



Review article

Possible bio cathode materials for usage in microbial fuel cells towards energy generation and wastewater treatment to sustain environment: A review

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ABSTRACT

The aim of this study is to review the effectiveness of bio-cathode materials usage in microbial fuel cells (MFCs) for power generation and wastewater treatment. The review focused on the Microbial fuel cell construction and design. The Anode and cathode materials of MFCs with their merits and demerits are compared. The first half of the study discusses the components for Anodes and cathodes. Typical anode and cathode materials are compared based on their power densities. The focus is narrowed down to discuss about bio cathode components and their materials including the most prominent/discussed ones such as Stainless steel and Graphite/carbon as bio cathode materials. Indirect electron transfer and direct electron transfer in MFCs are also reviewed. The second part of the review focused on bio cathode materials for electricity production and wastewater treatment. It was reported in many literatures that, MFCs can serve as supplementary, decentralized power sources. Also this review highlighted that MFCs can be employed with effective methods for removing sulfides from wastewater with certain microbes. It was reported that, a considerable coulombic efficiency of 80% can be achieved with MFCs. It was also found from the literatures that a well-designed MFC-membrane bioreactor for wastewater treatment could achieve good pollutant removal performance with a remarkable power density of 6 W/m³ at an average current of 0.4 mA to 1.9 mA. The limitations of current technology, as well as some possible future developments, were discussed in the last section. Therefore, this may open up possibilities for further development and the use of bio-cathode materials in the future.

1. Introduction

A device that transforms chemical energy from fuel and an oxidizing agent into electrical power is called a fuel cell. They are employed in many different fields, such as transportation, military applications, and power generating. Fuel cells function similarly to batteries, except they

don't need to be recharged or run down. As long as fuel is available, they can generate heat and power. A negative electrode, also known as the anode, and a positive electrode, sometimes known as the cathode, are positioned around an electrolyte to form a fuel cell. Fuel cell types include metal hydride, zinc-air batteries, electro-galvanic, direct formic acid, alkaline, proton-exchange membrane, direct carbon, direct

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borohydride, and microbial fuel cells, among others. The three main categories of fuel cells are microbial, enzymatic, and catalytic. Since the turn of the century, research on microbial fuel cells (MFCs) has exploded. Recently, there has been a lot of interest and in exploring anaerobic technology through microbial fuel cells (MFCs). Some of these microbial fuel cell types are still in the research stage and require further investigation for its commercialization. Many research work is ongoing on using bio-cathode materials in microbial fuel cells (MFCs). However, few restrictions on the concept would have hindered its implementation in an industrial setting. While these problems regarding engineering and research are still in their infancy, several novel experimental results have been generated to address them. Continuous experimental effort and evidence-gathering must be needed over the next few years for this integration notion to be generally accepted and implemented. Bio-cathodes are advocated for use in MFC to solve this problem and provide renewable power [1]. MFCs facilitate the transformation of electrical energy into the byproducts of microorganisms. The final electron acceptor at the biological cathode can be any number of substances, including transition metal complexes, inorganic salts, oxygen, and carbon dioxide. Multiple studies have demonstrated the importance of microorganisms in biological electron transfer, even if the underlying mechanism is still poorly understood. The bio-cathode has gained popularity due to its potential to harness microbial metabolism to produce useful industrial products while eliminating unwanted pollutants and its inexpensive construction and operation costs. Microbial fuel cells are a novel method of energy production also. They employ electrochemically active bacteria as catalysts to generate energy from various organic compounds [2]. MFCs can use microorganisms as catalysts instead of enzymes or inorganic compounds to convert chemical energy into electricity. In an MFC, a proton is transferred from the anode to the cathode across an ion exchange membrane (a cation exchange barrier or a proton exchange membrane) to block oxygen diffusion from the cathode site into the anode chamber [3]. The anode provides the microorganisms with an artificial, exogenous electron acceptor. Before arriving at the cathode, electrons go through a resistor or another electrically powered device. To keep the charge balance in the circuit, protons are transferred from the anodic chamber to the cathodic one via a proton exchange membrane. Protons and electrons join forces at the cathode to decrease the diffusion of an electron acceptor (like oxygen) over the membrane and into the circuit.

Most MFCs get their extract from biological cathodic and abiotic anodic chambers [1]. This technology has made it possible to convert the inherent chemical energy in organic and inorganic materials using electrochemical techniques [4,5]. It also has potential applications in wastewater treatment and bio-remediation of toxic chemicals [6]. Microbial gene editing and surface modification with nanomaterials have both been used by numerous researchers to boost MFC power generation [7].

The use of microbial electrochemical systems (MESs) has grown significantly in prominence recently as a possible method of producing bioelectricity. MFCs and microbial desalination cells (MDCs) are two examples of MESs that produce bioelectricity [8]. The built wetland system with vegetation and a microbial fuel cell (CW-MFC) fared better in terms of treatment efficiency than the unplanted system. The possibility of employing a vegetated CW-MFC system to accomplish sustainable wastewater treatment while concurrently generating renewable energy is demonstrated by the notable nutrient removal efficiencies and bioelectric power production, which will help to promote environmentally friendly waste management methods [9].

Studies have demonstrated the limitless advantages of adopting microbial fuel cells (MFCs) in modern scientific civilizations to convert organic waste materials into bio-energy through electrochemical processes aided by enzymatic-microbial influenced cathode and microorganism-catalyzed anode. Despite the undeniable advantages of this clean energy technology, a number of flaws that require further research have also been found. One important one is the requirement for

improved MFC cathodes in order to boost the production of bioenergy. Critical explanations of the existing circumstances and difficulties in applying MFC, together with the gaps that need to be addressed by researchers, were provided [10].

As an anode material, graphite flexible powder shows great potential due to its superior performance and up to 90% lower capital cost when compared to carbon felt. Although there is potential for using recycled chopped carbon fiber as MFC anodes, further work is needed to increase system stability and durability so that scale-up is possible [11].

The presence of hetero atoms on the carbon matrix, which enhances the stability of its surface chemistry, was discovered during the evaluation of the usefulness of activated carbon obtained from biomass as a cathode material. Because of this, the cathode surface can function in real-time scenarios without causing corrosion to the metal mesh collectors that are coated on it [12].

As discussed, many studies are currently being conducted on the use of bio-cathode materials in MFCs. However, few constraints on the notion would have prevented its commercialization. The literatures examined how the low power density of microbial fuel cells renders them unsuitable for industrial or commercial power generation. Despite several studies on MFC technology and operation, fuel cell materials, electron transport pathways relevant to power generation, and wastewater treatment have yet to be thoroughly investigated. The impact of bio-cathode materials in MFCs on electricity generation and wastewater treatment are the primary focus of this research. The review describes the essential structure of microbial fuel cell construction for a complete grasp of these types. This article examines cathodic restrictions in MFCs, current research into these limitations, and proposed solutions. Finally, the assessment suggested potential directions for the MFC concept.

2. Microbial fuel cell construction and design

Bioenergy systems are biological processes that produce electricity, hydrogen, or other valuable products from organic resources such as complex lingo cellulose or simple waste water [13]. Exo electrogens are charged particles created by bacteria outside the cell, and M.C. Potter was the first to identify them through his research and use of natural products.

The idea that the bacterial breakdown of organic matter generates electricity was proposed much later. Due to an electron-releasing bio-film, "Microbial Fuel Cell technology" [13] can simultaneously remove organic carbon from wastewater and generate sustainable bio-electricity. It is possible to use MFCs to clean sewage while also producing bio-energy from wastewater, which could reduce the costs of running existing wastewater treatment facilities [14]. A typical MFC setup separates the anode and cathode by a proton exchange membrane (PEM) in the anodic and cathodic chambers. Bio-catalysts oxidize organic substrates in the anodic chamber of a microbial fuel cell (MFC), releasing protons, electrons, and carbon dioxide gas. Electrons move from the anode to the negative electrode via an external circuit, whereas protons move from the anode to the cathode via a proton exchange membrane (PEM). Oxygen, charged particles, and electrons combine at the cathode to create water [15].

An MFC that cannot pollute the air or water provides energy and functions correctly [16]. Depending on the effluent content, an MFC can generate anywhere from 1.43 to 1.8 kWh/m³ of energy. However, its 0.024 kW of power consumption is far from the 0.3 kW required for anaerobic digestion. Compared to the activated sludge process, which uses 10 % more energy, MFC has more potential for providing renewable energy and treating wastewater cost-effectively.

More important than the bio-catalytic activity of an MFC are the materials utilized to construct it. An MFC creates electricity through the sequential actions of (a) microorganism catabolism of organic material, (b) anode electron capture, (c) cathode electron acceptor reduction, and (d) simultaneous proton transport from the anode to the cathode via PEM [17]. Due to the necessity of regularly sparging air into the cathode

chamber in this basic setup, the electricity cost of treating wastewater cannot be lowered [18]. Lui discovered that if the cathode is attached directly to the proton exchange membrane (PEM), atmospheric oxygen can react directly, causing the MFC to expand.

An anode chamber, a gas diffusion surface separating the cathode from the anode chamber, and a passive oxygen delivery route to the cathode comprise a single chamber unit. Unlike the more conventional two-chamber MFC, this setup did not require a separate, energy-intensive aeration stage [19]. Using spacers, the footprint of the Microbial fuel cell reactor can be reduced without sacrificing efficiency. Using 1.5 mm plastic spacers, the reactor could achieve an output of 97326 mW/m^2 , comparable to output without spacers. In addition, it was argued that power densities were reduced because oxygen could more easily enter the reactor when the spacer was 1.3 mm thick [20]. Ahn Y and Logan BE developed a single-chamber MFC using a carbon black fiber brush multi-anode and an air cathode [21]. A separator is linked to the bio-anode and wind cathode in a separator electrode assembly to decrease the design further with an efficiency of 85 % in columbic voltage. There is an 8-hour hydraulic retention time at a constant flow rate. It is well-known that continuously using a multi-electrolytic design can make it simpler to generate power and current. Later, a membrane-free cell (MFC) was combined with a device conceptually similar to a membrane bioreactor (MBR) to develop a hybrid MFC-MBR for treating wastewater and generating potable water [21]. Ren L et al. developed a microbial fuel cell (MFC) with an anaerobic fluidized bed cell wall reactor (AFMBR) for use in the lab. Another study was undertaken [22] to solve the issue of producing potable water from wastewater without much energy. TDS was nearly reduced with a 9-hour hydraulic retention time [22] after running the reactor system continuously with household sewage (total COD 21011 mg/L) at room temperature for 50 days. Wastewater with a COD concentration of 8720 mg/L and a peak energy density of 135.4 mW/m^2 was treated using a graphite electrode with 100 mM potassium Fe^{+3} catholyte, the results indicated that the concept might be scaled up to generate high power in a tiny footprint [23]. Under aerobic conditions, biocatalysts oxidize organic material, releasing charged particles into the anolyte. Increasing proton concentrations in the anode chamber diminish the operational stability of a two-chamber MFC. To solve this problem, researchers stacked single-chamber MFCs on each other and added a double-chambered MFC to form a hybrid MFC with a self-directed, PH-regulating stack. High output voltages and acetate conversion efficiencies were attained by hybrid stacking as compared to single cells [24]. Glass bead layers, a cathode, and an anode comprise the tubular MFCs. Fluid must first penetrate the anode from below to get to the cathode. The diffusion barrier between the electrodes provides the gradient necessary for MFCs to function effectively [25]. A two chamber microbial fuel cell is depicted in Fig. 1. Fig. 2 depicts a MBC-MFC hybrid

system.

3. Anode and cathode materials

The cathode material must be carefully chosen to maximize bacterial adhesion, electron transfer, and electrochemical efficiency in a bio-cathode microbial fuel cell. Most bio cathodes are made from carbon paper, stainless steel mesh, or graphite fold [26]. Cathode materials should have oxygen-reduction catalytic capabilities to improve MFC lifetime and bacterial adherence [27]. Materials for anodes and cathodes must be chosen with several factors in mind [28], including electrical conductivity, cost, availability, surface area, porosity, stability, and durability. Meanwhile, anodes should generally be biocompatible. Platinum-based catalysts can improve power generation; their high cost prevents their current widespread use [29]. Microbes at the anode of an MFC oxidize fuel anaerobically, producing electrons in the process. Electrons must move from the anode to the cathode via the external circuit to neutralize the oxidizing agent and generate electricity. Several electrode parameters can affect MFC performance [19]. These include biocompatibility, active surface area, excellent conductivity, and electrode surface features.

3.1. Components for Anodes

The effectiveness of an MFC is primarily determined by how well its anode performs. Therefore, the anode's components and design must be given top priority. Parametric properties of the anode, such as surface area, lifespan, chemical resistivity, and conductivity, significantly affect the efficiency of MFCs [30]. Synthetic nanomaterial, graphite powder, and wax (0.2 g) were heated at 50°C for 15 minutes to produce anodes [31]. Biofilm development and bacterial electron transfer to the electron acceptor are also profoundly affected by the anode material [28]. Carbon materials are widely used as anodes because of their high electric conductivity, adaptability in microbial cultures, large surface area, high micro-porosity, and catalytic activities. These are cheaper and more conductive [32,33]. When eight graphite anodes and a single cathode were used in a single-chamber MFC, the COD was reduced by 80% from the starting value [34], and the maximum power was 26 mW/m^2 . Anodically connected vertically produced multiwall carbon nanotubes generate 392 mW/m^3 of electricity [35]. Compared to using eight graphite anodes, the maximum current that could be generated when using eight graphite-felt electrodes was raised by a factor of 3. The maximal power density of anodes made from carbon fabric is 483 mW/m^2 [37]. In addition, carbon fabric is prohibitively expensive, limiting its widespread application. Carbon mesh anodes are much more cost-effective than carbon cloth, producing a power density of 1015 mW/m^2 [38]. The graphite/PTFE composite generated bioelectricity

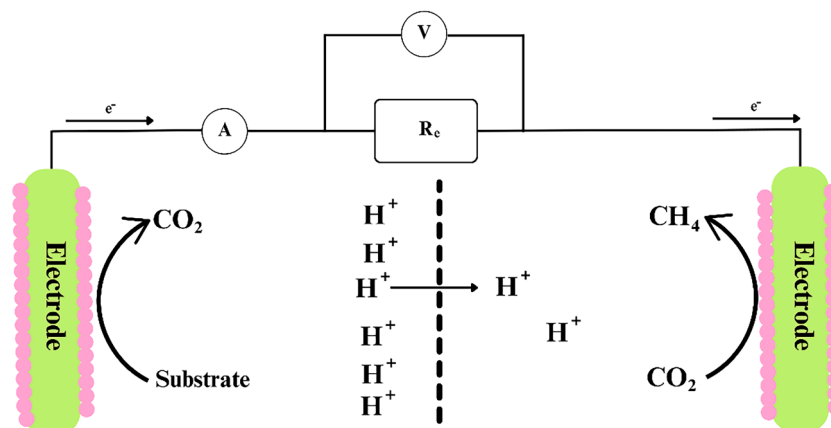


Fig. 1. A two-chamber microbial fuel cell.

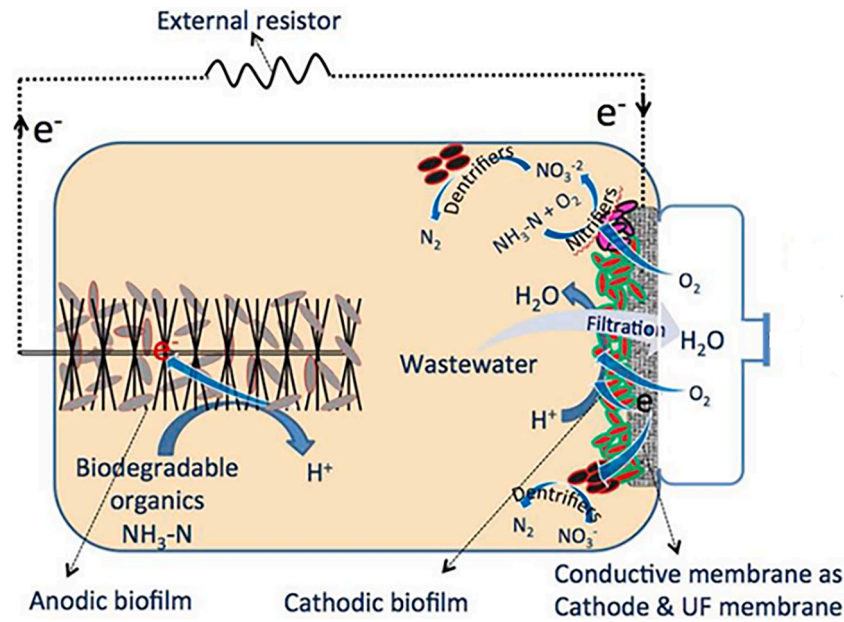


Fig. 2. A Typical MFC-MBR hybrid system.

with a power density of 760 mW/m^2 [39].

3.2. Components of a Cathode

An ideal cathode would have superior mechanical durability, excellent electrical conductivity, and powerful catalytic properties. Materials for the cathode can be based on carbon. However, they require an extra catalyst modification. Platinum is the most favored cathode catalyst because of its high efficiency, despite its practical application being debatable due to its high cost [19]. Aeration requires no additional energy in a cathode ray tube MFC because of the direct interaction with oxygen. Under the right conditions, MFC can also directly convert the chemical energy present in organic sources into electrical energy [40]. The majority of anode materials are also suitable for use as cathodes. Mechanical strength, electronic/ionic conductivity, and catalytic properties are all essential. Experiments have shown that a double-layered platinum-loaded/carbon cathode may produce up to 1610 mW/m^2 of power density [41]. Despite good power densities, Platinum-based cathodes are more susceptible to fouling when operated with minimal water [42]. At neutral pH, the power density of an iron phthalocyanine-Ketjenblack carbon cathode was 634 mW/m^2 , while the same circumstances with a pricey platinum catalyst only produced 593 mW/m^2 . An activated carbon air cathode achieved a maximum power density of 1220 mW/m^2 [43]. However, carbon-metal meshed cathodes offer an unexpected and beneficial air-based cathode option in a few different MFCs [19]. At the same time, transition metal-based macrocyclic catalysts are generally less expensive and can be used in large-scale MFCs [44]. Water is produced when protons and electrons are transferred to oxygen at the cathode. Necessary in this context is the oxygen reduction process (ORR), which, with the right cathode catalyst, changes oxygen into water. High catalytic performance for ORR has been the focus of all studies on low-maintenance, cost-effective, and easily fabricated cathode catalysts [45,46]. Table 1 compare some of the frequently used anode and cathode materials used in MFCs on their merits and demerits, Table 2. lists typical anode materials with their power densities and Table 3. lists typical cathode materials with their power densities.

4. Bio cathode components and materials

Fig. 3 depicts the configuration of a bio cathode MFC and Fig. 4

Table 1

Anode and cathode materials of MFCs and their merits and demerits.

	Materials	Advantages	disadvantages	Refs
Anode	<ul style="list-style-type: none"> graphite rod graphite filter brush carbon cloth carbon felt carbon paper 	<ul style="list-style-type: none"> High chemical stability and conductivity, relatively low cost, and simple accessibility superior focus and simple construction significant relative porosity extensive surface area simple wiring connector 	<ul style="list-style-type: none"> An increase in surface area is challenging Clogging comparatively pricey extreme resistance Fragile 	[30–34]
Cathode	<ul style="list-style-type: none"> Core-shell bimetallic gold-palladium alloy TiO₂ Graphene material 	<ul style="list-style-type: none"> heightened toughness, Low resistance to bulk Strong electro-catalytic performance extensive surface area Eco-friendly 	<ul style="list-style-type: none"> If carbon nanotubes are to become stable cathodes, more research must be done. Week-to-week, pricey catalyst Not as durable as carbon cloth coated with Pt, and pricey Pricier than nickel and stainless steel 	[35–37]

depicts the mechanism of it. Energy output and COD reduction are the foundational metrics for evaluating MFC effectiveness. Wastewater is known for its potential to generate significant levels of power while simultaneously reducing chemical oxygen demand (COD) and nitrogen (N) [47–49]. Microbial fuel cell-powered bio cathode sensors can be used to monitor water quality autonomously. However, significant electrode potential change occurs when the MFC-powered bio cathode detects changing analyte concentrations, reducing sensitivity and accuracy [50].

Table 2
Typical anode materials with their power densities.

Anode Material	Power Density in mW/m ²	Refs
8 Graphite anodes	26	[34]
multi-walled carbon nanotubes grown vertically and nickel-silicid anode	392	[35]
8 Graphite felt anodes	3x26	[36]
Carbon cloth anode	483	[37]
Carbon mesh anode	1015	[38]
Graphite/PTFE composite anode	760	[39]

Table 3
Typical cathode materials with their power densities.

Cathode Material	Power density in mW/m ²	Refs
Platinum loaded double layered PDMS/carbon cathode	1610	[41]
Iron phthalocyanine - Katzenbach carbon cathode at neutral PH	634	[42]
Expensive platinum cathode at similar conditions as the cathode mentioned above	593	[42]
Activated carbon air cathode	1220	[43]

Because of their unique properties, electrode materials play a pivotal role in the MFC setup. Electors’ Standard requirements are low cost, chemical stability, conductivity, and durability. Electro catalysts must be compatible, have a high surface hardness, and provide efficient electron exchange between the electrode surface and the bacteria since bio-electrodes are microorganism carriers [51,52]. The conductivity and surface quality of bio-electrodes are the two most influential factors. The high mechanical strength of carbon material’s rough surface is excellent for biofilm growth [53]. However, due to its brittleness, bulkiness, and

high electrical resistance, carbon material may present challenges for the massive process by increasing electrode resistance losses. A combination of graphite and carbon was used to combat this issue, together with conductive metal current collectors like stainless steel mesh [54, 55]. The material and design are the two most challenging parts of creating a practical and inexpensive bio-cathode MFC. Several cathode materials have been explored and confirmed viable for use as a bio-cathode in MFCs, particularly carbon-to-metal bases.

4.1. Stainless steel as bio-cathode material

Bio cathode power densities of 0.06 W/m² are possible at 1.89 A/m². Three bio cathode materials (carbon paper, graphite felt, and stainless-steel mesh) were tested for their electrochemical performance in an MFC application by Zhang et al. [56]. For example, fuel cell sediments often use stainless steel as the basic material for metal-based bio cathodes. In a saltwater environment, a biofilm is formed on a stainless-steel cathode [57]. Graphite surfaces may have been more conducive to biofilm formation than stainless steel ones because bacteria settle more easily on surfaces with a significantly coarser roughness. According to the research, stainless steel’s essential property, as opposed to its surface roughness, is responsible for its increased current production compared to graphite. Stainless steel is an ideal bio cathode support material due to its superior electro kinetic characteristics compared to graphite in biofilm-driven reduction processes [53]. Using a stainless-steel mesh bio cathode mounted on an activated carbon-coated fabric electrode, the performance of sulfate-reducing bacteria was analyzed [58]. Adding the stainless-steel mesh improved the bio cathode’s performance above that of a bio-cathode made from active carbon fabric alone. The current can be increased by a factor of three, and power was increased by a factor of five. Biofilms grown on metal substrates in a saltwater environment and used as oxygen-reducing cathodes are more effective. Seawater

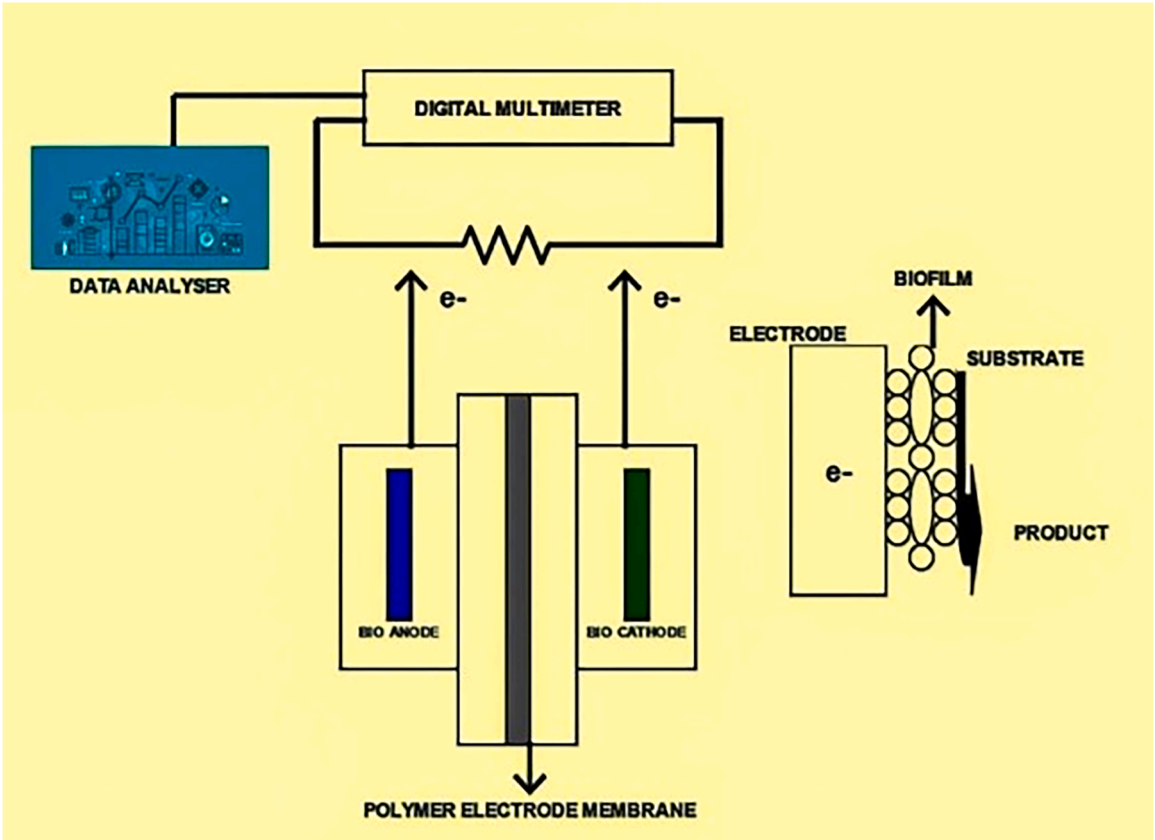


Fig. 3. Schematic of Bio cathode configuration.

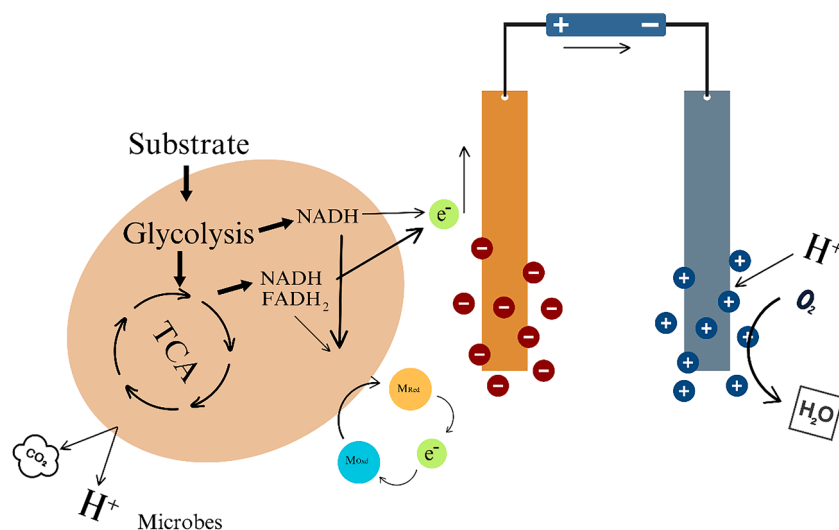


Fig. 4. Schematic of Bio cathode mechanism.

bio-cathodes assist in running high-salinity electrolytes despite microbial oxygen reduction catalysis being a significant source of sea aerobic corrosion [59]. The bio-cathode mesh made of stainless steel performed exceptionally well in MFC. Instead of a pricey membrane, it was tried to build an MFC out of *matkas* (earthen pots) [60]. This study used activated carbon flakes (CF/SM) as the bio-cathode in a stainless-steel mesh container. The CF/SM was made by fusing activated carbon flakes with a porous stainless-steel mesh. The cylindrical mesh container was opened at the top by its flat ends and made of stainless steel. Stainless steel mesh was employed as a current collector, while mesoporous carbon flakes were used as an oxygen reduction catalyst [61]. Among the three materials tested for use as bio-cathodes in MFC [26], the stainless-steel-based bio-cathode mesh was the most catalytically active, yielding the highest possible power and current densities.

4.2. Graphite/carbon as bio cathode materials

Bio cathodes in MFCs typically consist of flat materials such as carbon sheets, graphite plates, cloth, or felt. Carbon paper is significantly weaker than graphite plates. Although it's still quite thick, graphite felt is not as fragile as carbon paper. However, germs can cling strongly to carbon sheets and graphite plates due to their compact shape and smooth surface [62]. Graphite felt is more effective than carbon paper and materials made from stainless steel. Graphite felt and carbon paper was also tested frequently. Maximum power values were 8 W/m³ using granular activated carbon in a unit chambered MFC [63] to neutralize natural dye wastewater. Research showed that the granular activated carbon's high surface area made the MFC system's high activity possible. The benchmark is an effective alternative to platinum (Pt) and other chemical catalysts in boosting biofilm adhesion [64]. The surface area accessible for bacterial growth in MFCs is increased when carbon-based electrodes are used in dense arrays. It is most likely that granular graphite or carbon will be used as a bio cathode. Some of the most power was supposedly generated by a bio cathode MFC that used graphite granules as an electron donor. Freguia et al. employed graphite granules to boost cathodic oxygen reduction in a two-chamber MFC cell. The biofilm formed on the granular graphite cathode produced 110 W/m³ of electricity when operated continuously, and the process was stable for 9 months [65]. With their high porosity and extensive surface area, graphite brush electrodes seem tailor-made for bio cathodes since they facilitate microbial attachment and electron transmission. Additionally, Zhang et al. studied the polarization curve following 10, 50, 200, and 400 days of MFC operation to ascertain the impact of cathode type on MFCs' long-term productivity.

Compared to MFCs with abiotic graphite fiber brushes and carbon cloth cathodes, the MFC twin compartment with the bio-cathode performed better in the long run [66]. In a separate study, Zhang et al. used three methods: graphite granules (GG) and graphite fiber brushes (GFB), and both serve as bio cathodes in MFCs. Compared to graphite (73 W/m³) or graphite grains (73 W/m³) fiber brush, the MFC's Power density was approximately 99 W/m³ when GG-GFB was used as the bio-cathode foundation material combination. In addition, a FISH analysis showed a very dense bacterial population at 186 hours when the combined cathode materials had been improved. This result indicates that the combination technique can improve the electrode's overall area and surface properties, influencing bacterial growth and leading to a biological decrease in oxygen [67]. A different type of packed bio cathodic material was used in a study. Granular graphite, activated carbon, semi-coke, and carbon felt were used in its construction [68].

Graphite fiber was studied as a possible component in a novel method. Combining bio cathode MFC with a brush and other materials increases efficiency [69]. The electrode's physical characteristics change when various carbon compounds are applied to a graphite brush. The oxygen reduction process relies on bacterial growth and the catalytic process's efficiency, enhanced by adding components that increase porosity, microbial adsorption capacity, and specific area. The study found that the highest power output, pace of reducing chemical oxygen demands, and columbic efficiency all came from using a graphite fiber brush in conjunction with active carbon granules. A bio cathode MFC's performance can be enhanced by incorporating more carbon materials, as measured against a base electrode. Therefore, improving various cathode materials can significantly boost bio cathode MFC system performance generally [69]. Table 4 presents Biomaterials explored as anode and cathode support materials for MFC. The table gives the details the chamber design, source and substrate with the power density.

5. Electron transfer mechanisms

In a membrane fuel cell (MFC), electrons released by organic substances are transported to electrodes, where they are utilized to create electricity. Except for androphiles, bacteria cannot directly transfer electrons to the anode. Non-conductive lipid membranes, peptide-glycans, and lip polysaccharides are found on the outer layers of most microbial species [74]. Electron transmission and electrical output are strongly coupled, and high energy generation in MFCs systems relies on the conductivity of the biofilm. Ten years ago, much less was known about the physiological mechanics of electron transport. Mediators,

Table 4

Biomaterials as anode and cathode support materials for MFC.

Cathode materials	Anode materials	Power (mW/m ²)	Reactor design	Source or substrate	Refs
Granular carbon	Graphite rod	-	Double chamber	Salt acetate metabolically anaerobic sewage-related sludge disposal facility	[70]
Stainless steel	Pt	320	Double chamber	Biofilm seawater	[71]
graphite granules	graphite rod	-	two identical double chambers	acetate	[64]
carbon papers	carbon papers	50-214	Double chamber	Sludge and sediment	[72]
Stainless steel meshing/graphite plate	Stainless steel meshing	Graphite-20 Stainless steel meshing-4	Earthen pot	Sludge	[60]
Carbon cloth	Carbon fabric	103	Double chamber	Sludge	[73]
Graphite fiber brush embedded in graphite granules	Graphite fibre brushes	-	double chamber	topsoil	[66]
carbon paper, Graphite felt, stainless steel meshing	Graphite felt	33, 110, 3	Double chamber	Sludge	[26]

shuttles, pili-nanowires, and membrane-bound electrons are well-established mechanisms [75]. In indirect electron transfer mechanism, Scientists first zeroed in on yeast and other fermenting microorganisms due to their well-established pathways for producing energy. It was either explicitly stated or assumed that the reduced byproducts of microbial fermentation were oxidized at the anode surface to yield electrons. Some examples of these waste products are hydrogen, alcohol, and ammonia [76]. In direct electron transfer mechanism, when a bacterial cell membrane touches a cathode electrode, electrons are transferred directly between the two. Microorganisms' redox macromolecules, such as cytochromes, can immediately accept an electron from the cathode [77]. *Thiobacillus ferrooxidans*, an ano-cathophilic bacterium that forms a biofilm on the cathode and functions as an electron donor, is one such organism that has been the subject of research. To get the anode's endophilic bacteria to react appropriately, these organisms must alter the cathode's ability to create electricity [78]. In 1997, research by Hasvold et al. [79] showed that microorganisms at the cathode lowered MFC efficiency. They discovered that saltwater bacteria that lived on the cathode's surface produced slimes that helped reduce oxygen levels. Bergel et al. combined a Pt anode with a biocathode supported by stainless steel to create a one-of-a-kind, inexpensive cathode for oxygen reduction in fuel cells. The biofilm on the stainless-steel cathode generated up to 270 mW/m², while only 2.8 mW/m² was generated by a clean cathode [80]. In addition, Chen et al. revealed the electron transport method and the dynamic nature of the microbial community, finding that gamma proteo bacteria were the most prolific clone-forming bacteria in the sewage treatment cathode. Utilizing granular graphite as the anode and cathode, they determined the power density to be 2 W/m³ and 10 W/m³, respectively, utilizing nitrate and oxygen reduction. According to them, oxygen reduction is enhanced by the microbe near the cathode [81].

5.1. Artificial mediator

Artificial mediators are sometimes referred to as "electronic shuttles," this technology facilitates the transmission of electrons via synthetic intermediates. Condensed products are more electrochemically active than the other fermentation products because of the substances that bacteria use to generate them. These electron transporters typically transport electrons across cell membranes, pick them up from intracellular electron carriers, and then discharge them at the electrode [82]. Due to their inefficient electron transport across the cell's core metabolism, bacteria, including *Pseudomonas*, *Proteus*, *Escherichia coli*, and *Bacillus* species, need mediators in microbial fuel cells [74]. The most effective mediators are those that can easily cross through cell membranes, are inexpensive, have a high electrode reaction rate, are soluble in analytes, are not poisonous to bacteria, and do not biodegrade.

Some bacterial species can make extracellular electron transport mediators. To improve electron transport to Fe³⁺, this was initially postulated in *Shewanella oneidensis* [84].

The biosynthesis of an electron shuttle is a highly energy-intensive process. Therefore, it must be recycled multiple times to compensate for the energy lost each time. Thus, the microbes responsible for their production are expected to have a competitive disadvantage in environments where the shuttle would be lost soon after being released. This may partially explain the preponderance of *Geobacter* species in low-Fe³⁺ sedimentary environments. Possible electron transport to electrodes using phenazine electron shuttles, which *Pseudomonas aeruginosa* may produce. Although certain bacteria can build an electron shuttle, their energy-generating capacity is severely constrained since they only partially oxidize their organic fuels [85]. Table 5 highlights the specific bio cathodic component materials along with their MFC arrangement, catalyst choice, power density and durability.

6. Biocathode materials for electricity production and wastewater treatment

6.1. Electricity production

MFC technology is exceptional because it can generate bioenergy from microorganisms on various substrates and with various supporting materials [86]. Even if the power needs of individual systems are low, this remains true. The goal is to use sustainable power in the long run but not compromise public safety and health [87]. Clytonbetin (2006) showed that despite the relatively large surface area needed, an MFC would be sufficient for cardiac stimulation if it could transfer 25mW of electricity [88]. MFCs primarily power and supply remote electrical systems with enough current and power. A work that used a stacked MFC built as a power supply successfully lit 10 LEDs and ran a digital clock [86]. When fuel molecules are oxidized, the resulting chemicals are converted into electricity without generating heat. The chemical energy in biomass can be converted into electrical energy using MFCs. MFC power generation is still poor because electron abstraction/idea speed is slow. Using reusable devices to store electricity before delivering it to end users is one solution to this problem [87]. In underdeveloped regions, MFCs can serve as supplementary, decentralized power sources. Renewable energy can be produced locally from easily accessible biomass. MFCs have the potential to be used in aerospace applications due to their ability to generate electricity and decompose waste [88].

6.2. Wastewater treatment

Sanitary wastes, food processing, swine, and maize stover wastewater include organic matter that can be biodegraded to release energy [84]. The first method presented for wastewater treatment was in 1991 [87–93], MFC technology offers many benefits. It can function as a

Table 5

Bio cathodic components parameters.

Cathodic component	Microbial fuel celled arrangement	Catalyst choice	Power density (W/m ²)	durability	References
Graphitic felt	Double partition	Anaerobic sludge	2.5	Up-to 3000°C	[26]
Carbon paper	Dual partition	Anaerobic feed	0.81	400 - 500°C	[33]
Graphitic felt	Flat plated double partition	Aerobic/anaerobic	14	Up-to 2800°C	[81]
Carbon paper	Dual segregation	Mixed culture	0.185	300°C	[26]
Stainless steel based	Earthen vessel	Oxidation ditch feed	1.67	1200°C	[2]
Carbon nano tubing	Double segregation	Anaerobic disposal	5.77	2800°C	[26]
Semi coke	Twinned chamber	Aerobic/anaerobic	20	600°C	[33]
Manganese embedded graphitic felt	Two chambered	Digestive disposal	32.2	2200°C	[70]
Actuated carbon	Flat plated dual chamber	Aerobic/anaerobic	24.4	800°C	[62]
Granular graphite	Dual partition	Topsoil feed	72.9	Up-to 2600°C	[81]

hydrogen fuel cell or an electric power plant. An effective treatment system must have high operational sustainability and low material costs [92]. Studies show that nitrogen and organic compounds in leachate can be effectively removed through biological treatment [93,94]. High-strength waste waters are appropriate for anaerobic digestion operations with longer retention times because they may produce both power and methane from debris. Effective methods for removing sulfides from wastewater using MFCs with certain microbes were demonstrated by Rabaey et al. in 2006 [91,95]. It has been reported that the coulombic efficiency can approach 80% under optimal conditions (wherein up to 90% of the COD is removed) [92,96,97,98]. Scientists found that MFC's power output and CE decreased at lower concentrations after removing the salt from selenium-containing wastewater. Kim et al. [99] demonstrated that as electricity output grows toward the maximum 228 mW/m², odor removal improves with MFC-based technology. Biofuel cells were shown to be effective in treating biodegradable organic waste and generating power from landfill leachate. The removal rate of organic matter was 8.5 kgCODm³ d¹ when the energy capacity was 344 mWm³. It was recently reported that a novel MFC-membrane bioreactor for wastewater treatment could achieve a maximum power density of 6.0 W/m³ with an average current of 0.4 to 1.9 mA and good pollutant removal performance [92], thanks to its high biomass preservation and solid rejection.

7. Technical hindrances and limitations

One potential drawback of using microbial cells is that they might not provide enough power to maintain a portion of the system constantly operational [100]. The high price of the electrode materials and the difficulty in expanding MFC to connected industrial capabilities are also causing concern [101]. The poor power density and inability to produce enough electricity to fulfill everyday needs make the widespread implementation of MFCs challenging. Biofilm formation is hampered by the decreased electrode surface area available for microbial growth [102]. Most challenges in creating a high-performance MFC stem from the cathode materials and combinations [103]. Commercialization of MFCs is hampered by the high price of the cathode/anode and membrane materials required for scaling up [104]. MFCs are ineffective at low temperatures because microbial reactions are too slow [105]. Problems with industrial-scale biofuel production include research and development, regulatory constraints, industrial systems, raw material quality fluctuations, seasonal factors, storage costs, and other related issues [106]. Limitations in charge transfer, surface area, catalytic activity, and cost at the electrodes have slowed the progress of MFC technology [101].

8. Future directions

There is a pressing need to investigate and develop clean alternatives to fossil fuels, such as biofuels and fuel cells [100]. Researchers and scientists must improve MFCs to produce more power for practical applications. Since locally manufactured electrode materials have

improved charge transfer characteristics, durability, and surface area, further research is needed to construct effective MFC electrodes [101]. For biofuel power generation to become mainstream, related businesses must improve their standards and regulations [106]. More investigation into different cathode materials and combinations is needed to create high-performance MFC. Finding the optimal operating conditions for MFCs that use bio cathodes to enrich a more significant number of viable species [107] is an important area of research. Scientists must determine how to construct industrial-scale MFCs with high power output and stable performance [108]. According to several research, adding additional carbon materials can improve the performance of a bio cathode MFC as compared to a base electrode. Thus, enhancing different cathode materials may greatly improve the overall performance of bio cathode MFC systems. This finding suggests that the combination approach can enhance the electrode's surface characteristics and total area, which will affect bacterial growth and cause a biological drop in oxygen. Efficiency is increased by combining bio cathode MFC with a brush and other materials. It is clear that in order to improve performance and identify the optimal material combinations, an increasing number of materials and their combinations must be investigated.

One of the newer technologies in current trend is the sediment microbial fuel cells (SMFC). In the face of energy constraint, SMFCs are thought to be a very economical and ecologically beneficial electrochemical device. SMFC offers a lot of potential for advancement in sediment remediation as it can produce a constant current while breaking down water contaminants. Nevertheless, there are other obstacles in the way of SMFC's actual use. The use of SMFC was restricted by low electrical power and a small clean-up area.

Another promising scope in MFCs is to device a prominent experimental structure. Emerging Bio electro chemical systems (BES) are promising sustainable solutions for resource recovery and energy generation. The metabolic pathways and the electrode-microorganism interactions determine how well these technologies work. Since biofilm development and stability, as well as effective electron transmission, are the primary elements responsible for BES efficiency, significant research efforts have been undertaken to enhance electrode biocompatibility in order to reduce the ohmic resistance. Another promising experimental procedure is bio electro catalysis. By using materials generated from biological systems as catalysts to catalyse the redox processes happening at an electrode, the multidisciplinary study subject of bio electro catalysis combines bio-catalysis with electro catalysis. The advantages of electro catalysis and bio catalysis are combined in bio electro catalysis. High activity, high selectivity, broad substrate range, and benign reaction conditions are some of the benefits of bio catalysis. High energy conversion efficiency and the potential use of renewable power as an electron source are two benefits of electro catalysis [83].

9. Conclusion

One of the most modern approaches to producing energy from different substrates is using MFCs. The possibility of producing sustainable energy from various substrates, such as organic wastes, has

recently prompted an uptick in research into this subject. Using organic and inorganic substrates that can be effectively converted to power from domestic and industrial wastes (such as wastewater from breweries, paper mills, and sugar processing) would be a cost-effective solution to the energy problem. The bio-cathode made of stainless-steel mesh has also shown outstanding performance. Therefore, several different setups and selective modes have been developed to maximize the MFC while working around its drawbacks. MFC is a promising technology for waste water treatment and carbon-free energy generation. Different microorganisms are used to build different kinds of MFCs for waste water treatment, energy generation, and other purposes. However, there are a number of restrictions that limit this technology's viability. Improved electricity generation and cost reduction are examples of limitations that will be overcome by technical innovation. Recent developments in MFC have made it possible to produce bio hydrogen, clean wastewater, remove toxins, and use it for a variety of purposes. The large-scale, successful building is still a constraint, though. In wastewater treatment, carbon sequestration, bio-hydrogen production, green power generation, and environmentally sustainable wastewater treatment, the coupling technology with MFC may become a new treatment mode. In particular, the coupling of MFC with anaerobic fermentation will be a better option. Lastly, the advantages of MFC cannot be fully realized with the existing coupling mechanism. It is envisaged that future study may further increase the functionalities of MFC and open up a new and trustworthy way for wastewater purification and electricity production. More research and development are needed to optimize the MFC configuration to mitigate the over potential of MFCs on a large scale. Transition metal macrocyclic catalysts are less expensive and can be used in industrial MFCs to solve this issue. Improving MFCs' compatibility with bio-cathodes is a primary area of study. Making high-performance MFCs is challenging due to issues with materials and cathode designs.

CRedit authorship contribution statement

S. Baskar: Data curation. **J. Jayaprakash:** Writing – review & editing, Writing – original draft, Conceptualization. **Raman. A:** Funding acquisition, Formal analysis. **T. Surulivel Rajan:** Methodology. **J Aravind Kumar:** Investigation. **Nalini Ramachandran U:** Supervision. **Balaji E:** Resources. **Padmanabhan Sambandam:** Writing – review & editing, Project administration. **Jisha PK:** Validation. **M. Ruban:** Visualization.

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.

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Data availability

All data are available within the manuscript only.

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