton hopping via the Grotthuss mechanism, while maintaining superior thermal stability compared to imidazole-functionalized cellulose.

In a similar approach, Bayer et al. [129] introduced sulfonic groups into CNFs to enhance ion exchange capacity (IEC) and ionic conductivity. Using sodium periodate and sodium bisulfite, sulfonated CNF membranes (30 μm thick) achieved an IEC of 0.900 mmol g^{-1}—significantly higher than untreated CNF (0.016 mmol g^{-1}). The resulting membranes reached through-plane conductivities up to 2×10^{-3} S cm^{-1} and demonstrated comparable water uptake (26%) to Nafion®, achieving high power densities (156 mW cm^{-2}) under standard PEMFC conditions.

Cellulose and its derivatives though possess excellent intrinsic properties, including high mechanical strength, renewability, hydrophilicity, and chemical compatibility, however, their ion conductivity and dimensional stability still require enhancement to match commercial standards such as Nafion. Noted future research was on the emphasis on crosslinking and co-polymerization techniques to stabilize cellulose networks and tune hydrophilic–hydrophobic balance.

Cation polymeric materials (CPM)

Cation exchange membranes (CEMs) are ion-conducting polymers that contain negatively charged functional groups such as sulfonate ($–SO_3^-$), carboxylate ($–COO^-$), or phosphonate ($–PO_3^{2-}$). These functional sites selectively attract and transport cations including H^+, Na^+, K^+, and Li^+ while repelling anions, thereby maintaining charge balance and efficient proton transfer within the membrane matrix. This selective ion migration underpins the electrochemical performance of proton exchange membrane fuel cells (PEMFCs) [130].

To address the high production cost and limited durability of conventional commercial membranes such as Nafion®, researchers have focused on developing alternative CEMs using different structural and compositional strategies. These approaches include the modification of organic polymers, formation of organic–inorganic hybrid membranes, blending of compatible polymers, and chemical cross-linking to improve mechanical and thermal stability [131,132].

Recent advancements have also explored the incorporation of cellulose and its derivatives into CEMs to enhance sustainability and performance. Cellulose-based modifications provide improved hydrophilicity, ion conductivity, and mechanical robustness while reducing environmental impact. These bio-derived materials have demonstrated promising electrochemical behavior, making them attractive candidates for PEMFC applications [132].

Polyaryletherketone (PAEK) membranes

Hydrocarbon-based polymers, particularly polyaryletherketones (PAEKs), have emerged as viable alternatives to high-cost fluorinated membranes like Nafion, due to their superior thermal stability, mechanical strength, and lower production cost. These materials, when functionalized or combined with cellulose nanocrystals (CNCs), exhibit significant improvements in water retention, dimensional stability, and proton conductivity, making them promising candidates for proton exchange membrane fuel cells (PEMFCs) and redox flow batteries [133].

CNC-reinforced SFPEEKK and other hybrid membranes

Ni et al. [134], synthesized composite membranes based on sulfonated fluorenyl-containing poly(ether ether ketone ketone) (SFPEEKK) and CNC via a solution-casting process. Two variants, SFPEEKK-30 and SFPEEKK-60 were prepared with 30% and 60% fluorenyl units, respectively, and CNC loadings ranging from 0–10 wt.%. The optimal performance was

achieved at 4 wt.% CNC, which enhanced proton conductivity, ion exchange capacity, and mechanical strength due to strong hydrogen bonding between the $–SO_3H$ and –OH groups on CNC and SFPEEKK.

At 20 °C, proton conductivities of SFPEEKK-30-4%CNC and SFPEEKK-60-4%CNC were 0.03 and 0.076 S cm^{-1}, respectively, which increased to 0.109 and 0.245 S cm^{-1} at 90 °C. The results demonstrate that the CNC incorporation facilitates hydrogen bond networks that promote effective proton conduction while improving the membrane's dimensional [134]. Building on their previous work, Ni et al. [134] replaced SFPEEKK with sulfonated poly(aryletherketone) containing carboxylic acid groups (SPAEK-COOH-x) and employed surface-modified CNC as both a crosslinker and performance enhancer. The resulting CNC–SPAEK-COOH membranes exhibited improved mechanical integrity and proton conductivity while retaining thermal stability. In particular, the SPAEK-COOH-10/CNC composite achieved an excellent balance of conductivity, mechanical strength, and thermal endurance, demonstrating that CNC crosslinking effectively enhances the proton conduction network and overall fuel cell suitability [134].

Bano et al. [135], developed a crosslinked sulfonated poly(ether ether ketone) (SPEEK) composite membrane using CNC as a reinforcing agent and ethylene glycol (EG) as a crosslinker. This configuration improved the dimensional stability and mechanical strength of the membrane without compromising conductivity. Through interactions between CNC's surface hydroxyl and sulfonic groups and the ionic domains of SPEEK, an efficient proton transport network was established. The optimized 4 wt.% CNC–SPEEK membrane achieved a proton conductivity of 0.186 S cm^{-1} at 95 °C and 95% RH, comparable to that of Nafion 117, while maintaining superior thermal and oxidative stability [135].

Zhao et al. [136], synthesized sulfonated poly(ether ether ketone ketone) (Ph-SPEEKK) membranes incorporating aminated and sulfonated CNCs (Am-sCNC) via a direct sulfonation process. Functionalization involved introducing $^{-}SO_3H$ and $–NH_2$ groups using sulfonic acid and silane coupling agents, respectively. The resulting composite membranes (Am1-sCNC and Am3-sCNC) showed enhanced water uptake and proton conductivity due to the synergistic interaction of multiple hydrophilic groups ($–SO_3H$, $–NH_2$, –OH).

Among the tested formulations, Ph-SPEEKK–Am3-sCNC-5 exhibited the highest proton conductivity (0.133 S cm^{-1} at 80 °C) and delivered a superior power density of 227 mW cm^{-2}, compared to 104 mW cm^{-2} for pristine Ph-SPEEKK. The co-presence of hydrophilic groups facilitated both vehicular and Grotthuss proton transport mechanisms, leading to improved electrochemical performance [136].

Various polymers have been utilized in the synthesis of cellulose nanocrystal (CNC)-based membranes, including poly(acrylic acid) (PAA), poly(bis[2-(methacryloyloxy)ethyl] phosphate) (P(bisMEP)), poly(2-acrylamido-2-methylpropane sulfonic acid-co-methyl methacrylate) (P(AMPS-co-MMA)), poly(vinylphosphonic acid)-b-polystyrene (PVPA-b-PS), polyvinyl alcohol (PVA), polyaniline (PANI), and sulfonated polystyrene (sPS). These polymer matrices have been blended with cellulose derivatives such as CNC, cellulose nanofibrils (CNF), cellulose acetate (CA), and bacterial cellulose (BC) to produce proton exchange membranes (PEMs) for fuel cell applications.

Incorporating CNF into PAA matrices yielded flexible, mechanically durable electrolytes due to strong hydrogen bonding and reduced swelling behavior (Li et al., 2018). Similarly, P(bisMEP)/BC nanocomposites developed via in-situ polymerization achieved superior ion exchange capacity and high Young's modulus, owing to their anisotropic nano-fibrillar architecture [137].

Graft copolymer membranes derived from cellulose acetate and P(AMPS-co-MMA) exhibited improved ionic conductivity and hydrophilicity with increasing AMPS concentration, enabling tailored performance for fuel cells [138].

Low-acidity CNC@PVPA-b-PS membranes fabricated via RAFT polymerization demonstrated moderate proton conductivity, benefiting from the phosphonic acid functionality of PVPA [139]. Similarly, hybrid sulfonated CNC/PVA membranes containing triazole groups showed notable thermal stability and enhanced proton transport [140].

Further modification of bacterial cellulose with protic ionic liquids and conductive polymers, such as BG-BF_4 and polyaniline, enhanced both conductivity and mechanical integrity at elevated temperatures, making them suitable for high-temperature PEMFCs [141]. Additionally, the inclusion of phosphoric acid in sPS–bio-cellulose composites increased proton conduction, albeit lower than Nafion benchmarks [141]

CONCLUSION

Homopolymer, random copolymers and block, as well as graft copolymers possessing aromatic rings or double bonds, have been credited as suitable materials for PEMs in fuel cell application. Beyond this recognition, efforts in synthesizing alternative PEMs have been seen using perfluorinated, partially fluorinated, non-fluorinated and composite polymeric materials, in which the later has been rated as a more promising source materials for fuel cell application. This is because of the synergistic effects of the materials, which provided sustainable and enhanced high-performance PEM with relatively cost effectiveness, arising from the readily availability of some of the major base materials. Commercial production of some of these synthesized PEMs, which can compete favourably and better than Nafion, can now significantly address Nafion's monopolistic and expensive market.

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