

Review

Emerging Trends in fabrication and modification techniques for bioelectrochemical system electrodes: A review



Rizwan Khan, Sudipa Bhadra, Soubhagya Nayak, Anagha Bindu, Ashish A Prabhu,
Surajbhan Sevda*

Department of Biotechnology, National Institute of Technology Warangal, Warangal-506004, Telangana, India

ARTICLE INFO

Keywords:

Anode electrode
Cathode electrode
Modified electrode
Bioelectrochemical system
Bioremediation

ABSTRACT

Background: Bioelectrochemical systems (BES) are specialized systems that can convert chemical energy into electrical energy using bacteria as catalysts. Electrodes play an important role in electrical energy transfer through electrochemical reactions. Electrodes are selected based on their physiochemical properties to enhance biological reactions. In microbial fuel cells (MFC), the anode is crucial because electrogens adhere to its surface and produce electrons and protons. These electrons and protons are absorbed by the cathode surface to generate bioelectricity. Numerous substances, like carbon based, metal based, conductive polymers and gas diffused materials, can be used as anodes and cathodes.

Method: To improve their physiochemical properties, conductive polymers such as polypyrrole (PPy) and poly-aniline (PANI) are combined with other substances. In MFCs, both anode and cathode are important components. In anodic location, oxidation occurs, which produces electrons and protons. A reduction reaction produces molecules of water at the cathode location. Various materials can be utilised to create cathodes and anodes. Materials such as carbon based, CC, graphite and metals can be utilized to create anodes. Materials based on carbon, such as CC, carbon black, and so on, as well as materials based on metal and gas diffusion can be employed to create cathode. The electrode's surface material layer is created using electrode manufacturing techniques. Screen printing, electrochemical deposition, and chemical vapor deposition are the most commonly used methods. Applications for BESs are numerous and include bioremediation, biosensors, MFCs, and microbial electrolysis cells (MECs). Various waste products are used in anodic chambers of MFCs to create electrical energy. Methane, green hydrogen, formic acid, hydrogen peroxide, and other value-added compounds are produced by MECs, a modified form of MFCs. Toxic contaminants in BESs can be removed and transformed into products with increased value using bioremediation. Biosensors are essential tools for physiochemical parameter monitoring in real time in the current world. MFC is regarded as a biosensor for contrasting the energy generated with many other factors.

Significant Findings: This paper mainly focuses on the different materials of electrodes that are being used and fabrication techniques that enhance the productivity of electrodes in BES to reduce the organic waste load and generate bioelectricity.

1. Introduction

In the era of 21st century, as increasing in population exponentially the resources are reducing. The food and fossil fuel requirements are increasing day by day, and resources are depleting, i.e., crude oil, coal, and natural gases. These fossil fuels lead to a large amount of CO₂ emissions. The research shows that CO₂ emissions increased in 2019–2020, 2021, by 2%, 7.9%, and 1.5%, reaching up to 36.1 GtCO₂.

In 2020, CO₂ emissions were reduced due to the pandemic's continuous lockdown [1].

Coal has been the main source of electrical energy for many decades in India and other countries. Conventional oil, like crude oil, condensate, and natural gas liquid, is the major liquid fuel on which vehicles are dependent. These conventional oils are also depleting, and they are expected to last until 2050 [2,3]. The annual energy demand is around 13.5 terawatts worldwide and is increasing every year. It is estimated

* Corresponding author at: Department of Biotechnology, National Institute of Technology Warangal, Warangal, 506004, India.
E-mail addresses: sevdasuraj@nitw.ac.in, sevdasuraj@gmail.com (S. Sevda).

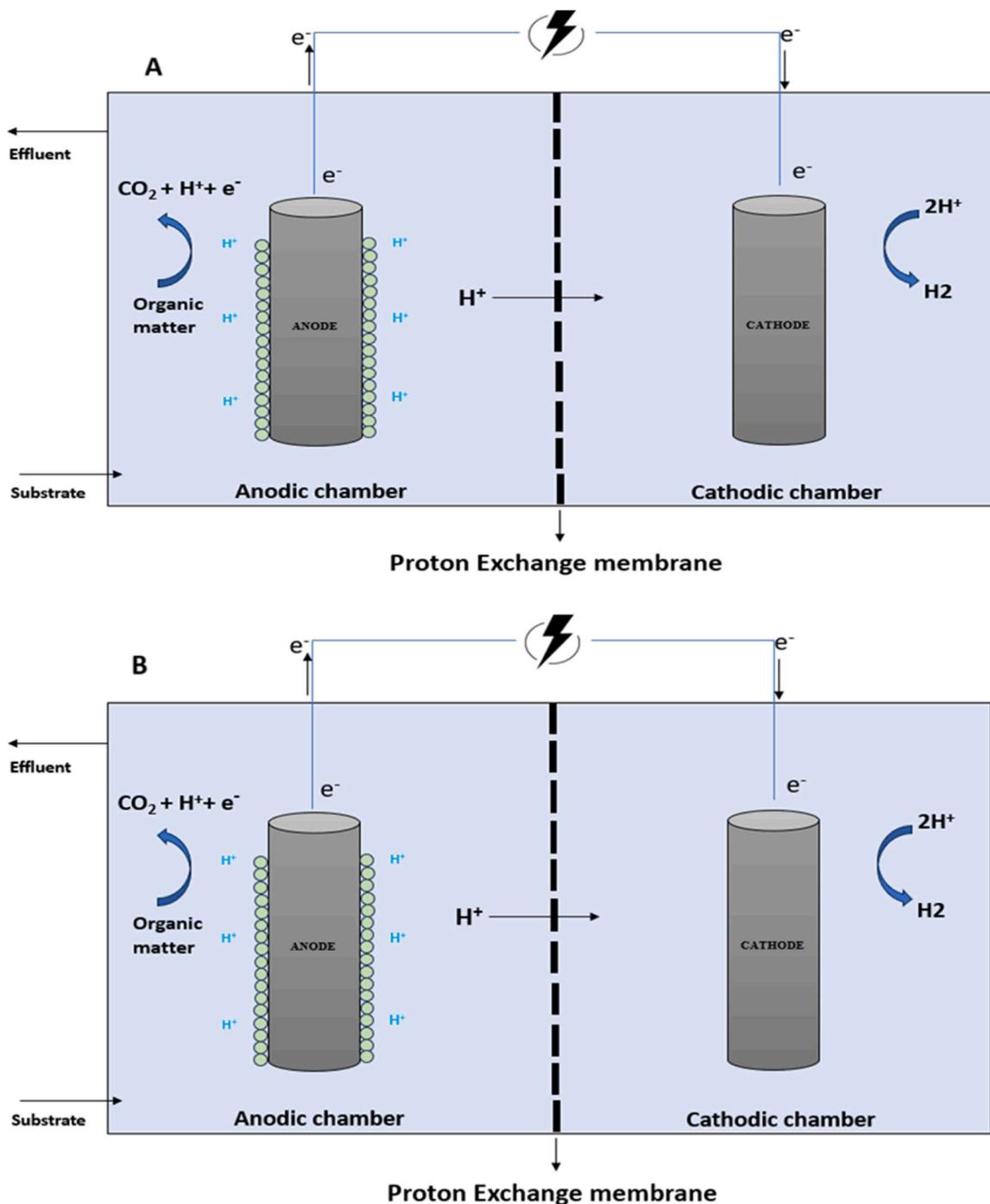


Fig. 1. Schematic diagram of (A) MFC and (B) MEC.

that in 2050 it will reach 23 TW. As per the scenario, due to the limited source of energy, we need a source that is economical, eco-friendly, and unlimited [4].

In this review, the focus is mainly on various materials for electrodes like anodes and cathodes. Electrodes play a major role in electrochemical reactions to reduce the organic load in waste. There are several kinds of materials which can be used in BES as electrodes. Traditional electrodes that are being used in BES systems face issues regarding low electricity generation, corrosion, less biocompatibility, chemical and physical instability, low bacterial adhesion which decrease the efficiency of BES. In this review, we discussed various electrode fabrication and modification techniques by which the mentioned problems can be solved. BES has various applications, like MFCs, MECs, bioremediation,

and biosensors. At the end of the review, the future and perspectives were discussed.

2. Bioelectrochemical systems

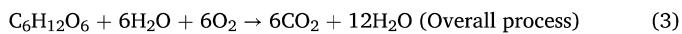
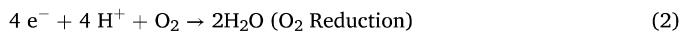
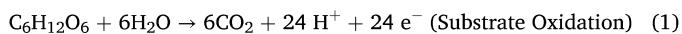
A BES is a system in which chemical energy is converted into electrical energy using microbes as a catalyst [5]. These microbes catalyse the biochemical reaction in which organic waste matter becomes a soluble compound. These organic wastes include waste water with low strength collected from sewage plants and lignocellulosic biomass mainly collected from agricultural wastes [4]. BES consists of MFCs, MECs, microbial electrosynthesis, enzymatic fuel cells, microbial solar cells, plant microbial fuel cells, and microbial desalination. The use

BESs, an innovative and sustainable technology for simultaneous energy production and wastewater treatment, has significantly increased in the past decades. Additionally, BESs have a distinct opportunity for the use of microbes in the clean and effective production of high-value compounds as fuel [6].

In the past decade, research on BES has increased rapidly. BESs mainly work on the principle of redox reactions, in which an oxidation reaction occurs on the anode and a reduction reaction on the cathode creates a potential difference that can cause the continuous movement of electrons from a low potential to a high potential. This flow of electrons through an external circuit is measured as electric current. The BES consists of two bioelectrodes, which are a biocathode and a bioanode, with microorganisms that generate electricity. In summary, BES are in vogue, developing quickly, and a wide range of applications involving various electron donors and acceptors have already been established [7]. BES can be classified into two categories: MFC and MEC. Electroactive microorganisms are used in MFCs to transform chemical energy into electrical energy. In MFCs, the proton exchange membrane (PEM) works as a barrier between the anodic and cathodic chambers to prevent oxygen migration from the cathode to the anode. Fig. 1. (A) shows the construction of MFC.

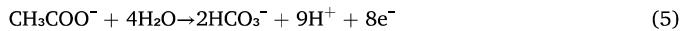
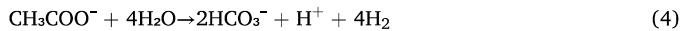
PEM facilitates the passing of only H⁺ or other cations across the membrane from the anode to the cathode. The two electrodes are simultaneously connected by a conductive substance to complete the external circuit. Organic and inorganic substrates are utilised as electron donors in the anode chamber and are then oxidised by bacterial consortia connected to the anode. The reduction process (often O₂ reduction) occurs when the electrons travel to the cathode.

The anodic and cathodic overall reactions that take place in the chamber are given below. (1)-(3)



Like MFCs, which produce electricity via the metabolic processes of microorganisms on organic substrates, MECs produce hydrogen through the application of an external potential to renewable biomass and wastewater. Single-chamber and double-chamber. There are two different types of MEC, which contain two electrodes, i.e., the cathode and the anode, which are separated by a membrane. Similar to the MFC, exoelectrogenic bacteria in a MEC transform organic matter (oxidise it) at the anode to CO₂, H⁺, and electrons, as shown in equations (4) and (5) and in Fig. 1 (B).

With the help of an external potential difference, these electrons are moved from the anode to the cathode through the external circuit [8]. According to eq. (6), hydrogen ions are reduced at the cathode.



In various life forms, electron transfer is the main component for processes like metabolism and respiration pathways, as well as for microbes. To enhance their energy uptake, microorganisms use the terminal electron acceptor with the highest potential available to transfer the electrons gained from the electron donor. When there is a lack of electron acceptors in the surrounding environment, they proceed to fermentation metabolism or make use of insoluble solid electron acceptors. In the latter scenario, bacteria use processes known as extracellular electron transfer (EET) to move electrons outside of the cells in order to perform the ultimate reduction reaction. Similar to this, in settings where soluble electron donors are scarce, microbes can also oxidise insoluble electron donors with EET. In natural settings, microbes use big organic molecules or solid minerals as electron acceptors or

donors.

The microorganisms permit the flow of electrons from an electron donor to an accessible electron acceptor in order to perform electron transfer to the cathode surface. Microbes must move electrons out of the cell for this reason via an external electron transfer mechanism, which is carried out via two main pathways [9]. In the indirect mechanism of BES, a mediator plays an important role in the electron transfer process. The system is operated in anaerobic conditions so that bacteria consume the substrate, catabolize it, and release electrons, reduced protons, and acids in order to generate the end product. An external mediator that can switch between the fermentative bacteria's anode and cell membrane is added to an indirect MFC system [10]. Mediators can enter the bacterium cell by reducing agents (reduced cytochromes, NADH, or NADPH) in their oxidised form inside the cell. In addition to being cell-permeable, the reduced mediator can diffuse from the cells to the electrode surface (anode), where it is oxidised electrocatalytically. Once mediators come out of the cell and are oxidised, they are free to repeat this cycle [11]. There are a few examples of mediators that are generally used: benzylviologen, 2,6-dichlorophenol, thionine, and 2-hydroxy-1, 4-naphthoquinone [10]. In a direct mechanism, the electrons are transferred via electrogens in bacteria without the help of a mediator in MFC. These electrogens capture electrons that are released by the organic material's oxidation and transfer them directly to the anode. The direct electron transfer method is further divided into three pathways. 1. Cytochrome-mediated 2. Nanowire 3. Electron shuttles or soluble mediators. In this mechanism, biofilm forms around the surface of the anode, which enables direct transfer through pili, nanowire, or cytochrome C. On the bacterial membrane surface, C-type cytochrome is present, which is a redox protein that aids in the electron's transmission to an external TEA (terminal electron acceptor), such as the MFC anode. These C-type cytochromes are multi-heme proteins that possess a redox potential range of almost volts and exhibit reasonable stability against chemical modifications. With these benefits, it is clear that C-type cytochromes play a crucial function in moving electrons from the inside of the cell to an external TEA [10]. CymA is an important example of CTC, which has N and C terminals in which the N terminal is tendered towards the inner membrane while the C terminal opens to the periplasm. CymA connects the inner membrane to the periplasmic area, which is why it is an important electron channel. It is a crucial part of anaerobic respiration and may interact with numerous terminal reductases, including fumarate reductase and nitrate reductase. In an experiment, observations have revealed that the inactivation or deletion of CymA leads to a drastic reduction in the current generation by approximately 80% [12].

Gram-negative bacteria secrete substances known as electron mediators, or shuttles. They encourage power production in MFCs [13]. These mediators should ideally have a redox potential that ranges between the anodic material and the bacterial membrane protein and be soluble, stable, reusable, and environmentally benign. A famous electron shuttle in MFCs is flavin, which Shewanella species manufacture on their own. They are mostly composed of flavin mononucleotide (FMN) and riboflavin (RF) [14]. These two flavones have distinct qualities and attributes. The outer membrane can allow FMN to seep through, and once it does, it changes into RF in the extracellular area. There is no way for the changed flavin to re-enter the periplasm. In the absence of a mediator, the electron transfer rate is incredibly low [15].

3. Electrodes in BES

Electrodes are an important part of the bioelectrochemical system, which is responsible for electricity generation through electrochemical reactions. So, it is crucial to identify the physicochemical characteristics that favour these BES in terms of performance. Based on these physicochemical characteristics, electrode materials are selected in order to achieve high electrical potential in wastewater treatment [16]. For it to be a good electrode material for BES, it should have good electrical conductivity, be stable chemically and mechanically, be inexpensive,

Table 1

Shows the comparison for anode material in BES.

S. No	Anode material	Anode modification	Cathode	PEM	Energy recovery	COD %	Reactor Configuration	Microbes/Inoculum source	Reference
1	Carbon cloth	Ammonia treatment	Carbon cloth	NA	1970 mW/m ²	NA	Single chamber	Domestic wastewater	[27]
2	Carbon mesh	Ammonia treatment	Carbon cloth	NA	992 mW/m ²	NA	Single chamber	Domestic wastewater	[30]
3	Carbon veil	Activated carbon powder	Activated carbon	NA	21.1 W/m ³	13.5	Single chamber	Anaerobic Activated sludge	[32]
4	Carbon felt	MnO ₂ coated	Carbon cloth	NA	615.2 mW/m ²	93.4	Single chamber	Municipal Wastewater	[34]
5	Graphite sheet	NA	Carbon paper	Nafion 112	2249 mW/m ²	NA	Dual chamber	<i>Escherichia coli</i>	[41]
6	Graphite rod	NA	Graphite rod	Nafion 117	7.74 W/m ²	50	Dual chamber	Aerobic sludge	[42]
7	Stainless Steel	PANI	NA	NA	167±7mW/m ²	NA	Single chamber	NA	[53]
8	Stainless steel	PANI	NA	NA	1190.94 mW/m ²	NA	Single chamber	Anaerobic granular sludge	[55]

and be capable of efficient electron transfer at the microbe-electrode contact. The degree of bacterial adhesion, bacterial growth potential, and electrode performance are all governed by the physicochemical parameters of the electrode [17]. Various types of electrodes were used in BES. Biofilms on the electrode surface are typically where microorganisms in bioanodes thrive. Since conductive pili and/or electron shuttles enable microorganisms to transmit electrons to the electrode at a distance of up to 40–50 mm, their synthesis is crucial for the development and operation of the biofilm.

Pili is thought to be essential for increasing biofilm thickness, which is considered an important part of anode performance because it correlates with the amount of active biomass that may use the electrode as the electron acceptor. Pili may also play a role in the structural support of anodic biofilms. The biomass densities in bioanodes are 20–40 times lower than the biomass densities seen in anaerobic reactors and can range between 10 and 20 g cell dry weight (CDW) L [18]. The performance of bioanodes is anticipated to be significantly improved by increasing biomass densities compared to those observed in other biotechnological applications. However, assuming reactor losses are not limited, larger biomass densities will just lead to a current generation [19].

3.1. Anode electrodes

In an MFC, the anode is the main component on which biofilm is produced by the growth of bacteria on its surface. These biofilm bacteria consume the substrate, decompose it with several metabolic reactions, and generate electrons and protons. Electrochemically active microorganisms (EAMs) in a bioanode oxidise electron donors (substrates), i.e., remove electrons from them, and then transfer these electrons to the electrode by a variety of electron-transferring mechanisms [20]. Those generated electrons are transferred to the cathodic site with the help of the given circuit, and those generated protons are transferred with the help of a membrane known as the PEM. These electrons and protons are taken into the cathode chamber. In the cathodic chamber, protons and oxygen, which came from the surrounding environment, combine to make molecules of water [21]. One of the latest techniques used for the transport of electrons is using microbial nanowires. These nanowires, also known as pilus, are present in bacteria; they were shown to be electrically conductive by employing the bacteria Geobacter sulfurreducens to reduce iron oxide. These pili are connected to membrane-bound cytochromes on the bacterial surface and permit electron transport to TEAs that are separated from the bacteria physically. As opposed to pili and flagella, which are homopolymers made up of a single subunit, nanowires are made up of several cytochromes as well as periplasmic and outer membrane proteins. Nanowires, which are a collection of pili-like outgrowths with a radius of 1.5–2.5 nm, are present in the low agitation regime, diffusion limiting regime, and/or

electron acceptor limiting regime of the *S. oneidensis MR-1*. Recently, it has been noted that *S. oneidensis MR-1* nanowires are extensions of the periplasm and outer membrane [22]. Anode material provides a good habitat for the bacterial population in order to perform an oxidation reaction, which is why anode material is more significant. As per studies, modification of anode material is more important than cathode material in order to enhance the performance of MFCs. However, a number of problems make the anode material selection criteria challenging, such as cost, availability, and stability for a long time. There are several properties of anodic material that are responsible for achieving performance in MFCs, like material surface area, biocompatibility of material, electrical conductivity, material stability and durability, and material availability and cost [21]. An ideal MFC anode electrode should have a high specific area, be highly conductive, biocompatible, and stable both chemically and physically [23]. There are various materials which can be used as anodes, which are mentioned in Table 1.

3.2. Material for anode

3.2.1. Carbon based material

Carbon is a rich element in nature that possesses several properties, like having inexpensive, having good chemical and thermal stability, having high conductivity, being good biocompatibility, and having fine electron transfer. graphite rod, graphite fibre brush, CC, carbon paper (CP), carbon felt (CF), and reticulated vitreous carbon. Some common carbon materials for anodes are CF, rod, fibre, cloth, mesh, paper, activated CC, glassy carbon, brushes, reticulated vitreous carbon, and graphite (block, felt, 3D graphite, graphite oxide, and granular graphite [24].

CC is a common anode material in MFCs, which is a carbonaceous substance. This substance ensures a large surface area and a comparatively high porosity while also showing strong electrical conductivity, mechanical strength, and flexibility when constructing more intricate 3D structures. The disadvantage is that the expense is typically rather expensive [25]. A carbon substance with a large surface area and an ideal area-to-volume ratio, CBs are very intriguing. CBs connection with titanium ensures their electrical conductivity. Most CBs are used as anodes, and current research is aimed at lowering their price [26]. CC is used in MFCs, which are treated with ammonia gas and phosphate buffer in order to enhance power generation. Untreated CC charges the electrode (from 0.38 to 3.99 meq/m²). The power was generated at around 1640 mW/m² (96 W/m³) using phosphate buffer and further to 1970 mW/m² (115 W/m³) using an ammonia-treated electrode [27].

Carbon mesh (CM) is easily accessible and affordable priced at the commercial level, but it has weak mechanical stability and low electric conductivity, which makes it less durable. In order to create 3D electrodes with a huge surface area, CM could be folded [28]. CM as a less expensive alternative to CC and CP materials as an anode electrode in an

MFC, Wang et al. discovered that in order to get good MFC performance, the CM has to be pre-treated (using heat, acetone, high temperatures, or an ammonia-gas process) [29]. A modified carbon is used for higher power density by heating it in a muffle furnace at 450°C for 30 min, producing a maximum power density of 992 mW/m² (46 W/m³). This was 3% more power than what was produced with a mesh anode that had been cleaned with acetone (893 mW/m²; 45 W/m³) [30].

Carbon veil, a low-cost carbon material with reasonably strong electric conductivity and a highly porous structure, is used as the anode electrode in order to increase the efficiency of energy production in MFCs. Although the single-layer carbon veil is quite fragile, it is versatile and may be folded to create a 3D anode electrode [31]. A MFC was constructed in which carbon veil was modified with activated carbon powder and 37.9 mW in comparison to the control (21.4 mW) and 13.5% COD reduction [32].

CF is one of the most commonly used materials as an anode. Both its porosity and electrical conductivity are high. Its cost is comparatively low, and depending on the material thickness, its mechanical stability is excellent [33]. A modified CF coated with manganese dioxide developed for MECs using the electrodeposition method is considered to have high electron transfer, enhance biofuel production, and dramatically lower MECs' costs. Organic wastewater treated using sludge CF has a higher power density (615.2 mW/m²) and lower power loss (5.4%) than that of a non-carbon (NC) electrode in long-term operation [34].

Carbon fibre brush is a material that provides a large surface area for microbial fuel cell to generate bioelectricity when used as an anode [35]. Metal-organic frameworks, or MOFs, are crystalline, have a large surface area, and come in a variety of morphologies. MOF performed admirably in a range of energy conversion and storage systems. A carbon fibre brush modified with Zn-MOF was constructed using a straightforward hydrothermal method. The produced electrodes were examined as a potential anode for MFC based on yeast. Maximum current and power densities of 317 mA/m² and 73.7 mW/m², respectively, were shown by the MFC using Zn-MOF carbon fiber brush, which are twice as high as those achieved utilizing brush anodes made of pure carbon [36].

3.2.2. Graphite based material

Graphite is made up of carbon and has a crystalline solid form with a SP2 hybridization structure. Graphite is a suitable material for bi-electrodes in MFCs because of its high stability and conductivity. Graphite has different forms, including rod, felt, sheets, and brushes used as bioanodes [37]. As anode electrodes for MFCs, graphite plates, rods, paper, cloth, granules, and brushes are typically more effective than ordinary carbon [38]. A novel graphite material sheet is highly flexible and conductive and made up of carbon fibre, carbon nanopowder, and graphite. In comparison with other carbon materials, it can be cut into desirable shapes and has good mechanical strength [39]. Additionally, as a carbon material, it is cost-effective and has good biocompatibility. As a result, it may be suitable for use as an anode material in MFCs with real-world applications. The performance of a dual-chamber MFC running with a GTS anode has been investigated for the first time in this work, which used graphite brushes as anodes in MFC and 2400 mW/m² [40]. A novel graphite sheet was used as an anode material for high performance in MFC and 2249 mW/m² power density with *Escherichia coli* (ATCC 25922) as a culture in dual chamber [41]. A MFC constructed using graphite both as electrode and cathode with dual chamber and 7.74 W/m² power density achieved a COD reduction of around 50% [42].

3.2.3. Metal based anode

Generally, the carbon-based anode material in BES is costly and difficult to fabricate, and it loses its conductivity when used for scale-up applications. So, there is a need to find an alternative to anode material that should be inexpensive, easy to process, and have good performance. In BESs, several metal bioanodes have also been identified in addition to carbon-based materials. Metal has excellent electrical conductivity, high

mechanical strength, and is relatively inexpensive. It serves as a current collector in BESs and has been used in structural supports [43]. The effectiveness of several metals, such as gold, silver, copper, nickel, cobalt, titanium, and stainless steel, as anodes in MFCs was examined. These findings show that all metals, with the exception of cobalt and titanium, could produce extremely effective electrochemically active biofilm, indicating the significant potential of metal-based bioanodes as anode materials [44]. Metals like gold and silver and other precious metals are very expensive. When compared to other common metals, copper has reportedly shown greater power generation performance [45]. The electrochemical properties of the electrode change as a result of metal corrosion, and if the metal ions get dissolved in the electrolyte solution, it can cause harmful effects for microbes on bioanodes [46,47].

3.2.4. Stainless Steel based material

Stainless steel is cheaper and has better corrosion resistance than other metals, which have been discussed earlier. Stainless steel is simple to manufacture and has outstanding biocompatibility. Consequently, stainless steel bioanodes are employed increasingly frequently in BESs. Additionally, it has been noted that, particularly for some sediment MFCs (SMFCs), the number of microbes adhering to carbon anodes is less than the amount on stainless steel anodes.

Stainless steel has good electron transfer efficiency, so it can be used as a material for bioanodes [48]. In an experiment, the biofilm was developed on the surface of stainless steel in order to achieve good organic and inorganic waste removal as well as electricity generation. They successfully removed 95.6% of the nitrate and 92.4% of the COD, whereas at a hydraulic retention time (HRT) of 150 minutes and 100 external resistance, 4.25 W/m³ power density and 18.32 W/m³ current density were attained [29].

3.2.5. Conductive polymers and its composites

Conductive polymers are widely used in chemosensors and other electronic devices because of their high electronic conductivity. In order to achieve high electronic conductivity in anode materials, a lot of research has been done on conductive polymers in MFCs [49]. Recently, they have attracted greater attention for their work on changing the anode to enhance MFC performance. PANI, PPy, and the composite materials based on them are two of the conductive polymers that have been shown to be highly successful for enhancing bioanode performance in MFC [50].

Carbon nanotubes (CNTs) have excellent properties as catalyst supports in MFCs, providing good electrical and biocompatible properties. In comparison with carbon black, CNTs are more reliable for the rate of reactions in the fuel cell for the PEM. The literature review shows that CNN shows cytotoxicity against microbes by inhibiting their growth, which leads to cell death. That's why CNN is not suitable for use as anode material until it gets modified [51].

The PANi/CNT nanocomposite, which was created using in situ oxidative chemical polymerization, has significant contacts between the microbe and electrode during biofilm attachment, which enhances its electroactive properties. When it comes to mechanical and thermal stability, hybrid nanocomposite materials outperform their respective polymer components. Because PANi and CNT have strong π-π interactions and stabilised bonding, using PANi/CNT nanocomposite results in good electrical conductivity and environmental stability [52]. CNTs with a di layer can provide thermal, electrical, and mechanical properties. The CNTs are mainly single-walled CNTs (SWCNT) with a carboxyl group, multi-walled CNTs with a carboxyl group (MWCNT-COOH), and multi-walled CNTs with a hydroxyl group (MWCNT-OH). They are fabricated with anode material. MVCNTs give a better result compared with SWCNT, especially when they have an OH group.

MWCNT-OH provides the highest power and treatment efficiency in MFC when used as an anode made up of MWCNT-OH and porelon membrane, with a PEM open circuit voltage of up to 0.74 V and an

average power density of 167 mW/m². The MWCNT are stable at high temperatures in the air up to 650 °C and decompose completely above 750 °C. The electrical conductivity of MWCNT was measured using a micro manipulator by the two-probe method, which gives an average conductivity of around 1000–2000 S/cm. The current density in a piece of individual nanotubes measured around 106 A/cm² [53].

In previous decades, stainless steel used as anode material in MFC had lost cost and high mechanical strength. However, it was still only used in limited situations due to its low biocompatibility and poor corrosion resistance. These problems can be overcome using conductive polymers, i.e., PPy, along with anode material. PPy is a conjugated polymer that is the most researched conductive polymer, as evidenced by the volume of publications devoted to its characteristics and uses. PPy is a very promising "smart" biomaterial because of its many great capabilities and stimulus-responsive characteristics. Most significantly, it possesses decently high conductivity under physiological settings and strong chemical stability [54].

The anode's ability to generate electricity and resistance to corrosion can both be considerably enhanced by modifying PPy. With PPy/SS anodes, MFCs were able to produce a maximum power density of 1190.94 mW/m², which was almost 29 times greater than that of naked SS anodes. Additionally, the SEM, CV, and electrochemical impedance spectroscopy (EIS) characterization results demonstrated that the MFC with a PPy/SS anode had higher capacitance and lower internal resistance than the MFC with a bare SS anode. These ensured that the PPy/SS had better biocompatibility, power density, and corrosion resistance, making it a potential anode material for MFCs [55,54]. To create nanostructured polyurethane/graphite/polypyrrole (PU/Graph/PPy) composites, polyurethane (PU) foams were covered with graphite. The pyrrole monomer was then chemically oxidised onto its surface. FeCl₃ was used to create the composite as the oxidant had a maximum output power density of 305.5 mW/m³. On the other hand, ammonium persulfate was used to create the composite, as the oxidizer had a maximum output power density of 128.6 mW/m³. The chemical oxygen demand (COD) removal was 48.2% and 45.5%, respectively [56].

3.3. Advantages and disadvantages of anode material

Carbon-based materials, metal/metal oxides and conductive polymers are the most commonly utilized materials for anodes in BES. Precious metals like gold have attracted a lot of attention in the past because of their exceptional mechanical strength and high conductivity. Later, in order to minimize the cost of the material of the anode, some metals like copper, nickel, aluminium, titanium, and stainless steel have also been utilized. In a similar way, a lot of research is still being done on carbon-based materials, including carbon rod, felt, fibre, and graphite. Conventional materials like these shown several drawbacks. For example, metal-based materials under long term-operation show corrosion, and they have a high price. Similarly, traditional conventional carbon materials showed low electric conductivity, ultimately making them less efficient. That why these conventional materials require surface modification in order to enhance their productivity and to reduce their limitations [21]. Graphite is a good conductor of electricity; it can stand in harsh physical and chemical environments. Along with advantages, graphite has disadvantages as well. Additionally, their research demonstrates that graphite fibre brushes can function as an electrode material in MFC more effectively than graphite granules. Even though graphite is one of the materials used in MFC the most frequently, one of the granules' technical disadvantages may be their high contact resistance, comparatively limited surface area, and potential for clogging.

Because of their comparatively large surface area, low ohmic resistance, and ability to unclog, graphite fibre brushes have a strong potential for enhancing the performance of biocathode MFCs [57].

There are some limitations in the application of conventional carbon materials. For instance, graphite-based materials have excellent

mechanical stability but comparatively less biofilm growth on the anode surface, which has an immediate impact on MFCs' ability to generate energy efficiently.

Although the reticulated glassy carbon anode, CP, and CC all have a rough surface area that is advantageous in the production of biofilms, they are not mechanically strong and cannot be used for long-term operations. Regarding the adherence of the bacteria, the CF demonstrated excellent conductivity and flexibility. Active bacterial colonisation is not supported by the formation of biofilm, which restricts the diffusion process of organic substrate from the exterior to the interior surface. This is a result of the CF material's extremely thick surface. Compared to other brushes, the carbon brush (CB) performs better in terms of energy output; nevertheless, because metal wires are needed to secure the CBs, they are not economically viable. Consequently, to create the modified anode, the vast majority of studies are using CP, CF, or graphite rod [58].

It is not easy to satisfy the requirement of an ideal anode in MFC. Due to various reasons, including cost, corrosion, lack of biocompatibility, and others, various forms of metal/metal oxide nanoparticles (NPs), such as Au, MnO₂, TiO₂, Pd, and many other strips, have not proven successful. For instance, stainless steel mesh satisfies a number of the criteria for the ideal anode, but with time, the gravity effect causes biofilm to disappear. In a similar way, while Au, Ag, and Cu also have great conductivity, they also demonstrated poor operational stability over extended periods of time when used to produce energy. Therefore, while looking for practical means to acquire them, modern anode materials must be integrated into the design in order to obtain a satisfying MFC's performance [57].

Single-walled CNTs (SWCNTs) have many advantages over other carbon materials. The single-walled CNTs have good mechanical strength due to their covalent bonds. It provides unique characteristics of electrical properties such as superconductivity, electroluminescence, photoconductivity, thermoelectricity, and good conductivity as well. Along with the advantages of SWCNTs, it has some disadvantages, like less purity, defects during functionalization, and high-cost synthesis methods.

Multi-walled CNTs (MWCNTs) have advantages like easier bulk synthesis, cheap synthesis methods, high purity, high thermal stability, and the lowest chances of defect development during functionalization. MWCNTs can be used over SWCNTs because they overcome all the disadvantages present in SWCNTs. There is a disadvantage to MWCNTs having less electrical property compared to SWCNTs [59].

4. Cathode material

Similar to the bioanode, the cathode is a fundamental part of MFCs. At the site of a cathode, water molecules are generated due to the reduction reaction [60]. The oxidation of organic matter is catalysed by exoelectrogens, resulting in a redox reaction in which electrons and protons are generated. The protons are entered into the cathode chamber through the PEM. Electrons are moved through an external circuit to the cathode. The electrons, protons, and oxygen combine to form water molecules.



Cathode materials are essential elements for electricity generation in MFCs. The cathode materials should be efficient, less expensive, stable, and easy to scale up for various substrates, i.e., wastewater. The stability of the cathode material is crucial to the continued operation of MFCs when they are exposed to water, composite organic matter, and bacteria [61]. Most anodic microbes have the ability to build biofilm on both the anode and cathode surfaces, which affects the catalytic activity of cathode materials [62].

Material selection is an important criterion that impacts the power capacity of MFCs and enhances their high redox potential and ease of gaining protons too. Graphite, CC, and CP are the common cathode

Table 2
Comparison of cathode materials in BES.

Cathode material	Cathode modification	Anode	Membrane type	Energy generation	COD %	Reactor configuration	Microbes/inoculum source	Reference
1 Carbon cloth	Activated carbon	Carbon cloth	NA	3.3 W/m ²	NA	Single-chamber	Wastewater Treatment Plant landfill leachate	[65]
2 Carbon paper	Copper-polyaniline	Stainless steel wool	Nafion	0.101 ± 0.01 mW/cm ²	NA	Single-chamber		[67]
3 Graphite plate	NA	Graphite plate	Nafion 117	76 mW/m ²	38.36	Single-chamber	Mixed photosynthetic consortia	[70]
4 Carbon Cloth	Coated with Pt	NA	GEFC-10N	300 mV	NA	Single-chamber	NA	[72]
5 Stainless steel mesh	Carbon nanotubes (CNTs)	Graphite felt	NA	147 mW/m ²	92	Dual chamber	Anaerobic sludge	[77]
6 Plain graphite blocks	Copper	Carbon brush	Nafion 117	0.6 A/m ²	NA	Dual chamber	NA	[78]
7 VITO-CoRE	Cold-rolled gas diffusion electrodes	Carbon cloth	Zirfon	19.06± 2.01 mW/m ²	92.68 ± 2.58	Dual chamber	Farm manure	[81]

materials. In order to improve the performance of the cathode material, modify a highly active catalyst like Pt, which is well known to increase the reaction rate and reduce the activation energy of the cathodic reaction. Modified cathodes containing graphite felt containing Pt in MFCs give a power density of up to 150 mW/m² which is three times higher than a pure graphite cathode [63]. There are various materials that can be used as cathode, which are mentioned in Table 2.

4.1. Carbon-based materials

4.1.1. Carbon black

Carbon black is a material frequently used as a support material for other ORR (oxygen reduction reaction) catalysts, having a high surface area, strong electron conductivity, practicality from an economic standpoint, and high stability. For instance, CB was amenable to PPy modification, and coating and dispersion techniques led to improved ORR performance. PPy modification facilitates ORR performance using dispersion and coating methods. In the experiment, the PPy/CB cathode having a higher ORR than the normal CB cathode and giving 260 mV showed high catalytic activity. In comparison with the maximum power density, PPy/CB gives 401.8 mW/m², which is higher than the normal CB with 90.9 mW/m² [64].

4.1.2. Carbon cloth

CC has a good conductivity, surface chemistry, pore size distribution, and surface area. Activated carbon with CC shows the good electrochemical performance as a base material. The quality of AC powders derived from hardwood, peat, coal, coconut, and bamboo sources is assessed. Among all the powders, bamboo-based AC showed the great energy generation, reaching 10.6 A/m², and maximum power generation, reached 3.3 W/m² [65].

4.1.3. Carbon paper

CP is a common material for electrochemical applications like MFCs, redox flow batteries, electrochemical capacitors, and electroanalysis. It has wide application because of its high surface area, electrochemical activity, electronic conductivity, porosity, ease of handling, and relatively good mechanical strength. In photomicrobial fuel cells, CP is used as a cathode material (7.2 cm²) and *p.limnetica* as is cultured with different anode materials like ITO-coated PET, CP, and stainless steel, which give power densities of 1.3×10^{-3} , 0.6×10^{-3} and 14.5×10^{-3} mW/m² [66]. A modified CP with PANI-copper hybrid was utilized as an air cathode for MFC. The CP/PANI-Cu hybrid cathode allows for a substantial oxygen reduction reaction (ORR) because of the uniform layer and relatively high adherence of PANI-Cu to CP and the given power density of 0.101 ± 0.01 mW/cm² [67].

4.1.4. Graphite

Graphite particles are the most often used filler in the anode chamber

of a 3D cell. Graphite is a good conductor of electricity and has excellent biocompatibility, which is why it can be used both as anode and cathode in culture. *C. reinhardtii* transformation F5 gives a power density of around 12.9 mW/m² [68]. There are various structures that can be made with graphite, like graphite felt, plates, rods and sheets. An MFC is designed to use graphite felt containing pt as the cathode and has a maximum power density of up to 150mW/m². It is estimated that this power density is three times greater than that of a pure graphite cathode [69]. A MFC system was made containing graphite plates both as anode and cathode with mixed photosynthetic consortia, given a power density of 76 mW/m² [70]. In this work, two microbial fuel cells (MFC) were used as the 3D cathode electrodes for oxygen reduction. The PB/GE nanocomposite and PB were deposited on the surface of active carbon particles. The two MFCs, designated as PB/GE-MFC and PB-MFC, had their long-term operational performances assessed. The effective deposition of PB/GE and PB on the particles was demonstrated by a number of characterization techniques. Following the extended. During the course of operation, the PB-MFC's cell voltage and maximum power density dropped significantly, which dropped. The PB/GE-MFC saw a slight decline, going from 530mV and $16.26\text{W}/\text{m}^3$ to 470mV and $15.88\text{W}/\text{m}^{-3}$, while the other two had a slight increase, from 530mV and $15.63\text{W}/\text{m}^3$ to 395mV and $7.5\text{W}/\text{m}^3$ [71].

4.1.5. Carbon nanomaterials

Nanomaterials like (CNFs) and CNTs (CNTs) are the most common materials that can be used as cathode materials and are considered the ideal material for the ORR catalyst in MFCs, along with the rapid advancement of nanotechnology. Nanomaterials are ultrafine particles (less than 100 nm in size) [61]. Treatment of acid and alkaline is a frequent modification approach for CFRs and CNTs, similar to the modification of CB, AC, and graphite/graphene. The increased surface area and charged pore size distribution of CNFs/CNTs activated by alkaline or acid may be responsible for their improved performance. [64]. constructed a CNT/chitosan nanocomposite using wastewater as a substrate and gained a maximum voltage of 300 mV with a 1000 Ω resistor, having two chamber modes and a total volume of 80L [72].

4.2. Metal based material

Metal-based electrodes are widely used in BES for cathode materials. The most commonly used materials are stainless steel, copper and nickel [73]. These materials provide good conductivity and mechanical strength. These properties can be an advantage while scaling up the BES system. They are extensively used in several kinds of foam, wire, mesh, and plate designs. Stainless steel is one of the most common materials among BES because it is cheaper than other metallic elements such as titanium and platinum [74]. Ni mesh yielded the best methane performance, followed by copper and steel [75]. When compared to carbon materials, the majority of 183 metal-based cathodes have a lower

surface area, the least corrosion resistance, and poor biocompatibility, except for their strong conductivity [76]. So, the surface of the electrode material needs to be modified in order to overcome this limitation and create a better microbe-electrode interaction.

Stainless steel is a metal widely used as a biocathode with modifications in order to make it more conductive, less corrosive, and more biocompatible. CNTs are nanomaterials coated on stainless steel mesh electrodes that have been fabricated using straightforward and scalable methods to improve the performance of biocathodes. The electron microscope showed a uniform distribution of CNTs all around the stainless-steel surface and created a three-dimensional network. The highest maximum power density of 147 mW/m^2 was achieved, which is 49 times larger than the MFCs (3 mW/m^2) with a bare stainless-steel biocathode [77].

Copper metal is also widely used as a cathode material in BES. A system was constructed to convert abiotic CO_2 into methane and organic chemicals. In this study, copper used as a biocathode was prepared using several different techniques in order to compare the performance of methanogenesis cells. The methane production rate of 201 nmol/cm^3 and the highest current density production of 0.6 A/m^2 were recorded by the electroless Cu deposition (electroless-Cu) cathode, whose performance remained consistent throughout time [78]. For hydrogen production, nickel-iron foam (Ni-Fe) cathode is made and used in BES for effluent from glucose fermentation. Since Ni-Fe is widely used, cheap, and has great catalytic qualities along with minimal microbial toxicity, it has emerged as a good alternative. The system's maximum hydrogen production rate and yield obtained were $500 \pm 80 \text{ m}^3/\text{m}^3/\text{d}$ and $470.2 \pm 11.2 \text{ mL/g COD}$, respectively [79].

4.3. Gas diffused biocathode

Microbial electrosynthesis, whose main application is the reduction of carbon dioxide (CO_2) to multi-carbon compounds at the cathode, is very appealing. Bacteria lower CO_2 by absorbing electrons or lowering their equivalents generated at the cathode. The effectiveness of the biological reduction process relies on the dissolution and transfer of CO_2 into the electrolyte, where it serves as the carbon source. We conducted research on a gas diffusion electrode (GDE) as a resolution for this issue. To facilitate the reduction of CO_2 at the biocathode, we introduced CO_2 into the MES reactor through the GDE. The electrode creates a three-phase interface by combining a catalyst layer (consisting of activated carbon and Teflon binder) with a hydrophobic gas diffusion layer (GDL). This arrangement allows the biocatalyst on the cathode surface to have access to both CO_2 and reducing equivalents [80].

Modified dual gas cathode MFC systems were operated separately in different operation modes, like batch mode (BM), continuous mode (CM), and semi-continuous mode (SCM), under dark fermentation effluent (DEF). BM showed a low power density of around $1.31 \pm 1.75 \text{ mW/m}^2$ due to the loss of electrons and the limitation of mass transfer. SCM and CM have shown power densities of $19.06 \pm 2.01 \text{ mW/m}^2$ and $15.53 \pm 2.51 \text{ mW/m}^2$ respectively [81]. Ammonia was recovered from MFC using a gas diffusion cathode. Ammonium migrated and diffused, resulting in the ammonium being transported to the cathode. Because of the high pH in the cathode chamber, ionic ammonium was transformed into volatile ammonia. A current density of 0.50 A/m^2 (compared to the surface area of the membrane) resulted in an ammonium recovery rate of $3.29 \text{ gN d}^{-1} \text{ m}^{-2}$. The energy balance revealed a surplus of 3.46 kJ gN^{-1} indicating that more energy was generated than was necessary for ammonium recovery. This groundbreaking approach demonstrated the feasibility of recovering ammonium and generating energy from urine [82].

5. Reference electrode

Reference electrodes are the most common electrodes that need to keep one of the electrodes in an electrochemical cell at a constant

potential in the measurement of electrochemicals. [83]. A reference electrode is mandatory to be used because the potential of a single phase cannot be measured to allow the measurement of the voltage (potential difference) between the indicator or measuring electrode and the reference electrode. Similar to the necessity for a ground in any electrical circuit, a reference electrode can be built in a number of ways to use the measuring electrode's signal of interest as a point of reference [84]. These reference electrodes are used to assess an indicator electrode (potentiometry, for example) or manage the working electrode potential (voltammetry) [83].

Electrode potentials and cell voltages may typically be accurately measured using widely accessible voltage meters, multimeter, and data gathering devices linked in parallel with the circuit. Electrode potentials can only be measured against a reference electrode that must be present in the electrode compartment; cell voltages can be found directly from the voltage differential between the anode and cathode [85]. Electrochemical sensors, which utilise transducers based on sensing principles, find applications in laboratory research, environmental monitoring, and biomedical devices due to their ability to detect a broad spectrum of important analytes. Among these transducers, the amperometric sensor stands out as a useful tool for analysing liquid analytes. The electronic interface for these transducers is provided by a circuit known as a potentiostat. A potentiostate consists of three electrodes: the auxiliary electrode (AE), the reference electrode (RE), and the working electrode (WE) [86]. The potentiostat is connected to the MFC electrode in order to get electrochemical properties, e.g., cyclic voltammetry, electrochemical impedance and linear sweep voltammetry.

5.1. Ag/AgCl reference electrode

An Ag/AgCl reference electrode which is frequently used in electrochemical experiments, including pH measurements and oxidation-reduction potential calculations. The electrode offers a stable, predictable potential in addition to its reversible redox activity and ease of miniaturization. Ag/AgCl is made up of an Ag wire partially converted to AgCl, dipped into a standard 1M KCl (internal solution) stored in a glass container. The bottom tip of the container is made of nanoporous glass that is only permeable to hydrogen ions. The Nernst equation provides the equilibrium potential of the Ag/AgCl reference electrode.

$$E = E_0 - (RT/F) \ln(CCl^-), \quad (8)$$

In reaction, E stands for equilibrium potential, E_0 represents the standard reduction potential in relation to the standard hydrogen electrode, R indicates the universal gas constant, T is the temperature in kelvin, F is faraday's constant and concentration of chloride in the electrode is represented by CCl^- . The nanoporous glass membrane inhibits the other analytes from migrating into the external solution and keeps a steady electrode potential by preserving a consistent concentration across different media [87].

5.2. Standard hydrogen electrode

A Standard hydrogen electrode (SHE) is made up of a platinum electrode bubbling with pure hydrogen gas at 100 kPa and immersed in a perfect acidic solution with 1 M (effective concentration) of protons. At 25°C , SHE's absolute potential is $4.44 \pm 0.02 \text{ V}$, but its potential is adjusted to zero so that it can act as a universal reference for zero potential at all temperatures. She can be reversed entirely. SHE is an ideal model that can never be created since there is never an optimal solution with 1 M protons. In the absence of any other indication, the potentials of redox half reactions are expressed with respect to SHE (vs. SHE) [88].

The standard hydrogen electrode in aqueous solutions is composed of a platinumized electrode (which can be wire, sheet, or mesh) and an acidic solution with proton (H^+) unit activity. This solution allows $\text{H}_2(\text{g})$ to supply data with a fugacity of 1.00 bar ($f(\text{H}_2) = 1.00 \text{ bar}$) and is ideally small enough to pass as small bubbles so that the electrolyte solution

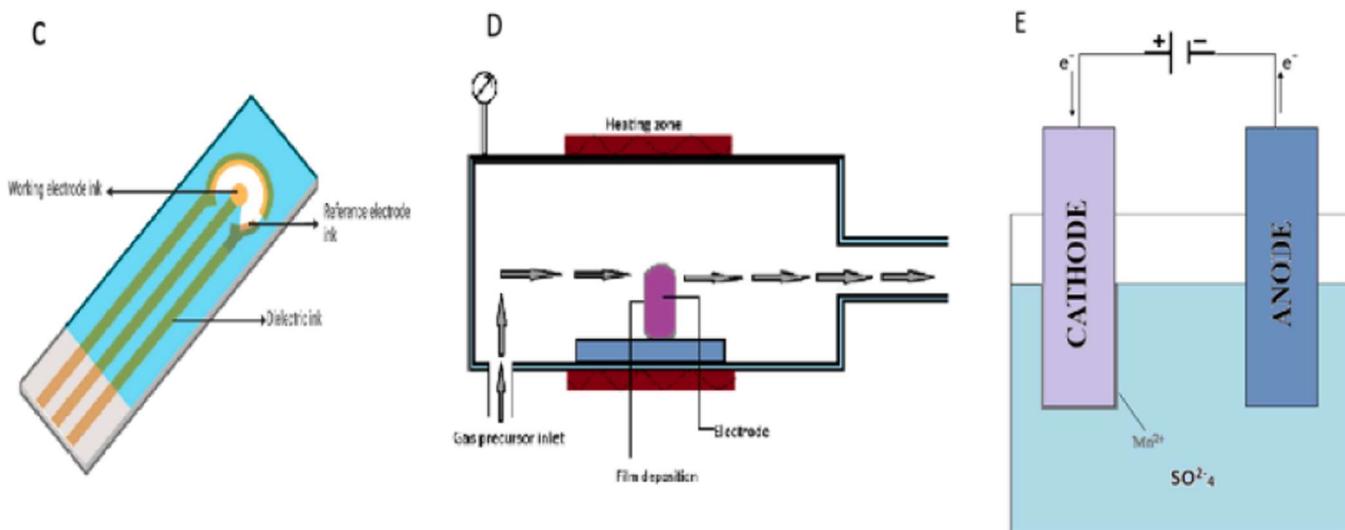


Fig. 2. Schematic representation of (C) screen printing, (D) chemical vapor deposition and (E) electrochemical deposition.

quickly becomes saturated with gas. One can locate a comprehensive process for platinizing Pt materials elsewhere [5]. At the electrode/electrolyte contact, the following general equilibrums spontaneously form themselves:



Because it promotes the dissociative adsorption of hydrogen, a crucial intermediate of the overall equilibrium, the platinized Pt is essential. The application of another noble metal, like gold, is not feasible because it does not support the dissociative adsorption of molecular hydrogen [89].

6. Electrode Fabrication and Modification Techniques

In MFCs, there are several factors that affect the productivity of microbes to produce electricity, including the chemical substrate, ionic concentration, proton exchange material, catalyst, internal resistance, electrode spacing and electrode materials. [90] lower extracellular electron transfer (EET). The primary barrier limiting MFCs from being used in practical settings is still their low extracellular electron transfer (EET) efficiency between the microbe and the electrode, which results in low power density and poor energy conversion efficiency. [91]. Generally, there are two main strategies to overcome these problems: first, surface treatment in order to improve the electrode property [92]. for example, by means of microbial reduction [93], electrostatic incorporation or ionic functionalization [91], the other involves creating novel electrode material to improve catalytic activity at the cathode or EET at the anode. Basically, in fabrication of electrodes three major techniques that is screen printing, chemical vapor deposition and electrochemical deposition being used which is shown in Fig. 2.

6.1. Fabrication methods

6.1.1. Screen printing

Screen printing is a fabrication technique used in the development of electrochemical sensors. These electrochemical sensors are used in biomedical, pharmaceutical, industrial, and environmental studies for in-situ monitoring and point-of-care testing. A screen-printed electrode is a combination of working, reference, and counter electrodes dipped in a substrate, which encourages the sensor's miniaturisation and portability. It's easy to mass produce screen-printed electrodes due to the ease of the fabrication process. There have been several types of screen-printed electrodes developed. Among these, carbon-based electrodes

fabricated gain a lot of interest. Here, a carbon working electrode, a reference electrode, and a counter electrode are combined on a substrate to form the screen-printed carbon electrode (SPCE) as shown in Fig 2. (C). The large potential window, low background current, inertness, and inexpensive cost of carbon material are what led to the widespread use of SPCE in electrochemical sensors. [94]. A screen printer generally consists of screen mesh, substrate, and squeeze. Screen mesh consists of unblocked pores, which collectively depict the intended pattern. The ink passes through these pores and deposits itself on the substrate underneath. The precise and desired pattern of the substrate is transferred onto the ink that seeps out of the pores in the screen mesh. A squeeze is used to force the ink through pores. The mechanical contact force is applied, so it becomes easier to seep through open pores. Carbon ink is widely used in fabrication of screen-printed electrodes. In Carbon inks have the most potential for electrochemical sensing applications because of their chemical inertness, stability over a wide range of potential windows, and reduced residual current contributions. Among these carbon inks, graphene is a marvel because of its intriguing mechanical, electrical, and optical characteristics. These features pave the way for flexible and transparent electronics [95].

Wang et al. explained the restrictions on screen printed carbon inks in relation to electrochemical applications and emphasized the significance of pre-treatment steps, where the Screen printing inks that contain polymeric binders and additives interfere with the filler material's ability to behave electrochemically, such as carbon or graphite [96].

Recombinant *E.coli* immobilised on the screen-printed carbon electrode using glutaraldehyde. The recombinant *E.coli* produces the organophosphorus hydrolase enzyme, which breaks methyl parathion into two products: dimethyl triphosphoric acid and p-nitrophenol [97]. Cyclic voltammetry and SPCE were related, and cyclic voltammograms were taken both before and after the hydrolysis of methyl parathion. Because of the redox behaviour of the hydrolysed product, p-nitrophenol, the detection was calibrated using the relationship between the changes in the current recorded at +0.1 V potential. Due to the increase in concentration of methyl parathion, the current also increased. A microbial biosensor developed for the determination of phenolic compounds, which were measured on the basis of oxygen consumption in relation to analyte oxidation. *Pseudomonas putida* DSM 50026 was immobilised on the surface of screen-printed graphite. Synthetic wastewater was used for the phenol detection [98].

6.1.2. Chemical vapor deposition

CVD is a process of electrode fabrication in which the electrode is fabricated or coated using the vaporization of chemicals at high

temperatures by an external heat source [99]. Additionally, at a lower processing temperature, it may create coating materials that are single layer, multilayer, composite nanostructured, and functionally graded with precisely regulated dimensions. Additionally, the advantage that CVD has over other deposition methods, such as its ability to deposit material outside of a line sight, has made it possible to coat intricate shape engineering components and create nanodevices, carbon-carbon (C-C) composites, ceramic matrix composites (CMCs), and free-standing shape components.

CVD materials are used in many different industries. The applications listed below make up a very minor portion of all the applications. On cutting tools, hard coatings made of materials like Al_2O_3 and TiC have been prepared. Moreover, CVD coatings that employ MoSi_2 , BN, tantalum, and SiC deposits can offer corrosion resistance. Tungsten has been used with steel to reduce erosion. Freestanding forms have been made from materials that traditional fabrication methods cannot fully utilize. It is necessary to ascertain whether a CVD reaction is thermodynamically feasible before considering its use. This will occur if the reactants' computed partial pressures (concentrations) in a state of chemical equilibrium are lower than their selected beginning concentrations. If not, the gas stream will quickly run out of reactant to reach the maximum deposition rate determined by the system's kinetics, and the rate will instead be thermodynamically limited. The equilibrium concentrations should ideally be much lower [100].

However, CVD is not a universal coating solution. Its greatest versatility occurs at temperatures of 600°C and above, when many substrates lose their thermal stability. This is just one of its numerous drawbacks. Nonetheless, this issue is somewhat mitigated by the advancements in metallo-organic CVD and plasma-CVD. The demand for high vapor pressure chemical precursors, or starting ingredients, which are sometimes exceedingly poisonous and frequently dangerous, is another drawback. Additionally, poisonous and caustic, the byproducts of the CVD processes need to be neutralized, which could be an expensive procedure [101].

Over the past 20 years, chemical vapour deposition (CVD) has expanded extreme quickly, and its application of manufacturing key elements in different industrial product such as optoelectronics, optics, semiconductors, cutting tools, refractory fibres and filters. Now a days, CVD is a significant technique on par with other significant technological fields like electrodeposition, power metallurgy, or conventional ceramic processing. As a result, CVD technology expanded and began to emphasise the deposition components of the process. Coating with the help of CVD improves many surface properties, such as protection against wear, corrosion, oxidation, chemical reactions, thermal shock, and neutron adsorption. Materials III-V and II-VI, C, B, Si, borides, carbides, nitrides, oxides, silicide's, and sulphides are among those used in these coatings [102].

It is no longer a lab curiosity [101]. The early research was done by van Arkel and de Boer on chemical vapour deposition. In a simplified ways CVD can be defined as the condensation of one or chemicals from the gas phase onto a substrate; thereafter, a reaction takes place to form a solid deposit. Fig. 2. (D) shows the process schematically, the material is heated and converted into a gas by volatilization from either liquid or solid, and it flows to the substrate through the action of a differential pressure. The reactant reacts with the substrate and forms a fabricated layer on its surface and byproduct vapour comes from outlets [100]. be gaseous, and the deposit's vapour pressure must be low enough to avoid volatilization.

A graphene electrode is modified by the chemical vapour deposition method and used in MFCs. It got attention for energy applications due to their excellent physical and chemical properties, by which they can greatly improve the efficiency of MFC in producing power. The graphene is mainly produced using transition metal materials, e.g., Cu and Ni, as the main substrates [103]. The resulting graphene films can be transferred to different surfaces while retaining their superior transparency and conductivity. By using this method, large-area and

high-quality graphene can be produced. Doping nitrogen on the surface of graphene will maximize the MFC power density of 1008 mW/m^2 at a current density of 6300 mA/m^2 . Due to the its overpriced and complex nature of the process its large-scale application will be limited. Even worse, the graphene quality is highly influenced by substrate. The catalyst's hydrophobic qualities improved the MFCs' endurance [104]. Constructed an anode with a nanocomposites film of novel CNTs and PANI modified indium-tin oxide (ITO) through graft polymerization of PANI after γ -aminopropyltriethoxysilane (APTES) treatment on the ITO substrate after γ -aminopropyltriethoxysilane (APTES) treatment on ITO substrate. It was followed by the alternative layer-by-layer (LBL) self-assembly of PANI and CNTs on its surface. With a maximum current density of $6.98 \mu\text{A/cm}^2$, the twelve layers of CNTs/PANI decorated ITO electrodes with an ideal nanoporous network demonstrated exceptional biocatalytic capabilities [105]. CNFs are modified with nickel (Ni) nanoparticles (NP) using chemical vapour deposition. Ni NPs were used as the catalyst to create the multiscale web of carbon micro-nanofibers (ACFs/CNFs), and benzene was used as a source of carbon for the CNFs to develop on the ACF substrate. During this experiment, power density ($710 \pm 5 \text{ mV}$) and OCP ($1145 \pm 20 \text{ mV/m}^2$) were measured, which were 9 times greater than ACF substrate-based MFCs [106,107].

6.1.3. Electrochemical deposition

The process of growing a film by electrochemically reducing the metal ions from the electrolyte to form a coating of metal on a base material is known as electrodeposition, as shown in Fig. 2. (E) A similar technique is frequently referred to as electroplating. The chemicals containing the target metal are dissolved in an appropriate solvent or heated to a liquid state to produce molten salts in the electrolyte, which is an ionic conductor. Water is often used as the solvent, however, recently, a variety of organic compounds, various ionic liquids and chemicals are utilized in specific electroplating procedures.

The primary steps in the electrodeposition process are submerging the item to be coated in a tank holding the electrolyte and the counter electrode, then connecting both electrodes to an external power source to generate current. In order for the metal ions to be reduced to metal atoms, which finally form the deposit on the surface, the object to be coated must be linked to the power supply's negative terminal.

In the last many years, electrochemical deposition has progressed from a precision science to an art. The ever-growing number and diverse range of potential uses of this field of applied science and engineering are attributed to this progress. A few technological domains where electrochemical deposition techniques and procedures play a crucial role include optics, optoelectronics, sensors of various kinds, electronics, both macro and micro.

The electrodeposition process can be influenced by current density and electrode potential, as well as other variables and process conditions like pH, temperature of the solution, concentration of reacting species, substrate, and parasitic processes like hydrogen evolution [110].

The following equation represent the reduction of the metal ion Mz^+ in aqueous solution.



There are two methods by which this can be achieved. The first one is a method of electrodeposition where z electrons (e) are supplied with power via an external source. An electroless (autocatalytic) deposition method where the electron source is a reducing chemical in the solution (no external power supply is involved). Electrochemical deposition is constituted by these two processes, which are electrodeposition and electroless deposition. Eq (1) represents the deposition reaction of charged particles at the interface between a liquid solution and a solid metal electrode. An electron and a metal ion are the two charged particle types that can pass through the contact. An electrodeposited graphene oxide is designed to enhance microbial growth on the anode surface in MEC. The anode is composed of river mud obtained from local river. The

system was operated in fed batch mode at 30°C. Acetate medium was added to the solution when the current started at 100 µA. Anode and cathode voltages were aligned at 1 V in the cell potential [111].

An inexpensive titanium-nickel (Ti/Ni) and graphite felt- nickel (GF/Ni) cathode was made using electrodeposition technique. The GF/Ni composite gave a highest maximum power density and coulombic efficiency of 113.4 ± 0.6 mW/m² and 29.6%, respectively. The composite of Ti/Ni gave highest maximum power density and coulombic efficiency of 110.7 ± 8.0 mW/m² /m² and 23.7%, respectively [112].

A novel electrode is fabricated in which manganese dioxide (MnO_2) is deposited on the surface of CF using electrochemical deposition. The electrodeposited manganese gave maximum power density of 3580 ± 130 mW/m² which was 24.7% higher than the normal CF anode (2870 mW m²) [113]. The CC electrode was electrochemically deposited with multiwalled CNTs-manganese oxide/ polypyrrole (MWCNT- MnO_2 /PPY). (MWCNT- MnO_2 /PPY) electrode demonstrated a high electrical conductivity of 0.1185 S m⁻¹. The modified electrode showed the higher power density of 1125.4 mW/m². With their excellent biocompatibility and high potential, the CC-modified MWCNT- MnO_2 /PPY nano-composite electrodes demonstrated a tremendous realised mediator-less MFCs for the production of bioelectricity from sewage wastewater [114]. Chitosan was modified with electrochemical deposition of the surface on CF and further modified with alginate. This process made a biocompatible platform that allowed microbes to grow prolifically on the anode (chit-Alg/ CF anode). The efficiency of electrode was tested on different substrates i.e., glucose, ethanol, acetate, and grape juice, in the dual chamber of MFC. Acetobacter aceti and Gluconobacter roseus showed the synergistic effect during utilization for the current generation. The power densities for glucose, ethanol, acetate, and grape juice were determined to be 1.55 W/m³, 2.80 W/m³, 1.73 W/m³, and 3.87 W/m³, in that order. The enhancement in performance was 20.75% more than that of the bare electrode [115].

6.2. Surface modification techniques

6.2.1. Nanomaterial coatings

Nanomaterials have become increasingly attractive because of their superior electrical, optical, thermal, catalytic, and mechanical strengths in environmental and electrochemical applications. When these electrodes are modified with nanomaterials it enhances their performance of electrode for to enhance performance in environmental and electrochemical applications. Materials such as silicon nanowires, gold nanoparticles, and carbon nanotubes have been regarded as novel electrode materials [117].

As was previously indicated, exoelectrogens in anodic biofilms create active areas where organic molecules supplied to MFCs can be oxidised. Because they affect the transfer of electrons and bacterial adhesion, the characteristics of the anode surface play a crucial role in the colonisation of exoelectrogenic bacteria [118]. An optimal material for an MFC anode must hasten electron transport and microbe attachment by conduction. Graphite (plate, rod, and brush), CP, CF, and CC are standard carbon-based materials that are readily available for commercial use as anodes in MFC systems. Carbon is generally thought to be an excellent conductor and anti-corrosion material for making electrodes for MFCs. However, because of the poor adhesion of bacteria, electron transport from microbial biofilm to the electrode surface is limited when utilising traditional anodes. This problem affects the MFC's ability to operate by lowering its power output, which impedes the technology's practical application. High internal resistance (IR), which results in a sluggish rate of charge transfer and expensive materials, is the other major drawback [119]. Cheap nanoparticles can improve microbial adhesion and increase the surface area available for bacterial growth on the anode. The MFC's function and effectiveness are boosted as a result of this enhancement, which is greater exoelectrogens colonisation through higher extracellular electron transfer (EET) and substrate metabolism. More electrons and protons are produced when the number of exoelectrogenic colonies increases, since this increases the anodic biofilm's

redox activity [120].

Enhancing the characteristics of MFC's component parts—microorganisms, electrodes (anode and cathode), and membrane—will improve the device's performance in proportion. Nanomaterials are useful and can possibly benefit of nanotechnology by enhancing the features of certain MFC components. A property of a nanomaterial can affect a membrane, anodes, cathodes, and microbes. Nanomaterials affect the rate of bacterial adhesion, biofilm development, and growth in microorganisms. It has a direct impact on the anode's large surface area, porosity, charge transfer, conductivity, and biocompatibility. Conductivity charge transfer capacitance has the greatest influence on the cathode. Water absorption, oxygen cross-over, and proton conductivity all have an impact on the membrane [121]. Carbon nanotube platinum (CNT/Pt) coated on the surface of CP and used as a cathode in MFC and gave the highest current density ((82.38 mA/m²) and maximum power density (16.26 mW/m²) in the investigated MFC system. [122] doped the CP with cobalt transition metal nanoparticles used as an anode material in MFC with sewage wastewater for mixed culture. The maximum power density 165.6 was achieved [123]. A PANI composite TiO_2 nanosheet was modified with CP electrodes. The co-modification of conductive PANI and vertically oriented (Improved microbial electrocatalysis with neutral red immobilized electrode) TiO_2 nanosheets (TiO_2 -NSs) is investigated. At TiO_2 -20PANI/CP anode, the PV-4's maximum output power density (813mW/m²) is raised by 63.6% more than at TiO_2 -NSs/CP anode [124].

6.2.2. Surface area enhancement method

The large specific surface area offered a high number of catalytically active spots, which improved the electrode's catalytic efficacy and added spaces for the microorganisms to adhere to and differentiate [125]. Utilizing dispersed carbon materials, like activated carbon granules, which are strong, inexpensive, and have a large surface area, is one way to increase the anode electrode's surface area [117]. An innovative carbon nanofiber electrode (MnCo/CNF) based on manganese cobalt metal-organic framework was created and utilized as the anode for microbial fuel cells (MFCs). In the anode chamber (MnCo-Py_MFC), pyrite was added. MnCo/CNF has shown good synergistic effects and facilitate removal of waste and generate electricity. MnCoPy_MFC contributed the highest COD reduction ($82 \pm 1\%$) and highest columbic efficiency ($35 \pm 1\%$). MnCo/CNF has a high surface area and a porous structure that provides many attachment sites for electroactive microorganisms and greatly increased the biocatalytic effectiveness of MnCoPy_MFC. This work demonstrated the synergistic relationship between pyrite and the MnCo/CNF anode, offering a fresh approach to the use of composite anode MFC in energy recovery and heavy metal removal [6].

The performance of MFC was optimized by changing the electrode-surface area/anode compartment volume (ESAVR). Five ESVRs, ranging in size from 0.15 to 0.75 cm²/cm³, were evaluated in independent MFCs using actual effluent from a winery factory. Results showed an increase in electricity generation by decreasing the anode compartment volume. Therefore, the maximum current density rose from 583 to 2416 mA/m² by increasing ESVR. Nevertheless, it was discovered that lowering the ESVR (from 590 to 1075 mg COD L⁻¹ d⁻¹) improved the efficiency of COD elimination. In both chambers, CF electrodes (3 cm² each) were utilised. The fuel cell operating with 20 cm³ of anode compartment had the lowest average cell voltage (21 mV), whereas the MFCs operating with 4 and 8 cm³ showed the highest average cell voltage (87 mV, with a maximum peak of 117 mV) [126]. The performance of a single chamber MFC was enhanced by increasing the surface area of the anode. Here, three different thicknesses of graphite granules of 0.3, 1, and 3 cm with three different volumes of the reactor chamber of 3.75, 12.5 and 37.5 cm³, respectively and a maximum power density of 0.043, 0.247 and 8.1 W/m³ were achieved [127]. The carbon veil anode was modified with activated carbon for enhanced surface area and power performance. When compared to the

control (CV), which produced 21.4 mW (11.9 W/m³), the stack fitted with modified anodes (MF-CV) produced up to 37.9 mW (21.1 W/m³), indicating a 77% increase in power production. Excellent power output and a greater treatment rate were achieved by the MFC stack due to the unique combination of highly porous activated carbon particles deposited onto the conduction network of carbon fibres, which simultaneously boosted electrocatalytic activity and increased surface area. Compared to the control stack, it enhanced COD reduction by 13.5% [128].

7. Applications of BES electrodes

7.1. MFCs

MFCs are BES that convert chemical energy into electrical energy via the metabolism of organic waste by microorganisms. It is considered an alternative way to generate electricity for small to large scale applications [11]. The relationship between electricity and metabolic processes in living organism was began in eighteenth century. An Italian scientist, Luigi Galvani, initially proposed his hypothesis of "animal electricity" in the eighteenth century after observing the production of electricity in a frog's legs. This observation was considered the beginning of research into relationship between electricity and metabolic processes in living organism [11]. The MFCs work on the principle of extraction and transfer of electrons from microbial cells onto the anode electrode. The anode is connected with cathode via an external circuit, through which electrons flow to generate current. Because their different liquid solutions have different redox potentials, electrons go from the anode (negative) to the cathode (positive). The anode and the cathode are the two chambers that make up a standard double-chamber MFC. Between these two chambers, a membrane known as PEM is fixed, which only permits protons generated at the anode to flow through itself to the cathode. The microbes at the anode chamber oxidise the organic substrates, producing carbon dioxide, protons, and electrons. Redox-active proteins, or cytochromes initially transmit the electrons produced by the metabolic activity of microorganisms to the anode surface, where they are subsequently sent to the cathode via an electrical circuit [129].

In MFCs, the culture can be a culture can be either pure culture or mixed culture to be used in order to produce cell biomass. The mixed culture of electrogens bacteria is readily available in sewage sludge and can be used as a starter culture for MFCs [11].

7.2. MECs

MECs are a type of bioelectrochemical fuel cell that converts the chemical energy into electrical energy and permits water electrolysis. Electrons pass from anode to cathode by external power given to the BES electrical circuit, which facilitates the cathode's production of hydrogen. As opposed to the MFCs, the cathodic chamber of MECs works in an anaerobic condition, which promotes the production of hydrogen. However, once CO₂ and methanogens are present, the anoxic environment in MECs, together with high quantities of hydrogen synthesis, can also encourage methane formation. There are a few methods that lower the methane production, like the cathode chamber's aeration in between batches, lowering the pH, functioning for brief retention periods, delivering the inoculum a heating shock, and suppressing the growth of methanogens by adding chemicals [4]. The energy is supplied to a MEC for its functioning by another independent MFC, which serves as a power source. By using these two-fuel cell systems, a hydrogen production rate of 0.24 m³ H₂/m³ d and a recovery of energy of around 23% use a substrate of fermentation effluent [130]. Unlike other BESs, there is no requirement to use expensive metals like platinum for bioanode and biocathode in MEC. Preferably, the carbon cathode's microbial enrichment shortens the startup time and generates current densities that are similar to those of the bioanode. There are several factors that can improve the performance of MEC. Electroactive microorganisms or Exoelectrogens which catalyse electron transfer organic matter to

electrodes. Exoelectrogens are important for anode or cathode reactions. The habitats in which the electrogenic bacteria have been discovered are diverse, such as sewage wastewater, marine and ocean sediments, and anaerobic sewage sludge. There are few commonly Exoelectrogens which isolated and belong to diverse group α -Proteobacteria (*Rhodopseudomonas*, *Ochrobactrum* and *Acidiphilum*), β -Proteobacteria (*Rhodoflexax*). External factors such as pH, buffer strength, temperature can affect the electrogenic microorganism [131,132].

Unlike other systems, the MECs electrode is also classified into three categories, namely anode, cathode, and PEM. Generally, the low-cost metals, carbon materials are used for construction or selection of materials for anode, cathode and membrane respectively. The anode is a main component of MECs because the Exoelectrogens adhere on it. MEC anodes may employ the same anode material as MFC anodes. An ideal anode material should possess following features; good conductivity and low resistance, strong biocompatibility, chemical stability and ant corrosiveness, wide surface area; and a high shelf life. [133]. Wagner et al., constructed a MEC system using plain CC anode and CP containing 0.5 mg pt/cm² as cathode used. The system produces 2-3 mol H₂/mol glucose by combining with hydrogen fermentation, has the potential to produce ca. 8-9 mol H₂/mol glucose at an energy cost equivalent to 1.2 mol H₂/ mol glucose [133]. A chamber was made of poly (methyl methacrylate). In this, anode is made up of graphite felt, which is disc-shaped. The external voltage 0.5V was applied to produce approximately 0.02 m³ H₂/m³ reactor liquid volume/day from acetate with a 53±3.5% total efficiency [134]. Similar to the anode, the cathode is one of the most important parts of the MECs, where H₂ as well as other value-added chemical compounds are produced. On a plain carbon electrode the hydrogen evolution reaction (HER) is very low but in order to generate H₂ high overpotential is needed [135]. Additionally, efforts have been undertaken to investigate whether nickel and nickel-based alloy cathodes are suitable for producing hydrogen in MECs. A single-chamber MEC reactor was constructed in which nickel oxide catalyst was used, which has shown an improved energy efficiency (31-137%) and volumetric HPR (0.08–0.76 m³ H₂/m³ d) [136]. Due to poor mechanical stability of this MEC reactor decreased its performance over time. A separator or membrane is always included in MEC reactors, which is probably employed to inhibit microbes from consuming hydrogen at the anode and to increase hydrogen purity as a product. Additionally, it serves as a divider to prevent short circuits. There are various membranes being used in MECs; the most common membrane is PEM for proton transport known as Nafion [137,138,134]. Substrate used in MEC is considered one of the most important factors that affects the H₂ generation. The reaction process and H₂ yield is determined by the type, concentration and feeding of substrate in MEC [139]. Since acetate (CH₃COONa) is a frequent end product of dark fermentation, it is the most commonly employed substrate in MECs. A two chamber MEC developed and applied voltage of 1V and 50 m³ H₂/m³ d HPR (hydrogen production rate) was achieved [140]. Wastewater is also used as a substrate in MEC. Wastewater consists of variety of mixture of organic waste that need to be treated before discharge into the environment. Generally, the production of H₂ with acetate is higher than wastewater. It was found that using single chamber MEC, it generated 0.9-1.0 m³ H₂/m³ using graphite fibre brush as an anode and diluted swine wastewater, and in the test of 20 h, 8 to 29 % and in longer test of 184 h using full strength wastewater, 69%-75% COD removal was achieved [133]. Other than hydrogen generation, recently more uses for MEC cathodes have been developed.

7.3. Electrode-assisted bioremediation

7.3.1. Bioremediation

The word "bioremediation" is composed of two parts: "to remediate," which implies to find a solution to an issue, and "bios," which means life and refers to living things. Utilising biological organisms to address environmental issues like contaminated soil or groundwater is known as

"bioremediation." Using live microorganisms to break down or stop pollution in the environment is known as bioremediation. Otherwise, it's a technique that eliminates contaminants from the environment, returning it to its original state and stopping new pollution. The biological process of decontaminating a contaminated area is known as bioremediation. The surroundings could be aquatic, terrestrial, or both.

7.3.1.1. In-situ bioremediation. The most common method for getting rid of contaminants in polluted soils and groundwater is in situ bioremediation. Because it uses safe microorganisms to remove chemical contamination and reduces transportation costs, it is an excellent method for cleaning contaminated areas. It is preferable for these microbes to have a positive chemotactic attraction for pollutants. This characteristic raises the likelihood of bioremediation at nearby locations where bioremediants have not yet dispersed. Furthermore, the approach is preferred since it disturbs the contaminated area the least. This would be extremely relevant in places with hazardous contamination (like those tainted with chemical or radioactive materials) or in areas with the least amount of investment and pollution (like factories).

7.3.1.2. Ex-situ bioremediation. Since the bioremediation process in this case takes place some distance from the source of pollution, contaminated soil must be transported there or groundwater must be pumped there. There are more drawbacks to this method than benefits. Ex situ bioremediation is categorised as follows based on the condition of the pollutant during the bioremediation step:

(i) The solid phase system, which also includes soil piles and land treatment, is used to bioremediate organic wastes as well as problematic industrial and residential wastes, municipal solid wastes, and sewage sludge. Composting, soil biopiling, and land farming are the three methods used in solid-phase soil bioremediation. (ii) Slurry phase systems: Compared to the other treatment methods, slurry phase bioremediation is a somewhat faster procedure. This includes solid-liquid suspensions in bioreactors [141]. Many studies have been conducted in the past year that have shown that BES can be a useful approach for removing environmental pollutants such as hydrocarbons and their derivatives, percolates, chlorinated organic compounds, heavy metals, and azo dyes [142]. Recovery of uranium from contaminated subsurface was the first BES remediation study with electrodes serving as the electron donor. BESs electrodes, which are non-exhaustible electron acceptors or doners for degradation of contaminants, require almost no external energy and no modification of chemical additionally, even when some energy is produced on-site for onsite purposes. In comparison with traditional physical, chemical or biological remediation methods, this method has huge advantages. Either they required a large amount of energy consumption, such as biosparging, bioventing, or soil vapour extraction or they needed external chemical addition such as bioremediation or chemical oxidation. BESs can have cheap operational costs by reducing through the elimination or reduction of energy and chemical expenses [143].

As mentioned earlier, MFC has been shown to be a green and encouraging technology to eliminate emerging contaminants, such as chemicals from wastewater, phenols, dyes, and surfactants. In research, it was reported that about 50 mg L^{-1} of acid orange 7 (A07) which is 80.6% removal was achieved in addition to an $8.57 \pm 0.2 \text{ mW/m}^2$ reduction of power with the help of a single chamber upflow MFC. The MFC consisted of carbon plate ($2 \text{ cm L} * 5 \text{ cm W}$) and CF ($3 \text{ cm L} * 2.5 \text{ cm W} * 2 \text{ cm H}$) used as cathodes and anodes. It was noted that power generation decreased to $7.07 \pm 1.4 \text{ mW/m}^2$ when concentration of A07 was increased to 75 mg L^{-1} [144]. This study suggests that there was competition between azo dye and anode in order to receive electrons from oxidized substrate and toxicity of azo dye and its intermediate by products inhibit the activity of electricity generation by bacteria in MFC [145]. Similarly, in an additional study, simultaneous electricity generation and degradation at the cathode of 200 mg L^{-1} of direct red 80

dye were examined. A dual chamber of MFC was constructed with graphite felt and platinum coated graphite as the anode and cathode [146]. A study was conducted in which phenolic compounds (phenol and trichlorophenol) with maximum power density of 522.7 mW/m^2 were produced under oxic conditions using cyclic voltammetry (CV). The power density produced was 1.15 folds greater than what is found in anoxic conditions (454.81 mW/m^2). Furthermore, in the cathode and anode chambers made up of CC whose surface is coated with PAN-I/SnO₂, respectively, approximately 75.66% and 70.93% of the organic content removal were achieved under oxic and anoxic conditions, with a combined starting phenol and trichlorophenol concentration of 300 mg L^{-1} [147]. Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that consist of two or more fused benzene rings and are among the most common contaminants in soil due to anthropogenic sources like leaking underground storage tank, abandoned manufactured gas sites. Several microbes, like aerobic bacteria, fungi and enzymes, can consume it as a source of energy. A graphite plate was used as anode and cathode ($10.16 \text{ cm} * 10.16 \text{ cm} * 0.318 \text{ cm}$). The results showed a power density of 6.02 ± 0.34 and $3.63 \pm 0.37 \text{ mW/m}^2$ with an external resistance of 1500 for aerobic and anaerobic MFC in sediment MFC [148]. A modified graphene oxide anode (L-GO) derived from oil palm biomass waste is used for remediation of lead (Pb^{2+}) in double chamber of MFCs. To improve electron transfer, L-GO was fabricated with zinc (L-GO/ZnO). The fabricated graphene (L-GO/ZnO) anode MFC has a 91.07% efficiency of removal of metal ions (Pb^{2+}) with a maximum power density of $1350 \times 10^{-3} \text{ mW/m}^2$ while, unmodified L-GO has an 85% efficiency of removal and maximum power density = $20 \times 10^{-3} \text{ mW/m}^2$ [149].

Pesticides are another class of emerging contaminants that are used every year, more than 2.5 million of tons, in order to withstand problems associated with agriculture fields due to insects, weeds and other organisms that are harmful for crops [150]. These residues of contaminants are mixed in water, which has serious impact on the environment. That's why these pesticides should be eliminated from contaminated water before they are released into water sources. In this sense, MFC can have a major role in the biodegradation of these contaminants. Zhang et al., demonstrated the performance of MFC in eliminating fipronil from wastewater. Approximately 94.22% fipronil degradation was seen at a nearly neutral pH of 7.02 throughout a 72-hour operational period, starting at 74 mg L^{-1} . Species like *y*, *Azospirillum* (51.35%), *Azoarcus* (4.98%), *Sphaerochaeta* (8.95%), *Pseudomonas* (3.39%), *Chryseobacterium* (4.26%), were observed in anodic biofilm in anodic chamber of MFC, which caused the biodegradation of fipronil. Furthermore, the extremely acute toxicity to zebra fish was eliminated following the MFC treatment, given a 96- hour exposure in which no zebra fish died during this period.

A modified type of MFC, a MEC, may transform the organic matter in wastewater into various by-products, such as H_2O_2 , formic acid, and other valuable-added goods, as well as valuable-added products like H_2 and CH_4 . In MEC, the exoelectrogenic bacteria in the anodic chamber oxidise the organic waste, releasing CO_2 , protons into the solution, and electrons to the anode. The organic waste in MEC undergoes oxidation through the action of exoelectrogenic bacteria that live in the anodic chamber. This process releases carbon dioxide, protons into the solution, and electrons to the anode.

Protons are moved from the anodic chamber to the cathodic chamber via PEM at the same time as the electrons released to the anode flow through an external circuit towards the cathode. Apart from the production of hydrogen (H_2) and methane (CH_4) at the cathode, MEC is widely used in the removal of dyes, chlorinated compounds, pharmaceuticals, EDCs, and heavy metals from wastewater. There are various advantages to choosing MECs to over other technologies, such as minimum running costs, recovery of value-added products, self-assembling biocatalysts and producing less sludge [151]. During an investigation, a single chamber MEC operated with molybdenum disulphide ($\text{MoS}_2\text{-GO}$) nickel foam (NF) cathode for decolorization of AYR (Alizarin Yellow R) dye along with H_2 production. In this investigation, it was

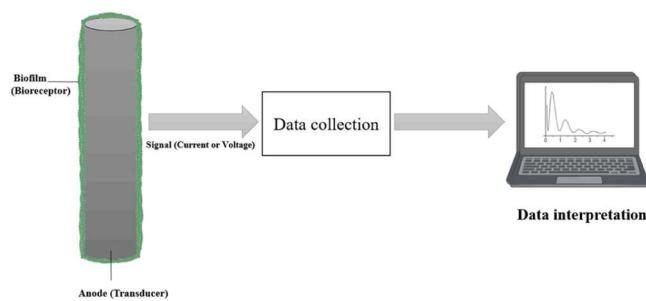


Fig. 3. MFC as a biosensor.

concluded that 93% of the decolorization of AYR dye occurred within 10 hours of period, with an initial concentration of 30 mg L^{-1} and sodium acetate (NaAc) of 1 g L^{-1} as co-substrates. The H_2 production of 0.119, 0.169, and $0.183 \text{ m}^3 \text{ day}^{-1} \text{ m}^3$ with different co substrates such as NaAc, glucose, and NaAc with glucose was achieved. [152]. PFAS(per- and polyfluoroalkyl substances) are synthetic chemicals that are widely used in daily basis products like non-sticking pans, paper coatings and fire-fighting foams. The contamination of PFAS is a serious concern, having adverse effects such as affecting the immune system, hormone interference and increasing the chances of cancer. The PFAS was defluorinated using an anaerobic autotrophic bacterium, *Acidimicrobiaceae sp. strain A6* (A6). Melany Ruiz-Urigüen (Continued).

A coupled recirculatory microbial desalination-MEC ((MDC-MEC) is a novel technology that generates power, treats wastewater, and supports desalination through a process that is eco-friendly. This research mainly focuses on simultaneous efficient removal of Fe^{2+} and Pb^{2+} in the MEC and ammonium ions in the MDC. The single chamber MEC (SCMEC) and double chamber MEC (DCMEC) run for a 48-hour cycle, in which SCMEC has higher Pb^{2+} (74.61%) and Fe^{2+} (85.05%) removal efficiency. The DCMEC exhibited a greater current density of 753.62 mA/m^2 in comparison to 463.77 mA/m^2 in the SCMEC [153].

7.4. Biosensors and bioelectronics

In the modern era, measurement of molecular entities such as proteins, ligands, and cell heavy metals in a sample is a big challenge [154]. Biosensors have critical applications in BES, highlighting the various analytical applications like detecting several parameters, monitoring water quality, electrochemicals evaluation detecting toxicity and metabolic processes. Previous researches indicates that the use of biosensors in MFC can increase instant, onsite monitoring and toxic detection, which are needed for testing the water quality [155]. BES has applications for producing electricity generation(at the anode), bioremediation and chemicals (at the cathode) and biosensing tools, as shown in Fig. 3 [156]. In research, biosensing tools are less studied, but they might be with great interest and be implemented more quickly. BES has the potential to be applied for the detection of harmful chemical compounds as an alternative to traditional analytical methods such as high-performance liquid chromatography (HPLC), mass spectrometry (MS), gas chromatography (GC) and atomic adsorption. These techniques are costly, time consuming, demand sophisticated technological knowledge and are unsuitable for in-situ or on-site testing.

MFC is also considered a biosensor for the detection of various parameters. There is a potential application likely for the shock biosensor of MFC for biosensing. When a high number of heavy metals or organic compounds are present in wastewater, "shock" occurs, which is higher than the normal concentration. The operating system of a wastewater treatment plant may be harmed by shock events because these facilities are constructed to function at average contamination concentrations. That's why early detection is needed to minimize damage of the treatment plant. There are various dedicated sensors available in the market that sense the shocks, but it is difficult to sense a wide variety of shocks.

The ability to use a single gadget that can identify a variety of shocks is therefore crucial [156]. Planktonic cells are used for heavy metal shock detection, including lead and copper [157]. Recently, MFCs have been used to detect a number of shocks, including formaldehyde, cadmium (Cd^{2+}), copper (Cu^{2+}), and chromium (Cr^{6+}) [158]. The presence of excess heavy metals can be identified by the electrical responses of MFC in which shocks provoke a perturbation in normal operating condition.

Water quality monitoring is an immediate application of MFC as a biosensor. The biochemical oxygen demand (BOD) parameter, which is established via the 5-day biochemical oxygen demand test (BOD_5), is frequently used to quantify the extent of organic contamination in water systems. BOD_5 is a test that has been used worldwide, but 5 days of incubation are needed. That's why using it in one line for BOD monitoring is impossible, and hence, new analytical approaches are required. The research has demonstrated that there is a linear relationship between the current output of MFC and BOD parameter when non-saturated operating conditions are applied to the device. Here graphite felt is used as both anode and cathode, with nafion as the cation exchange membrane [159]. Biofouling is a process in which material performance is affected due to the presence of microbial biofilms on metal surfaces. It is seen that extracellular polymeric materials produced by microbes are essential for cell attachment on the surface of metal. The amount of protein, lipids, and polysaccharides in the exopolymers varies according to the type of bacteria and the growing environment. The interaction between bacteria and metal surfaces causes microbially influenced corrosion (MIC) [160,161]. According to reports, MIC seriously damaged industrial plants, particularly the cooling systems that were used with contaminated water. Therefore, from an industrial perspective, the ability to continuously monitor the state and corrosion protection of the pipelines would be of utmost importance, with the potential to save hundreds of thousands of dollars for regular and critical maintenance. Several reports from the early 2000s discuss the use of BES for MIC monitoring. Mollica and Cristiani demonstrated that a specific M3C, wherein a quasi-galvanostatic polarisation is given to the stainless-steel element to be monitored, can be used to track the biofilm settlement on industrial pipelines. A zinc electrode is used as an anode and connected to a high resistor so that it might be thought of as a pseudo reference electrode. The growth of biofilm is clearly indicated by the ohmic drop between the zinc anode and the stainless-steel element. Biofilm settlement on a metal surface can be used as a monitoring the presence of corrosion and changes in electrochemical parameters shown its metabolism [156].

8. Challenges and future perspectives

BES and MFC offer a novel approach that is used in electricity generation and wastewater treatment, along with several advantages and limitations that need to be considered. These systems use microorganisms' metabolic processes to remediate wastewater and produce energy at the same time. It is essential for the successful application of MFCs in wastewater treatment to comprehend the possible advantages and difficulties related to their use. This section discusses the benefits and limitations of MFC anodes, cathodes, and membranes, highlighting their potential and areas in need of development. Carbon-based electrodes like the anode and the cathode have certain limitations. This anode is less conductive compared with metal-based electrodes and the cathode has a limited oxygen diffusion rate [162]. Graphite plate (Gpc) served as the cathode and stainless-steel mesh (SSMa) as the anode in the third CW-MFC unit. Stainless steel mesh was used as the anode and graphite plate as the cathode in the unit that produced the highest amount of electricity (9 mW/m^2). Metal-based MFC anodes have a lower surface area and limited biocompatibility [163]. In polymer-based MFCs, the cathode's oxygen diffusion rate is limited, while the anode's membrane fouling limits long-term performance [164]. The anodes in ceramic-based MFCs are constrained by scalability, whereas the cathode is constrained by the rate of oxygen diffusion [165,166]. When

Table 3

Shows various anode and cathode electrode modification in single and dual chamber BES systems.

Anode	Anode modification	Cathode	Membrane type	Energy generation	Reactor configuration	Microorganism/inoculum source	Reference
1 Carbon micro-nanofibers	Nickel (Ni) nanoparticles	Carbon micro-nanofibers	Nafion 117	1145±20mW/m ²	Dual chamber	<i>Escherichia coli</i> K12	[106]
2 Graphene nano sheets	Nitrogen doped	Carbon cloth	Nafion115	1008 mW/m2	Dual chamber	<i>Escherichia coli</i> ATCC 27325	[104]
3 Indium-tin oxide	Polyaniline/Carbon Nanotubes Composite	Carbon cloth	Dupont	34.51 mW/m2	Dual chamber	<i>Shewanella loihica</i>	[105]
4 Stainless steel	Carbon nanofiber	NA	NA	1.28 mA/cm2	Single chamber	Domestic wastewater	[108]
5 Carbon fibre	Carbon nanotube	Carbon cloth	NA	1876.62mW/m2	Single chamber	Sludge water	[109]

Table 4

Shows various anode electrode modification in single and dual chamber BES systems.

Anode	Anode modification	Cathode	Membrane type	Energy generation	COD %	Reactor configuration	Microorganism/inoculum source	Reference
1 Carbon Cloth	MWCNT-MnO ₂ /PPy	NA	Nafion 117	1125.4 mW m ²	92	Dual chamber	Sewage waste water	[114]
2 Carbon felt	MnO ₂	Carbon brush	CMI7000	3580 ± 130 mW m ²	NA	Dual chamber	Mixed bacterial cultures collected from the effluent	[113]
3 Carbon felt	Chit-Alg/carbon felt anode (Prussian blue)	Carbon felt	Nafion 115	3.87 W/m ³	44	Dual chamber	<i>A. aceti</i> (NCIM No. 2116) and <i>G. roseus</i> (NCIM No. 2049)	[115]
4 Carbon brush	Graphene oxide (GO)	Stainless steel mesh (AISI304)	NA	NA	NA	Single chamber	Mixing river mud	[116]
5 Carbon cloth	CC-NS + CC-AN + CC-AS	Carbon air-cathodes	NA	NA	NA	Single chamber	Wastewater treatment plant	[107]

compared to conventional MFCs, the anode in microbial desalination cells can only generate a limited amount of power [167]. BES is used for wastewater treatment, energy production, heavy metals removals and valuable molecules extraction. But there are various challenges for BES which need to implement for future perspectives. Improvement in the BES system will widen the understanding of the process, reduce the cost of production, and make it a more sustainable wastewater treatment method. It will also give advantage to the recovery of resources and bioenergy. In the Past two decades, the BES has improved significantly but still faces many challenges in order to commercializing low power generation, pricey electrode accessories, costly membrane separators and proper scaling up. Ecological pollution and energy constraints are growing global issues obstructing human advancement. Future waste biorefinery, pollution control, CO₂ removal and recycling, and microbial electrosynthesis of sustainable and renewable biofuels or commercially viable molecules are all made possible by the MEC platform. This method makes natural energy more adaptable and environmentally beneficial by enabling its harvesting and storage. The current rigorous efforts to create and improve next-generation BES significantly expand the field of potential and advance BES technological advancements. This suggests that this approach might be used instead of the conventional waste biorefinery processes [168].

As we know, carbon dioxide can be utilized by microbes in bioelectrochemical systems and converted to chemicals and gaseous or liquid energy in this way to moderate the percentage of CO₂ in the atmosphere. Products like acetate and methane are the most widely produced. In order to obtain financial benefits from the manufacturing system, the MES system looks for high-value and unique items. Only when high titres and purity can be achieved in the final product will the application of MES technology become appealing [169]. The essential step in the WL pathway of CO₂ reduction is acetyl-CoA, which is also a primary precursor for the synthesis of numerous commercial molecules [170]. MES technology transforms electrical energy into new, high-value compounds or biofuels, opening up a wealth of potential opportunities through clever improvements. MES is a promising technology that has the ability to store electricity directly in the form of precursor chemicals or biobased energy carriers. In contrast to alternative biomass-to-biofuel strategies, this electricity-powered

bioproduction technique doesn't require fertile soil. While plants' net photosynthetic efficiency in the creation of organic matter is only about 0.5%, photovoltaic systems have an efficiency of roughly 10-15% in converting solar energy to electricity. Even if a MES system operates at 25% efficiency, the overall efficiency of producing organic matter will be 3.75% when it is powered by a photovoltaic system. This suggests that when bioproduction is done in MES powered by a photovoltaic system, at least 7.5 times more organic matter may be gathered per m² of land. As a result, MES bioproduction requires a comparatively small amount of land, which does not necessarily need to be fertile. Compared to agricultural production, the bioproduction of chemicals can save large volumes of nutrients and fresh water. In addition to being a clean technique, microbiological electrosynthesis has these amazing benefits [169].

The review article "Emerging Trends in Fabrication and Modification Techniques for Bioelectrochemical System Electrodes" explores recent advancements in creating and enhancing electrodes used in bioelectrochemical systems. New methods for constructing electrodes, potentially involving nanomaterials, 3D printing, or other innovative approaches. Techniques to improve the performance and functionality of electrodes, such as incorporating enzymes or other biomolecules. Surface modification techniques, such as electrode functionalization with biomolecules or polymers, are likely discussed for improving biocompatibility, stability, and electron transfer efficiency. Additionally, the review may explore strategies for immobilizing enzymes, microbial cells, or other biocatalysts onto electrode surfaces to enhance BES performance. [Tables 3 and 4](#)

Funding source

This research work was supported by Science and Engineering Research Board (SERB) Grant no SRG/2021/001460. This research work was supported by the Scheme for Promotion of Academic and Research Collaboration (SPARC), India, Grant no SPARC/2024-2025/ENSU/P3267.

CRediT authorship contribution statement

Rizwan Khan: Writing – original draft, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sudipa Bhadra:** Investigation, Formal analysis. **Soubhagy Nayak:** Methodology, Investigation. **Anagha Bindu:** Formal analysis, Data curation. **Ashish A Prabhu:** Writing – review & editing. **Surajbhan Sevda:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Dr. Surajbhan Sevda reports financial support was provided by Science and Engineering Research Board India. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] Liu Z, Deng Z, Davis S, Ciais P. Monitoring global carbon emissions in 2022. *Nat Rev Earth Environ* 2023;4:205–6. <https://doi.org/10.1038/s43017-023-00406-z>.
- [2] Goswami S. Impact of Coal Mining on Environment. *European Researcher* 2015; 92:185–96. <https://doi.org/10.13187/er.2015.92.185>.
- [3] Sorrell S, Speirs J, Bentley R, Brandt A, Miller R. Global oil depletion: A review of the evidence. *Energy Policy* 2010;38:5290–5. <https://doi.org/10.1016/j.enpol.2010.04.046>.
- [4] Bajracharya S, Sharma M, Mohanakrishna G, Dominguez Benneton X, Strik DPBTB, Sarma PM, et al. An overview on emerging bioelectrochemical systems (BESs): Technology for sustainable electricity, waste remediation, resource recovery, chemical production and beyond. *Renew Energy* 2016;98: 153–70. <https://doi.org/10.1016/j.renene.2016.03.002>.
- [5] Zhang Y, Zheng Y, Zhang Q, Sun J, Wang S, An L, et al. Catalytic Membrane Cathode Integrated in a Proton Exchange Membrane-free Microbial Fuel Cell for Coking Wastewater Treatment. *J Taiwan Inst Chem Eng* 2022;132:104117. <https://doi.org/10.1016/j.jtice.2021.10.017>.
- [6] Jiang N, Yan M, Li Q, Zheng S, Hu Y, Xu X, et al. Bioelectrocatalytic reduction by integrating pyrite assisted manganese cobalt-doped carbon nanofiber anode and bacteria for sustainable antimony catalytic removal. *Bioresour Technol* 2024;395. <https://doi.org/10.1016/j.biortech.2024.130378>.
- [7] Hamelers HVM, Ter Heijne A, Sleutels THJA, Jeremiassie AW, Strik DPBTB, Buisman CJN. New applications and performance of bioelectrochemical systems. *Appl Microbiol Biotechnol* 2010;85:1673–85. <https://doi.org/10.1007/s00253-009-2357-1>.
- [8] Mier AA, Olvera-Vargas H, Mejia-López M, Longoria A, Verea L, Sebastian PJ, et al. A review of recent advances in electrode materials for emerging bioelectrochemical systems: From biofilm-bearing anodes to specialized cathodes. *Chemosphere* 2021;283. <https://doi.org/10.1016/j.chemosphere.2021.131138>.
- [9] Savla N, Anand R, Pandit S, Prasad R. Utilization of Nanomaterials as Anode Modifiers for Improving Microbial Fuel Cells Performance. *J Renew Mater* 2020; 8:1581–605. <https://doi.org/10.32604/jrm.2020.011803>.
- [10] Yang Y, Xu M, Guo J, Sun G. Bacterial extracellular electron transfer in bioelectrochemical systems. *Process Biochemistry* 2012;47:1707–14. <https://doi.org/10.1016/j.procbio.2012.07.032>.
- [11] Ieropoulos IA, Greenman J, Melhuish C, Hart J. Comparative study of three types of microbial fuel cell. *Enzyme Microb Technol* 2005;37:238–45. <https://doi.org/10.1016/j.enzmictec.2005.03.006>.
- [12] Nevin KP, Kim BC, Glaven RH, Johnson JP, Woodward TL, Methé BA, et al. Anode biofilm transcriptomics reveals outer surface components essential for high density current production in Geobacter sulfurreducens fuel cells. *PLoS One* 2009; 4. <https://doi.org/10.1371/journal.pone.0005628>.
- [13] Rimboud M, Pocaznoi D, Erable B, Bergel A. Electroanalysis of microbial anodes for bioelectrochemical systems: Basics, progress and perspectives. *Physical Chemistry Chemical Physics* 2014;16:16349–66. <https://doi.org/10.1039/c4cp01698j>.
- [14] Pandit S, Khilari S, Roy S, Pradhan D, Das D. Improvement of power generation using Shewanella putrefaciens mediated bioanode in a single chambered microbial fuel cell: Effect of different anodic operating conditions. *Bioresour Technol* 2014;166:451–7. <https://doi.org/10.1016/j.biortech.2014.05.075>.
- [15] Pandit S, Khilari S, Roy S, Ghangrekar MM, Pradhan D, Das D. Reduction of start-up time through bioaugmentation process in microbial fuel cells using an isolate from dark fermentative spent media fed anode. *Water Science and Technology* 2015;72:106–15. <https://doi.org/10.2166/wst.2015.174>.
- [16] Sharif HMA, Farooq M, Hussain I, Ali M, Mujtaba MA, Sultan M, et al. Recent innovations for scaling up microbial fuel cell systems: Significance of physicochemical factors for electrodes and membranes materials. *J Taiwan Inst Chem Eng* 2021;129:207–26. <https://doi.org/10.1016/j.jtice.2021.09.001>.
- [17] Sharma M, Alvarez-Gallego Y, Achouak W, Pant D, Sarma PM, Dominguez-Beneton X. Electrode material properties for designing effective microbial electrosynthesis systems. *J Mater Chem A Mater* 2019;7:24420–36. <https://doi.org/10.1039/c9ta04886c>.
- [18] Kandpal R, Nara S, Shahadat M, Ansari MO, Alshahri A, Ali SW, et al. Impedance spectroscopic study of biofilm formation on pencil lead graphite anode in microbial fuel cell. *J Taiwan Inst Chem Eng* 2021;128:114–23. <https://doi.org/10.1016/j.jtice.2021.09.002>.
- [19] Pham TH, Aeiterman P, Verstraete W. Bioanode performance in bioelectrochemical systems: recent improvements and prospects. *Trends Biotechnol* 2009;27:168–78. <https://doi.org/10.1016/j.tibtech.2008.11.005>.
- [20] Qi Q, Huang G, Li R, Yu J, Chen X, Liu Z, et al. Improving bioelectrochemical performance by sulfur-doped titanium dioxide cooperated with Zirconium based metal–organic framework (S-TiO₂@MOF-808) as cathode in microbial fuel cells. *Bioresour Technol* 2024;394:130288. <https://doi.org/10.1016/j.biortech.2023.130288>.
- [21] Yaqoob AA, Ibrahim MNM, Guerrero-Barajas C. Modern trend of anodes in microbial fuel cells (MFCs): An overview. *Environ Technol Innov* 2021;23. <https://doi.org/10.1016/j.jeti.2021.101579>.
- [22] Pirbadian S, Barchinger SE, Leung KM, Byun HS, Jangir Y, Bouhenni RA, et al. Shewanella oneidensis MR-1 nanowires are outer membrane and periplasmic extensions of the extracellular electron transport components. *Proc Natl Acad Sci U S A* 2014;111:12883–8. <https://doi.org/10.1073/pnas.1410551111>.
- [23] Abbas AA, Farrag HH, El-Sawy E, Allam NK. Microbial fuel cells with enhanced bacterial catalytic activity and stability using 3D nanoporous stainless steel anode. *J Clean Prod* 2021;285. <https://doi.org/10.1016/j.jclepro.2020.124816>.
- [24] Wilberforce T, Abdelkareem MA, Elsaied K, Olabi AG, Sayed ET. Role of carbon-based nanomaterials in improving the performance of microbial fuel cells. *Energy* 2022;240. <https://doi.org/10.1016/j.energy.2021.122478>.
- [25] Santoro C, Arbizzani C, Erable B, Ieropoulos I. Microbial fuel cells: From fundamentals to applications. A review. *J Power Sources* 2017;356:225–44. <https://doi.org/10.1016/j.jpowsour.2017.03.109>.
- [26] Cai T, Meng L, Chen G, Xi Y, Jiang N, Song J, et al. Application of advanced anodes in microbial fuel cells for power generation: A review. *Chemosphere* 2020;248. <https://doi.org/10.1016/j.chemosphere.2020.125985>.
- [27] Cheng S, Logan BE. Ammonia treatment of carbon cloth anodes to enhance power generation of microbial fuel cells. *Electrochim Commun* 2007;9:492–6. <https://doi.org/10.1016/j.elecom.2006.10.023>.
- [28] Sun H, Zhu J, Baumann D, Peng I, Xu Y, Shakir I, et al. Hierarchical 3D electrodes for electrochemical energy storage. *Nat Rev Mater* 2019;4:45–60. <https://doi.org/10.1038/s41578-018-0069-9>.
- [29] Wang K, Liu Y, Chen S. Improved microbial electrocatalysis with neutral red immobilized electrode. *J Power Sources* 2011;196:164–8. <https://doi.org/10.1016/j.jpowsour.2010.06.056>.
- [30] Wang X, Cheng S, Feng Y, Merrill MD, Saito T, Logan BE. Use of carbon mesh anodes and the effect of different pretreatment methods on power production in microbial fuel cells. *Environ Sci Technol* 2009;43:6870–4. <https://doi.org/10.1021/es900997w>.
- [31] Artyushkova K, Roizman D, Santoro C, Doyle LE, Fatima Mohidin A, Atanassov P, et al. Anodic biofilms as the interphase for electroactive bacterial growth on carbon veil. *Biointerphases* 2016;11. <https://doi.org/10.1116/1.4962264>.
- [32] Gajda I, Greenman J, Ieropoulos I. Microbial Fuel Cell stack performance enhancement through carbon veil anode modification with activated carbon powder. *Appl Energy* 2020;262. <https://doi.org/10.1016/j.apenergy.2019.114475>.
- [33] Huang Le TX, Bechelany M, Cretin M. Carbon felt based-electrodes for energy and environmental applications: A review. *Carbon N Y* 2017;122:564–91. <https://doi.org/10.1016/j.carbon.2017.06.078>.
- [34] Li M, Li YW, Yu XL, Guo JJ, Xiang L, Liu BL, et al. Improved bio-electricity production in bio-electrochemical reactor for wastewater treatment using biomass carbon derived from sludge supported carbon felt anode. *Science of the Total Environment* 2020;726. <https://doi.org/10.1016/j.scitotenv.2020.138573>.
- [35] Feng Y, Yang Q, Wang X, Logan BE. Treatment of carbon fiber brush anodes for improving power generation in air-cathode microbial fuel cells. *J Power Sources* 2010;195:1841–4. <https://doi.org/10.1016/j.jpowsour.2009.10.030>.
- [36] Sayed ET, Olabi AG, Mouselly M, Alawadhi H, Abdelkareem MA. Zinc-based metal organic framework on carbon fiber brush as a novel anode of yeast-based microbial fuel cell. *Int J Hydrogen Energy* 2024;52:856–64. <https://doi.org/10.1016/j.ijhydene.2023.06.016>.
- [37] Yaqoob AA, Ibrahim MNM, Rodriguez-Couto S. Development and modification of materials to build cost-effective anodes for microbial fuel cells (MFCs): An overview. *Biochem Eng J* 2020;164:107779. <https://doi.org/10.1016/j.bej.2020.107779>.
- [38] ter Heijne A, Hamelers HVM, Saakes M, Buisman CJN. Performance of non-porous graphite and titanium-based anodes in microbial fuel cells. *Electrochim Acta* 2008;53:5697–703. <https://doi.org/10.1016/j.electacta.2008.03.032>.
- [39] Ouzzi ZA, Abes S, Nofouzi K, Khajeh RT, Rezaei A. Carbon paste/LDH/bacteria biohybrid for the modification of the anode electrode of a microbial fuel cell. *J Taiwan Inst Chem Eng* 2023;142:104668. <https://doi.org/10.1016/j.jtice.2022.104668>.
- [40] Logan B, Cheng S, Watson V, Stadt G. Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. *Environ Sci Technol* 2007; 41:3341–6. <https://doi.org/10.1021/es062644y>.

- [41] Gao X, Zhang Y, Li X, Ye J. Novel graphite sheet used as an anodic material for high-performance microbial fuel cells. *Mater Lett* 2013;105:24–7. <https://doi.org/10.1016/j.matlet.2013.04.044>.
- [42] Nayak S, Bhadra S, Sevda S. Optimization of human urine to synthetic wastewater ratio for pollutants removal, power generation in a bioelectrochemical system. *J Water Process Eng* 2024;57. <https://doi.org/10.1016/j.jwpe.2023.104643>.
- [43] Hao W, Lee SH, Peera SG. Xerogel-Derived Manganese Oxide/N-Doped Carbon as a Non-Precious Metal-Based Oxygen Reduction Reaction Catalyst in Microbial Fuel Cells for Energy Conversion Applications. *Nanomaterials* 2023;13. <https://doi.org/10.3390/nano13222949>.
- [44] Baudler A, Schmidt I, Langner M, Greiner A, Schröder U. Does it have to be carbon? Metal anodes in microbial fuel cells and related bioelectrochemical systems. *Energy Environ Sci* 2015;8:2048–55. <https://doi.org/10.1039/c5ee00866b>.
- [45] Karchiyappan T. Study of electrochemical process conditions for the electricity production in microbial fuel cell. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects* 2018;40:951–8. <https://doi.org/10.1080/15567036.2018.1468506>.
- [46] Srikanth S, Pavani T, Sarma PN, Venkata Mohan S. Synergistic interaction of biocatalyst with bio-anode as a function of electrode materials. *Int J Hydrogen Energy* 2011;36:2271–80. <https://doi.org/10.1016/j.ijhydene.2010.11.031>.
- [47] Zhu X, Logan BE. Copper anode corrosion affects power generation in microbial fuel cells. *Journal of Chemical Technology and Biotechnology* 2014;89:471–4. <https://doi.org/10.1002/jctb.4156>.
- [48] Pu K-B, Bai J-R, Chen Q-Y, Wang Y-H. Modified Stainless Steel as Anode Materials in Bioelectrochemical Systems. In: ACS Symposium Series. 1342. American Chemical Society; 2020. p. 165–84. <https://doi.org/10.1021/bk-2020-1342.ch008>.
- [49] Kumar GG, Sarathi VGS, Nahm KS. Recent advances and challenges in the anode architecture and their modifications for the applications of microbial fuel cells. *Biosens Bioelectron* 2013;43:461–75. <https://doi.org/10.1016/j.bios.2012.12.048>.
- [50] Li C, Zhang L, Ding L, Ren H, Cui H. Effect of conductive polymers coated anode on the performance of microbial fuel cells (MFCs) and its biodiversity analysis. *Biosens Bioelectron* 2011;26:4169–76. <https://doi.org/10.1016/j.bios.2011.04.018>.
- [51] Flahaut E, Durrieu MC, Remy-Zolghadri M, Bareille R, Baquey C. Study of the cytotoxicity of CCVD carbon nanotubes. *J Mater Sci* 2006;41:2411–6. <https://doi.org/10.1007/s10853-006-7069-7>.
- [52] Yellappa M, Sravan JS, Sarkar O, Reddy YVR, Mohan SV. Modified conductive polyaniline-carbon nanotube composite electrodes for bioelectricity generation and waste remediation. *Bioresour Technol* 2019;284:148–54. <https://doi.org/10.1016/j.biortech.2019.03.085>.
- [53] Thepusparangsiluk N, Ng TC, Lefebvre O, Ng HY. Different types of carbon nanotube-based anodes to improve microbial fuel cell performance. *Water Science and Technology* 2014;69:1900–10. <https://doi.org/10.2166/wst.2014.102>.
- [54] Balint R, Cassidy NJ, Cartmell SH. Conductive polymers: Towards a smart biomaterial for tissue engineering. *Acta Biomater* 2014;10:2341–53. <https://doi.org/10.1016/j.actbio.2014.02.015>.
- [55] Pu K-B, Ma Q, Cai W-F, Chen Q-Y, Wang Y-H, Li F-J. Polypyrrole modified stainless steel as high performance anode of microbial fuel cell. *Biochem Eng J* 2018;132:255–61. <https://doi.org/10.1016/j.bej.2018.01.018>.
- [56] Pérez-Rodríguez P, Ovaldo-Medina VM, Martínez-Amador SY, Rodríguez-de la Garza JA. Bioanode of polyurethane/graphite/polypyrrole composite in microbial fuel cells. *BioTechnology and Bioprocess Engineering* 2016;21:305–13. <https://doi.org/10.1007/s12257-015-0628-5>.
- [57] You SJ, Ren NQ, Zhao QL, Wang JY, Yang FL. Power generation and electrochemical analysis of biocathode microbial fuel cell using graphite fibre brush as cathode material. *Fuel Cells* 2009;9:588–96. <https://doi.org/10.1002/fuce.200900023>.
- [58] Sonawane JM, Yadav A, Ghosh PC, Adelouj SB. Recent advances in the development and utilization of modern anode materials for high performance microbial fuel cells. *Biosens Bioelectron* 2017;90:558–76. <https://doi.org/10.1016/j.bios.2016.10.014>.
- [59] Singla S, Sharma S, Basu S, Shetty NP, Aminabhavi TM. Photocatalytic water splitting hydrogen production via environmental benign carbon based nanomaterials. *Int J Hydrogen Energy* 2021;46:33696–717. <https://doi.org/10.1016/j.ijhydene.2021.07.187>.
- [60] Jatoi AS, Akhter F, Mazari SA, Sabzoi N, Aziz S, Soomro SA, et al. Advanced microbial fuel cell for waste water treatment-a review. *Environ Sci Pollut Res Int* 2021;28:5005–19. <https://doi.org/10.1007/s11356-020-11691-2>.
- [61] Qiu S, Guo Z, Naz F, Yang Z, Yu C. An overview in the development of cathode materials for the improvement in power generation of microbial fuel cells. *Bioelectrochemistry* 2021;141. <https://doi.org/10.1016/j.bioelechem.2021.107834>.
- [62] Chandrasekhar K. Effective and nonprecious cathode catalysts for oxygen reduction reaction in microbial fuel cells. *Biomass, Biofuels, Biochemicals: Microbial Electrochemical Technology: Sustainable Platform for Fuels, Chemicals and Remediation*, Elsevier 2018:485–501. <https://doi.org/10.1016/B978-0-444-64052-9.00019-4>.
- [63] Zhou M, Chi M, Luo J, He H, Jin T. An overview of electrode materials in microbial fuel cells. *J Power Sources* 2011;196:4427–35. <https://doi.org/10.1016/j.jpowsour.2011.01.012>.
- [64] Yuan H, Hou Y, Abu-Reesh IM, Chen J, He Z. Oxygen reduction reaction catalysts used in microbial fuel cells for energy-efficient wastewater treatment: A review. *Mater Horiz* 2016;3:382–401. <https://doi.org/10.1039/c6mh00093b>.
- [65] Janicek A, Gao N, Fan Y, Liu H. High Performance Activated Carbon/Carbon Cloth Cathodes for Microbial Fuel Cells. *Fuel Cells* 2015;15:855–61. <https://doi.org/10.1002/fuce.201500120>.
- [66] Bombelli P, Zarrouati M, Thorne RJ, Schneider K, Rowden SJL, Ali A, et al. Surface morphology and surface energy of anode materials influence power outputs in a multi-channel mediatorless bio-photovoltaic (BPV) system. *Physical Chemistry Chemical Physics* 2012;14:12221–9. <https://doi.org/10.1039/c2cp42526b>.
- [67] Sonawane JM, Pant D, Ghosh PC, Adelouj SB. Fabrication of a Carbon Paper/Polyaniline-Copper Hybrid and Its Utilization as an Air Cathode for Microbial Fuel Cells. *ACS Appl Energy Mater* 2019;2:1891–902. <https://doi.org/10.1021/acsaem.8b02017>.
- [68] Lan JCW, Raman K, Huang CM, Chang CM. The impact of monochromatic blue and red LED light upon performance of photo microbial fuel cells (PMFCs) using Chlamydomonas reinhardtii transformation F5 as biocatalyst. *Biochem Eng J* 2013;78:39–43. <https://doi.org/10.1016/j.bej.2013.02.007>.
- [69] Moon H, Chang IS, Kim BH. Continuous electricity production from artificial wastewater using a mediator-less microbial fuel cell. *Bioresour Technol* 2006;97:621–7. <https://doi.org/10.1016/j.biortech.2005.03.027>.
- [70] Chandra R, Venkata Subhash G, Venkata Mohan S. Mixotrophic operation of photo-bioelectrocatalytic fuel cell under anoxygenic microenvironment enhances the light dependent bioelectrogenic activity. *Bioresour Technol* 2012;109:46–56. <https://doi.org/10.1016/j.biortech.2011.12.135>.
- [71] Xu L, Zhang G, Chen J, Yuan G, Fu L, Yang F. Prussian blue/graphene-modified electrode used as a novel oxygen reduction cathode in microbial fuel cell. *J Taiwan Inst Chem Eng* 2016;58:374–80. <https://doi.org/10.1016/j.jtice.2015.06.013>.
- [72] Liu XW, Sun XF, Huang YX, Sheng GP, Wang SG, Yu HQ. Carbon nanotube/chitosan nanocomposite as a biocompatible biocathode material to enhance the electricity generation of a microbial fuel cell. *Energy Environ Sci* 2011;4:1422–7. <https://doi.org/10.1039/c0ee00447b>.
- [73] Peera SG, Maiyalagan T, Liu C, Ashmath S, Lee TG, Jiang Z, et al. A review on carbon and non-precious metal based cathode catalysts in microbial fuel cells. *Int J Hydrogen Energy* 2021;46:3056–89. <https://doi.org/10.1016/j.ijhydene.2020.07.252>.
- [74] Noori MT, Vu MT, Ali RB, Min B. Recent advances in cathode materials and configurations for upgrading methane in bioelectrochemical systems integrated with anaerobic digestion. *Chemical Engineering Journal* 2020;392. <https://doi.org/10.1016/j.cej.2019.123689>.
- [75] Sangeetha T, Guo Z, Liu W, Cui M, Yang C, Wang L, et al. Cathode material as an influencing factor on beer wastewater treatment and methane production in a novel integrated upflow microbial electrolysis cell (Upflow-MEC). *Int J Hydrogen Energy* 2016;41:2189–96. <https://doi.org/10.1016/j.ijhydene.2015.11.111>.
- [76] Dumas C, Mollica A, Féron D, Basséguy R, Etcheverry L, Bergel A. Marine microbial fuel cell: Use of stainless steel electrodes as anode and cathode materials. *Electrochim Acta* 2007;53:468–73. <https://doi.org/10.1016/j.electacta.2007.06.069>.
- [77] Zhang Y, Sun J, Hu Y, Li S, Xu Q. Carbon nanotube-coated stainless steel mesh for enhanced oxygen reduction in biocathode microbial fuel cells. *J Power Sources* 2013;239:169–74. <https://doi.org/10.1016/j.jpowsour.2013.03.115>.
- [78] Baelk G, Shi L, Rossi R, Logan BE. Using copper-based biocathodes to improve carbon dioxide conversion efficiency into methane in microbial methanogenesis cells. *Chemical Engineering Journal* 2022;435. <https://doi.org/10.1016/j.cej.2022.135076>.
- [79] Satar I, Bakar MHA, Daud WRW, Mohd Yasin NH, Somalu MR, Kim BH. Performance of nickel-iron foam (Ni-Fe) cathode in bio-electrochemical system for hydrogen production from effluent of glucose fermentation. *Materials Science and Engineering: B* 2020;260. <https://doi.org/10.1016/j.mseb.2020.114613>.
- [80] Bajracharya S, Vanbroekhoven K, Buisman CJN, Pant D, Strik DPB. Application of gas diffusion biocathode in microbial electrosynthesis from carbon dioxide. *Environmental Science and Pollution Research* 2016;23:22292–308. <https://doi.org/10.1007/s11356-016-7196-x>.
- [81] Pasupuleti SB, Srikanth S, Venkata Mohan S, Pant D. Continuous mode operation of microbial fuel cell (MFC) stack with dual gas diffusion cathode design for the treatment of dark fermentation effluent. *Int J Hydrogen Energy* 2015;40:12424–35. <https://doi.org/10.1016/j.ijhydene.2015.07.049>.
- [82] Kuntke P, Śmiech K, Bruning H, Zeeman G, Saakes M, Sleutels THJA, et al. Ammonium recovery and energy production from urine by a microbial fuel cell. *Water Res* 2012;46:2627–36. <https://doi.org/10.1016/j.watres.2012.02.025>.
- [83] Kahlet H. Reference electrodes. *Electroanalytical Methods: Guide to Experiments and Applications*. Berlin Heidelberg: Springer; 2010. p. 291–308. https://doi.org/10.1007/978-3-642-02915-8_15.
- [84] Wilson DM, Hoyt S, Janata J, Booksh K, Obando L. Chemical sensors for portable, handheld field instruments. *IEEE Sens J* 2001;1:256–74. <https://doi.org/10.1109/7361.983465>.
- [85] Logan BE, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, et al. Microbial fuel cells: Methodology and technology. *Environ Sci Technol* 2006;40:5181–92. <https://doi.org/10.1021/es0605016>.
- [86] Martin SM, Gebara FH, Strong TD, Brown RB. A Fully Differential Potentiostat. *IEEE Sens J* 2009;9:135–42. <https://doi.org/10.1109/JSEN.2008.2011085>.
- [87] Brezinskit DP. Kinetic, Static and Stirring Errors of Liquid Junction Reference Electrodes*. vol. 108. 1983. doi:10.1039/AN9830800425.

- [88] Wahyuni WT, Putra BR, Fauzi A, Ramadhanti D, Rohaeti E, Heryanto R. A Brief Review on Fabrication of Screen-Printed Carbon Electrode: Materials and Techniques. *Indo J Chem Res* 2021;8:210–8. <https://doi.org/10.30598/ijcr.2021.7-wul>.
- [89] Jerkiewicz G. Standard and Reversible Hydrogen Electrodes: Theory, Design, Operation, and Applications. *ACS Catal* 2020;10:8409–17. <https://doi.org/10.1021/acscatal.0c02046>.
- [90] Kim KY, Chae KJ, Choi MJ, Ajayi FF, Jang A, Kim CW, et al. Enhanced Coulombic efficiency in glucose-fed microbial fuel cells by reducing metabolite electron losses using dual-anode electrodes. *Bioresour Technol* 2011;102:4144–9. <https://doi.org/10.1016/j.biortech.2010.12.036>.
- [91] Zhao C, Wang Y, Shi F, Zhang J, Zhu JJ. High biocurrent generation in shewanella-inoculated microbial fuel cells using ionic liquid functionalized graphene nanosheets as an anode. *Chemical Communications* 2013;49:6668–70. <https://doi.org/10.1039/c3cc42068j>.
- [92] Zhao CE, Gai P, Song R, Chen Y, Zhang J, Zhu JJ. Nanostructured material-based biofuel cells: Recent advances and future prospects. *Chem Soc Rev* 2017;46: 1545–64. <https://doi.org/10.1039/c6cs00044d>.
- [93] Yuan Y, Zhou S, Zhao B, Zhuang L, Wang Y. Microbially-reduced graphene scaffolds to facilitate extracellular electron transfer in microbial fuel cells. *Bioresour Technol* 2012;116:453–8. <https://doi.org/10.1016/j.biortech.2012.03.118>.
- [94] Wahyuni WT, Riza Putra B, Fauzi A, Ramadhanti D, Rohaeti E, Heryanto R. Indonesian Journal of Chemical Research A Brief Review on Fabrication of Screen-Printed Carbon Electrode. *Materials and Techniques* 2021;8.
- [95] Su W-Y, Wang S-M, Cheng S-H. Electrochemically pretreated screen-printed carbon electrodes for the simultaneous determination of aminophenol isomers. *Journal of Electroanalytical Chemistry* 2011;651:166–72. <https://doi.org/10.1016/j.jelechem.2010.11.028>.
- [96] Suresh RR, Lakshmanakumar M, Arockia Jayalatha JBB, Rajan KS, Sethuraman S, Krishnan UM, et al. Fabrication of screen-printed electrodes: opportunities and challenges. *J Mater Sci* 2021;56:8951–9006. <https://doi.org/10.1007/s10853-020-05499-1>.
- [97] Kumar J, D'Souza SF. Microbial biosensor for detection of methyl parathion using screen printed carbon electrode and cyclic voltammetry. *Biosens Bioelectron* 2011;26:4289–93. <https://doi.org/10.1016/j.bios.2011.04.027>.
- [98] Timur S, Della Setta L, Pazarlıoğlu N, Pilloton R, Telefoncu A. Screen printed graphite biosensors based on bacterial cells. *Process Biochemistry* 2004;39: 1325–9. [https://doi.org/10.1016/S0032-9592\(03\)00265-6](https://doi.org/10.1016/S0032-9592(03)00265-6).
- [99] Nagel S, MacChesney J, Walker K. An overview of the modified chemical vapor deposition (MCVD) process and performance. *IEEE J Quantum Electron* 1982;18: 459–76. <https://doi.org/10.1109/JQE.1982.1071596>.
- [100] Bryant WA. Review The fundamentals deposition of chemical vapour. vol. 12. Pittsburgh: 1977. doi:[10.1007/BF00540843](https://doi.org/10.1007/BF00540843).
- [101] Pierson HO. *Handbook of chemical vapor deposition : principles, technology, and applications*. Noyes Publications; 1999.
- [102] Choy K. Chemical vapour deposition of coatings. *Prog Mater Sci* 2003;48:57–170. [https://doi.org/10.1016/S0079-6425\(01\)00009-3](https://doi.org/10.1016/S0079-6425(01)00009-3).
- [103] Yu F, Wang C, Ma J. Applications of graphene-modified electrodes in microbial fuel cells. *Materials* 2016;9. <https://doi.org/10.3390/ma9100807>.
- [104] Kirubaharan CJ, Santhakumar K, Gnana Kumar G, Senthilkumar N, Jang JH. Nitrogen doped graphene sheets as metal free anode catalysts for the high performance microbial fuel cells. *Int J Hydrogen Energy* 2015;40:13061–70. <https://doi.org/10.1016/j.ijhydene.2015.06.025>.
- [105] Wu W, Niu H, Yang D, Wang S, Jiang N, Wang J, et al. Polyaniline/Carbon nanotubes composite modified anode via graft polymerization and self-assembling for microbial fuel cells. *Polymers (Basel)* 2018;10. <https://doi.org/10.3390/polym10070759>.
- [106] Singh S, Verma N. Fabrication of Ni nanoparticles-dispersed carbon micro-nanofibers as the electrodes of a microbial fuel cell for bio-energy production. *Int J Hydrogen Energy* 2015;40:1145–53. <https://doi.org/10.1016/j.ijhydene.2014.11.073>.
- [107] Li B, Zhou J, Zhou X, Wang X, Li B, Santoro C, et al. Surface modification of microbial fuel cells anodes: Approaches to practical design. *Electrochim Acta* 2014;134:116–26. <https://doi.org/10.1016/j.electacta.2014.04.136>.
- [108] Wang J, Li M, Liu F, Chen S. Stainless Steel Mesh Supported Carbon Nanofibers for Electrode in Bioelectrochemical System. *J Nanomater* 2016;2016. <https://doi.org/10.1155/2016/4246568>.
- [109] Zhao N, Ma Z, Song H, Xie Y, Zhang M. Enhancement of bioelectricity generation by synergistic modification of vertical carbon nanotubes/polypyrrole for the carbon fibers anode in microbial fuel cell. *Electrochim Acta* 2019;296:69–74. <https://doi.org/10.1016/j.electacta.2018.11.039>.
- [110] Gamborg YD, Zangari G. Theory and Practice of Metal Electrodeposition. Theory and Practice of Metal Electrodeposition 2011. <https://doi.org/10.1007/978-1-4419-9669-5>.
- [111] Paunovic M, Schlesinger M. Fundamentals of Electrochemical Deposition. Wiley; 2006. <https://doi.org/10.1002/0470009403>.
- [112] Satar I, Daud WRW, Kim BH, Somalu MR, Ghasemi M, Bakar MHA, et al. Performance of titanium–nickel (Ti/Ni) and graphite felt-nickel (GF/Ni) electrodeposited by Ni as alternative cathodes for microbial fuel cells. *J Taiwan Inst Chem Eng* 2018;89:67–76. <https://doi.org/10.1016/j.jtice.2018.04.010>.
- [113] Zhang C, Liang P, Jiang Y, Huang X. Enhanced power generation of microbial fuel cell using manganese dioxide-coated anode in flow-through mode. *J Power Sources* 2015;273:580–3. <https://doi.org/10.1016/j.jpowsour.2014.09.129>.
- [114] Mishra P, Jain R. Electrochemical deposition of MWCNT-MnO₂/PPy nano-composite application for microbial fuel cells. *Int J Hydrogen Energy* 2016;41: 22394–405. <https://doi.org/10.1016/j.ijhydene.2016.09.020>.
- [115] Navanietha Krishnaraj R, Karthikeyan R, Berchmans S, Chandran S, Pal P. Functionalization of electrochemically deposited chitosan films with alginate and Prussian blue for enhanced performance of microbial fuel cells. *Electrochim Acta* 2013;112:465–72. <https://doi.org/10.1016/j.electacta.2013.08.180>.
- [116] Alonso RM, San-Martín MI, Sotres A, Escapa A. Graphene oxide electrodeposited electrode enhances start-up and selective enrichment of exoelectrogens in bioelectrochemical systems. *Sci Rep* 2017;7. <https://doi.org/10.1038/s41598-017-14200-7>.
- [117] Sharma RK. *Advancements in Nanotechnology for Energy and Environment*. Singapore: Springer Nature Singapore; 2022. <https://doi.org/10.1007/978-981-19-5201-2>.
- [118] Lv C, Liang B, Zhong M, Li K, Qi Y. Activated carbon-supported multi-doped graphene as high-efficient catalyst to modify air cathode in microbial fuel cells. *Electrochim Acta* 2019;304:360–9. <https://doi.org/10.1016/j.electacta.2019.02.094>.
- [119] Ghasemi M, Daud WRW, Hassan SHA, Oh SE, Ismail M, Rahimnejad M, et al. Nano-structured carbon as electrode material in microbial fuel cells: A comprehensive review. *J Alloys Compd* 2013;580:245–55. <https://doi.org/10.1016/j.jallcom.2013.05.094>.
- [120] Lv C, Liang B, Zhong M, Li K, Qi Y. Activated carbon-supported multi-doped graphene as high-efficient catalyst to modify air cathode in microbial fuel cells. *Electrochim Acta* 2019;304:360–9. <https://doi.org/10.1016/j.electacta.2019.02.094>.
- [121] Mashkour M, Rahimnejad M. Effect of various carbon-based cathode electrodes on the performance of microbial fuel cell. *Biofuel Research Journal* 2015;2: 296–300. <https://doi.org/10.18331/BRJ2015.2.4.3>.
- [122] Mohamed HO, Sayed ET, Obaid M, Choi YJ, Park SG, Al-Qaradawi S, et al. Transition metal nanoparticles doped carbon paper as a cost-effective anode in a microbial fuel cell powered by pure and mixed biocatalyst cultures. *Int J Hydrogen Energy* 2018;21560–71. <https://doi.org/10.1016/j.ijhydene.2018.09.199>.
- [123] Mashkour M, Rahimnejad M. Effect of various carbon-based cathode electrodes on the performance of microbial fuel cell. *Biofuel Research Journal* 2015;2: 296–300. <https://doi.org/10.18331/BRJ2015.2.4.3>.
- [124] Yin T, Zhang H, Yang G, Wang L. Polyaniline composite TiO₂ nanosheets modified carbon paper electrode as a high performance bioanode for microbial fuel cells. *Synth Met* 2019;252:8–14. <https://doi.org/10.1016/j.synthmet.2019.03.027>.
- [125] Wang Y, Zheng H, Lin C, Zheng J, Chen Y, Wen Q, et al. Development of a 3D porous sponge as a bioanode coated with polyaniline/sodium alginate/nitrogen-doped carbon nanotube composites for high-performance microbial fuel cells. *J Appl Electrochem* 2020;50:621–30. <https://doi.org/10.1007/s10800-020-01410-7>.
- [126] Penteado ED, Fernandez-Marchante CM, Zaiai M, Gonzalez ER, Rodrigo MA. Optimization of the performance of a microbial fuel cell using the ratio electrode-surface area /anode-compartment volume. *Brazilian Journal of Chemical Engineering* 2018;35:141–6. <https://doi.org/10.1590/0104-6632.20180351s20160411>.
- [127] Di Lorenzo M, Scott K, Curtis TP, Head IM. Effect of increasing anode surface area on the performance of a single chamber microbial fuel cell. *Chemical Engineering Journal* 2010;156:40–8. <https://doi.org/10.1016/j.cej.2009.09.031>.
- [128] Gajda I, Greenman J, Ieropoulos I. Microbial Fuel Cell stack performance enhancement through carbon veil anode modification with activated carbon powder. *Appl Energy* 2020;262. <https://doi.org/10.1016/j.apenergy.2019.114475>.
- [129] Kumar R, Singh L, Zularisam AW. Microbial fuel cells: Types and applications. *Waste Biomass Management - A Holistic Approach*. Springer International Publishing 2017:367–84. https://doi.org/10.1007/978-3-319-49595-8_16.
- [130] Wang A, Sun D, Cao G, Wang H, Ren N, Wu WM, et al. Integrated hydrogen production process from cellulose by combining dark fermentation, microbial fuel cells, and a microbial electrolysis cell. *Bioresour Technol* 2011;102:4137–43. <https://doi.org/10.1016/j.biortech.2010.10.137>.
- [131] Kadier A, Kalil MS, Abdeshahian P, Chandrasekhar K, Mohamed A, Azman NF, et al. Recent advances and emerging challenges in microbial electrolysis cells (MECs) for microbial production of hydrogen and value-added chemicals. *Renewable and Sustainable Energy Reviews* 2016;61:501–25. <https://doi.org/10.1016/j.rser.2016.04.017>.
- [132] Catal T, Kavanagh P, O'Flaherty V, Leech D. Generation of electricity in microbial fuel cells at sub-ambient temperatures. *J Power Sources* 2011;196:2676–81. <https://doi.org/10.1016/j.jpowsour.2010.11.031>.
- [133] Wagner RC, Regan JM, Oh SE, Zuo Y, Logan BE. Hydrogen and methane production from swine wastewater using microbial electrolysis cells. *Water Res* 2009;43:1480–8. <https://doi.org/10.1016/j.watres.2008.12.037>.
- [134] Rozendal RA, Hamelers HVM, Euverink GJW, Metz SJ, Buisman CJN. Principle and perspectives of hydrogen production through biocatalyzed electrolysis. *Int J Hydrogen Energy* 2006;31:1632–40. <https://doi.org/10.1016/j.ijhydene.2005.12.006>.
- [135] Conway B. Nature of electrosorbed H and its relation to metal dependence of catalysis in cathodic H₂ evolution. *Solid State Ion* 2002;150:93–103. [https://doi.org/10.1016/S0167-2738\(02\)00266-7](https://doi.org/10.1016/S0167-2738(02)00266-7).
- [136] Selembio PA, Merrill MD, Logan BE. The use of stainless steel and nickel alloys as low-cost cathodes in microbial electrolysis cells. *J Power Sources* 2009;190: 271–8. <https://doi.org/10.1016/j.jpowsour.2008.12.144>.

- [137] Selembo PA, Merrill MD, Logan BE. The use of stainless steel and nickel alloys as low-cost cathodes in microbial electrolysis cells 2009;190:271–8. [doi:10.1016/j.jpowsour.2008.12.144](https://doi.org/10.1016/j.jpowsour.2008.12.144).
- [138] Madadi R, Maljacec H, Serafim LS, Ventura SPM. Microalgae as contributors to produce biopolymers. *Mar Drugs* 2021;19:1–27. <https://doi.org/10.3390/MD19080466>.
- [139] Cheng S, Logan BE. Sustainable and efficient biohydrogen production via electrohydrogenesis. *Proceedings of the National Academy of Sciences* 2007;104: 18871–3. <https://doi.org/10.1073/pnas.0706379104>.
- [140] Jeremiassie AW, Hamelers HVM, Buisman CJN. Microbial electrolysis cell with a microbial biocathode. *Bioelectrochemistry* 2010;78:39–43. <https://doi.org/10.1016/j.bioelechem.2009.05.005>.
- [141] Sardrood BP, Goltapeh EM, Varma A. An Introduction to Bioremediation, 2013, p. 3–27. [doi:10.1007/978-3-642-33811-3_1](https://doi.org/10.1007/978-3-642-33811-3_1).
- [142] Wang H, Luo H, Fallgren PH, Jin S, Ren ZJ. Bioelectrochemical system platform for sustainable environmental remediation and energy generation. *Biotechnol Adv* 2015;33:317–34. <https://doi.org/10.1016/j.biotechadv.2015.04.003>.
- [143] Gregory KB, Lovley DR. Remediation and recovery of uranium from contaminated subsurface environments with electrodes. *Environ Sci Technol* 2005;39:8943–7. <https://doi.org/10.1021/es050457e>.
- [144] Thung WE, Ong SA, Ho LN, Wong YS, Ridwan F, Oon YL, et al. A highly efficient single chambered up-flow membrane-less microbial fuel cell for treatment of azo dye Acid Orange 7-containing wastewater. *Bioresour Technol* 2015;197:284–8. <https://doi.org/10.1016/j.biortech.2015.08.078>.
- [145] Oon YS, Ong SA, Ho LN, Wong YS, Oon YL, Lehl HK, et al. Disclosing the synergistic mechanisms of azo dye degradation and bioelectricity generation in a microbial fuel cell. *Chemical Engineering Journal* 2018;344:236–45. <https://doi.org/10.1016/j.cej.2018.03.060>.
- [146] Miran W, Rasool K, Nawaz M, Kadam A, Shin S, Heo J, et al. Simultaneous electricity production and Direct Red 80 degradation using a dual chamber microbial fuel cell. *Desalination Water Treat* 2016;57:9051–9. <https://doi.org/10.1080/19443994.2015.1049410>.
- [147] Khan N, Anwer AH, Ahmad A, Sabir S, Khan MZ. Investigating microbial fuel cell aided bio-remediation of mixed phenolic contaminants under oxic and anoxic environments. *Biochem Eng J* 2020;155. <https://doi.org/10.1016/j.bej.2019.107485>.
- [148] Sherafatmand M, Ng HY. Using sediment microbial fuel cells (SMFCs) for bioremediation of polycyclic aromatic hydrocarbons (PAHs). *Bioresour Technol* 2015;195:122–30. <https://doi.org/10.1016/j.biortech.2015.06.002>.
- [149] Yaqoob AA, Ibrahim MNM, Yaakop AS, Umar K, Ahmad A. Modified graphene oxide anode: A bioinspired waste material for bioremediation of Pb²⁺ with energy generation through microbial fuel cells. *Chemical Engineering Journal* 2021;417. <https://doi.org/10.1016/j.cej.2020.128052>.
- [150] Fenner K, Canonica S, Wackett LP, Elsner M. Evaluating Pesticide Degradation in the Environment: Blind Spots and Emerging Opportunities. *Science* (1979) 2013; 341(1979):752–8. <https://doi.org/10.1126/science.1236281>.
- [151] Priyadarshini M, Ahmad A, Das S, Ghangrekar MM. Application of microbial electrochemical technologies for the treatment of petrochemical wastewater with concomitant valuable recovery: A review. *Environmental Science and Pollution Research* 2021. <https://doi.org/10.1007/s11356-021-14944-w>.
- [152] Hou Y, Tu L, Qin S, Yu Z, Yan Y, Xu Y, et al. Dye wastewater treatment and hydrogen production in microbial electrolysis cells using MoS₂-graphene oxide cathode: Effects of dye concentration, co-substrate and buffer solution. *Process Biochemistry* 2021;102:51–8. <https://doi.org/10.1016/j.procbio.2020.12.008>.
- [153] Koomson DA, Huang J, Li G, Miwonrunyuine N, Ewusi-Mensah D, Darkwah WK, et al. Comparative studies of recirculatory microbial desalination cell-microbial electrolysis cell coupled systems. *Membranes (Basel)* 2021;11. <https://doi.org/10.3390/MEMBRANES11090661>.
- [154] Gu N, Liu S. Introduction to Biosensors. *J Mater Chem B* 2020;8:3168–70. <https://doi.org/10.1039/d0tb90051f>.
- [155] Ivasi TJP, Nyakuma BB, Oladokun O, Abu PT, Hassan MN. Review of the principal mechanisms, prospects, and challenges of bioelectrochemical systems. *Environ Prog Sustain Energy* 2020;39. <https://doi.org/10.1002/ep.13298>.
- [156] Grattieri M, Hasan K, Minteer SD. Bioelectrochemical Systems as a Multipurpose Biosensing Tool: Present Perspective and Future Outlook. *ChemElectroChem* 2017;4:834–42. <https://doi.org/10.1002/celc.201600507>.
- [157] Patil S, Harnisch F, Schröder U. Toxicity response of electroactive microbial biofilms-a decisive feature for potential biosensor and power source applications. *ChemPhysChem* 2010;11:2834–7. <https://doi.org/10.1002/cphc.201000218>.
- [158] Olias LG, Di Lorenzo M. Microbial fuel cells for in-field water quality monitoring. *RSC Adv* 2021;11:16307–17. <https://doi.org/10.1039/d1ra01138c>.
- [159] Hong Kim B, Seop Chang I, Cheol Gil G, Soo Park H, Joo Kim H. Novel BOD (biological oxygen demand) sensor using mediator-less microbial fuel cell. vol. 25. 2003. [doi:10.1023/A:1022891231369](https://doi.org/10.1023/A:1022891231369).
- [160] Beech IB, Sunner JA, Hiraoka K. Microbe-surface interactions in biofouling and biocorrosion processes. *Int Microbiol* 2005;8:157–68. <https://doi.org/10.2436/IM.V8I3.9522>.
- [161] Beech IB. Corrosion of technical materials in the presence of biofilms - Current understanding and state-of-the art methods of study. *Int Biodeterior Biodegradation* 2004;53:177–83. [https://doi.org/10.1016/S0964-8305\(03\)00092-1](https://doi.org/10.1016/S0964-8305(03)00092-1).
- [162] Hassan M, Kanwal S, Singh RS, Ali SA M, Anwar M, Zhao C. Current challenges and future perspectives associated with configuration of microbial fuel cell for simultaneous energy generation and wastewater treatment. *Int J Hydrogen Energy* 2024;50:323–50. <https://doi.org/10.1016/j.ijhydene.2023.08.134>.
- [163] Mashkour M, Rahimnejad M, Raouf F, Navidjouy N. A review on the application of nanomaterials in improving microbial fuel cells. *Biofuel Research Journal* 2021;8:1400–16. <https://doi.org/10.18331/BRJ2021.8.2.5>.
- [164] Zhang B, Jiang Y, Han J. Facile fabrication of PVAc-g-PVDF coating on surface modified cotton fabric for applications in oil/water separation and heavy metal ions removal. *Fibers and Polymers* 2017;18:1754–62. <https://doi.org/10.1007/s12221-017-1224-4>.
- [165] Palanisamy G, Thangarasu S, Dharman RK, Patil CS, Prithvi Pal Singh Negi T, Kurkuri MD, et al. The growth of biopolymers and natural earthen sources as membrane/sePARATOR materials for microbial fuel cells: A comprehensive review. *J Energy Chem* 2023;80:402–31. <https://doi.org/10.1016/j.jechem.2023.01.018>.
- [166] Kumar AG, Singh A, Komber H, Voit B, Tiwari BR, Noori MT, et al. Novel Sulfonated Co-poly(ether imide)s Containing Trifluoromethyl, Fluoranyl and Hydroxyl Groups for Enhanced Proton Exchange Membrane Properties: Application in Microbial Fuel Cell. *ACS Appl Mater Interfaces* 2018;10:14803–17. <https://doi.org/10.1021/acsami.8b03452>.
- [167] Jafary T, Al-Mamur A, Alhimali H, Baawain MS, Rahman MS, Rahman S, et al. Enhanced power generation and desalination rate in a novel quadruple microbial desalination cell with a single desalination chamber. *Renewable and Sustainable Energy Reviews* 2020;127. <https://doi.org/10.1016/j.rser.2020.109855>.
- [168] Dattatraya Saratale G, Rajesh Banu J, Nastro RA, Kadier A, Ashokkumar V, Lay CH, et al. Bioelectrochemical systems in aid of sustainable biorefineries for the production of value-added products and resource recovery from wastewater: A critical review and future perspectives. *Bioresour Technol* 2022;359. <https://doi.org/10.1016/j.biortech.2022.127435>.
- [169] Bajracharya S, Srikanth S, Mohanakrishna G, Zacharia R, Strik DP, Pant D. Biotransformation of carbon dioxide in bioelectrochemical systems: State of the art and future prospects. *J Power Sources* 2017;356:256–73. <https://doi.org/10.1016/j.jpowsour.2017.04.024>.
- [170] Schiel-Bengelsdorf B, Dürre P. Pathway engineering and synthetic biology using acetogens. *FEBS Lett* 2012;586:2191–8. <https://doi.org/10.1016/j.febslet.2012.04.043>.