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Metal–Organic Frameworks in Proton-Exchange Membrane for Intermediate-to-High-Temperature Fuel-Cell Applications: A Review

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ABSTRACT

A proton-exchange membrane (PEM) is a vital component in fuel cells as a solid electrolyte that conducts ions. The high cost and degradation of Nafion® membrane in low-temperature fuel cells limits the technology's commercialization. The development of intermediate (IT-PEMFCs) to high-temperature (HT-PEMFCs) fuel cells operating within the range of 80–200 °C has made progress over the last few decades, and improvements in water management addressing the issues of low-temperature PEMFCs have been observed. However, these types of PEM fuel cells (IT-PEMFCs and HT-PEMFCs) still face considerable challenges, such as unsatisfactory performance stability at high temperatures. Particularly, in HT-PEMFC, despite the high acid doping level (ADL) in membranes as a potential means to improve proton conductivity, high ADL decreases the membrane's mechanical stability. Recently, metal–organic frameworks (MOFs) have achieved satisfactory results in applications of PEM modification. This manuscript reviews the development in applying MOFs in improving the properties of composite membranes in IT- and HT-PEMFCs by using SPEEK and PBI, respectively. The synthesis strategies using MOFs in the PEM are discussed together with the electrochemical properties obtained. The success of incorporating of MOFs into PEMs could shed light on the synthesis of new-generation IT- and HT-PEMFCs, which could improve several properties such as mechanical and thermal stability, oxidative stability, and acid-retention capacity.

Keywords: Metal-organic frameworks; proton exchange membrane; fuel cell

INTRODUCTION

Proton-exchange membrane fuel cells (PEMFCs) have numerous advantages as future energy-generation devices, including high energy efficiency and zero emissions (Moreno et al. 2015). The key component in PEMFCs is their membrane-electrode assembly (MEA), which converts the chemical energy of reactants into electrical energy through redox reactions. Researchers are particularly interested in the development of alternative materials for proton-exchange membranes (PEMs), which act as carriers for proton transfer and serve as physical barriers to separate the anode and cathode fuels. Owing to the high cost of the state-of-art Nafion® membrane, potential alternative new materials including sulfonated polysulfone, sulfonated poly(ether ether ketone) (SPEEK), polybenzimidazole (PBI), chitosan (CS) polymer and poly (vinyl alcohol) (PVA) have been proposed and investigated under different operating conditions. These alternative membranes operating within the range of 120–200 °C have been reported and developed rapidly, and favorable properties such as high proton conductivity have been reported (Wu et al. 2021).

Intermediate-temperature PEMFCs (IT-PEMFCs) operating at around 80–140 °C (Li et al. 2003) have also attracted considerable interest in recent years. Compared with LT-PEMFCs, IT-PEMFCs show superior performance with increased temperature and can overcome most of the shortcomings associated with LT-PEMFCs' operation over 100 °C, such as overcoming the water-management issue in LT-PEMFCs, simplifying the cooling and water-control system in fuel cells, and dramatically enhancing tolerance to impurities (such as CO and SO_2) (Xiao et al. 2020).

High-temperature PEMFCs (HT-PEMFCs) operating above 120 °C have received considerable research attention in recent years owing to their superior performance. Among HT-PEMFCs, SPEEK N,N′-dimethylacetamide (DMAc)/

DMF membrane (Carbone et al. 2006), phosphorus acid doped-PBI/sulfonated polysulfone membrane (Hasiotis et al. 2001), and aquivion/ePTFE membrane (Xiao et al. 2013) have been studied and found to have promise as a solid-state PEM for HT-PEMFCs. However, considerable challenges in HT-PEMFCs remain to be addressed, such as the degradation rate at elevated temperatures, increased rate of thermal decomposition at >150 °C, as well as under anhydrous or low-humidity conditions (Authayanun et al. 2015). This review summarizes the performance improvement of IT- and HT-PEMs with different categories of metal–organic frameworks (MOFs) applied in HT-PEMFCs.

MOFs are a family of crystalline porous materials with periodic network structures. MOFs are scientifically compelling and functionally evolving as meso-, micro-, and ultramicro porous materials. As a kind of organic–inorganic hybrid materials, intramolecular pores form by the self-assembly of organic ligands and inorganic metal ions or clusters through coordination bonds. They differ from inorganic porous materials and general organic complexes as they simultaneously exhibit the rigidity of inorganic materials and the flexibility of organic materials. MOFs comprise metal nodes and organic linkers that can be systematically tuned in terms of chemical composition and precise arrangement. Hence, as a new material, they are rapidly becoming a research hotspot and frontiers in the field of materials. Over the last two decades, they have developed at an amazing speed, and various MOFs have been developed one after another. Recently, MOFs have been explored for application in HT-PEMFCs. Their enhanced PEM performance and durability overcome the existing challenges in IT- and HT-PEMs. Some MOFs include UiO-66-SO_3H, UiO-66-NH_2, Cr-MIL-101-NH2, Fe-MIL-101-NH2, ZIF-8, ZIF-67, and MOF 1 (Liu et al. 2020).

TYPES OF MOF-MODIFIED PEMS FOR IT- AND HT-PEMFCs

In recent years, different types of MOFs have been doped into PEM substrate, showing promising membrane performance. UiO-series MOFs (UiO stands for University of Oslo) have been found to possess a high-density spatial structure and outstanding stability under water and acid conditions that can significantly improve the stability of PEMs. MIL-series MOFs (stands for Materials of Institute Lavoisier) in PEMs contain numerous CUSs, which can provide abundant hydroxyl groups through hydrolysis to promote proton conductivity in composite PEMs. Zeolite imidazolate framework (ZIF)-series MOFs have unique hydrophobic pores and surface structure, endowing them with high selectivity and chemical stability in alkaline aqueous solution that can greatly reduce methanol permeability. Moreover, increasing the content of acid groups and mixing MOFs have exerted an astonishing effect on performance improvement, which has greatly improved the performance of PEMFCs. Other types of MOFs such as JUC-200 (a hexaphosphate ester-based 3D MOF) and MOF 1 (a chiral 2-D MOF) have been fabricated. They have increased the capacity of MOF particles to absorb water and the adsorption and humidification of water by polyvinyl pyrrolidone (PVP). This is particularly beneficial for retaining water molecule or the acid within the polymeric matrix at high operation temperature, crucial for enhancing the proton conductivity. In addition, MOFs' self-coordination skeleton could provide more ion channels, and proton-transport carriers within the polymer electrolyte (Rosli et al. 2021).

Various strategies have been proposed for MOF/PEM composite membranes, such as the following: (1) compositing polymers with MOFs through hybridization and chemical functionalization (Kitao et al. 2017), (2) loading MOF particles into the matrix as proton carriers (Liu et al. 2018), and (3) encapsulating MOF pores in a polyelectrolyte with different proton carriers, such as phytic@MIL, PIL@MIL, and acids@MIL (Dong et al. 2017), and/or modifying the organic ligands of MOFs with functional groups, such as -SO_3H, -NH_2, and −COOH.

High-temperature PEMs modified by MOFs can be divided into four different types, including UiO series, ZIF series, MIL series, and others. Table 1 summarizes the MOF composite membranes in HT-PEMFCs with their respective activation energy and proton conductivity value.

TABLE 1. Summary of MOF composite membrane in IT- and HT-PEMFCs

Compound	Synthesis strategy/prominent features	MOFs	Conditions	Ea (eV)	Proton Conductivity σ (S cm^{-1})	Ref.
SPEEK/S-UiO-66@GO-10	In-situ growth/hybridizing	UiO-series	100°C, 40% RH	-	0.268	Sun et al. 2017a
CS/UiO-66-NH2+UiO-66-SO3H	Hybridizing/moulding	UiO-series	100°C, 98% RH	0.131	5.2×10^{-2}	Dong et al. 2018
CS/UiO-66-NH2+UiO-66-SO3H	Hybridizing/moulding	UiO-series	120°C, anhydrous	0.131	3.78×10^{-3}	Dong et al. 2018
CS (Chitosan)	-	MIL-series	100°C, 100% RH	0.189	0.030	Dong et al. 2018
CS/MIL-101	Nitrogen atoms from -NH_2 groups line channels / lattice water	MIL-series	100°C, 100% RH	0.183	0.034	Dong et al. 2017
CS/S-MIL-101	Nitrogen atoms from -NH_2 and Oxygen atoms from SO_3- on the pore surface/water	MIL-series	100°C, 100% RH	0.174	0.064	Dong et al. 2017
CS/H2SO4@MIL-101	Nitrogen atoms from –NH_2 and Oxygen atoms from H_2SO_4 in backbone facilitate H- bonding/water	MIL-series	100°C, 100% RH	0.181	0.095	Dong et al. 2017
CS/H3PO4@MIL-101	Nitrogen atoms from –NH_2 and Oxygen atoms from H_3PO_4 in backbone facilitate H– bonding/water	MIL-series	100°C, 100% RH	0.175	0.083	Dong et al. 2017
CS/CF3SO3H@MIL-101	Nitrogen atoms from –NH_2 and Oxygen atoms from CF_3SO_3H in backbone facilitate H- bonding/water	MIL-series	100°C, 100% RH	0.179	0.094	Dong et al. 2017
SA-EIMS@MIL-101	heterogeneously impregnating procedure	MIL-series	150°C, anhydrous	0.262	1.89×10^{-3}	Chen et al. 2018
MSA-EIMS@MIL-101	heterogeneously impregnating procedure	MIL-series	150°C, anhydrous	0.304	1.02×10^{-4}	Chen et al. 2018
PTSA-EIMS@MIL-101	heterogeneously impregnating procedure	MIL-series	150°C, anhydrous	0.424	2.78×10^{-4}	Chen et al. 2018
PES/Cr-MIL-101	Solution casting	MIL-series	160°C, anhydrous	-	41.00×10^{-3}	Anahidzade et al. 2018
SPPO/NAPI@MIL	Amino-functionalized particles immersing in water and $CHCl_3$	MIL-series	160°C, 0.15% RH	-	4.0×10^{-2}	Wu et al. 2014a
NAPI/Fe-MIL-101-NH2	Amino-functionalized particles immersing in water and $CHCl_3$	MIL-series	160°C, 0.15% RH	-	0.25	Wu et al. 2014a
EIMS-HTFSA@MIL	A heterogeneous mixing and grinding method, together with capillary action	MIL-series	140°C	-	2×10^{-4}	Sun et al. 2017c
SPEEK@ZCN	Hybrid cross-linked networks (ZCN) synthesis/ hybridizing	ZIF-series	120°C, 30% RH	-	5.0×10^{-2}	Sun et al. 2017b
PBI@ZIF-8	Solution casting	ZIF-series	180°C, anhydrous	-	3.1×10^{-3}	Escorihuela et al. 2018
PBI@ZIF-67	Solution casting	ZIF-series	180°C, anhydrous	-	4.2×10^{-2}	Escorihuela et al. 2018
PBI@ZIF-Mix	Solution casting	ZIF-series	180°C, anhydrous	-	9.2×10^{-2}	Escorihuela et al. 2018
SPEEK@ZIF-8	Solution casting	ZIF-series	100°C	-	1.6×10^{-2}	Barjola et al. 2018
SPEEK@ZIF-67	Solution casting	ZIF-series	100°C	-	1.5×10^{-2}	Barjola et al. 2018
SPEEK@ZIF-Mix	Solution casting	ZIF-series	100°C	-	2.9×10^{-2}	Barjola et al. 2018
MOF 1	Embedded into PVP polymer matrix by spin-coating method	Others	180°C, anhydrous	-	3.2×10^{-4}	Liang et al. 2013
SPPESK nanofiber/ZCCH	Solution casting	Others	160°C, anhydrous	-	$(8.2\pm0.16) \times 10^{-2}$	Wu et al. 2014b

The above-mentioned different types of MOFs improved the proton conductivity of the membranes through the introduction of protonic charge carriers (water, acids, or heterocycles) in composite membranes (Ma et al. 2013).

TRANSPORT MECHANISMS AND PROPERTIES OF MOFS

The ion-transport mechanism in PEMs is critical, with two commonly known processes, i.e., Grotthuss mechanism and vehicle mechanism. In the Grotthuss mechanism (structure diffusion), protons are transferred between the charge-carrying solvent groups via hydrogen bonds, i.e., the solvated proton of H_3O^+ hops from one anion to another. In the vehicle mechanism, the protons are typically transported by charge carriers and freely diffuse in a liquid (Lafitte et al. 2007). As reported by other researchers, surface (or interface) transport is mentioned as a third type (Weber et al. 2004; Kreuer et al. 2004). This process involves structure diffusion via surface or interface.

Moreover, in the Grotthuss mechanism, free proton transport tends to become more dominating at higher temperatures and lower humidity; conversely, vehicle transport dominates at low temperatures and higher humidity. Thus, the Grotthuss mechanism plays the most important role in proton transport under high-temperature and anhydrous conditions. Figure 1 shows the Grotthuss-type transport properties of GO@UiO-66-SO3H, as demonstrated in SPEEK (Sun et al. 2017a). Proton hopping occurs at the interface of the neighboring acidic donor/acceptor sites on the polymer backbone with gas or water medium, in dry or hydrated membranes, and represents Grotthuss-type transport mechanism (Luduena et al. 2011). Furthermore, the synergy between backbone properties such as morphology and hydrophilicity (governed by the type of polymeric materials) and the proton-transport site (governed by the type of acid and its concentration), strongly influences the overall proton conductivity of the polymeric membrane (Sun et al. 2019).

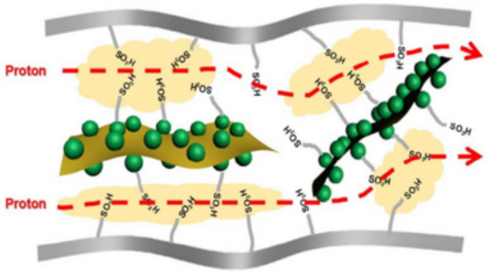

FIGURE 1. Schematic of Grotthuss-type transport properties of SPEEK/GO@UiO-66-SO_3H (Sun et al. 2017a)

MECHANICAL PROPERTIES OF MOFS IN IT- AND HT-PEMFC APPLICATION

PEMs should have good long-term mechanical stability, such as high tensile strength, Young's modulus, and elongation at break under the desired operating conditions. Table 2 shows the mechanical properties with various types of MOFs in HT-PEMs.

Anahidzade et al. (2018) synthesized sulfonated poly(ether sulfone)-MOF (SPES-MOF) membrane) by post-grafting. The amino-functionalized Cr-MIL-101 (Cr-MIL-101-NH_2) was anchored onto chlorosulfonated poly(ether sulfone) as a flexible polymer with the aryl ether backbone to form a cross-linked bond. This composite membrane develops the pathway for proton transfer, thereby maintaining the acid-retention capacity and preventing acid leaching. The mechanical features of SPES-MOF membrane outperform those of SPES membrane, with a tensile strength of 43.72 and 40.21 MPa under dry and wet conditions at 25 °C, respectively (Anahidzade et al. 2018).

As a kind of effective reinforcer, ZIF compounds increase the mechanical stability of composite membranes, as studied by Barjola et al. In their study, Young's modulus increased from 1.5 GPa for recast SPEEK membrane and up to 2.2 GPa for SPEEK/ZMix-10. The tensile strength increases from 95 MPa to 123 MPa, as shown in Figure 2A. Owing to the interfacial interactions between ZIFs and the SPEEK polymeric matrix, which inhibits the mobility of SPEEK chains, the mechanical properties can be enhanced. Furthermore, the dispersing conditions are excellent to ensure that the MOFs are dispersed uniformly throughout the polymer matrix, thereby improving the mechanical performance. In SPEEK/ZMix membranes, the elongation at break (%) of the composite membranes is slightly lower than that of recast SPEEK owing to the higher stiffness of ZIF particles in the polymeric matrix. This finding indicates that MOFs have superior mechanical stability in composite membranes.

A SPEEK/S-UiO-66@GO (graphene oxide) composite membrane has been prepared through the post-sulfonation of PEEK (Sun et al. 2017a). Sun and his co-authors compared three different GO concentrations and applied them in SPEEK. They obtained the highest tensile strength and Young's modulus in SPEEK/S-UiO-66@GO-15. S-UiO-66 is a stable MOF with the –SO_3H functional group in its ligands. The resultant hybrid nanosheets yield a uniform dispersion of S-UiO-66 onto GO nanosheets, eliminating the agglomeration of S-UiO-66 in the membrane matrix. Moreover, the mechanical performance of the composite membranes is substantially strengthened. They also found that GO is responsible for the improvement in the mechanical properties.

Figure 2B shows that SPEEK@ZIF-Mix (10wt.%) has the highest tensile strength of 123 MPa.

TABLE 2. Mechanical properties of MOF composite membrane in IT- and HT-PEMs

Composite PEMs	MOFs	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Toughness (MJ·m^{-3})	Ref.
SPEEK	-	41.1	1.511	48.0	-	Sun et al. 2017a
SPEEK/S-UiO-66@GO-5	UiO-series	47.8	2.023	45.8	-	Sun et al. 2017a
SPEEK/S-UiO-66@GO-10	UiO-series	53.5	2.190	31.0	-	Sun et al. 2017a
SPEEK/S-UiO-66@GO-15	UiO-series	66.1	2.211	10.8	-	Sun et al. 2017a
Sulfonated poly(ether sulfone) (SPES)/Cr-MIL-101	MIL-series	40.21(wet)	-	16.51(wet)	-	Anahidzade et al. 2018
Sulfonated poly(ether sulfone) (SPES)/Cr-MIL-101	MIL-series	43.72(dry)	-	11.26(dry)	-	Anahidzade et al. 2018
PBI dry	-	174 ± 4	2.52 ± 0.17	2.0 ± 0.1	0.5 ± 0.1	Escorihuela et al. 2018
PBI (75% RH)	-	81 ± 3	1.22 ± 0.12	242 ± 6	96 ± 2	Escorihuela et al. 2018
PBI@ZIF-8	ZIF-series	79 ± 2	1.53 ± 0.08	79 ± 5	50 ± 8	Escorihuela et al. 2018
PBI@ZIF-67	ZIF-series	77 ± 3	1.44 ± 0.10	26 ± 6	13 ± 4	Escorihuela et al. 2018
PBI@ZIF-Mix	ZIF-series	87 ± 2	1.61 ± 0.15	180 ± 17	119 ± 3	Escorihuela et al. 2018
SPEEK@ZIF-8 (5wt.%)	ZIF-series	118	1.8	-	-	Barjola et al. 2018
SPEEK@ZIF-67 (5wt.%)	ZIF-series	121	1.9	-	-	Barjola et al. 2018
SPEEK@ZIF-Mix (10wt.%)	ZIF-series	123	2.2	-	-	Barjola et al. 2018

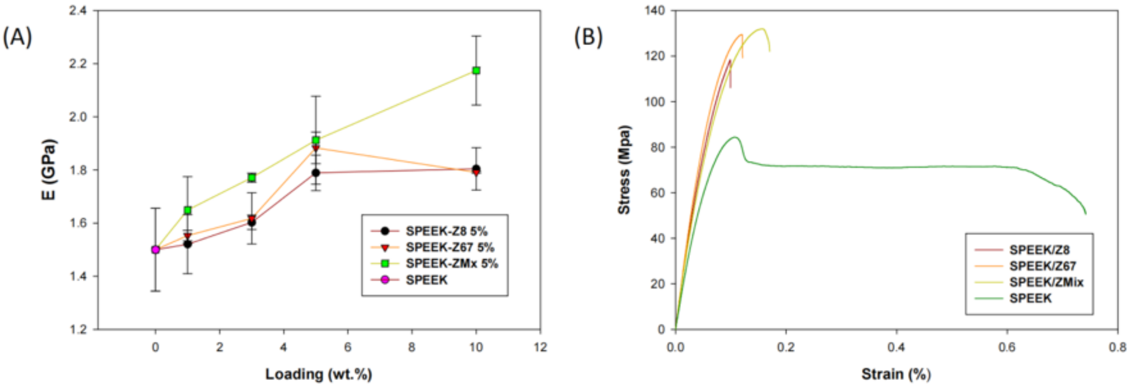

FIGURE 2. (A) Young's modulus and (B) stress–strain curves for composite membranes containing 5wt.% of ZIFs and pristine SPEEK membrane (Barjola et al. 2018)

Referring to the discussion on the mechanical properties of MOF composite membrane in HT-PEMFCs, SPEEK and PBI membranes are the most commonly mentioned membranes for IT- and HT-PEMFCs. Accordingly, the authors focus on SPEEK and PBI composite PEMs in the following sections.

PBI/MOF COMPOSITE PEM

Recently, ZIF-series MOFs have been developed and applied in high-temperature PEMs. ZIF is a kind of effective reinforce that can increase the mechanical stability of composite membranes. PBI@ZIF composite membranes are a kind of hybrid membranes (Vega et al. 2017; Escorihuela et al. 2018). Unlike single ZIF doping, ZIF mixed doping can enhance proton conductivity. Escorhuela et al. (2018) actively reported their works on PBI/ZIF-series composite PEM. They synthesized and characterized composite polybenzimidazole (PBI) membranes containing ZIF-8 and ZIF-67. Phosphoric acid-doped PBI composite membranes display increased proton conductivity from 100 °C to 200 °C under anhydrous conditions. In the case of PBI@ZIF-8 composite membrane, proton conductivity reaches 3.1 × 10^{-2} S·cm^{-1} at 200 °C, and higher values are obtained for PBI@

ZIF-67 membranes (up to 4.1 × 10^{-2} S·cm^{-1}). Furthermore, a composite membrane containing a mixture of 5wt.% ZIF-8 and ZIF-67 reaches a maximum of (9.1 ± 0.2) × 10^{-2} S·cm^{-1} at 200 °C, as shown in Figure 3. As we reviewed, these observed values show that the proton conductivity of PBI@ ZIF-mix membranes is higher than those of other reported HT-PEMs based on MOFs under anhydrous conditions. The above-mentioned enhancement in proton conductivity is owing to the additional proton charge carriers provided by ZIFs in the composite membranes. The higher affinity of phosphonate anions causes it to bind to Co (II) rather than to Zn (II), similar to the observations in a study on H_3PO_4 uptake and swelling ratios. Thus, hybrid PBI@ZIF-mix membrane can synergistically promote proton conductivity.

Moreover, Escorihuela et al. (2018) studied PBI/ZIF composite membrane and tested PBI with 5wt.% of ZIF-8, ZIF-67, and ZIF-mix. They measured the Young's modulus, tensile strength, elongation at break, and toughness values of PBI and PBI/ZIF composite membranes at room temperature. They found that the Young's modulus of PBI@ZIF-mix reaches 1.61 ± 0.15 GPa and its tensile strength is 87 ± 2 MPa. These values are better than those of pristine PBI under the condition of 75% relative humidity (RH). Meanwhile, oxidative stability is a critical parameter in high-temperature PEM fabrication as it affects the long-term operation and lifetime of membranes (Escorihuela et al. 2018). Owing to the peroxide radicals (HO• and HOO•) generated from incomplete oxygen reduction reactions at the cathode of fuel cells, the composite membrane's resistance to degradation is very important (Rafidah et al. 2020). Escorihuela et al. (2018) utilized Fenton's test to demonstrate the chemical stability of composite membranes. All ZIF-containing membranes display a similar level of oxidative stability and are superior to pristine PBI membrane. Among three samples, PBI@ZIF-mix shows the highest resistance to degradation, as shown in Figure 4.

The long-term operation of phosphoric acid (PA)-doped membranes could be affected by acid leaching. One of the key degradation factors is the PA-retention capability of PBI membranes in HT-PEMFCs (Escorihuela et al. 2018). Acid-leaching experiments for all membranes by weighing PA-doped membranes after immersion in boiling water have been conducted. Results show that the acid-leaching degree of 5wt.% PBI@ZIF-8 hybrid membrane is 28%, that of 5wt.% PBI@ZIF-67 is 29%, and that of 5wt.% PBI@ZIF-mix is 30%. These values reveal that PBI@ZIF hybrid membranes retain higher amounts of acid than pristine PBI membrane (the acid-leaching degree of pristine PBI membrane is 36%). Herein, the degree of acid leaching of PBI@ZIF composite membranes is reduced, showing that ZIF compounds have the capacity to trap more acid molecules, thereby limiting the leaching out of membranes (Escorihuela et al. 2018).

Escorihuela et al. has investigated the size and morphology of the synthesized ZIF-8 and ZIF-67 particles, as shown in Figure 3, the typical ZIF rhombic dodecahedral shape has been seen. The obtained average particle size by SEM was approbably 350 to 400 nm for the ZIF-8 and the ZIF-67. Since smaller particles display better dispersion in the solution, and benefit for the properties and stability of the colloidal solution. Futhermore, as shown in Figure 3(c,f), ZIF particles into the PBI matrix showed a certain tendency to form small aggregates, which may achieve a larger effective contact area for transport carriers via smaller particles.

The above studies indicate that proton conductivity increases with increased temperature even under anhydrous conditions operating within 120–180 °C, which benefits operation at high temperatures. Thus, PBI@ZIF-mix composite membrane has promising applications in MEAs for automotive applications.

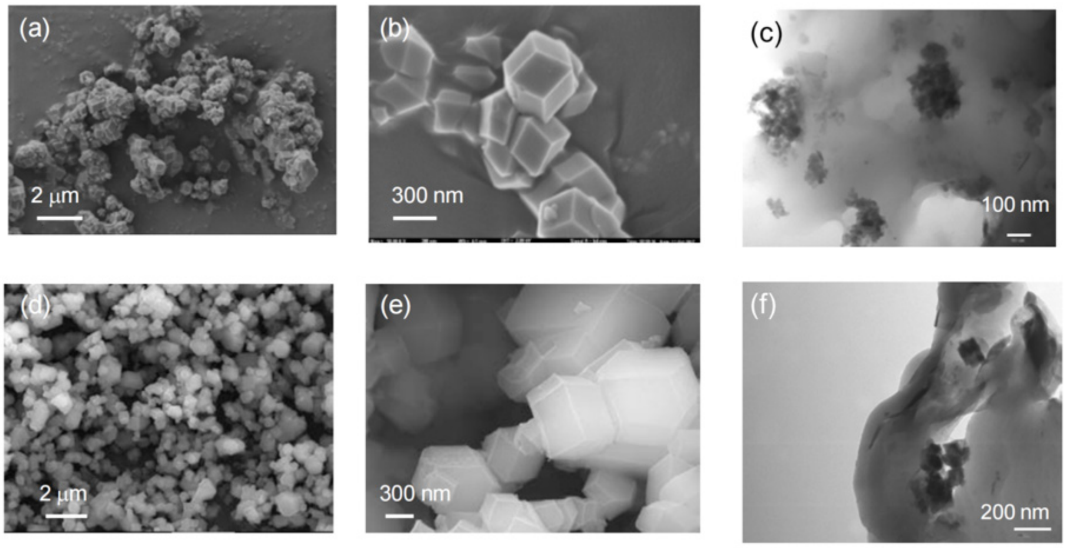

FIGURE 3. (a) Low and (b) high-magnification field-emission scanning electron microscopy (FE-SEM) images of the ZIF-8; (c) transmission electron microscopy (TEM) image of the PBI composite membrane containing ZIF-8 (5 wt.%); (d) low and (e) high-magnified FE-SEM images of the ZIF-67; (f) TEM image of the PBI composite membrane containing ZIF-67 (5 wt.%). (Escorihuela et al. 2018)

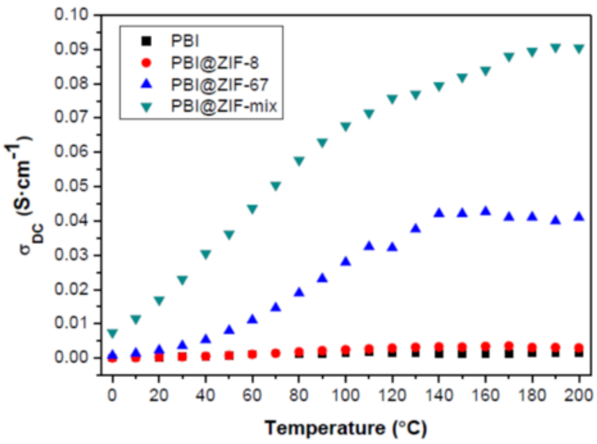

FIGURE 4. Proton conductivity of PBI composite membranes containing 5wt.% ZIF-8, ZIF-67, and ZIF-mix under increasing temperatures and anhydrous conditions (Escorihuela et al. 2018)

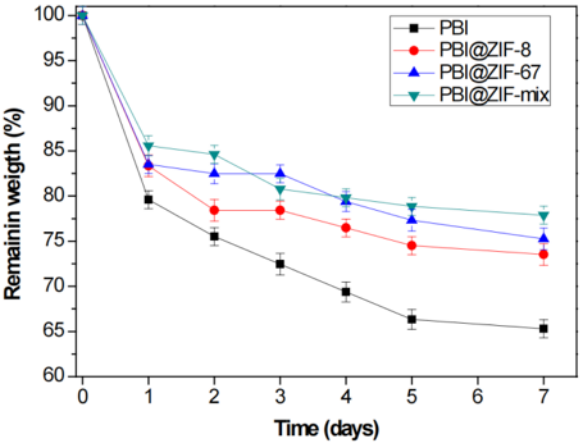

FIGURE 5. Fenton's test (3% H_2O_2 containing 4 ppm Fe^{2+} at 70 °C) for the degradation of PBI@ZIF-8, PBI@ZIF-67, and PBI@ZIF-mix composite membranes (Escorihuela et al. 2018)

SPEEK/MOF COMPOSITE PEM

A SPEEK/S-UiO-66@GO composite membrane has been prepared through the post-sulfonation of PEEK by Sun et al. (2017a). Sun and his co-authors compared GO with three different concentrations and applied them in SPEEK. They obtained the highest tensile strength and Young's modulus in SPEEK/S-UiO-66@GO-15. They also tested a pristine SPEEK membrane with a tensile strength of 41.1 MPa and Young's modulus value of 1.511 GPa. However, SPEEK/S-UiO-66@GO-15 with hybrid nanosheets have higher values, reaching 66.1 MPa (tensile strength) and 2.21 GPa (Young's modulus). Conversely, the 15wt.% GO concentration in SPEEK/S-UiO-66@GO-15 hybrid membranes benefits the increase in tensile strength. Proton conductivity also reaches 0.268 $S \cdot cm^{-1}$ under the conditions of 100 °C and 40% RH, and this proton conductivity is the highest reported for MOF composite PEMs to date. This study demonstrates that S-UiO-66@GO-15 effectively enhances the proton conductivity of SPEEK composite membranes.

The sulfuric acid-doped SPEEK/S-UiO-66@GO membranes and 99.8% DMAc-doped SPEEK@ZIF membranes reportedly show high thermal stability and retain higher amounts of the acid than pristine SPEEK membrane (Sun et al. 2017a; Barjola et al. 2018). However, SPEEK composite membranes display slightly lower thermal stability than pristine SPEEK membrane, and the membrane retains thermal stability when operated at 100–140 °C (Barjola et al. 2018).

Barjola et al. (2018) prepared composite SPEEK membranes with the zeolitic imidazolate frameworks ZIF-8, ZIF-67, and a mixture of ZIF-8 and ZIF-67 (ZIF-mix), which enhance proton transport relative to pristine SPEEK or ZIFs. They reported that the direct current conductivity of composite membranes are three orders of magnitude higher than that of pristine SPEEK at different temperatures, and that of the SPEEK/ZIF-mix membrane is higher than that of SPEEK/Z8 and SPEEK/Z67. They also revealed that the proton conductivity of SPEEK/ZIF-mix is 8.5×10^{-3} $S \cdot cm^{-1}$ rather than those for SPEEK/Z8 and SPEEK/Z67 membranes, which are 2.5×10^{-3} and 1.6×10^{-3} $S \cdot cm^{-1}$ respectively, at 120 °C. Compared with SPEEK/S-UiO-66@GO-10 composite membranes, the proton conductivity of SPEEK/ZIF-mix composite membranes is lower, i.e., 2.9 × 10^{-2} S·cm^{-1}. Notably, the Young's modulus reaches 2.2 GPa for SPEEK/ZMix-10 and the tensile strength reaches 123 MPa, as shown in Figure 2A. As expected, the mechanical properties can be enhanced by the interfacial interactions between ZIFs and SPEEK polymeric matrix, and their study has demonstrated that SPEEK/ZIF-mix composite membranes have outstanding mechanical properties and the highest tensile strength reported so far.

CONCLUSIONS AND FUTURE PERSPECTIVES

We review different types of MOFs doped in PEMs and summarize the recent application and progress of MOFs in high-temperature PEMs for fuel cells. The incorporation of MOFs is found to be more beneficial for enhancing proton conductivity and mechanical stability. In particular, for the doping of intermediate- to high-temperature fuel-cell membranes, MOFs achieve satisfactory results. Owing to the abundant water molecules and acidic groups on the surface of MOFs, the composite membrane possesses the pendant porous. It has various promising properties, including high proton conductivity, mechanical stability, chemical durability, and oxidative stability. There properties result in enhanced performance of the composite membrane when operated at high temperatures in fuel cells under low RH and anhydrous conditions. Hence, these MOF composite membranes have great merits in commercial application.

However, several challenges remain in the development and fabrication of MOF/PEM composite membranes:

1. selection of potential MOF types (with certain properties) and the type of polymer with potential as PEM for IT- and HT-PEMFCs;
2. solutions to identify the dispersing conditions and ensure that MOFs disperse uniformly throughout the polymer matrix;
3. identify the optimum range of doping concentration of MOFs to attain the optimum performance of composite membranes; and
4. the MOFs' grain boundary and diverse crystal structures restricting the proton conductors' migration (Taylor et al. 2015; Van Goethem et al. 2018), which confers difficulty in directly synthesizing MOFs.

Although some challenges and issues at high temperatures remain to be addressed, composite MOFs/PEMs derived from various composite polymers show multiple advantages. The different types of MOFs enhance the performance of high-temperature PEMs. The aforementioned methods reveal that the developed MOF/SPEEK and MOF/PBI composite membranes can be considered as promising candidates for HT-PEMFCs. Furthermore, MOFs play an outstanding role in improving mechanical stability and maintaining high proton conductivity at high temperatures.

Overall, the properties of PEMs at high temperatures can be improved and optimized by doping suitable MOFs. These types of MOFs can significantly affect the proton conductivity, mechanical durability, and chemical stability of the PEM composite membranes and enhance the performance of IT- and HT-PEMFCs. More MOF/PEM composite membranes will be developed through the rational design of novel PEM materials with high electrochemical performance and long lifetime.

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DECLARATION OF COMPETING INTEREST

None

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