

Review Paper

Recent developments in high-performance Nafion membranes for hydrogen fuel cells applications



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ABSTRACT

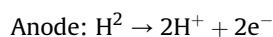
As a promising alternative to petroleum fossil energy, polymer electrolyte membrane fuel cell has drawn considerable attention due to its low pollution emission, high energy density, portability, and long operation times. Proton exchange membrane (PEM) like Nafion plays an essential role as the core of fuel cell. A good PEM must have satisfactory performance such as high proton conductivity, excellent mechanical strength, electrochemical stability, and suitable for making membrane electrode assemblies (MEA). However, performance degradation and high permeability remain the main shortcomings of Nafion. Therefore, the development of a new PEM with better performance in some special conditions is greatly desired. In this review, we aim to summarize the latest achievements in improving the Nafion performance that works well under elevated temperature or methanol-fueled systems. The methods described in this article can be divided into some categories, utilizing hydrophilic inorganic material, metal-organic frameworks, nanocomposites, and ionic liquids. In addition, the mechanism of proton conduction in Nafion membranes is discussed. These composite membranes exhibit some desirable characteristics, but the development is still at an early stage. In the future, revolutionary approaches are needed to accelerate the application of fuel cells and promote the renewal of energy structure.

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1. Introduction

The growing global energy demand poses severe challenges to environmental protection, energy security, human health, and the sustainable development of natural resources (Wang et al., 2020). Due to the heavy utilization of fossil energy, enormous quantities of critical air pollutants and greenhouse gases have been released (Yuan et al., 2018; Chen et al., 2020). In the process of moving towards a low-carbon and green economy, many countries are striving to find alternatives to traditional energy sources to deal with the energy crisis. In recent years, with the rapid development of green energy applications, the technical and economic feasibility of hydrogen energy applications has steadily improved, and the replacement of fossil energy by hydrogen energy is gradually becoming a reality (Abe et al., 2019). To realize the vision of sustainable development of the hydrogen economy, the fundamental science of hydrogen production, storage, and transportation requires significant progress (Thomas et al., 2020).

Proton exchange membrane fuel cell (PEMFC) represents a crucial step in the development of the hydrogen economy. It has aroused widespread attention due to its high energy efficiency, long operation times, easy scale-up, low (or zero) pollution emission, and convenient fuel supply (Zhang and Shen, 2012; Prykhodko et al., 2021). Fuels such as H₂, ethanol, and methanol have been commonly used in fuel cells. The reaction occurring in the fuel cell can be explained as follows:



The primary compartments of the PEMFCs have been shown in Fig. 1. The fuel cell is an electrochemical device that converts the chemical energy of fuel into electrical energy continuously, and this energy conversion is carried out under constant pressure and temperature (Gao et al., 2020). The fuel of the anode is dissociated into hydrogen protons and releases electrons under the action of the catalyst. The hydrogen protons pass through the proton exchange membrane to reach the cathode, electrons flow from the

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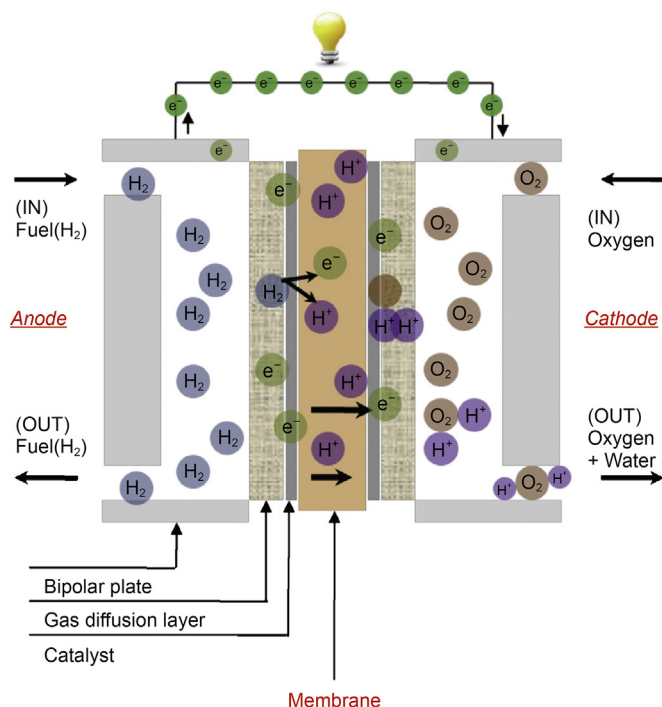


Fig. 1. Schematic design of the PEM fuel cell. Reprinted with permission from ref (Kim et al., 2015). Copyright (2015) Elsevier.

external circuit to the cathode. The oxidant (oxygen or air) is reduced by the cathode catalyst and combines with hydrogen ions and external circuit electrons to produce water (Kiani et al., 2018; Shen et al., 2020). Fuel cell technology has been widely used in cars, buses, ships, stationary power generation equipment, and portable mobile energy (Wang and Jiang, 2017). High cost, lagging industrial technology, poor performance, and short service life of fuel cells has hindered the broad commercialization of PEMFC technology (Vengatesan et al., 2011; Kim et al., 2015; Li et al., 2020a).

Polymer electrolyte membrane (PEM) is the core component of PEMFC, which plays a crucial role in cell performance. Nafion has been used as PEMs since inception due to its unique hydrophilic/hydrophobic nanophase structure. In Nafion, it is known that the hydrophobic perfluorinated polyethylene backbone and highly hydrophilic sulfonic acid-terminated perfluoro vinyl ether side groups can form nanoscale domains with ion migration (Mauritz and Moore, 2004). The chemical structure of Nafion and the cluster network model are shown in Fig. 2. It is a random copolymer consisting of perfluoro ether side chains, in which sulfonic acid groups are randomly distributed along the polymer backbone (Yin et al., 2018). The cluster network in the Nafion membrane is created by connecting 4 nm sulfonated ion clusters and 1 nm narrow channels (Fernandez Bordín et al., 2018). Ionic clusters are formed by the aggregation of Nafion's highly hydrophilic sulfonic acid groups, which made the water and proton passed through (Fruhvirt et al., 2020). Despite its advances of ideal chemical/mechanical stabilities and considerable proton conductivity, there remain several defects for Nafion used as PEMs, including the fuel penetration, excessive swelling, and water loss at high temperature (Motz et al., 2018). Moreover, given any alteration to the assembly environment or the chain structure could cause damage to the nanophase structure of Nafion, it is hard to simultaneously maintain the mechanical/chemical stabilities and improve the proton conductivity. Enhancing the comprehensive properties of the Nafion membrane has become an indispensable but challenging

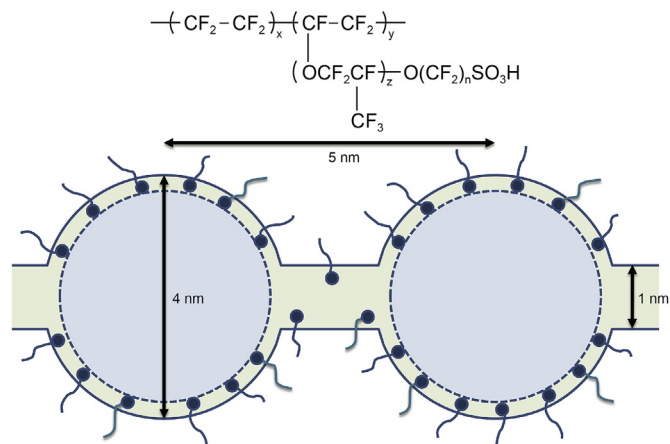


Fig. 2. Chemical structure of Nafion and cluster network model.

problem for further development of high-performance PEM based on Nafion.

It is worth mentioning that the advanced PEM should meet the following requirements: (i) excellent chemical and thermal stability; (ii) high proton conductivity; (iii) superior mechanical properties; (iv) easy to fabricate MEA; (v) low cost and satisfactory durability; (vi) low fuel permeability and sufficient water uptake.

To further realize the vision of the widespread application of fuel cells, it is necessary to rationally design novel membranes based on a deep understanding of proton transport, fuel permeability, and membrane material stability. Current research on Nafion membranes is mainly focused on the development of excellent water retention ability at high temperatures or good proton conduction ability in the absence of water. In this review, we discuss various strategies for achieving a high-performance Nafion membrane and evaluate their feasibility in the process of fuel cell applications.

2. Proton conduction mechanism in PEMs

The key to understanding the proton conduction mechanism is the competitive relationship between the electrostatic interactions and proton's solvation energy, where the solvation energy is numerically proportional to the reciprocal of the dielectric constant (Li et al., 2020b). For the interpretation of proton conduction phenomenon in PEMs, two mechanisms are generally accepted: the vehicular and Grotthuss hopping (Chopade et al., 2016). The vehicular mechanism elucidates the conductivity based on the diffusion of protons and involving the water molecules such as H_3O^+ , $H_5O_2^+$, and $H_9O_4^+$ in combination with the diffusion of uncharged molecules. After the combination of proton and carrier, a concentration gradient phenomenon occurs during the diffusion process, which makes the remaining carriers reversely diffuse and promotes the transport of protons (Kusoglu and Weber, 2017). The vehicular mechanism dominants especially at incomplete hydrogen-bond and low hydration conditions as hydrogen bonds begin to break and elongate (Li et al., 2020c). The Grotthuss mechanism explains the conduction of protons within a hydrogen-bonded network of water molecules (Lim et al., 2019). According to this model, the transport of a hydrated proton along the water network channel involves the continuous conversion between two hydrated complexes. This mechanism is characterized by high proton mobility and activation energy (0.1–0.4 eV) since the hydrogen-bond cleavage requires an energy loss of about 0.11 eV.

The industry standard PEM for fuel cells in Nafion, the water

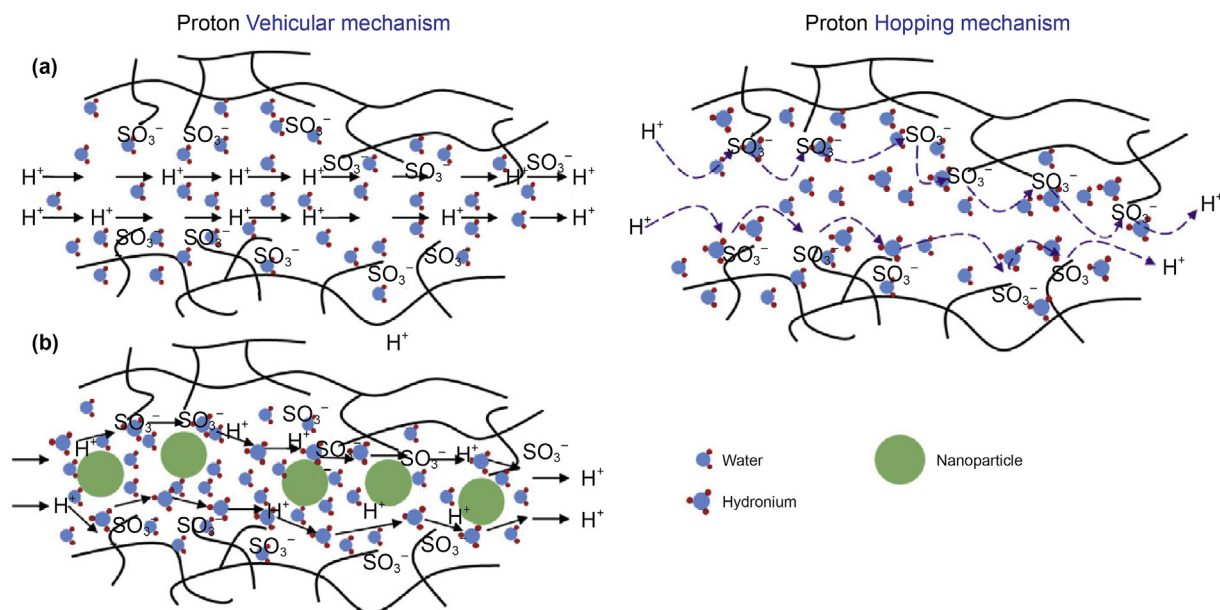


Fig. 3. The schematic illustration of the Vehicular mechanism and hopping mechanism as proton conduction in (a) pristine membranes and (b) polymer/nanoparticle composite membranes. Reprinted with permission from ref (Peighambaroust et al., 2010). Copyright (2010) Elsevier.

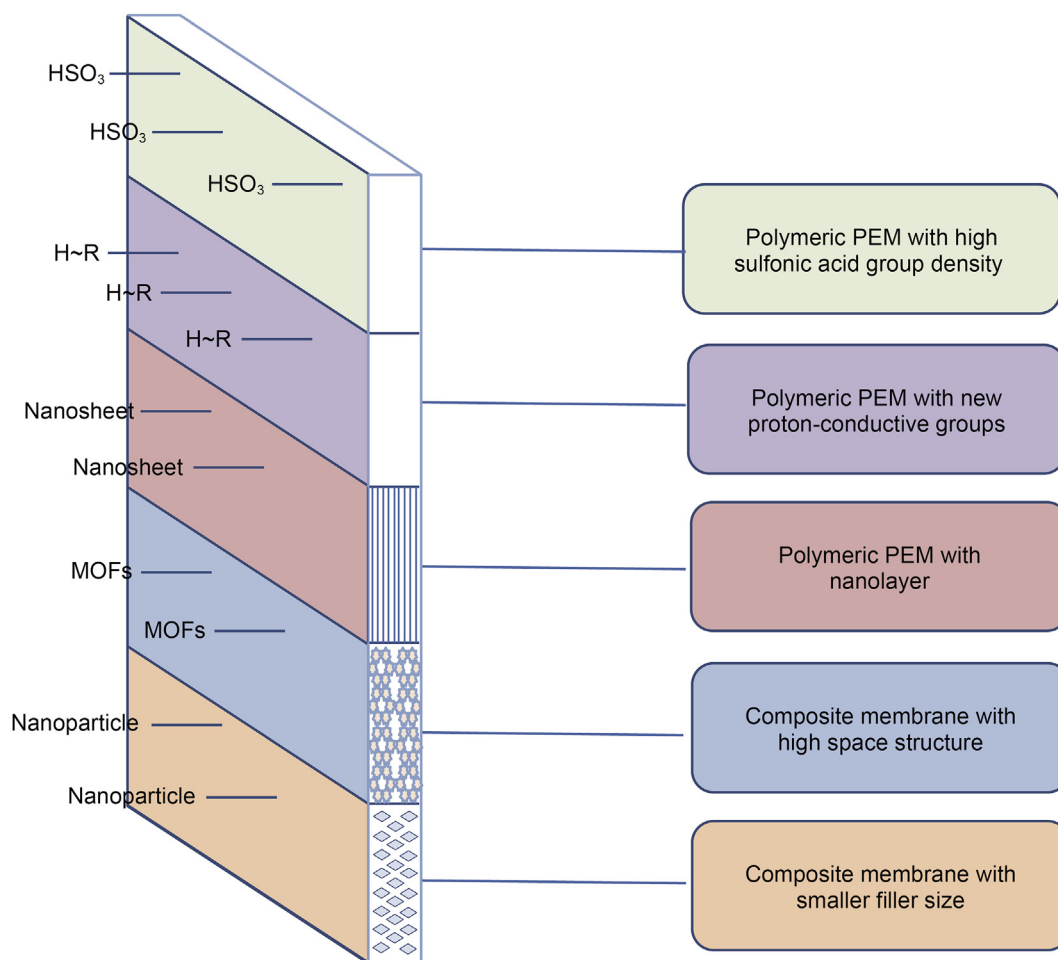


Fig. 4. Possible approaches to improve the performance of Nafion membrane in the future.

molecules and sulfonic acid groups produce conductivities of approximately 10^{-1} – 10^{-2} S cm^{-1} . The activation energies typically exist between 0.1 and 0.5 eV due to the hydration levels, likely caused by a Grotthuss-like conduction mechanism (Paul et al., 2011).

The schematic of the vehicular mechanism and hopping mechanism are shown in Fig. 3. The mechanism of proton transport in a hybrid system depends on the chemical properties and surface of the interface between the organic phases and inorganic phases (Li et al., 2020d).

3. Nafion-based composite membrane

Nafion membrane is the most promising proton exchange membrane due to its superior performance. However, the proton conductivity is greatly affected by the surrounding water environment (Bai et al., 2020). Introducing the filler into the membrane is a common method to reduce membrane dehydration at elevated temperatures (Li et al., 2020b). Possible mechanisms are still under discussion, but there are indications that the high water retention due to the increased tortuosity and crystallinity of the fillers inside the membrane can significantly enhance proton conduction (Liu L. et al., 2021). Moreover, the novel PEMs requires high stability at high temperatures and can be synthesized at a low cost. So many different research groups have made a lot of effort in various aspects to solve these problems in the Nafion membrane. Fig. 4 illustrates some suggestions for the future development of PEMs.

3.1. Inorganic material

It has been reported that the sulfonic acid groups of Nafion can be dynamically cross-linked with dispersed “hygroscopic” oxides, such as Al_2O_3 , TiO_2 , SiO_2 and ZrO_2 , thereby improving the water retention, increasing the porosity, and decreasing the gas crossover (Son et al., 2019). Additionally, better proton conductivity can be obtained by adding sulfonated oxides. The incorporation of these hygroscopic fillers to Nafion can significantly enhance the water retention properties, reduce the methanol crossover, and so on (Sun

et al., 2020). However, introducing the hygroscopic fillers into Nafion membranes by direct blending method usually leads to low proton conductivities due to the proton insulation of these hygroscopic fillers. The physical and mechanical properties of the membranes may be affected by the low compatibility between the Nafion and hygroscopic fillers. Thus, the Nafion membrane containing hygroscopic fillers was prepared by the in-situ sol-gel method. The results indicated that the composite membrane not only retained water but also increased water absorption. The water retention capacity of the membranes with ZrO_2 increased by 33% and 45% at 90 and 120 °C, respectively, while the water retention capacity of the membranes containing TiO_2 and SiO_2 at 120 °C increased by 25% and 15%, respectively. However, the results of conductivity measurement showed that TiO_2 and SiO_2 did not increase the conductivity, and ZrO_2 only increased 8–10% compared with pure Nafion (Fig. 5).

Zirconia, silica, and their combinations were similarly used as inorganic “dopants” for Nafion membranes due to their excellent thermal phase and surface stability. The prepared inorganic particles were mixed into Nafion solution and heated at 80 °C for 12 h to make the membrane (Park et al., 2008). The results showed that the water uptake of the silica doped membrane was higher than the recast Nafion and the Nafion 112. At 90% relative humidity (RH) and 80 °C, the conductivity of the zirconia-modified membrane showed the highest conductivity of 100 mS/cm, while the conductivity of recast Nafion, silica doped membrane, and the commercial Nafion 112 both had a conductivity of 70 mS/cm (Fig. 6a). It should be noted that the conductivity of recast Nafion membrane and Nafion 112 membrane was 17.5 mS/cm at 120 °C and 50% RH, while the membrane with one part zirconia and two parts silica as the inorganic dopant had a conductivity of 30 mS/cm (Fig. 6b). The water management and mechanical properties of the membrane are improved due to the specific interactions between the organic and inorganic in membranes.

The chemical degradation caused by reactive oxygen species (ROS) is one of the most serious problems that can affect the performance of a PEMFC. According to Vinothkannan et al. (2020), adding CeO_2 can scavenge free radicals generated in the membrane

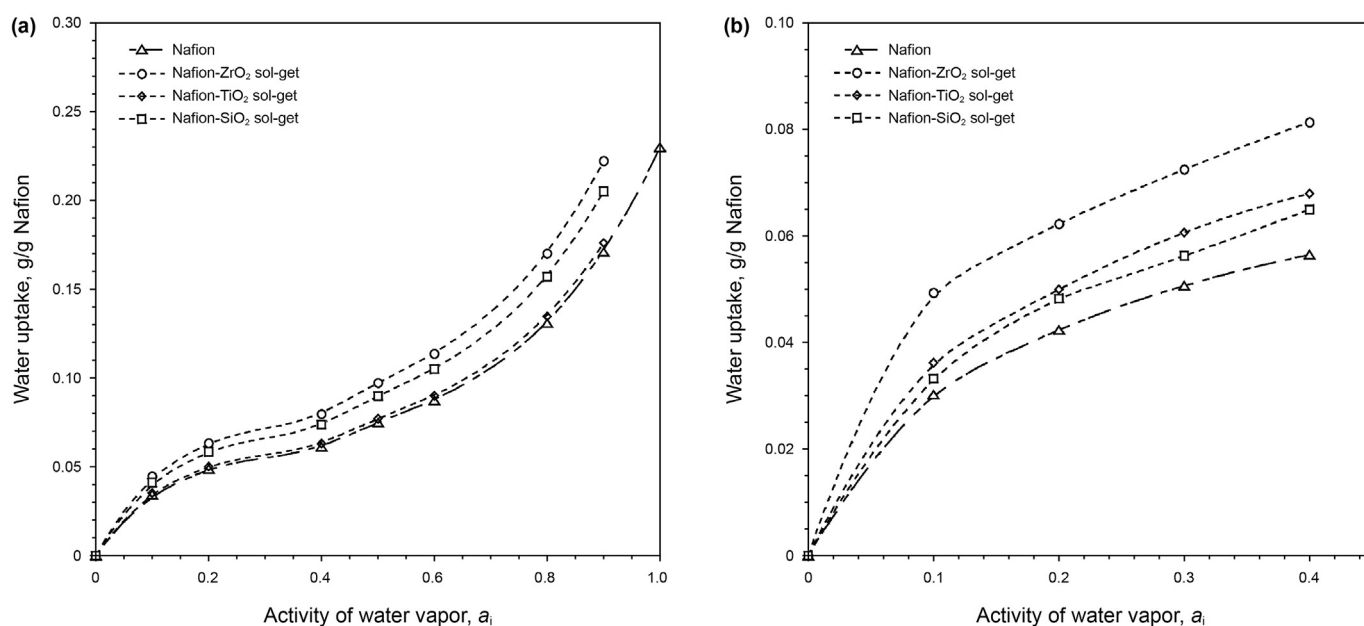


Fig. 5. The conductivity of the different inorganic composite membranes at 90 °C (a) and 120 °C (b). Reprinted with permission from ref (Jalani et al., 2005). Copyright (2005) Elsevier.

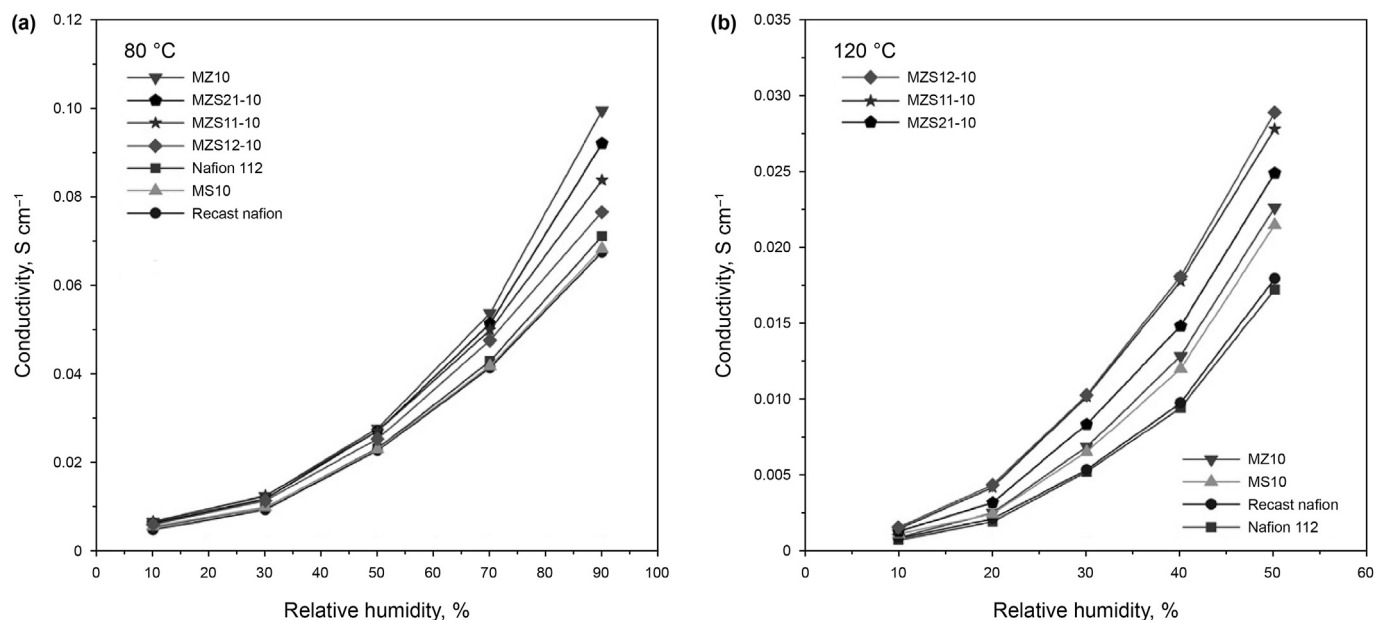


Fig. 6. The conductivity of the membranes measured at different RH levels, where the membranes are labeled MZSxy-10 and x: y is Zr: Si (b). Reprinted with permission from ref (Park et al., 2008). Copyright (2008) Elsevier.

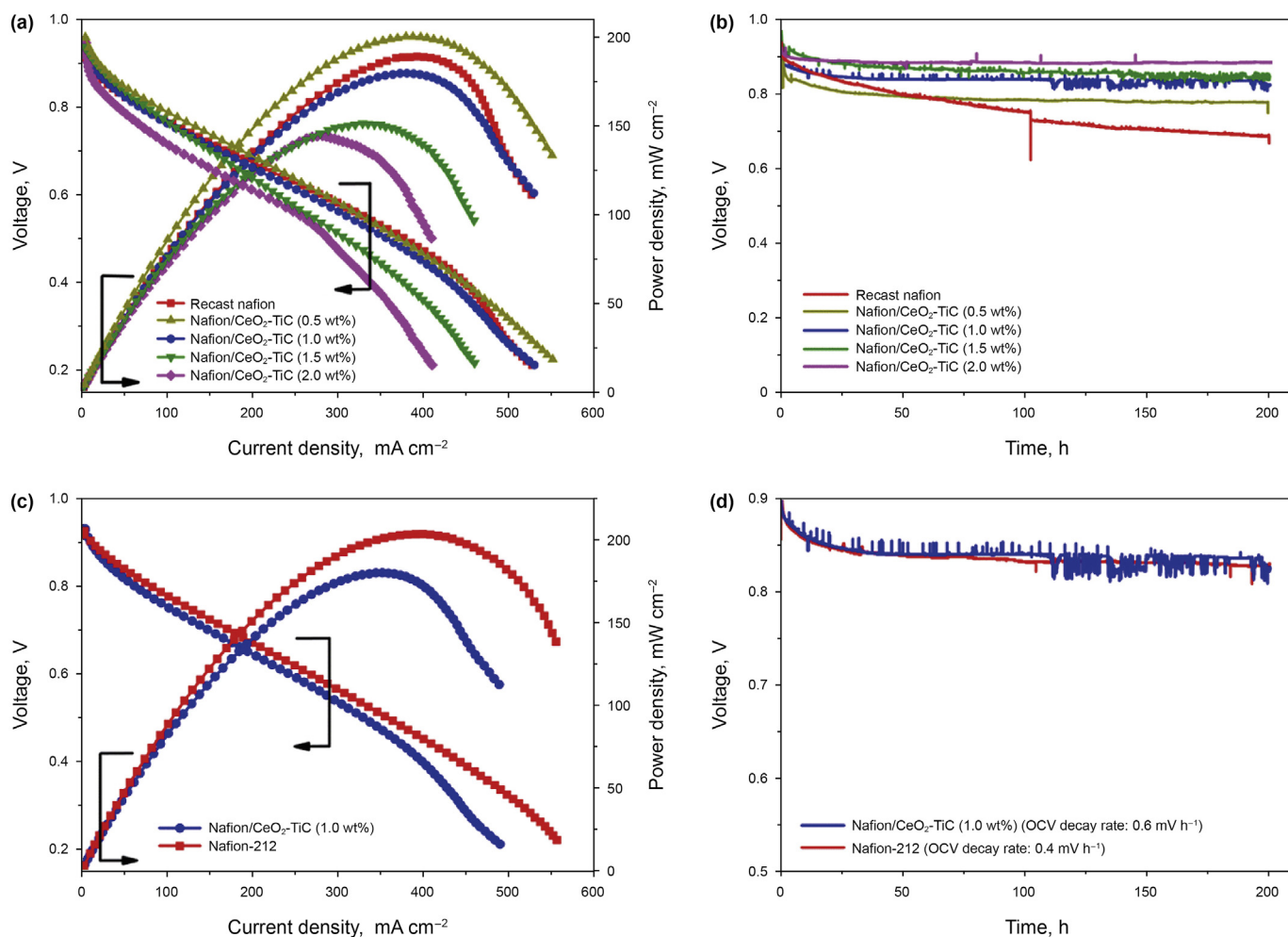


Fig. 7. (a) PEMFC polarization curves of pristine Nafion and hybrids at 60 °C and 100% RH; (b) Durability curves; (c) PEMFC polarization curve of Nafion/CeO₂-TiC (1 wt%) and Nafion-212; (d) Durability curves. Reprinted with permission from ref (Vinothkannan et al., 2020). Copyright (2020) American Chemical Society.

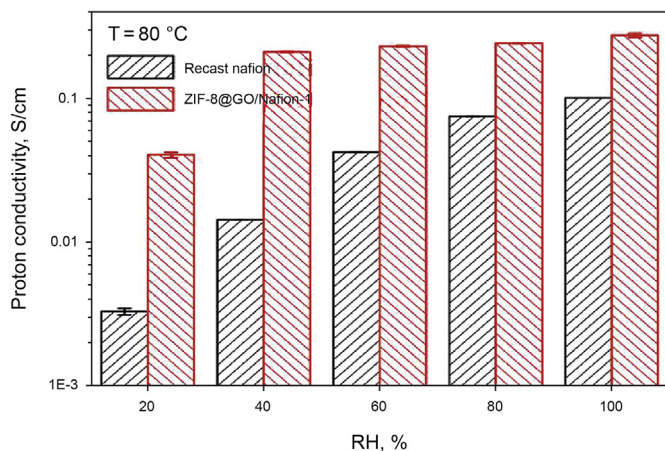


Fig. 8. The proton conductivity of recast Nafion and ZIF-8@GO/Nafion (80 °C). Reprinted with permission from ref (Yang et al., 2015). Copyright (2015) The Royal Society of Chemical.

to improve the durability of PEM, and the addition of TiC can enhance the tensile strength of PEM. However, the pure CeO₂ may dissolve in the PEM during the operation of PEMFC, which will reduce the effect of scavenging free radicals. Studies have found that TiC can be used to stabilize bare CeO₂ and reduce the solubility of CeO₂ in PEM. Incorporating CeO₂-TiC can strengthen the intermolecular force of Nafion through electrostatic interactions, which increases tensile strength and thermal stability by 1.3 and 1.4 fold, respectively. Moreover, the composite membrane showed a reasonable power output and remarkable durability after 200 h at 60 °C and 100% RH (Fig. 7).

In response to the issues discussed above, Rui et al. (2019) first added quercetin as a free radical scavenger to mitigate this problem. It was found that the incorporation of 1 wt% quercetin significantly increased service life and reduced chemical degradation. Additionally, the comparison between quercetin and CeO₂ indicated that the quercetin had better free radical scavenging performance than CeO₂.

3.2. Metal-organic frameworks (MOFs)

Metal-organic frameworks (MOFs) are a class of crystalline porous materials with a three-dimensional network structure formed by self-assembly of organic ligands and transition metal ions (Zhang et al., 2020). Compared with other porous materials, the properties of MOFs can be customized to suit unique target

applications. Owing to the special characteristics, MOFs have potential applications in improving the water retention ability and proton conductivity of Nafion-based membranes (Yang et al., 2017; Moi et al., 2020). Generally, polymer/MOF composites can improve proton conductivity in two ways, saturating the pores of MOFs with proton carriers, or modifying the organic ligands with functional groups to increase the hydrophilicity and acidity (Yang et al., 2015; Nguyen et al., 2018).

Yang et al. (2015) developed a high-performance Nafion/MOFs composite membrane. The porous metal-organic framework ZIF-8 was grown on graphene oxide (GO) and then introduced into Nafion matrix in this work. In addition, the synergetic effect between ZIF-8 and GO was found to enhance the proton conductivity significantly. At 120 °C and 40% RH, the ZIF-8@GO/Nafion membrane displayed a proton conductivity as high as 280 mS/cm, almost 55 times higher than that of recast Nafion membrane (5 mS/cm). The significant increase in proton conductivity is due to the unique single-layer space structure and strong water retention of ZIF-8@GO. Besides, the dependence of proton conductivity on the humidity of the hybrid membrane is also conducted in this work. Based on their results, the proton conductivity was observed to decrease when the humidity was lower than 40% RH (Fig. 8). However, the authors did not test this composite membrane in an actual PEMFC to verify the positive performance in a real operating environment.

Tsai et al. (2014) studied the practical application of Nafion/MOFs composite membrane in PEMFCs. Herein, two 1-D channel microporous MOFs, MIL-53(Al) and CPO-27(Mg) were used as fillers for PEMFCs. The maximum amount of filler that can be maintained for preparing a homogeneous and flat membrane is 3 wt%. At 50 °C and 100% RH, the composite membrane with CPO-27(Mg) had higher water uptake and proton conductivity. Besides, it exhibited higher power densities at all temperatures and the performance was 74% higher than that of recast Nafion at 50 °C. However, the authors tested this composite membrane only at a low RH of 15%. The Nafion/CPO-27(Mg) composite membrane exhibited higher power densities at low RH values compared to the high one. For example, at 50 °C, the power density of the Nafion/CPO-27(Mg) was 853 mW/cm² at 15% RH and 818 mW/cm² at 100% RH.

Li et al. (2014) added phytic@MIL101 as a novel filler to add to Nafion to fabricate a PEM with ultra-high proton conductivity. The phytic acid was extracted from plants with unique properties such as good chemical stabilities, excellent iron-chelating ability, and the highest phosphate group content. There were abundant coordinatively unsaturated metal sites in MIL-101, which could be chelated by phytic acid. The morphology of MIL101 and phytic@MIL-101 were observed by FESEM, and the results were

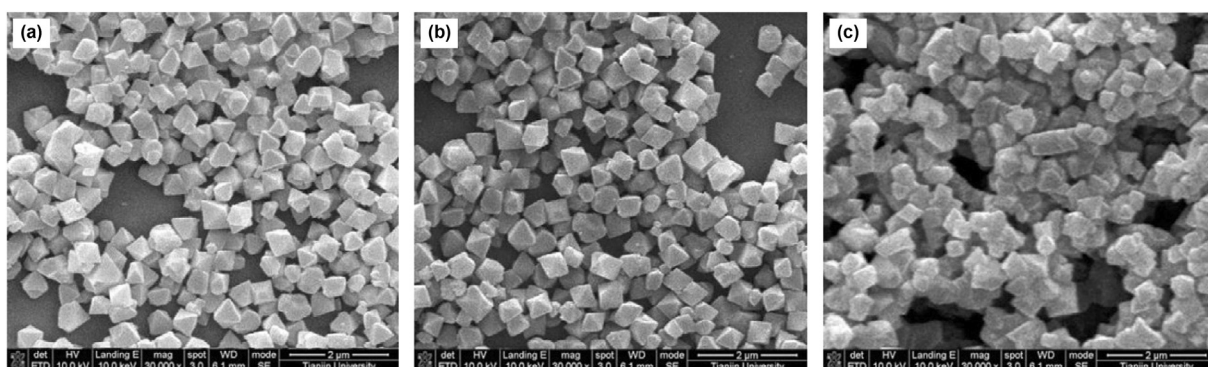


Fig. 9. FESEM images of raw-MIL101 (a), pure-MIL101 (b) and phytic@MIL101(c). Reprinted with permission from ref (Li et al., 2014). Copyright (2014) American Chemical Society.

shown in Fig. 9. Phytic acid had no significant effect on the octahedral shape of MIL101. At 80 °C, the conductivities of the composite materials were 61 mS/cm and 0.7 mS/cm at 57% and 11% RH, which was about 2.8 and 11 times higher than recast Nafion. This remarkable enhancement in proton conductivity was maintained by coordinated bond and cage effect in phytic@MIL101: (i) Continuous channels could be formed for proton transport with the common frameworks of MIL101. (ii) Phosphate groups showed less dependence on water. (iii) MIL101 maintained rapid proton conduction due to the high mobility of phosphate groups. Additionally, the mechanical properties and swelling resistance of the hybrid membrane were also substantially improved. The developed composite membrane shows great application potential in PEMFC.

Recently, Rao et al. (2017) incorporated GO@UiO-66-NH₂ into the Nafion matrix. At 90 °C, the proton conductivity of the composite membrane was 3.4 mS/cm under anhydrous conditions and 303 mS/cm under 95% RH, which was about 1.88 and 1.57 times higher than recast Nafion, respectively. Additionally, continuous proton conduction channels of UiO-66-NH₂ were built by using the binding effect of GO surfaces and good interconnection among MOFs. The superior proton transport was promoted by the synergistic effect between Ui-66-NH₂ and GO and significantly decreased the conducting barriers under high humidity and anhydrous conditions. A better match between smaller particle sizes and a higher specific surface area has a positive effect on the proton conductivity of PEM. The schematic diagram of the proton conduction mode in a different environment is shown in Fig. 10.

4. Proton conducting medium in the Nafion

The ionic channels of Nafion in the dry state are prone to collapse, which limits its proton conduction (Rosli et al., 2017). Therefore, some suitable sorbents should be used to expand

collapsed ionic channels of Nafion to obtain an ideal proton conductivity.

4.1. Water and alcohols

The mechanical properties of the Nafion membrane are significantly influenced by the sorbent uptake. Therefore, sorbents should have appropriate uptake in the membrane, which could not affect its mechanical properties (Li J. et al., 2020). According to some studies, the clusters and channels can be formed between methanol and Nafion, but the degree of disorder is greater than that of Nafion membrane saturated with water (Simari et al., 2020). Zhao et al. (2012) studied the diffusion of water and methanol in Nafion membranes. Their results showed that the adsorption and transport characteristics of methanol, ethanol, and water are mainly due to differences in molar volumes. Further, the proton conductivity will decrease with increasing solute molar volume.

It should be pointed out that the hygroscopicity of Nafion is greatly affected by cationic. Therefore, the Nafion ionic cluster can be used to expand by different sorbents, but we should also consider that higher sorbent uptake may affect Nafion mechanical properties.

4.2. Ionic liquids (ILs)

As we all know, the water content of Nafion has a significant influence on proton conductivity. In the systems of proton conduction, protons have been conducted through Vehicle and Grotthuss mechanisms (Chopade et al., 2016). Proton conductive channels are provided by the water in the membranes. However, the operating temperature of the fuel cell systems is lower than 80 °C due to the loss of water. Therefore, the modification of Nafion membrane with ILs at high temperatures is considered a promising

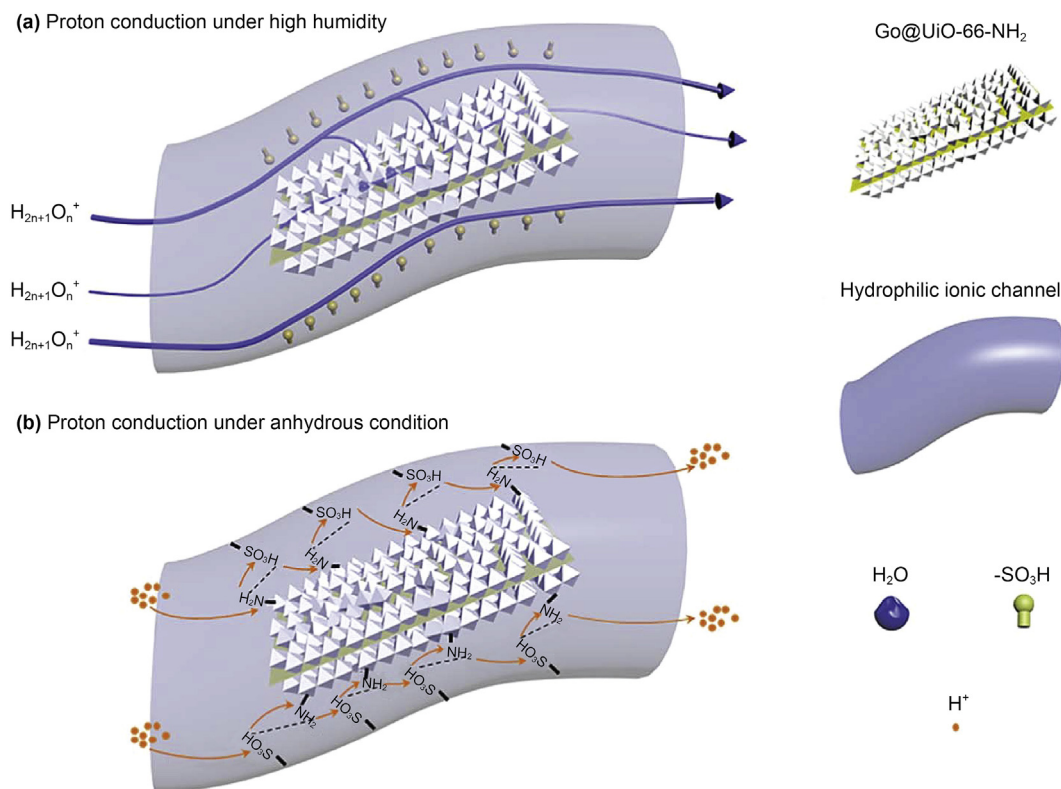


Fig. 10. Schematic diagram of proton conduction. Reprinted with permission from ref (Rao et al., 2017). Copyright (2017) Elsevier.

alternative for water (Liu et al., 2017; Elwan et al., 2021).

ILs are organic salts that are liquid at room temperature, which have some special properties including high ionic conductivities, high thermal stability, and strong chemical stability (Vázquez-Fernández et al., 2021). Using ionic liquid instead of water as the protic solvent can effectively improve the working temperature and conductivity of Nafion membrane.

Yang et al. (2011) studied the effect of IL containing imidazolium cation to enhance the doping level of phosphoric acid in the Nafion membrane under the anhydrous condition. In their works, the membranes were prepared by incorporating the polymer with ILs and doping with phosphoric acid. Their results showed that using ILs and phosphoric acid can significantly improve the proton conductivity when the temperature rises without humidification (Fig. 11). The presence of ILs cation can form hydrogen bonds with sulfonic acid in Nafion to increase the doping level of phosphoric acid and significantly improve the conductivity under anhydrous conditions. However, the ILs have low compatibility with polymers. The leakage of ILs will occur when the membrane is used for a long time, which will lead to a decrease in conductivity and stability. Nonetheless, with the in-depth understanding of the structure and properties of ILs, the preparation of ILs with good compatibility with polymer matrix, the application of ILs in proton exchange membranes will have a better prospect.

Schmidt et al. (2008) studied the effect of various ionic liquids (imidazolium, pyridinium) that were impregnated into the Nafion membrane. As the temperature rises, the proton conductivity of Nafion decreases due to the evaporation of water. However, the proton conductivity of composite membrane showed 100 times higher than dry Nafion 117 at 120 °C, mainly because ILs can maintain the thermal stability of these systems and reduce the water expansion of dry membrane. It is foreseeable that in the application and development of high-temperature PEMs, the use of ILs to modify Nafion seems very promising.

5. Nafion fuel cell performance

Single cell performance is substantially regarded as an indispensable parameter to evaluate the performance of membranes used in fuel cell applications (Sabet-Sharghi et al., 2013; del Río et al., 2014). As mentioned above, the conductivity and performance of Nafion membrane can be significantly reduced due to water loss at elevated temperatures. Several strategies can be

implemented, including (i) Preparation of nanocomposite proton exchange membranes; (ii) Polymer blending; (iii) Improvement of skeleton materials of proton exchange membrane; (iv) Adjusting the internal structure of the membrane.

5.1. Pristine Nafion fuel cell performance

The actual operating conditions of the fuel cell determine the conductivity of the membrane to a certain extent. According to Table 1, when the cell voltage is 0.5 V, the current densities of the pristine Nafion membrane can change from 3 to 1041 mA/cm² due to the change of humidity in the membrane. Maiti et al. (2018) evaluated the performance of Nafion 117 under anhydrous conditions. The results showed that Nafion fuel cell displayed a low current density at a cell potential of 0.5 V. However, Lin et al. (2006) presented the Nafion 117 fuel cell performance showed satisfactory improvement at 75 °C and 95% RH. And the current density raised to 784 mA/cm² with the potential is 0.4 V. These results support that water has a positive effect on the performance of Nafion fuel cells.

Scientists have evaluated different commercial proton exchange membranes, such as Nafion 112, Nafion 115, and Nafion 117. The thickness of these membranes is arranged in the following order; Nafion 112 < Nafion 115 < Nafion 117. Based on their results, the low thickness membrane for the fuel cell system provided higher performance and showed higher proton conductivity. In their works, the membrane thickness has a significant effect on the current density of fuel cell at a cell potential is 0.5 V; Nafion 112 > Nafion 115 > Nafion 117. It had been shown that the cell with a thicker membrane gave a better performance at lower current densities, and the cell with a thinner membrane exhibited better performances at higher current densities. The membrane thickness has an essential effect on charge/discharge voltage and time, and it also directly determined the electrolyte crossover and membrane resistance.

Although increasing the thickness of the membrane will improve the mechanical properties, the increase in ohmic resistance will also cause performance degradation (Sun and Zhang, 2019).

5.2. Effect of fuel type on Nafion fuel cell performance

H₂ and methanol are widely studied by researchers among the various fuels used for fuel cell. As shown in Table 1, the fuel cell system powered by H₂ have higher performance. It is worth mentioning that methanol has a higher energy density than H₂, but its high permeability in Nafion will reduce its utilization, increase the polarization of oxygen electrode, and reduce the performance of DMFC. Therefore, a low concentration of methanol should be used in the practical application system of the fuel cells. Meanwhile, Deluca and Elabd (2006) studied the effect of methanol concentration on the performance of DMFCs. The methanol concentration increased from 2 M to 16 M, the current density decreased from 300 mA/cm² to 91 mA/cm² at a constant potential of 0.2 V. The reduction of fuel cell performance is mainly due to the cathode polarization loss caused by the high permeability of methanol (Dutta et al., 2015). Therefore, many modifications to Nafion have been expected to reduce its high permeability, including impregnation (Choi et al., 2008), polymerization (Ram et al., 2020), incorporation of nanoparticle fillers into the polymers (Guo et al., 2020; Wang et al., 2021), casting (Yang et al., 2019), high-temperature processing (Ramya and Dhathathreyan, 2008), and electrochemical modification (Liu B.L. et al., 2021). Unfortunately, the reduction of methanol permeability always results in the loss of proton conductivity.

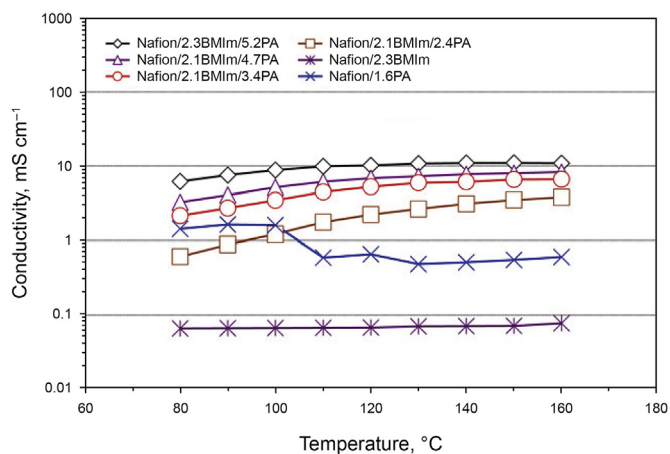


Fig. 11. The proton conductivity of acid-doped and BMIm composite membranes versus temperature. Reprinted with permission from ref (Yang et al., 2011). Copyright (2011) Elsevier.

Table 1
Nafion fuel cell performance.

Type	Nafion type/fuel	Reinforcement	Voltage, V	Current density, mA/cm ²	Operation conditions	References
Pristine Nafion	Nafion 117/H ₂	–	0.5	3	110 °C/anhydrous	Maiti et al. (2018)
	Nafion 117/H ₂	–	0.4	784	75 °C/95% RH	Lin et al. (2006)
	Nafion 112/H ₂	–	0.5	1041	90 °C/95% RH	
	Nafion 115/H ₂	–	0.5	736		
	Nafion 112/methanol (2M)	–	0.3	160	80 °C	Lin et al. (2010)
	Nafion 117/methanol (6M)	–	0.3	40	60 °C	Dutta et al. (2015)
	Nafion 117/methanol (2M)	–	0.3	62	60 °C	
Ionic liquids	Nafion solution/H ₂	Hydroxyl functionalized imidazolium IL + SiO ₂	0.5	700	160 °C/anhydrous	Li et al. (2016)
			0.5	880	180 °C/anhydrous	
	Nafion 117/H ₂	1-butyl-3-methylimidazolium tetrafluoroborate	0.5	153	80 °C/60% RH	da Trindade et al. (2018)
		Without IL	0.5	135	80 °C/60% RH	
Blend	Recast Nafion 117/methanol (2 M)	Partially sulfonated polyaniline (SPANi)	0.3	51	60 °C	Dutta et al. (2015)
	Recast Nafion 117/methanol (6 M)					
	Nafion solution	Chemically modified PVDF	0.5	476	80 °C/100% RH	Song et al. (2003)
			0.5	701	90 °C/100% RH	
			0.5	905	100 °C/100% RH	
Nanocomposite	Nafion solution/H ₂	Sulfonic acid functionalized carbon nanotubes (MWCNTs) (0.25 wt%)	0.5	808	60 °C/20%RH	Steffy et al. (2018)
				1541	60 °C/60%RH	
	Nafion solution/H ₂	Sulfated Zr-MOF (SZMOF) (1 wt%)	0.5	505	80 °C/35% RH	Patel et al. (2016)
	Nafion 117/H ₂	Zwitterion-functionalized covalent organic framework	0.5	306	80 °C/100% RH	Li Y. et al. (2018)
	Nafion 115/H ₂	Zirconium Phosphate (25% wt.%)	0.6	820	80 °C/Immersed in water	Yang et al. (2004)

5.3. Fuel cell performance of Nafion blends

The motivation of blending Nafion with other polymers is usually to increase the performance of DMFC by reducing the permeability of methanol through Nafion. As discussed in the previous section, the properties of Nafion can be reduced by increasing the methanol concentration. The polymer blended with Nafion should have superior compatibility and low methanol permeability (Ahmed and Dincer, 2011; Ru et al., 2019).

Deluca and Elabd (2006) successfully prepared Nafion/polyvinyl alcohol (PVA) composite membranes for DMFC. PVA is used in DMFCs due to its abundant hydroxyl groups with remarkable methanol resistance. According to their results, the Nafion/PVA blend (20 wt% PVA) presented lower performance compared to pristine Nafion. However, the Nafion/PVA blend (5 wt% PVA) showed higher performance due to its lower methanol permeability. Their results indicated that the penetration and cross-over of methanol in proton exchange membranes greatly affected the efficiency and performance of fuel cells in DMFC.

Dutta et al. (2015) studied the performance of sulfonated polyaniline/Nafion composite membranes in DMFC applications. This new PEM material presents very high membrane selectivity and extremely low methanol permeability. Based on their results, the blend composition consisting of 30 wt% SPAni and 70 wt% of Nafion showed the best-optimized results. Also, all properties of the blend membranes were better than Nafion membranes, such as the swelling ratios and single cell performance. By analyzing the results, the low methanol permeability of the new material may be the reason for these results.

5.4. Fuel cell performance of Nafion nanocomposites

Nanofillers were used to improve the Nafion performance under low humidity conditions in recent years (Steffy et al., 2018). As it is observed in Table 1, nanocomposite membranes present higher performances among different types of composite membranes. It can be seen that functionalized sulfonic acid nanocomposites exhibited better performance in fuel cells compared to the

unmodified nanoparticles. Due to the incorporation of unmodified nanoparticles, the number of sulfonated groups per unit volume of each domain in the Nafion structure is reduced, resulting in lower fuel cell performance (Sasikala et al., 2016). Nevertheless, the two-dimensional metal frames, mesoporous carbon fillers, and carbon nanotube have higher performance than other fillers among various available nanoparticles. It has been reported that the size of nanoparticles can also have a significant impact on the performance of the PEM. Based on the research of Li et al. (2018), by increasing the sizes of the nanoparticles, the performance of the fuel cell will be reduced by covering the sulfonic acid cluster channels in the Nafion membrane.

6. Summary

The PEM is an essential component of the fuel cell system, and its successful application paves the road for the commercialization of PEMFCs. In this review, different approaches to improve proton conductivity and fuel cell performance were evaluated, including the incorporation of hydrophilic inorganic materials, metal-organic frameworks, and ionic liquids (ILs) within the Nafion matrix.

Nafion has been widely commercialized, and its production has been achieved at an industrial scale. Judging from the research and actual commercial use in recent years, it will be difficult to completely replace Nafion due to its superior comprehensive performance, such as good proton conductivity and excellent oxidative stability. However, the original Nafion also has some intricate problems, there is still a broad room for improvement in the application of fuel cells. Based on the dilemma of Nafion, various types of PEMs have been developed due to their unique complementarity and designability.

By now, researchers have adopted various strategies and methods to improve PEM performance. Modification methods such as crosslinking, blending, and introduction of fillers have been proven to improve certain specific properties of the membrane to meet better actual needs. Meanwhile, these PEMs also have some problems that need to be solved urgently. For example, the crosslinking could cause membrane brittleness and nanofiller may form

more tortuous and complex proton conductive pathways. Additionally, the compatibility of these modified Nafion membranes with MEA components may be different from that of pure Nafion, more research is needed to explore the bipolar plates, flowrates of reactants, electrolytes, and catalyst quantities. The shortcomings of the examples in this article are that some composite membranes were not tested in PEMFC systems so that their stability is not assessed. Although the proton conductivity is the most widely used indicator for evaluating the membrane properties, it is not the only consideration for membrane development. Morphological and chemical stability, physical properties, compatibility with electrode materials, and cost are important considerations.

Nevertheless, the cost advantage of nonfluorinated acid exchange membranes makes them play an important role in the research and development of fuel cells. A thorough understanding of the fundamental properties of the polymer and various aspects of the membrane is required to produce PEMs with superior properties successfully. Moreover, the development and application of novel PEM require a delicate balance between physical properties, MEA compatibility, electrochemical properties, cost, and durability.

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