Polymer Reviews

ISSN: 1558-3724 (Print) 1558-3716 (Online) Journal homepage: https://www.tandfonline.com/loi/lmsc20

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To cite this article: Chun Yik Wong, Wai Yin Wong, Kee Shyuan Loh, Wan Ramli Wan Daud, Kean Long Lim, Mohammad Khalid & Rashmi Walvekar (2019): Development of Poly(Vinyl Alcohol)-Based Polymers as Proton Exchange Membranes and Challenges in Fuel Cell Application: A Review, Polymer Reviews, DOI: 10.1080/15583724.2019.1641514

To link to this article: https://doi.org/10.1080/15583724.2019.1641514

POLYMER REVIEWS
https://doi.org/10.1080/15583724.2019.1641514

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REVIEW

Development of Poly(Vinyl Alcohol)-Based Polymers as Proton Exchange Membranes and Challenges in Fuel Cell Application: A Review

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ABSTRACT

Poly(vinyl alcohol) (PVA) is a biodegradable, water-soluble membrane that has low methanol permeation and reactive chemical functionalities. Modification of these features makes PVA an attractive proton exchange membrane (PEM) alternative to Nafion^{TM}. However, the pristine PVA membrane is a poorer proton conductor than the Nafion^{TM} membrane due to the absence of negatively charged ions. Hence, modification of PVA matrixes whilst complying with the requirements of projected applications has been examined extensively. Generally, three modification methods of PVA membranes have been highlighted in previous reports, and these are (1) grafting copolymerization, (2) physical and chemical crosslinking, and (3) blending of polymers. The use of each modification method in different applications is reviewed in this study. Although the three modification methods can improve PVA membranes, the mixed method of modification provides another attractive approach. This review covers recent studies on PVA-based PEM in different fuel cell applications, including (1) proton-exchange membrane fuel cells and (2) direct-methanol fuel cells. The challenges involved in the use of PVA-based PEM are also presented, and several approaches are proposed for further study.

ARTICLE HISTORY
Received 13 March 2019
Accepted 1 July 2019

KEYWORDS
Poly(vinyl alcohol) (PVA); proton exchange membrane (PEM); modification methods; fuel cells

1. Introduction

Fuel cell technology is an attractive green energy alternative that can replace fossil fuel technology. Current research in this area is inspired by the enthusiastic promotion of the Japanese government of hydrogen energy as the next generation energy sources in Japan.[1] However, the durability and cost of membrane materials and platinum catalyst in the electrodes have been identified as critical factors that inhibit the commercial success of fuel cell technology.

Toyota Mirai is one of the first fuel cell vehicles propelled by a fuel cell stack that comprises 370 cells, each of which is incorporated with GORE-SELECT® membrane

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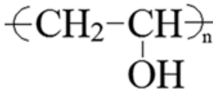
technology.[2] The total active area of the fuel cell stack is estimated to be 9 m^2, and the price of the polymer electrolyte membrane (PEM) alone (Nafion^{TM} N117-type membrane) is expected to be \$17,919 according to the Nafion^{TM} Store; this price is approximately 31% of the vehicle's selling price (\$57,500).[3] Hence, establishing an alternate approach to the conventional Nafion^{TM} membrane is essential for achieving commercial success. As a potential candidate, PEM needs to fulfill the requirements of resistance to aqueous acid solutions, biocompatibility, appropriate water content (for proton conduction) and constrained swelling (for mechanical stability).[4,5] Various types and techniques of PEM preparation (i.e. copolymerization, grafting, polymer blending or crosslinking) have been presented by researchers. For example, a polyetheretherketone (PEEK)-based film prepared through radiation-induced crosslinking and grafting was reported by Chen et al.[6] Overall enhancement in mechanical properties and reactant permeability were observed, and the film was proven to be durable for direct methanol fuel cell (DMFC) setup at high temperatures. The authors reported that the PEEK-based film achieved a maximum power density of 106 mW/cm^2 at 95 °C during the membrane electrode assembly (MEA) fuel cell test.

Among all potential candidates, one that meets the requirements is poly(vinyl alcohol) (PVA), a polyhydroxy polymer that is widely used for packaging and producing polarizer films. PVA membranes have a good film-forming capacity, relatively low production cost, wide-ranging crystallinity, complete biodegradability, crystal modulus and a considerable amount of hydroxyl groups that serve as a proton transfer bridge.[7] According to Pivovar et al.,[8] PVA membranes employed in pervaporation possess better methanol permeability than Nafion^{TM} membranes. However, in terms of electrical properties, PVA membranes are a poorer proton conductor compared with Nafion^{TM} membranes due to the absence of negatively charged ions. For this reason, PVA has to be modified through the incorporation of proton sources to enhance its proton conductivity and hydrophilicity. Filho et al.[9] produced a PVA-based membrane doped and cross-linked with phosphotungstic acid (HPW) and diethylenetriaminepentaacetic acid (DTPA). The resulting hybrid membrane displayed a remarkable reduction in swelling behavior whilst maintaining a high proton conductivity of 8.59×10^{-3} S/cm at 30 °C. According to Ye et al.,[7] PVA-based membranes for PEM applications can be grouped into two preparation methods, namely, (1) incorporated into PEM as a cross-linked partner via condensation and (2) esterification to form a 3D network structure. Several properties, such as swelling and chemical and mechanical properties, are effectively controlled by the degree of crosslinking of PVA-based membranes through the tuning of the dense molecular network structure.

This review focuses on the recent development of PVA-based PEM whilst highlighting its potential as a replacement for conventional Nafion^{TM} membranes in fuel cell applications.

2. Background and application of PVA

PVA as shown in Figure 1 is an excellent biodegradable and water-soluble polymer. Unlike most vinyl polymers, PVA is not prepared by polymerization of the corresponding monomer but through various indirect methods that involve the alcoholysis (also



$$-\!\!\left(CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}\right)\!\!-_n$$

Figure 1. Monomer structure of PVA.

known as saponification or hydrolysis) of polyvinyl acetate.[10] The conversion process can be catalyzed through strong acids or bases. As a polymeric material, PVA possesses exceptional properties, such as excellent film-forming capacity, structural flexibility, hydrophilicity, and biocompatibility.[11,12] Thus, PVA is widely used in various industrial applications, such as recovery of acids and valuable metals from waste solutions, membrane fuel cell applications, biological and biomedical applications, catalysis in organic and inorganic syntheses, and pervaporation separation of liquid mixtures.[13–17] Research related to PVA is constantly reinvigorated by different applications. For example, Kadri et al.[18] produced a PVA hydrogel membrane for tissue engineering. Although the results had inconsistencies, the preliminary data acquired were sufficient to conclude that PVA can be used as artificial membranes.

El-Kader et al.[19] illustrated the potential of utilizing PVA films as a replacement for commercial polyethylene films in technological applications (such as food packaging material). A PVA film was prepared by simple casting without the aid of additives or UV-cured coatings. The ranges of different PVA film thickness were synthesized (0.08, 0.2, 0.23, and 0.42 mm) for comparison with those of commercial polyethylene films. Correlations were observed between the two transmission spectra (samples of PVA and commercial polyethylene film) in the region of 190–350 nm and a 20% increase in the transmission of the PVA film over that of the commercial polyethylene film was noted in the region of 350–1500 nm. In terms of mechanical properties, Young's modulus and strength at break of the PVA films were better than those of the commercial polyethylene film by two orders of magnitude. Hence, the authors acknowledged PVA film as a promising replacement for commercial polyethylene films.

Moreover, Kusumaatmaja et al.[20] produced a PVA nanofiber by needle electrospinning for smoke filtration. The authors set up a test under three different smoke sources, namely, cigarette, waste, and vehicle combustion, for 1 min. The morphology of PVA nanofibers were demonstrated in Fig. 2. It was shown that the polymer matrix of PVA nanofibers was covered by various particles of cigarette smoke. Smoke particles of waste- and vehicle-combusted sources were as well attached to the nanofibers. The interaction between small particles and fibers could have resulted in adsorption with the PVA nanofiber membrane. Mohrova et al.[21] fabricated a thin PVA nanofibrous membrane for sound absorption applications. Several attempts were conducted with water vapor annealing to modify the structure of the PVA nanofibrous membrane owing to its water-soluble properties.

Accordingly, the numerous fabricated PVA nanofibrous membranes were oriented with different surface structures, as presented in Fig. 3. Figure 3b, c show that the structure of the thin membrane after water vapor action exhibited local area weight irregularity. After further analysis, the authors concluded that the absorbed frequency range increases with increasing irregularity in the polymer structure. However, the irregularity in the material surface decreases when the limit is exceeded due to the formation of

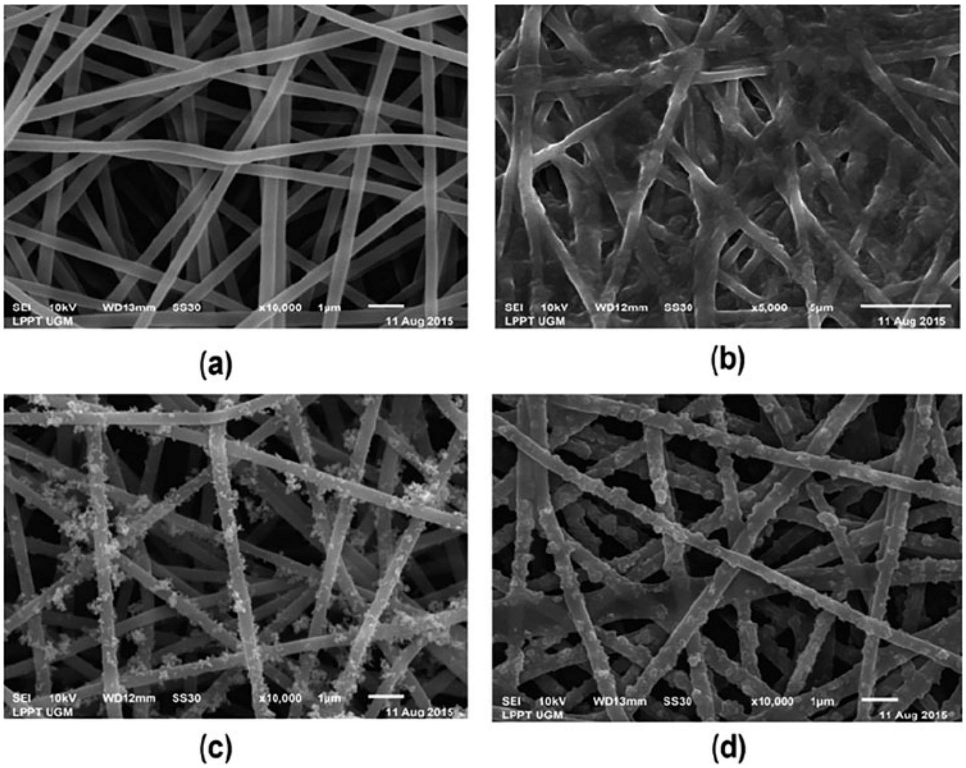


Figure 2. Morphology of PVA nanofiber membrane (a) before filtration and after filtration with (b) cigarette smoke, (c) waste-combusted smoke and (d) vehicle-combusted smoke.[19]

merged fibers, as shown in Fig. 3d. The absorbed frequency range reverts to being a function of peak again.

The low mechanical strength, thermal stability and proton conductivity of PVA hinder its use as a potential alternative for Nafion^{TM} membranes. Hirankumar et al.[22] reported that the proton conductivity value of a pure PVA membrane is 3.7×10^{-10} S/cm at room temperature. Notably, virgin PVA possesses secondary alcohol functionality, which is a pre-requisite of the successful functionalization of polymers. Moulay et al.[23] reported the functions of PVA functionalization in various applications. In this review, different modifying agents in the form of molecular and macromolecular compounds (i.e., graphene, hyaluronic acid (HA), β-cyclodextrin, polystyrene, poly(4-vinylpyridine), and poly(L-lactic acid)) were covered in tuning PVA matrixes to meet requirements in projected applications.

3. PVA-based polymer membrane

The interest in using PVA in DMFC applications began with PEM's high permeation selectivity of water to alcohol, which is believed to be a much better methanol barrier property than that of Nafion^{TM} membranes. Hydroxyl groups in PVA might also interact with other host polymers to maintain stability in the blend composite system. Yang et al.[24] performed a preliminary study of sulfonated poly(ether ether ketone) (SPEEK)/

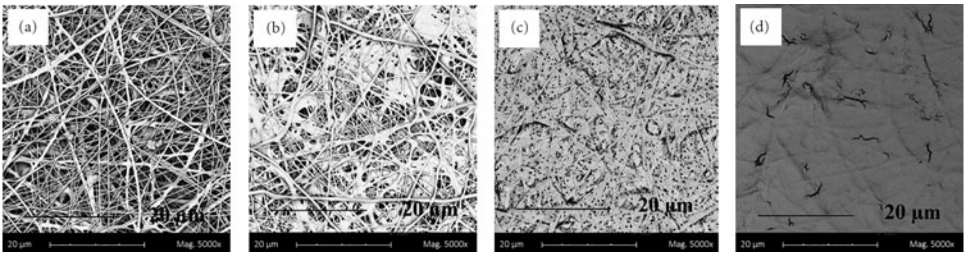


Figure 3. Surface morphology of PVA nanofiber structures (a) without water vapor action and after water vapor action for (b) 60 seconds and (c) 120 seconds; (d) structure after water vapor action in the liquid condition to the nanofiber layer for 60 seconds.[21]

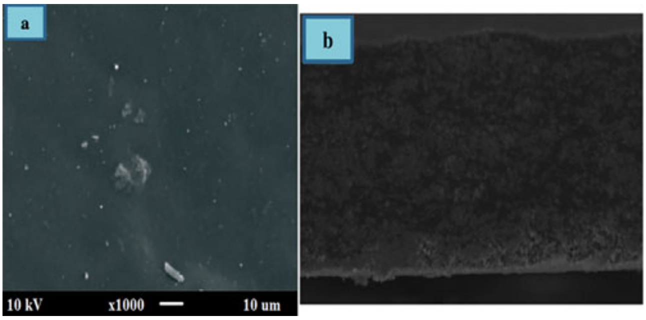


Figure 4. SEM images of SPVA-MOR membranes: (a) surface morphology at 1000× magnification and (b) cross-sectional.[27]

PVA composite membrane for DMFC applications. The composite membrane displayed low methanol permeability at a high PVA content (lowest at 3.588×10^{-6} cm^2/s at 50 wt.% of PVA). Although the addition of PVA results in excellent methanol resistance of the composite membrane, proton conductivity and ion exchange capacity (IEC) is reduced at a higher PVA content. The authors postulated that a reaction took place between hydroxyl groups of PVA and sulfonic groups of SPEEK, which in return inhibited or limited the number of active sites for proton transport. From there, we speculate that the blending of SPEEK and PVA formed an acid–base interaction that counteracts some sulfonic acid groups and offsets the proton conductivity by restricting the amount of ionic pathways.[25] Aside from that, a possibility of PVA agglomerates (7–12 µm) that dispersed through SPEEK matrix that resulted ionic pathways more tortuous could also be one of the reasoning in reduced conductivity.[26]

An integration of studies on sulfonated PVA-mordenite (SPVA-MOR) membrane for DMFC application was presented by Uctug et al.[27] Sulfonation of PVA was carried out in accordance with the procedure described by Yun et al.,[28] where sodium hydride (NaH) was added slowly to the PVA/ethanol mixture with constant mechanical stirring. During stirring, propane sultone was added drop-wise to the mixture, and the reaction was allowed to take place by heating at 80 °C for 3 h. The resulting SPVA was then mixed with the fully dispersed MOR in an oil bath at 100 °C for 1 h. The results revealed an effectively mixed MOR particle in the polymer matrix, and no voids were observed under scanning electron microscope (SEM) images (in Fig. 4). The SPVA-MOR membranes (0.052 S/cm) displayed approximately 50% higher proton conductivity than the PVA-MOR membrane (0.036 S/cm) at room temperature. Overall, the SPVA-MOR membrane outperformed the PVA-MOR membrane in the fuel cell test at low-temperature settings (below 75 °C). Although the result still did not match the power levels of Nafion^{TM} membranes, the potential of PVA-based membranes elicited much attention due to many positive aspects, such as low production cost and enhanced biodegradability.

Maiti et al.[29] reviewed more than 40 related studies on modified PVA for DMFC applications. PVA-based membranes are becoming more competitive than Nafion^{TM} membranes due to two essential characteristics, namely, proton conductivity and methanol crossover. The PVA modifications highlighted in the review are as follows:

1. Copolymerization: Coupling can be achieved by hydrophilic and hydrophobic copolymerization or through a chemical grafting-induced method by irradiation or chemical activation.
2. Crosslinking: Crosslinking of PVA can be achieved in many ways, such as freezing, heat treatment, irradiation and chemical treatment.
3. Blending: Blending of PVA can be realized with various sulfonated polymers (i.e. SPEEK, Nafion^{TM}, poly(styrene sulfonic acid) (PSSA) and PSSA-co-maleic acid (PSSA-MA)).

Among notable studies on the use of PVA in DMFC applications, the following highlighted numerous modification techniques to induce desired characteristics and improve membrane performance.

3.1. Modification by copolymerization of PVA membrane

Graft copolymerization of polymer effectively mixes the characteristics of two or more polymers in a single unit.[30] Natural polymers in their native form are generally unsuitable due to their high swelling and poor stability in biological environments.[31] Graft polymerization provides a research platform for modifying such characteristics and further obtaining novel polymeric materials with hybrid properties.

Several studies have examined PVA graft copolymerization with various hydrophilic and hydrophobic monomers to improve physical, mechanical or biological properties.[32–34] According to Chen et al.,[35] ceric ion-induced redox initiated grafting is favored in mild conditions with high graft yields and minimum side reactions. They conducted an experiment by graft co-polymerization of 2-[(acryloyloxy)ethyl]trimethylammonium chloride (AETMAC) monomer on PVA with ceric ammonium nitrate (CAN) as a redox initiator. The results revealed a close relationship amongst equilibrium swelling ratio, water vapor transmission and grafting extent. When grafting of AETMAC increases to 40%, the quantity of water absorbed increases to 587.8% ± 19.6 from 289.5% ± 6.6 of 10% AETMAC. This result is due to the relatively hydrophilic surface and low degree of crystallinity of AETMAC that subsequently dominated the grafted polymer matrixes and induced high hydrophilicity towards the membrane. Furthermore, Koohmareh et al.[36] developed a novel approach through reversible addition-fragmentation chain transfer method for synthesizing a grafted polymer of styrene from PVA. This method is ideal for the synthesis of polymers with a predetermined molar mass and low dispersion index compared with other controlled free-radical polymerization techniques, in which monomers can be polymerized through a controlled manner with requiring reaction conditions. According to Rohatgi et al.,[37] molar mass of PVA did played a significant role in fabrication of polymeric membrane. From the analytical results (three different molar mass of PVA were studied including (A) 13,000–23,000; (B) 89,000–98,000; (C) 124,000–186,000), we draw a hypothesis that low molar mass of PVA are able to interact more effectively between polymer chains during polymerization process which resulted lower mobility and swelling of polymer matrix.

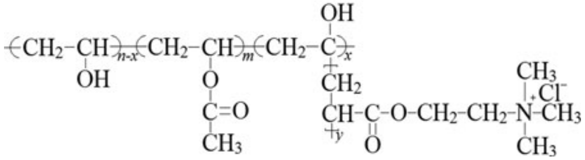
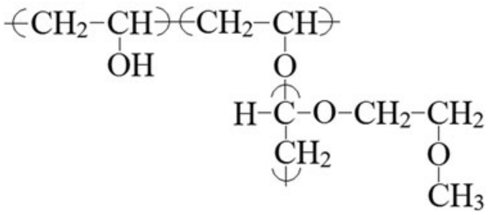
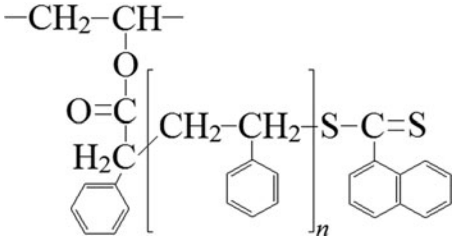
Aoshima et al.[38] presented a new method of synthesizing PVA graft copolymers via living cationic polymerization with a new coupling reagent of partially hydrolyzed poly (vinyl acetate) (PVAc-OH). Better solubility was achieved in comparison with that of pure PVA. The grafted PVA could be dissolved in water, dimethyl sulfoxide (DMSO) and many organic solvents, such as toluene and chloroform ($CHCl_3$). The film obtained from PVA-*graft*-poly(2-methoxyethyl vinyl ether) (poly(MOVE)) was translucent and tough, whereas an almost transparent film was obtained from the mixture of PVA and PVA-*graft*-poly(MOVE). Although the study did not present an informative explanation, differences in appearance are expected due to the low refractive index of poly(MOVE) that potentially leads to a translucent-like film.[39] Table 1 shows a summary of several studies on grafted PVA membranes.

3.2. Modification by crosslinking of PVA membrane

Polymer crosslinking alters the properties of a basic polymer, especially the water-uptake capacity of the polymer, degree of swelling, thermal, chemical and mechanical stability and capacity to retain acid functionality.[29] General crosslinking of polymers can facilitate low solubility due to covalent bonding that prevents polymer molecules from sliding over each other easily. However, this feature can be undone by increasing crosslinking, which can result in membrane brittleness. Several methods, such as freezing, heat treatment, irradiation, and chemical treatment, have been utilized for PVA crosslinking. The freeze-thaw cyclic processing method was first implemented by Stauffer et al.[40] as a novel method for the preparation of PVA hydrogel that is free of chemical or reinforcing agents. The tensile strength, stability and swelling ratio of the hydrogel were a function of solution concentration, freezing time and number of freeze-thaw cycles. The authors reported that the “best” PVA hydrogels were obtained by freezing 15 wt.% PVA solution at $-20\,^{\circ}C$ for 24 h followed by thawing at $23\,^{\circ}C$ for 24 h. As for freeze-thaw cycles, the PVA structures became increasingly dense as the number of cycles increased. This result is consistent with that of Yokoyama et al.,[41] who concluded that increasing the freeze-thaw cycles can increase crystallites and result in densely packed polymer matrixes.

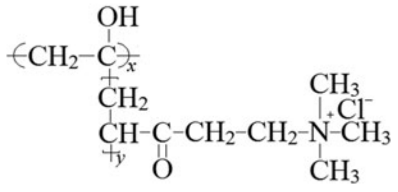
In the heat treatment crosslinked method, a previous study reported that a PVA film shows a decrease in permeability as the heating times increase.[42] Heating of PVA film can increase crystallinity and reduce the solubility and swelling in water. These effects may be due to the heat treatment that readily induces inter- and intramolecular crosslinking of polymers. Subsequently, the process reduces the mobility of the polymer

Table 1. Example of copolymerization methods studied with PVA membrane.

Method	Condition	Application	Chemical Structure	Ref.
Ceric ion-induced redox initiation method	• 10–40% by weight of AETMAC is added to the PVA solution under nitrogen • Aqueous CAN of 20 wt.% is added drop-wise to initiate graft co-polymerization • Reaction takes place at a constant temperature of 40 °C for 12 h	Wound dressing		Chen et al.[35]
Living cationic polymerization	• Living cationic polymerization of MOVE is carried out at 0 °C under dry nitrogen atmosphere • An initiator solution ($Et_{1.5}AlCl_{1.5}$ in hexane) is added to initiate the reaction • PVAc-OH in toluene is added to the mixture at 0 °C and subsequently added to methanol • Reaction mixture is diluted with dichloromethane and washed with water	-		Aoshima et al.[38]
RAFT Process	• Pre-treat the PVA-RAFT sample with dry toluene for 24 h • Styrene monomer and an initiator are dissolved in toluene and added to the flask to initiate polymerization • Tighten the flask and purge with nitrogen and heat the solution under oil bath at 60 °C for 48 h • Pour the mixture into excess methanol to precipitate the polymer	Biological application		Koohmareh et al.[36]

(continued)

Table 1. Continued.

Method	Condition	Application	Chemical Structure	Ref.
Ceric ion technique	• Add PVA to the flask and keep at 35 °C under nitrogen atmosphere • Add methacryloxyehtyl trimethylammonium chloride (DMC) monomer into the flask and purge with nitrogen for 30 min • Nitric acid and CAN are added to the flask to initiate graft copolymerization	Packaging materials		Zheng et al. [34]

solution and improves mechanical strength. The irradiation crosslinked method is similar to heat treatment in terms of changes in elastomer properties due to vulcanization. Petrova et al.[43] reported the effect of microwave irradiation on PVA crosslinking. Heating of PVA from 100 to 150 °C can result in crosslinking through ether bridges.[44] Further heating to 220 °C leads to the formation of double bonds and imparts a dark color to the polymer. The authors performed a study with temperature ranging from 70 to 170 °C and holding time ranging from 5 to 30 min to observe the correlation between the two factors. They found that temperature is proportional to crosslinking time, and an increase in the two parameters increases the degree of crosslinking and decreases swelling. Microwave irradiation resulted in a higher degree of crosslinking compared with convection heating. The results implied a great contribution of intermolecular etherification reactions with microwave irradiation. Convection heating oversees the increase in double bond contents as temperature rises from 150 °C (2.5 relative units) to 170 °C (5.4 relative units). This foresee that microwave irradiation technique was more effective in providing intense heat energy for greater intermolecular etherification reactions in comparison with convection heating technique. Therefore, the number of hydroxyl groups on PVA are effectively reduced that make the polymer matrix much more moisture resistant.[45]

Chemical treatment involves various chemical reagents (i.e. sulfosuccinic acid (SSA), poly (acrylic acid) (PAA), glutaraldehyde (GA), and 4-sulfophthalic acid (sPTA)[46] to promote changes in the chemical structure of the modified membrane. The adjustment of inter- and intramolecular reaction modes can be achieved by opting for specific crosslinker reagents and/or operational conditions.[47] For example, MA,[48] formaldehyde (FA)[49] and GA[50] can serve as crosslinking polymers without thermal treatment to drive the reaction. Other crosslinkers that contain proton sources have been incorporated into PVA to form crosslinked membranes by covalently linking the sulfonated groups of the crosslinker and the hydroxyl groups of PVA.[7] This type of crosslinkers is eliciting increased research attention due to the addition of sulfonic acid groups that can play a decisive role in proton conduction through the promotion of ionic channels for $–SO_3^-H^+$ to transport. Moreover, it serves as a barrier to methanol transport while crosslinking with the host polymer. Hou et al.[51] indicated that the IEC value improves when the amount of SSA content is increased. However, the addition of excessive crosslinkers might lead to a rigid and compact polymer structure, which supports the authors' findings that 20 wt.% SSA results in a lower proton conductivity than 15 wt.% SSA. Similar results have been obtained for PVA-based crosslinked membranes by using sulfoacetic acid as the crosslinker and proton source.[52] Water uptake and proton conductivity decrease with an increase in sulfoacetic acid content. Similarly, a study chemically crosslinked PVA with 2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS).[53] The modified membrane attained an optimum of 1.2×10^{-2} S/cm 1.53 meq/g for proton conductivity and IEC value, respectively, at room temperature with a mass ratio of 3.0 in PAMPS/PVA membrane. On these modified PVA membranes, a resemblance outcome of the swelling ratio decreased with the time of crosslinking, which was accompanied by improved mechanical properties and a slight weakening in proton conductivity. In that regards, the strong hydrocarbon matrix of the modified PVA membranes was thought to be highly impermeable to methanol despite the group not evaluating the value through methanol permeability analysis. Hence, the authors concluded that a crosslinker with sulfonic acid groups plays a dominant role in enhancing proton conductivity and methanol resistivity and obstructing the mobility of protonic charge carriers that facilitate reduced proton conductivity when surpassing the concentration limit. Maintaining a balance between sulfonic acid groups and water content within the polymer matrix is thus essential.

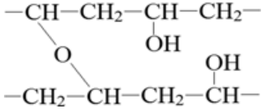
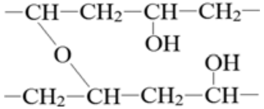
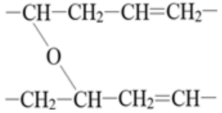
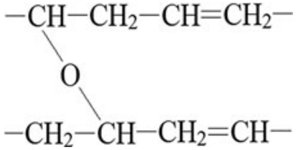
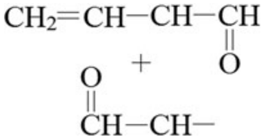
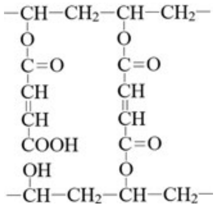
In summary, modification by crosslinking can generally be categorized under two methods, namely, physical (freeze-thawing, heat treatment, and irradiation) and chemical crosslinking. According to Chang et al.,[54] physical modification via freeze–thawing exhibits greater mechanical properties compared with chemical modification. However, chemical crosslinking is preferred over physical crosslinking for PEM applications due to its wide range of freedom in inducing desired characteristics (i.e. proton conductivity) towards the host polymer. Table 2 shows several studies on crosslinking methods of PVA membranes.

3.3. Modification by blending of PVA membrane

Polymer blending is a more attractive and facile method of improving properties, such as biological, mechanical and degradation, in comparison with using an individual polymer. The combination of synthetic and natural polymers is preferred for environmentally friendly production. Compared with natural polymers, synthetic polymers generally possess functional groups that can be tailored according to the desired mechanical and chemical properties. An important characteristic that influences blending behavior is the miscibility between polymers. Park et al.,[57] Srinivasa et al.[58] and Lewandowska[59] reported that blending of PVA and chitosan (CS) results in poor miscibility. Fourier transform infrared (FTIR) analysis indicated the existence of weak hydrogen-bonding interactions. On the basis of this result, Lewandowska et al.[59] showed that using different degrees of hydrolysis PVA could result in low miscibility with CS. In addition, only the PVA sample with a relatively low degree of hydrolysis (88%) had a low degree of crystallinity. It was demonstrated through the reduction in crystallinity and melting point of PVA upon addition of CS that further suggests partial miscibility between CS and PVA.

A study has also been conducted on the use of low-density polyethylene (LDPE), which is an extensively used synthetic plastic material, to blend with PVA.[60] The LDPE/PVA blend film showed improved oxygen permeability that favored its application as a packaging material. The thermogravimetric (TGA) curve of the LDPE/PVA blend film revealed a three-step degradation in comparison with pure LLPE that had a single degradation stage only. This finding also revealed that the blend film can withstand the impact of extensive applications with improved thermal stability. Salleh et al.[61] presented a blend film that includes PVA and starch fiber to improve water resistivity. Starch fibers were blended at a composition ranging from 50 wt.% to 90 wt.% in the study. The results indicated that increases in starch fiber content reflect the blend film thermal stability with high onset degradation temperature (from 50 wt.% starch fiber of 301.01 °C to 90 wt.% starch fiber of 356.40 °C). By contrast, an increase in starch fiber content shows high water absorption due to the nature of natural polymers that are hydrophilic.

Table 2. Examples of PVA crosslinked membrane through physical and chemical methods.

Type	Crosslink Method	Crosslinker	Application	Condition	Structure	Ref.
Physical	Freeze-thawing	-	-	• Freeze in an electric freezer at −15 °C for 23 h • Release at room temperature for 1 h		Yokoyama et al.[41]
	Freeze-thawing cycle	-	-	• Freeze at −20 °C for 24 h • Thaw at 23 °C • Up to five freeze-thaw cycles		Stauffer et al.[40]
	Heat treatment	-	Drug delivery	• Heat at a temperature ranging from 100–200 °C		Byron et al.[42]
	Microwave irradiation	-	-	• Heat in a microwave at a temperature ranging from 70–170 °C		Petrova et al.[43]
	γ irradiation	-	Integrated electronic	• Subject the film to ^{60}Co-γ-rays with doses of 0–300 kGy and a rate of 1.19 Gy/s		E-Sawy et al.[55]
Chemical		MA	Separation of organic liquid mixtures	• MA added corresponds to a theoretical crosslinking degree of 1–10 wt.% to PVA weight		Meng et al.[48]

(*continued*)

Table 2. Continued.

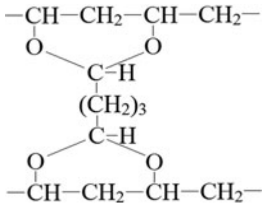
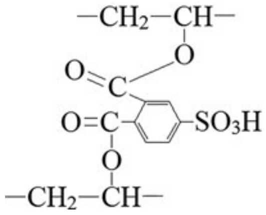
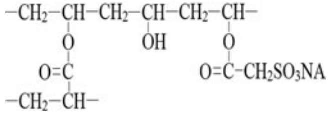
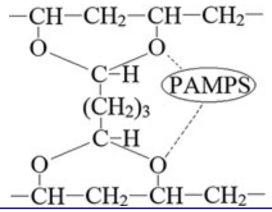
Type	Crosslink Method	Crosslinker	Application	Condition	Structure	Ref.
		GA	Widespread application	• GA/PVA mass ratio varies from 0.005 to 1, with temperatures of 10, 25, and 40 °C		Figueiredo et al.[50]
		sPTA	DMFC	• sPTA in the range of 10–40 wt.% (by mole of COOH group per OH group of PVA) added drop-wise, followed by continuous stirring at room temperature for 24 h • Dried membrane heated at 120 °C for a given time (between 5 and 60 min) to complete sulfonation and crosslinking		Chanthad et al.[56]
		Sulfoacetic acid sodium salt and poly(acrylic acid) (PAA)	DMFC	• Amount of sulfoacetic acid sodium salt (between 5 and 20% by weight of PVA) added drop-wise, followed by continuous stirring at room temperature for 24 h • Dried membrane heated at 140 °C for 4 h to complete sulfonation and crosslinking		Seeponkai et al.[52]
		PAMPS	Artificial muscle application	• Ratios of polymer solution (PVA/PAMPS) at 1:0.5, 1:1, and 1:2 are prepared • Dried membranes are annealed at 85–100 °C in over for 24 h to complete crosslinking		Dai et al.[53]

Table 3 illustrates several recent studies on PVA membrane with blending modifications. These extensive studies have shown that the modification of counterpart polymers (i.e. SPI, ODADS and PANI) impart targeted properties, which subsequently enhance the performance of the hybrid membrane.

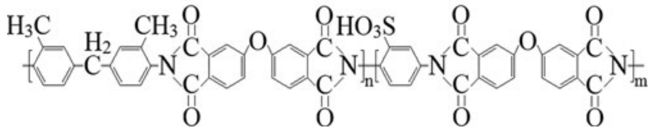
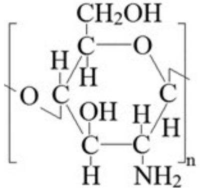
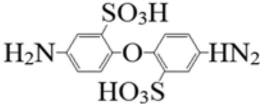
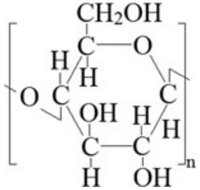
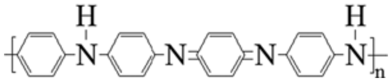
3.4. Modification through mixed methods of PVA membrane

Although a modified PVA membrane can achieve remarkable results, a mixed method of modification is proven to counteract the tradeoff effect. Chang et al.[71] reported the synthesis of PVA/sulfonated polyhedral oligosilsesquioxane (sPOSS) hybrid membrane. The hybrid membrane was prepared through simple methods involving the solution blending of PVA and sPOSS, followed by crosslinking with ethylenediaminetetraacetic dianhydride (EDTAD). The authors suggested that blending of sPOSS significantly enhances proton conductivity, with the highest reported at 50 wt.% (0.042 S/cm at 25 °C). In addition, the thermal stability of the hybrid membrane is improved compared with pristine PVA.

In this study, EDTAD functioned as a crosslinker that promotes the linking of polymer chains to the hybrid membrane and induces ionizable carboxylic acid groups into the network that ideally improve electrical and mechanical properties. Figure 5 demonstrates the proposed model structure of the crosslinked PVA/sPOSS hybrid membrane, which suggests probable ionic channels for proton transportation.

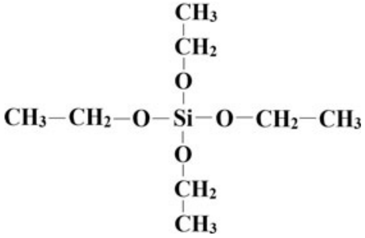
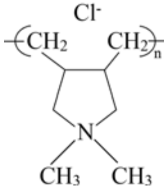
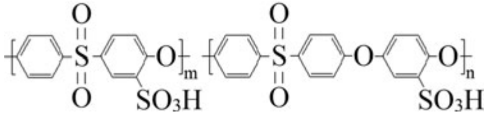
A modified membrane structure of PVA crosslinked with potassium hydroxide (KOH) and formaldehyde (CH_2O) was also presented. Further improvements in water uptake, IEC value and mechanical properties of the membrane can be achieved by the addition of vanadium oxide (Va_2O_5) as an inorganic filler. The unmodified membrane (without the aid of Va_2O_5) demonstrated a 101.1% water uptake due to the high degree of hydrolysis of the PVA (99.8%). Young's modulus was recorded at 122.9 MPa. The modified membrane showed an improvement in water uptake compared with the unmodified membrane. This higher water uptake was due to the laminar orthorhombic structure of Va_2O_5 that improved the interaction between Va_2O_5 and the polymer network, which then provided room for water absorption and an appropriate medium for the two main proton transfer mechanisms (Grotthuss and vehicular mechanism).[72] As Va_2O_5 loading increased (from 0.5 to 1.5%) in the modified polymer, the IEC value increased to 1.1 meq/g from the unmodified membrane of 0.5 meq/g. However, the increase in Va_2O_5 came with a compromise in mechanical properties, in which 0.5% loaded Va_2O_5 was found to be more favorable with a tensile strength of 35.9 MPa in comparison with 1.5% loaded Va_2O_5 of 30.6 MPa tensile strength. This particular finding may be due to the increase in inorganic filler loading that exceeded the limit and resulted in the uneven distribution of the excess load particles over the membrane that led to mechanical rupture.[73] Alamaria et al.[74] differentiated the effects of crosslinking techniques on a blend polymer consisting of Sago and PVA. Three approaches, namely, (1) using glutaraldehyde only, (2) using heat treatment (80 °C) only, and (3) using both glutaraldehyde and heat treatment, were studied. TGA analysis showed that the three techniques exhibit three consecutive weight loss steps. However, the Sago/PVA blend

Table 3. Types of polymers studied to perform blending modification with PVA membrane.

Polymer	Polymer Structure	Application	Condition	Ref.
Novel sulfonated polyimide (SPI)		Redox flow battery	• Blend the dissolved solution and cast onto a flat glass • The dried membrane is crosslinked with 3.6 wt.% FA in 25 wt.% H_2SO_4 solution	Liu et al.[62]
CS		DMFC	• Blend the dissolved solution and cast onto a glass plate • The dried membrane is crosslinked with a mixture of 10 wt.% GA solution and 2 M sulfuric acid solution for 24 h	Danwanichakul et al.[63] and Gopi et al.[64]
4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS)		DMFC	• Blend the dissolved solution with varying amounts of ODADS by weight ratios of PVA (5–30%)	Boroglu et al.[65]
Cellulose fiber		Packaging materials	• Disperse the microcrystalline cellulose under continuous stirring in distilled water and sonicate using an ultrasonicator • The resulting cellulose nanofiber is then blended with PVA to prepare the nanocomposite film	Frone et al.[66]
Polyaniline (PANI)		Conductive polymer	• Dissolve PVA in distilled water at 85 °C with continuous stirring for 1 h • Pour the solution into a three-mouth flask together with 100 mL 1 mol/L HCl	Wang et al.[67]

(*continued*)

Table 3. Continued.

Polymer	Polymer Structure	Application	Condition	Ref.
			• Add aniline to the flask and drop 1 mol/L of ammonium persulphate into the mixture solution • Hold the reaction in a water bath (25 °C) for 6 h	
TEOS		Micro-supercapacitor device	• Dissolve PVA in distilled water at 60 °C • Filter the filtrate and add TEOS and HCl (concentration, 1 ml) as catalyst for sol-gel reaction • Stir the solution for overnight at room temperature before casting onto glass plate	Anand et al.[68]
Poly(diallyldimethyl-6#ammonium chloride) (PDDA)		Alkaline fuel cell (AFC)	• Prepare PVA solution in water at 80 °C • Mix PVA and PDDA at a mass ratio of 1:0.5 under continuous stirring for 2 h until a homogeneous solution is obtained	Zhou et al.[69]
Sulfonated poly(ether sulfone) (SPES)		DMFC	• Blend the prepared polymer solutions with varying amounts of SPES by weight ratios of PVA (0–25%)	Divya et al.[70]

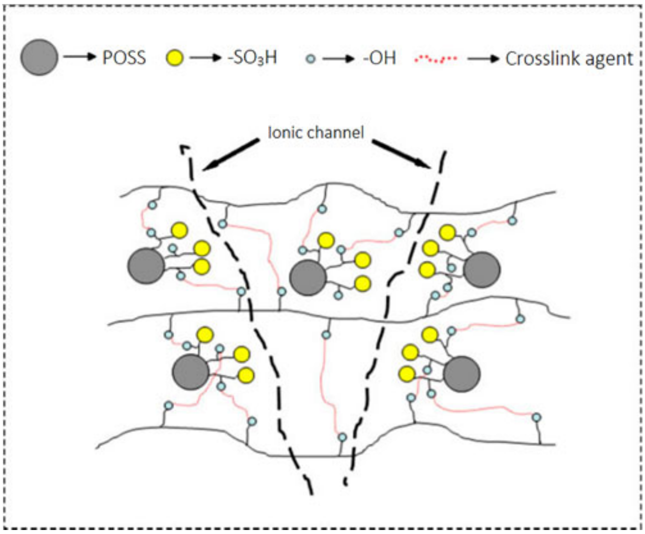


Figure 5. Proposed model structure of crosslinked PVA/sPOSS hybrid membrane.[71]

membrane with chemical and thermal crosslinked has the best thermal stability amongst the compared approaches.

Mittal et al. examined a PVA/starch blend film and further crosslinked it with urea formaldehyde. Urea formaldehyde is a crosslinker commonly used to modify polysaccharides, such as starch. Crosslinking between polysaccharides induces a covalent bonding between $-CH_2$ groups of formaldehyde and –OH groups of polysaccharides. According to the authors, the water uptake of crosslinked PVA/starch blend films is reduced by the formation of macromolecular crosslinking of PVA and starch with urea formaldehyde. The crosslinking reduces the molecular mobility of the polymer chains. As a compromise, the tensile strength of the blend films increases.

4. Integration of PVA-based membrane in fuel cell applications

PVA is a versatile, environmentally benign and readily available commercial polymer.[75] Global consumption of PVA in 2006 exceeded one million metric tons due to PVA's multiple usages and applications. The utilization of PVA biopolymers for fuel cell technologies is a novel and challenging research area and it promotes a cost-effective alternative to conventional Nafion^{TM} membranes. Though recent attempts are made to develop high performance bio-membranes for better environmental friendly production of PEM (i.e. chitosan, alginate, and cellulose),[76] but the interest in PVA-based PEM in fuel cell applications is significant due to the relatively low methanol permeation and reactive chemical functionalities available for modification. Extensive studies on PVA modification have proven that the latter is essential in promoting the desired properties for fuel cell applications.

4.1. PVA-based membrane for proton-exchange membrane fuel cell (PEMFCs)

The development of PEMFCs has attracted significant attraction due to the viability of hydrogen energy, which is virtually pollution free. In pristine form, PVA has a low proton conductivity of 10^{-10} S/cm. Beydaghi et al.[77] crosslinked this polymer with sulfonated graphene oxide (SGO) to improve performance. The obtained crosslinked PVA/SGO membranes were compared with Nafion^{TM} 117, and the former showed better thermal stability ($T_m = 223$ to 137 °C of Nafion^{TM} 117), mechanical strength (67.8–43 MPa of Nafion^{TM} 117) and proton conductivity (0.05–0.021 S/cm of Nafion^{TM} 117). The same study developed organic-inorganic nanocomposite membranes through chemical crosslinking with sulfonated nanoporous silica (SBA-15-propyl-SO_3H) in PVA.[78] Porous silica is commonly used as an inorganic filler in PEMFC application and by means of sulfonation, porous silica speeds up proton transport through additional sulfonic acid groups that serve as ionic pathways. Recently, a new species of inorganic nanofiller in the form of lanthanum cerium oxide ($La_2Ce_2O_7$) is proposed by Hooshyari et al.[79] $La_2Ce_2O_7$ nanoparticles co-exist as a cubic fluorite structure that are thermally and mechanically stable under long annealing process at 1673 K.[80] In that, PVA-$La_2Ce_2O_7$ composite was reported with an improved mechanical stability (29.35 MPa compared to 25.29 MPa of PVA membrane) which is adequate for fabricating MEA.

A blending polymer consisting of SPEEK, PVA and tetraethyl orthosilicate (TEOS) was produced by Sahin et al.[81] SPEEK is a front-runner for alternative PEM due to its high proton conductivity and thermal and chemical stability. With the inclusion of PVA, the author revealed the possibility of increasing the presence of modifiable groups, thus leading to improved proton transport and oxidative and hydrolytic stability upon adding TEOS. This finding was supported by the results reported by the author, in which the blend of SPEEK/PVA/TEOS outperformed other samples (pure SPEEK, PVA, and SPEEK/PVA composite) in terms of oxidative and hydrolytic stability. The addition of TEOS decreased the presence of –OH groups and subsequently improved water resistivity whilst leading to enhanced hydrolytic stability. Furthermore, the composite membrane comprises of Nafion^{TM} and PVA as well presented for the fabrication of ultrathin ($<20\,\mu m$) PEM.[82] In term of mechanical properties, the composite membranes were measured with much higher elastic modulus associated with the significant mechanical reinforcement provided by PVA nanofibers. However, such composite membranes are reported with lower proton conductivity to pristine Nafion^{TM} which may be attributed to the nonionic conducting behavior of the bulk PVA phase. Despite that, the contribution of PVA nanofibers did demonstrate interesting result at relative humidity under 40% whereby proton conductivity of the Nafion^{TM}/PVA composites were relatively similar to pristine Nafion^{TM}.

The study of PVA-based PEM has also been extended to high-temperature PEMFCs. High-temperature PEMFCs are a promising technology that corresponds to an operating temperature ranging from 120 to 180 °C. It is understood that such operating condition is profitable towards more effective proton transportation while also nullify the formation of liquid water. However, polymeric membrane under such a condition is challenging as the heat generation would causes the membrane to dry up and thus losses energy due to increased change in transport resistance.[83] For that, an advanced membrane with adequate physical and chemical properties is required. Hence, a novel proton-conducting membrane consisting of PVA, PAMPS and 1,2,4-triazole was fabricated by physical blending, casting and solvent evaporation techniques.[84] The resulting composite of PVA/PAMPS/1,2,4-triazole showed a thermal stability of up to 200 °C, which is ideal for use as a PEM in high-temperature PEMFCs. The composite also exhibited good dimensional stability when exposed to water and had a proton conductivity of 0.002 S/cm at 150 °C. Besides that, Anis et al.[85] also reported a study through the blending of sulfonated PVA and polybenzimidazole (PBI) for high-temperature PEMFC application. The involvement of sulfonated PVA demonstrates better control over resolving the usual mechanical stability issue of phosphoric acid (PA)/PBI composite as reported by Suryani et al.[86] The sulfonation of PVA polymer matrix has furnished a lower crosslinking sites for the composite, and thus increase the flexibility of polymer chains which leads to an increase in percent elongation and tensile strength. Aside from that, the protonated species of additional sulfonic groups also warranted higher proton conductivity with highest at 2.72×10^{-3} S/cm tested under 90 °C. Research on this class of PEMFCs (high-temperature PEMFCs) with PVA-based PEM is relatively new and challenging. Another related work is dedicated to phosphorus acid (H_3PO_4) imbibed polyacrylamide (PAM)/PVA semi-interpenetrating polymer network (semi-IPN) hydrogel.[87]

Table 4 summarizes the literature on PVA-based PEM. The studies are partly distinguished based on low-temperature and high-temperature PEMFCs.

4.2. PVA-based membrane for direct-methanol fuel cell (DMFCs)

For application in DMFCs, PEM is designed to have low methanol crossover to prevent the cathode catalyst from poisoning. This effect consequently causes decrements in performance. Nafion™ membrane is the commonly used PEM for fuel cell applications, but is unsuitable for DMFCs due to its sulfonic acid groups that causes excessive swelling in methanol (strong affinity between sulfonic acid groups and alcohol).[94] PVA has been employed as a promising PEM for DMFC applications due to its low production cost, good film-forming capacity, and methanol barrier.[95] Lue et al.[96] reported a methanol permeability of 3.57×10^{-7} cm^2/s for pure PVA membrane. Further enhancement was demonstrated by chemically crosslinking with sulfoacetic acid sodium salt and PAA, as per Seeponkai et al.[52] An improvement in methanol resistivity boosted methanol permeability to 5.21×10^{-9} cm^2/s with 10 wt.% sulfoacetic acid sodium salt to PVA weight. The resulting sulfonated membrane also displayed an improvement in proton conductivity (3.06×10^{-3} S/cm to 0.57×10^{-3} S/cm of pure PVA) and IEC (0.462–0.092 meq/g of pure PVA) and was regarded as a potential polymeric membrane for DMFC application. Besides that, these decisive results also in agreement that chemical crosslinking of pure PVA by imparting proton sources, sulfoacetic acid sodium salt are capable to resolve the intrinsic result of low conductivity in pure PVA.

Palani et al.[97] conducted a study on protonated montmorillonite (H^+MMT) crosslinked PVA membrane. Protonating MMT increased the available protonated particles that were consequently held with low affinity with water. As a result, the PVA/H^+MMT membrane showed lower methanol uptake than the unprotonated membrane. Interestingly, H^+MMT drew attention through the formation of an acid–base complex between the acidic sulfonic groups of the polymer electrolyte and the basic groups of the MMT compound. The highest proton conductivity was revealed to be 0.9572 S/cm

Table 4. Literatures on PVA-based PEM for PEMFC applications.

Type of PEMFCs	[a]PEM	[b]WU (%)	[c]IEC (meq/g)	[d]PC (S/cm)	[e]FC (mW/cm^2)	Ref.
Low-temperature	PVA/ SBA-15-propyl-SO_3H	80 (at 25 °C)	-	0.006 (at 25 °C)	-	Beydaghi et al.[78]
	PVA/SGO	58.3 (at 25 °C)	0.92 (at 25 °C)	0.050 (at 25 °C)	16.15 (at 30 °C)	Beydaghi et al.[77]
	SPEEK/PVA/TEOS	65 (at 80 °C)	2.02 (at 25 °C)	0.084 (at 80 °C)	336 (at 80 °C)	Sahin et al.[81]
	PVA/SSA	-	-	0.056 (at 70 °C)	72.8 (at 70 °C)	Ebenezer et al.[88]
	PVA/SSA	-	-	0.077 (at 70 °C)	99 (at 70 °C)	Ebenezer et al.[89]
	PVA/PAMPS/zeolitic imidazole framework (ZIF)	328 (at 25 °C)	1.52 (at 25 °C)	0.134 (at 80 °C)	-	Erkartal et al.[90]
	25 kGy irradiation doses 10% PVA	-	-	0.340 (at 25 °C)	-	Stosevski et al.[91]
	PVA/SSA/graphene oxide (GO)	-	-	0.003 (at 30 °C)	155.4 (at 23 °C)	Gonzalez-Guisasola et al.[92]
	PVA/sulfonic acid	–	–	0.156×10^{-5} (at 25 °C)	–	Ali et al.[93]
High-temperature	PVA/PAMPS/1,2,4-triazole	248 (at 25 °C)	1.62 (at 25 °C)	0.002 (at 150 °C)	-	Erkartal et al.[84]
	H_3PO_4-imbibed PAM/PVA	-	-	0.053 (at 183 °C)	225 (at 183 °C)	Tang et al.[87]

[a] PEM refers to proton exchange membrane.

[b] WU refers to water uptake.

[c] IEC refers to ion exchange capacity.

[d] PC refers to proton conductivity.

[e] FC refers to fuel cell performance.

with 10 and 20% of PVA and H^+MMT, respectively. Presumably, an increase in PVA concentration resulted in higher water swelling due to the presence of more apparent –OH groups and was thus remotely beneficial with higher proton conductivity when crosslinked with H^+MMT. Additionally, the methanol permeability exhibited by the composite membranes was displayed with a slope of the straight line in corresponding to increase in H^+MMT concentration. According to Altaf et al.,[98] the reduction in methanol permeability may be attributed by the exfoliation of H^+MMT (inorganic filler) that act upon as the tortuosity factor and hence improve the barrier properties of the composite.

Furthermore, a blend composite membrane comprising PVA, CS, and cellulose nanocrystals (CNCs) was reported as an eco-friendly and cost-effective candidate for DMFC application.[99] The complex membrane was prepared by blending PVA and CS with GA as the crosslinker. Crosslinking of the membrane adversely converted the crystalline phase of the membrane into a more dominant amorphous phase. Hence, adding CNCs as the biofiller created a tortuous path that suppressed the water uptake to 70% ± 2 from 253% in the case of pure PVA membrane. The methanol permeability of the PVA/CS/CNC membrane also decreased by a magnitude of 10^{-8} cm^2/s due to the crosslinked effect and improved filler–matrix interaction. Extensive studies have also been conducted on the effects of varying preparation methods on performance. Yang et al.[100] prepared two blend membranes of PVA and CS via solution casting and electrospinning methods, respectively. The composite blend prepared via electrospinning method had an appropriate ionic conductivity (0.010 S/cm), low methanol permeability (2.28×10^{-7} cm^2/s) and high selectivity (43.9×10^3 $S/cm^{-3}s$). Xi et al.[101] supported this finding in their study, which showed that electrospun membranes exhibit shifted and more distinct small-angle X-ray scattering ionomer peaks compared with a solution-casted membrane. This result implies larger proton transport channels and better phase separation with the electrospinning method compared with the solution casting method.

In term of mechanical improvement, Danwanichakul et al.[63] demonstrated graft copolymerization of PVA and CS along with glutaraldehyde and sulfuric acid as a crosslinking agent and catalyst respectively. From the obtained results, the group advanced with statement of CS-graft-PVA/PVA membrane provides more reliable properties at fully hydrate state than polymer blending of CS and PVA due to its less flexible structures of the crosslinking network. Though the initiation of graft copolymerization is capable to form a dense polymeric structure with improved mechanical properties, however proton conductivity channels are reduced in the process whereby some amino groups are grafted with PVA chains. In agreement to the statement, characterization study of polyethylene-graft-sulfonated polyarylsulfone (PE-g-s-PAES) proton exchange membrane conducted by Kim et al.[102] clearly revealed that graft copolymerization indeed provides a uniquely strong and stable matrix that effectively limits water swelling. In addition, contact angle measurement has shown water droplet being stable on the membrane surface as a comparison to Nafion^{TM} 117 (immediately diffused into the PEM matrix). Evidently, the graft copolymerization had taken effect on forming a dense and compact structure with greater hydrophobicity and well-organied microphase separated bulk morphology.

Nevertheless, both chemical crosslinking and polymer blending strategies are shown to be more matured for DMFC application, but physical crosslinked via freezing/thawing method does immerse with promising properties as per reported by Gupta et al.[103] The physically crosslinking of PVA has increased the polymer matrix interaction and disfavors chain mobility that remotely reduces the void volume in the membrane. For that reason, barrier properties of the PVA membranes are improved with a lower water uptake and methanol permeability reported. Although the reduction in water uptake may indicate a drop in proton conductivity, however, the properties of lower methanol permeability is practically useful parameter towards DMFC. The single cell DMFC performance of the in-house synthesized PVA membrane was shown with a maximum power density of 1.79 mW/cm^2 at 30 °C.

Table 5 shows recent studies on PVA-based PEM in DMFC applications.

5. Challenges in using PVA-based PEM in fuel cell applications

To develop a new PEM for fuel cell applications, several specifications are required, namely, (1) low cost, (2) high thermal and chemical stability, (3) excellent mechanical strength, (4) high proton conductivity, and (5) low methanol crossover.[113] Utilizing water-soluble polymers, such as PVA, PAM, poly(ethylene oxide) (PEO), poly(vinylpyrrolidone) (PNVP) and poly(hydroxyethyl acrylate) (PHEA), are suitable due to their high affinity for water. Consequently, large amounts of water molecules are imbibed within the polymer matrixes. High water uptake increases proton conductivity due to the formation of flexible polar side chains that facilitates many carrier ions and the formation of hydrogen bridges between polymer matrixes.[114] However, this statement contradicts current research revealing that a reduction in water swelling of the membrane is desirable for methanol resistivity, which is essential for DMFC applications.[115,116] Therefore, the balance between methanol permeability and proton conductivity must be effectively optimized.

Water swelling and methanol permeability can be reduced by modification. Kim et al.[117] demonstrated a crosslinked membrane of PVA/SSA. The methanol permeability and proton conductivity of the PVA/SSA were measured to be 2.63×10^{-7} cm^2/s and 0.012 S/cm, respectively. This result is comparable to that of the pure PVA membrane that excels in methanol blockage (methanol permeability $= 3.46 \times 10^{-7}$ cm^2/s for pure PVA) but with a high proton conductivity (proton conductivity $= 0.57 \times 10^{-3}$ S/cm for pure PVA). The addition of inorganic fillers, such as SiO_2, could decrease methanol permeability (PVA/SSA/SiO_2 $= 4.48 \times 10^{-8}$ cm^2/s) due to the strong interaction between the organic polymer matrix and SiO_2 in the hybrid that restricts methanol uptake.[117] Although the results of crosslinking PVA-based membranes are impressive, completely replacing the conventional Nafion^{TM} membrane is still infeasible. Kasai et al.[110] compared a synthesized CL-SEC/PVA blend composite and Nafion^{TM} NRE-212 as alternative candidates to DMFC application. The power density obtained through a DMFC performance test was about three times higher in Nafion^{TM} NRE-212 than in CL-SEC/PVA under 1 M of methanol. In this regard, using a high degree of substitution of sulfoethyl groups on sulfoethylcellulose (SEL) could result in increased proton conductivity.

Table 5. Literatures on PVA-based PEM for DMFC applications.

PEM	[a]MP (cm^2/s)	[b]WU (%)	[c]IEC (meq/g)	[d]PC (S/cm)	[e]FC (mW/cm^2)	Ref.
PVA/sulfoacetic acid sodium salt/PAA	5.21×10^{-9}	80	0.462	0.0030	-	Seeponkai et al.[52]
PVA/H^+MMT	-	610	-	0.9572	-	Palani et al.[97]
PVA/CS/CNCs	5.39×10^{-8}	-	-	0.0004	-	Gaur et al.[99]
Composite electrospun-PVA/CS	2.28×10^{-7}	-	-	0.0100	30 (at 50 °C)	Yang et al.[100]
20% Zwitterionic functionalized PVA/ (3-mercaptopropyl)trimethoxysilane (MPTMS)	1.45×10^{-6}	145	5.000	0.0070	-	Gao et al.[104]
2% carbon nanotubes (CNT)-poly (diallyldimethylammonium chloride) (PDDA)-HPW/PVA	4.02×10^{-7}	116.8	-	0.0053	16 (at 60 °C)	Li et al.[105]
In situ prepared SPVA/titanium oxide (TiO_2)	1.11×10^{-9}	123.1	1.010	0.0822	0.75 (at 70 °C)	Solanki et al.[106]
SPEEK/PVA	8.12×10^{-6}	24	0.621	0.0175	-	Yang et al.[24]
ODADS crosslinked PVA	7.65×10^{-8}	69.9	-	0.0163	-	Boroglu et al.[65]
PVA/sPOSS	3.45×10^{-7}	135	0.605	0.0420	-	Chang et al.[71]
SPVA-MOR	-	22.3	0.470	0.0520	2.9 (at 75 °C)	Uctug et al.[27]
PVA/pectin/nano-TiO_2	2.63×10^{-6}	247	-	0.0015	-	Raj et al.[107]
KOH-doped PVA	-	70	4.090	0.0056	1.79 (at 30 °C)	Gupta et al.[103]
KOH-doped PVA/PSSA/TiO_2	-	5	-	0.0042	-	de Oliveira et al.[108]
Orthophosphoric acid modified PVA/HA/ hydroxyapatite (HAP)	-	140	-	0.0570	90 (at 55 °C)	Kamoun et al. [109
Crosslinked sulfoethylcellulose (CL-SEC)/PVA	0.24×10^{-6}	44	1.100	0.0220	23.6 (at 50 °C)	Kasai et al.[110]
Polytetrafluoroethylene (PTFE)/Zirconium phosphate (ZrP)/PVA	14.5×10^{-7}	30.65	1.280	0.0281	–	Pagidi et al.[111]
SPVA/nano-TiO_2	1.29×10^{-9}	114.32	0.931	0.0783	0.72 (at 70 °C)	Gohel et al.[112]
Freeze-thawed PVA	–	70	4.090	0.0056	1.79 (at 30 °C)	Gupta et al.[103]

[a] MP refers to methanol permeability.
[b] WU refers to water uptake.
[c] IEC refers to ion exchange capacity.
[d] PC refers to proton conductivity.
[e] FC refers to fuel cell performance.

Incorporating functionalized nanofillers and further impregnating them with imidazole-type ionic liquid (IL) is a novel approach in preparing PEM with high proton conductivity. Wu et al.[118] constructed a composite membrane by incorporating various functionalized GO (i.e. vinyl imidazole functionalized GO (V-GO) and p-styrenesulfonic acid functionalized GO (S-GO)) and further filling with 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIm]^{+}BF_4^{-}$, IL) to activate many proton transfer channels. The inclusion of IL in the polymer matrix distinguished the crosslinking method as the imidazolium salt functional groups exhibited superior stability chemically and thermally. Although the imidazole group is hydrophilic and could significantly increase the water uptake, the methanol uptake reported by Guo et al.[119] was only 3.54% at the highest copolymerization content of 1.387% (1-allyl-3-methylimidazolium chloride (AmimCl) to polymer). In addition, the resulting composite demonstrated a high proton conductivity of 0.0333 S/cm.

Despite that strategy for formulating PVA-based PEM for fuel cell applications is promising, as justified by prevailing research. Intrinsic properties of PVA being water soluble remained a doubt for fuel cell application to serve the requirement of long operation hours and thermal stabilities that demand for successful PEM. Nevertheless, the incorporation of inorganic fillers demonstrated a glimpse of improvement in term of thermal stabilities and proton conductivity of PVA-based PEM. But the enhancement in water retention capacity might ease up the water management and consequently lead to failure operation due to dimensional instability of PEM. For instances, the incorporation of $La_2Ce_2O_7$ nanoparticles into PVA as described by Hooshyari et al.[79] The vacancies of La^{3+}, Ce^{4+}, and O_2 sites have led to a higher surface area for water transportation in the nanocomposite membranes and hence proton conductivity increases. Meanwhile, the water uptake was reported at 148% which signified twofold of mass increases upon immersing into the water. In correspondence, the plausible structural expansion would accommodate along the increases and may prompt with severe mechanical problems that affect the integrity of MEA (such as flooding due to the accumulation of excessive water).[120]

Aside from that, a major hindrance towards DMFC application is down to its relatively poor power densities, ranging from 1 to 24 mW/cm^{-2} at temperatures between 25 and 80 °C.[121] Nevertheless, integration of different modifying methods towards PVA-based PEM are shown promising in properties such as chemical, thermal and mechanical properties. However, one could not assure the possible arrangement of polymer matrix upon modification. According to Yee et al.,[122] the reported conductivity of buckypaper/PVA composite is reduced upon addition of multiwall carbon nanotubes (MWCNTs). Based on the experimental compiled, the authors summarized a possible action on the penetration of electrically insulating PVA into the porous MWCNTs network which lead by reduced the availability of electrically conductive pathways.

As a result, extensive investigation of improving thermal stability whilst maintaining a balance between water management and mechanical properties are essential to a proposing study of polymer blending and incorporation of functionalized inorganic fillers (such as sulfated metal oxides and SGO). Furthermore, analysis on proton conduction properties as well as single cell performance are vital to measure its potential as a PEM.

6. Summary and perspectives

PVA-based membrane is a potential PEM for fuel cell applications. Although the maturity level is yet to be achieved, this PEM type has gained attention due to its low methanol permeation and reactive chemical functionalities available for modification. In this work, multiple modification methods involving with PVA membrane are reviewed, including copolymerization, crosslinking, polymer blending, and mixed method that adopted multiple modifications to further enhance PVA with desirable properties. Furthermore, it summarizes the current work that employs PVA-based membrane into the study of fuel cell application. Two types of fuel cells, namely, PEMFC and DMFC are both involved. With that being mentioned, we foresee PVA-based PEM may soon be a front-runner in fuel cell technology for commercial usage in real-world applications.

Though there are several challenges such as long-term and thermal stabilities awaiting to be rectified in order to achieve the state. From that, it can be perceived that PVA-based PEM are lacking practicality, whereby it proved vital towards replacing conventional Nafion^{TM} in commercialization. In correspondence with those challenges, the future direction of such PEM can be done by prolong existing research. For instance, thermal stability in term of polymeric masses over time can be measure at specific operating temperature (i.e. 80 °C to resemble the operating condition of low-temperature PEMFC application) or measure the power density of single stack MEA over time. This can reserve as the real-time performance of PVA-based membrane while examining its potential as an alternative PEM.

Funding

The authors acknowledge the financial support given by the Universiti Kebangsaan Malaysia research grants through project no. DIP-2018-012 & GGPM-2017-043.

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