Review Article

Additives in proton exchange membranes for low- and high-temperature fuel cell applications: A review

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ABSTRACT

Polymer electrolyte membranes, also known as proton exchange membranes (PEMs), are a type of semipermeable membrane that exhibits the property of conducting ions while impeding the mixing of reactant materials across the membrane. Due to the large potential and substantial number of applications of these materials, the development of proton exchange membranes (PEMs) has been in progress for the last few decades to successfully replace the commercial Nafion® membranes. In the course of this research, an alternate perspective of PEMs has been initiated with a desire to attain successful operations at higher working temperatures (120 −200 °C) while retaining the physical properties, stability and high proton conductivity. Both low- and high-temperature PEMs have been fabricated by various processes, such as grafting, cross-linking, or combining polymer electrolytes with nanoparticles, additives and acid-base complexes by electrostatic interactions, or by employing layer-by-layer technologies. The current review suggests that the incorporation of additives such as plasticisers and fillers has proven potential to modify the physical and chemical properties of pristine and/or composite membranes. In many studies, additives have demonstrated a substantial role in ameliorating both the mechanical and electrical properties of PEMs to make them effective for fuel cell applications. It is notable that plasticiser additives are less desirable for the development of high-temperature PEMs, as their inherent highly hydrophilic properties may stiffen the membrane. Conversely, filler additives form an inorganic-organic composite with increased surface area to retain more bound water within the polymer matrices to overcome the drawbacks of ohmic losses at high operating temperatures.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) are regarded as clean energy generation devices because they use electrochemical reactions to produce electricity. The membrane and electrodes used in these devices govern the reaction mechanisms and thus the overall performance of the system. In fuel cell systems, a solid proton exchange membrane (PEM) is required to ensure the transport of protons or hydrogen ions to allow the completion of a redox reaction [1,2]. One of the most widely used PEMs in PEMFCs is the Nafion® membrane, which consists of an aliphatic perfluorinated backbone with ether-linked side chains that end in sulfonated cation exchange sites that resemble Teflon membranes [3,4]. This structural build-up provides the Nafion® membrane with long-term stability in oxidative and reductive conditions [5]. Under a dry state, the polymer matrix of the Nafion® membrane will have a reverse micelle morphology, in which the ionic clusters are dispersed in a continuous tetrafluoroethylene phase. In contrast, the ionic domains will swell and form proton-conducting channels above a critical water content when hydrated [6]. However, further increases in water content result in a diminished concentration of protons, which causes a reduction in conductivity.

The Nafion® membrane contains a sulfonic acid group pendant to the polytetrafluoroethylene backbone, which impels proton transport across the membrane when hydrolysed with water. However, this type of membrane demonstrated severe drawbacks at temperatures lower than 0 °C and at temperatures greater than 100 °C [7,8]. The Nafion® membrane displayed poor proton conductivity at elevated temperatures due to the dehydration of water, which restricted the number of water-filled channels [9–11]. To address this issue, researchers have developed several alternatives by proposing other polymeric materials and by incorporating additives (i.e., plasticisers and fillers) [12].

Integration of inorganic fillers such as phospho-tungstic acid into the Nafion® membrane supports greater proton-transfer reactions and aids the water retention capability by reducing the vapor pressure when free water is low [13]. As a result, the Nafion® composite membrane proved competent in the temperature range of 110–120 °C. There have also been attempts to develop different polymeric materials with the primary intention of lowering the production cost while retaining the proton conductivity and mechanical properties (comparable to Nafion®) under low-temperature operating conditions (60–80 °C). Wafiroh et al. [14] demonstrated a practical composite membrane composed of sulfonated chitosan and sodium alginate with a water uptake and methanol permeability of 31.86% and 1.9×10^{-8} g/cm²s, respectively. These results were promising compared to those for the Nafion® 117 membrane, which had a water uptake and methanol permeability of 21.30% and 27.6×10^{-8} g/cm²s, respectively [15,16]. In addition, Matos et al. [17] also demonstrated that the addition of inorganic fillers (titanate nanotubes) into Nafion® is promising, as they yielded a power density that was approximately 60% greater than that of the unmodified Nafion® membrane at 120–130 °C. This increase in power density may be attributed to the remarkably large specific surface area of the titanate nanotubes, which provided a larger water retention capacity and thus resulted in the sustained performance at T ≥ 120 °C. Furthermore, there is another type of additive called plasticisers. Garaev et al. [18] reported the use of plasticisers in ionic liquids and demonstrated that they provided no substantial changes to mechanical strength while they decreased the elastic modulus and increased the creep compliance upon blending with Nafion® 112. PEMs can be differentiated by their operating temperature, whereby low-temperature PEMs fall in the range of 60–80 °C and high-temperature PEMs fall in the range of 100–200 °C. An investigation carried out by Casciola et al. [19] determined the effect of hygrothermal cycling on a Nafion® 117 membrane under a temperature range of 70–130 °C,

which depicted irreversible structural changes and a substantial reduction in the proton conductivity during heating. Thus, two operating temperatures for PEMFCs have been suggested with high-temperature PEMFCs emerging as an alternative solution to improve the limitations of the Nafion® membrane.

To date, most review papers have focused on the advancement of different types of membranes, whereas few have provided in-depth discussions regarding the role of additives in PEMs. The focus of this review paper is to cover the recent progress on PEMs under both low- and high-temperature operating conditions, while compiling cutting-edge studies related to the inclusion of additives.

## Proton exchange membrane (PEM) fabrication and transport mechanisms

The performance of PEMs is greatly influenced by the synthesis technique, which affects the PEM properties and thus its proton transport mechanisms. Chatterjee et al. [20] recently reviewed PEM fabrication techniques, which covered chemical polymerisation [21], UV polymerisation [22], plasma irradiation [23], the sol-gel method [24], the ultrasonic coating method [25], the phase inversion method [26], the solution casting method [27] and the layer-by-layer self-assembly technique [21]. Based on the discussion, solution casting, chemical polymerisation and UV polymerisation methods are the most widely used techniques in the preparation of PEMs for fuel cell applications. For solution casting, the polymer solution is first obtained through dissolution under the respective solvent prior to casting on Teflon/glass petri dishes, which is followed by the evaporation of the solvent. The resulting membranes from this method are often asymmetric in structure and consist of dense, thin-skin layers and rough, porous support layers [28]. The sol-gel method has been used in an attempt to solve both CO poisoning and water management issues on Nafion® membranes, and some of the results have been promising. Through research efforts, the preparation of Nafion®/sol-gel composites can be performed with two different approaches: (1) infiltration of the Nafion® with the sol-gel solution and (2) mixing of the sol-gel and Nafion® solutions [29]. For instance, Mauritz et al. [30] demonstrated the infiltration of Nafion® with silicon alkoxides to prepare Nafion®/SiO$_2$ composites. They showed that sulfonic acid group ($SO_3^-H^+$) clusters of Nafion® are responsible for catalysing the sol-gel reaction upon immersion in an alcohol/water solution. Then, a mixture of tetraethylorthosilicate (TEOS) and alcohol was added to the swelling solution to allow the migration of the TEOS into the clusters. Upon completing the sol-gel reactions, the in situ inorganic phase is cured [30]. The mixing approach in sol-gel reactions is more straightforward when the Nafion® solutions and silicon alkoxides are prepared in a mutual solvent prior to casting into a petri dish; this approach offers a wider variation in the silica content in the Nafion® matrix. However, this wider variation in silica content leads to an increase in the film brittleness.

The proton transfer phenomena within the polymer matrices can be categorised into two basic mechanisms: vehicular and Grotthuss. The vehicular mechanism refers to the proton diffusing and migrating with a so-called "vehicle", such as a hydronium ion (H_3O^+), through the medium of water. Conversely, the Grotthuss mechanism refers to the proton hopping between the water molecules by hydrogen bonding [31]. Luduena et al. [32] concluded that the Grotthuss-type hopping mechanism is dominant compared to the vehicle transport mechanism in a PEM because it is supported by the short-distance transport of hydronium ions to neighbouring conductive sites as shown in Fig. 1 [32].

According to Choi et al. [33], an environment that is advantageous to the Grotthuss-like proton transfer mechanism is equally advantageous to water transfer in the presence of a homogeneous electric field. Specifically, the free water molecules in the membrane are responsible for the water bridge formation within the membrane and thus facilitate the proton transfer through the functional groups, such as the sulfonic groups in the Nafion® membrane [34,35]. Thus, the Grotthuss mechanism is known to be a relay mechanism that not only aids the "slow" proton transport of the vehicular mechanisms but also accommodates the unexpectedly high transfer rate of protons through the continuous formation and breakage of hydrogen bonding from one functional group to another. Sun et al. [6] explained that H_3O^+ is the dominant transfer particle at low water content and that the hydrated ion of $H^+(H_2O)_2$ is the main transfer particle at higher water content. It was thought that under low water content, each of the protons was capable of binding with only one free water molecule and forming H_3O^+; conversely, at a higher water content, more free water molecules readily combined with protons to form $H^+(H_2O)_n$ [6]. The proton conductivity in a PEM can be visualised as an increase in the dominance of H_3O^+ transport through the support of the Grotthuss mechanism at high temperature.

The role of water in the PEMFC system is to establish H-bonding bridges between the conductive sites. The Grotthuss-type transport mechanism also exhibits greater proton mobility than the vehicular mechanism (approximately ten times higher in speed) owing to the small lifetime of the H_3O^+ ions (approximately 3×10^{-12} s) [36]. A study on the proton transport in the zeolite membrane indicates that the vehicular-type mechanism is dominant over the Grotthuss
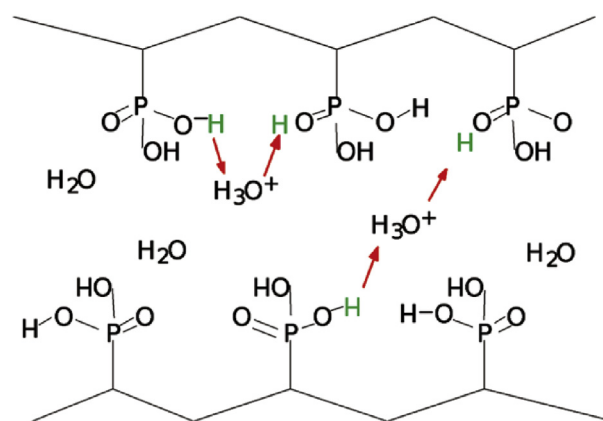
Fig. 1 — Schematic of the Grotthuss-type transport mechanism, which indicates the short-distance transport of hydronium (H_3O^+) ions to the neighbouring acids [32].

mechanism at temperatures above 473 K ($\approx 200\ °C$) [37]. Based on this, one could hypothesise that the increase in temperature results in a decrease in relative humidity and simultaneously leads to a disconnection of the ion channels. Therefore, the proton transfer occurs by the molecular motion of water between the clusters [38]. Hence, it can be summarised that the transport mechanisms and proton transport rate are mainly impacted by the operating temperature, which has a direct correlation with the water content in the membrane.

Types of proton exchange membranes (PEMs)

Despite the market dominance of the Nafion® or perfluorosulfonic acid membrane for PEMFC applications, alternative materials are being developed to overcome some of the drawbacks of the commercial membrane [39]. Some critical drawbacks exhibited by the Nafion® membrane are the poor mechanical and chemical stabilities at elevated temperatures due to dehydration of the membrane; these drawbacks cause severe degradation, high fabrication cost, and high methanol crossover, which reduces the fuel efficiency and poisons the cathode catalyst by oxidising the methanol [40—47].

In practice, the common materials that are being extensively studied to replace Nafion® membranes include sulfonated poly (ether ether ketone) (SPEEK), polybenzimidazoles (PBI), chitosan and poly (vinyl alcohol) (PVA) [48—51]. These materials show their respective strengths in different aspects of proton conductivity, water uptake, and mechanical and thermal stabilities. The selection of materials is divided on the basis of the operating temperature of the membrane. The criterion beneath low- and high-temperature PEMs will be discussed briefly in this section.

Low-temperature proton exchange membranes (PEMs)

Low-temperature PEMFCs are the current state-of-the-art fuel cells used in transportation and mobile devices, and they have an operating temperature in the range of approximately 60—80 °C [52]. The challenges in the development of PEMFCs for low temperature applications, specifically for transportation applications, include the tolerance to fuel impurities, such as carbon monoxide (CO) and hydrogen sulfide (H_2S) (<20 ppm) and heat rejection [53]. In an effort to find more efficient or lower cost membranes, attempts have been made using different types of polymeric materials, such as chitosan composites, sulfonated polysulfone (SPSf) composites, sulfonated polyimide (SPI) and more [54—56]. These materials have excellent water uptake characteristics (Feng et al. [57] reported an improvement of 8.4% by the addition of graphene oxide (GO) in the Nafion® membrane), good thermal stability (Ozden et al. [55] demonstrated that a SPSf/zirconium hydrogen phosphate (ZrP) composite membrane was thermally stable up to 200 °C), and methanol crossover (Purwanto et al. [58] reported that a biocomposite membrane composed of chitosan and organophilic montmorillonite (MMT) exhibited a methanol permeability of $3.03 \times 10^{-7}\ cm^2s^{-1}$, which was substantially lower than that of a pristine Nafion® membrane, which was $2.19 \times 10^{-6}\ cm^2s^{-1}$ [59]). Different methodologies and strategies have been applied to improve the conductivity

and stability of membranes for low-temperature PEMs, such as grafting, cross-linking, or combining polymer electrolytes with nanoparticles, additives (e.g., carbon nanotubes (CNTs), GO), and acid-base complexes by electrostatic interactions or by employing layer-by-layer technologies [60—66]. A composite membrane that consists of an intermolecular ionic crosslinked SPEEK/amino-substituted PEEK (APEEK) membrane was prepared by Li et al. to evaluate its potential in PEM applications [67]. When the APEEK content increased from 1% to 10%, the resultant membrane exhibited a substantial reduction in the proton conductivity owing to the losses in water uptake—which restricted the formation of continuous proton transfer channels—the decrease in methanol permeability and the increase in relative selectivity; these results are shown in Fig. 2. The composite membrane was considered to be a suitable PEM for direct methanol fuel cell (DMFC) applications.

Apart from varying synthesis strategies, there is also a wide range of studies with biocompatible material-based membranes, which have the intrinsic advantages of low cost, abundant natural availability and biodegradability; these membranes are mainly useful in DMFC and PEMFC applications because of their lower operating temperatures. Suganthi et al. [68] evaluated the effectiveness of a PVA/citric acid (CA) composite membrane with citric acid (CA) as a crosslinker in DMFC applications. The group reported that the addition of a CA crosslinker substantially improved the membrane properties with a proper ratio of hydrophobic/hydrophilic domains, which enhanced the electrochemical selectivity and reduced the methanol permeability [68]. Smitha et al. [50] also reported a membrane with high proton conductivity (3.8×10^{-2} S/cm) and low methanol permeability ($3.9 \times 10^{-8}\ cm^2/s$) that is composed of a 50:50 wt% ratio of ionically crosslinked chitosan and poly (acrylic acid) (PAA).

In addition, a nanocomposite membrane prepared using bacterial nanocellulose (BC) and Nafion® for low-temperature PEMFCs was also reported by Jiang et al. [69]. The experiment was conducted at room temperature with and without annealing to analyse the performance efficiency in PEMFC and DMFC applications. It was demonstrated that an annealed membrane with a BC-to-Nafion® ratio of 1:7 (B1N7) was
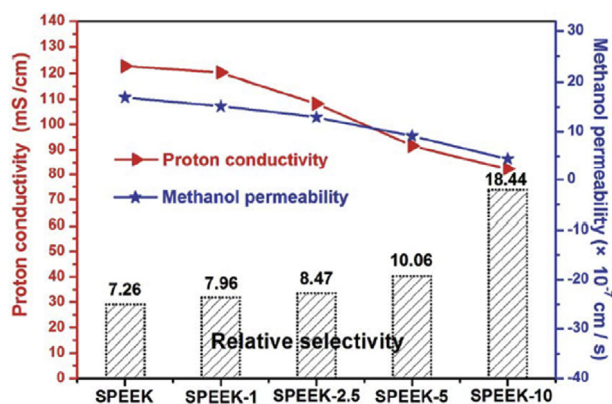
Fig. 2 — Relative selectivity, proton conductivity and methanol permeability of the pristine SPEEK- and APEEK-modified composite membranes [67].

capable of delivering a larger maximum power density—106 mW/cm^2 in PEMFCs and 20.4 mW/cm^2 in DMFCs—than that of other BC-based membranes [69]. In addition, a morphology study of the nanocomposite membrane also revealed that the annealing process is capable of stiffening the structure of the membrane while increasing the mechanical strength. There are a number of studies related to the development of biopolymers because of their economical and sustainable perception. Wafiroh et al. [14] reported the synthesis of biocomposite PEMs composed of chitosan and sodium alginate as the host polymers and sulfuric acid (H_2SO_4) as the sulfonating agent for PEMFC applications. The group demonstrated a low methanol permeability of 2.0×10^{-8} g/cm^2s; in comparison, the methanol permeability of Nafion® 117 is 27.6×10^{-8} g/cm^2s [70]. Despite the many types of materials studied for low-temperature PEMFCs, there has been limited discussion with regard to the mechanical stability of the alternative membranes.

High-temperature proton exchange membranes (PEMs)

The intention of developing an alternative PEM technology at temperatures > 100 °C is to overcome the following shortcomings of low-temperature PEMFCs: (1) in water management control, perfluorinated-based PEMs become less conductive under high temperature conditions due to the evaporation of water, which causes the reduction in ion channels and proton transport within the polymer electrolyte; (2) a mixture of liquid- and gas-phase water co-exists during the operation and requires complicated electrode preparation techniques such as impregnating the Nafion® solution by spraying/brushing methods in preparation of the gas diffusion layer; and (3) a low tolerance to CO and other impurities (up to a maximum of 25 ppm at 80 °C) [71—73]. Thus, this sums up the principle for the implementation of a high-temperature PEMFC system.

The development of polymeric materials to be utilised in high-temperature conditions is a considerable challenge for researchers because there are few important criteria that must be addressed, such as (1) the degradation rate of PEMs, where the parameter must be high enough for it to be sustained under elevated temperatures, (2) the operational startup time and (3) the ability of the membrane to operate under high temperatures and to exhibit high conductivity at low humidity [74]. The phosphoric acid-doped PBI membrane is recognised as one of the most promising polymer systems for high-temperature PEMFCs [75]. This membrane possesses attractive intrinsic properties, such as high thermal and mechanical stabilities (indicating a break-in period of 120 h under continuous load conditions with H_2 as the fuel source) and is categorised under the development of high-temperature fuel cell applications (in the range of approximately 120—200 °C) [76]. One of the earliest studies was executed by Wainright et al. [77] with unmodified phosphoric acid-doped PBI membranes under varying temperature ranges from 120 to 192 °C. According to the conducted experiment, although the conductivity of the membrane at low temperatures is less than that of other fuel cell electrolytes, the conductivity of the membrane increases substantially at higher temperatures, which indicates its application in high-temperature

operations (the proton conductivity reached a maximum value of approximately 0.039 S/cm at approximately 190 °C).

A study by Kim et al. [78] on sulfonated poly (phthalazinone ether sulfone ketone) (SPPESK)/silica hybrid membranes was used to correlate the state of water and the ion conducting mechanism, which changes with operating temperature. Accordingly, the state of water within a polymer can be distinguished as free water (water that is not intimately bound to the polymer chain), freezing bound water (water that is either weakly bound to the polymer chain or interacts weakly with non-freezing water and displays relatively broad melting endotherms) and non-freezing bound water (water that shows no phase transition within temperature ranges from −73 to 0 °C and arises from a strong interaction with the polymer) [79]. According to Ren et al. [80], the group reported that an increase in temperature would diminish the hydrogen bonding that bound due to the fast evaporation of the absorbed water. As mentioned, the bound water participates in the Grotthuss mechanism, while free water takes part in both the vehicular and Grotthuss mechanism. Therefore, it is crucial to consider the polymeric materials that are used in high-temperature PEMs, which are capable of retaining the water content, particularly the bound water, within the polymer matrix at high temperatures.

Li et al. [81] prepared a high-temperature PEMFC system by utilising a blend polymer electrolyte of PBI and sulfonated polysulfone for a DMFC system with an operational temperature up to 200 °C. The group evaluated the performance of blend PEMs, and the system demonstrated a power density of >0.4 W/cm^2 at a cell voltage of 0.6 V under atmospheric pressure and with a noble catalyst loading of 0.45 mg/cm^2 [81]. PBI-based PEMs also exhibit exceptional high-temperature stability, which allows the membrane to operate at a higher working temperature of approximately 200 °C; the resulting tolerance level to CO is 10,000 to 30,000 ppm [67,82,83]. This resulted in the possibility of using an integrated system with reformed hydrogen directly from a methanol reformer without further CO removal throughout the operation cycles, as shown in the literature by Das et al. [84]. Furthermore, a maximum power density of 400 mW/cm^2 was obtained for the SPEEK DMAc/DMF at 0.5 V using humidified H_2/air in a single cell at 130 °C; conversely, the maximum power density of the a Nafion®-112 (N112) membrane was 270 mW/cm^2 under the same conditions. Although the SPEEK membrane exhibits good proton conductivity at a high water content, the proton conductivity gradually decreases when the hydration level is low (increasing from room temperature to 80 °C) [85].

PBI-based membranes are among the most widely used and studied high-temperature PEMs due to the high reactivity of their polymer backbone, which allows chemical modifications, such as sulfonation, to modulate its physicochemical properties, including the thermo-oxidative stability, polymer solubility, and film processing behaviour [86]. In principle, there are two different approaches to sulfonate the polymer backbone of the PBI membrane: (1) synthetically modifying the benzimidazole monomers prior to polymerisation and (2) post-polymerisation substitution of the polymer [87]. Hasiotis et al. [88] focused on the development of PBI and sulfonated polysulfone composite membranes that were doped with phosphorus acid. The blending of the PBI/sulfonated

polysulfone system was intended to chemically modify the composite to produce both anionic and cationic sites, which resulted in a strong electrostatic interaction through the ionic cross-linking between the polymers. These results produced substantial increases in mechanical strength compared to that of pure PBI membranes. Furthermore, the acid doping level of phosphorus acid was also found to play a substantial role in defining the ionic conductivity of the PBI/sulfonated polysulfone composites. The ionic conductivity was 7×10^{-1} S/cm at an acid doping level of 2300 mol% at 160 °C. Ion migration through the membrane increased because of the extraneous phosphoric acid, which was introduced as the conducting active species apart from sulfonate-water clusters.

Although PBI-based membranes have received considerable attention as promising polymeric materials for high-temperature PEMFC technologies, other polymers and composite systems have also been proposed in the last few decades. Gautier-Luneau et al. [89] proposed the use of organic-inorganic proton-conducting PEMs synthesised by the hydrolysis-condensation process of three different alkoxy silanes (benzyltriethoxysilane, n-hexyltrimethoxysilane, and triethoxysilane) followed by sulfonation under stoichiometrically equivalent dichloromethane and chlorosulfonic acid. The resulting solutions were then cross-linked with divinylbenzene using a platinum complex as a catalyst to improve the polymer-polymer interactions through divinyltetramethyldisiloxane covalent bonding in tetrahydrofuran (THF) for the hydrosilylation reaction. The TGA data showed an endothermic peak, which indicated that the composite membrane was thermally stable up to 250 °C [89]; therefore, the membrane shows promise as a solid state PEM for high-temperature PEMFC technologies.

In accordance with Bose et al. [90], the group reviewed recent advances and challenges in the development of high-temperature PEMs. Although it was previously elaborated that the PBI-based membrane was effective at high operating temperatures, the conductivity of such PEMs reportedly exhibited a gradual decrease from 125 to 175 °C (125 °C = 0.078 S/cm and 175 °C = 0.045 S/cm) [91]. This decrease in conductivity is due to the absence of humidification in high-temperature PEMFCs, which then causes large ohmic losses that subsequently lower the efficiency of the membrane. The introduction of filler additives could be effective in achieving improved water retention capacity, which would result in an increase in membrane swelling at lower relative humidity and offer a conducting path to ease the transport of protons through the membrane [90].

Table 1 summarises the types of membranes that are used in both low-temperature and high-temperature PEMFCs.

Integration of additives in polymer electrolyte membranes

Additives are defined as substances that are intentionally added to a polymer mixture through physical mixing [95]. With the intensive development of PEMs based on polymeric materials, the introduction of additives has received much attention in recent years due to their ability to further alter the

Table 1 — Examples of PEMs under different operating conditions.

	PEM	FC[a] Type	WU[b] (%)	WS[c] (%)	MP[d] ($\times 10^{-8}$ g/cm²s)	PC[e] ($\times 10^{-2}$ S/cm)	Single-cell (mW/cm²)	Ref.
Low-temp.[f]	SPEEK membrane	DMFC	25.0	—	14.5	1.6800	—	Li et al. [85]
	Nafion® 115 membrane	DMFC	20.0	—	493.5	4.1800	—	Li et al. [85]
	Annealed bacterial nanocellulose/Nafion® composite	PEMFC	21.0	7.2	133.0	4.8000	106.0 (room temp.)	Jiang et al. [69]
	Sulfonated chitosan-alginate brown membrane	PEMFC	—	31.9	1.9	0.0009	—	Wafroh et al. [14]
	PVA/citric acid composite	DMFC	42.5	—	20.4	0.1240	—	Suganthi et al. [68]
	SPEEK/APEEK composite	DMFC	25.1	—	44.7	1.7200	—	Li et al. [67]
	Chitosan/PAA composite	DMFC	26.0	—	3.9	0.0380	—	Smitha et al. [50]
	PVA/sulfosuccinic acid membrane	DMFC	22.0	—	140.0	3.2000	—	Rhim et al. [92]
High-temp	SPEEK DMAc/DMF membrane	PEMFC	31.0	—	—	—	400.0 (at 130 °C)	Carbone et al. [93]
	PBI/sulfonated polysulfone	DMFC	—	—	—	—	494.0 (at 200 °C)	Li et al. [81]
	Phosphorus acid doped-PBI/sulfonated polysulfone	PEMFC	—	—	—	2.1000 (at 175 °C)	—	Hasiotis et al. [88]
	Poly (benzyl sulfonic acid)siloxane	DMFC	—	—	—	1.6000	—	Gautier-Luneau et al. [89]
	Aquivion/expanded-polytetrafluoroethylene (ePTFE)	PEMFC	28.4	—	—	18.0000 (at 120 °C)	—	Xiao et al. [94]

^a FC refers to the fuel cell.
^b WU refers to the water uptake.
^c WS refers to the water swelling.
^d MP refers to the methanol permeability.
^e PC refers to the proton conductivity.
^f temp. refers to the temperature.

physical and chemical properties of the pristine polymer matrix. Additives play a role in either softening or hardening the polymer skeletal structure, which is dependent on its intrinsic properties. For instance, the addition of inorganic fillers, such as silica, may utilise the combined advantages of organic polymers (e.g., flexibility, processability) and inorganic materials (e.g., mechanical strength, thermal stability) to counteract the drawbacks of dehydration and mechanical instability at higher temperatures [96]. Altering the properties of the membrane could create certain advantages in the development of PEMs. In this review, the additives will be categorised into plasticisers and fillers.

Plasticiser additives

In general, plasticisers are low molecular weight compounds that can be attached to high molecular weight polymers to improve their processability, impact strength, and elongation. When added to the polymer system, the plasticisers will penetrate into the amorphous regions of the polymer matrix, which establishes the polar attractive forces between the polymer chains; this leads to an increase in the segmental mobility and thus a decrease in the glass transition temperature (T_g) and crystalline region proportion. The main effect generated by plasticisation can be rationalised as an increase in the "free volume" of the polymer-plasticiser system. The plasticisers form secondary bonds (intermediate hydrogen bonding) with the polymer and reduce the secondary bonds between polymer chains with a continuous distribution of interstitial "free volume" to spread the polymer chains apart for greater swelling of the plasticised polymer [97]. Thus, the flexibility of the plasticised polymer is enhanced by this plasticisation effect; moreover, the plasticised polymer experiences a decrease in tensile strength and an increase in elongation at break. Fig. 3 illustrates an example of the plasticisation effect that occurs after adding the plasticiser into the polymer system as described by Fong et al. [98].

In practice, the mutual miscibility between plasticisers and polymers is an important factor to improving their effectiveness on dispersion throughout the polymer and disrupting the intermolecular interactions. The plasticiser is meant to form a polymer-plasticiser system with permanent or semi-permanent interactions and to prevent the tendency of the
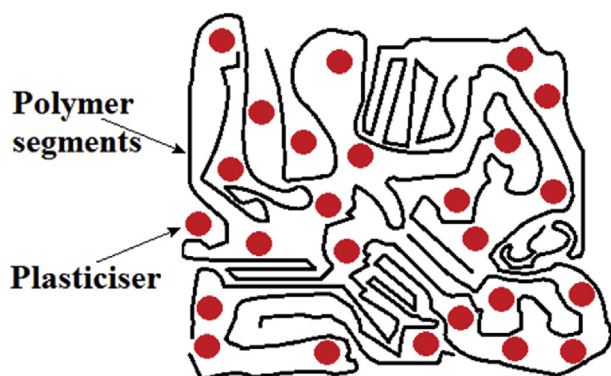
plasticiser to wear off due to evaporation or volatilisation. A non-soluble plasticiser will lead to brittleness in the system owing to ineffective diffusivity of the plasticiser in the polymer matrices. The use of plasticisers can be categorised into two major forms. If a plasticiser is said to be soluble at a high concentration of polymer, it is classified as a primary plasticiser. Primary plasticisers are capable of strongly and rapidly attaching to the polymer under a normal processing temperature range and are not exuded from the polymer matrices [99]. A secondary plasticiser is represented with two phases upon plasticisation: (1) a single phase that represents the semi-plasticised effect and (2) a phase that represents the fully plasticised effect between the plasticiser and polymer. The secondary plasticiser has a lower gelation capacity and limited compatibility with the polymer. Further breakdown of the mechanisms and characteristics related to plasticisers will be skipped, as an in-depth review was attempted under a previous study [100].

A comprehensive work investigating the compatibility of plasticisers to non-miscible starch/zein biocomposite blends was attempted by Favero et al. [101]. Five sets of plasticisers ((1) glycerol, (2) 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) ionic liquid (IL), (3) urea-choline chloride deep eutectic solvent (DES), (4) glycerol-choline chloride DES, (5) cholinium acetate IL) were evaluated through mechanical property testing, morphological study and finite element modelling that employs the representative elementary size (RES) concept. The results of the study indicated that the cholinium acetate plasticised blend outperformed other candidates, as it had the highest miscibility and exhibited high elongation at break and tensile strength [101]. The three ionic plasticisers ((1) [BMIM]Cl, (2) urea-choline chloride DES, and (3) glycerol-choline chloride DES) lead to an imperfect interphase (leading to bad plasticisation effect) due to the presence of chloride anions. Although Biswas et al. [102] concluded that [BMIM]Cl is an efficient solvent for both starch and zein, the zein polymer was found to be insoluble in choline chloride-based DESs. An imperfect interfacial effect created by the three ionic plasticisers resulted in material failure upon stretching the polymer blend.

Oliveira et al. [103] demonstrated the feasibility of using a nylon 6,6 plasticiser to mechanically stabilise a sulfonated-PVA (SPVA)/chitosan membrane. Amide groups in the backbone chain of nylon (a polyamide) allowed hydrogen bond formations with other polymers. SPVA/chitosan membranes with nylon as a plasticiser exhibited greater thermal stability due to improvements in the polymer-plasticiser interaction, which was attained through an increase in hydrophobicity that induced mechanical stability. However, a drawback of the plasticisation was the narrowing of the hydrophilic channel size of the polymer, which lead to decreased proton diffusion across the membrane [103]. Hence, the work reflected a good interpretation of the positive and negative effects that a plasticiser could potentially deliver when added to a pristine or composite membrane.

In general, plasticisers are non-volatile substances that are applied to penetrate into the polymer and combine into a uniform mass to form a soft and flexible structure. The addition of plasticisers into the polymer electrolyte membrane can be summarised by different approaches according

Fig. 3 — Graphical illustration of the addition of the plasticiser into the polymer system.

to the situational requirements. Dimensional instability is one of the major drawbacks in most water-soluble polymers due to the high water affinity that is formed between the water molecules and the membrane [104]. As such, hydrophobic plasticisers (water insoluble) are proven to be more favourable for increasing the resistance to water vapor permeation due to the collapse of micro-voids in the membrane. Such plasticiser types are widely used in the pharmaceutical industry for the production of biodegradable materials to prevent the increase in water permeability and susceptibility of the matrix to environmental humidity [105]. For instance, Hung et al. [106] presented a work with various hydrophobic plasticisers for use in drug delivery systems. Based on this work, the group anticipated that the addition of hydrophobic plasticisers within polymer films would create a more hydrophobic environment for water permeation and thus result in a decrease in the diffusion coefficient of water. However, there are substantial drawbacks to having this type of plasticiser for PEM applications because the increase in concentration would cause a reduction in the mechanical properties (tensile strength and elongation at break) of the PEM [107,108]. Furthermore, these types of plasticisers also contain the drawback of potential phase separation that subsequently leads to flexibility losses or to the formation of discontinuity zones during the membrane drying process [109].

On the other hand, hydrophilic plasticiser types are well established for PEM applications. Some of the common uses of these plasticiser types are found in propylene glycol, glycerol and water. For instance, Fong et al. [98] demonstrated the impact of the addition of hydrophilic plasticisers on PVA films. It was suggested by this group that the introduction of such plasticisers enable the disruption of inter-chain hydrogen bonding through penetration of the polymer system while promoting higher chain mobility via the increases in the size of the free volume cavities [110]. Table 2 illustrates some examples reported by researchers who used either hydrophilic and hydrophobic plasticisers in PEM applications.

Filler additives

Filler additives have been thoroughly studied with the aim of changing and improving the physical and mechanical properties of polymers while also reducing the fabrication cost. In earlier studies, the fillers were intended to improve or overcome the fire resistance of plastics without modifying the other properties. Fillers are solid particles that are either fine particles (particulate fillers such as China clay) or fibrous in nature (glass fibre) [117]. Fillers may be classified into two categories: (1) inorganic and (2) organic fillers. Prior to the selection of effective fillers, a complete understanding of the individual characteristics is essential because each class of filler appears to exhibit specific characteristics suited to a given application. Depending on the application, a filler may be selected based on its advantages, such as low cost, abundant supply characteristics, compatibility and ease of mixing with other additives, high mechanical strength, low moisture absorption, high heat resistance, good electrical characteristics, ease of moulding and absence of abrasive or chemical reactions on the mould [118].

Table 2 — Types of plasticisers reported in the literature.

Plasticiser Types	Plasticiser Additives	Polymer System	PC^g (mS/cm)	WU^h (%)	EM^i (MPa)	Ref.
Hydrophilic	1-Butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$)	Poly (3,4-ethylenedioxythiophene) (PEDOT)	–	–	–	Bircan et al. [111]
	1-Hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (MC$_6$)	PBI	35.0 (at 25 °C)	–	80.0	Hooshyari et al. [112]
	Glycerol	PVA	–	–	–	Fong et al. [98]
	Water	PVA-sodium alginated (SA)/SPVA	–	–	–	Fong et al. [98] and Bo et al. [113]
	Choline chloride:urea (ChCl:urea)	Chitosan/carboxymethyl cellulose (CMC)	15.7 (at 25 °C)	49.4	–	Wong et al. [114]
Hydrophobic	Tributyl citrate (TB)	Gelatin	–	–	30.7	Andreuccetti et al. [105]
	Acetyltributyl citrate (ATB)	Gelatin	–	–	27.7	Andreuccetti et al. [105], Yu et al. [115] and Hoglund et al. [116]
	Nylon 6,6	SPVA/chitosan	7.3 (at 50 °C)	32.4	3.4	Oliveira et al. [103]
	Dibutyl phthalate (DBP)	Surelease	–	–	15.1	Hung et al. [106]

g PC refers to the proton conductivity.
h WU refers to the water uptake.
i EM refers to the elastic modulus.

Inorganic fillers

Inorganic-type fillers are by far the most common filler additive used in PEMs to reduce the crystallisation ability and improve the mechanical strength and ionic conductivities of the polymer [119]. There are several categories of materials that can be added as the filler phase, including oxides, heteropolyacids and their pyrophosphates, carbon-based materials, reinforcing polymer phases, and ionic liquids (ILs) [120]. Carbon black (CB) and SiO_2 are by far the most widely studied inorganic fillers for use in the rubber industry, in which CB can impart strength and toughness to elastomers, which results in materials with greater durability and resistance towards tearing, abrasion, and flexural fatigue [121].

Although the addition of inorganic fillers into polymers improves many useful properties, the fillers also introduce certain complex phenomena, such as an increase in the percentage of voids present and/or changes in the weight of the filled product, which ultimately influence the density of the polymer system [122]. Agrawal et al. [122] reported such phenomena for all sets of composites with a proportional increase in both the filler content and polymer density. For instance, the study found that an increase in the filler content will consecutively lead to a higher number of voids within the polymer matrices and that a decrease in the fatigue resistance will increase the susceptibility of the matrix to water penetration. Exceeding the upper limit of the filler content may lead to inter-particle interference, which can potentially degrade the properties of the filler and the composite. Subsequently, the filled composite would be mechanically unstable due to improper wetting conditions.

However, we shall not overlook the advantages of the filled polymer system. As mentioned in Section Filler additives, a list of properties may be enhanced by the addition of fillers. Oyama et al. [123] studied the effect of inorganic fillers on both the thermal and mechanical properties of isotactic polypropylene (iPP) composites. In this study, magnesium hydroxide (MH) inorganic fillers were modified with dodecanoic acid (DA) and dodecylphosphate (DP) to enhance the interfacial adhesion between the filler and the polymer matrix. It was demonstrated that the modification by DA and DP produced ionic interactions with the MH surface and enabled a substantial improvement in the toughness and ductility (>300%) of the PP/MH composite. In addition, thermal analyses indicated an increase in the crystallinity and a decrease in the T_g after adding MH inorganic fillers to the matrix. These results are probably caused by the presence of a non-wetted interface in the PP/MH composite; images of this non-wetted interface are compared to those of the surface modified MH composites in Fig. 4 [123]. To interpret the thermal analysis results, the authors constructed a hypothetical explanation that suggests the possibility of a plasticisation effect in the iPP/MH-DA and/or iPP/MH-DP composites by the organic reagent (DA and DP), which justifies the additional increase in crystallinity and decrease in T_g.

An interesting study was conducted by Handayani et al. [124] to clarify the effect between organic and inorganic fillers on the polymer system. Two sets of SPEEK membranes composed of an acrylonitrile butadiene styrene (ABS) organic polymer and a SiO_2 inorganic powder were prepared. It was found that the SPEEK/ABS composite membrane had higher
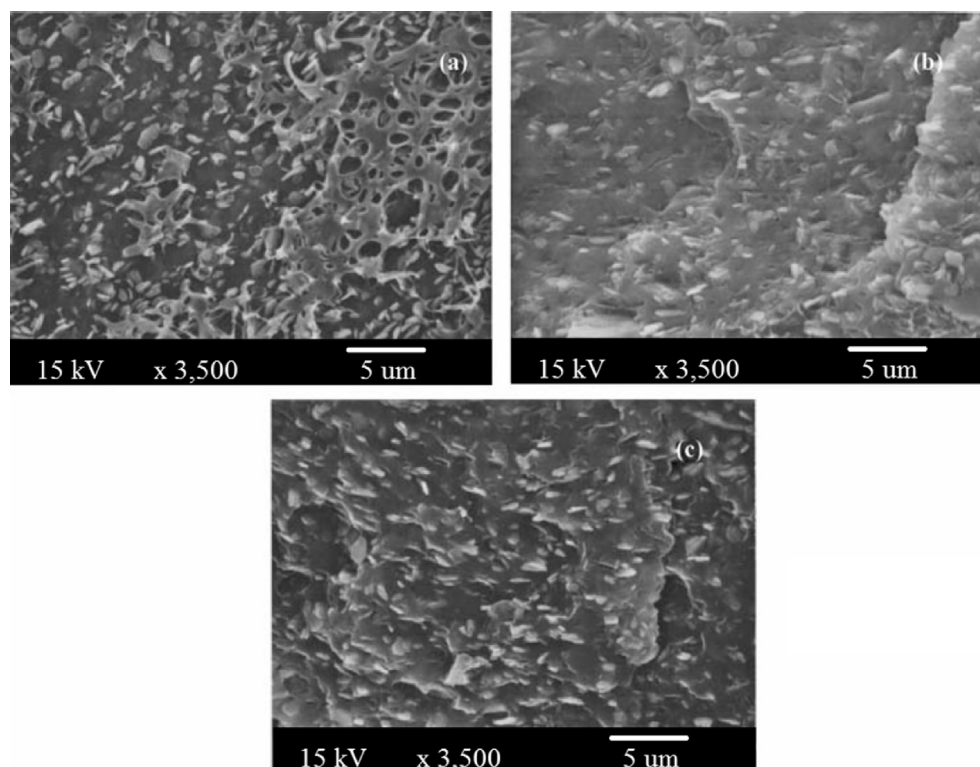

Fig. 4 — SEM micrographs of the (a) iPP/MH, (b) iPP/MH-DA, and (c) iPP/MH-DP composites [123].

crystallinity, which limited the segmental motion of the polymer chains and thus, reduced the flexibility and proton conductivity compared to those of the SPEEK/SiO_2 composite membrane.

The involvement of such filler additives is shown to be able to develop moderate interactions between the PEMs and the inorganic fillers. Inorganic fillers are mostly in the form of hygroscopic oxides, which aim to increase the water retention of the membranes under hotter and drier operating conditions or to decrease the methanol permeation during operation as a DMFC [125].

SiO_2 has been one of the most popular inorganic fillers used in the development of PEMs. According to Arico et al. [126], the incorporation of SiO_2 will narrow the hydrophilic channels of a PEM (small-angle X-ray scattering (SAXS) shows a size decrease from 7.9 to 6.5 mm). However, such an effect was not reflected on the proton conduction properties, as the Arrhenius plots of the proton self-diffusion coefficients for both the pristine and SiO_2-filled composites demonstrated a similar activation energy, E_a. Moreover, the addition of SiO_2 also increases the crystallinity of the PEM through a shift of the crystalline peak to higher Bragg angles [11]. This statement is further proven by Liu et al. [127], who performed a related study with talc, $Mg_3Si_4O_{10}(OH)_2$, as an inorganic filler in the PLA membrane. The group suggested that the interfacial adhesion between the polymer and inorganic filler is vital. Their work demonstrated that the addition of hydroxyapatite (HA) into the PLA led to a reduction in crystallinity, which may be attributed to the presence of voids adjacent to the HA particles that led to early failure of the composite and thus limited the mechanical properties [127,128]. Nevertheless, both inorganic fillers (talc and HA) were proven capable of improving the mechanical properties of the composite in terms of the toughness. The authors believed that the crystallinity and interfacial properties that affect the tensile strength can be improved by optimising the filler content.

In relation to the filler content and polymeric properties, Solanki et al. [129] reported a study of titanium oxide (TiO_2)-filled SPVA membranes. Through thermal stability analyses, it was determined that increasing the TiO_2 content up to 20% improved the thermal stability by approximately 20% compared to that of $TiO_2 = 5\%$. The enhancement is thought to be attributable to the higher TiO_2 content that contributed towards better polymer matrix crystallinity, which limits the movement of the chain segment of the polymer and thus results in higher thermal stability. In addition, the hygroscopic properties of TiO_2 also reacted to a higher water uptake of composite; which can create more hydrogen bonding between the water molecules and assist in greater ion mobility between polymer matrices.

Organic filler additives

Organic fillers, such as wood flour, are among the first organic-type fillers that have been commercially produced since 1906 for various applications, including soil amendments, extenders for glues, and absorbents for explosives [130]. Organic fillers are attractive as filler additives for various plastic materials because of their low price, low density and renewable nature. These fillers consist of a sub-category of cellulosics, lignins, proteins and synthetics. Steven et al. [131] added the organic filler ((1) N,N' −dimethylacrylamide (NNPAAM), (2) poly (acrylamide) (PAAM)) to a PEO-based membrane. The results demonstrated that the addition of PAAM organic fillers produced an effective reduction in the crystallisation of the PEO-$LiClO_4$ composite system and gradually separated into a flexible amorphous phase, which led to a reduced T_g value. A similar trend was observed with NNPAAMs that contain PEO-$LiClO_4$-based composite electrolytes.

The utilisation of organic fillers is extremely uncommon when fabricating a PEM, as there have not yet been any positive results reported in the development of a greater amorphous phase that led to an increase in the proton conductivity compared to that of pristine polymers. Mantia et al. [132] suggested that this phenomenon occurs because of the flammable nature of the natural organic materials during the study of their mechanical properties. The addition of organic fillers (i.e., wood fibres, kenaf fibres, and sago starch) lowered the heat deflection temperature when compared to that of the inorganic fillers. Due to the higher heat absorption associated with the usage of organic fillers, limited work has been performed on organic fillers, which is a drawback to the development of PEM technologies [133].

Additives for PEMs in fuel cells based on the operating temperatures

Additives for low-temperature proton exchange membranes (PEMs)

A few of the key properties that are essential to consider when evaluating the proton conductivity of polymer-additive systems that are used as PEMs are listed hereafter: (1) the compatibility between polymers and additives, (2) dispersibility of the additives during processing and (3) the orientation and exfoliation of the additives. Currently, nanofillers such as nanosilicas and nanoclays have been actively investigated for PEMs in an attempt to modify the ionic channels and increase the ionic transport [53,134]. Mishra et al. [135] attempted to study the ion transport enhancement by introducing IL-functionalised nanostructured silica fillers into Nafion® electrolyte composites. The study showed that an increase in the T_g was observed after adding the IL-silica fillers into the Nafion® (from 112 °C to 121 °C), which implies an improvement in the thermo-mechanical stability due to the good compatibility between the inorganic silica and Nafion® [135]. Ionic conductivity analysis was also carried out for both the unmodified and IL-functionalised silica for comparison. Three sets of temperatures (30, 60, and 90 °C) and relative humidities (30, 60, and 90%) were studied to speculate the changes in ionic conductivity from hydrous to anhydrous conditions of the composite membrane. At 90 °C and 90% relative humidity, the Nafion®/IL-functionalised silica composite membrane exhibited the highest conductivity, which was 0.375 S/cm; these results are ascribed to the presence of highly hydrophilic and conductive ILs that modified the proton conduction mechanism and assisted the ion transport within the polymer chains of Nafion®. At 90 °C and 30% relative humidity, the IL-functionalised silica-filled Nafion® composite membrane measured a conductivity of 0.0546 S/cm

compared to pristine Nafion® membrane conductivity of 0.015 S/cm [135]. The increases in the ionic conductivity were believed to be supported by the high water retention capability of the inorganic filler, in which the additional IL functionalisation substantially improved the formation of interconnected ion channels in the Nafion® membrane and delivered promising results under both high and low relative humidity conditions [90].

In a study conducted by Yu et al. [115], CB and acetyl tributyl citrate (ATBC) were selected as the filler and plasticiser, respectively, for poly (lactic acid) (PLA) polymers. The group reported that the addition of ATBC in the PLA/CB composite could potentially lower the processing viscosity and exhibit a strong interaction between the PLA/ATBC matrix and CB particles (favouring CB dispersivity with lower agglomeration), as demonstrated in Fig. 5. In addition, it was demonstrated that the increase in ATBC content from 0 to 30 wt% decreased the percolation threshold of the carbon black and hence increased the ionic conductivity [136]. It was further indicated that the excessive ATBC could potentially form its own phase domain while also demonstrating a synergistic effect on the formation of a conductive network along with CB [136].

Beydaghi et al. [137] reported the synthesis of a PEM composed of PVA and sulfonated GO as the host polymers and glutaraldehyde (GLA) as the crosslinker for low-temperature class PEMFC applications. The particular study conducted by this group demonstrated improved thermal stability for PVA/ sulfonated GO composite membranes among the various membranes (pristine PVA and PVA/GO membranes). The
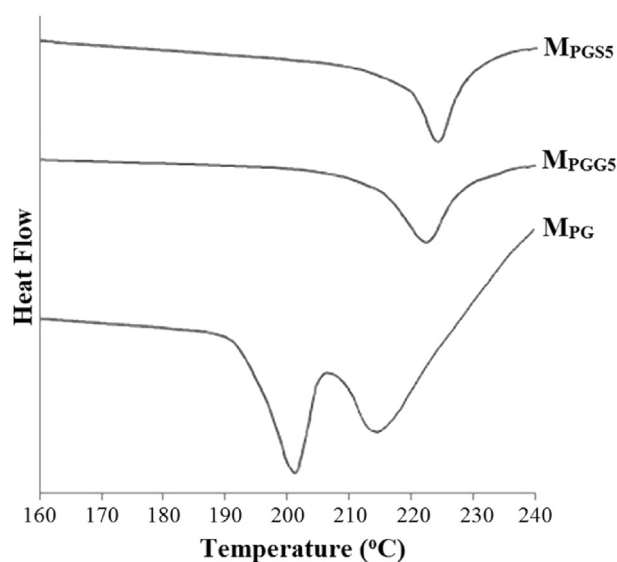

Fig. 6 — DSC thermogram for pristine PVA (M_{PG}), PVA/GO (M_{PGG5}) and PVA/sulfonated GO (M_{PGS5}) membranes [137].

melting temperature of $T_m = 223 \, °C$ for the PVA/sulfonated GO composite membrane, which was obtained by differential scanning calorimetry (DSC), surpassed the 137 °C melting temperature of Nafion® 117, as shown in Fig. 6 [137]. Ionic conductivity of 0.05 S/cm was obtained with the PVA/ sulfonated-GO composite membrane, which highlights its potential in PEMFC applications. Hence, it was seen as a
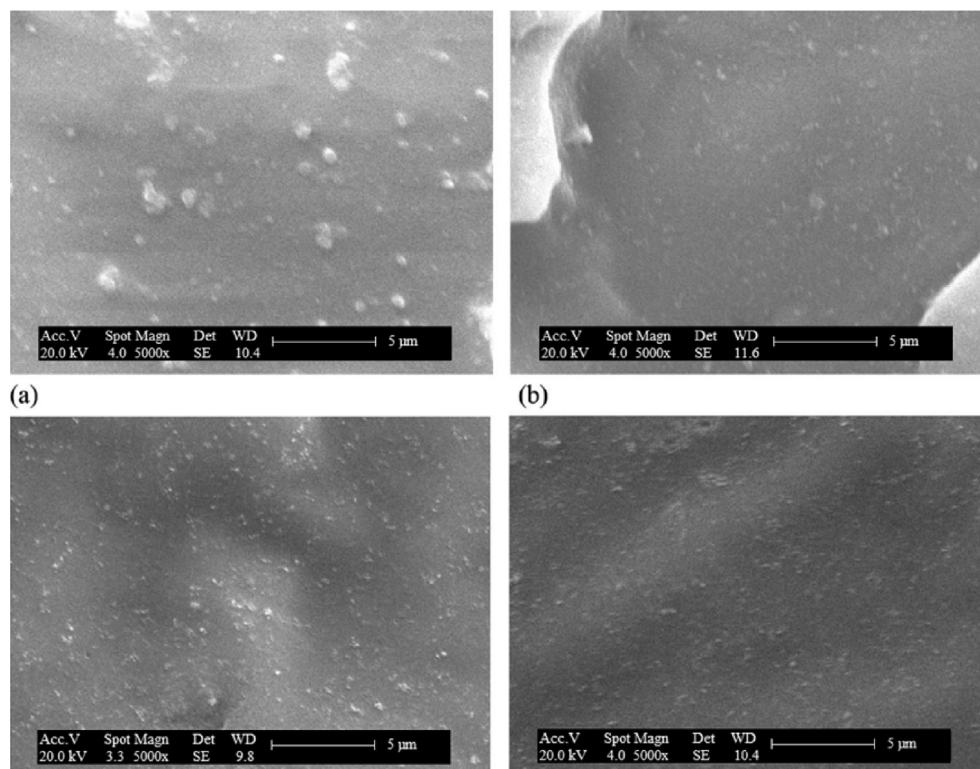

Fig. 5 — — SEM micrographs of the PLA/ATBC/CB composites: (a) PLA/ATBC (100/0) with 1.39 vol% CB, (b) PLA/ATBC (100/10) with 2.46 vol% CB, (c) PLA/ATBC (100/20) with 1.2 vol% CB, and (d) PLA/ATBC (100/30) with 2.03 vol% CB [115].

strategy to incorporate additives in small amounts to appreciably improve the properties of the membranes and produce the desired high conductivity and thermal stability.

Additives for high-temperature proton exchange membranes (PEMs)

With the aforementioned drawbacks and incompetency of the commercialised Nafion® membranes under high-temperature operating conditions, there are generally three solutions that can be followed to overcome the disadvantages: (1) incorporate hydrophilic or proton conductive inorganic nanoparticles into the polymer matrix to fabricate inorganic-organic composite membranes; (2) substitute water with non-volatile or low-volatile polar solvents to prevent evaporation or volatilisation; and (3) prepare a new material that can conduct protons independent of water [138–140]. The concept of incorporating additives aligns with one of the solutions stated above to rectify the drawbacks of Nafion® membranes at high-temperature working conditions.

Ramani et al. [141] performed a study that utilised different techniques to add heteropolyacid (HPA)-based inorganic fillers ((1) phosphotungstic acid (PTA), (2) phosphomolybdic acid (PMA), (3) silicotungstic acid (STA), and (4) silicomolybdic acid (SMA)) into a Nafion® membrane to overcome the large resistive losses that result in the reduction in cell voltage encountered in pristine Nafion® membranes. Out of the three different techniques used for fabricating Nafion®-HPA composites, the method of formulating the composite with a 0.5 M solution of sodium hydroxide (NaOH) demonstrated the best thermal stability. The high boiling point of the solvent with NaOH resulted in composites with positively charged sodium ions (Na+) and improved the interfacial stability between the filler and Nafion® polymer with a decomposition temperature of approximately 340–350 °C as opposed to the decomposition temperature of 300 °C for the composites prepared without using the high boiling point solvent [141]. To further justify the advantages of incorporating inorganic fillers, the group demonstrated cell performance analyses to evaluate the compatibility of these fillers under a harsh heat treatment. It was shown that at a cell temperature of 120 °C and a cathode inlet RH (CIRH) of 35%, the PMA- and SMA-filled Nafion® composites demonstrated poor performance due to the strong adsorption of the molybdenum-based additives into the carbon support of the electrode [142]. However, based on the observed endurance, the filled composite exhibited an extensive interaction with the polymer systems and subsequently improved the resistivity to polymer dissolution and the mechanical properties [143,144].

In addition, there are also extensive studies on PBI-based membranes with the incorporation of inorganic filler additives, and one study performed by Matos et al. [145] pushed through the boundary while evaluating the potential of such membranes for high-temperature PEMFC applications. This group assessed the behaviour of titania-filled Nafion® membranes with respect to an increase in temperature while determining the relationship between the proton conductivity and α-relaxation. Unlike the pristine Nafion® membrane, an irreversible phenomenon of proton conduction was observed in the Nafion®-titania composite after two successive heating.

In the first heating cycle, the Nafion®-titania composite had less proton conductivity at lower temperatures (T > 60 °C) than that of the pristine Nafion® membrane, which was ascribed to the ionomer glass transition [146]. In the second heating, the Nafion®-titania composite exhibited higher proton conductivity than that observed in any temperature range during the first heating cycle; conversely, the Nafion® membrane displayed lower proton conductivity at temperatures >90 °C. Additionally, the group also distinguished the advantages of the filled composite by conditioning both the Nafion® and Nafion®-titania composites at 130 °C with a transitional RH (40–100%). The α-relaxation of the Nafion®-titania composite was shown to be capable of displacing to higher frequencies in all RH ranges. However, the Nafion® membrane was only allowed to displace the α-relaxation at higher frequencies up to 60% RH, and an inversion displacement was shown to follow after that. The presence of the α-relaxation possibly restricts the segmental motion of the polymer chains and thus restricts the water swelling for ion transport [147]. However, the amount of water allowed by the composite is only beneficial up to a certain extent (approximately RH <60%), and the excess water content will eventually cause the proton conductivity to become more predominantly dependent on the polymer relaxations. These results demonstrated that the advantages of the Nafion®-titania composite are due to the extensive displacement of the α-relaxation over the entire RH ranges at 130 °C. Such a characteristic presents an important contribution to the development of high-temperature PEMFCs to overcome the obstacles associated with proton conductivity reduction in the Nafion® membrane.

Lee et al. [148] presented a novel composite membrane that consisted of a silica (SiO_2)/SPEEK nanofibre mat impregnated with Nafion®. The SiO_2/SPEEK inorganic-organic composite nanofibre mats were fabricated via electrospinning and impregnated with an adequate amount (5 wt%) of Nafion® to evolve the membrane from the nanofibre composite to a dense composite while also reducing the fabrication cost. The addition of SiO_2 was suggested to improve both the thermal stability and hygroscopic properties of the composite, which indicates that it is a potential PEM for high-temperature PEMFC technologies [149]. The composite membrane was observed to possess better water retention and resistance to swelling due to the presence of a hygroscopic nanofibrous skeleton. The nanofibrous skeleton structurally reinforced the composite membrane and substantial reduced the linear membrane swelling in both the x- and y-axes [148]. The maximum power density of the composite membrane was 170 mW/cm² at 120 °C and 40% relative humidity and was lower than that of the PBI-based membrane (0.4 W/cm²) under the same conditions. The result was remarkably higher than that of the recast Nafion® (71 mW/cm²) and SPEEK membrane (failed during the test) under similar conditions.

Ye et al. [150] studied IL-functionalised inorganic fillers, with carbon materials (CB, MWCNTs, and rGO) instead of silica, and indicated that they improved the conductivity by shifting the physical geometry of the ionic channels in the polymer matrix and by enhancing the proton mobility along the transport mechanism pathway [151]. The group reported homogeneous dispersion trends on all functionalised-carbon materials within the polymer matrix and supported the

Table 3 – Types of additives in different polymeric membranes and their proton conductivity properties for low- and high-temperature PEMs.

	Types of Additives (*P[j]/*F[k])	PEM	Condition	WU[l] (%)	IEC (mmol/g)	PC[m] ($\times 10^{-2}$ S/cm)	Ref.
Low-temp.[n]	IL-functionalised nanostructured SiO_2*F	Nafion®	90 °C and 100% relative humidity (RH)	41.3	—	37.50	Mishra et al. [135]
	Modified laponite clay*F	Nafion®	85 °C and 100% RH	—	—	4.99	Fatyeyeva et al. [159]
	CB*F, ATBC*P	PVA	Room temperature	—	—	160.00	Yu et al. [115]
	Aluminium oxide (Al_2O_3) ceramic*F	PEO-lithium bis(oxalate)borate (PEO-LiBOB)	90 °C	—	—	0.10	Croce et al. [160]
	Platinum deposited GO*F	Nafion®	80 °C and 100% RH	19.5	—	10.50	Lee et al. [161]
	Dibutyl phthalate (DBP)*P, SiO_2*F	Sulphonated poly (styrene-ethylene-butylene-styrene) (SSEBS)	Room temperature	—	2.000 (without additives)	0.26	Lee et al. [162]
	Nylon 6,6*P	Sulphonated PVA/chitosan	50 °C and 100% RH	34.5	3.920	1.028	Oliveira et al. [103]
	1-Butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$)*P	PEO	—	—	—	—	Bircan et al. [111]
	Phosphoric acid (H_3PO_4) and phytic acid (PA)*P	Bacterial cellulose	Room temperature	38.0 (H_3PO_4) 20.0 (PA)	—	12.00 (H_3PO_4) 8.00 (PA)	Jiang et al. [163]
	IL-functionalised TiO_2	PEO/poly (methyl methacrylate) (PMMA) composite	Room temperature	—	—	0.11	Lee et al. [164]
High-temp	Heteropolyacid (HPA)-based inorganic filler ((1) PTA, (2) PMA, (3) STA, and (4) SMA)*F	Nafion®	120 °C and 35% RH	7.8 (PTA)	—	1.50 (PTA)	Ramani et al. [141]
	Titania*F	Nafion®	130 °C and 100% RH	—	—	9.00	Matos et al. [145]
	IL-functionalised carbon materials ((1) CB, (2) MWCNTs, and (3) RGO)*F	Sulphonated polyimide (SPI)/IL composite	100 and 160 °C	—	2.310 (without additive)	2.30 (CB) 2.95 (MWCNTs) 4.10 (RGO)	Ye et al. [150]
	(1) 1,3-Di (3-methylimidazolium) propane bis (trifluoromethylsulfonyl) imide (PDC$_3$)*P (2) 1-Hexyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide (PMC$_6$)*P	PA-doped PBI	180 °C	—	—	(1) 8.10 (PDC$_3$) (2) 6.10 (PMC$_6$)	Hooshyari et al. [112]
	$Ti_3C_2T_x$*f	Nafion®	120 °C	35.6	0.204 (under 30 °C)	14.70	Liu et al. [165]
	Nano-silicate*f	Nafion®/PTFE	60–110 °C	—	—	—	Jung et al. [166]
	TiO_2*f	PBI	150 °C	17.5	—	11.70	Lobato et al. [91]
	(1) Phosphoric acid-modified silica*f (2) Imidazole-modified silica*f	PBI	120 °C and 70% RH	—	—	(1) 0.35 (2) 4.50	Grandi et al. [167]
	Nano-sized zeolitic imidazole framework-11 (nZIF-11)*f	PBI	70–200 °C	—	—	—	Sanchez-Lainez et al. [168]
	Phosphate-modified titanium zirconium oxide (TiO_2/ZrO_2/phosphate)	Aquivion composite	120 °C and 40% RH	32.8	—	27.00	Lee et al. [169]

[j] *P refers to the plasticiser.
[k] *F refers to the filler.
[l] WU refers to the water uptake.
[m] PC refers to the proton conductivity.
[n] temp. refers to the temperature.

Table 4 — —Unmodified and modified fillers for fuel cell applications in the literature.

	Filler types	PEM	WU° (%)	IEC^p (mmol/g)	T_d^q (°C)	PC^r (×10^{-2} S/cm)	Ref.
Unmodified filler	SiO$_2$	Nafion®-based composite	55.0 (at 80 °C)	–	–	3.46 (at 40 °C)	Li et al. [170]
	SiO$_2$	PVA/PAA composite	38.0 (at 90 °C)	1.470	123.0	31.00 (at 80 °C)	Kim et al. [171]
	SiO$_2$	SPPESK composite	18.5	0.960	278.3	36.00 (at 30 °C)	Kim et al. [78,129]
	Nano-silicate	Nafion®/polytetrafluoroethylene (PTFE) composite	–	–	–	–	Jung et al. [166]
Modified filler	TiO$_2$	SPVA composite	123.1	1.010	112.8	82.20	Solanki et al. [129]
	S–SiO$_2$	Nafion®-based composite	43.0 (at 80 °C)	–	–	4.30 (at 40 °C)	Li et al. [170]
	Sulphonated nanoporous silica (SBA-15-propyl-SO$_3$H)	PVA composite	80.0	–	–	6.00	Beydaghi et al. [172]
	Zeolitic imidazolate framework-8 (ZIF-8)	PVA composite	–	–	–	20.4 (at 60 °C)	Hsu et al. [173]
	ZIF-8	PVA/poly (2-acry-lamido-2-methylpropanesulfonicacid) (PAMPS) composite	328.0	1.520	180.0	134.0 (at 80 °C)	Erkartal et al. [174]

° WU refers to the water uptake.
p IEC refers to the ion exchange capacity.
q TS refers to the temperature that corresponds to a weight loss of 5%.
r PC refers to the proton conductivity.

formation of ion clusters that readily contributed to the proton conductivity [152]. The proton conductivity was observed to be temperature dependent, and its highest output occurred at 160 °C (7.8 × 10^{-2} S/cm). Hence, these results revealed the potential of adding modified inorganic fillers, such as IL-functionalised carbon materials, as the group illustrated that they achieved a high proton conductivity while being mechanically stable at higher working temperatures. Furthermore, the application of sulfated metal oxides as fillers has raised substantial awareness from researchers due to their higher stability and acidity, which are beneficial for the development of fuel cell membranes. One of the strongest superacids among all known solids with a Hammett acidity (H_0) < −16 is sulfated zirconia (SZrO$_2$). According to Hara et al. [153], the surface SO$_4$ species existed as bidentate complexes strongly bonded with ZrO$_2$ in a SZrO$_2$ powder calcined at 620 °C. SO$_4$-species are electron-withdrawing, and thus the Lewis acidity of the zirconium is strengthened [154,155]. For that reason, the acidic surface functionalities exhibited improved proton transport and stiffened the composite, which resulted in higher dimensional stability at elevated temperatures [156]. Chen et al. [157] presented a preliminary study of having sulfated tin oxide (S−SnO$_2$) as a filler into Nafion® composite membranes; the group reported that the introduction of S−SnO$_2$ facilitates additional acidic sites, which improved the proton transport characteristics and increased the degree of crystallinity with respect to lower methanol crossover through XRD analysis.

Table 3 summarises the proton conduction properties of various composite membranes with additives used as low- and high-temperature PEMs. Table 4 demonstrates the use of modified and unmodified inorganic fillers for fuel cell applications. Although many of the presented results are without ion exchange capacity (IEC), such parameters are vital as alternative methods to gauge the ionic conductivity of membranes. It refers to the number of functional groups present per mass of material of a membrane. According to Navessin et al. [158], the IEC correlates with the cell performance, whereby the reduction of the IEC leads to a reduction in the mass-transport limited current due to a decrease in the O$_2$ diffusion coefficient and a decrease in the O$_2$ permeability.

In summary, the potential of polymer-additive systems for low- and high-temperature PEMs has been discussed. In general, the incorporation of additives has presented phenomenal results with improvements in both the mechanical properties and ion/proton conducting properties. However, the incorporation of a plasticiser additive is not desirable for high-temperature PEMs because of its inherently high hydrophilic properties, which may stiffen the membrane while forming hydrogen bonds within ionic clusters [175]. Despite that, including additives into polymer systems for fuel cell applications have improved the overall membrane properties.

Conclusion and future perspectives

In conclusion, the addition of additives plays a substantial role in ameliorating both the mechanical and electrical properties of PEMs to make them effective for fuel cell applications. For example, the addition of titania fillers into Nafion® membranes

has improved their proton conductivity at high temperatures (at temperatures >120 °C). The addition of a plasticiser introduces the capability of PEMs to form their own domain to facilitate more proton-conducting channels, whereas the filler additive demands a critical concentration to achieve the percolation threshold. Optimisation of the contents of the plasticiser and filler additives is essential if both are to be involved in the fabrication of PEMs. Some additives that are capable of delivering improved performance in low-temperature PEMs are glycerol, [BMIM]Cl, sulfonated-GO and nylon 6,6. In high-temperature PEMs, fillers are found to be more suitable than plasticisers due to the inherently high hydrophilic properties of the plasticiser upon incorporation into the polymer system. This hydrophilicity could potentially affect the mechanical stability of the polymer membrane while operating at high temperatures. Some of the additives involved in the manufacture of high-temperature PEMs are TiO_2, SiO_2, CB, MWCNTs and rGO. The inclusion of the aforementioned additives is capable of forming extensive interactions with polymer systems and thus improving the polymer degradation and stability while operating at high temperatures.

Moreover, this review highlighted that the application of filler additives is better suited to high-temperature PEM operating systems due to their ability to improve the water retention capacity of the composite. In the case of plasticiser additives, it is suggested that their inherently high hydrophilic properties may stiffen the membrane while forming hydrogen bonds within the ionic clusters. For that reason, the involvement of plasticiser additives may not be helpful for the development of high-temperature PEMs. It is concluded that the employment of suitable additives can help develop a cost-effective and commercialisable PEM for fuel cell application usage, such as in automotive applications and in portable and stationary power generators.

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REFERENCES

[1] Fang J, Qiao J, Wilkinson DP, Zhang J. Electrochemical polymer electrolyte membranes: electrochemical energy storage and conversion. 7 ed. Boca Raton: Taylor & Francis Group; 2015.

[2] Behling NH. Fuel Cells: current technology challenges and future research needs. 1 ed. Oxford: Elsevier; 2013.

[3] La Conti AB, Hamdan M, Mcdonald RC. Mechanisms of chemical degradation. In: Vielstich W, Lamm A, Gasteiger H, editors. Handbook of fuel cells - fundamentals, technology and application. New York: John Wiley & Sons; 2003.

[4] Feldheim DL, Lawson DR, Martin CR. Influence of the sulfonate counter cation on the thermal stability of nafion† perfluorosulfonate membranes. J Polym Sci B Polym Phys 1993;31:953—7.

[5] Panchenko A. Polymer electrolyte membrane degradation and oxygen reduction in fuel cell: an EPR and DFT investigation. Online Publikationen der Universität Stuttgart: Universität Stuttgart; 2004.

[6] Sun H, Yu M, Li Z, Almheiri S. A molecular dynamic simulation of hydrated proton transfer in perfluorosulfonate ionomer membranes (nafion 117). J Chem 2015;2015:1—10.

[7] Uosaki K, Okazaki K, Kita H. Conductivity of Nation membranes at low temperatures. J Electroanal Chem Interfacial Electrochem 1990;287:163—9.

[8] Cappadonia M, Erning JW, Niaki SMS, Stimming U. Conductance of Nafion 117 membranes as a function of temperature and water content. Solid State Ionics 1995;77:65—9.

[9] Adjemian KT, Srinivasan S, Benziger J, Bocarsly AB. Investigation of PEMFC operation above 100 °C employing perfluorosulfonic acid silicon oxide composite membranes. J Power Sources 2002;109:356—64.

[10] Kim YM, Choi SH, Lee HC, Hong MZ, Kim K, Lee H-I. Organic—inorganic composite membranes as addition of SiO2 for high temperature-operation in polymer electrolyte membrane fuel cells (PEMFCs). Electrochim Acta 2004;49:4787—96.

[11] Antonucci PL, Arico AS, Creti P, Ramunni E, Antonucci V. Investigation of a direct methanol fuel cell based on a composite Nafion®-silica electrolyte for high temperature operation. Solid State Ionics 1999;125:431—7.

[12] Lin J-C, Kunz HR, Fenton JM. Composite membranes for proton exchange membrane fuel cell operation at higher temperature. In: Ryan MA, Surampudi S, Jain M, editors. Power sources for the new millennium: proceedings of the international symposium. New Jersey: The Electrochemical Society Inc; 2001.

[13] Malhotra S, Datta R. Membrane-supported nonvolatile acidic electrolytes allow higher temperature operation of PEMFC. J Electrochem Soc 1997;144:L23—6.

[14] Wafiroh S, Pudjiastuti P, Sari II . The production of sulfonated chitosan-sodium alginate found in brown algae (Sargassum sp.) composite membrane as proton exchange membrane fuel cell (PEMFC). 2016.

[15] Zawodzinski TA. Water uptake by and transport through Nafion® 117 membranes. J Electrochem Soc 1993:140.

[16] Li C, Yang Z, Liu X, Zhang Y, Dong J, Zhang Q, et al. Enhanced performance of sulfonated poly (ether ether ketone) membranes by blending fully aromatic polyamide for practical application in direct methanol fuel cells (DMFCs). Int J Hydrogen Energy 2017;42:28567—77.

[17] Matos BR, Santiago EI, Fonseca FC, Linardi M, Lacerda RG, Lavayen V, et al. Titanate nanotubes as inorganic fillers of nafion membranes for PEM fuel cell operating at high temperatures. ECS Transactions 2007:143—50.

[18] Garaev V, Pavlovica S, Reinholds I, Vaivars G. Mechanical properties and XRD of Nafion modified by 2-hydroxyethylammonium ionic liquids. IOP Conf Ser Mater Sci Eng 2013:49.

[19] Casciola M, Donnadio A, Sassi P. A critical investigation of the effect of hygrothermal cycling on hydration and in-plane/through-plane proton conductivity of Nafion 117 at medium temperature (70—130 °C). J Power Sources 2013;235:129—34.

[20] Chatterjee A, Hansora DP. Fabrication techniques for the polymer electrolyte membranes for fuel cells. In: Imnamuddin Mohammad A, Asiri AM, editors. Organic-

inorganic composite polymer electrolyte membranes. Cham: Springer; 2017. p. 359—80.

[21] Tripathi BP, Shahi VK. Organic-inorganic nanocomposite polymer electrolyte membranes for fuel cell applications. Prog Polym Sci 2011;36:945—79.

[22] Lemus J, Eguizabal A, Pina PM. Endurance strategies for the preparation of high temperature polymer electrolyte membranes by UV polymerization of 1-H-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide for fuel cell applications. Int J Hydrogen Energy 2016;41:3981—93.

[23] Jiang Z, Jiang Z-J. Plasma techniques for the fabrication of polymer electrolyte membranes for fuel cells. J Membr Sci 2014;456:85—106.

[24] Neburchilov V, Martin J, Wang H, Zhang J. A review of polymer electrolyte membranes for direct methanol fuel cells. J Power Sources 2007;169:221—38.

[25] Kim DJ, Choi DH, Park CH, Nam SY. Characterization of the sulfonated PEEK/sulfonated nanoparticles composite membrane for the fuel cell application. Int J Hydrogen Energy 2016;41:5793—802.

[26] Lian F, Wen Y, Ren Y, Guan H. A novel PVB based polymer membrane and its application in gel polymer electrolytes for lithium-ion batteries. J Membr Sci 2014;456:42—8.

[27] Sforc ML, Yoshida IVP, Nunes SP. Organic-inorganic membranes prepared from polyether diamine and epoxy silane. J Membr Sci 1999;159:197—207.

[28] Uragami T. Functional separation membranes from chitin and chitosan derivatives. In: Thakur VK, Thakur MK, Kessler MR, editors. Handbook of composites from renewable materials: functionalization. California: Wiley-Scrivener; 2017. p. 69—120.

[29] Klein LC. Sol-gel process for proton exchange membranes. Key Eng Mater 2008;391:159—68.

[30] Mauritz KA. Organic-inorganic hybrid materials: perfluorinated ionomers as sol-gel polymerization templates for inorganic alkoxides. Mater Sci Eng C 1998;6:121—33.

[31] Gao W, Li Z, Sammes N. An introduction to electronic materials for engineers. 2 ed. Singapore: World Scientific; 2011.

[32] Ludueña GA, Kühne TD, Sebastiani D. Mixed Grotthuss and vehicle transport mechanism in proton conducting polymers from Ab initio molecular dynamics simulations. Chem Mater 2011;23:1424—9.

[33] Choe YK, Tsuchida E, Ikeshoji T, Yamakawa S, Hyodo SA. Nature of water transport and electro-osmosis in nafion: insights from first-principles molecular dynamics simulations under an electric field. J Phys Chem B 2008;112:11586—94.

[34] Sun H, Sun Z, Wu Y. Proton transfer mechanism in perfluorinated sulfonic acid polytetrafluoroethylene. Int J Hydrogen Energy 2012;37:12821—6.

[35] Knox CK, Voth GA. Probing selected morphological models of hydrated nafion using large-scale molecular dynamics simulations. J Phys Chem B 2010;114:3205—18.

[36] Szasz A, Szasz N, Szasz O. Oncothermia: principles and practices. Dordrecht: Springer; 2011.

[37] Franke ME, Simon U. Solvate-supported proton transport in zeolites. ChemPhysChem 2004;5:465—72.

[38] Hase K, Nakano T, Koiwai A. Performance of high-density of acid electrolyte and analysis of proton conduction mechanism. ECS Transactions 2007;11:159—64.

[39] Beuscher U, Cleghorn SJC, Johnson WB. Challenges for PEM fuel cell membranes. Int J Energy Res 2005;29:1103—12.

[40] Wu J, Yuan XZ, Martin JJ, Wang H, Zhang J, Shen J, et al. A review of PEM fuel cell durability: degradation mechanisms and mitigation strategies. J Power Sources 2008;184:104—19.

[41] Ghi LJ, Park NR, Kim MS, Rhee HW. Nafion/silane nanocomposite membranes for high temperature polymer electrolyte membrane fuel cell. J Nanosci Nanotechnol 2011;11:5749—53.

[42] Tang Y, Karlsson AM, Santare MH, Gilbert M, Cleghorn S, Johnson WB. An experimental investigation of humidity and temperature effects on the mechanical properties of perfluorosulfonic acid membrane. Mater Sci Eng, A 2006;425:297—304.

[43] Healy J, Hayden C, Xie T, Olson K, Waldo R, Brundage M, et al. Aspects of the chemical degradation of PFSA ionomers used in PEM fuel cells. Fuel Cells 2005;5:302—8.

[44] Rodgers MP, Bonville LJ, Kunz HR, Slattery DK, Fenton JM. Fuel cell perfluorinated sulfonic acid membrane degradation correlating accelerated stress testing and lifetime. Chem Rev 2012;112:6075—103.

[45] Kusoglu A, Karlsson AM, Santare MH, Cleghorn S, Johnson WB. Mechanical response of fuel cell membranes subjected to a hygro-thermal cycle. J Power Sources 2006;161:987—96.

[46] Shi S, Chen G, Wang Z, Chen X. Mechanical properties of Nafion 212 proton exchange membrane subjected to hygrothermal aging. J Power Sources 2013;238:318—23.

[47] Dutta K, Das S, Kundu PP. Partially sulfonated polyaniline induced high ion-exchange capacity and selectivity of Nafion membrane for application in direct methanol fuel cells. J Membr Sci 2015;473:94—101.

[48] Amir Al A, Sultan AS, Zaidi SMJ. Sulfonated poly(ether ether ketone) (SPEEK): a promising membrane Material for polymer electrolyte fuel cell. Ion exchange technology 2012:437—51.

[49] Araya SS, Zhou F, Liso V, Sahlin SL, Vang JR, Thomas S, et al. A comprehensive review of PBI-based high temperature PEM fuel cells. Int J Hydrogen Energy 2016;41:21310—44.

[50] Smitha B, Sridhar S, Khan AA. Polyelectrolyte complexes of chitosan and poly(acrylic acid) as proton exchange membranes for fuel cells. Macromolecules 2004;37:2233—9.

[51] Smitha B, Sridhar S, Khan AA. Solid polymer electrolyte membranes for fuel cell applications—a review. J Membr Sci 2005;259:10—26.

[52] Edlund D. Methanol fuel cell systems: advancing towards commericialization. Boca Raton: Taylor & Francis Group; 2012.

[53] Li Q, He R, Jensen JO, Bjerrum NJ. Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100 °C. Chem Mater 2003;15:4896—915.

[54] Shaari N, Kamarudin SK. Chitosan and alginate types of bio-membrane in fuel cell application: an overview. J Power Sources 2015;289:71—80.

[55] Ozden A, Ercelik M, Devrim Y, Colpan CO, Hamdullahpur F. Evaluation of sulfonated polysulfone/zirconium hydrogen phosphate composite membranes for direct methanol fuel cells. Electrochim Acta 2017;256:196—210.

[56] Adanur S, Zheng H. Synthesis and characterization of sulfonated polyimide based membranes for proton exchange membrane fuel cells. J Fuel Cell Sci Technol 2013;10.

[57] Feng K, Tang B, Wu P. Evaporating" graphene oxide sheets (GOSs) for rolled up GOSs and its applications in proton exchange membrane fuel cell. ACS Appl Mater Interfaces 2013;5:1481—8.

[58] Purwanto M, Atmaja L, Mohamed MA, Salleh MT, Jaafar J, Ismail AF, et al. Biopolymer-based electrolyte membranes from chitosan incorporated with montmorillonite-crosslinked GPTMS for direct methanol fuel cells. RSC Adv 2016;6:2314—22.

[59] Mollá S, Compañ V, Luis Lafuente S, Prats J. On the methanol permeability through pristine Nafion® and

nafion/PVA membranes measured by different techniques. A comparison of methodologies. Fuel Cells 2011;11:897—906.

[60] Chen J, Li D, Koshikawa H, Asano M, Maekawa Y. Crosslinking and grafting of polyetheretherketone film by radiation techniques for application in fuel cells. J Membr Sci 2010;362:488—94.

[61] Qiao J, Ikesaka S, Saito M, Kuwano J, Okada T. Life test of DMFC using poly(ethylene glycol)bis(carboxymethyl)ether plasticized PVA/PAMPS proton-conducting semi-IPNs. Electrochem Commun 2007;9:1945—50.

[62] Kim J-H, Kim S-K, Nam K, Kim D-W. Composite proton conducting membranes based on Nafion and sulfonated SiO$_2$ nanoparticles. J Membr Sci 2012;415—416:696—701.

[63] Heo Y, Yun S, Im H, Kim J. Low methanol permeable sulfonated poly(ether imide)/sulfonated multiwalled carbon nanotube membrane for direct methanol fuel cell. J Appl Polym Sci 2012;126:E467—77.

[64] Tseng C-Y, Ye Y-S, Cheng M-Y, Kao K-Y, Shen W-C, Rick J, et al. Sulfonated polyimide proton exchange membranes with graphene oxide show improved proton conductivity, methanol crossover impedance, and mechanical properties. Adv Energy Mater 2011;1:1220—4.

[65] Zhao Q, An QF, Ji Y, Qian J, Gao C. Polyelectrolyte complex membranes for pervaporation, nanofiltration and fuel cell applications. J Membr Sci 2011;379:19—45.

[66] Mochizuki T, Uchida M, Uchida H, Watanabe M, Miyatake K. Double-layer ionomer membrane for improving fuel cell performance. ACS Appl Mater Interfaces 2014;6:13894—9.

[67] Li G, Zhao C, Cui Y, Rong T, Zhu C, Na H. Intermolecular ionic cross-linked sulfonated poly(ether ether ketone) membranes with excellent mechanical properties and selectivity for direct methanol fuel cells. RSC Adv 2016;6:23025—32.

[68] Suganthi S, Mohanapriya S, Raj V. Biocomposite proton-exchange membrane electrolytes for direct methanol fuel cells. J Appl Polym Sci 2016;133.

[69] Jiang G-p, Zhang J, Qiao J-l, Jiang Y-m, Zarrin H, Chen Z, et al. Bacterial nanocellulose/Nafion composite membranes for low temperature polymer electrolyte fuel cells. J Power Sources 2015;273:697—706.

[70] Laomongkonnimit P, Soontarapa K. Chitosan-zeolite proton exchange membrane. Fuel Research Center; 2009.

[71] Rikukawa M, Sanui K. Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers. Prog Polym Sci 2000;25:1463—502.

[72] Lee H-K, Park J-H, Kim D-Y, Lee T-H. A study on the characteristics of the diffusion layer thickness and porosity of the PEMFC. J Power Sources 2004;131:200—6.

[73] Li Q, He R, Gao J-A, Jensen JO, Bjerrum NJ. The CO poisoning effect in PEMFCs operational at temperatures up to 200°C. J Electrochem Soc 2003;150:A1599—605.

[74] Authayanun S, Im-orb K, Arpornwichanop A. A review of the development of high temperature proton exchange membrane fuel cells. Chin J Catal 2015;36:473—83.

[75] Hickner MA, Ghassemi H, Kim YS, Einsla BR, McGrath JE. Alternative polymer systems for proton exchange membranes (PEMs). Chem Rev 2004;104:4587—612.

[76] Zhou F, Araya SS, Grigoras IF, Andreasen SJ, Kær SK. Performance degradation tests of phosphoric acid doped PBI membrane based high temperature PEM fuel cells. In: ASME 2014 12th international conference on fuel cell science, engineering and technology. Boston, Massachusetts, USA: ASME; 2014. 021002-1—021002-9.

[77] Wainright JS. Acid-doped polybenzimidazoles: a new polymer electrolyte. J Electrochem Soc 1995:142.

[78] Kim DS, Shin KH, Park HB, Lee YM. Preparation and characterization of sulfonated poly(phthalazinone ether sulfone ketone) (SPPESK)/silica hybrid membranes for direct methanol fuel cell applications. Macromol Res 2004;12:413—21.

[79] Higuchi A, Iijima T Dsc. Investigation of the states of water in poly(vinyl alcohol) membranes. Polymer 1985;26:1207—11.

[80] Ren X, Gottesfeld S. Electro-osmotic drag of water in poly(perfluorosulfonic acid) membranes. J Electrochem Soc 2001;148:A87—93.

[81] Li Q, Hjuler HA, Hasiotis C, Kallitsis JK, Kontoyannis CG, Bjerrum NJ. A quasi-direct methanol fuel cell system based on blend polymer membrane electrolytes. Electrochem Solid State Lett 2002;5:A125—8.

[82] Li Q, Hjuler HA, Bjerrum NJ. Phosphoric acid doped polybenzimidazole membranes: physicochemical characterization and fuel cell applications. J Appl Electrochem 2001;31:773—9.

[83] Zhang J, Tang Y, Song C, Zhang J. Polybenzimidazole-membrane-based PEM fuel cell in the temperature range of 120—200°C. J Power Sources 2007;172:163—71.

[84] Das SK, Reis A, Berry KJ. Experimental evaluation of CO poisoning on the performance of a high temperature proton exchange membrane fuel cell. J Power Sources 2009;193:691—8.

[85] Li L. Sulfonated poly(ether ether ketone) membranes for direct methanol fuel cell. J Membr Sci 2003;226:159—67.

[86] Quartarone E, Mustarelli P. Polymer fuel cells based on polybenzimidazole/H$_3$PO$_4$. Energy & Environ Sci 2012;5.

[87] Li Q, Jensen JO, Savinell RF, Bjerrum NJ. High temperature proton exchange membranes based on polybenzimidazoles for fuel cells. Prog Polym Sci 2009;34:449—77.

[88] Hasiotis C, Li Q, Deimede V, Kallitsis JK, Kontoyannis CG, Bjerrum NJ. Development and characterization of acid-doped polybenzimidazole/sulfonated polysulfone blend polymer electrolytes for fuel cells. J Electrochem Soc 2001;148:A513—9.

[89] Gautier-Luneau I, Denoyelle A, Sanchez JY, Poinsignon C. Organic—inorganic protonic polymer electrolytes as membrane for low-temperature fuel cell. Electrochim Acta 1992;37:1615—8.

[90] Bose S, Kuila T, Nguyen TXH, Kim NH, Lau K-t, Lee JH. Polymer membranes for high temperature proton exchange membrane fuel cell: recent advances and challenges. Prog Polym Sci 2011;36:813—43.

[91] Lobato J, Cañizares P, Rodrigo MA, Úbeda D, Pinar FJ. A novel titanium PBI-based composite membrane for high temperature PEMFCs. J Membr Sci 2011;369:105—11.

[92] Rhim J, Park H, Lee C, Jun J, Kim D, Lee Y. Crosslinked poly(vinyl alcohol) membranes containing sulfonic acid group: proton and methanol transport through membranes. J Membr Sci 2004;238:143—51.

[93] Carbone A, Pedicini R, Portale G, Longo A, D'Ilario L, Passalacqua E. Sulphonated poly(ether ether ketone) membranes for fuel cell application: thermal and structural characterisation. J Power Sources 2006;163:18—26.

[94] Xiao P, Li J, Tang H, Wang Z, Pan M. Physically stable and high performance Aquivion/ePTFE composite membrane for high temperature fuel cell application. J Membr Sci 2013;442:65—71.

[95] Daniels CA. Polymers: structure and properties. 1 ed. Lancaster: CRC Press; 1989.

[96] Mulmi S, Park CH, Kim HK, Lee CH, Park HB, Lee YM. Surfactant-assisted polymer electrolyte nanocomposite membranes for fuel cells. J Membr Sci 2009;344:288—96.

[97] Jimenez A, Peltzer M, Ruseckaite R. Poly(lactic acid) science and technology: processing, properties, additives and

applications (polymer chemistry series). Cambridge: Royal Society of Chemistry; 2015.

[98] Fong R, Robertson A, Mallon P, Thompson R. The impact of plasticizer and degree of hydrolysis on free volume of poly(vinyl alcohol) films. Polymers 2018;10:1036.

[99] Chanda M, Roy SK. Plastics technology handbook. 4 ed. New York: CRC Press; 2007.

[100] Wong CY, Wong WY, Loh KS, Mohamad AB. Study of the plasticising effect on polymer and its development in fuel cell application. Renew Sustain Energy Rev 2017;79:794–805.

[101] Favero J, Belhabib S, Guessasma S, Decaen P, Reguerre AL, Lourdin D, et al. On the representative elementary size concept to evaluate the compatibilisation of a plasticised biopolymer blend. Carbohydr Polym 2017;172:120–9.

[102] Biswas A, Shogren RL, Stevenson DG, Willett JL, Bhowmik PK. Ionic liquids as solvents for biopolymers: acylation of starch and zein protein. Carbohydr Polym 2006;66:546–50.

[103] Oliveira PNd, Mendes AMM. Preparation and characterization of an eco-friendly polymer electrolyte membrane (PEM) based in a blend of sulphonated poly(vinyl alcohol)/chitosan mechanically stabilised by nylon 6,6. Mater Res 2016;19:954–62.

[104] Rachipudi PS, Kariduraganavar MY, Kittur AA, Sajjan AM. Synthesis and characterization of sulfonated-poly(vinyl alcohol) membranes for the pervaporation dehydration of isopropanol. J Membr Sci 2011;383:224–34.

[105] Andreuccetti C, Carvalho RA, Grosso CRF. Effect of hydrophobic plasticizers on functional properties of gelatin-based films. Food Res Int 2009;42:1113–21.

[106] Hung SF, Hsieh CM, Chen YC, Wang YC, Ho HO, Sheu MT. Characterizations of plasticized polymeric film coatings for preparing multiple-unit floating drug delivery systems (muFDDSs) with controlled-release characteristics. PLoS One 2014;9. e100321.

[107] Cheng LH, Abdul Karin A, Seow CC. Characterization of composite films made of konjac glucomannan (KGM), carboxymethyl cellulose (CMC) and lipid. Food Chem 2008;107:411–8.

[108] Karbowiak T, Debeaufort F, Voilley A. Influence of thermal process on structure and functional properties of emulsion-based edible films. Food Hydrocolloids 2007;21:879–88.

[109] Vieira MGA, da Silva MA, dos Santos LO, Beppu MM. Natural-based plasticizers and biopolymer films: a review. Eur Polym J 2011;47:254–63.

[110] Hodge RM, Bastow TJ, Edward GH, Simon GP, Hill AJ. Free volume and the mechanism of plasticization in water-swollen poly(vinyl alcohol). Macromolecules 1996;29:8137–43.

[111] Bircan H, Seshadri V, Padilla J, Invernale M, Otero TF, Sotzing GA. Use of polymer/ionic liquid plasticizers as gel electrolytes in electrochromic devices. J Phys Conf 2008;127.

[112] Hooshyari K, Javanbakht M, Adibi M. Novel composite membranes based on PBI and dicationic ionic liquids for high temperature polymer electrolyte membrane fuel cells. Electrochim Acta 2016;205:142–52.

[113] Bo S, Zhang L, Han S, Li Y, Li W, Xing W. Fabrication of bilayer catalytic composite membrane PVA-SA/SPVA and application for ethyl acetate synthesis. J Membr Sci 2018;563:10–21.

[114] Wong CY, Wong WY, Walvekar R, Loh KS, Khalid M, Lim KL. Effect of deep eutectic solvent in proton conduction and thermal behaviour of chitosan-based membrane. J Mol Liq 2018;269:675–83.

[115] Yu J, Wang N, Ma X. Fabrication and characterization of poly(lactic acid)/acetyl tributyl citrate/carbon black as

conductive polymer composites. Biomacromolecules 2008;9:1050–7.

[116] Hoglund A, Hakkarainen M, Albertsson A-C. Migration and hydrolysis of hydrophobic polylactide plasticizer. Biomacromolecules 2010;11:277–83.

[117] Whelan A. Polymer technology dictionary. 1 ed. Netherlands: Springer; 1994.

[118] Misra GS. Introductory polymer chemistry 1ed. New Delhi: Wiley; 1993.

[119] Singh NK, Verma ML, Minakshi M. PEO nanocomposite polymer electrolyte for solid state symmetric capacitors. Bull Mater Sci 2015;38:1577–88.

[120] Quartarone E, Angioni S, Mustarelli P. Polymer and composite membranes for proton-conducting, high-temperature fuel cells: a critical review. Materials 2017;10.

[121] Zhang Y, Ge S, Tang B, Koga T, Rafailovich MH, Sokolov JC, et al. Effect of carbon black and silica fillers in elastomer blends. Macromolecules 2001;34:7056–65.

[122] Agrawal A. Thermal and dielectric behavior of polymer composites with hybrid fillers [Doctoral Thesis]. Rourkela, India: National Institute of Technology Rourkela; 2015.

[123] Oyama HT, Sekikawa M, Ikezawa Y. Influence of the polymer/inorganic filler interface on the mechanical, thermal, and flame retardant properties of polypropylene/magnesium hydroxide composites. J Macromol Sci, Part B 2011;50:463–83.

[124] Handayani S, Dewi EL, Hardy J, Christiani L, Kurniawan. Influence of composite electrolyte membrane for proton exchange membrane fuel cells. Procedia Chem 2012;4:123–30.

[125] Herring AM. Inorganic–polymer composite membranes for proton exchange membrane fuel cells. J Macromol Sci Polym Rev 2006;46:245–96.

[126] Arico AS, Baglio V, Antonucci V, Nicotera I, Oliviero C, Coppola L, et al. An NMR and SAXS investigation of DMFC composite recast Nafion membranes containing ceramic fillers. J Membr Sci 2006;270:221–7.

[127] Liu X, Wang T, Chow LC, Yang M, Mitchell JW. Effects of inorganic fillers on the thermal and mechanical properties of poly(lactic acid). Int J Polym Sci 2014;2014:1–8.

[128] Michael FM, Khalid M, Hoque ME, Ratnam CT. PLA/GNP/NHA: application of poly-lactic acid reinforced with graphene nano-platelets and nano-hydroxy apatite hybrids in load bearing bone implants. In: 5th international conference on nanotek and expo. San Antonio, USA: Journal of Nanomedicine & Nanotechnology; 2015. p. 41.

[129] Solanki JN, Mishra PS, Murthy ZVP. Situprepared Tio2nanoparticles cross-linked sulfonated Pva membranes with high proton conductivity for Dmfc. Química Nova.; 2016.

[130] Xanthos M. Functional fillers for plastics. 2 ed. Weinheim: Wiley-VCH; 2010.

[131] Stevens JR, Wieczorek W. Ionically conducting polyether composites. Can J Chem 1996;74:2106–13.

[132] Mantia FPL, Morreale M, Ishak ZAM. Processing and mechanical properties of organic filler-polypropylene composites. J Appl Polym Sci 2005;96:1906–13.

[133] Donskoi AA, Shashkina MA, Zaikov GE. Fire resistant and thermally stable materials derived from chlorinated polyethylene. 1 ed. Netherlands: CRC Press; 2003.

[134] Mishra AK, Bose S, Kuila T, Kim NH, Lee JH. Silicate-based polymer-nanocomposite membranes for polymer electrolyte membrane fuel cells. Prog Polym Sci 2012;37:842–69.

[135] Mishra AK, Kuila T, Kim D-Y, Kim NH, Lee JH. Protic ionic liquid-functionalized mesoporous silica-based hybrid membranes for proton exchange membrane fuel cells. J Mater Chem 2012;22.

[136] De SK, White JR. Short fibre-polymer composites. 1 ed. Cambridge: CRC Press; 1996.

[137] Beydaghi H, Javanbakht M, Kowsari E. Synthesis and characterization of poly(vinyl alcohol)/sulfonated graphene oxide nanocomposite membranes for use in proton exchange membrane fuel cells (PEMFCs). Ind Eng Chem Res 2014;53:16621–32.

[138] Yen C-Y, Lee C-H, Lin Y-F, Lin H-L, Hsiao Y-H, Liao S-H, et al. Sol–gel derived sulfonated-silica/Nafion® composite membrane for direct methanol fuel cell. J Power Sources 2007;173:36–44.

[139] Yan X-M, Mei P, Mi Y, Gao L, Qin S. Proton exchange membrane with hydrophilic capillaries for elevated temperature PEM fuel cells. Electrochem Commun 2009;11:71–4.

[140] Rodgers MP, Shi Z, Holdcroft S. Transport properties of composite membranes containing silicon dioxide and Nafion®. J Membr Sci 2008;325:346–56.

[141] Ramani V, Kunz HR, Fenton JM. Investigation of Nafion®/HPA composite membranes for high temperature/low relative humidity PEMFC operation. J Membr Sci 2004;232:31–44.

[142] Wu Y, Ye X, Yang X, Wang X, Chu W, Hu Y. Heterogenization of heteropolyacids: a general discussion on the preparation of supported acid catalysts. Ind Eng Chem Res 1996;35:2546–60.

[143] Moore RB, Martin CR. Procedure for preparing solution-cast perfluorosulfonate ionomer films and membranes. Anal Chem 1986;58:2569–70.

[144] Moore RB, Martin CR. Chemical and morphological properties of solution-cast perfluorosulfonate ionomers. Macromolecules 1988;21:1334–9.

[145] Matos BR, Santiago EI, Fonseca FC. Irreversibility of proton conductivity of Nafion and Nafion–Titania composites at high relative humidity. Mater for Renew and Sustain Energy 2015;4.

[146] Matos BR, Santiago EI, Muccillo R, Velasco-Davalos IA, Ruediger A, Tavares AC, et al. Interplay between α-relaxation and morphology transition of perfluorosulfonate ionomer membranes. J Power Sources 2015;293:859–67.

[147] Kreuer K-D. The role of internal pressure for the hydration and transport properties of ionomers and polyelectrolytes. Solid State Ionics 2013;252:93–101.

[148] Lee C, Jo SM, Choi J, Baek K-Y, Truong YB, Kyratzis IL, et al. SiO2/sulfonated poly ether ether ketone (SPEEK) composite nanofiber mat supported proton exchange membranes for fuel cells. J Mater Sci 2013;48:3665–71.

[149] Aparicio M, Durán A. Hybrid organic/inorganic sol-gel materials for proton conducting membranes. J Sol Gel Sci Technol 2004;31:103–7.

[150] Ye YS, Wang H, Bi SG, Xue Y, Xue ZG, Liao YG, et al. Enhanced ion transport in polymer–ionic liquid electrolytes containing ionic liquid-functionalized nanostructured carbon materials. Carbon 2015;86:86–97.

[151] Choi BG, Hong J, Park YC, Jung DH, Hong WH, Hammond PT, et al. Innovative polymer nanocomposite electrolytes: nanoscale manipulation of ion channels by functionalized graphenes. ACS Nano 2011;5:5167–74.

[152] Ueno K, Tokuda H, Watanabe M. Ionicity in ionic liquids: correlation with ionic structure and physicochemical properties. Phys Chem Chem Phys 2010;12:1649–58.

[153] Hara S, Miyayama M. Proton conductivity of super acidic sulfated zirconia. Solid State Ionics 2004;168:111–6.

[154] Tominaka S, Momma T, Scrosati B, Osaka T. Sulfated zirconia as proton conductor for fuel cells: stability to hydrolysis and influence on catalysts. J Power Sources 2010;195:4065–71.

[155] Scipioni R, Gazzoli D, Teocoli F, Palumbo O, Paolone A, Ibris N, et al. Preparation and characterization of nanocomposite polymer membranes containing functionalized SnO2 additives. Membranes 2014;4:123–42.

[156] Casciola M, Capitani D, Comite A, Donnadio A, Frittella V, Pica M, et al. Nafion–zirconium phosphate nanocomposite membranes with high filler loadings: conductivity and mechanical properties. Fuel Cells 2008;8:217–24.

[157] Chen F, Mecheri B, D'Epifanio A, Traversa E, Licoccia S. Development of nafion/tin oxide composite MEA for DMFC applications. Fuel Cells 2010;10:790–7.

[158] Navessin T, Eikerling M, Wang Q, Song D, Liu Z, Horsfall J, et al. Influence of membrane ion exchange capacity on the catalyst layer performance in an operating PEM fuel cell. J Electrochem Soc 2005;152:A796–805.

[159] Fatyeyeva K, Chappey C, Poncin-Epaillard F, Langevin D, Valleton J-M, Marais S. Composite membranes based on Nafion® and plasma treated clay charges: elaboration and water sorption investigations. J Membr Sci 2011;369:155–66.

[160] Croce F, Scrosati B, Settimi L, Zane D. Nanocomposite, PEO-LiBOB polymer electrolytes for low temperature, lithium rechargeable batteries. J N Mater Electrochem Syst 2006;9:3–9.

[161] Lee DC, Yang HN, Park SH, Kim WJ. Nafion/graphene oxide composite membranes for low humidifying polymer electrolyte membrane fuel cell. J Membr Sci 2014;452:20–8.

[162] Lee W. Preparation and ionic conductivity of sulfonated-SEBS/SiO2/plasticizer composite polymer electrolyte for polymer battery. Solid State Ionics 2003;164:65–72.

[163] Jiang G, Qiao J, Hong F. Application of phosphoric acid and phytic acid-doped bacterial cellulose as novel proton-conducting membranes to PEMFC. Int J Hydrogen Energy 2012;37:9182–92.

[164] Lee L, Kim I-J, Yang S, Kim S. Filler effect of ionic liquid attached titanium oxide on conducting property of poly(ethylene oxide)/Poly(methyl methacrylate) composite electrolytes. J Nanosci Nanotechnol 2014;14:8010–3.

[165] Liu Y, Zhang J, Zhang X, Li Y, Wang J. Ti3C2Tx filler effect on the proton conduction property of polymer electrolyte membrane. ACS Appl Mater Interfaces 2016;8:20352–63.

[166] Jung G, Weng F, Su A, Wang J, Leonyu T, Lin H, et al. Nafion/PTFE/silicate membranes for high-temperature proton exchange membrane fuel cells. Int J Hydrogen Energy 2008;33:2413–7.

[167] Grandi S, Mustarelli P, Carollo A, Tomasi C, Quartarone E, Magistris A. New fillers for PBI-based composite electrolytes in polymer fuel cells. Compos Interfac 2012;17:649–62.

[168] Sánchez-Laínez J, Zornoza B, Téllez C, Coronas J. On the chemical filler–polymer interaction of nano- and micro-sized ZIF-11 in PBI mixed matrix membranes and their application for H2/CO2 separation. J Mater Chem 2016;4:14334–41.

[169] Lee C, Park J, Jeon Y, Park J-I, Einaga H, Truong YB, et al. Phosphate-modified TiO2/ZrO2 nanofibrous web composite membrane for enhanced performance and durability of high-temperature proton exchange membrane fuel cells. Energy Fuels 2017;31:7645–52.

[170] Li X, Ke C, Qu S, Li J, Shao Z, Yi B. High temperature PEM fuel cells based on Nafion®/SiO2 composite membrane. In: Carbone R, editor. Energy storage in the emerging era of smart grids. Rijeka: InTech; 2011. p. 279–98.

[171] Kim D, Park H, Rhim J, Lee Y. Proton conductivity and methanol transport behavior of cross-linked PVA/PAA/silica hybrid membranes. Solid State Ionics 2005;176:117–26.

[172] Beydaghi H, Javanbakht M, Badiei A. Cross-linked poly(vinyl alcohol)/sulfonated nanoporous silica hybrid membranes for proton exchange membrane fuel cell. J Nanostruct in Chem 2014;4.

[173] Hsu P-Y, Hu T-Y, Kumar S, Chang C-H, Wu K, Tung K-L, et al. Highly zeolite-loaded polyvinyl alcohol composite membranes for alkaline fuel-cell electrolytes. Polymers 2018;10:102.

[174] Erkartal M, Usta H, Citir M, Sen U. Proton conducting poly(vinyl alcohol) (PVA)/poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS)/zeolitic imidazolate framework (ZIF) ternary composite membrane. J Membr Sci 2016;499:156—63.

[175] Satterfield MB, Benziger JB. Viscoelastic properties of Nafion at elevated temperature and humidity. J Polym Sci B Polym Phys 2009;47:11—24.