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Review

Review on Material and Design of Anode for Microbial Fuel Cell

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Abstract: Microbial Fuel Cell (MFC) is a bio-electrochemical system that generates electricity by anaerobic oxidation of substrates. An anode is the most critical component because the primary conversion of wastewater into electrons and protons takes place on the surface of the anode, where a biofilm is formed. This paper describes the essential properties of the anode and classifies its types according to the material used to make it. Anode material is responsible for the flow of electrons generated by the microorganism; hence biocompatibility and conductivity can considered to be the two most important properties. In this paper, the various modification strategies to improve the performance of anodes of MFC are explained through the review of researchers' published work in this field. The shape and size of the anode turned out to be very significant as the microbial growth depends on the available surface area. The attachment of biofilm on the surface of an anode largely depends on the interfacial surface chemistry. Methods for improving MFC performance by altering the anode material, architecture, biocompatibility, and longevity are discussed with a future perspective giving special importance to the cost.

Keywords: microbial fuel cell; properties of anode; carbon-based material; conductive polymer; advanced Hummer's method; polymer coating; nanocomposite material; metal-based anode; scaleup challenges

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1. Introduction

In 1780, Luigi Galvani and his wife Lucia discovered during an experiment that when an electrical spark struck the legs of a dead frog, their muscles twitched. This incident was one of the first explorations into the field of bioelectricity, which investigates the electrical patterns and signals produced by tissues such as nerves and muscles. This observation turned into one of the most important inventions. It led to different research aspects, including the development of bio-electrochemical systems such as microbial desalination cells, microbial fuel cells (MFCs), and microbial electrolysis cells (MECs). The latter two are particularly attractive as the MFC can treat wastewater and recover energy by directly generating electricity.

In contrast, in the MEC, the process is reversed to generate hydrogen or methane from organic material by applying electrical energy. However, the technology is still in its infancy, and most research is at a lab scale. Similar to MFCs, various electrochemical systems are made of the membrane electrode assembly, such as iron redox flow batteries, vanadium redox flow batteries, polymer electrolyte fuel cells, etc. [1,2]. These electrochemical systems often require heavy metals and expensive gases for operation [3]. The operational expenditure of these systems is always higher compared to MFCs. MFC is a self-sustainable and inexpensive process that only requires wastewater as a fuel for operation. The performance of the MFC needs to be improved further to employ MFC as an alternative technology for wastewater treatment and make the system economically viable. The design of the MFC plays a significant role in achieving the best performance.

The crucial components, such as electrodes and membranes, are selected based on the required properties and cost. This paper considers the key characteristics of the anode and reviews various potential materials and their impact on performance and cost. It also describes the design strategy for selecting the most appropriate anode material with the goal of improving the overall performance of the device.

In MFC, the conversion of organic matter into electricity occurs through bacterial metabolism. A typical MFC consists of two chambers, the anode and the cathode, each containing an electrode. The two electrodes are separated by a proton exchange membrane (PEM) (Figure 1). Membrane plays a significant role in MFC. Nafion, the most commonly used membrane, has a hydrophobic polytetrafluoroethylene (PTFE) backbone with excellent chemical stability. A lot of research work also has been carried out irrespective of MFC on Nafion membrane to enhance the crucial properties such as resistance to fouling, species crossover, chemical degradation, mechanical fatigue degradation/ageing, etc. [4]. A research study showed that the Tungsten oxide dispersed into the Nafion matrix formed two layers of inorganic and organic ion exchange membrane. This modified membrane was used in vanadium redox flow battery (VRFB) instead of Nafion 212, which showed an increase in Coulombic efficiency from 88% to 93% [5]. Table 1 lists the main components, and potential materials need to design MFC. The selection of proper microorganisms influences a lot in the overall performance of MFC. The microbes oxidize the organic substrate to produce protons (H^+) and electrons in the anode chamber. The electrons are transferred to the cathode chamber through an external circuit that produces electricity. H^+ ions flow through the membrane to the cathode chamber and react with oxygen to form water. All three components contribute to the cell's functionality. However, an anode is where bacteria grow and oxidize substrate into electrons, H^+, and CO_2. The wastewater acts as a fuel in this device, and microbial activity in the anodic chamber depends on the characteristics of wastewater. The concentration of organic matter (substrate), pH, total dissolved solids, etc., influences the kinetics of the biochemical reaction in an anodic chamber. Necessary batch studies are often required to optimize the flow rate of the wastewater according to the bacterial growth kinetics [6]. The sensitivity of microbial growth towards pH, substrate inhibition, etc., needs to be optimized prior to the continuous steady-state operation.

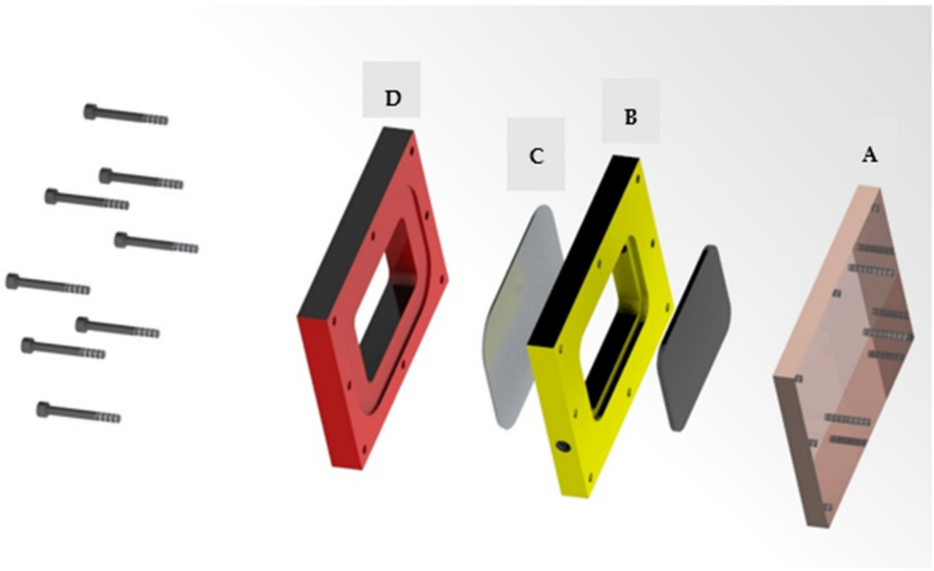

Figure 1. Schematic configuration of a Microbial Fuel Cell (A: End Plate; B: Anode Chamber; C: Membrane; D: Cathode Chamber).

Table 1. Major three components of microbial fuel cell and material used.

Component	Materials	Remarks	Reference
Anode	Carbon felt, carbon paper, carbon cloth, Reticulated vitreous carbon (RVC), graphite-felt, graphite-brush, graphene-oxide, graphene-nano tubes, Pt black	Essential	[7,8]
Membrane	Ion exchange, cation exchange, anion exchange, proton exchange (Nafion 117, Ultrex, SPEEK), salt bridge	Optional	[4,7,9,10]
Cathode	Carbon felt, carbon catalyst with stainless steel mesh, carbon cloth, graphite, reticulated vitreous carbon (RVC), biocathode	Essential	[7,11–13]

2. Role of Anode Material and Characterization

The output of MFC is sensitive towards the selection of anodic material and its design as it affects the biocatalytic activity. Anode design is key to providing the bacteria with the necessary environment and surface area to grow. The process by which microbes transfer electrons to the electrode is a rate-limiting step of the MFC [8]. Various materials can be used as an anode to boost the output of the MFC. The anaerobic condition in an anodic chamber often enhances the microbial growth on the surface of the anode [14].

For the efficient transfer of electrons, the other essential property of the anode is conductivity. Metals such as copper, platinum, and stainless steel are conductive and can be considered suitable for the anode. However, these metals or alloys may be ideal for the electrochemical activity of the fuel cells but not so good for the microbial activity. Some metals such as platinum and titanium stood out due to their ability to carry electrons over long distances and their effectiveness in large-scale operations. However, using such precious metals increases the system cost and introduces new research areas for finding alternative materials when scaling up a typical MFC [15].

Previous research on anode development was based on two philosophies. The earlier study aimed to increase anode surface area to accommodate more biofilm. In contrast, the concept worked well in small-scale operations or lab studies. However, a scaled-up system or stacked MFC requires more than increasing electrode surface area. It requires proper electron migration between anode and cathode [16]. Recent research has focused on long-distance electron transport from anode to cathode rather than small-scale operation.

There are several techniques to modify the properties of the carbon-based anode, such as treatment with acid, electrochemical treatment, coating with polymer, etc. The main focus behind these techniques is to increase the surface area and perturb the surface chemistry, which improves the adhesion of biofilm on the surface of an anode. A research paper describes the method of determining the increased surface area after modification was carried out using acids and electrochemical treatment. The Brunauer-Emmett-Teller (BET) gas adsorption method has been used to characterize the increase in the surface area of anode after chemical treatment and modification [17].

2.1. Essential Properties of Anode

The electrode materials were investigated in order to improve the efficiency of the treatment of wastewater and energy generation. The electrode material should have excellent mechanical strength, chemical stability, biocompatibility, and electrical conductivity, among other characteristics [18]. The conductive property of materials offers a high flow of electrons which is very important for MFC to perform well [19]. The surface area of the electrode plays a significant role in microbial activity. Better performance was obtained by offering a higher surface area of the anode. For microbial activity, both surface area and material of anode are very sensitive. A good technique of measuring the surface area of monolayer graphene was presented in the paper [20]. The major influential properties of the anode affecting the performance of MFC is summarized below.

2.1.1. Surface Area

In MFC, energy production is primarily influenced by the anode's surface area [21]. The Ohmic loss of MFC largely depends on the internal resistance of the anode. Increasing the surface area enhances electrode kinetics as it promotes microbial activity. An indirect electron transfer from the cell membrane to the anode electrode is possible with Gram-negative proteobacteria [22]. These gram-negative proteobacteria become adhered to on the surface of the anode and form biofilm. The roughness of the surface offers a better attachment to the biofilm. An increase in the rough surface area of the anode enhances the active sites and is suitable for microbial attachment.

2.1.2. Chemical Compatibility

Electrodes are directly exposed to bacterial respiration. Copper, silver, gold, and other metals are used as an anode, and they are incompatible with biological activity [23] because they tend to corrode in acidic environments. Moreover, copper has a toxic effect on microbial activity; thus, such kinds of metals, even they are good conductors, are not considered suitable anode materials from the bacterial point of view [24].

2.1.3. Durability

The low durability and mechanical instability of conventional anode materials may cause swelling and affect the lifespan of anode material [25]. Exposure to anode material in an acidic environment over a more extended period may lead to corrosion and often becomes swelled. Thermal instability, the low mechanical strength of anode material and chemical corrosion because of the high local concentration of H^+ ions lead to this kind of electrode swelling. The rough surface area of the anode also helps to remove moisture and offers more active sites to the microbes [24].

2.1.4. Electrical Conductivity

Bacteria emit electrons transferred to the anode electrode and then to the cathode via the external circuit. The suitable conductive materials offer a higher electron transfer rate. The selection of conductive anode material should be so that it can provide low resistance to the substrate present in anodic solution for a better flow of electrons. Resistance and interfacial impedance can be reduced by using highly conductive materials [26].

2.1.5. Porosity

The porous surface of the anode enhances the biocatalytic conversion by microorganisms. The porous surface effectively immobilizes the microorganisms, promoting direct electron transfer. Porosity reduces ohmic loss and internal resistance. Increasing porosity indirectly increases anode surface area, encouraging bacterial and biofilm growth. Researchers have used carbon allotropes and even porous graphite brushes to improve biofilm and biochemical activities [22].

3. Classification of Anode

The two most important properties of anode influence the performance of MFC; One is biocompatibility, and another is electron conductivity. Based on these properties, various research works have been reported. A research study showed that the use of porous three-dimensional interconnecting conductive Polypyrrole (PPy) material with a larger rough surface area showed maximum power density around 2420 mW/m^2 due to its porous three-dimensional structure and huge rough surface area. A rough surface always offers better adhesion to the biofilm formed by microorganisms on the surface of anode [27]. Thus, an increase in the surface area and the roughness of the surface increases the biocompatibility of the anode. The classification of anode material is presented and discussed based on the past research studies in the following section.

3.1. Carbon Based Anode

Due to its biocompatibility and electron transfer kinetics, carbon-based materials are used as anodes in microbial fuel cells. The selection of anode material is guided by the biochemical reaction which takes place in an anodic chamber [28]. The conversion of electrons and protons is determined by reaction kinetics. The reaction occurs on the surface of the anode, where the biofilm is formed. The kinetics of this biochemical reaction determines the conversion of electrons and protons from the organic matter present in the wastewater. Carbon-based materials used as an anode include brush, felt, cloth, mesh, paper, rod, RVC, graphite, etc. [29–31]. The use of carbon fibers material as an anode showed more promising results in output because of the larger surface area, three-dimensional structure, high chemical stability, and electrical conductivity. A research study on iron-chromium redox flow battery explained the essential physical and chemical properties of polyacrylonitrile-based graphite felt (GF) and carbon felt (CF) in detail [32]. However, these materials have their own benefits and drawbacks. Carbon paper/cloth significantly improved output power densities in lab-scale tests due to its higher effective surface area than graphite rod [33]. Scaling up using carbon cloths/sheets is technically simple due to their flexibility but using large carbon cloths makes the system very expensive. Many researchers have used cheaper carbon mesh instead of carbon cloth, and it worked well even in large-scale operations. The atomic ratio of nitrogen is to carbon of anode material proved to be favorable for microbial growth and attachment. A research study on the development of anode showed better performance when the ratio of nitrogen is to carbon was increased by heating the carbon mesh followed by treatment with ammonia gas [34]. Another research work showed that the plasma modified carbon paper performed better than carbon mesh because of its high surface area but failed to scale up due to its high cost [35]. A research study with porous activated carbon granules showed promising results in large-scale MFC operation due to its higher porosity and charge holding capacity. Granular activated carbon (GAC) based anode produced twice the output energy compared with regular carbon felt [36]. Most of the wastewater is turbid and often contains a lot of suspended materials. Using GAC as an anode in such wastewater resulted in a low-pressure drop and better efficiency due to the higher surface area. Graphite, another important allotrope of carbon, has a crystalline structure and is a good conductor of electricity.

A group of researchers studied the carbon nanotubes as an anode of MFCs and showed a promising result with remarkable electrochemical properties and possibilities of larger-scale operation [37]. Carbon nanotubes fiber mat material was used to make three-dimensional electrodes to enhance the output of MFC. Geobacter sulfurreducens microorganisms were used as proteobacteria and showed around 7.5 mA/cm^2 maximum output current density [38]. Another research study reported that the use of multi-walled carbon nanotubes provided a better result than the single-walled carbon nanotube as an anode in the presence of a hydroxyl group. Moreover, the open-circuit voltage was achieved around 0.75 V, and the maximum power density obtained was around 167 $mW/m^{2,}$ which is 130% higher than that of carbon cloth [39].

A research study showed that the polished surface of graphite rod is not suitable as an anode material for the attachment of biofilm, leading to low output of MFC. The output power density increased with an increase in roughness of the graphite rod surface [40], but its limited surface area restricts the growth of the biofilm compared to the graphite brush or GAC. Bruce Logan had used a large surface area graphite brush as an anode for enhancing MFC performance [8]. Following the concept of anode's design, another research work has been carried out using graphite brush as an anode material to remove COD and other pollutants from wastewater [41]. Subsequently, the review of anode material concluded that the most promising anode material is proved to be graphite brush for the scaled-up system. The shape and structure of graphite brush electrodes were studied further to optimize their design. A research study showed that shorter diameter brushes performed better than longer diameter brushes, although the longer one has more surface area. The poor performance of longer brushes was attributed to the coulombic loss, which is more

in long brushes [41]. Using multiple short brushes instead of one long brush improved the performance of MFC. This is because a shorter path has less resistance to electron flow. Observing the concept of electron flow in the least resistance path, scaling up the system can be carried out by stacking multiple small graphite brush type anode to achieve higher output power densities.

Graphene is more stable, durable, mechanically, and diamagnetically more robust than graphite. Graphene is highly conductive and biocompatible and is often used as an anode in MFC. Due to these two properties of graphene, researchers have carried out several studies on this material. Commercial graphene is very expensive, so a cheaper alternative is always needed. Compared to commercial graphene materials, using waste to carbonize graphene powder appears to be significant and cost-effective [23]. Moreover, waste-derived graphene powder provided microbes with more surface area to grow.

The most popular method for carbonizing waste materials is Hummer's method because it is eco-friendly and produces no toxic fumes as a byproduct [42]. At the early stage of work, researchers were more focused on the production of graphene oxide (GO). Later the focus shifted to synthesizing three-dimensional graphene oxide (GO). Mesoporous structure, high electrical conductivity, ultra-light weight, enzyme immobilization, and large surface area of three-dimensional GO outperformed two-dimensional GO [43]. Graphene oxide (GO) is synthesized in several steps [44]. Natural waste is carbonized in the presence of inert gas at around 1050 °C to obtain fine nanoparticles. The nanoparticles are created by oxidizing reagents such as hydrogen peroxide and potassium permanganate (Figure 2). Nitrate was used to dope nitrogenous substances to increase the nitrogen-to-carbon ratio and oxidize the material. A research study showed that the smaller mesh fine particles provided more surface area for microbial activity and enhanced MFC's performance [45]. Although the entire process takes a long time, it is still cheaper than commercial graphene.

Figure 2. Schematic diagram of advanced Hummer's method for graphene oxide electrode.

Modifications of Hummer's method were reported in various studies. In one study, the modification was carried out by introducing three major steps: drying, heating, and oxidation (Figure 2) [43]. According to the stoichiometry, graphite powder and sodium nitrate were added in concentrated sulfuric acid under stirring for 30 min. After that, potassium permanganate was added in a controlled way under slow stirring to the same solution. Since the reaction is exothermic, the beaker was placed in an ice bath to maintain the temperature below 20 °C. The endpoint of this step was determined by the change of the color from violet to brownish violet. Subsequently, demineralized water was added in a very controlled way while the temperature was kept around 95 °C using a water bath. Finally, the reaction was completed by adding 30% hydrogen peroxide dropwise to form bright yellow graphene oxide (GO). After oxidation, the graphene oxide was dispersed in an L-Cysteine solution using ultrasonication and rapid stirring to form an aerogel or hydrogel. In order to improve the system performance, the hydrogel was mixed with a polymeric binder such as PTFE (Polytetrafluoroethylene) or PES (Polyether sulfonate) to form a paste. This modified graphene oxide paste was further used to make electrodes in various shapes and sizes. A porous and three-dimensional structure with a larger anode surface area is always preferable to a denser graphite rod with less porosity and surface area in MFCs.

In another research study, ice templates were used to form 3D graphene loofah and used as an anode. The output power density achieved by using loofah graphene anode was around 427 W/m^3 [46]. It was reported that doping of nickel in graphene helped to increase the conductivity and the overall performance of the electrode. The power density was increased to 1024 mW/m^2 [47]. A research study showed graphene hydrogel's formation by dispersing graphene powder in L-cysteine. This graphene hydrogel anode was used, and the obtained output power density was around 679.9 mW/m^2 [48].

The various research studies show that the use of graphene as an anodic material showed the best performance among other carbon-based electrodes [49]. Nevertheless, the use of graphite brush type anode, which performed well in large-scale operations, was reported in a few papers. Combining these two philosophies by forming graphene oxides brush could result in a revolutionary change in the field of wastewater and its treatment methodology.

3.2. Natural Material Based Anode

The electrodes are chosen based on their physicochemical and biological properties in a microbial fuel cell. In search of cheap carbon-based material, natural waste materials enriched with organic matter can be a good alternative to commercial carbon-based materials. Raw waste is readily available and inexpensive, but it must be treated to be compatible with the system. It takes a long time to process but is cheaper than other materials due to its stability, availability, and biocompatibility. Most importantly, recycling can be carried out by using waste material. A research study was carried out to improve the performance of the MFC using layer corrugated carbon (LCC) anode. The research work showed that the layer corrugated carbon anode increased the surface and facilitated microbial growth (Table 2). It also indicated that the output current density for a single layer was around 70 A/m^2, for three-layered corrugated carbon was 200 $A/m^{2,}$ and for six-layered corrugated carbon was 390 A/m^2 [50]. The mesoporous structure of natural waste-derived anode materials showed promising output because of its 3D structure, which also helped to optimize the internal resistance. The use of natural egg white protein (EWP) developed carbon-based material doped with titanium dioxide as capacitive layers showed a significant result around 2590 mW/m^2 when it was integrated into loofah sponge carbon (LSC) due to its mesoporous 3D structure [51]. This is 63% higher than normal loofah sponge carbon (LSC) and two times higher compared to graphite anodes due to the favorable surface functionalization for the interfacial microbial electron transfer.

Table 2. Natural material-based anode and output performances.

Natural Source of Anode Material	Electrode Dimensions (cm)		Effective Surface Area $2\pi R(R + L)$ cm^2	Fuel Source	Output Power Densities mW/m^2	References
	Radius	Length				
Loofah sponge dopped with PANI	0.5	3.0	10.99	Mixed Sludge	2590	[51]
Bamboo Charcoal	2.4	1.57	59.83	Mixed sludge	1652	[52]
Coconut shell	0.5	3.0	10.99	Mixed sludge	1069	[53]
Chestnut shells	0.3	66.4	125.65	Anaerobic mixed sludge	850	[54]
Coffee wastes	—	——	1.0	Domestic sludge	3927	[55]

The use of bamboo charcoal anode showed 50% better performance (1652 mW/m^2) than conventional graphite tube (1102 mW/m^2) (Table 2) because it has a better C-N bond, which facilitated the electron transfer biocompatibility and minimized the internal resistance against the flow of electron. Moreover, due to the tubular shape of the bamboo charcoal, it is easier to scale up as per requirement [52]. Thermal hydrolysis of sludge is a popular way to recycle sludge and convert them into valuable materials. Sewage sludge was converted into biochar by heat treatment and pressed with different coconut shells to form carbon monoliths. The produced carbon monoliths were used as an anode material, and the powdered form of carbon monoliths was used as a catalyst for oxygen reduction at the cathodic chamber. This produced 2.4 folds more current density than conventional graphite anode and platinum cathode. The research showed significant results by using naturally available sewage sludge material to prepare electrodes. At the same time, it replaced the expensive platinum cathode with low-cost powdered carbon monoliths [53]. Another important aspect of the research has been carried out on the chestnut shell. It was dried under vacuum initially around 80 °C followed by carbonization and activation at 900 °C to form chestnut carbon powder. The produced carbon powder contained pyridinic groups, which were favorable for the electron transfer between the anode surface and the biofilm and suitable for microbial adhesion. The output power density obtained by using chestnut shell-derived carbon powder was 2.3 times higher than carbon cloth anode due to the activation process, which created more microporous and mesoporous structures inside it [54]. Among all the natural materials, activated carbon derived from coffee waste had produced a maximum output current density around 3927 mW/m^2, higher than commercially available activated carbon. An increase in power density was observed due to suitable pore size distribution, which helped microorganisms to grow fast, resulting in a better electron transfer and adhesion to the surface. The research showed that the use of coffee waste-derived activated carbon material as an anode in the long term produced 2000 mW/m^2 current output till 100 h. In addition, the potassium hydroxide (KOH) concentration played an important role as an activating reagent [55]. So, for further development on the synthesis of natural waste material as an alternative to commercial carbon-based material, the source of the natural waste material and its characterization played an important role in long-term operation to make the system cost-effective and more sustainable.

3.3. Metal-Based Anode

Metals have lower interfacial impedance and internal resistance than carbon-based materials. Metal anode use has some benefits and drawbacks. The most important and favorable property of a metal-based anode is its conductivity and the flow of electrons [56]. However, there are several disadvantages too. Among them, the major reason is the corrosiveness. Most metal electrodes are very much corrosive and not at all biocompatible.

In addition to corrosiveness, metals have a smooth surface area, which is also not good for microorganisms to grow. A smooth surface inhibits bacterial adhesion leading to lower performance. Research has revealed that the use of non-corrosive metal such as stainless steel as an anode has not produced a good output because of its smooth surface area, which inhibited the adhesion of bacterial growth on the surface of the electrode. The maximum output power density obtained using stainless steel anodes was around 70 mW/m^2 [57]. Again, the use of stainless-steel mesh combined with carbon cloth produced a higher current density than conventional graphite electrodes. Carbon cloth offered a more extensive and rough surface area for microbial growth and attachment and coated stainless steel from direct exposure the low pH water [58]. However, the use of a few precious metals such as Gold, Platinum, and Titanium also showed a significant result on the output performance of the MFC. Still, it is impossible to construct a large-scale MFC using such precious metals due to cost-effectivity. This promotes new approaches for finding the derivative of metals that can be an alternative to precious noble metals. Using metal oxides instead of noble metal had exhibited good results when metal oxide nanoparticles were dopped with carbon material. Better results were obtained due to a decrease in internal resistance and improved surface roughness, facilitating the growth of the microorganism. These nano metal oxides also lowered the toxic effect on bacterial growth [59,60]. Instead of using pure, expensive noble metal, doping more nano metallic particles such as Titanium Oxide (TiO_2), Zinc Oxide (ZnO) having a catalytic effect on various carbon-based materials as an anode, could yield a remarkable change in the field of the research area.

The advantages of the use of carbon-based anode materials are very high electrical conductivity, high specific surface area, better hydrophilicity, and definitely good biocompatibility. In contrast, the disadvantages are particular bio toxification, comparatively high cost, and often the pointed edge of the carbon-based material can damage the cell wall during adhesion of the biofilm on the surface of an anode. The advantages of using natural material-derived anode are lower cost, good biocompatibility, and porous three-dimensional structure that offers high substrate diffusion inside the electrode. However, the major disadvantages of using natural material-derived anodes are durability and poor electrical conductivity. Metal-based anode materials are very good in electrical conductivity, superior in catalytic activity, and easy to scale up the system. However, these materials are inferior in corrosion and stability for long-term operation [6].

4. Modification of Anode Material

In this section, different development strategies are discussed by classifying them according to their modification technique carried out by several researchers. There are mainly three kinds of modification strategies that have been observed from the previous research work. The surface modification is primarily carried out to improve biofilm adhesion and microbial activities. Coating of anode material is another way of enhancing the electrode's durability and electron transfer rate. Coating materials such as Polypyrrole, PANi, etc., help sustain the anode even at low pH. Several articles described the performance of modified nanocomposite anode materials but still need more research work to acquire maximized output performance. Introduction of conductive materials such as Copper, Titanium, and Pyrolyzed Iron Phthalocyanine (FePc) by nano synthesis with carbon material improved the performance of MFC. This way of modification enhances the electron transfer rate and is also biocompatible with good electrical conductivity.

4.1. Surface Treatment of Anode

The idea of treating electrode surfaces comes from the concept of charge and force. The attraction force between an electrode and cell wall increases bacterial adhesion. The adhesion of bacteria to the anode surface depends on surface charge and interfacial surface chemistry. Previous research showed two ways to improve the potential difference between an anode and bacterial cell wall for better adhesion. In order to form a positive charge on a quaternary ammonium group (Figure 3), the electrode is reacted with ammonia gas at

700 °C in the presence of helium gas [31]. The increased surface charge of the anode accelerated microorganism adhesion, increasing output from 1640 mW/m^2 to 1970 mW/m^2. Another way to improve the surface of an electrode is to treat it with acid for a more extended period. The surface protonation of a nitric acid quenched electrode as an anode has been shown to nearly double the output of an MFC [29]. A research study showed that the biochemically nano synthesized palladium coating on the surface of the carbon cloth improved the output power densities of an MFC by 14% [28].

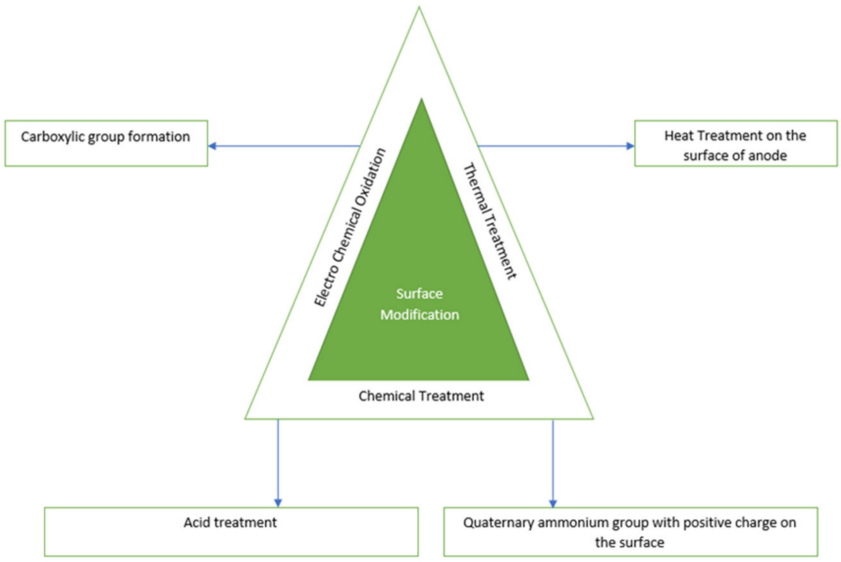

Figure 3. Classification of surface-modified anode based on the physicochemical treatment.

The heat treatment process helps to increase the surface area of an anode (Figure 3). A research study showed that the increased surface area encouraged the microbial film to grow after heat treatment, but there was no significant change in output. The increase in output performance was only by 3% [34].

Another research study showed that continuous electrochemical oxidation of graphite felt anode carried out for 12 h with constant exposure to a current density around 30 mA/cm^2 formed a carboxylic group. In order to transfer electrons from the bacterial cell wall to the anode surface, the carboxylic functional group (COOH-) forms a peptide bond (-CO-NH$_2$-). It was found that the output power density of MFC using anodes with peptide bond formations formed by carboxylic groups was 1.4 times higher than that of graphite felt due to the very strong hydrogen bond between bacterial cytochromes and a carboxylic acid group [61].

Substrates such as glucose or acetate contain carboxylic groups. They provide a better pathway for electron transfer from bacterial cell walls to anode surface and are easier to scale up. Although utilizing ammonia gas to form a positive charge on the electrode surface showed significant results, scaling up poses a challenge due to the use of ammonia gas, storage, handling, and high-temperature operation. In fact, using nitric acid for surface modification overcomes heat and ammonia treatment, but using strong mineral acid and storing it can be a hassle in large scale operations.

4.2. Coating of Anode Material

Microbial activities in the anodic chamber are strongly dependent upon the mechanism related to the rate of electron transfer, the surface area of the anode, and the roughness of the anode's surface where biofilm formation occurs. As it has been already discussed, the rough surface area of the anode is suitable for the adhesion of bacteria. Stainless steel has good conductivity, but its smooth surface is unfavorable to bacterial activity. Once the bacterial activities occur in the anodic chamber under anaerobic conditions, it produces

H^+ ions, leading to a low pH. Research revealed that coating of Polypyrrole (PPy) onto the surface of Stainless Steel (SS) increased the biocompatibility and corrosion resistivity. PPy coating also helped lower the impedance and internal resistance to the system, leading to a high electron transfer rate (ETR), which enhanced the output from 39 mW/m^2 to 1190.94 mW/m^2 [62].

In wastewater treatment, a research study exhibited 100% removal of chemical oxygen demand from wastewater with an output current density of around 440 mW/m^2 when MnO_2 coated polypyrrole stainless steel plates were used as an anode in MFC. The electrodeposition of the thin layer of MnO_2 acted as a catalyst to enhance the surface roughness and conductivity [63]. As per the literature, Polypyrrole improved the penetration capacity of the cell membrane and transported electrons through the metabolic trail. By galvanostatic polymerization of aniline in the presence of 0.7 M Nitric acid, the formation of a thin layer on the surface of the pristine stainless-steel plate (SS-P/PANi) used as an anode showed almost 10 times better output power density 780 mW/m^2 compared to regular stainless-steel plate (SS-P). The study also showed that by using PANi on the surface of the SS-P the output current was enhanced by around 13 times (1400 mA/m^2) of the current produced using regular SS plates. This was attributed to the lower impedance and resistance and uniform coating, which helped bacteria adhere to its surface [64]. Coating of PANi on the surface of graphite felt was used as an anode, which produced around 4000 mW/m^3, which was 2.3 times higher than the normal graphite felt [65]. Polyethene dioxythiophene (PEDOT) is another kind of conductive polymer used in various biosensors, semiconductor materials, solar cells, etc. Chemical polymerization followed by Electrochemical deposition (Figure 4) of a definite amount of (2.5 mg/m^2 of electrode) PEDOT on the surface of various carbon-based electrodes such as graphite plate, carbon cloth, and graphite felt were compared in terms of output current densities. Among these three classes of electrodes, graphite felt coated with PEDOT showed significant results by producing a current density of 3.5 A/m^2, with 51% coulombic efficiency and 86% removal of chemical oxygen demand (COD) [66]. Carbon nanotubes were also used to enhance the electron transfer rate (ETR) from bacterial cell walls to electrodes [67]. However, the toxic effects of various conductive metals such as Silver, Copper, etc., on microbial activities were discussed earlier. Suppose sufficient coating of conductive polymers such as polyaniline can be made on the surface of such conductive metal oxides such as Titanium oxide and Zinc oxide. In that case, it may offer a valuable opportunity to modify a new generation of electrodes combining the synergistic effects. Efforts to prepare unconventional polymeric composite-based electrodes using this technique have not been significant, probably due to the considerable cost.

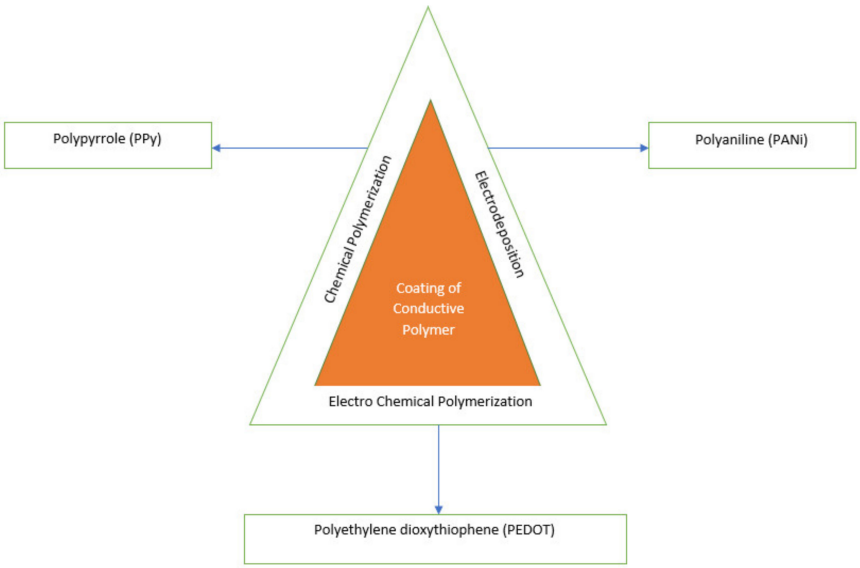

Figure 4. The different coating methods of the anode.

The three most commonly used processes for the preparation of composite anode materials using precursors to enhance the nucleate growth are Hydrothermal, Solvothermal, and Sol-gel technology [68,69]. Depending on the treatment process, various dimensional nanomaterials can be formed, such as nanoclusters, nanofibers, nanoparticles, nanowires, nanotubes, nanosheets, etc. In the above mentioned three processes, if the dispersion of colloidal nanoparticles takes place in solvent form followed by heat treatment, this process is called the Solvothermal process. Dispersion of nanoparticles in an aqueous medium is known as the Hydrothermal process, while the Sol-gel process involves hydrolysis followed by polycondensation during heat treatment to form nanoparticles. These nanocomposite materials can enhance the conductive properties of the anode material favorable to the electron transfer rate. The radius of the nanoparticles formed by any of these processes depends on the material's surface energy, atomic volume, thermal energy, and supersaturation. The use of proper precursors appropriately showed better nucleation and improved the colloidal growth of nanoparticles. Dispersed nanoparticles were formed in the presence of various solvents followed by a vacuum drying to acquire dry amorphous nanoparticles. The temperature of the vacuum drying process largely depends on the solvent's boiling point. The use of solvents such as ethanol, acetonitrile, and methanol in the solvothermal process proved superior to the hydrothermal mixing method to produce nanoparticles. This paper [70] obtained $CuCO_2S_4$/rGO nanocomposite material by a simple one-step solvothermal method. Graphene oxide was dispersed in ethylene glycol, and then the suspension was mixed under ultrasonication, followed by mixing of copper acetate monohydrate, cobalt acetate tetrahydrate and thiourea. The mixture was then autoclaved under high pressure at 180 °C for 24 h to form a black precipitate (Figure 5a,b). The precipitated material was then centrifuged after washing it with ethanol, followed by vacuum drying to obtain a dry powder. This modified nanocomposite material $CuCO_2S_4$/rGO showed excellent results in terms of output, firstly because of the nonaggregating property of the reduced graphene oxide, which helped to avoid the aggregation of the $CuCO_2S_4$/rGO nanoparticles and minimized the void fraction between the nanoparticles by reducing the volume variation. Secondly, the electronic conductivity of the reduced graphene oxide facilitated the fleet electron and the ionic conduction [70].

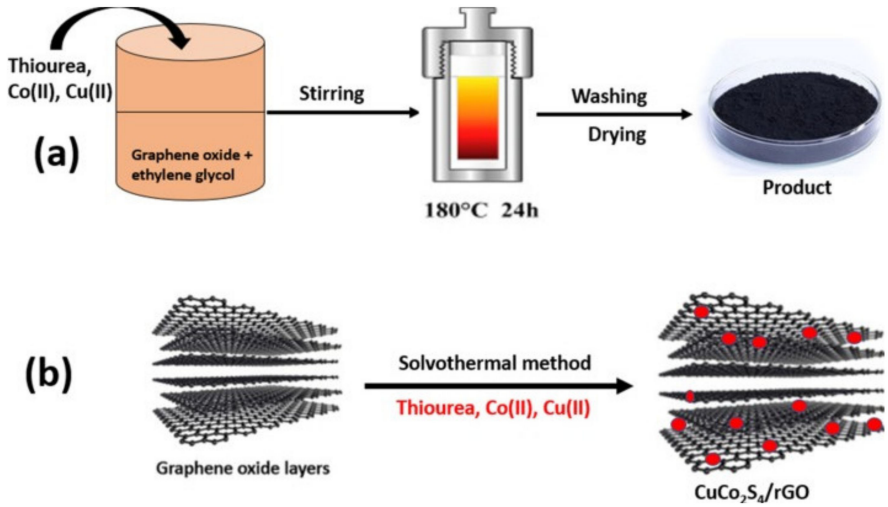

Figure 5. Schematic diagram of (**a**) synthesis and (**b**) formation of CuCO2S4/rGO [70].

Similar to different kinds of synthesis of nanoparticles, various research studies have been carried out on the formation of nanosheets. One of the studies that showed significant results in MFC output performance is the fabricated TiO_2 nanotubes on carbon paper composite anodes using the Sol-gel method. The maximum power density was enhanced 1.63 times using TiO_2 nanosheets layer on the surface of the carbon paper due to its three-dimensional open porous interface, which provided good biocompatibility, huge surface

area for adhesion of bacteria, better mass transport, and enhanced direct electron transfer to the electrodes [71]. The two-dimensional carbon nanotube (CNT) based electrodes are also good, but they may need more surface modification to reduce the lag time, activation losses, and metal toxicities [72]. To increase the carbon to nitrogen ratio of the material as well as conductivity, Pyrolyzed Iron Phthalocyanine (FePc) coated activated carbon brush was used as an anode material. Surface treatment of activated carbon brush was achieved by dispersion of FePc in dimethylformamide solvent. Then the dispersed material was dried under vacuum, followed by pyrolysis in an argon atmosphere. The pyrolyzed sample was leached out in sulfuric acid solution and washed until neutralized. This surface developed anode material exhibited the maximum output power density of 1092 mW/m^2, 63% higher than untreated activated carbon [73]. Thus, various research works on graphene-based nanocomposite anode material showed promising results by changing the shape, dimensions, or chemical modifications. The modified anode materials should also be analyzed in terms of sustainability, stability, and cost-effectivity.

5. Future Perspective

Finding a suitable material that is biocompatible and at the same time electrically conductive is quite challenging. Cost-efficiencyis another critical factor that needs to be considered while searching for the most suitable electrode material. Commercially available graphene oxides turned out to be the most effective material for anodes, but the material is very expensive. Natural carbon-based materials are always cheaper. The power cost of the MFC can be obtained by dividing the cost of the unit cell by the maximum power density. Therefore, the use of inexpensive materials to construct MFC can lead to a cheaper cost of power. A research work showed that the material cost for natural biomass-derived anode varied from (51–381) US dollar per ton of the material whereas, commercially available granular activated carbon or graphite granules cost around (800–2500) US Dollar per ton of the material [74]. The dilemma can be solved by turning waste materials into carbonized anode rods, brushes, or plates. Very few reports exist on the process and modification technique for converting waste into graphene oxide. Yet, a lot of work still needs to be carried out to improve synthesized graphene oxide properties from natural waste sources.

There is another way of anode modification by developing metal-polymer composites. This development process enhances the electron transfer rate and makes it more durable. The material needs to be assessed in more detail over a more extended period to ensure stability, strength, and compatibility with various wastewater sources.

Anode fabrication relies heavily on the size and design of the electrode. The electrode spacing and surface area are responsible for bacterial growth. In large scale operations, the stability of the material is a challenging issue. Over a more extended period of operation, industries need standard operating protocols for a system to run smoothly. Very few articles have been reported explaining the stability guidelines of electrode material in large-scale operations. These areas need to be investigated further in future research work.

The graphite brush type architecture proved to be very efficient as an anode material in MFC. On the other hand, metal-polymer composite materials have also shown better results in some research works. Commercially available graphene is expensive, but it can also be derived from waste materials, as discussed earlier. Therefore, if waste material-derived graphene oxides are binded with Nafion or PES then coated on the surface of a metal composite brush, It would form an efficient MFC electrode. Further testing is required to analyze the performance of the combined effect.

6. Conclusions

Many research studies have shown that the design and architecture of an anode control the overall performance of the MFC. The architecture and the individual components of MFC impact the output performance. The proper selection of anode material plays an essential role in MFC operation. Based on the review of available research results, the following conclusions can be made:

- Carbon-based materials are proved to be very good as an anode. Biocompatibility and electrical conductivity are the two most important properties of the anode, which primariessentially controls the system's performance. The surface area of the electrode should be maximized to enhance the formation of the biofilm. The use of commercially available graphene oxide as an anode showed excellent results. However, graphene oxides are very expensive and may not be suitable for large-scale and commercial applications.
- Among all the past research work, biomass-derived anode electrodes are very attractive in terms of the low cost, high surface area, good bacterial adhesion, and compatibility with microbial activities. However, the major drawback of natural waste-derived materials is poor electrical conductivity and durability.
- To enhance the conductivity of the biomass-derived anode materials, doping of metal oxide and hybridization of the copolymer and different surface treatments may be needed. From the past research studies on the modification of anode, the most popular and effective method used by researchers to fabricate anodes was Hummer's method which indicated the effectiveness of graphene materials derived from various natural biowastes.
- The electrodeposition, chemical polymerization and electrochemical polymerization techniques for making conductive polymer-based anodes are very good in terms of eco-friendliness, large surface area, and chemical stability. Still, the major drawback of these materials is the risk of shedding of polymers and not suitable physical properties that affect the electrical conductivity.
- At the same time, carbon-based brush type material and carbon nanotubes are also exhibited good performance by increasing the surface area of the electrode in large-scale operation but lagged in conductive properties. Often the sharp edge of the brush can rupture the cell wall of microorganisms, which leads to overall poor performance. Further research work should be carried out with more focus on improving the mechanical strength of graphene by combining with metal oxides or with some composite copolymers, followed by giving them a brush or nanotubes type architecture. These type of materials can lead to a new generation of the anode to acquire a combined effect. These modifications can be tested on a small scale with proper optimization and can be scaled up to use in commercial applications.

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