



Review Paper

Porous Proton Exchange Membrane Based Zeolitic Imidazolate Framework-8 (ZIF-8)

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Highlights

- MOFs is intrigued for fuel cell application since it can act as proton conductor
- Decreasing in ZIF-8 crystal's size, the water uptake is increase by two times
- The outer surface of smaller ZIF-8 crystals can induce more water sorption
- -N-H unit of ZIF-8 can increase proton conduction pathway when interact with water

Abstract

Metal-organic frameworks (MOFs) are emerging material class for the past few years due to its tailorability characteristics for various applications. However, the research and development (R&D) of MOFs is still scarce for fuel cell system. This may be due to several difficulties faced in selecting a good MOFs based electrolyte, which consequently affects both proton conduction and methanol crossover especially for direct methanol fuel cell (DMFC) system. Owing to excellent thermal and chemical stability with controllable pore size possessed by Zeolitic imidazole framework-8 (ZIF-8) crystal structure has make it most widely been investigated. Furthermore, super-hydrophobicity of ZIF-8 allows high proton conductivity and methanol barrier properties especially in DMFC system. In fact, there has been a huge development on fabricating ZIF-8 membrane, regardless the effects on proton conduction and methanol permeation for fuel cell application. Thus, in this paper, the specialty possessed by MOFs as proton conductors been discussed; in conjunction with the properties, synthesis and fabrication of ZIF-8 membrane as alternative proton conductor and methanol barrier for DMFC application also been highlighted.

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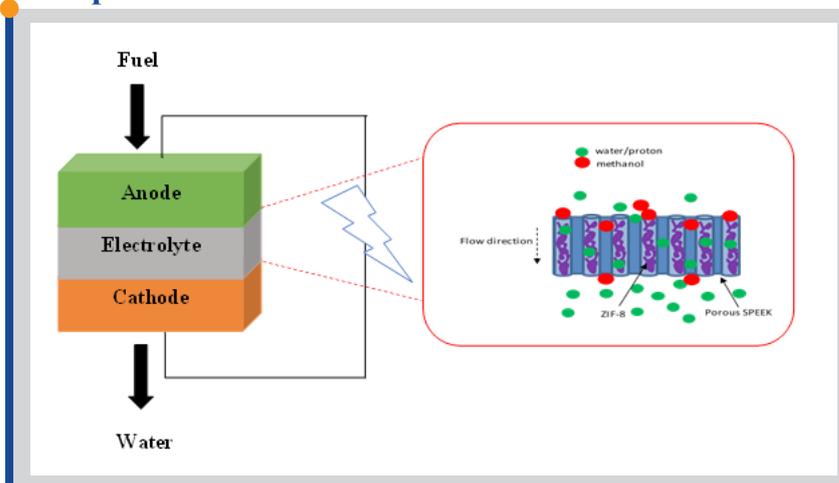
1. Introduction

In past decades, fossil fuel has been the main sources in generating power either for urban or rural used. However, due to rapid depletion of fossil fuel had limited the demand and the time for recovery was too long consequently contributed to fuel's price increment [1]. The worsening scenario is fossil fuel also has led to the environmental problem, climate change, human health, global warming and etcetera. These problems had forced all the researchers around the world to find the solution for these matters. After long term run of numbers research and development (R&D), the renewable energy was then being introduced since it had shown a potential to replace current dependency on fossil fuel. In addition, this renewable energy had offered several advantages

which make it more special than fossil fuel. The advantages offered are as follow [2]:

- 1) Not directly compete with fossil fuel in mainstream of the world.
- 2) Wholesale price was not depended on fossil fuel price.
- 3) Provide electricity to digital devices.
- 4) Financial aspect can be easily estimated and possible to decrease with increasing the technology.
- 5) Demand was depended on government policy not the fossil fuel price.
- 6) Mainly used in electricity system which the prices were not depend on

Graphical abstract



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fossil fuel prices.

“Renewable energy” is a term which referred to self-renewing energy which derived from a variety of resources such as sunlight, wind, flowing water, biomass, geothermal heat and etcetera [3]. As compared to others, fuel cell-based energy supply has captivated a huge potential in research field since it can provide an environmental friendly [4]. The first fuel cell was accidentally fabricated by William Grove in 1838 with respect to the first extensive research work on electrolysis process using electricity to break water into hydrogen and oxygen by William Nicholson and Anthony Carlisle in 1800. The idea for reinventing water by reverse process of electrolysis by William Grove is eventually end up with gas battery or “Grove cell”. This gas battery generated current of 12 Amps with 1.8 Volts. Fuel cell essentially consists of three main parts which are electrode (anode and cathode), electrolyte and fuel [5]. Among all, electrolyte is the vital part in fuel cell system since it can control the fuel cell operation. Most of the electrolyte was define as “polymer electrolyte membrane (PEM)” since it was generally created using polymer electrolyte membrane as proton conductor [6]. These PEMs should have intrinsic properties such as high proton conductivity, high methanol barrier properties as well as high mechanical and chemical stability. The most notable PEM was Nafion[®] which provided the conductivities of 10 Scm⁻¹ at 80°C and 100% relative humidity (RH) whereas, 5-20 Scm⁻¹ at 150°C and 0% relative humidity (RH) [7]. However, despite the higher value of proton conductivity, Nafion had suffered from high fuel permeability especially when operating on direct methanol fuel cell (DMFC) system. Thus, several approaches have been introduced to refine performance of fuel cell performance such as: (1) modifying perfluorinated ionomer membrane/ acid-base blends; (2) modifying ionomer membrane and (3) preparing new electrolyte composite membrane based on proton conducting materials. The latter approach has mark up the R&D for new designed electrolyte in past few decades.

Metal organic frameworks (MOFs) is one type of the inorganic compound which is a new family of hybrid material made up of metals connected by organic linkers called ligands [8]. MOFs are intrigued for fuel cell application since it can act as proton conductor. MOFs has been designed for many applications especially in laboratory scale unit for gas separation, drug delivering, sensors, gas storage, catalyst and etcetera due to its tuneable structure and function. Generally, MOFs is a high crystalline ordered solid, possessed high porosity (depend on metal cations), has huge variety of structures, ultrahigh surface area, flexible structure and high thermal stability [9] which make it unique material to be used as new proton electrolyte membrane. A simple modification to chemical functional groups along the linkers can dramatically enhanced MOFs desired properties in accordingly to the type of application. Therefore, this paper was carried out to discuss on the new direction in developing new MOFs which is ZIF-8 that may attain the desired performance of fuel cell system.

2. General proton conduction mechanism in polymer electrolyte membrane

Process of proton conduction across the polymer electrolyte membrane (PEM) can be diverged into two mechanisms which are (1) the Grotthuss

mechanism and (2) vehicle mechanism [10]. The similarity shared by these two mechanisms is the type of carrier ion involved which is protons. However, after close comparison, the carrier process between the two does defer as the proton transport in vehicle mechanism is mobile, whereas in Grotthuss it is static as illustrated in Figure 1.

Grotthuss mechanism was first introduced by Theodore von Grotthuss in 1804. In his study, he proposed the proton transport mechanism between the water molecules involves the exchanges of covalent bonding to hydrogen bonding of hydrogen (H) atom and oxygen (O) atom. Figure 1 depicted the discussed proton transport via hydrogen bonding based on Grotthuss’ mechanism which is known as proton ‘hopping’. This is due to the fact that involved protons migrate from one carrier to another, without modifying the carrier molecules [11]. On the contrary, protons in vehicle mechanism are transported together with the carrier, simultaneously reshape its chemical structure [10]. In this process, the proton is transported as H₃O⁺ or NH₄⁺ rather than H⁺ and then bonded with the “vehicle” to form H₂O or NH₃ [12]. Thus, both mechanisms do possess distinct functionality at different operating temperature, allowing it to be identified through the temperature itself. Grotthuss mechanism is said to be carried at a dominant temperature under 120°C, whereas higher temperature (120°C-200°C) is preferable for vehicle mechanism.

Primarily, the state of art for polymer electrolyte membrane (PEM) fuel cell technology was conquered by Nafion and other related perfluorosulfonic acid membranes [13]. The concept of using this as an ion exchange membrane was first introduced by General Electric in 1955. However, due to the limitation dwell by these types of electrolyte membranes in fuel cell system, a new direction was being introduced. The most common drawback of these perfluorosulfonic acid polymer especially Nafion, has leads to fuel crossover which eventually decreased the fuel cell overall performance. Previously, as replacement of Nafion by sulfonated poly (ether ether ketone) (SPEEK) by Li *et al.* [14] has shown the improvement in methanol barrier properties for DMFC performance, but, the proton conductivity barely changed at temperature of 80°C. This due to the fact that the proton transport properties of the polymer membrane depend on the presence of water. At higher temperature, for instances, 100°C, the membrane will suffer from dehydration which eventually affected the proton conduction activity [15]. Since then, the evolution of electrolyte membrane fabrication was outrageously increased in order to cater the aforementioned problem regarding proton conductivity, methanol barrier properties and stability of the fabricated PEMs.

3. Composite polymer electrolyte membranes

Composite electrolyte membranes are one of the interest sub-topic in PEM evolution to be discussed due to its specialties provided by inorganic and polymeric materials. The combination of both properties can induce higher selectivity and permeability in some extreme conditions as compared to polymeric membranes [16]. The inorganic compound such as zeolite, talc, mica, carbon black, fumed silica and clay mineral are widely used as a reinforcer for polymeric-based materials. These reinforcers were used by means to reduce the methanol crossover and water permeability in polymeric electrolyte membrane [17]. Table 1 tabulated some of the type of polymer inorganic membranes for DMFC applications.

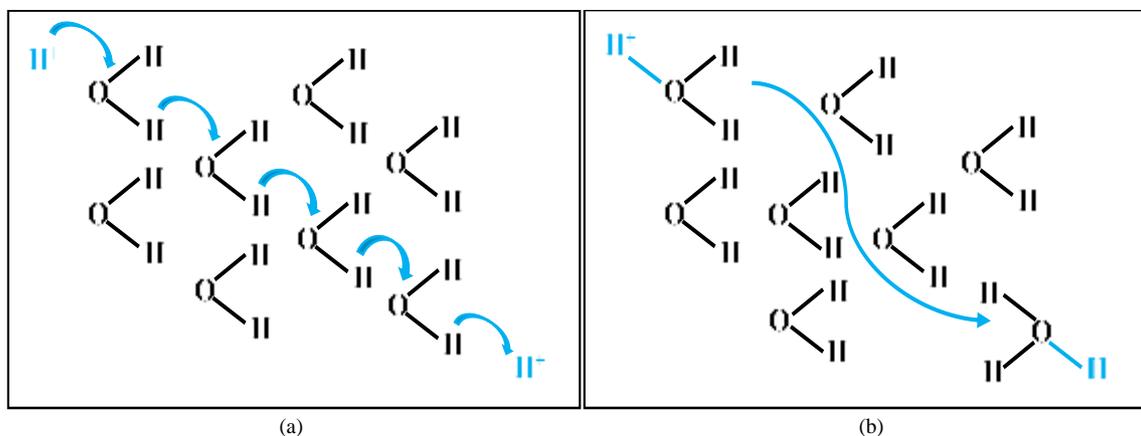


Fig. 1. Proton conduction modelling: (a) Grotthuss mechanism and (b) vehicle mechanism.

Table 1
Polymer-inorganic electrolyte membranes for DMFC applications.

Composite Membrane	Abbreviation	Proton Conductivity (Scm ⁻¹) *	Methanol Permeability (cm ² s ⁻¹) *	Operating Temperature (°C)	Author/s
Poly (vinyl alcohol) /montmorillonite (10 wt.%)	PVA/MMT (10 wt%)	36.8 x 10 ⁻³	3.67x10 ⁻⁶	30	[18]
Sulfonated poly(styrene- <i>b</i> -ethylene/butylenes- <i>b</i> -styrene) copolymer/Cloisite®Na+	S-SEBS/Na ⁺	142 x 10 ⁻³	0.62 x 10 ⁻⁶	NA	[19]
Sulfonated poly (ether ether ketone)/Cloisite15A® (2.5 wt.%) /triaminopyrimidine (5 wt.%)	SPEEK/Cloisite (2.5wt%)/TAP (5.0wt%)	16.3 x 10 ⁻³	1.3 x 10 ⁻⁶	RT	[20]
Sulfonated poly (arylene ether nitrile)/sulfonated graphene oxide	SPEN/SGO (1wt%)	109 x 10 ⁻³	0.17 x 10 ⁻⁶	20	[21]
Sulfonated poly (ether sulfone)/ Graphene oxide (1 wt.%)	SPES/GO (1wt%)	4.3 x 10 ⁻³	0.0492 x 10 ⁻⁶	NA	[22]
Nafion/Nanoporous carbon (1 wt.%)	Nafion/NPC (1 wt%)	75.1 x 10 ⁻³	0.98 x 10 ⁻⁶	80	[23]
Nafion/Ceria (1 wt.%)	Nafion/CeO ₂ (1 wt%)	176 x 10 ⁻³	Decreasing	70	[24]
Sulfonated poly (cynlidene fluoride)/sulfonated magnetite@silica (3 wt.%)	sPVdF/sFe ₃ O ₄ @SiO ₂ (3 wt%)	64 x 10 ⁻³	2x10 ⁻⁶	60	[25]
Sulfonated polysulfone/sulfonated ZSM-5 zeolite	SPSF/SZSM5	9.65 x 10 ⁻³	Two orders of magnitude lower than Nafion 117	30	[26]

*RT = room temperature

*NA = not available

*all measurement be compared with pristine Nafion and parent membrane respectively

Table 2
MOF-polymer composite membrane for fuel cell application.

MOF-polymer	Abbreviation	Proton Conductivity (Scm ⁻¹)	Temperature (°C)	Relative Humidity (RH)	Methanol Permeability (cm ² /s)	Author/s
Zeolitic Imidazolate Framework-Carbon Nanotube Hybrid/Sulfonated Poly (ether ether ketone)	ZCN/SPEEK	50.24 x 10 ⁻³	120	30	0.245 x 10 ⁻⁸	[27]
Zeolitic Imidazolate Framework-8/Sulfonated Poly (ether ether ketone)	ZIF-8/SPEEK	24.1 x 10 ⁻³	120	30	1.459 x 10 ⁻⁸	[27]
Iron -MIL = Mate'riaux de l'Institut Lavoisier '101-amine/Sulfonated Poly (2, 6-dimethyl-1,4-phenylene oxide)	Fe-MIL-101-NH ₂ /SPPO	0.10 x 10 ⁻³ 0.25 x 10 ⁻³	RT 90	NA NA	NA	[29]
Sulfonated - Mate'riaux de l'Institut Lavoisier '101 (Chromium)/Sulfonated Poly (ether ether ketone)	Sul-MIL101 (Cr) /SPEEK	0.306	75	100	slightly higher	[30]
Zeolitic Imidazolate Framework-8/Poly (vinyl phosphonic acid)	ZIF-8/PVPA	3.2 x 10 ⁻³	139.85	NA	NA	[31]
Zeolitic Imidazolate Framework-8/ Poly (vinyl alcohol/ Poly (2-acrylamido-2-methyl propane sulfonic acid) (PAMPS)/	ZIF-8/PVA: PAMPS	0.134 x 10 ⁻³	80	100	NA	[32]
Phosphotungstic acid - encapsulating Mate'riaux de l'Institut Lavoisier '101 (Chromium)/ Poly (ether ether sulfone)	HPW@MIL101/ SPEEK	272 x 10 ⁻³ 6.51 x 10 ⁻³	65 60	100 40	NA	[33]
Zeolitic Imidazolate Framework-8/ deoxyribonucleic acid	ZIF-8@DNA	17 x 10 ⁻³	75	97	1.25 x 10 ⁻⁸	[34]

*RT = room temperature, NA = not available

Other than that, newly reinforce such as metal organic frameworks (MOFs) has been extensively studied for application in DMFC system due to its ability to act as both proton conductor and methanol barrier simultaneously that will be discussed in detail in later subtopic. However, the realization utility of MOFs in fuel cell application still limited due to its crystal structure which hinder the membrane fabrication process [27]. Thus, a combination of MOF-polymer will provide a good synergy between MOF-polymer which eventually induced a great performance in fuel cell application. For instance, Yang *et al.* [28] have worked on Nafion incorporated with graphene oxide and zeolitic imidazolate framework-8 (GO@ZIF-8) fillers. In their work, they found that the fuel crossover especially on DMFC has reduced as compared to pristine Nafion membrane whereas the value of proton conductivity was extremely increase to 0.28 Scm⁻¹ as compare to Nafion (0.005 Scm⁻¹). Table 2 summarize the MOF-polymer composite membranes for fuel cell application. From Table 2, it was proven that the combination of both polymer and MOF indeed increased the proton conductivity of the membrane as compared to the pristine polymer and MOF itself.

4. Metal organic framework (MOF) proton conductor

Most of the times, proton conductor is referred as an electrolyte, specifically a solid electrolyte in which H⁺ is the main charge carrier. It

embodies a porous body to hold proton-conducting polymers, which are covalently bonded. Two main vital properties to a proton conductor comprising of great components are: (1) for operation below than 100°C and (2) can unlock the cost efficiencies at operation temperature higher than 100°C [9]. As for metal-organic frameworks (MOFs), they are a new class of porous crystalline solids assembled from metal ions/clusters coordinated by organic linkers with a strong bond [35-40]. Only recently that MOFs have shown some intrinsic properties, simultaneously potentials that allowed them to be used as proton conductors instead. Due to their extraordinarily, yet controllable structure, its flexibility makes MOFs to be broadly studied for its gas storage, sensing, separation medium, catalysis and biomedical applications [35, 41]. Consecutively, the specialty of MOFs with highly crystalline solid is elucidated, emphasising its proton conducting site which gives a vision into molecular-level transport properties mechanism [42]. This transport mechanism is crucial in order to understand the structural relationships in electrolyte membranes [43]. When it comes to both Grotthuss and vehicle mechanism transport properties, these two relationships are involved: (a) relationship of morphology of hydrated PEMs and the interfaces and (b) relationships of transport in PEMs (morphology) [42]. The detailed of these two consecutive transport mechanism relationships have been demonstrated by Sanabria-chinchilla and colleagues [42] via simulation methods.

In addition to that, organic linkers seem to be an important part of MOFs

synthesis, given how it can be adjusted to the MOFs' properties for a targeted application by altering the geometry, length, ratio and functional group [36]. Table 3 summarizes the types of organic linkers for MOFs. The incorporation of active functional linkers with inherent porosity (sulfonic, phosphonic, carboxylic or hydroxyl group) and proton carrier molecules/ions (water, imidazole, NH_4^+ , H_3O^+ , Emim⁺) in MOFs' proton-carrier channels led to an exceptional opportunity for proton transport mechanism [9].

From Table 3, there are various type of organic linkers such as ditopic, tritopic, tetratopic, hexatopic, octatopic, mixed-linkers, desymmetrized linkers, metallo, N-heterocycle linkers and dhhdc linkers. These organic linkers and its twisted angles may affect the dimension and topology of MOFs' structure [36]. For an example, the formation of MOF-601 [36] is defined due to its 90° bend angle of bridging ligand [44] by one of the ditopic linkers which eventually led to *nbo* topology [36]. To further elucidate, ditopic linkers are the receivers that hold two binding areas in which coordinate with a metal cluster [45]. As for other types of MOF, they too possess the same characteristics as the binding angle, though the latter plays a role with different types of cluster; all discussed in detail by [36]. Linkers such as tritopic, tetratopic, hexatopic, octatopic however, are formed when there are more than two site binding areas connected to a metal cluster. Mixed-linkers on the other hand are a combination from different types of organic linker that lead to formation of varying types of MOF.

Besides that, for desymmetrized linkers, the formation of modified MOF does differ from untainted ones, albeit the two possess same number of site binding. For instance, UMCM-151 displays a different topology compared to UMCM-150 (see Figure 2). This phenomenon was achieved by adding ring to the symmetrized linkers [36]. Metallo-linkers are referred to the ones with another metal added to the MOF, then categorised based different types of donor groups attached to organic linkers. N-heterocycle linkers can be divided into two types which are ditopic and polytopic, both are consisted of nitrogen donors coordinated with metal clusters.

Excellent materials for proton-conducting MOFs can be divided into three parts which are: (1) water-assisted proton-conducting MOFs, (2) anhydrous proton-conducting MOFs and (3) combination of (1) and (2) proton-conducting MOFs [41, 46]. Such requirements for selected materials can assist the potential of MOFs to be used at relatively high temperature and in anhydrous conditions [40]. To add on, the tuneable porosity possessed by MOFs can give an impact to the performance of fuel cell since it can be selective to certain molecules that are passing through.

Water-assisted proton conducting MOFs usually involve the presence of water-based molecules (oxalated-based, carboxylate-based, sulphonate-carboxylate-based, phosphonate-based and mixed linkers-based) in which not only form hydrogen-bonding interaction with the framework, but also act as

proton carriers [46]. Aside from that, they only operate at low and moderate temperature. Though for anhydrous proton-conducting MOFs, a higher temperature which is usually greater than 80°C is preferable. These types of MOFs basically contain organic molecules such as pyrazole and imidazole, whereby both act as proton conductor in absence of water molecules [47]. Smart materials that combine both features of proton conduction at hydrate and anhydrous condition had been studied greatly within the past few years. They have shown remarkable proton conductivity at both conditions. Such discovery is supported a study conducted by Nagarkar et al. [41], whereby it was proven that the new 3D MOFs $\{[(\text{Me}_2\text{NH}_2)_3(\text{SO}_4)]_2[\text{Zn}_2(\text{ox})_3]\}_n$ had performed a high proton conductivity for both conditions. In comparison to the distinguished Nafion membrane, proton conductivity at hydrate ($4.2 \times 10^{-2} \text{ Scm}^{-1}$) and anhydrous condition ($1 \times 10^{-4} \text{ Scm}^{-1}$) are respectively likewise [41].

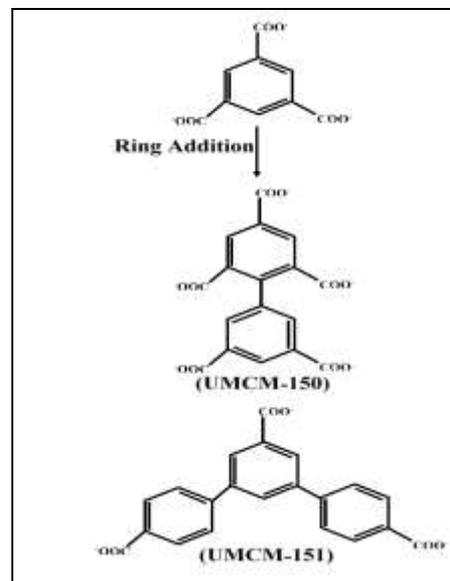


Fig. 2. Desymmetrized linkers.

Table 3
Type of organic linkers for MOFs.

Type of Linker	Linkers and Cluster Types
Ditopic	i. Ditopic carboxylate linkers with 4-connected paddle-wheel clusters ii. Ditopic carboxylate linkers with 6-connected octahedral clusters iii. Ditopic carboxylate linkers with 6-connected trigonal-prismatic clusters iv. Ditopic carboxylate linkers + 12-connected clusters v. Ditopic carboxylate linkers with infinite chain clusters
Tritopic	i. Tritopic carboxylate linkers with 4-connected paddlewheel clusters ii. Tritopic carboxylate linkers with 6-connected octahedral clusters iii. Tritopic carboxylate linkers with 6-connected trigonal-prismatic clusters iv. Tritopic carboxylate linkers with multiple SBUs
Tetratopic	i. Tetrahedral carboxylate linkers with 8-connected cubical clusters ii. Tetrahedral carboxylate linkers with 4-connected square planar clusters iii. Tetrahedral carboxylate linkers with 8-connected hexagonal bipyramidal clusters iv. Non-regular tetrahedral carboxylate linkers
Hexatopic	i. Hexatopic linkers with 1,3-benzenedicarboxylate units ii. Hexatopic linkers with 4,4'-azanediyldibenzoate units. iii. Hexatopic linkers with 1,1':3',1''-terphenyl-4,4''-dicarboxylate units
Octatopic	-NA
Mixed	i. Ditopic-ditopic linear linkers ii. Tritopic carboxylate-ditopic carboxylate linkers iii. Carboxylate-pyridine linkers iv. Linkers coordinatively identical but distinct in shape
Desymmetrized	-NA
Metallo	i. Metallo-linkers with oxygen and sulfur donors ii. Metallo-linkers with nitrogen and phosphine donors iii. Metallo-linkers with mixed donor groups
N-heterocyclic linkers	i. Ditopic N-heterocyclic linkers ii. Polytopic N-heterocyclic linkers
dhhdc linker	Abbreviation for linkers with different metals attached

Table 4
Summarization of MOF-based electrolyte for fuel cell.

MOF-based electrolyte	Proton conductivity (Scm ⁻¹)	T (°C)	RH (%)	Author/s
{[(Me ₂ NH ₂) ₃ (SO ₄) ₂ [Zn ₂ (ox) ₃] _n }	42 x 10 ⁻³ 0.1 x 10 ⁻³	NA	100 0	[41]
H ₂ SO ₄ @MIL-101	10 x 10 ⁻³	150	NA	[52]
H ₃ PO ₄ @MIL-101	3 x 10 ⁻³	RT	NA	[54]
UiO-67(Im)	1.44 x 10 ⁻³	120	NA	[54]
PCMOF2 ^{1/2}	21 x 10 ⁻³	85	90	[57]
(NH ₄) ₂ (adp)[Zn ₂ (ox) ₃].3H ₂ O	8 x 10 ⁻³	25	98	[58]
β-PCMOF2	0.5 x 10 ⁻³	150	0	[59]
Histamine@[Al(μ ₂ -OH)(1,4-NDC)] _n	1.7 x 10 ⁻³	150	0	[60]
(NH ₄) ₄ [MnCr ₂ (ox) ₆].4H ₂ O	1.1 x 10 ⁻³	RT	NA	[61]
[Zn(<i>l</i> -LCl)(Cl)](H ₂ O)	0.00445 x 10 ⁻³	30.85	98	[62]
[Zn(<i>d</i> -LCl)(Cl)](H ₂ O)	0.00442 x 10 ⁻³			
MgH ₆ ODTMP.6H ₂ O	1.6 x 10 ⁻³	19	100	[63]
{[(Zn _{0.25}) ₃ (O)]Zn ₆ (L) ₁₂ (H ₂ O) ₂₅ (DMF) ₆₉ (NO ₃) ₂] _n }	2.3 x 10 ⁻³	25	95	[64]
Cu-TCPP	3.9 x 10 ⁻³	NA	98	[65]
PCMOF ₁₀	35.5 x 10 ⁻³	70	95	[66]
UiO-66-SO ₃ H	3.4 x 10 ⁻³	29.85	-97	[67]
UiO-66-2COOH	1.0 x 10 ⁻³			
ZIF-8	0.46x10 ⁻³	94	98	[68]
MFM-500(Ni)	0.45 x 10 ⁻³	25	98	[69]
(Me ₂ NH ₂)[Eu(L)] (H ₄ L = 5-(phosphonomethyl) isophthalic acid)	3.76 x 10 ⁻³ 1.25 x 10 ⁻³	100 150	98 0	[70]

*RT = room temperature, NA = not available

4.1. Proton conductor medium for metal organic frameworks (MOFs)

Metal organic frameworks (MOFs) have flourished over the years due to its amenability, inclusively on its architecture design which possessed a porous structure in range of microporous (pore sizes <2 nm) to mesoporous (2–50 nm) scale [48, 49]. The tailorable porosity and dynamic behaviour of MOFs have strengthened its potential as proton conductors [37]. As a matter of fact, they can be loaded with guest molecules [50], demonstrating greater potential in proton conduction and gas tight properties. Nevertheless, the open structure of MOFs may appear brittle, allowing fuel to permeate instead [37]. Since 2003, several approaches have been investigated, with emphasis proton-conducting MOFs for both hydrate and dehydrate conditions [7] and came upon three approaches which are: (1) as-synthesized MOFs (controlled hydrophilicity and acidity), (2) introduction of guest molecules/inorganic nano-structure (imidazole/triazole, polyoxometalates) into MOFs and (3) chemically modified MOFs in post-synthesis step.

The hydrophilicity of PEMs is important for proton conduction, mainly at ambient temperature and condition with low humidity [51]. Thus, a smart material like MOFs should comply for both operating conditions either in hydrate or anhydrous. Controlling the hydrophilicity of the pores is one of the key components in achieving high proton conduction, proven by Sadakiyo and co-worker [51], who worked on {NR₃(CH₂COOH)}[MnCr(ox)₃]_n.H₂O with different functional groups. It was found that the bigger amount of hydrophilic compound present in these functional groups, the higher the proton conductivity would be. Ponomareva and co-worker [52] then elucidated that a good proton conductor should have strong amount of H⁺ ion carriers such as sulphuric acid (H₂SO₄) and phosphoric acid (H₃PO₄), based on the impregnation of carboxylic group in MIL-101 structure. From their study, the findings shown that the proton conductivity of H₂SO₄@MIL-101 (1 x 10⁻² Scm⁻¹) and H₃PO₄@MIL-101 (3 x 10⁻³ Scm⁻¹) are remarkably higher than other PEMs such as Nafion at 150°C and ambient temperature.

As previously mentioned, porosity is one of MOFs' amazing features, one that traps guest molecules within the insulated pores and eventually increases the proton conductivity of particular MOFs. Said guest molecules can be adapted as a medium for proton transport which interacts with nearby functional group for a dynamic transportation of proton [53]. Given the concern that PEMs commonly collapse when operating at high temperature (>80°C), a new approach in regard to MOFs' materials is studied to cater this problem. Introduction to guest molecules like imidazole in the MOFs's channel is indeed substantial. In the study of Liu *et al.* [54], the incorporation of imidazole group within UiO-67's channel has been proven by the presence

of high proton conductivity (1.44 x 10⁻³ Scm⁻¹) at 120°C.

Post-synthesis modification (PSM) usually occurs when the alteration on its functionality cannot be done at the beginning of synthesis process. This PSM can be classified into three methods which are (a) modification of the linkers, (b) modification of metal containing nodes and (c) building block replacement (BBR) that have being explained in details by Deria and colleague [55]. To simplify, these modifications may include all parts of the frameworks as well as the linkers, metal and inorganic clusters [56]. One of the examples would be the modification on the ligand through the replacement method. Kim and co-worker [57] have introduced C₃-symmetric tris (hydrogen phosphonate) ligand on β-PCMOF2 which eventually formed a new MOF named PCMOF2^{1/2}. In their study, they also found that the proton conduction of modified MOF (PCMOF2^{1/2}) exhibited proton conductivity of 2.1 x 10⁻² Scm⁻¹ at 85°C and 90%RH higher than its parents β-PCMOF2. Summarization of MOF-based electrolyte for fuel cell can be found in Table 4.

The exceptional functional properties of MOFs can be clarified as diverse and have tuneable porosities as well as high surface area [35, 36]. These amenabilities of structure MOFs with extraordinary porosity, excellent electrochemical properties as well as large surface area give merits in further investigating compact films and membranes [35, 36, 40, 71]. The designed framework with pores and channels had given an insight with added value for MOFs to act as proton conductor, given that various conducting media can be added to these structural properties [68]. Aside from the channels within MOFs, Xu *et al.* [65], had revealed in their study that the surface of MOFs nanocrystal also gave an impact on proton transport mechanism as shown in Figure 3. This new pathway has given a discernment of MOFs' idiosyncrasy as an excellent medium of proton conductor.

Reasonably, when the size of the MOF crystal is reduced to nanoscale, the outer surface area also increases exceptionally. When dealing with the process of proton conduction, it is worth noting that the relative humidity (RH) may play a big role for transport condition. When RH increases, the added value for proton conduction by water molecules also increases due to high uptake of water molecules in electrolyte membrane. In a condition whereby, the water uptake is greatly increased, the conductivity of MOFs becomes saturated [65]. There are two possible mechanisms that would occur throughout the process of proton transport MOFs, either in the pore's channel or surface of the crystal; or simply both. From Figure 3, it can be clearly seen that the dangling carboxyl groups of nanosheet gives an impact upon the surface.

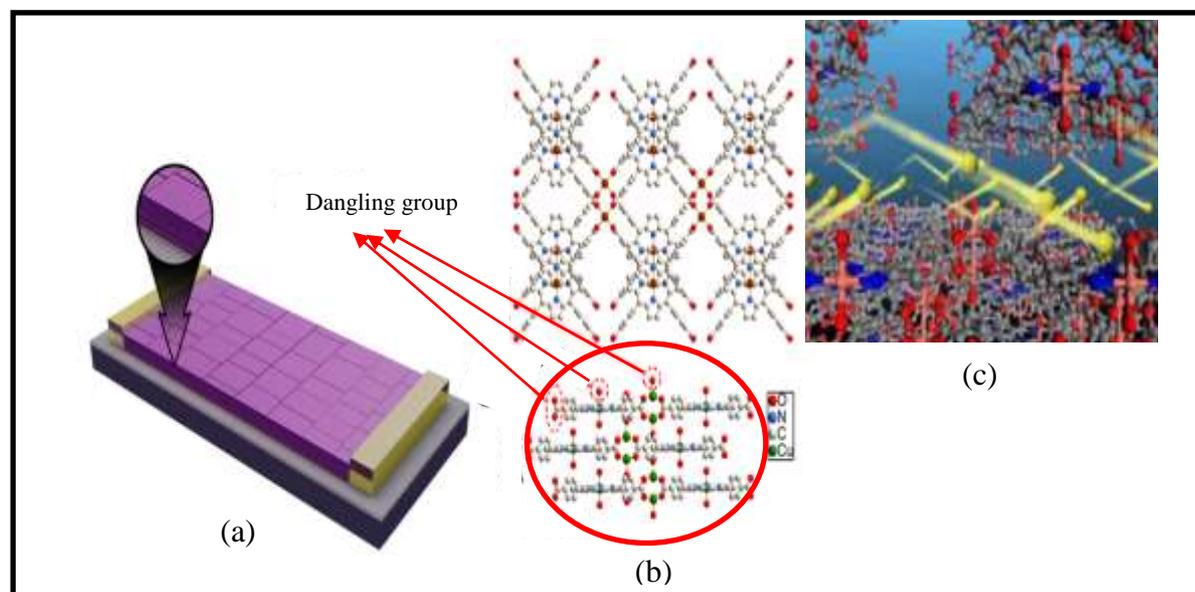


Fig. 3. (a) nanosheets of Cu-TCPP, (b) crystal structure with dangling carboxyl groups on CU-TCPP nanosheet surface and (c) schematic of proton conducting medium on the surface of Cu-TCPP [65] Copyright© 2013 American Chemical Society.

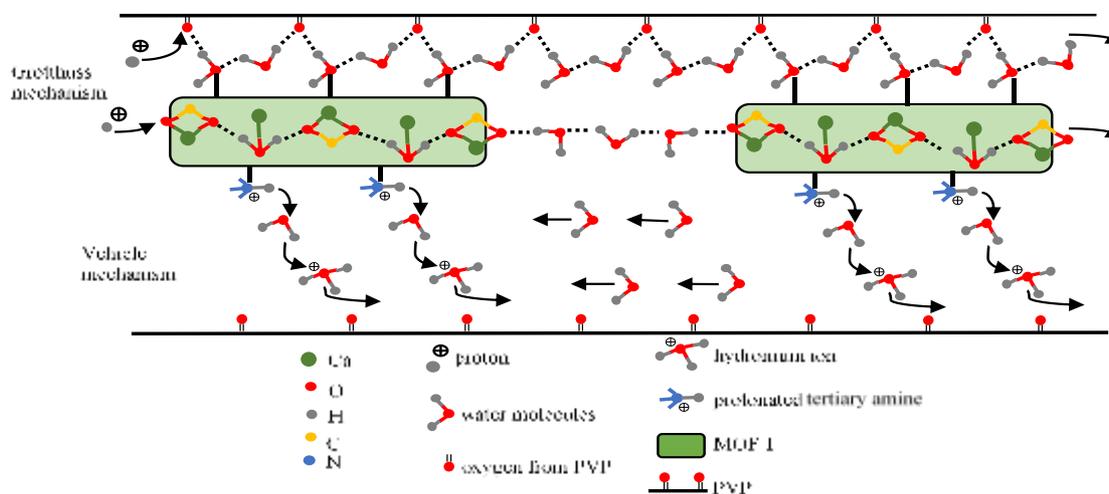


Fig. 4.1 Possible transport mechanisms in MOF-1-PVP composite membrane [73].

The hydrogen-bonding network was created when these dangling carboxyl groups interact with hanging water molecules that are present on the surface due to rejection of micropores adsorption. Such phenomenon occurs when the absorbed water molecules cannot pass through the small micropore size channel, causing the water molecules to appear on the surface of nanosheets [65]. This Cu-TCPP type of MOFs exhibits a high proton conductivity which is $3.9 \times 10^{-3} \text{ Scm}^{-1}$ at 98% RH.

5. Mechanism of proton transport in metal organic frameworks (MOFs)

Mechanism of proton transport in metal organic frameworks (MOFs) can be both Grothuss and vehicle depending on the type of metal and organic linkers involved. Higher activation energy apparently can be a sign for both mechanisms to appear. This was clarified by Wang *et al.* [72] in their paper in which discussed on $\{(\text{NH}_4)_2(\text{adp}) [\text{Zn}_2(\text{ox})_3] \cdot 3\text{H}_2\text{O}\}_n$ (ox = oxalic acid, adp = adipic acid) proton-conducting MOF. They discovered that the activation energy for $\{(\text{NH}_4)_2(\text{adp}) [\text{Zn}_2(\text{ox})_3] \cdot 3\text{H}_2\text{O}\}_n$ (ox = oxalic acid, adp = adipic acid) was at 0.63 eV which is higher than Nafion (0.22 eV). Liang *et al.* [73] had found that whether vehicle or Grothuss mechanism would appear in proton transport process is depending on the relative humidity [74]. Based on

the research, at low relative humidity (~53% RH), only small water molecules were required to act as vehicles, while others were inclined to accept protons which eventually led to higher activation energy (0.65 eV). However, at high relative humidity (~65% RH), Grothuss mechanism took place. At this point, the activation energy was recorded to be low (0.54 eV) given that more water molecules were required to form an effective hydrogen bonding. Figure 4 depicts the possible proton transport mechanism occurred in MOF-1, $\{[\text{Ca}(\text{D-Hpmpc})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ ($1, \text{D-H}_3\text{pmpc} = \text{D-1-(phosphonomethyl) piperidine-3-carboxylic acid}$) / Poly (vinylpyrrolidinone) (PVP), (MOF-1-PVP) composite membrane.

From Figure 4, vehicle mechanism occurred when proton diffused together with water molecules, thus the protonated tertiary amines of MOF-1 transferred the proton to adsorb water molecules. Whereas for Grothuss mechanism, it is stated to have occurred by proton hopping from one proton carrier to other neighbouring carrier through hydrogen bonding. In these interactions, there are two possible types of hydrogen bonding involved [73]: (1) hydrogen bonding among oxygen atoms of PVP, adsorbed water molecules in PVP, coordinated aqua molecules interact on the surface of MOF-1 crystal and (2) hydrogen bonding among adsorbed water molecules in PVP, coordinated carboxylate oxygen atoms and coordinated aqua molecules in MOF-1. In fact, Talin *et al.* [75] once had claimed that the thin films of

MOFs compound are generally poor conductors due to the π -orbital conjugation within the organic linking groups that act as an insulator [76]. However, the insulator properties of MOFs are seemingly insignificant since the structure and morphology of MOFs are more crucial to be concerned of as it can greatly impact the proton conductivity.

6. Proton conductive MOFs

MOFs can be divided into two large notable families which are: (1) metal-organic polyhedras wherein transition metal ions are coordinated by either nitrogen or carboxylate electron-donor organic units, and (2) zeolitic imidazolate frameworks (ZIFs) with various imidazole groups coordinating of ZnII (ZIF -1 to -4, -6 to -8, and -10 to -11) or CoII (ZIF -9 and -12) and adapted zeolite topology [7]. Zeolitic imidazolate frameworks (ZIFs) are novel subclasses of MOFs consisting of tetrahedral transition metal ions such as zinc or cobalt that are bridged by imidazole type linkers [77, 78]. This ZIFs-type MOFs offer a permanent porosity with more topology structure and coordinate factors compared to pure zeolites; in fact, the strong bonding between centre metal ions and nitrogen atom from ligands offers robust chemical and thermal stability to ZIFs [77, 78]. ZIFs structure is analogous to zeolite-like topologies such as Si or Al tetrahedral unit and bridging O is being replaced by Zn²⁺ or Co²⁺ and imidazolate-derived ligands, respectively [77, 79-80]. Among all, zeolitic imidazolate framework -8 (ZIF-8) has shown an exceptional thermal and chemical stability, as well as contributing imidazole proton and high surface area which indeed may provide a good proton conductivity ($0.46 \times 10^{-3} \text{ Scm}^{-1}$) [68].

7. Zeolitic imidazolate framework-8 (ZIF-8)

Generally, zeolitic imidazolate framework-8 (ZIF-8) is a subclass of ZIFs with chemical formula C₈H₁₀N₄Zn, constructed from binding Zn²⁺ metal ions by bridging ligand of 2-methylimidazole (Hmim). This type of ZIF has

sodalite (SOD) topology with pore size of 0.34 nm and internal cavities of 1.16 nm in diameter [48, 77, 79-82]. ZIFs-8 however, has a simple synthesis route, yet possesses high chemical and thermal stability [78, 82]. Papporello et al. [48] even discussed on the stability of ZIF-8 in liquid solution. In general, from the findings collected, ZIF-8 was found to be stable in boiling water, organic solvent (methanol and benzene) condition for 7 days, whereas only 24 hours in alkaline solution [83]. However, the flexibility of structure makes it possible for the biggest molecule to enter the window spacing [48].

8. Synthesis methods for ZIF-8 crystals

The synthesis of ZIF-8 commonly involved two step processes which are nucleation and crystallization [84]. The formation of ZIF-8 mainly involved of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O and 2-methylimidazole (MeIM). Synthesis for ZIF-8 can be divided into few techniques [79, 85] as depicted in Figure 5.

From Figure 5, it can be deduced that the formation of ZIF-8 crystals can be divided into two large notable groups which are solvent-based synthesis and solvent-free synthesis. The common solvents that have been used in practical applications were *N, N*-dimethylformamide (DMF), *N, N*-diethylformamide (DEF), *N*-methyl pyrrolidine (NMP), methanol (MeOH) and water (H₂O). Potential solvent likes ammonia, ionic liquid and eutectic mixture were still in the early stage of study. A detailed discussion on synthesis type of ZIF-8 crystals can be found in literature by Chen *et al.* [86]. Other than types of synthesis procedure, the operating condition for each method also need to be addressed in detail to obtain a good structure of ZIF-8 crystal for specific applications. These factors can be divided into four large groups which are: (1) adjustment the concentration of reactants and solvents, (2) altering the synthesis conditions such as temperature and time, (3) different heating types such as for solvothermal and microwave-assisted synthesis and lastly (4) using specific additives as deprotonated agent [87]. Figure 6 depicted the ZIF-8 crystallization phase over time interval.

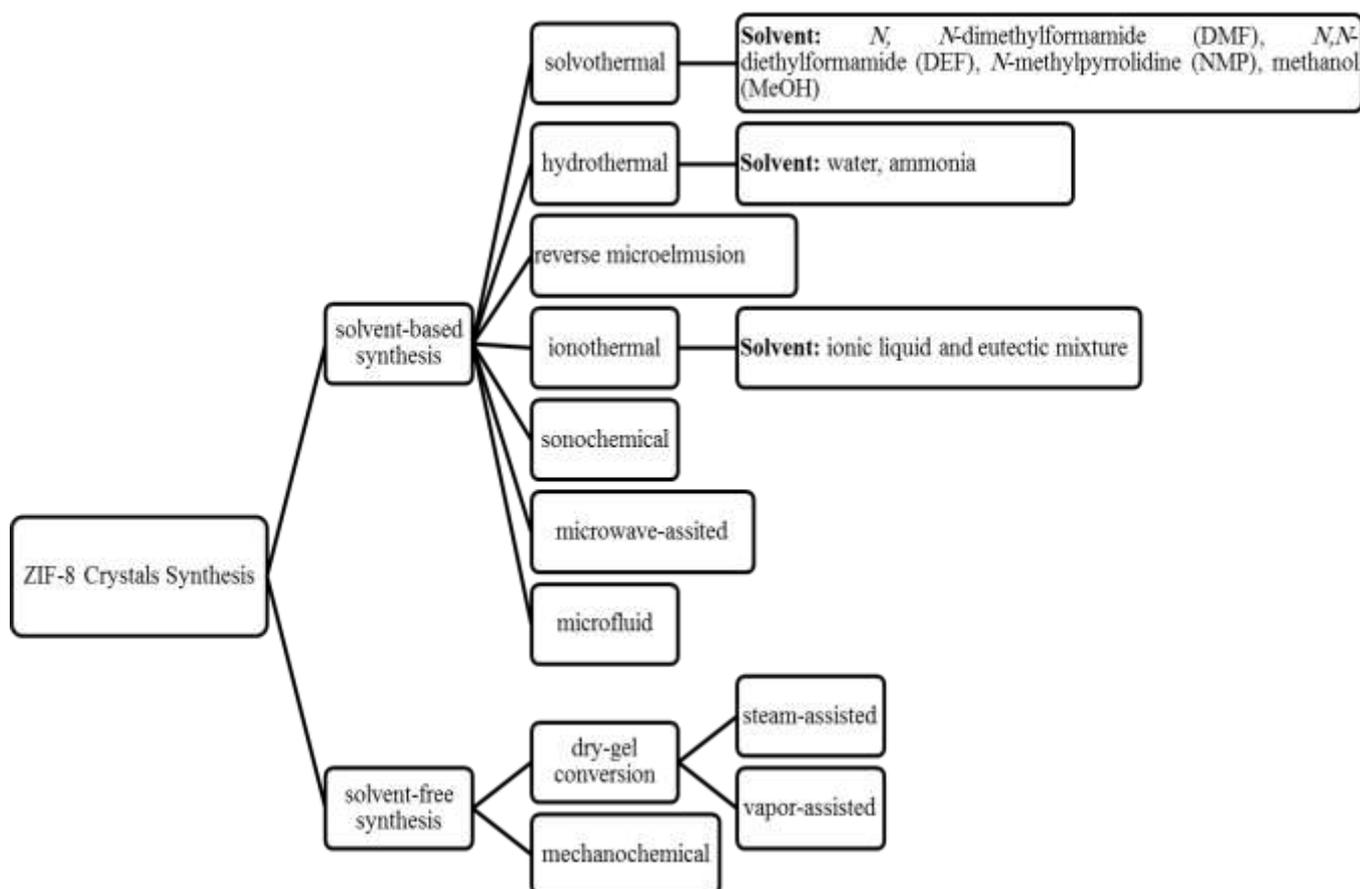


Fig. 5. Methods involved in preparing ZIF-8 crystals.

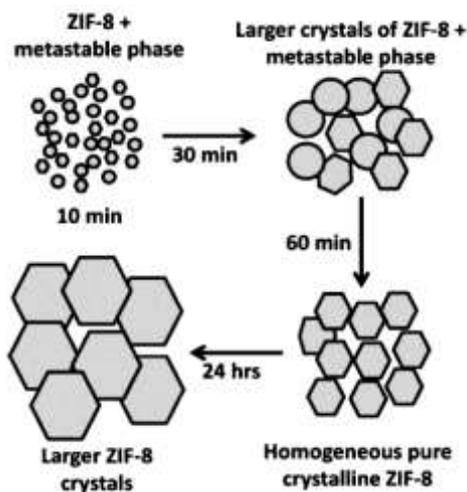


Fig. 6. Crystallization phase of ZIF-8 over time interval [88]. @Copyright (2010) American Chemical Society.

The evolution of ZIF-8 crystals have been proposed by Venna *et al.* [88] in their study. These proposed routes over time intervals were matched with XRD and TEM analyses from their experimental work. From Figure 6, at 10 minutes reaction time, the seed ZIF-8 crystals were formed (~ 50 nm in diameter) in metastable phase. However, upon reaching 30 minutes, the ZIF-8 was believed in aggregate metastable phase changing from smaller to larger crystals. After 60 minutes of equilibrium reaction, a homogeneous crystalline ZIF-8 was formed and larger homogeny ZIF-8 crystals were induced at higher reaction time (24hours). As conclusion from those proposed routes, they found that there were 4 different stages for evolution of ZIF-8 which are (1) nucleation, (2) crystallization, (3) growth and (4) equilibrium. The transformation of these crystals was from semi crystalline (nucleation) to fully crystalline structure at equilibrium phases. The formation of ZIF-8 crystals with sodalite framework morphology was first induced by liquid phase diffusion methods of Zn^{2+} ions and bridging ligands (Hmim) precursors to form a $Zn(Hmim)_4$ tetrahedral in cubic crystal form [89]. The repetition growth of sodalite cage (6-rings) will end up with complete ZIF-8 crystals with internal diameter of 11.6Å as depicted in Figure 7. Detailed mechanism for ZIF-8 crystal formation can be found in Yan [89].

9. ZIF-8 proton conductor and methanol barrier

The actual structure of ZIF-8 causes it to act as super hydrophobic framework which resists the water uptake. Somehow, when the average size of these crystals is decreased, the water uptake is likewise to increase by two times, proposing that the outer surface does involve in water sorption [68]. Thus, it indicates that these ZIF-8 crystals indeed can cause proton conduction to occur with the addition of higher surface areas. Furthermore, it is indicated that some of the water may be trapped by the cage of ZIF-8 crystal [28] which ultimately increased the potential for proton to transport through ZIF-8. The ZIF-8 with -N-H from terminating imidazole linker may donate proton via interaction with water, hence increasing the proton pathway for conduction [28]. In addition, methanol permeation is crucial for DMFC application, thus, a small aperture size of zeolitic imidazolate framework 8 (ZIF-8) which is ~3.4Å can give a tortuous pathway for methanol (kinetic diameter ~ 3.8Å) (see Figure 7) to passing through the pores and eventually will decrease the methanol permeation. Table 5 tabulated some of ZIF-8/polymer composite membrane that have been studied for DMFC applications.

From Table 5, the value of proton conductivity and methanol permeability for all ZIF-8/polymer composite membranes were exceeding the theoretical value which are $5 \times 10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}$ and $< 10^{-6} \text{ moles min}^{-1} \text{ cm}^{-2}$ for both proton conductivity and methanol permeability, respectively. It worth to note that, the -N-H units from terminating imidazole linker is the main contribution for proton conduction process in composite membrane. These linkers can act as both proton donors and acceptors by sharing protons in between N-H linkers and through non-coordinated N atom respectively [27]. Nevertheless, the cage of ZIF-8 was believed has potential to trap the water

molecules which lead to higher and faster proton conduction even at high operating temperature [28].

The hydrophobic nature of ZIF-8 may tighter the hydrophobic backbone domain of polymer chain and simultaneously constructed the new hydrophobic domains on parent polymer matrix. These hydrophobic domains make more tortuous pathway for methanol to passing through and eventually reduce the methanol permeability [27, 28, 34]. Been said earlier, the contribution of small aperture size of ZIF-8 has suppressed the methanol permeation yet allowing more protons to diffuse.

For instance, Yang *et al.* [28] in their study has found that at first degree, the methanol transports through ZIF-8@GO/Nafion composite membrane looked smooth due to the low larger separation between hydrophilic and hydrophobic regions. However, at point when encounter ZIF-8, the methanol molecules seemly bouncing to original place due to narrower interconnected channel between ZIF-8 particles as well as rejection of methanol molecules by smaller pore size of porous ZIF-8. Even though the inclusion of ZIF-8 seem to have a little effect on proton transportation (kinetic diameter of water 2.6 ~ 3.2Å), yet these crystals can hold/trap water molecules in its cages which eventually leading to higher proton conduction. In addition, the narrower separation of hydrophobic and hydrophilic regions gives merits to protons for faster and easier transportation.

10. Techniques preparing ZIF-8 based membrane

As previously mentioned, the electrolyte used in DMFC system was made up from solid state which is in membrane form. Thus, in order to comply with this requirement, ZIF-8 need to be presented in membrane form. Some modification or strategy need to be adhered for ZIF-8 membrane formation. ZIF-8 membrane fabrications can be divided into two synthesis routes which are in-situ growth and seeded secondary growth [71, 78, 81]. For seeding growth secondary growth, or also known as stepwise layer by layer deposition [53] can be divided into other sub-synthesized [81, 86] route as depicted in Figure 8.

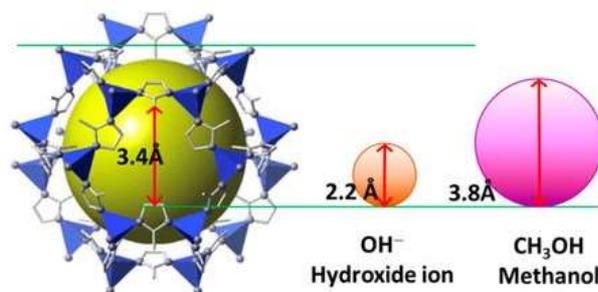


Fig. 7. Comparative of kinetic diameter of ZIF-8, hydroxide ion and methanol molecules. The yellow sphere indicates the internal diameter (11.6Å) [90] @ Copyright Polymers.

Table 5
ZIF-8/polymer composite membrane for DMFC application.

ZIF-8/ Polymer	Abbreviation	Proton Conductivity (Scm^{-1})	Methanol Permeability (cm^2/s)	Author/s
Zeolitic Imidazolate Framework-8 @ Graphene	ZIF-8@ GO/Nafion	0.28	6.82×10^{-8}	[28]
Zeolitic Imidazolate Framework-8/ Deoxyribonucleic Acid	ZIF-8@ DNA	17×10^{-3}	1.25×10^{-8}	[34]
Zeolitic Imidazolate Framework-8/ Sulfonated Poly (ether ether ketone)	ZIF-8/ SPEEK	24.1×10^{-3}	1.459×10^{-8}	[91]

*all the measurement being compared with pristine polymer and commercial Nafion, respectively.

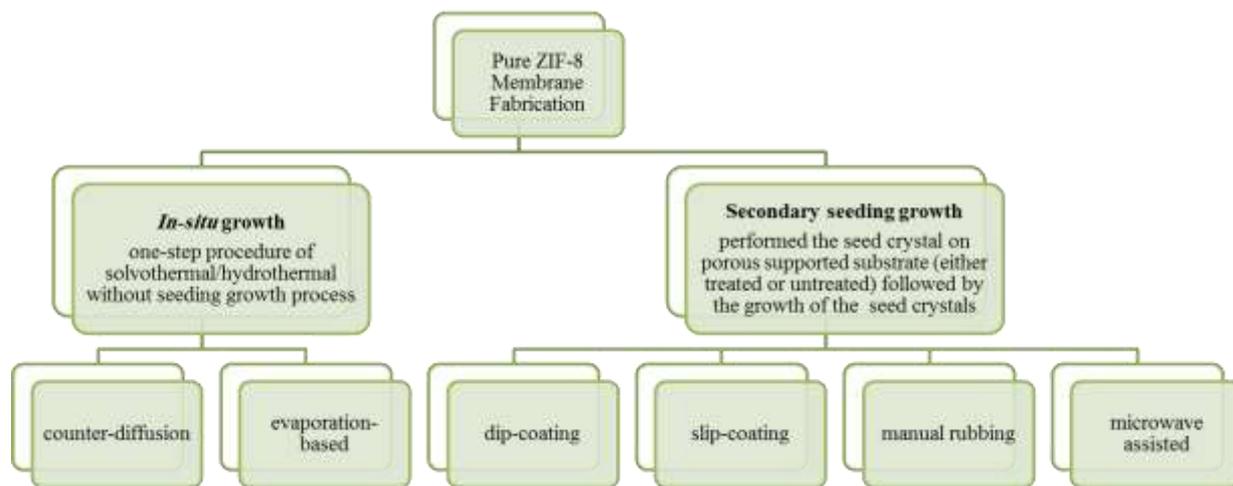


Fig. 8. Synthesis routes for ZIF-8 membrane formation.

Table 6
Few types of support used for ZIF-8 membrane fabrication.

Type of support	Method	Application	Remarks	Author/s
Copper-based foils	Dip-coating	NA	Metallic supports high thermal conductivity and discursivity	[48]
α -alumina	Dip-coating	Water stability testing	Repetition on the method is necessary in order to fabricate a continuous membrane	[78]
α -alumina	Hydrothermal	Separation	-	[80]
α -alumina	Microwave irradiation	Separation	Rapid crystal formation	[81]
Glass/silicon wafer slides	NA	Selective sensor for chemical vapours and gases	-	[93]
Dense substrate			Gold surfaces, silicon wafers, graphite, polymers or sapphire surface functionalization with specific functional groups	[94]
Porous substrate			Alumina or polymeric non-woven materials	[94]

Moreover, Bux and co-worker [92] have been successful fabricated the continuous ZIF-8 membrane solvothermal method (in-situ synthesis route) by using aqueous methanol. It worth to note that, since the ZIF-8 crystals was in the powder form, thus it required a support to make it able functioning as membrane. Table 6 summarize few of the supports for ZIF-8 membrane fabrication.

Stassen *et al.* [82] had demonstrated the synthesis process of ZIF-8 films through solvent-free transformation strategy method (see Figure 9). A 3-step procedure was outlined as depicted below, whereby the pattern was separately drawn according to three different precursor approaches which were dense, patterned and flat-like precursors.

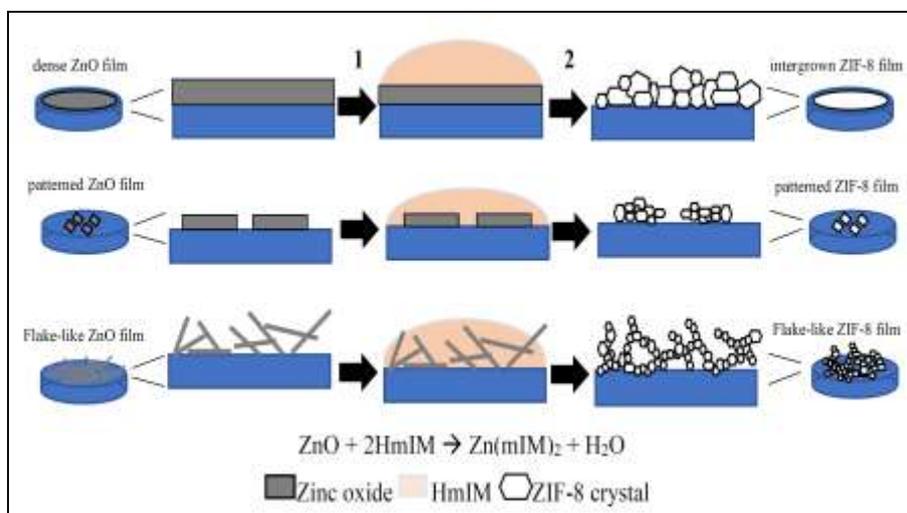


Fig. 9. Process involved in ZIF-8 films formation with different pattern of ZnO precursor [82].

From Figure 9, an intergrown ZIF-8 films was formed by sputtering the ZnO precursor on silicon wafer substrate, therefore the patterned ZIF-8 film was shaped via microcontact printing of ZnO patterns. Whereas, the flake-like ZIF-8 film was designed by electrochemically depositing flake-like ZnO precursor on a carbon steel support. As conclusion, there are many ways to develop a ZIF-8 membrane, but the difference is depended on the purpose of application to these fabricated ZIF-8 membranes. As for electrolyte membrane fabrication, the fabricated ZIF-8 membrane should have possessed the intrinsic properties, required for an excellent electrolyte membrane.

11. Conclusion and outlook

Conclusively, the vital aspect that influenced the performance of fuel cell in terms of proton conductivity and methanol permeability has been methodically reviewed. Large scale commercialization of the designed PEM has not only reducing cost, but also increasing the durability and performance of fuel cell by optimizing the proton conductivity and methanol permeability. Over the past decade, extensive research works have been carried out on designing the PEM especially on structural aspects such as dense, thin membrane, thick, sandwich, layered as well as pore-filling type. The structural ability of ZIF-8 crystals as a super hydrophobic yet allowing the water sorption at low average size of the crystal has made it as one of smart materials used in DMFC system. One step procedure in preparing porous ZIF-8 membrane by contra-diffusion techniques has given merits to this material. Finding the subtle equilibrium between membrane morphology and transport process is the key challenge to achieve a high performance of cell, which depends on several variables such as thickness of ZIF-8 crystals on the membrane's surface, the diameter of the pores, the porosity of the membrane as well as the hydrophilicity of the membrane. In addition, as compared to Nafion, this proposed material could provide a sophisticated fuel cell that is beneficial in term of costing, durability and selectivity. The alteration on porous based membrane is required by the means of introducing a hydrogen-bonding site which is essential for proton-conducting pathways yet blocking methanol crossover. In conjunction to these newly designed materials, the profound problem by commercial Nafion due to fuel crossover and low oxidation value will be solved for Direct Methanol Fuel Cell (DMFC) systems. Furthermore, the availability of the materials in fabrication of this membrane is easily accessible due to its widely used in other researches and importantly, these materials also has a low toxicity which make it easier to handle.

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