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A Review on the Potential of UiO-66-NH₂ Metal-Organic Framework as a Proton Exchange Membrane in Microbial Fuel Cells

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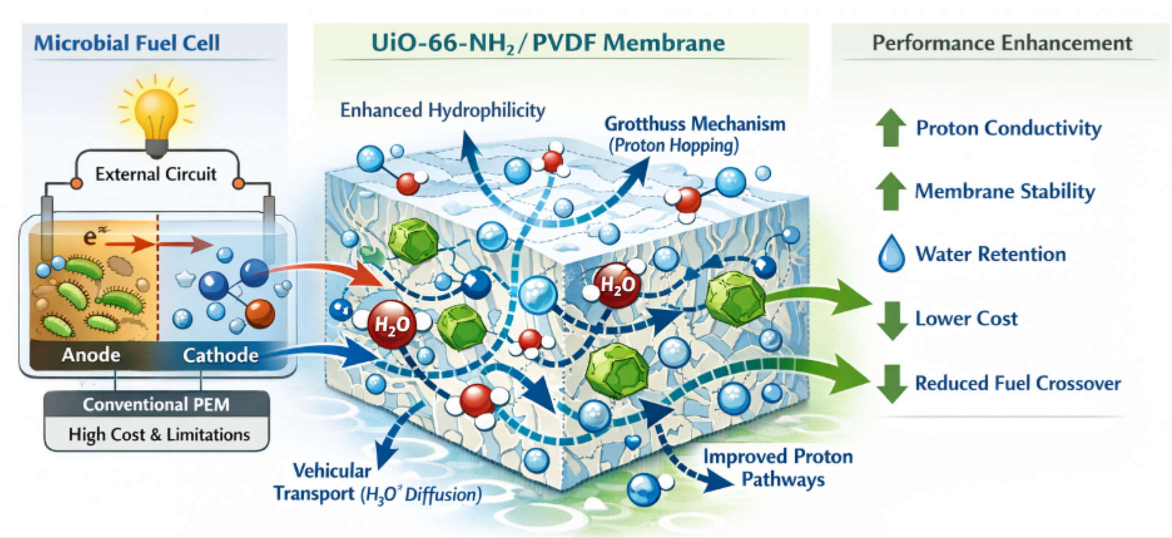
GRAPHICAL ABSTRACT



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ABSTRACT

The growing global demand for energy has intensified efforts to develop sustainable, efficient renewable energy technologies. Microbial fuel cells (MFCs) have emerged as promising bioelectrochemical systems capable of converting chemical energy from organic substrates into electrical energy through microbial metabolism. A key component influencing MFC performance is the proton exchange membrane (PEM), which enables selective proton transport between the anode and cathode while limiting substrate crossover. However, conventional PEM materials such as Nafion are associated with several limitations, including high cost and performance constraints under certain operational conditions. Consequently, recent research has focused on the development of mixed-matrix membranes (MMM), which combine polymer matrices with inorganic fillers to improve membrane performance. Among various candidates, the metal-organic framework UiO-66-NH₂ has attracted considerable attention due to its exceptional chemical stability and the presence of amine (-NH₂) functional groups that enhance hydrophilicity and facilitate proton transport. This review examines the potential of UiO-66-NH_2 as a functional filler in polyvinylidene fluoride (PVDF)-based membranes for PEM applications in MFC systems. Recent studies indicate that incorporating UiO-66-NH_2 into PVDF matrices can improve proton conductivity, membrane stability, and structural integrity. Overall, UiO-66-NH_2/PVDF composite membranes show strong potential as alternative PEM materials for improving the efficiency and sustainability of bioelectrochemical energy systems.

1. INTRODUCTION

The increasing demand for sustainable energy technologies has intensified research into alternative systems capable of simultaneously generating energy and reducing environmental impacts [1-3]. Among these technologies, microbial fuel cells (MFCs) have attracted significant attention as bioelectrochemical systems that convert chemical energy stored in organic substrates into electrical energy through microbial metabolic processes [4]. In addition to electricity generation, MFCs offer the advantage of simultaneously treating organic waste streams, highlighting their potential for integrated energy recovery and wastewater treatment applications [5].

Despite these advantages, the practical performance of MFC systems remains strongly influenced by the efficiency of proton transport between the anode and cathode compartments. The proton exchange membrane (PEM) plays a critical role in this process by facilitating selective proton transport while preventing oxygen diffusion and substrate crossover that can reduce electrochemical efficiency [6]. The most commonly used membrane is Nafion due to its high proton conductivity, good thermal, and chemical stability [7]. However, its high cost, fuel permeability, and performance limitations under certain operating conditions have motivated the development of alternative membrane materials [8].

One promising strategy is the development of mixed-matrix membranes (MMM), which combine polymer matrices with inorganic fillers to improve membrane performance. In such systems, the polymer provides mechanical stability and processability, while the inorganic component can enhance proton conductivity, water retention, and structural stability. Polyvinylidene fluoride (PVDF) is commonly used as a polymer matrix due to its chemical resistance, mechanical strength, and thermal stability [9]. However, the intrinsic hydrophobicity of PVDF limits its proton transport capacity, leading to increased interest in incorporating functional inorganic fillers, such as metal-organic frameworks (MOFs), to improve membrane performance [10].

MOFs are porous coordination polymers composed of metal ions and organic ligands held together by coordination bonds. Their high surface area, tunable pore structures, and functionalizable frameworks make them attractive candidates for various applications, including their use as functional fillers in MMM [11]. Among the wide range of MOF materials, zirconium-based MOF such as UiO-66 and its derivatives have attracted particular interest because of their superior structural stability and tunable functional groups, making them promising candidates for proton conducting membrane application. In particular, UiO-66-NH_2 contains amine functional groups that enhance membrane hydrophilicity and facilitate the formation of hydrogen-bond networks, thereby promoting proton transport within hydrated membrane structures [12]. Previous studies have shown that incorporating UiO-66-NH_2 into PVDF matrices can improve proton conductivity, mechanical stability, and resistance to membrane degradation [5, 11]. These findings suggest that PVDF/UiO-66-NH_2 composite membranes represent a promising alternative to conventional PEM materials for MFC applications.

Nevertheless, several challenges remain unresolved, including the long-term stability of MOF-polymer interfaces, potential particle agglomeration within polymer matrices, and the durability of these composite membranes under real MFC operating conditions. Addressing these challenges requires a deeper understanding of the structure-property relationships of UiO-66-NH_2 and its interaction with polymer matrices.

Based on these considerations, this review focuses on the potential of UiO-66-NH_2 as a function filler for PEM in MFC systems. Compared with many other MOFs, UiO-66-NH_2 possesses exceptional chemical and hydrothermal stability due to its $Zr_6O_4(OH)_4$ cluster framework. In addition, the presence of amine functional groups ($-NH_2$) enhances membrane hydrophilicity and promotes the formation of hydrogen-bond networks that facilitate proton transport. Therefore, understanding the structure-property relationships of UiO-66-NH_2 and its integration into polymer matrices, such as PVDF, is essential for designing high-performance PEMs for MFC applications.

2. METAL-ORGANIC FRAMEWORKS (MOF)

2.1. Structure and Characteristics of Metal-Organic Frameworks (MOF)

Metal-organic frameworks (MOF) have emerged as a versatile class of porous crystalline materials composed of metal nodes connected by organic ligands through coordination bonds (Figure 1) [13]. Their exceptionally high surface area, tunable pore structures, and chemically functionalizable frameworks have made them attractive candidates for a wide range of applications, including gas storage, catalysis, and membrane technologies [14]. In recent years, MOFs have attracted particular attention as inorganic fillers in mixed-matrix membranes (MMMs), where their porous structures and functional groups can facilitate proton transport and enhance membrane stability [13].

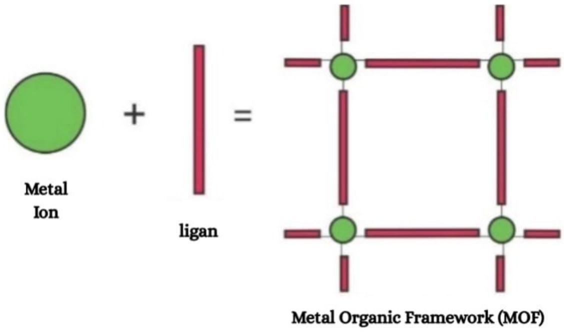

Figure 1. The general process of MOF formation [13].

Compared with conventional porous materials such as zeolites and activated carbon, MOFs offer greater structural tunability by selecting different metal centers and organic linkers. This flexibility allows the design of materials with tailored pore environments and functional groups that can enhance ion transport or water retention within membrane structures [15]. However, the practical use of many MOFs in electrochemical systems is limited by their chemical instability in aqueous or acidic environments.

To address this limitation, zirconium-based MOFs have attracted considerable interest due to their superior chemical and thermal stability. Among them, UiO-66 and its derivatives are particularly notable because of their robust $Zr_6O_4(OH)_4$ cluster framework, which forms strong coordination bonds with carboxylate ligands and provides high structural stability under harsh conditions [16]. This stability makes Zr-based MOFs promising candidates for membrane-based electrochemical applications.

Several MOF structures have been investigated as fillers in proton-conducting membranes, including UiO-66, HKUST-1, MIL-101, and ZIF-8 (Figure 2). These materials offer different structural characteristics that influence their performance in mixed-matrix membranes. For instance, HKUST-1 provides open metal sites that can enhance adsorption interactions, while MIL-101 exhibits extremely large surface areas and mesoporous structures ($> 2000\ m^2/g$) [15,16]. ZIF-8 offers high chemical stability and uniform pore sizes, making it suitable for molecular separation [17]. Nevertheless, among these materials, UiO-66 has attracted particular interest for membrane applications due to its superior hydrothermal stability [6].

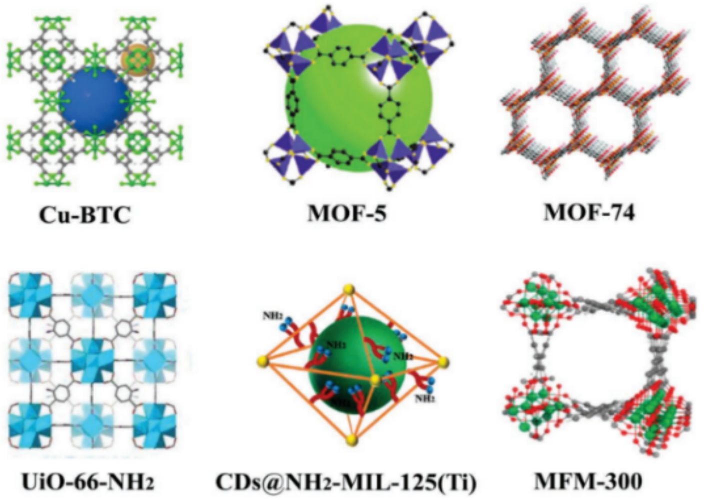

Figure 2. Various types of MOFs [15].

Functionalized derivatives such as UiO-66-NH_2 further expand the potential of MOF-based membranes. The presence of amine groups increases the hydrophilicity of the material and promotes hydrogen-bond interactions with water molecules, which can facilitate proton transport through hydrated networks within the membrane structure [6]. Previous studies have shown that incorporating UiO-66-NH_2 into polymer matrices can improve proton conductivity, water retention capacity, and membrane durability, highlighting its potential as a functional filler for proton exchange membranes in microbial fuel cell systems.

2.2. Synthesis Methods for Metal-Organic Frameworks (MOF)

Various synthesis strategies have been developed for the preparation of metal-organic frameworks (MOF), including solvothermal, hydrothermal, microwave-assisted, mechanochemical, and electrochemical methods [18,19]. These approaches enable control over key structural parameters such as crystallinity, particle size, and morphology, which strongly influence the performance of MOF materials in practical applications.

Among these techniques, solvothermal synthesis is the most widely applied method for producing highly crystalline MOF structures. In this method, metal precursors and organic ligands are typically dissolved in organic solvents such as dimethylformamide (DMF) and heated in sealed reactors at elevated temperatures, promoting the formation of ordered coordination frameworks (Figure 3) [20,21]. This approach has been widely used to synthesize zirconium-based MOFs, including UiO-66 and its derivatives, which are commonly investigated for membrane applications due to their high structural stability.

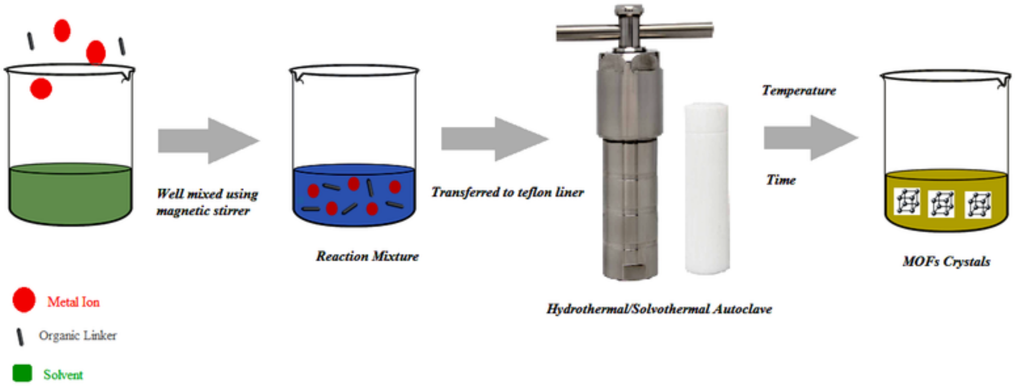

Figure 3. Schematic of the solvothermal method in MOF synthesis [21].

Alternative synthesis methods have also been explored to improve synthesis efficiency or environmental sustainability. Hydrothermal synthesis uses water as the reaction medium and is considered a more environmentally friendly approach, although it may produce less uniform crystal structures in some cases [22,23]. Microwave-assisted synthesis can significantly reduce synthesis time by providing rapid and homogeneous heating of the reaction mixture.

Mechanochemical synthesis, which involves solvent-free grinding of metal precursors and organic ligands, has attracted attention as a green synthesis strategy due to its reduced solvent consumption. Electrochemical synthesis has also been reported as an alternative method in which metal ions are generated by anodic dissolution of a metal electrode in the presence of organic ligands, enabling MOF formation directly on conductive substrates [24]. This method enables controlled growth of MOF films and is particularly attractive for electrochemical devices such as sensors or catalytic electrodes (Figure 4).

However, for the production of bulk MOF particles for mixed-matrix membrane fabrication, solvothermal synthesis remains the most commonly used method due to its ability to yield highly stable, well-defined crystalline structures. Overall, the choice of synthesis method can significantly influence the structural properties of MOF, including particle size, crystallinity, and surface functionality, which ultimately affect their dispersion within polymer matrices and their performance as fillers in mixed-matrix membranes.

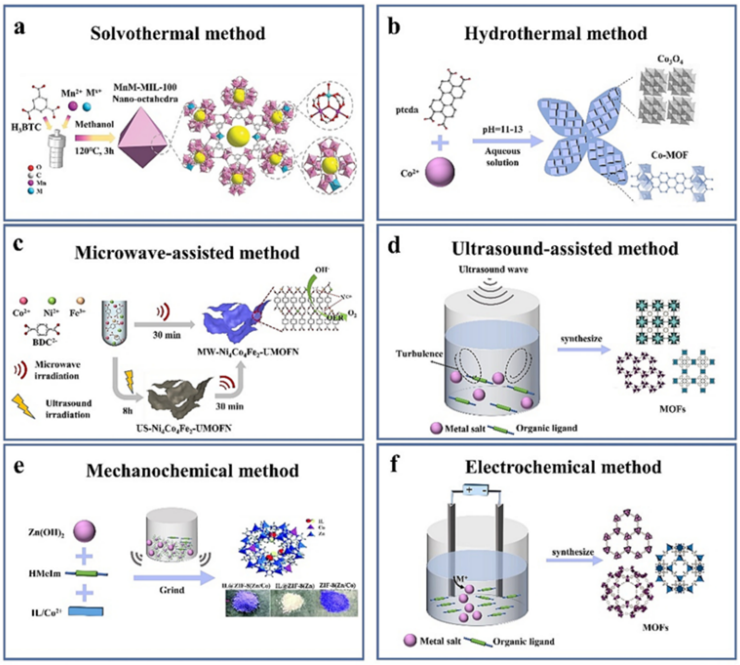

Figure 4. MOF synthesis methods [24].

3. MOF UiO-66-NH₂

UiO-66-NH_2 (University of Oslo-66-NH_2) is one of the most stable types of MOF. The structure of this material consists of $Zr_6(OH)_4O_4$ groups connected to 2-aminoterephthalate ligands ($H_2BDC-NH_2$), also known as 2-Aminobenzene-1,4-dicarboxylic acid, forming a strong three-dimensional structure (Figure 5) [25]. Compared to other MOFs, such as HKUST-1, which is easily degraded by moisture, or ZIF-8, which tends to be fragile in acidic conditions, UiO-66-NH_2 is much more stable in aqueous environments and under extreme conditions with peat-water substrates. This is the reason UiO-66-NH_2 MOF is used in renewable energy applications, including bioelectrochemical systems.

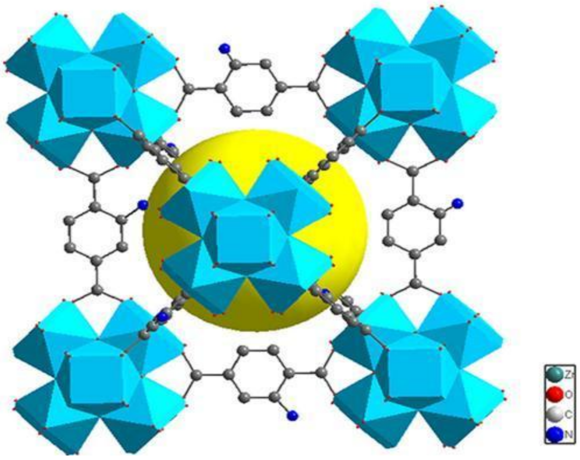

Figure 5. Structure of UiO-66-NH_2 [25].

The synthesis of UiO-66-NH_2 is typically carried out by solvothermal reaction of the $ZrCl_4$ precursor with 2-aminoterephthalate ligands in organic solvents such as dimethylformamide (DMF) at high temperatures (Figure 6). In addition to the solvothermal method, other methods, such as hydrothermal, mechanochemical, microwave-assisted, sonochemical, and post-synthetic modification, can be used to enhance the functionality of the amine group within the MOF framework (Figure 7) [26]. These variations in synthesis method allow the production of UiO-66-NH_2 crystals with different sizes, morphologies, and surface areas, tailored to application requirements.

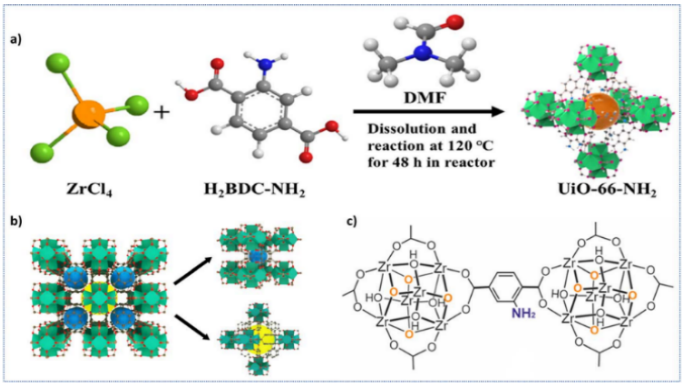

Figure 6. Synthesis scheme of UiO-66-NH_2 [26].

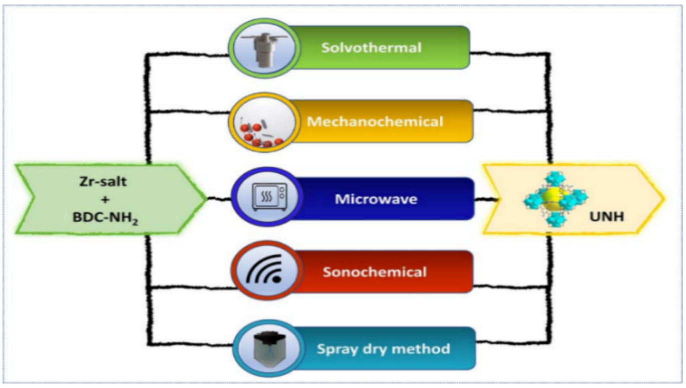

Figure 7. Synthesis method of UiO-66-NH_2 [26].

One of the distinctive properties of UiO-66-NH_2 is the presence of amino groups, namely (-NH_2) groups, on its ligands. These groups make the structure more hydrophilic, enabling it to form hydrogen bonds with water molecules. This hydrogen-bonding pathway is important because it serves as an additional proton transport channel absent in MOFs lacking polar functional groups [27]. This distinguishes UiO-66-NH_2 from other MOFs such as MIL-101 or ZIF-8, which tend to be more hydrophobic. In addition, the amine group also acts as a chemically active site that can be further modified to enhance interactions with polymers or ions in membrane systems [11]. Characterization of UiO-66-NH_2 was performed using various techniques. XRD showed a typical cubic crystal pattern with main reflections consistent with the UiO-66 structure. FTIR was used to identify the vibrations of the -NH_2, C=O, and Zr-O groups, indicating the successful formation of the coordination framework. Meanwhile, BET analysis showed that UiO-66-NH_2 has a very large specific surface area, typically above 1000 m^2/g, enabling high water adsorption capacity. TGA showed that this material is stable up to temperatures above 500°C, indicating excellent thermal stability [25].

In membranes, UiO-66-NH_2 has proven to be an effective filler. The addition of these particles to polymers such as PVDF, SPEEK, or Nafion can increase proton conductivity, water retention, and membrane selectivity towards H^+ ions. This is due to the combination of high porosity and additional proton pathways from the -NH_2 groups that support the polymer matrix [6]. Previous studies have reported that PVDF/UiO-66-NH_2 composite membranes exhibit improved mechanical stability and structural durability compared with pristine PVDF membranes [7]. These findings are primarily based on membrane characterization results, including morphology, mechanical strength, and proton conductivity. Although these properties are important for MFC operation, not all studies report direct electrochemical performance metrics of MFCs. Therefore, the reported improvements should be interpreted primarily as enhancements in membrane properties that may contribute to improved MFC performance.

However, despite the excellent chemical and hydrothermal stability of UiO-66-NH_2 reported in numerous studies, its performance under real microbial fuel cell (MFC) operating conditions may still face several practical limitations. In operational MFC environments, membranes are continuously exposed to microbial communities, fluctuating pH conditions, and prolonged immersion in aqueous electrolytes, all of which may compromise membrane durability and proton transport efficiency. Biofilm formation on membrane surfaces can increase mass transfer resistance and hinder proton migration, thereby reducing the overall efficiency of MFC systems [28]. Moreover, pH fluctuations and long-term exposure to electrolyte solutions may weaken the structural integrity of MOF-polymer interfaces, potentially leading to gradual degradation of composite membranes during extended operation [23]. These factors indicate that, although UiO-66-NH_2-based membranes demonstrate promising properties at the laboratory scale, systematic investigations of their long-term stability and durability under realistic MFC conditions remain necessary.

4. MICROBIAL FUEL CELL (MFC)

Microbial fuel cells (MFCs) are bioelectrochemical systems that convert organic substrates into electricity through microbial metabolism. In these systems, electrogenic microorganisms oxidize organic compounds at the anode and transfer electrons to an external circuit, enabling simultaneous electricity generation and wastewater treatment [4]. MFC technology has various models that have been developed, as shown in Figure 8.

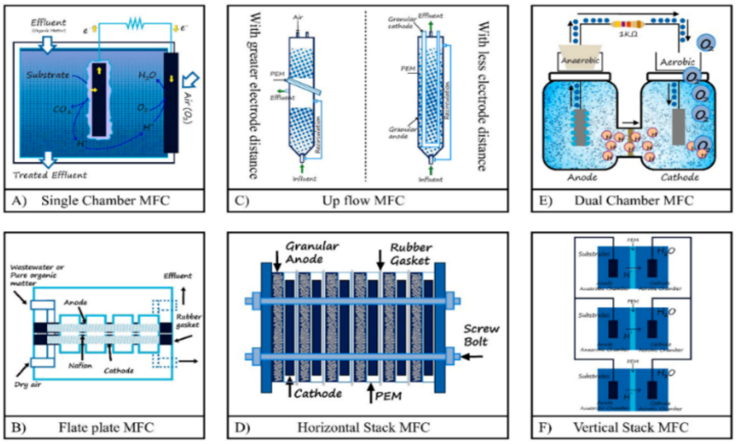

Figure 8. Models of Microbial Fuel Cells (MFC) [4].

In general, an MFC consists of three main parts, namely an anode, a cathode, and a proton exchange membrane (PEM). In the anode chamber, microorganisms degrade organic substrates under anaerobic conditions, thereby forming electrons and protons. Electrons flow to the cathode through an external circuit, while protons pass through the membrane. At the cathode, protons react with oxygen and electrons to produce water, while the flow of electrons in the external circuit generates an electric current [29]. The membrane plays an important role in this process, functioning as a separator between the anode and cathode chambers and as a proton transport pathway. If the membrane does not function properly, oxygen leakage or substrate diffusion toward the anode can occur, reducing the MFC's efficiency. Therefore, membrane performance is a key factor in improving MFC performance [5].

The advantage of MFC is that the substrate used can be simple compounds such as acetate, glucose, ethanol, and methanol, as well as complex substrates such as peat water, which is rich in humic and fulvic compounds [30]. This opens up great opportunities for utilizing local resources as bioelectrochemical fuels [5]. The working scheme of MFC is shown in Figure 9 [28].

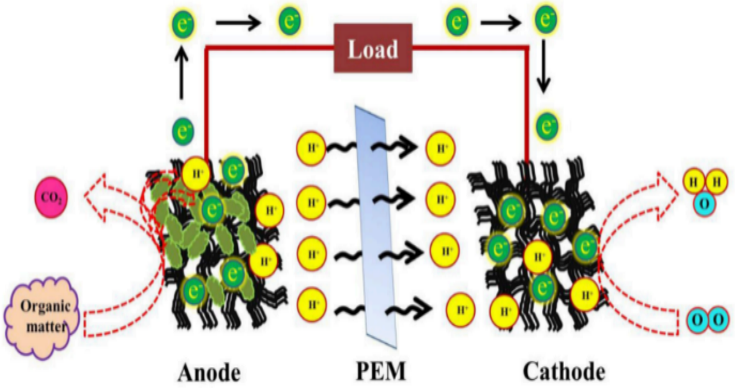

Figure 9. MFC working scheme [28].

5. MIXED-MATRIX MEMBRANE (MMM) AS PROTON EXCHANGE MEMBRANE

The proton exchange membrane (PEM) is a key component of the MFC system. Its main function is to transport H^+ ions from the anode chamber to the cathode while preventing the back diffusion of oxygen and substrates. PEM maintains anaerobic conditions at the anode and supports the oxygen reduction reaction at the cathode. This makes the membrane highly influential on the stability and efficiency of MFC operation [5]. Nafion is widely used as a standard PEM membrane due to its high proton conductivity and good chemical stability. However, its use faces several challenges, including high cost, relatively high fuel permeability, and long-term performance degradation [9]. These limitations have driven the development of more economical and stable alternatives, one of which is the Mixed-Matrix Membrane (MMM) concept (Figure 10). Conventional Nafion membranes typically exhibit proton conductivity values in the range of approximately 0.05-0.10 cm^{-1} under fully hydrated conditions.

In contrast, MOF-based mixed matrix membranes usually demonstrate conductivity in the range of 10^{-3}-10^{-2} $S.cm^{-1}$ depending on the type of polymer matrix, MOF loading, and operational humidity. For example, SPEEK/UiO-66 composite membranes have been reported to exhibit proton conductivity of approximately 0.085 $S.cm^{-1}$ at elevated temperatures, significantly higher than pure SPEEK membranes [31]. Although the conductivity of MOF-based membranes may still be slightly lower than that of Nafion, they offer several advantages, including lower cost, tunable pore structures, improved thermal stability, and enhanced resistance to chemical degradation, making them promising alternatives for sustainable MFC applications.

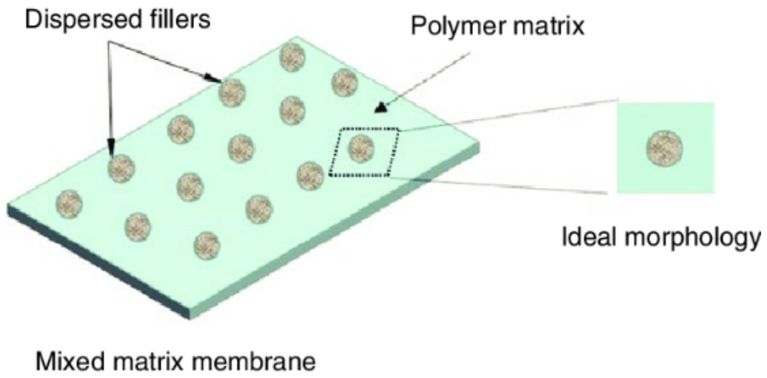

Figure 10. Schematic of Mixed-Matrix Membrane (MMM) [32].

MMM is a composite membrane that combines a polymer matrix with inorganic filler materials [32]. Previous studies have shown that applying MMM can significantly improve membrane performance. For For example, research by [9] reported that adding UiO-66 to the Nafion matrix improved proton conductivity while reducing methanol permeability, resulting in better performance than pure Nafion (Figure 11) [9]. Similar results were also reported by [8] for SPEEK/UiO-66, in which the hydrophilic properties of the sulfonate group in SPEEK were combined with MOF pores to create a more ordered proton transport pathway [8]. Another study by by Ashtiani et al. (2021) on UiO-66-NH_2/PEI showed that amine groups (-NH_2) can strengthen hydrogen bonds with water molecules, thereby increasing proton conductivity and improving ion selectivity [33]. Previous research indicates that combining polymers with inorganic fillers via the MMM approach can overcome the limitations of single membranes, particularly in terms of stability, mechanical strength, and ion transport efficiency. While many studies emphasize improvements in proton conductivity in MMM, membrane selectivity remains a critical parameter that must be considered for efficient MFC operation.

Although the incorporation of MOF fillers into polymer matrices has been widely reported to enhance proton conductivity in mixed-matrix membranes (MMM), membrane selectivity remains a critical factor for efficient microbial fuel cell (MFC) operation. The highly porous structure of MOF can create additional proton transport pathways and improve membrane hydration. However, excessive porosity or poor polymer-MOF interfacial compatibility may introduce non-selective transport channels. Such defects can facilitate undesired mass transfer, including substrate diffusion and oxygen crossover between the anode and cathode compartments, which may reduce coulombic efficiency and overall MFC performance. Recent studies on MOF-based MMM have highlighted this conductivity-selectivity trade-off, emphasizing the need to balance enhanced proton transport with adequate membrane selectivity and structural stability [34]. Consequently, controlling MOF loading, improving filler dispersion, and optimizing membrane microstructure are essential strategies for achieving high proton conductivity without compromising membrane selectivity in MMM systems.

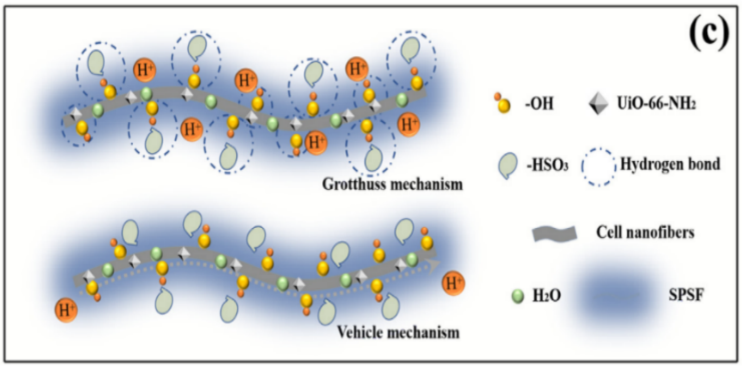

Figure 11. Proton transfer pathway in the UiO-66-NH_2 membrane [9].

Beyond structural factors, the interfacial compatibility between UiO-66-NH_2 fillers and polymer matrices is crucial for determining the performance of mixed-matrix membranes. Poor compatibility at the polymer-filler interface may lead to the formation of interfacial voids or defects that create non-selective transport pathways [35]. Another important challenge is particle agglomeration, which may occur when MOF loading exceeds the dispersion capacity of the polymer matrix. Aggregation of filler particles during membrane formation can disrupt membrane morphology and reduce the effective surface area of MOF particles, ultimately affecting separation performance [36,37]. Therefore, optimizing filler loading is essential to balance the benefits of enhanced proton conductivity with the risk of structural defects. Previous studies have shown that the relationship between proton conductivity and MOF filler loading is not linear. Excessive addition of fillers may offset the beneficial effects on transport properties, while internal agglomeration of MOF particles can introduce additional resistance to proton conduction [38]. For example, in Nafion-based systems, moderate MOF loading often produces the best proton conductivity while maintaining membrane mechanical stability [9]. Consequently, improving polymer-MOF interfacial interactions and controlling filler dispersion are key factors in designing high-performance UiO-66-NH_2-based mixed-matrix membranes. Surface modification of MOF fillers has also been widely explored as an effective strategy to minimize particle agglomeration and improve membrane performance [39].

In addition to MOF-based membranes, several alternative proton-conducting materials have been widely explored for microbial fuel cell applications. Sulfonated polymers such as sulfonated poly(ether ether ketone) (SPEEK) and sulfonated polysulfone (SPSF) have attracted considerable attention as non-fluorinated alternatives due to their lower cost compared with Nafion, with studies showing that composite PES/SPEEK membranes can significantly improve proton conductivity during MFC operation [40,41]. SPEEK is a promising material due to its excellent thermal stability, mechanical properties, and tunable proton conductivity, which can be controlled by adjusting the degree of sulfonation to balance conductivity with dimensional and mechanical stability [42]. Inorganic-acid-based membranes, including those incorporating phosphoric acid or heteropolyacids, can provide high proton conductivity under specific conditions but often suffer from acid leaching and long-term stability issues. Phosphoric acid (PA)-doped membranes have demonstrated satisfactory proton conductivity at high temperatures and anhydrous conditions; however, the persistent challenge of PA leaching remains a critical limitation that compromises membrane durability and long-term performance [43]. While the introduction of PA into the membrane improves proton conductivity, it does so at the cost of mechanical strength, and acid leaching, along with chemical and mechanical degradation, represent major obstacles hindering further commercialization [44].

Meanwhile, bio-based membranes derived from materials such as bacterial cellulose or chitosan offer advantages in terms of sustainability and low production cost, although their proton conductivity and chemical durability are generally lower than those of synthetic polymer membranes. Bacterial cellulose (BC) is advantageous due to its renewable nature, low cost, environmental compatibility, and biodegradability; however, its practical applications have been limited by its poor intrinsic proton conductivity and high-water dispersion during fuel cell operation [45]. Similarly, pristine chitosan membranes exhibit low proton conductivity due to the absence of mobile hydrogen ions and exhibit excessive swelling, which negatively impacts their mechanical properties, limiting their performance in fuel cell applications [46]. Despite these advances, each membrane category still presents specific limitations in terms of cost, durability, or proton transport efficiency. Compared with these alternatives, UiO-66-NH_2-based mixed-matrix membranes offer several advantages, including tunable pore structures, structural stability, and the ability to form interconnected ionic nanochannels that facilitate proton transport. UiO-66-NH_2 has been recognized as a highly promising dopant for enhancing proton conductivity owing to its large pore volume and structural tunability, with its -NH_2 functional groups promoting high water-channel connectivity, which is favorable for proton transport [47]. Nevertheless, challenges related to MOF dispersion within polymer matrices, membrane fabrication scalability, and overall material cost still need to be addressed for practical deployment.

Proton transport in UiO-66-NH_2-based membrane generally occurs through a combination of two mechanisms: the vehicular mechanism and the Grotthuss proton hopping mechanism [48]. In the vehicular mechanism, protons are transported by the diffusion of protonated species such as hydronium ions (H_3O^+), which migrate through hydrated membrane channels. Meanwhile, the

Grotthuss mechanism involves proton hopping along a hydrogen-bond network formed by water molecules and functional groups within the membrane. The presence of amine groups (-NH_2) in UiO-66-NH_2 facilitates hydrogen bonding with water molecules, thereby creating efficient pathways for proton hopping [49]. As a result, the incorporation of UiO-66-NH_2 into polymer matrices can enhance proton conductivity by promoting both diffusion-based and hopping-based proton transport.

In addition to this combination, MMM development also uses many other polymers, such as SPEEK, SPSF, PBI, and PVDF, each with its own advantages. SPEEK is known to be hydrophilic due to its sulfonate groups; SPSF has good mechanical properties and solvent resistance; PBI has high thermal stability; and PVDF has strong chemical stability [8]. The inorganic fillers used also vary, ranging from silica and zeolite to graphene oxide and MOFs, which have large surface areas and modifiable pore structures [33]. Recent research shows that MOFs, particularly UiO-66, offer potential due to their regular porous structures and chemical properties that can be modified as needed [33]. Therefore, the use of polymers such as PVDF and MOF-based filler materials, particularly UiO-66-NH_2, is increasingly being researched because the two are considered complementary (Figure 12). A summary of reported UiO-66-NH_2 composite membranes, including polymer matrices, filler loading, fabrication methods, proton conductivity, and MFC performance, is presented in Table 1.

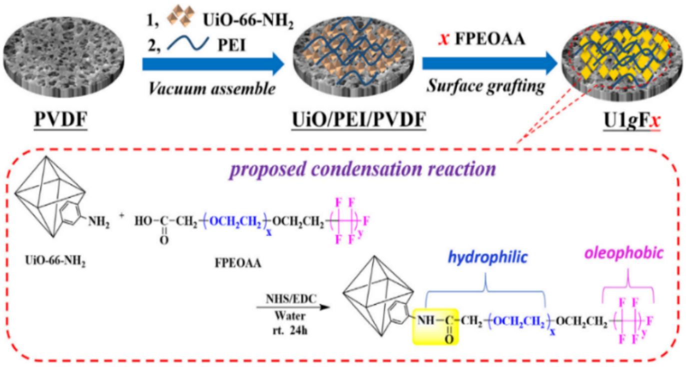

Figure 12. Membrane preparation scheme [6].

TABLE I. Summary of UiO-66-NH_2 composite membranes for MFC applications.

Polymer Type	Filler Loading	Fabrication Method	Proton Conductivity	MFC Performance	Ref
Nafion composite membrane	5-15 wt% UiO-66 / SO_3H-UiO-66	Solution casting	Significant enhancement of proton conductivity due to sulfonated MOF proton pathways	Improved mechanical properties and proton transport	[9]
PVDF composite membran	5 wt% UiO-66	Phase inversion/ solution casting	Increased proton conductivity due to hydrophilic MOF channels	Improved proton conduction and membrane stability	[50]
PVDF nanofiber membrane	In-situ grown UiO-66-based MOF	Electrospinning + in-situ MOF growth	Enhanced proton conductivity and dimensional stability	Reduced ionic resistance and improved membrane transport	[12]
PVDF membran	UiO-66-NH_2 surface layer	Deposition-grafting surface modification	Improved water uptake and ion transport properties	Enhanced membrane stability and	[6]

				separation performance	
Sulfonated polysulfone membrane	UiO-66-NH_2 functionalized CNF	Solution casting	High proton conductivity due to additional proton hopping sites	Improved proton exchange pathway and membrane stability	[8]
Mixed Matrix Membrane	UiO-66- NH_2 dispersed filler	MMM fabrication	Improved ion transport due to well-dispersed MOF structure	Enhanced separation and membrane functionality	[32]

6. PVDF POLYMERS AS MIXED-MATRIX MEMBRANE

In the development of Mixed-Matrix Membranes (MMM), polymers serve as the main matrix in which inorganic fillers, such as MOFs, are dispersed. The main function of polymers is to maintain the mechanical stability of the membrane while supporting proton transport within it [9]. The types of polymers used in MMM vary greatly depending on the application. In general, commonly used polymers include Nafion, Sulfonated Polyether Ether Ketone (SPEEK), Polybenzimidazole (PBI), Polysulfone (PSf), Sulfonated Polysulfone (SPSf), Polyether Sulfone (PES), and Polyvinylidene Fluoride (PVDF) (Figure 13) [6]. Nafion is the most commonly used polymer for proton exchange membrane (PEM) applications because it has high proton conductivity and good electrochemical stability [5]. The structure of Nafion consists of a hydrophobic perfluorocarbon main chain and a hydrophilic side chain containing sulfonate (-SO_3H) groups [32]. The combination of these two properties enables the formation of an efficient proton-conduction pathway. However, Nafion has several drawbacks, such as its high price and decreased performance at high temperatures or low humidity conditions [8]. Therefore, many studies have sought to replace Nafion with other polymers that are more economical yet retain good proton conductivity. One alternative is Sulfonated Polyether Ether Ketone (SPEEK). This polymer is obtained by sulfonating PEEK with sulfonic acid, yielding -SO_3H groups that enhance hydrophilicity and proton conductivity. According to the study by Wang et al. (2021), the addition of UiO-66 to SPEEK produces a membrane with proton conductivity of up to 0.085 S/cm at 80°C, an increase of almost twofold compared to pure SPEEK [51]. In addition, the added MOF also helps maintain the mechanical stability of the membrane at high temperatures.

Another widely used polymer is Polybenzimidazole (PBI). PBI is known to have thermal resistance up to 400°C and excellent stability in acidic or alkaline environments [10]. However, its proton conductivity is low due to its hydrophobic nature. Therefore, modifications are usually made by adding phosphoric acid or fillers such as ZIF-8 and UiO-66 to improve its conductivity [51]. In addition to SPEEK and PBI, Polysulfone (PSf) and Sulfonated Polysulfone (SPSf) are also often used as membrane base materials. PSf is known to have good mechanical strength and solvent resistance, while SPSf has sulfonate groups that increase water absorption and facilitate proton conductivity [52]. Research by Li et al. (2023) shows that adding ZIF-67 to SPSf produces a membrane with a conductivity of 0.074 S/cm and a reduced methanol permeability of up to 50% compared to pure PSf membranes [52]. Polyether sulfone (PES) has also been used in several studies due to its strong mechanical properties and its ability to interact with various inorganic fillers [10]. In addition, natural polymers such as chitosan and cellulose acetate are gaining attention due to their environmental friendliness and biodegradability. In a study by Liu et al. (2022), a chitosan-based membrane modified with MIL-101 MOF was developed, resulting in an increase in proton conductivity to 0.032 S/cm [10].

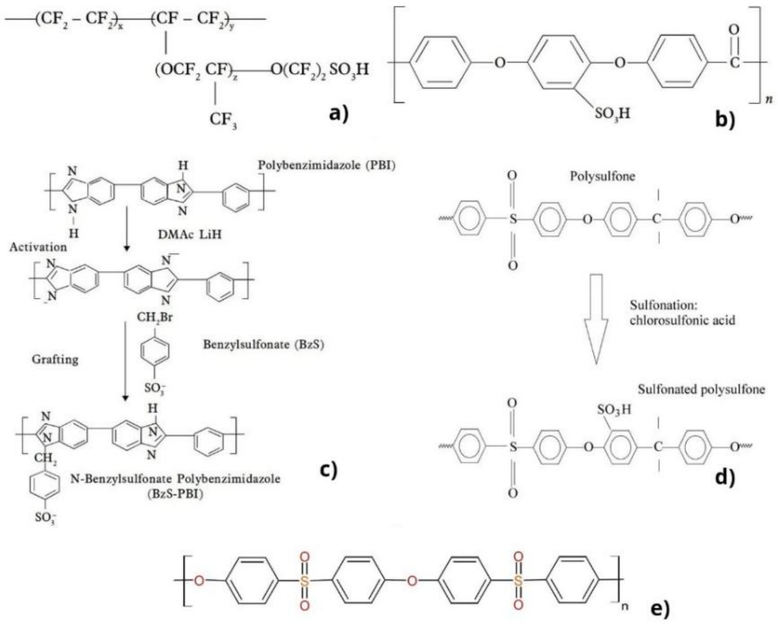

Figure 13. Structure of various polymers: a) Nafion [52], b) SPEEK [52], c) PBI [52], d) Psf and SPsf [52], and e) PES [10].

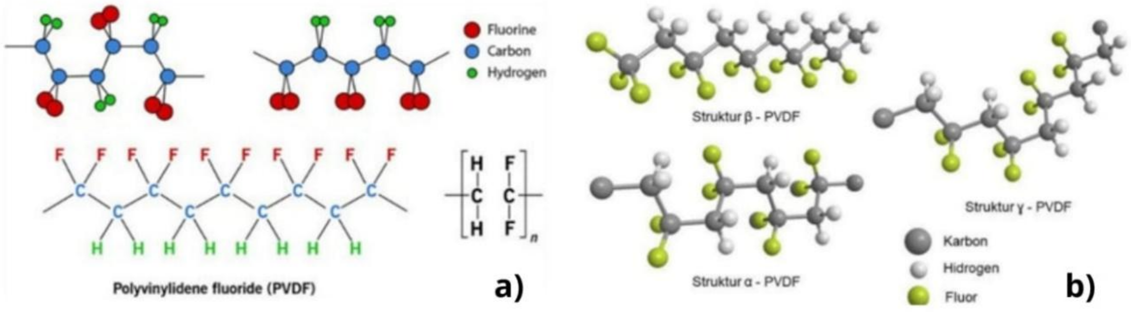

Figure 14. a). Structure of PVDF polymer, b). Structure of PVDF polymorph [53].

Among these polymer types, PVDF (Polyvinylidene Fluoride) is among the most attractive for the development of composite membranes, especially in Microbial Fuel Cell (MFC) applications. PVDF is a semi-crystalline polymer with stable chemical properties, resistance to organic solvents, and high mechanical strength [50]. The PVDF structure consists of -CH_2-CF_2- units that can form α (non-polar) and β (polar) crystal phases, where the β phase is important in conductivity because its dipole orientation supports proton movement [54]. The advantage of PVDF over other polymers is its ability to interact with various types of inorganic fillers without reducing its mechanical stability (Figure 14) [50]. Despite these advantages, PVDF also has several limitations when used as a proton exchange membrane matrix. The intrinsic hydrophobicity of PVDF can limit water uptake, a critical factor for efficient proton conduction in hydrated membranes.

Furthermore, differences in surface chemistry between hydrophobic PVDF chains and inorganic fillers, such as MOF, may lead to interfacial incompatibility issues, including particle agglomeration or the formation of non-selective voids within the membrane structure [55]. These interfacial defects may reduce membrane selectivity and mechanical stability. To overcome these challenges, strategies such as MOF surface functionalization, incorporation of hydrophilic additives, and polymer modification have been explored to improve filler dispersion and interfacial interactions in PVDF-based composite membranes.

Research by Shen et al. (2022) reported that the addition of UiO-66-NH_2 to PVDF through the Evaporation Induced Phase Separation (EIPS) method produces a membrane with homogeneous particle distribution, more regular pores, and an increase in proton conductivity up to twice that of pure PVDF [6]. In addition, PVDF is easy to fabricate using phase inversion or casting methods, making it more economical and efficient than Nafion. Although many polymers have been used in the development of MMMs, PVDF is the most promising choice for combination with MOF UiO-66-NH_2 [56]. This combination has been shown to improve proton conductivity and mechanical stability of the membrane. These improvements in membrane properties are considered beneficial for electrochemical systems such as MFCs, although further validation is still needed through direct testing under MFC operating conditions.

7. FABRICATION OF UiO-66-NH_2 MEMBRANES

Membrane fabrication is an important step in determining the morphological properties, porosity, and performance of membranes in separation applications and electrochemical systems. Figure 15 presents the general scheme for phase-separation-based membrane fabrication, in which a polymer is dissolved in a solvent to form a homogeneous solution that subsequently undergoes phase separation. This process results in the formation of a porous membrane structure following solvent removal.

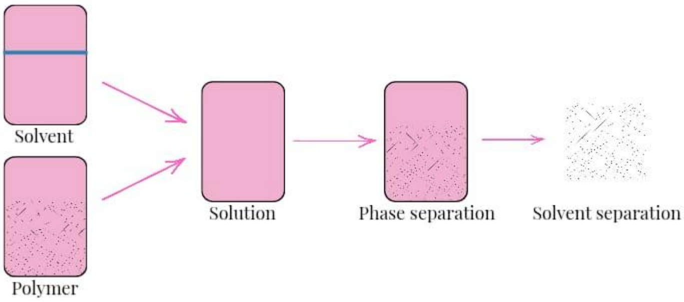

Figure 15. General scheme of phase separation-based fabrication methods.

Various methods have been developed to produce membranes with specific characteristics, such as Evaporation-Induced Phase Separation (EIPS), Non-Solvent-Induced Phase Separation (NIPS), Thermally-Induced Phase Separation (TIPS), and Vapor-Induced Phase Separation (VIPS) (Figure 16). The choice of fabrication method depends heavily on the type of polymer, solution properties, and the membrane's final application.

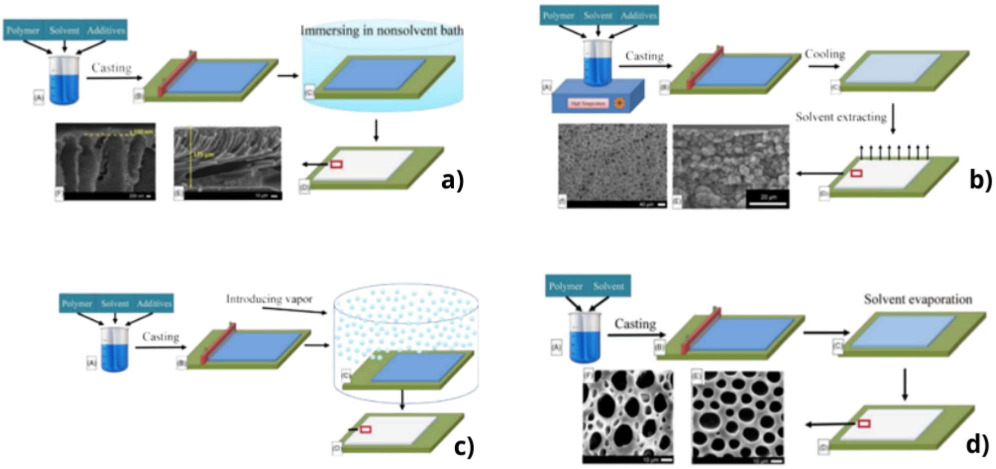

Figure 16. Method types of membrane production: a) NIPS, b) TIPS, c) VIPS, d) EIPS [57].

Membrane fabrication plays a crucial role in determining the morphology, porosity, and proton transport properties of mixed-matrix membranes. Various phase separation techniques have been reported for polymer membrane fabrication, including Non-Solvent Induced Phase Separation (NIPS), Thermally Induced Phase Separation (TIPS), Vapor Induced Phase Separation (VIPS), and Evaporation Induced Phase Separation (EIPS) [58–60]. Among these methods, NIPS and EIPS are most widely used in the fabrication of UiO-66-NH_2-based composite membranes, as they enable the formation of controlled porous structures and facilitate the uniform dispersion of MOF fillers within the polymer matrix. The resulting membrane morphology can significantly influence proton transport pathways and membrane stability in electrochemical systems such as microbial fuel cells. Several studies have reported the advantages of the EIPS method in PVDF-based membranes. For example, morphological modification of PVDF membranes prepared by EIPS has been shown to enhance mass transfer performance [6], while PVDF/UiO-66-NH_2 membranes fabricated using this approach exhibited improved proton conductivity, lower cross-ion resistance, and enhanced mechanical stability [12]. These properties indicate that EIPS-fabricated membranes may offer structural advantages for electrochemical applications. However, further studies involving full MFC performance evaluation are still required to confirm their practical benefits under real operating conditions.

8. CHARACTERIZATION

Characterization techniques play a crucial role in understanding how the structural properties of MOF-based membranes influence proton transport and overall performance in microbial fuel cell (MFC) systems. Key parameters such as crystallinity, pore structure, surface chemistry, and particle dispersion significantly affect proton mobility within the membrane matrix. For example, uniform dispersion of MOF particles in the polymer matrix can create continuous proton conduction pathways, while appropriate pore structures and water uptake capacity facilitate proton transport through hydrated channels. Therefore, characterization methods including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and porosity analysis are commonly used to evaluate the structural integrity and performance of UiO-66-NH_2-based composite membranes for MFC applications.

8.1. XRD

X-ray diffraction (XRD) analysis is widely used to verify the crystalline structure of UiO-66-NH_2 and to evaluate its structural stability after incorporation into polymer matrices [61]. Previous studies have reported characteristic diffraction peaks of UiO-66-NH_2 at 2θ values around 7-9°, corresponding to the formation of the $Zr_6O_4(OH)_4$ framework coordinated with aminoterephthalate ligands (Figure 17) [11]. Figure 18 shows that these peaks remain clearly visible when UiO-66-NH_2 is incorporated into PVDF membranes, although their intensity may slightly decrease due to polymer dispersion effects [7]. The preservation of these characteristic diffraction peaks indicates that the MOF's crystalline structure remains stable within the composite membrane.

Several studies also report that increasing UiO-66-NH_2 loading within PVDF matrices can enhance membrane crystallinity and contribute to the formation of more stable proton transport pathways [6]. These findings suggest that maintaining the structural integrity of MOF particles is an important factor for improving membrane performance.

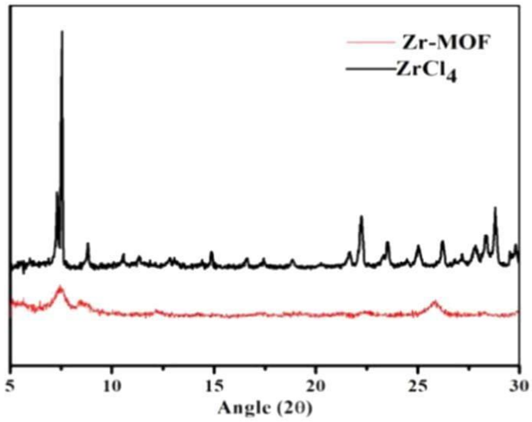

Figure 17. XRD diffractogram of Zr-MOF and $ZrCl_4$ [11].

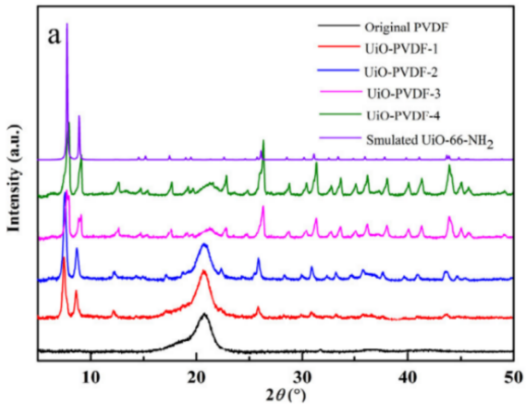

Figure 18. XRD diffractogram of PVDF/UiO-66-NH_2 [7].

8.2. FTIR

Fourier transform infrared (FTIR) spectroscopy is commonly used to investigate the chemical interactions between UiO-66-NH_2 and polymer matrices. The FTIR spectra of UiO-66-NH_2 typically exhibit characteristic absorption bands associated with amine groups (-NH_2) around 3500 cm^{-1}, carbonyl (C=O) vibrations near 1650 cm^{-1}, and Zr-O bonds in the range of 500-700 cm^{-1} (Figure 19) [7]. These peaks confirm the presence of UiO-66-NH_2 within the composite membrane structure. When UiO-66-NH_2 is incorporated into PVDF matrices, shifts in the absorption bands of the -NH_2 and C=O groups are often observed, indicating interactions between the MOF functional groups and the polymer chains (Figure 20) [6,18]. Such interactions can enhance membrane hydrophilicity and promote hydrogen-bond formation with water molecules.

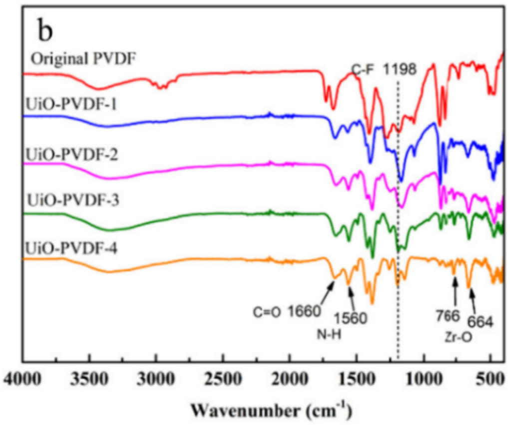

Figure 19. FTIR spectrum of PVDF/UiO-66-NH_2 [7].

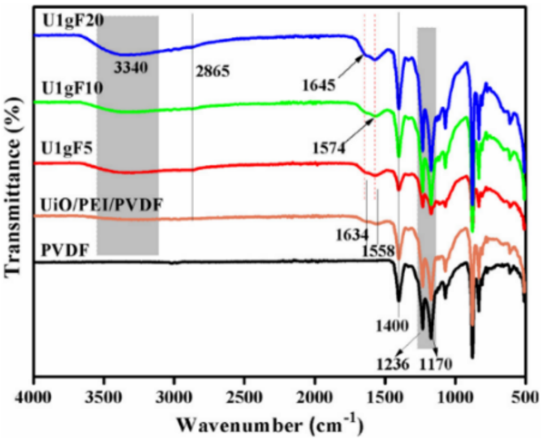

Figure 20. FTIR spectrum of PVDF/UiO-66-NH_2 [6].

Several studies have reported that changes in the intensity of these absorption bands are associated with increased hydrogen-bonding networks within the membrane, which can facilitate proton transport through hydrated channels [6]. These findings suggest that chemical interactions between UiO-66-NH₂ and the polymer matrix play an important role in improving proton conductivity and overall membrane performance in MFC applications.

8.3. SEM

Scanning electron microscopy (SEM) is commonly used to examine the surface morphology and filler dispersion in MOF-based composite membranes. SEM observations provide important insights into the distribution of UiO-66-NH₂ particles within the polymer matrix and the resulting membrane pore structure. Previous studies have reported that UiO-66-NH₂ particles can be relatively well dispersed within PVDF matrices, as shown in Figure 21, although particle agglomeration may occur at higher filler loadings [6]. A homogeneous distribution of MOF particles contributes to the formation of more uniform pore structures, which can facilitate proton transport by shortening the diffusion pathway of H^+ ions within the membrane.

In addition, the membrane fabrication method also influences membrane morphology. For example, phase inversion techniques have been reported to produce elongated pore structures that enhance ion permeability and improve electrochemical performance [11]. Similar observations were reported by Yu et al. (2023), who found that PVDF/UiO-66-NH₂ membranes exhibited finer, more interconnected pore structures after MOF incorporation (Figure 22) [7].

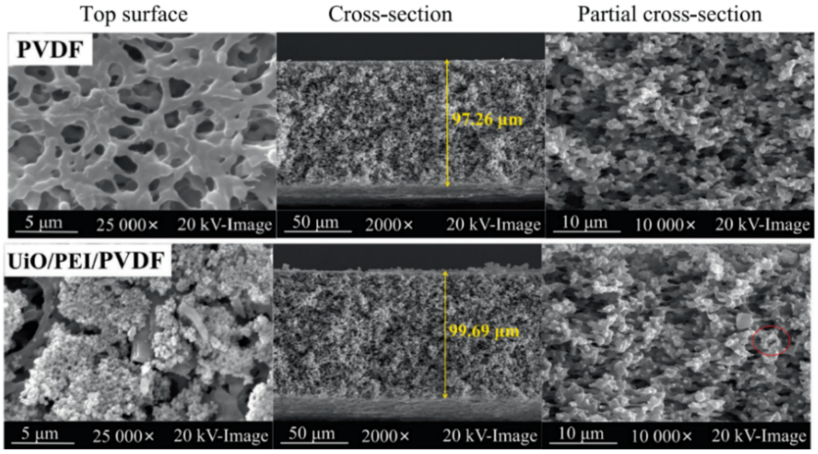

Figure 21. SEM morphology of PVDF/UiO-66-NH₂ [6].

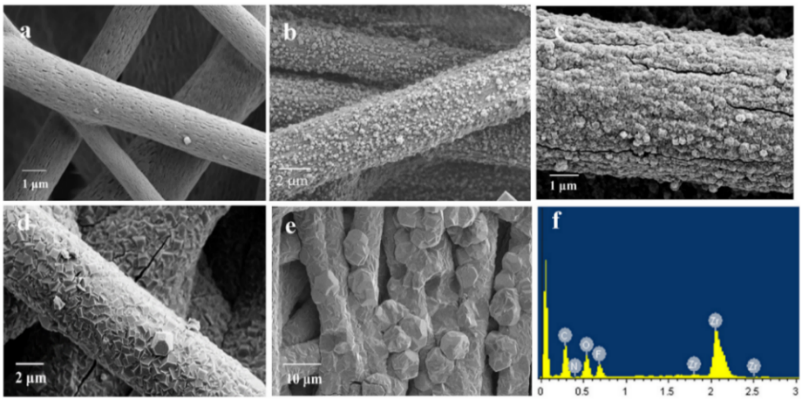

Figure 22. SEM morphology of PVDF/UiO-66-NH₂ [7].

Overall, SEM analysis demonstrates that the dispersion of UiO-66-NH₂ within the polymer matrix plays a crucial role in determining membrane morphology and transport pathways. Improved particle distribution and pore connectivity are, therefore, key factors contributing to enhanced proton conductivity and overall membrane performance in MFC systems.

8.4. Porosity Test and Swelling Test Using the Archimedes Method

Porosity and swelling behavior are important parameters influencing proton transport and water management in proton exchange membranes used in microbial fuel cell (MFC) systems. Membranes with appropriate pore structures can provide interconnected channels that facilitate proton migration while maintaining sufficient mechanical stability.

Membrane porosity is commonly evaluated using the Archimedes method, which estimates pore volume from the difference between the membrane's dry and water-saturated masses. The porosity can be calculated using the following equation:

$$\% \text{ Porosity} = \frac{W_w - W_d}{V\,x\,\rho}\ x\ 100\%$$

Where W_w is the weight of the wet membrane, W_d is the weight of the dry membrane, V is the bulk volume of the membrane, and ρ is the density of water. Porosity is widely recognized as an important factor controlling mass transport in polymer membranes, as a higher pore volume can enhance water permeability and ion mobility within the membrane matrix [62]. Previous studies from Almanassra et al. (2023) have shown that incorporating MOF particles into polymer matrices can significantly increase membrane porosity and hydrophilicity, thereby enhancing permeability and ion-transport properties. The porous structure of MOF provides additional transport pathways and enhances water retention within the membrane, thereby improving membrane performance (Figure 23) [63].

Swelling behavior is another important parameter used to evaluate the dimensional stability of proton exchange membranes. The swelling ratio is typically determined from the weight difference between hydrated and dry membranes, as expressed by:

$$\% \text{ Swelling} = \frac{W_w - W_d}{W_d}\ x\ 100\%$$

Where W_w and W_d represent the weight of the wet and dry membrane, respectively, swelling reflects the ability of the membrane to absorb water, which plays a critical role in forming hydrated proton transport pathways [62]. The higher the swelling value, the greater the membrane's ability to conduct ions, but a value that is too high can reduce its mechanical strength [37]. Studies on MOF-based composite membranes suggest that the structure of the incorporated MOF strongly influences swelling behavior. The report by Zheng et al. (2020) showed that CS/fle-MOF composite membranes exhibited distinct swelling behavior depending on the MOF framework, with MIL-88B-based membranes exhibiting lower swelling but improved structural stability in aqueous environments (Figure 23) [47]. This indicates that controlled swelling can provide sufficient hydration while preserving membrane integrity. Such hydrated environments facilitate the formation of hydrogen-bond networks that support proton transfer through mechanisms such as the Grotthuss pathway [47].

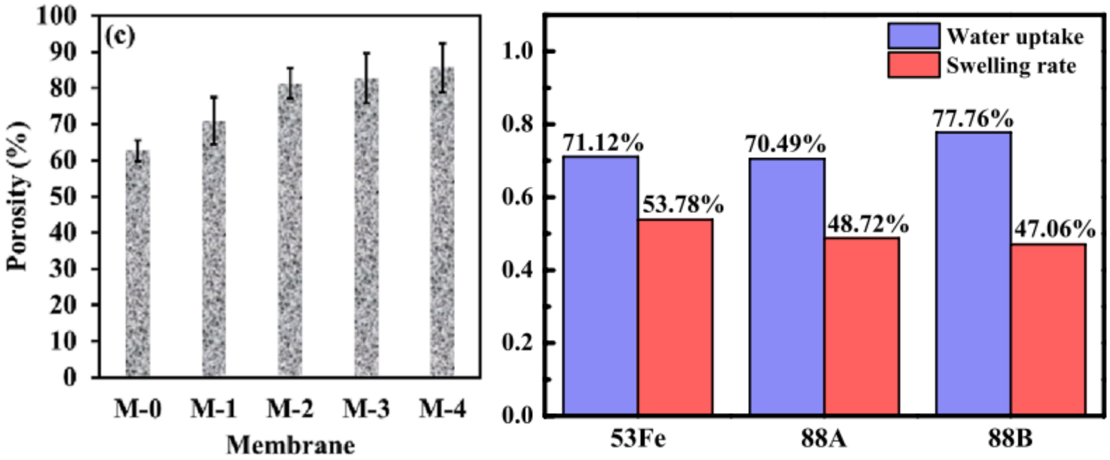

Figure 23. Membrane porosity (left) and swelling rates (right) test graph [45,62].

For PVDF/UiO-66-NH_2 composite membranes, optimizing both porosity and swelling behavior is therefore essential. Adequate porosity can provide efficient proton transport pathways, while controlled swelling ensures sufficient hydration without compromising membrane stability.

Achieving this balance is crucial for improving the electrochemical performance and long-term durability of proton exchange membranes in MFC applications.

9. FUTURE PERSPECTIVES AND CHALLENGES

Despite the promising performance of UiO-66-NH_2-based mixed-matrix membranes, several challenges remain for their practical implementation in microbial fuel cell (MFC) systems. One important issue concerns the scalability of MOF synthesis and the manufacturability of membranes. The synthesis of UiO-66-NH_2 commonly relies on solvothermal processes that require relatively high temperatures, long reaction times, and organic solvents, which may increase production costs when scaled to industrial levels. In addition, achieving uniform dispersion of MOF particles within polymer matrices during large-scale membrane fabrication remains challenging. Poor dispersion or particle agglomeration can generate interfacial defects that create non-selective transport pathways and reduce membrane efficiency. Therefore, the development of cost-effective synthesis routes, scalable fabrication methods, and improved polymer-MOF interfacial compatibility will be essential for translating laboratory-scale materials into practical MFC technologies.

Another important consideration is the long-term operational stability of MOF-based membranes in real MFC environments. In practical systems, membranes are exposed to microbial activity, pH fluctuations, and prolonged immersion in aqueous electrolytes, which may affect membrane durability and proton transport efficiency. Although MOF incorporation can enhance proton conductivity, excessive porosity or poor polymer-MOF compatibility may create non-selective pathways that promote substrate diffusion or oxygen crossover. Therefore, future research should focus on improving membrane durability, optimizing MOF loading and dispersion, and designing membrane structures that balance proton conductivity with selectivity and structural stability.

10. CONCLUSION

Metal-Organic Frameworks (MOFs), particularly UiO-66-NH_2, show promising potential as fillers in proton exchange membranes for microbial fuel cell (MFC) systems due to their porous structures and amino functional groups, which can enhance membrane hydrophilicity, thermal stability, and proton transport pathways. When incorporated into polymer matrices such as PVDF, UiO-66-NH_2 can produce composite membranes with improved proton conductivity, chemical resistance, and mechanical stability compared with conventional polymer membranes. However, several challenges remain, including the long-term stability of membranes under real MFC operating conditions, resistance to biofouling, durability of the MOF-polymer interface, and the scalability of MOF synthesis and membrane fabrication. Therefore, future studies should focus on evaluating long-term membrane performance in real MFC environments and on developing more durable, fouling-resistant composite membrane structures.

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