



Review article

Hydrogel-derived materials for microbial fuel cell



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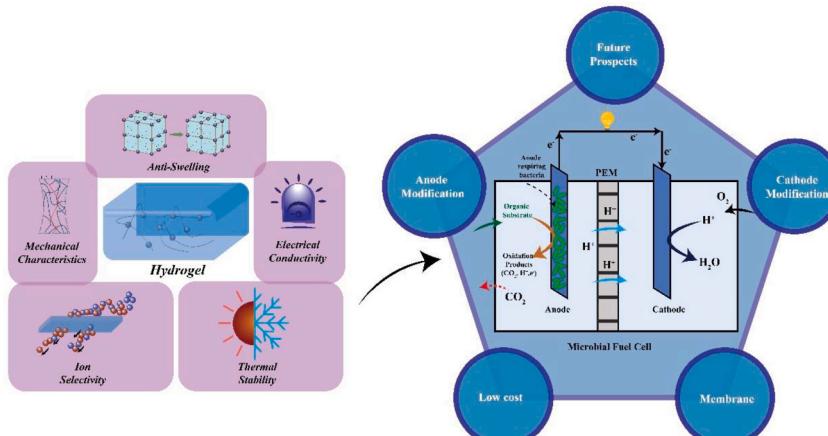
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HIGHLIGHTS

- Hydrogels boost MFC performance by enhancing electrodes, membranes, and microbe stability.
- Biocompatibility and tunable porous properties are ideal for MFC applications.
- Reviewed general concepts and impact of hydrogel as electrode and membrane for MFC.
- Hydrogel has great potential to boost MFC performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cells (MFCs) represent a promising renewable energy source, harnessing the metabolic processes of microorganisms to generate electricity through substrate oxidation. Hydrogels have recently garnered significant attention for their potential to enhance MFC performance and efficiency by addressing critical challenges associated with electrode materials, proton exchange membranes, microbial immobilization, and overall system stability. This review comprehensively explores the latest advancements in hydrogel-based approaches for MFC applications. The article begins with the unique properties of hydrogels related to fuel cells, including their

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biocompatibility, porosity, ionic transport capability, and tunable physicochemical properties, which make them ideal candidates for MFC applications. Moreover, the review discusses diverse methodologies for incorporating hydrogels into MFCs, including electrode modification, microbial consortium immobilization matrices, and separators. Research findings indicate that incorporating conductive elements into hydrogels or fabricating hybrid hydrogel-based anodes has led to notable improvements in electrical conductivity and power density output. However, further research is imperative to enhance power generation efficiency, long-term stability, and scalable preparation for sustainable MFC operation. This review concludes by discussing the challenges and opportunities associated with the use of hydrogels in MFCs.

1. Introduction

The global population surge, urbanization, and industrial growth have intensified the demand for alternative sources of energy rather than fossil fuels and nuclear power [1–4]. Addressing both energy demand and pollution management is critical for a sustainable future. In case of energy demand, microbial fuel cells (MFC) promise to generate green energy from wastewater by utilizing bacteria like *E. coli* and *Geobacter* spp. [3]. MFC is a bioelectrochemical fuel cell designed to produce electric current by directing electrons generated from microbial oxidation on the anode to reduce oxygen on the cathode through an external electrical connection [5,6]. This highlights the urgent need for advancements in green energy technologies and environmental protection efforts.

A typical MFC contains an anodic and a cathodic chamber divided by a proton exchange membrane (PEM) [7,8]. An electrogenic biofilm containing anaerobic bacteria can form on the anode (the negative terminal) and generate electrons and protons by oxidizing substrates, such as organic pollutants [9]. Microbial Fuel Cells (MFCs) offer several advantages, such as wastewater treatment, low carbon emissions, and electricity generation. However, some key issues need to be addressed to ensure the sustainability of MFCs. These include low power generation, poor long-term stability, and challenges related to scaling up the technology [7]. Regarding the efficiencies of MFCs, microbial and electrode, especially anode, interaction, and microbial community play a significant role [10,11].

Using hydrogel as an electrode or membrane in MFCs has great advantages. Hydrogel can be prepared physically or chemically cross-linked, ensuring structural stability during water adsorption [12,13]. Several unique properties, such as swelling, porous structure, biocompatibility, non-toxicity, and self-healing, make them suitable for improving the performance and stability of the MFC [12,14]. The hydrogel's porous structure provides ample space for microbial colonization, while its unique swelling properties maintain a stable internal environment, ensuring the long-term viability of the microbial community [15,16]. Additionally, the hydrogel facilitates the simple flow of waste products and nutrients into and out of the matrix, giving the microorganisms the resources they need to survive [17]. The ability to alter the matrix polymers' functional group can help facilitate electron transport and microbe binding [18]. By exposing bacteria immobilized in hydrogel to acidic assaults, Du et al. [19] established the protective properties of hydrogels. The immobilized bacteria demonstrated outstanding electrocatalytic activity with a rise in current density.

Hydrogels have been modified and tailored for MFC research to enhance anodic biofilm metabolic activity and electron transfer efficiency. Furthermore, hydrogel materials have been employed in the fabrication of anodes, cathodes, separators/membranes, and electrolytes for diverse applications. While hydrogels have been widely utilized in MFCs [20–22], conducting hydrogels and carbon composite-based hydrogels have gained prominence as anode materials due to their ability to augment microbial electrocatalytic activity and facilitate electron transfer [23–25]. For instance, the high electrical conductivity and bio-adhesive qualities of polyaniline (PANI) and polypyrrole (PPy) have made them popular choices for anode modification [24]. Adding titanium dioxide to the PANI-bacterial cellulose composite showed

further improvement in conductivity [26]. Moreover, numerous reports are available on the benefits of integrating carbon-based materials such as carbon nanotubes (CNT), graphite, carbon brushes, and graphene oxide (GO) with various conductive polymers. This integration enhances the conductivity and significantly improves the power density output of MFC [27,28]. These findings show that incorporating various conductive elements into hydrogels or making hybrid hydrogels has improved their conductivity as well as power density output.

Hydrogels have also been used in certain research to enhance oxygen reduction reactions (ORRs) at the MFC cathode. Hydrogel-based cathodes are being explored to enhance ORR efficiency and address the affordable cost and scarcity associated with current catalysts. For example, Yang et al. [29] created the most effective MFC using a nitrogen and iron chitosan gel on an activated carbon substrate by an economically viable approach, which showed high stability (up to 120 h) and power density. Additionally, evaporation impacts power output stability, which is a problem in air cathodes, especially in small MFCs [30]. This is diminished by the hydrophilic nature of hydrogel polymers, which maintain internal pressure while absorbing water. Enhancing ion transport in horizontal air cathodes can improve interface contact in membrane electrode assembly air cathodes and create self-sustaining MFCs [21,31]. Therefore, hydrogel materials have great potential for MFC applications.

Hence, this review focused on several objectives. They are: (i) to provide a fundamental understanding of recent progress in hydrogel-based MFC development; (ii) to discuss the tailororable properties of hydrogel material for MFCs; (iii) to provide details about hydrogel materials and electrodes specifically relevant to MFC; (iv) to discuss practical implications possibilities; and (v) to include discussion related to future studies. Thus, this review will provide a comprehensive examination of each topic, presented section by section. Furthermore, we will delve into the future prospects of hydrogel materials for MFC applications, emphasizing the innovative and rational design potential of hydrogels for sustainable energy solutions. Finally, we will offer our insights on the remaining challenges and areas for further research.

2. Tailorable properties of Hydrogel for fuel cells

2.1. Water uptake and retention

Hydrogels are polymer networks that can absorb and retain large amounts of water due to their three-dimensional and hydrophilic nature [32]. By adjusting the crosslinking density of the hydrogel, we can control its water absorption and retention capabilities, which are crucial for transporting ions within the MFC. However, sometimes hydrogel may experience lower swelling capabilities due to different preparation methods and crosslinking density variation among polymers. Hydrogels for MFCs can be modified for improved performance, with customizable properties such as water retention capacity, proton conductivity, thermal stability, mechanical durability, and catalytic activity (Fig. 1) [33–36]. Furthermore, the overall efficiency of microbial fuel cell processes can be enhanced by using hydrogel coatings on electrodes. These coatings can boost catalytic activity at the electrodes. An important aspect of PEM fuel cells is their ability to transport protons while impeding electron flow. The ion transport capabilities directly relate to

the water uptake and retention capacity. Therefore, a hydrogel with a higher swelling capacity and favorable ion-transport capability can be an ideal material for MFC applications.

Hydrogels can absorb and retain large amounts of water, which increases their porosity and water uptake capacity. Controlling water uptake and porosity through adjustments in crosslinking density and hydrogel thickness is crucial. This can enhance proton transfer rate and ionic conductivity but may lead to membrane swelling and mechanical issues. Balancing proton and oxygen mass transfer coefficients through hydrogel composition and structure optimization is highly required to improve MFC performance, efficiency, and durability.

2.2. Ionic conductivity

Hydrogels with ion-conductive properties can be used as electrolytes in MFCs, facilitating ion transfer between the anode and cathode to enhance electrochemical processes [37]. The ability of a hydrogel to conduct ions is essential for the efficient operation of MFC. Hydrogels can significantly impact the proton mass transfer coefficients, oxygen mass transfer coefficients, and water uptake and porosity in MFCs compared to non-hydrogel-based MFCs. For example, hydrogels can increase proton mass transfer coefficients due to their high water content and ionic conductivity. The proton transfer rate can be enhanced by 1–2 orders of magnitude compared to traditional membranes. Also, hydrogels can reduce oxygen mass transfer coefficients due to their hydrophilic nature and water absorption. This can lead to decreased oxygen diffusion and increased oxygen transfer resistance. Some hydrogels may have lower ion transport capability due to their lower ionic conductivity, which can lead to decreased operational performance. The ionic conductivity of a hydrogel can be adjusted by including ion-conductive groups in the polymer network or by using a salt solution as the solvent for the hydrogel. Research is ongoing to identify potential membrane materials, specifically focusing on hydrogels with strong proton conductivity. Hydrogels play a crucial role in

fuel cell membranes because they form a hybrid polymer gel electrolyte, which manages the interfacial charge transfer kinetics and enhances the stability of the MFC [38]. Hydrogel-based solutions have shown high reversibility and ion diffusivity, which is desired in many MFC applications [39]. Hydrogels provide several benefits, including high water retention, flexibility, and adjustability.

2.3. Mechanical properties

The mechanical properties of a hydrogel, such as its stiffness and strength, are important for its ability to withstand the stresses that can be encountered in a MFC environment. The mechanical properties of a hydrogel can be tailored by varying the crosslinking density of the polymer network or by incorporating reinforcing agents. In this case, using only natural polymers to prepare hydrogels may result in lower mechanical properties and stabilities. Therefore, a combination of different natural and synthetic polymers is utilized to prepare highly mechanically stable hydrogels. Therefore, increasing the membrane's mechanical strength, water retention, and proton conductivity can improve the membrane's overall performance. Also, hydrogel-derived materials can be employed in MFCs as catalyst supports [39]. These materials give the MFC a more effective overall performance by offering a porous and conductive structure for effective catalyst deposition [40].

2.4. Selectivity

The hydrogel should be selective for certain ions in some MFC applications. For example, in a PEM fuel cell, the hydrogel should be selective for protons and should exclude other ions, such as hydroxide ions. The selectivity of a hydrogel can be tailored by incorporating charged groups into the polymer network or by using a charged salt solution as the solvent for the hydrogel.

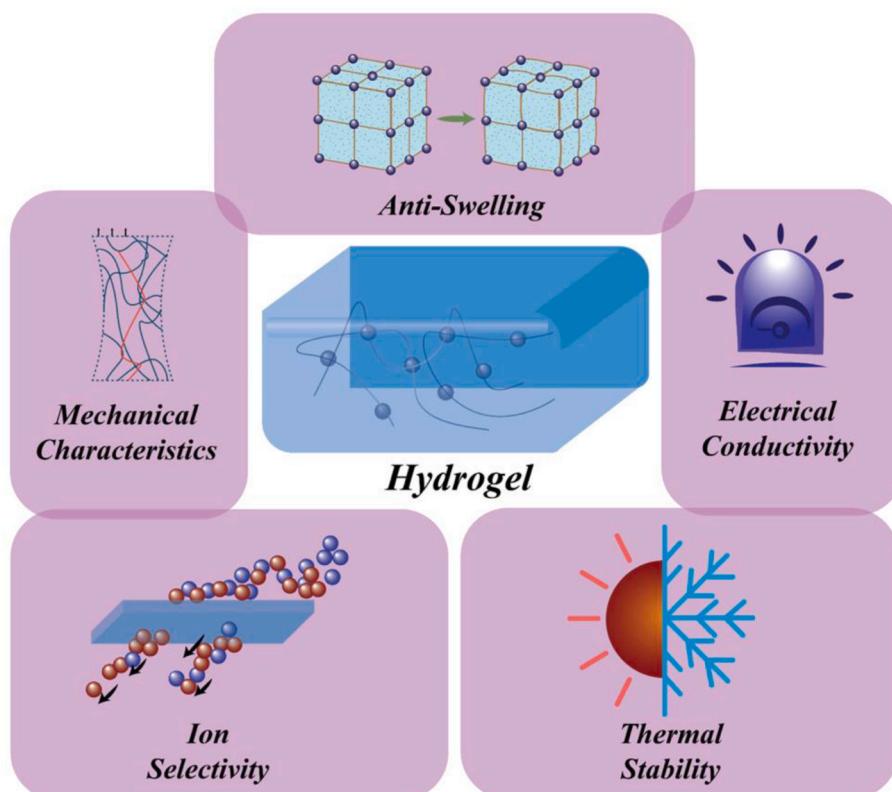


Fig. 1. A graphical illustration of tailored properties of hydrogel for fuel cell-based applications.

3. Hydrogel materials in microbial fuel cell

Hydrogel can be prepared with different polymers. However, the basic principle of all hydrogel's formulation for MFC is that hydrogel can form biofilm which helps proton transfer and microbial growth. Then the biofilm or hydrogel can act as a microbial anode and can promote antimicrobial activities. It can be simply expressed as the following schematic.

Hydrogel → Biofilm Formation → Proton Transfer → Microbial Growth
→ Microbial Anode → Antimicrobial Activity

The above schematic is a simplified representation and actual hydrogel structures may vary. The main aims of hydrogels in MFCs are to (i) enhance proton transfer and ionic conductivity; (ii) support microbial growth and biofilm formation; (iii) regulate oxygen and electrolyte diffusion; and (iv) improve overall MFC performance and

efficiency. However, the specific hydrogel properties and performances may vary depending on the application and MFC design.

3.1. Catalyst supports in MFC

Hydrogels can be used as catalyst supports in MFCs. MFCs are electrochemical cells that use the electrochemical reaction between fuels (like H₂, methanol, and ethanol) and other oxidizing agents (usually O₂) to convert the chemical energy of fuels into electrical energy [41,42]. Until now, the most effective electrodes for promoting cathodic ORR and anodic hydrogen oxidation reactions have been Pt-based catalysts. Nonetheless, Pt-based materials' high cost and poor durability prevent their widespread use in MFCs. Reducing Pt loadings, for instance, less than 0.1 mg_{Pt}/cm², is an easy way to cut costs without sacrificing durability or activity. To achieve long-term MFC durability, carbon frameworks must address the problem of poor stability. High oxygen concentrations, high water contents, high electrode potentials, high

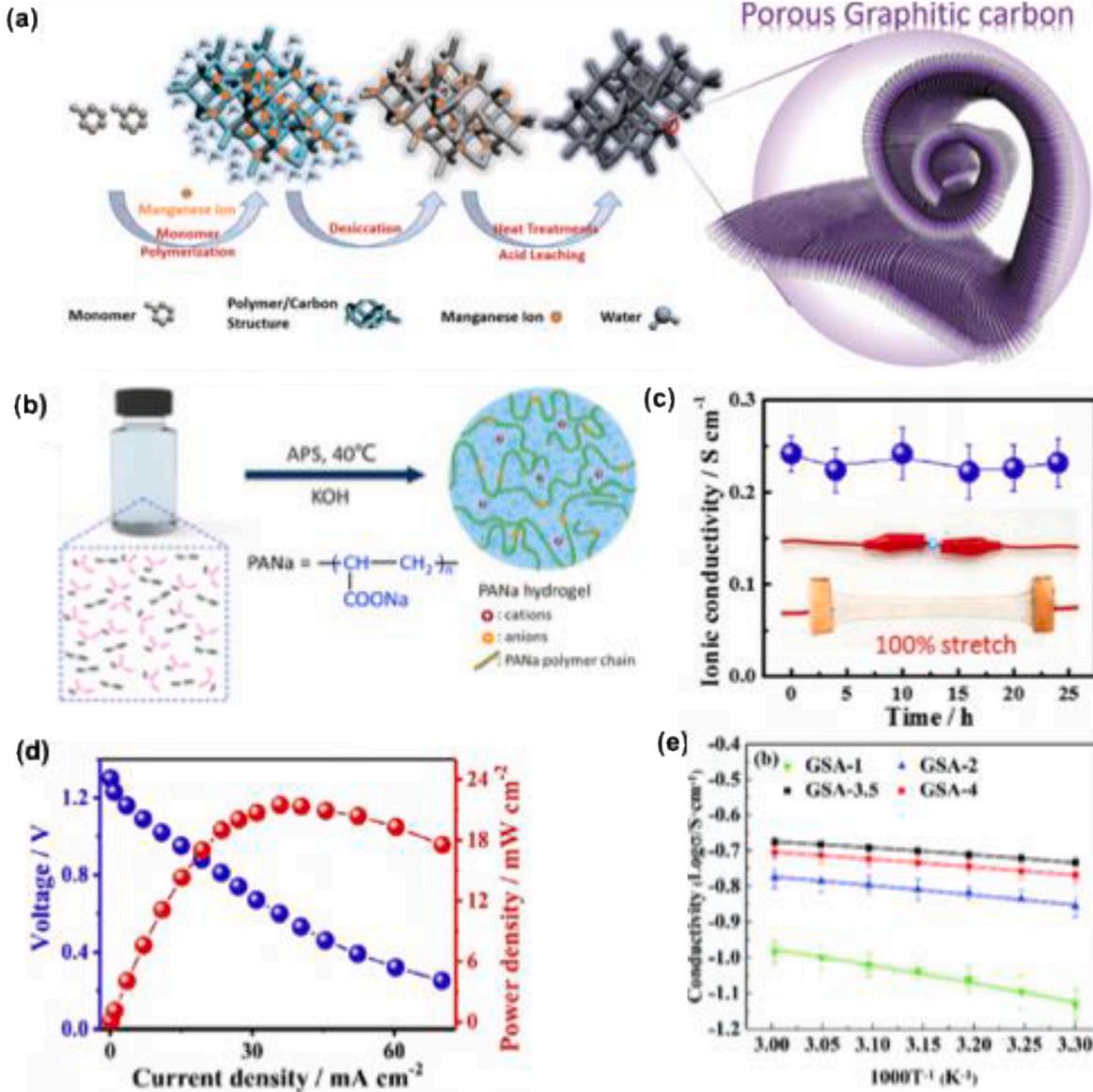


Fig. 2. (a) Synthesis scheme for a polymer hydrogel-derived porous graphitic carbon as the support for Pt particles [43]. (b) The preparation of sodium polyacrylate hydrogels (PANa) alkaline hydrogel membrane [46]. (c) Long-time ionic conductivities of PANa and the 100% stretched PANa as an ionic conductor to connect the LED circuit (in the inset) [46]. (d) Polarization curve and corresponding power densities of the assembled direct ethanol fuel cell with ethanol and air as fuels at room temperature and atmospheric pressure [46]. (e) The result of conductivity as a function of temperature, where GSA-n indicated the acid hydrogels, and n represented the molar concentration of H₂SO₄ in the resultant hydrogel [50].

temperatures, and low pH are typical operating conditions for PEM fuel cells. On the other hand, the amorphous state and low degree of graphitization of commercial carbon supports make them unstable. Recently, Qiao et al. [43] have investigated the use of a polyaniline-polypyrrole hybrid hydrogel-derived 3D porous graphitic carbon support that may be used to load Pt nanoparticles as an active and long-lasting Pt catalyst for MFCs (Fig. 2a). The outcome was that Pt nanoparticles deposited on polyaniline-polypyrrole hybrid hydrogel-derived carbon networks showed remarkable electrochemical stability with ignorable decay at a current density of 1.5 A/cm^2 after 5000 cycles under actual MFC operating conditions, surpassing the

United State Department of Energy's durability target of $<30 \text{ mV}$. Several studies on MFC materials made from polymers were described by Chung et al. [44]. One of these pioneering experiments used polyaniline as a carbon-nitrogen template to integrate iron and cobalt [45]. However, not much research has been carried out on polymer hydrogels made from non-precious carbon catalysts for use as MFC air electrodes.

3.2. Gas diffusion layers in MFC

Hydrogels can be used as gas diffusion layers in MFCs. Gas diffusion layers allow for the transport of reactant gases (such as hydrogen and

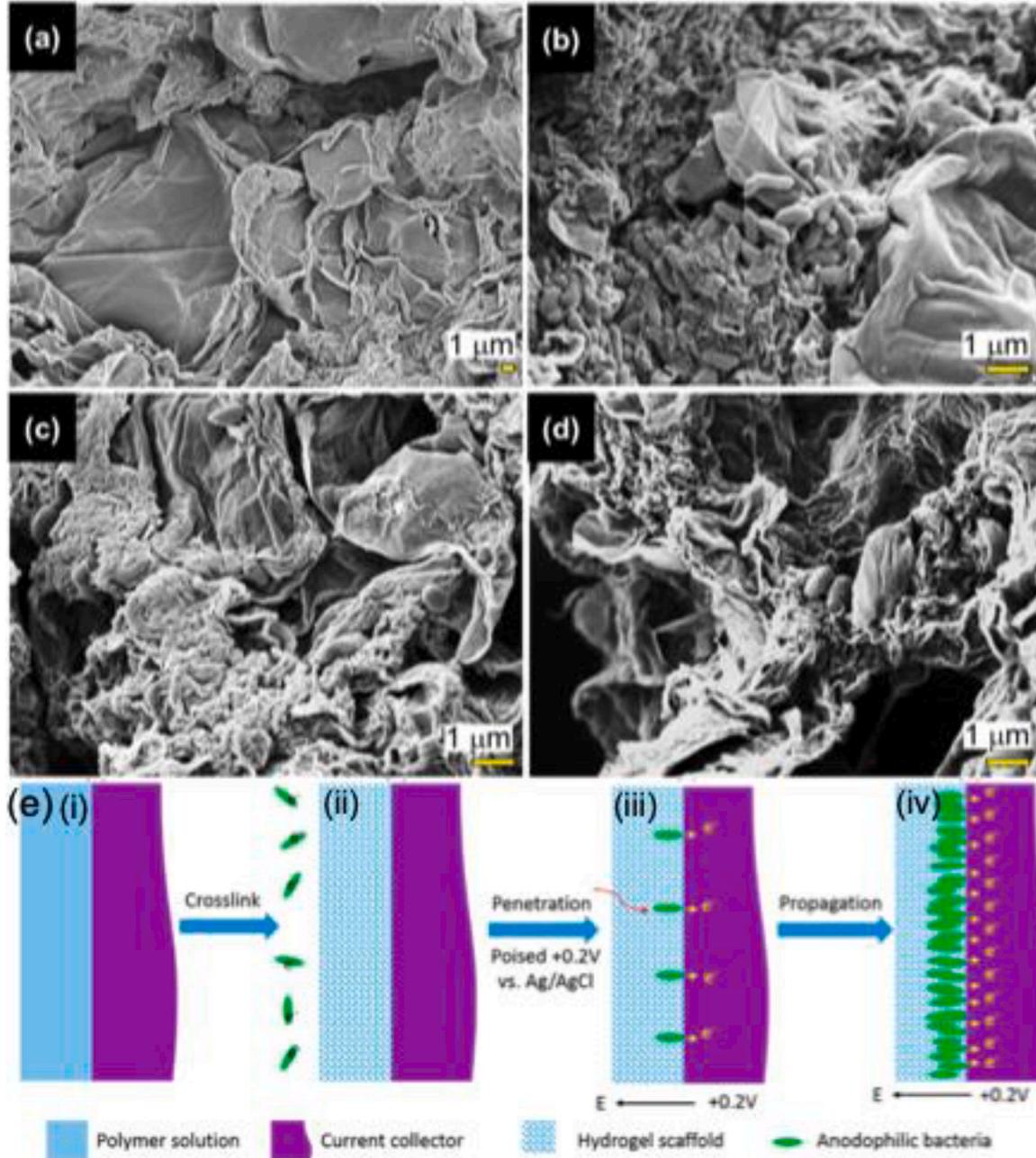


Fig. 3. SEM images of the complex of GO and rGO-GO-respiring bacteria. (a) GO's SEM image was utilized in this investigation. (b-d) SEM images of the rGO-GO-respiring bacteria complexes in the following cultures: river water (b), paddy soil (c), and water channel sediment (d) [88]. (e) The schematic diagram illustrates the fabrication process of HBA: (i) Coating of PVA or CB/PVA solution onto the SSM/CB current collector. (ii) Formation of a hydrogel scaffold electrode through freezing/thawing crosslink. (iii) Penetration of anodophilic bacteria in the media through the macroporous hydrogel scaffold, reaching the surface of the CB/SSM current collector under the driving force of the electric field generated by the poised positive potential ($+0.2\text{ V}$ vs. Ag/AgCl). (iv) Propagation of the anodophilic bacteria in situ led to the formation of thick biofilms on the surface of the CB/SSM current collector.

oxygen) to the catalyst sites within the MFC. However, although it has several notable features, the commercial Nafion membrane used in fuel cells is costly and eventually loses its ability to conduct ions when dehydrated.

The flexible fuel cell is a relatively new technology that was initially suggested in the early 21st century. Its primary purpose is to power wearable electronics, which can be integrated into clothing or attached directly to the skin. Soft, thin, and lightweight materials must be used for all cell components to achieve the desired flexibility. These components include the electrodes, electrolyte, and reactant channel. For example, the flexible direct ethanol MFC was initially studied by Wang et al. [46]. It was constructed using porous N, S-co-doped carbon catalyst as the cathode and highly ionic conductive sodium polyacrylate hydrogels as the alkaline membrane (Fig. 3b). Sodium polyacrylate hydrogels show higher ionic conductivity in highly concentrated alkaline environments, even in its stretchy condition, because of its super absorbing and water-retaining properties (Fig. 2c). The completed system was remarkably able to outperform numerous rigid MFC and batteries, reaching remarkable power and energy densities of 21.48 mW/cm^2 and 1.41 mWh/cm^2 (Fig. 2d). Ionic conductivity of gel-based hydrogels was reported between 10^{-4} to 10^{-5} S/cm in temperature range between 20 and 70°C [47,48]. A direct methanol fuel cell uses a quasi-solid potassium polyacrylate hydrogel as an electrolyte, achieving storage power density greater than 8.00 mW/cm^2 at 303 K with high stability and robustness and offers great flexibility under different bending degrees [49]. The mentioned electrolyte shows potential as a promising power source with rechargeable cycles of up to 54 h and flexible hydrogel by allowing diversified designs for fuel cells.

3.3. Polymer electrolytes in MFC

Hydrogels can be used as polymer electrolytes in PEM fuel cells. Polymer electrolytes offer several advantages over traditional liquid electrolytes, such as improved mechanical stability. Hydrogel polymer electrolytes require specific improvements in the following areas: (i) conductivity: Enhance ionic conductivity to enable faster charging and discharging; (ii) mechanical strength: Improve mechanical stability and durability to withstand repeated swelling and deswelling; (iii) water retention: Optimize water retention capacity to maintain electrolyte performance; (iv) electrochemical stability: Enhance stability to prevent degradation and ensure long-term performance; (v) interfacial compatibility: Improve compatibility with electrodes and other components; (vi) scalability: Develop scalable synthesis methods for large-scale applications; (vii) cost-effectiveness: Reduce material and production costs; (viii) temperature range: Expand operating temperature range for diverse applications; (ix) self-healing: Develop self-healing properties to extend lifespan; and (x) sustainability: Explore biodegradable and eco-friendly materials. Addressing these areas will enhance the performance, reliability, and practicality of hydrogel polymer electrolytes for MFC applications, including energy storage, sensors, and bioelectronics applications.

Several Hydrogels also have significant volume or gel solution phase transitions due to different physical and chemical stimuli, including temperature, electric pulse, magnetic fields, volume change, and pressure [49,50]. The physical structure and characteristics of monomer, charge intensity, and cross-linkage degree determine the response and reflex action of the hydrogel. Gel membranes synthesized from aqueous sulfuric acid liquid electrolytes have been used in various electrochemical applications and synthesized into gel membranes with concentrations of 1.0–4.0 mol/L through in-situ polymerization of acrylic amide monomer and divinylbenzene as a cross-linker for MFC applications. The synthesized gel membrane demonstrated the highest proton conductivity of 180 mS/cm with $3.5 \text{ mol/L H}_2\text{SO}_4$ concentration at 30°C temperature (Fig. 2e) [50]. The developed membrane had high tensile strain and could withstand pressures above 50 kPa and was tested using thermos-gravimetric analysis, showing high thermal

stability up to 231°C with a peak power density of 74 mW/cm^2 [50]. The mentioned hydrogel could withstand steady operations over 200 h. Research is still ongoing to replace Nafion in MFCs with a more affordable and highly conductive membrane electrolyte.

Three-dimensional (3D) macromolecular network polymeric hydrogels demonstrate exceptional water retention and chemical stability in both acidic and alkaline conditions, suggesting their significant potential for MFC applications. However, the cost-effective formulation of these hydrogels remains a crucial consideration. The hydrogel anion exchange membrane based on polyvinyl alcohol (PVA) has shown promising results for alkaline fuel cells [51]. It was able to obtain a hydroxide conductivity of 150 mS/cm at 80°C as well as strong alkaline stability and ultrahigh water absorption of up to 726 %. On the other hand, cell performance can be enhanced if oxide fillers, such as SiO_2 and ZnO , are added to the hydrogel membrane [52]. Moreover, polymer-based hybrid hydrogel exhibited high cationic and anionic permeability, good ionic conductivity, and a high retention rate [53]. Hence, these properties and the performance of hydrogel-based materials in MFCs and other energy storage devices influence the use of hydrogel and hydrogel-derived material for microbial fuel cells.

4. Hydrogel derived electrodes and materials in MFC

4.1. Hydrogel derived electrodes for MFC

Hydrogel has emerged as a versatile material in MFC research, offering tailored solutions to enhance the metabolic activity of anodic biofilms and improve electron transfer efficiency. Numerous studies have highlighted that significant improvement in power densities can be achieved through appropriate modifications in MFCs [54–57]. Several factors influence the performance of MFCs, including the type of microorganism and its inoculation between microorganisms and electrodes [58], the design of the MFC unit [59], and operating conditions [59]. One of the biggest obstacles to the practical applications of MFC is still the electrode's poor performance [60]. The subsequent subsections will delve into the various types of hydrogel electrodes employed in MFC applications.

4.1.1. Hydrogel derived anode in MFC

Table 1 provides a comprehensive overview of hydrogel-based components, summarizing their key features across different MFC applications. Despite the environmentally friendly and straightforward nature of MFCs, the characteristics of the anode electrode material are pivotal and have been a significant factor contributing to the relatively low efficiency observed in various prototypes [70,71]. The selection of anode materials and design significantly influences performance parameters in MFC systems, including microbial adhesion, electron transfer, and fuel oxidation. Achieving higher power density in MFCs necessitates the choice of an anode that facilitates efficient electron transfer from the bacterial community to the external circuit. Factors such as bacterial attachment and the promotion of electron flow can be influenced by the type and composition of the anode material [72]. Additional considerations include whether the MFC operates in continuous flow or batch culture and whether organisms primarily utilize indirect extracellular electron transfer (IEET) or direct extracellular electron transfer (DEET). The presence of a hydrogel may influence MFC behavior by immobilizing and anchoring bacterial cells in close proximity to the electrode. This effect can vary depending on the specific species involved and their preferred method of electron transfer. This effect varies depending on the type of species present and their method of electron transfer. For instance, species like *Geobacter* or *Rhodoferrax*, which use DEET, behave differently from species that rely on indirect transfer using a soluble mediator [73]. In continuous flow conditions, if the feedstock is carbon-energy limiting, the growth rate and power output of the MFC depend on the substrate supply rate, similar to a chemostat. The monolayer of the former species grows on the anode,

Table 1

Hydrogel application in microbial fuel cell.

Material	Synthesis technique	Used as	Anode/ Cathode Material	Membrane Material	MFC Type	P & C	Running time	Remarks	Ref
GO/CNT/PNIPAM	Suspension polymerization	Anode	Cathode: Bare carbon cloth	Nafion	Dual chamber	434 mW/ m ² 3606 mA/m ²	300h ^a	- High MFC performance with excellent durability - low cost and easier preparation method	[61]
CNT/Chitosan/ Carbon paper	Electrodeposition	Anode	Cathode: Carbon cloth	Nafion	Dual chamber	132 mW/ m ² , 320 mA/m ²	–	- Maximum power and current density increased by 65 % and 23 %, respectively, compared with the control	[62]
BC/PANI	In situ chemical oxidative polymerization	Anode	Cathode: Graphite plate	Nafion	H-type Dual Chamber	117 mW/ m ² & 617 mA/m ²	–	- BC can improve the output of mixed culture cells with the help of PANI conductivity - Nutrient transfer can be facilitated by capillary between BC's fibre	[63]
BC/PANI/TiO ₂	In situ oxidative Polymerization	Anode	Cathode: Graphite sheets	Nafion	Dual chamber	38.89 W/ m ³	30h ^a	- Maximum power density was 15-fold higher than bare anode	[64]
Alginate/PANI/ TiO ₂ /Graphite	In situ doping polymerization	Anode	Cathode: Woven graphite fibre	Nafion	Dual Chamber	7.88 W/ m ³	168 ^a	- Use of bio-anode significantly enhances the direct electron transfer rate and improves power density - Open opportunity to miniaturize the bio anode - Operation of the MFC at flow rate higher than 3 mL/min did not result in an increase in power density	[64]
PPY-CMC-Titanium nitride/Carbon brush Hydrogel	Direct oxidative polymerization	Anode	Cathode: Carbon rod	Nafion	Dual Chamber	14.11 W/ m ³	201 ^b	- The modified anode had a power density of 4.72-fold higher than the bare anode. - The modified anodes exhibited good energy storage performance	[27]
SA/PANI/CB	In situ polymerization	Anode	Cathode: Graphite rod	Nafion	Dual Chamber	515 mW/ m ²	–	- the modified anode had a power density of 1.38-fold higher than the pristine CB anode - COD removal efficiency was much higher than CB electrode	[65]
PPy/PANI/CNT/ Iron oxide PPy/CMC/ Nitrogen doped Carbon sponge	In-situ polymerization polymerization	Anode Anode	Cathode: Carbon rod Cathode: Graphite rod	Nafion Nafion	Dual chamber Dual chamber	5.9 W/m ³ 4.88 W/ m ³	– 153 h ^b	- Power output was twice compared with PPy anodes - Power density was 1.34 and 1.71 times greater than the PPy/N-CNT/S and N-CNT/S anodes	[28] [66]
AC, Fe(III)-chitosan-N N & FeCl ₃ .6H ₂ O self-doped AC and gel PVA, Water	Direct pyrolysis	Cathode	Anode: Graphite fibre brush	–	Single	2400 mW/m ²	120 h ^a	- Slightly more costly to fabricate, costing \$2.2 per meter square of catalyst	[29]
PVA, water, Clay aggregate	–	Cathode	Anode: Graphite felt	–	H-type dual chamber	977 mW/ m ²	400 h ^a	–	[67]
PVA, water, Clay aggregate	–	Separator	Anode: PVA-coke Cathode: carbon cloth	PVA	Tubular	38 mW/ m ²	120 days ¹	- Removed 95 % of benzene	[68]
PVA, water, Clay aggregate	–	Separator	Anode: carbon rod + coke Cathode: carbon cloth	PVA + Clay aggregate	Tubular	25.14 mW/m ²	–	- 50 mL of Toluene was completely degraded in 6 days	[69]

Maximum power (P) mW/m² and current (C) density mA/m².^a Overall running time.^b Running time of each cycle.

while daughter cells not in direct contact with the electrode are shed and washed away due to the flow rate, preventing biofilm accumulation and ensuring nutrient supply through advective transport. However, with hydrogel present, daughter cells accumulate, leading to thicker biofilms that can limit substrate supply due to diffusion, resulting in decreased power output [74]. On the other hand, if the anodic microbes are

predominantly reliant on indirect electron transfer and the MFC operates in batch culture mode, thick biofilms and an accumulation of redox mediators can lead to increased power output. Therefore, the type of microbial species and the operating mode of the MFC are important factors to consider rather than simply generalizing the MFC.

The anode material for MFCs should facilitate microbial attachment

and electron transfer. Inadequate attachment can impede electron transfer, reducing MFC performance and hindering practical implementation [75]. Other contributing factors to low efficiency include high internal resistance due to charge and mass transfer losses [76,77]. Developing cost-effective anode materials that enhance microbial attachment, substrate metabolism, and extracellular electron transfer (EET) can significantly improve MFC component performance [78]. An optimal anode for MFCs should possess good biocompatibility, a large surface area, great conductivity, and low cost.

Carbon-based materials like carbon paper, carbon cloth, activated carbon cloth, and activated carbon fiber felt are commonly used as anodes for MFC [79]. Their hydrophobic properties and low specific area hinder bacterial adherence despite being stable, relatively inexpensive, and exhibiting good conductivity and power density [80]. Recent advancements in anode materials reflect a growing interest in non-conventional carbonaceous materials. These materials and surface-modified metal-based anodes show promise in enhancing MFC performance, with some studies reporting high power densities [81–83]. However, 3D microporous anodes with large surface areas have been developed. A hydrophilic 3D microporous skeleton is a way to improve MFC performance [84]. An ideal anode material for MFCs should be biocompatible, promote strong microbial attachment, and facilitate electron transfer. It should also have good electrical conductivity, low resistance, large surface area, chemical inertness, anti-corrosion properties, and suitable mechanical strength. Achieving a balance among these attributes is challenging due to variations in material properties for microbial attachment and electron transfer.

The use of hydrogel-embedded anodes has resulted in improved voltage output in certain cases. This advancement is particularly beneficial for microorganisms with high electrogenic potential but limited biofilm formation genes, as hydrogel provides a way to enhance their immobilization [83]. Hydrogels have clear benefits in transporting and immobilizing bacteria when combined with graphene to create an anode. The combination supports cell colonization, efficient substrate transport, and favorable mechanical contact between the anode surface and microbial biofilms, optimizing the composite's performance in microbial fuel cells [85]. For example, a study by Neethu et al. [86] observed the feasibility of using different anode materials for MFCs. These materials included stainless-steel (SS) mesh cages filled with sodium alginate beads containing bacterial inoculum (Ic), activated carbon (AC), or a combination of both (AC-Ic); respectively. These anodes were prepared by solution-based and drop-casting methods. The performance of these materials was compared with MFCs that used bare carbon felt and SS mesh as anode materials. The MFC with an anode containing a bead matrix with AC-Ic in an SS mesh cage showed the best performance, with a maximum power density of 2.6 W/m^3 and a COD removal efficiency of $91.6 \pm 2.1\%$. This was attributed to enhanced bacterial-electrode interaction. Another recent study by Sun et al. [87] investigated the degradation of sulfamethoxazole using MFC technology and analyzed its electricity generation performance. Nano-ferro nickel sulfide (NiFe_2S_4) was prepared using a hydrothermal method and co-doped with ferro oxide (Fe_3O_4) nanoparticles to modify the poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT: PSS) hydrogel, which served as the bioanode of MFC. It was found that the presence of Ni and Fe ions can promote electron transfer, and S ions can enhance material biocompatibility. High throughput results showed the presence of enriched electro-producing bacteria and demonstrated the synergistic effect of bimetallic sulfides with metal oxides, accelerating the EET process. The maximum power density obtained was 3.67 W/m^3 .

Yoshida et al. [88,89] research suggests that the growth of specific electrogenic microbes is associated with GO reduction, leading to the formation of a complex termed rGO (Fig. 3). This rGO-hydrogel amalgam has been applied in MFCs to extract electricity from dialysis wastewater. However, the generated current fell short of expectations, which was attributed to an incomplete GO reduction [89]. To rectify this issue, an extended incubation period between GO and microbial species

is recommended [90]. A study by Li et al. [91] prepared a bioanode that can tolerate air by immobilizing bacteria that thrive in the presence of an anode. This bioanode was designed for use in MFCs that operate under aerobic conditions. The bioanode was made by using electrochemical methods to embed anodophilic bacteria into a 3D hydrogel scaffold. The hydrogel protected the bacteria and allowed them to efficiently catalyze electrochemical reactions even when exposed to continuous oxygen aeration, producing a current density similar to that achieved under anaerobic conditions. In another study, a 3D composite hydrogel by incorporating reduced GO and polyacrylamide (rGO/PAM) was developed and coupled with a graphite brush current collector to serve as the anode in MFCs (Fig. 4a) [92]. This hydrogel composite was prepared through free-radical polymerization and crosslinking processes. The graphite brush/rGO/PAM anode demonstrated an outstanding maximum power density and volumetric power density by reaching 758 mW/m^2 and 53 W/m^3 , respectively (Fig. 4b). Notably, the orientated rGO/PAM contributed to boast conductivity which further enhanced the maximum power density up to 782 mW/m^2 . These results significantly surpassed those obtained with traditional graphite brush, plain carbon cloth, and the control graphite brush/GO/PAM and carbon cloth/rGO/PAM-based electrodes when measured under identical conditions. Despite its notable biocompatibility, the GO/PAM scaffold demonstrated poor electrochemical performance due to the insulation of graphene oxide [92].

A novel CNT hydrogel was created by electrodepositing CNT and chitosan onto a carbon paper electrode, which serves as an efficient anode material for MFCs [93]. The MFC equipped with the CNT hydrogel demonstrated a significant increase in power generation and maximum power density compared to the control (Fig. 4c) [62]. The remarkable conductivity of CNT and the abundant functional groups on its surface were identified as key contributors to improved electron transfer and enhanced power generation in the MFC with the hydrogel anode [94]. Further enhancements in MFC performance have been demonstrated by incorporating CNT into composite polymer hydrogel. For instance, a hydrogel anode composed of GO, CNT, and poly N-isopropyl acrylamide (PNIPAM) exhibits 100 % in both power and current densities [61]. Moreover, CNT is commonly paired with PPy to form composite materials. Examples include the development of PPy-CNT hydrogels [95] and PPy, carboxymethylcellulose (CMC), and nitrogen-doped CNT hydrogels [66] (Fig. 4d–e). A new bio-anode was developed using gel-entrapped bacteria in alginate/polyaniline/- TiO_2 /graphite composites via an in-situ doping polymerization technique, and its electrical properties were examined [64]. The addition of polyaniline and graphite powder resulted in significant increases in conductivity and power density. The optimized concentrations were found to be 0.02 g/mL for polyaniline and 0.05 g/mL for graphite powder. The modified hydrogel anode was successfully used in semi-continuous and continuous microbial fuel cell systems operations. In semi-continuous mode, a power density of about 7.88 W/m^3 was achieved after 13 h of fermentation, with a glucose consumption rate of approximately $7 \text{ mg/h}/1.2 \times 10^7 \text{ CFU}$ immobilized cells.

To increase the amount of electricity produced by MFCs, a low-cost Fe-N-C catalyst was developed using affordable ferric chloride and chitosan precursors on an activated carbon support [29]. MFCs utilizing the Fe-N-C/AC catalyst achieved a maximum power density of $2.4 \pm 0.1 \text{ W/m}^2$, a 33 % improvement compared to control MFCs using a plain AC catalyst ($1.8 \pm 0.03 \text{ W/m}^2$). Using chitosan and ferric chloride added only 6 % more in material costs but resulted in a substantial 33 % increase in maximum power density, highlighting the cost-effectiveness and efficiency of this approach [29]. These results highlight the superior performance of the hydrogel anode in terms of power density and current generation in microbial fuel cells.

Polymer hydrogels are utilized in MFC as anodes due to their ability to interact physically with cell membranes, which facilitates electron transfer [96]. For example, the performance of the anode can be improved by combining cellulose hydrogels with PANI and PPy via an

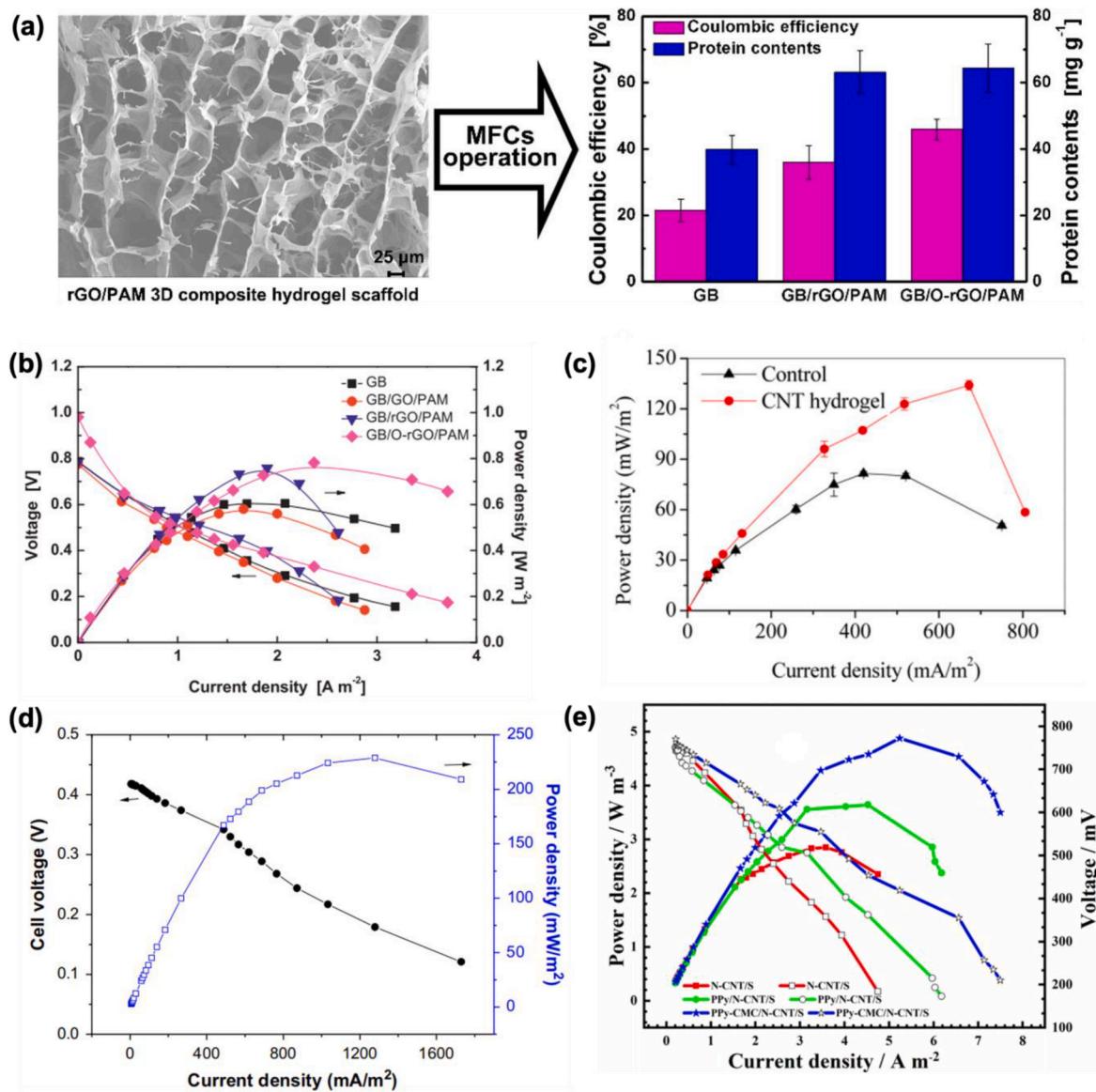


Fig. 4. (a) Fabricated reduced graphene oxide/polyacrylamide (rGO/PAM) 3D composite hydrogel and compare their biocompatibility and Coulombic efficiency as an anode in MFC with different types of hydrogel composite [92]. (b) polarization and power density curve of the MFCs with different kinds of hydrogel-based anode [92]. (c) The power output of the MFCs with controlled and CNT hydrogel anodes [62]. (d) Power output and polarization curves with polypyrrole-CNTs modified carbon paper anode [95]. (e) MFC performance with polarization curves and power density when fitted with various anodes [66].

in-situ chemical oxidative polymerization technique. PPy-bacterial cellulose produced a somewhat higher power density of 136 mW/m^2 , while PANI-bacterial cellulose had a power density of 117.76 mW/m^2 , as reported by Mashkour et al. [63] (Table 1). Using in situ polymerization, polyaniline-sodium alginate/carbon brush, a self-supporting hydrogel, was created to function as an MFC anode. As an electrode material, the PANI-sodium alginate-conducting hydrogel showed encouraging properties, resulting in a maximum power density of 515 mW/m^2 in MFCs, a 1.38-fold increase over a blank carbon brush anode [65]. Mashkour et al. [97] introduced a new bioanode, i.e., polyaniline-modified conductive bacterial cellulose (BC-CNT-PANI), for MFC membrane. In this process, BC is coated with CNT to form a conductive electrode (BC-CNT) and then the conductive side is coated with PANI through electro-polymerization to create BC-CNT-PANI. Both anode electrodes were studied in supercapacitive MFCs (using impedance analysis before and after biofilm formation). Biofilm formation on the surface showed that BC-CNT-PANI had lower charge transfer resistance and higher capacitance compared to BC-CNT. Tests indicated a 20 % improvement

in power density with the PANI-modified anode. Yuyang et al. [27] developed polypyrrole-CMC-titanium nitride/carbon brush (PPy-CMC-TiN/carbon brush) hydrogels as a bioanode for enhancing the energy output of MFCs (Fig. 5). The maximum power density of the MFC with the PPy-CMC-TiN/carbon brush hydrogel anode (14.11 W/m^3) was 4.72 times larger than that of the blank carbon brush anode. During the operation, the average peak current density of MFCs equipped with the PPy-CMC-TiN/carbon brush hydrogel anode was 10.12 times higher than that of the carbon brush anode [27]. In a different study, researchers created a double-layer hydrogel bioanode using sodium alginate. The inner layer contained encapsulated Fe₃O₄ and electroactive microorganisms for efficient electron transfer. The outer layer, formed by crosslinking sodium alginate with PVA, provided protection and promoted stable electricity production through its 3D porous structure [98].

4.1.2. Hydrogel derived cathode in MFC

While much research on hydrogel-based MFCs focuses on enhancing

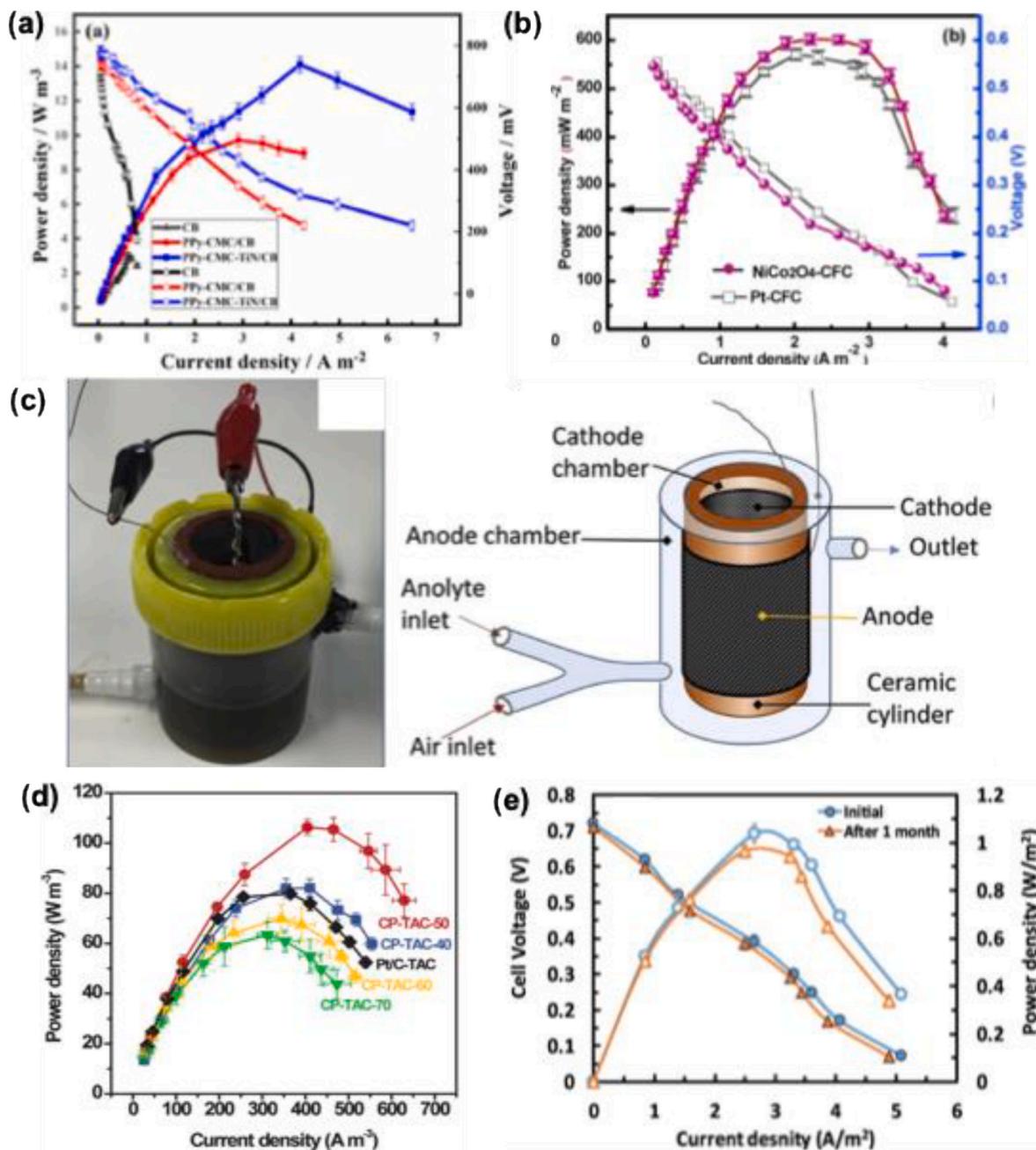


Fig. 5. (a) MFC performance with polarization curves and power density when fitted with various anodes [27]. (b) The output power density plots of Pt-MFC and NiCo₂O₄-Carbon fiber cloth-MFC [107]. (c) The cathode chamber of MFC using hydrogel [108]. (d) Power density curves of MFCs with a different cathode, where carbon paper-TAC means Chlorella pyrenoidosa-tubular air cathode and carbon paper-TAC-40, carbon paper-TAC-50, carbon paper-TAC-60 and carbon paper-TAC-70 means the 40, 50, 60 and 70 mL, respectively, deionized water that was equivalent to 4.4–6% agar concentrations of the total slurry was used to prepare the mixture [20]. (e) Electrochemical performance of MFC with an AC cathode modified with 10 mg/cm² OKH hydrogel polarization curves and power outputs after 1.0 months [21].

microbe-anode interactions and electron transfer efficiency, some studies have explored using hydrogel in MFC cathodes to improve ORR. ORR involves the reduction of oxygen to water or hydrogen peroxide and is crucial for electric energy production. The implementation of air-cathode membrane-less MFCs has laid a robust foundation for practical MFC technology application. This simplified design enables passive oxygen supply from the air, minimizing the energy required for continuous operation [99]. Despite these advantages, the performance of air cathodes is constrained by the sluggish and intricate kinetics of the ORR [100].

A typical air cathode for a MFC is composed of multiple layers,

including a waterproof polytetrafluoroethylene (PTFE) layer, a porous gas diffusion layer, and a catalyst layer on a conductive macroporous substrate. The conventional fabrication methods, such as hot pressing or rolling pressing, involve the use of binders like Nafion and PTFE to enhance triple-phase interfaces and provide mechanical strength to the electrodes. These triple-phase interfaces are critical intersections where electrochemically active sites, electrolytes, and gas pores meet in the cathode structure [101]. Using conductive polyacrylonitrile fiber, agar gel, and microalgae on the cathode, Li et al. [20] produced a hydrogel that increased power density over Pt electrodes by 33 %. But its longevity was hampered by carbonate precipitation. Another study used

tofu gel, nitrogen, and iron co-doped carbon for ORR electrocatalysis, producing a 30.62 % power boost over Pt electrodes [67].

While effective ORR catalysts in neutral pH electrolytes, platinum and its alloys are expensive and susceptible to poisoning under MFC conditions [102]. To mitigate these issues, previous research has focused on heteroatom-doped carbons, such as those containing S, B, N, and P, owing to their advantageous four-electron pathway and resistance to poisoning species [103]. Notably, self-doped ORR catalysts derived from renewable biomass materials are gaining attention for their intrinsic porous structure, environmental sustainability, and ability to avoid toxic dopants. Additionally, the architecture of the air cathode, influencing the accessibility and utilization of catalysts, significantly impacts cathode performance in MFCs. In the pursuit of efficient non-precious metal catalysts for the ORR in MFCs, an environmentally friendly and cost-effective Fe–N-doped carbon foam catalyst has been studied [104]. This catalyst is derived from Fe-embedded poly (acrylamide-co-acrylonitrile) hydrogel-based carbon foam, with poly (Am-co-An) hydrogel serving as the carbon and nitrogen precursor. Four variants of the catalyst were prepared based on different metal ratios, with Fe@Am-co-An/carbon fiber (2:22) displaying the highest power density (736.06 mW/m² at a current density of 1132.04 mA/m²) among the tested catalysts. Comprehensive characterization and electrochemical analyses indicate that Fe@Am-co-An/carbon fiber (2:22) stands out as a promising catalyst for ORR activity in MFCs.

The typical electrochemical binders used in microbial fuel cells are both electrochemically inert and insulative. Consequently, their use leads to an increase in the ohmic resistance of the electrodes, along with coverage of the catalyst surface, obstructing the pathway for oxygen and ion transfer [105]. This dual effect significantly hampers the performance of MFCs. To overcome issues associated with conventional binders in MFC air cathodes, a solution involves adopting free-standing cathodes where catalysts grow directly on the electrode surface [106]. Methods such as chemical vapor deposition on a nickel mesh and in situ electrodepositing NiCo₂O₄ nanoplatelets on carbon cloth have demonstrated improved conductivity and catalyst utilization, resulting in higher maximum power density and long-term stability (Fig. 5b) [107]. In addition, hydrogel-based cathodes outperform Pt electrodes in MFCs, offering an expanding hydrogel with catholyte-improved electrical output by 182 %, considerably more than the 33 %33 % power density increase as found by Winfield et al. [108] (Fig. 5c).

While previous techniques involve complex layering, recent proposals introduce free-standing, monolithic air cathodes with simplified fabrication processes and macroporous structures, promising enhanced accessibility and utilization of active sites in the ORR. Li et al. [20] developed a simple free-standing air cathode using a sol-gel-based method where chlorella pyrenoids serve as the catalyst precursor, polyacrylonitrile fiber as the conductive and supporting skeleton precursor, and deionized water as the solvent and pore former. Agar is incorporated as a gelling agent to facilitate the formation of 3D porous networks within the cathodes. This process produced mechanically robust and highly electrically conductive tubular air cathodes and established an interconnected hierarchical porous structure with distinct transport paths for air supply and ion transfer. The resulting air cathode, devoid of polymer binders or other modifications, demonstrated superior performance in an MFC with a maximum power density (P_{max}) of 106.3 ± 5.9 W/m³, approximately 33 % higher than that of Pt/C (79.8 ± 4.1 W/m³) (Fig. 5d) [20]. However, this cathode was limited by carbonate precipitation during prolonged operations. Another study introduces an alternative air cathode for MFCs without a diffusion layer, utilizing a crosslinked hydrogel called oxidized konjac glucomannan/2-hydroxypropyltrimethyl ammonium chloride chitosan (OKH) for ion bridging [21]. To mitigate the impact of high hydraulic pressure, the cathode is positioned horizontally. Sustained ion transportation is achieved with a minimal crosslinked hydrogel (i.e., OKH, oxidized konjac glucomannan/2-hydroxypropyltrimethyl ammonium chloride chitosan hydrogel) loading of 10 mg/cm², resulting in a

maximum power density of 1.0 ± 0.04 W/m², slightly lower than common air cathodes. The cost-effectiveness of the OKH hydrogel, priced at \$0.12/m², reduces approximately 85 % of the cathode cost, providing a low-cost strategy for stable MFC operation and demonstrating the significant potential for practical applications in MFC technology (Fig. 5e) [21]. However, the main limitation of such cathode is the requirement of a sufficient amount of OKH hydrogel coated on the AC cathode for effective proton transport.

4.2. Hydrogel based membrane and electrolyte for MFC

Nafion and other non-fluorinated polymers (i.e., conductivity $\sim 10^{-1}$ S/cm) have conventionally served as PEM in MFCs due to their exceptional proton conductivity, thermal and mechanical stability, and durability in hydrated conditions. However, their high cost has prompted exploration into more economical alternatives, notably exemplified by the adoption of hydrogels. Hydrogel-based membranes (i.e., conductivity $\sim 10^{-2}$ - 10^{-3} S/cm) have shown promising results in MFC applications, although they have lower conductivity than Nafion. However, their performance compared to traditional Nafion membranes varies depending on factors like hydration levels and environmental conditions. However, some hydrogel-based membranes have shown comparable or even higher proton conductivity. In the case of long-term performance and stability, Nafion membranes can undergo degradation over time, leading to reduced performance, while hydrogel-based membranes may exhibit improved long-term stability and durability due to their hydrophilic nature and ability to retain water. This transition towards hydrogel, though departing from conventional choices, signifies a strategic shift aimed at improving affordability without sacrificing the crucial functionalities necessary for efficient MFC operation. In hydrated polymeric matrices, proton transport occurs via two primary mechanisms, 'hopping' and 'vehicular', as illustrated in Fig. 6 [109]. Protons, including H⁺, H₃O⁺, and NH₄⁺, are transferred from one protonic site to another within the membrane. The vehicular mechanism involves hydrated protons moving through the medium in response to an electrochemical gradient. Protons attach to a vehicle site, typically water molecules, and diffuse through the medium, facilitating proton transport.

Hydrogel-based membranes are also used in MFCs as they have hydrated polymeric matrices in their structure. Thus, they can follow the above-mentioned mechanisms. For example, PVA undergoes a process of repeated freezing and thawing, which imparts elastomeric properties to the resulting membrane [110]. The membrane's remarkable capacity to facilitate proton exchange is noteworthy. Furthermore, when this hydrogel membrane is strategically integrated with the cathode to create a unified electrode assembly, the synergistic effects significantly enhance the overall electricity production efficiency of the microbial fuel cell system [111]. The use of PVA-hydrogel (PVA-H) has primarily been observed in the realm of air cathodes, proving to be effective tools for removing or degrading contaminants from water reservoirs. Chang et al. [68] devised a novel cylindrical MFC configuration, integrating a PVA-H proton exchange membrane to extract benzene from groundwater. Likewise, Wu et al. [110] developed a cascading MFC setup to tackle the presence of organic compounds in molasses wastewater, highlighting the versatile application of PVA-H in various environmental remediation strategies. Another study was conducted in a parallel endeavor aimed at eliminating azo dye [112]. However, the efficacy of PVA-H faced a challenge due to its inadequate water uptake and retention capabilities, thereby restricting its ability to facilitate proton transference. To overcome this limitation, Liu et al. [69] ingeniously introduced a water-retaining clay into the PVA-H composition. This strategic enhancement resulted in a remarkable 2.87-fold increase in proton conductivity compared to the conventional PVA-H MFC.

The evaporation challenge presents a common limitation in numerous air cathodes, especially in miniature microbial fuel cells, resulting in unstable power generation [30]. Hydrogel polymers, known

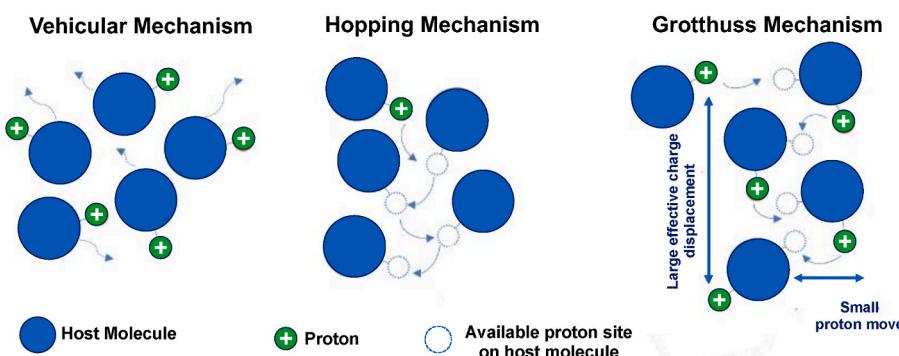


Fig. 6. Different mechanisms of proton transport through the membrane.

for including hydrophilic functional groups, demonstrate a remarkable ability: as water evaporates, the internal pressure decreases, prompting the hydrogel to draw in the substrate. This phenomenon has been strategically utilized in various applications, such as sustaining ion transport in horizontal air cathode designs [21]. Furthermore, it has improved the interaction between the ion exchange membrane in the MEA air cathode [113]. Additionally, the concept has been applied to develop an auto-feeding MFC capable of autonomously pulling up substrates, resembling a transportation-like process [31]. Significantly, hydrogel electrolytes prove valuable in enhancing cathode potential without disrupting critical ion exchange mechanisms. In summary, hydrogel-based membranes offer promising advantages, but their performance varies depending on the specific application and conditions. Further research is needed to overcome challenges and fully realize their potential in MFCs.

5. Practical implementation of hydrogel-based MFC

Conductive PPY hydrogels mixed with CNTs increased the stability and power density, reaching above 870–1900 mW/m², and enhanced power production in MFC [23,27]. In addition, it has been reported that the techniques are scalable and applicable as anode in MFCs with high electrocatalytic activity and reduced charge transfer resistance [64]. It is reported that agar chemical hydrogel is used to enhance the mass and charge transport rendered by the hydrophilic nature and water retention characteristics. Cost-effective agar chemical hydrogel binders could replace conventional Nafion polymers for fuel electrolyte-fed fuel cells [114]. The transfer rate of reactants in the hydrogel phase is much higher than in the dissolved phase. Chitosan chemical hydrogels are used in fuel electrolyte direct borohydride fuel cells, yielding a power density above 80 mW/cm² [115].

Agar hydrogels also can absorb large amounts of water and dissolve in hot water at 85–90 °C, created by water-insoluble acrylic acid hydrogel (ACH) binders by a chemical crosslinking reaction [116]. ACH-based electrodes yield a peak power density of 170 mW/cm² at 60, achieving a maximum current density of 470 mA/cm² [117]. The agar-based fuel cell delivers the highest power density of 100 W/m³, achieving 33 % higher power than conventional fuel cells [118]. Integration of hydrogels offers promising pathways and new routes for electricity storage and high-power density in fuel cells. Hydrogel frameworks are used to synthesize high-temperature proton exchange membrane fuel cells and have been shown to enhance the swelling kinetics, proton conducting performances, and electrochemical behavior of fuel cells [119]. Three-dimensional hydrogel frameworks are designed for high-temperature PEM fuel cells, delivering higher power density by 33 % than conventional fuel cells [120].

Besides the applicability in MFCs, hydrogels have significantly impacted other fuel cell applications besides microbial fuel cells, owing to preserved structural integrity, exceptional water content, and increased ionic conductivity [121]. They have been used in the

development of alkaline exchange membrane fuel cells (AEMFCs), which depend on AEMs to conduct hydroxide ions (OH⁻) while maintaining gas separation. Since OH⁻ ions are larger than H⁺ ions, they exhibit slower mobility in liquid water, resulting in lower conductivity compared to proton membranes like Nafion [122]. Hydrogel enhances OH-conductivity by promoting water absorption within AEMs. In a study, Yuan et al. [51] prepared a series of multi-cation crosslinked PVA hydrogel AEMs, and with ultrahigh water uptake up to 726 %, a hydroxide conductivity of 150 mS/cm at 80 °C was achieved. It was possible as large quantities of water molecules facilitate ion transportation as well as good alkaline stability. Moreover, the single fuel cell based on the as-prepared hydrogel AEM demonstrated a remarkable 715 mW/cm² peak power density. However, despite its positive impact on OH-conductivity, incorporating hydrogel poses challenges during MEA preparation and fuel cell water management, particularly concerning dimensional swelling and electrode flooding at high current densities. Hence, integrating hydrogel into AEMs can help progress in the AEMFC technology. In alkaline water electrolysis as the oxygen-evolving electrode, porous hydrogel electrodes are also expected to repair cracked surfaces by recombining microparticles and exhibiting enhanced mass transport at high current density. Hydrogel electrodes with larger pore sizes exhibited better mass transport to achieve higher OER activity at high current density [123]. Larger pore-size hydrogels can be synthesized using various methods, such as incorporating a porous network in the core structure of the hydrogel. Additionally, a 3D pore network can also be integrated into the hydrogel.

Hydrogels can significantly improve high-temperature PEM conductivities. A fuel cell synthesized with a thick membrane as a PEM, according to Li et al., demonstrated a peak power density of 635 mW/cm² at 150 °C when O₂ and H₂ were used as the fuel and oxidant, respectively. Additionally, an increase in the H₃PO₄ content per unit volume of the PAAm-PEG semi-IPN matrix is expected to accelerate the proton transfer via hydrogen bonds formed between individual H₃PO₄ molecules or the H₃PO₄ matrix. At 180 °C, the maximum anhydrous proton conductivity is 0.18 S/cm. Hydrogel materials have the potential to be used in high-temperature PEM fuel cells because of their strong proton conductivities at high temperatures, easy fabrication, low cost, and scalable hosts and proton conductors [124]. Furthermore, Tang et al. [125] reported using a polyacrylamide/polyacrylamide interpenetrating polymer network (PAM/PAM IPN) hydrogel for high-temperature PEM, demonstrating a proton conductivity of 0.0833 S/cm at 183 °C in dry air that remained stable for 80 h. This hydrogel can absorb a significant amount of aqueous solution to achieve high H₃PO₄ loading. Additionally, PEM based on polybenzimidazoles and polyacrylamide hydrogels for wide temperature application has been described by Yin et al. [126]. They stated because of the porous and hydrophilic polyacrylamide hydrogel, poly[2,20-(p-oxydiphenylene)-5, 50-bibenzimidazole] (OPBI)-acrylamide membranes showed higher phosphoric acid and water uptake than the original OPBI membrane. This led to higher conductivity at both high and low temperatures.

Without humidification, the OPBI-0.8AM sample's proton conductivities ranged from 0.0159 S/cm to 0.104 S/cm over a 40–180 °C temperature range. Its maximum peak power density was 200 mW/cm² at 80 °C and 560 mW/cm² at 160 °C at 0 % RH. The OPBI-0.8AM membrane demonstrated cell performance that was close to PBI-based membranes, opening the way for the development of PEMFCs that can be used in a broad temperature range and offer the benefits of low-cost and a simple preparation process. In addition, functional hydrogels for energy storage technologies and enhanced physicochemical properties achieve improved mechanical strength, flexibility, and charge transport, which enhance fuel cells by fabricating stimuli-responsive, self-healing, and highly stretchable hydrogels [127,128]. The versatility of hydrogels allows new approaches in the design of materials with great potential for energy storage for fuel cell applications [129].

6. Future prospects

Hydrogels have already shown enough potential for MFC applications. However, the evaporation challenge presents a common limitation in numerous air cathodes, especially in miniature MFCs, resulting in unstable power generation. One of the major challenges for hydrogel-based membrane applications in MFC is to improve proton conductivity and long-term stability. Hydrogel-based membranes are also required to optimize the membrane design and composition for specific MFC applications.

Hydrogel polymers, known for including hydrophilic functional groups, demonstrate a remarkable ability: as water evaporates, the internal pressure decreases, prompting the hydrogel to draw in the substrate. This phenomenon has been strategically utilized in various applications, such as sustaining ion transport in horizontal air cathode designs. Furthermore, it has improved the interaction between the ion exchange membranes in membrane electrode assembly air cathode. Additionally, the concept has been applied to develop an auto-feeding MFC capable of autonomously pulling up substrates, resembling a transportation-like process. Significantly, hydrogel electrolytes prove valuable in enhancing cathode potential without disrupting critical ion exchange mechanisms.

It is anticipated that additional research examining the impacts of hydrogel composites on MFC performances will surface, given the obvious advantages of employing hydrogels for MFC applications. More research should be done on customizing hydrogel composites for various MFC components. Hydrogels are excellent materials for automated manufacturing processes like 3D printing because of their high flexibility and adaptability. This special feature will undoubtedly significantly impact MFC applications in the real world going forward. Natural hydrogels based on polymers are also eco-friendly, helping to prevent any plastic contamination.

Subsequent studies should prioritize the advancement of microbial fuel cells (MFCs) for diverse applications such as sensing platforms and focus on refining various materials and design arrangements. Hydrogel composites come in a wide range of variations, each with customizable features. It is important to investigate how these hydrogel composites affect MFC applications. MFCs show great promise as a variety of application platforms. Subsequent studies should build upon current work by examining the impact of hydrogel on MFC performance. This could lead to fresh advancements in the technological domains of energy and the environment.

MFC stacks using urine have been tested in field trials, which have shown them to be sustainable, have good long-term stability, and have stack units that can be easily built up into larger and larger stacks without loss of power density [130]. Some of the recent works suggest that MFC power outputs are sufficient for practical applications [131, 132]. Finally, MFC can be downsized to increase power density and then stacked to form larger arrays, resulting in higher power output, which may add new dimensions for new applications.

7. Conclusion

This article comprehensively discusses hydrogel materials for microbial fuel cells (MFCs). Much research in the MFC field has been dedicated to anode hydrogels, focusing on optimizing their properties to improve MFC efficiency and electricity generation. Anode hydrogels such as conductive polymer hydrogels and carbon composite hydrogels are commonly used to enhance the electrocatalytic activity of microbes and facilitate electron transfer at the MFC anode. The addition of carbon-based materials and various conductive polymers has been found to improve conductivity and significantly increase the power density output of MFCs. Incorporating various conductive elements into hydrogels has improved their electrical conductivity and power output. Hydrogel-based cathodes are being explored to increase ORR efficiency and address the high cost and scarcity of current catalysts.

CRediT authorship contribution statement

I.M.R. Fattah: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jahangir Alom:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Jahid Uz Zaman:** Writing – review & editing, Writing – original draft, Data curation. **Sagar Ban:** Writing – review & editing, Visualization, Resources. **Ibham Veza:** Writing – review & editing, Writing – original draft, Project administration, Methodology. **M.A. Kalam:** Writing – review & editing, Supervision. **Volker Hessel:** Writing – review & editing, Supervision. **Mohammad Boshir Ahmed:** Writing – review & editing, Writing – original draft, Project administration, Methodology, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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