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Review

Anode Modification as an Alternative Approach to Improve Electricity Generation in Microbial Fuel Cells

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Abstract: Sustainable production of electricity from renewable sources by microorganisms is considered an attractive alternative to energy production from fossil fuels. In recent years, research on microbial fuel cells (MFCs) technology for electricity production has increased. However, there are problems with up-scaling MFCs due to the fairly low power output and high operational costs. One of the approaches to improving energy generation in MFCs is by modifying the existing anode materials to provide more electrochemically active sites and improve the adhesion of microorganisms. The aim of this review is to present the effect of anode modification with carbon compounds, metallic nanomaterials, and polymers and the effect that these modifications have on the structure of the microbiological community inhabiting the anode surface. This review summarizes the advantages and disadvantages of individual materials as well as possibilities for using them for environmentally friendly production of electricity in MFCs.

Keywords: microbial fuel cells; anode modification; electrode materials; nanomaterials; polymers; microbial community; exoelectrogens

1. Introduction

In view of the growing demand for electricity, there is a need to develop environmentally friendly technologies. In the European Union, there is a trend towards production of energy from renewable resources, particularly by using waste from biomass management [1]. The sustainable production of electricity from renewable sources by microorganisms is considered an attractive alternative to producing energy from fossil fuels. One of the trialed solutions are microbial fuel cells (MFCs), in which the metabolic activity of microorganisms is utilized to produce electricity by oxidation of organic substances on the anode and transfer of electrons to the cathode [2]. Electrochemically active biofilms in MFCs can be also successfully used for the synthesis of nanoparticles and band gap narrowing of metal oxides [3,4].

In recent years, research on MFCs technology for sustainable electricity production has increased (Figure 1).

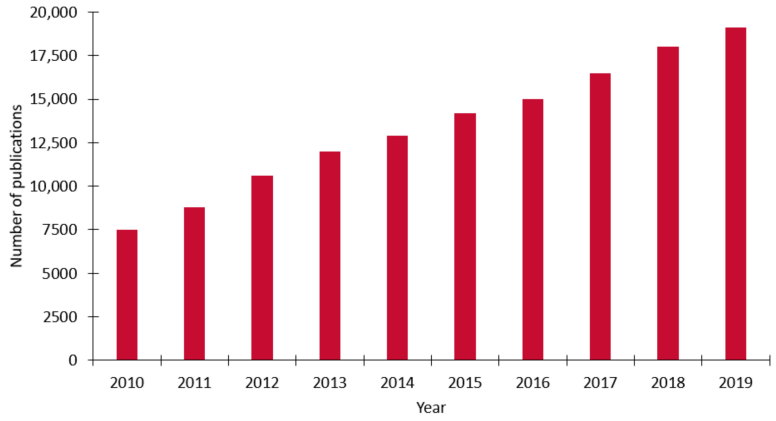

Figure 1. Number of publications per year found in the Google Scholar database using the search term "microbial fuel cells" (MFCs); (data acquired on 29 October 2020).

Wastewater contains large amounts of organic compounds that can be used as a potential carbon source in MFCs [5,6]. Current economic trends and legal regulations require that facilities such as wastewater treatment plants should be modernized to not only remove nutrients but also produce bioproducts and energy [5–7]. The use of MFCs in wastewater treatment systems can bring many benefits at the environmental, economic, operational stability, and energy management levels (Figure 2).

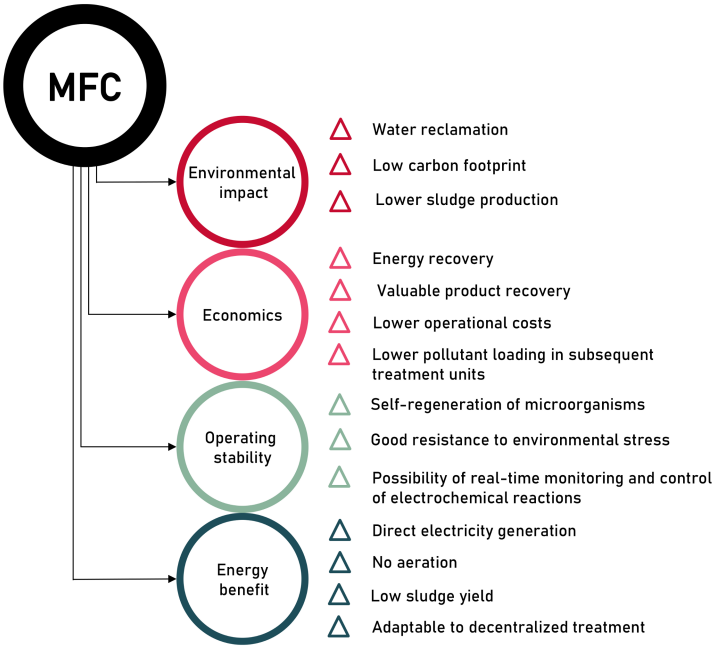

Figure 2. Potential benefits of MFCs for energy, environmental, operational, and economic sustainability.

Usually, MFCs are designed as single- or two-chamber systems [8,9]. A two-chamber MFCs has one chamber with an anode and one with a cathode, separated from each other by a proton exchange membrane (PEM). Single-chamber MFCs are more economical because the cathode is constantly exposed to air (so-called air cathodes), and there is no need to aerate the cathode chamber. Another advantage of one-chamber MFCs is the smaller distance between the anode and the cathode, which favors the efficient production of electricity [10]. The activity of microorganisms in the anode biofilm causes the decomposition of organic substances into electrons and protons. The electrons are transferred to the cathode by the external circuit, while the protons are transferred through the PEM to the cathode compartment (Figure 3). Some species, instead of transporting electrons to the exogenous acceptor, pass them directly to the anode. Such a phenomenon is called electrogenesis,

and the groups of electrochemically active microorganisms capable of carrying out this process are exoelectrogens [11]. Some bacteria are capable of producing secondary metabolites, which can act as redox shuttles [12]. Bacteria such as *Shewanella* sp. or *Escherichia coli* produce flavins, while *Pseudomonas* sp. produce phenazines (e.g., pyocyanin, pyorubin or oxychlororaphin)—these metabolites take part in an extracellular electron transfer. Other organisms (e.g., *Enterococcus faecalis* or *Faecalibacterium prausnitzii*) can use them, and as a result, electron transfer can take place over longer distances [13–16]. Biofilm formation by bacteria on the anode electrode is by far the most important mode of electrode–microbe interaction. To avoid competition between oxygen and electron carriers (mediators), anaerobic conditions should be ensured for the operation of the anodes of most MFCs [17]. The presence of oxygen, which is a terminal electron acceptor, in the anode compartment resulted in a lower power generation [18].

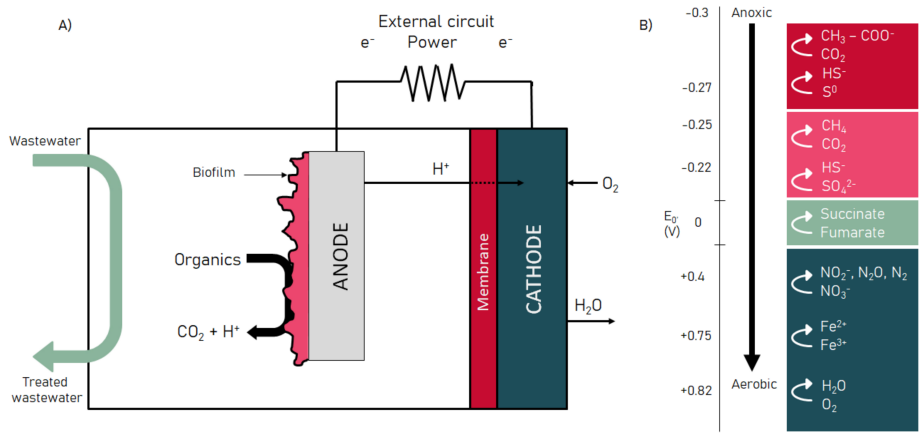

Figure 3. Diagram of an MFC reactor (**A**) and chemical changes in an MFCs depending on the oxygen conditions (**B**).

In MFCs, both pure bacterial cultures and mixed microbial consortia [19,20] are used, but pure cultures generate lower electrical voltage than diverse microbial consortia [21,22]. The advantage of using complex microbial consortia is that they can utilize complex substrates more efficiently due to syntrophic interactions between fermentative bacteria and exoelectrogens; such cooperation may enhance exoelectrogenic activity [23,24]. Syntrophic interactions are also observed between the exoelectrogens themselves [23]. However, pure bacterial cultures are important in elucidation of the electron transfer mechanisms in the biofilm [25].

Anaerobic respiration and fermentation are the main metabolic pathways of oxidation of organics by bacteria. Complex organic compounds are initially hydrolyzed into simpler chemical compounds such as fatty acids, sugars, amino acids, or aromatic compounds (Figure 4). Then, these simple organics can be either fermented or completely oxidized to CO_2, which results in the transfer of electrons to the anode. The ideal conditions for effective oxidation with maximum electron generation can be achieved if the exoelectrogens oxidize the organic matter completely to CO_2. The extracellular electron transfer can take place directly through cytochromes (redox proteins) because their outer cell membrane with exposed *c*-type cytochromes is in a direct or indirect (pili) contact with the electrode surface. Type IV pili are the conductive nanowires that transport the electrons from cell to cell inside the biofilm as well as from cells to the electrode surface. In addition to direct electron transport, microorganisms can also donate electrons indirectly via soluble electron shuttles [25]. Electron transfer from bacteria to the anode is facilitated by extracellular heteropolysaccharides as well as the cytochrome-*c* protein complexes present on bacteria cell walls [26].

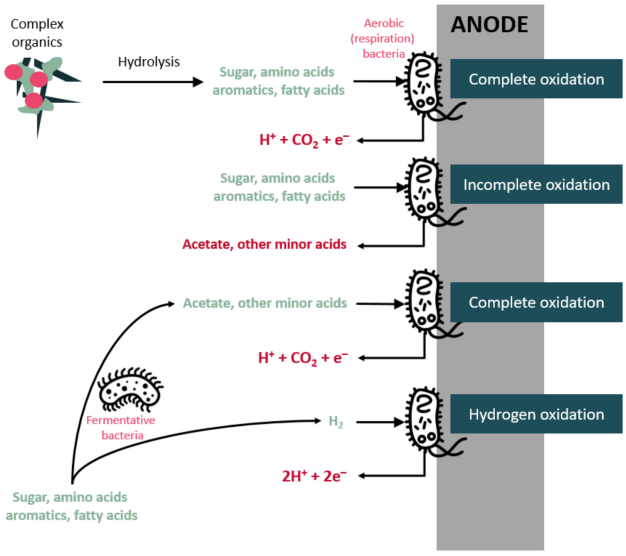

Figure 4. Conceptual representation of electricity generation from organic waste on the anode biofilm.

The diversity of the microbial community in the MFCs is determined not only by the origin of the inoculum, but also by the type of fuel used to power the cell, the presence of redox mediators, the oxygen conditions in the bioreactor, and the type of anode [27]. Studies by Eyiuche et al. [28] showed that, in an acetate-fed community on stainless steel (SS) anodes, *Desulfuromonas* sp. was abundant (15.4%) and *Geobacter* sp. was markedly less abundant (0.7%). On a carbon cloth (CC) anode, both genera were present in similar amounts (6.0–9.8%), indicating that an anode material affected exoelectrogenic genus enrichment in biofilms. In MFCs with an SS anode modified with carbon nanotubes (SS/CNTs), in the biofilm, such fermenting bacteria as *Chlorofexi* sp. and *Rhodanobacter lindaniclasticus* predominated, which resulted from the fact that the MFC was powered with the filtrate from fermentation of primary sludge. Exolectrogenic bacteria such as *Desulfovibro* sp., *Geobacter* sp., *Desulfobulbus* sp., and *Rhodopseudomonas* sp. occurred with a share of less than 1% [29]. *Geobacter* sp. was able to actively inhibit other microorganisms in the biofilm by production of extracellular proteins [30]. *Geobacter* sp. may have a competitive advantage over other genera in MFCs, due to this inhibitory activity as well as its robust capabilities for anaerobic respiration and flagellar chemotaxis, which allows it to gain proximity to the anode surface.

The studies have shown that the performance of MFCs increased with the increase in an anode's potential. Positive potential selected for, e.g., *Shewanella putrefaciens* biofilm [31], while negative anode potential promoted the growth of electrochemically active anode-respiring *Geobacter* sp. [32]. Bacteria such as *Geobacter sulfurreducens* and *Thermincola ferriacetica* that form thick multilayer biofilms of 38–50 µm at anodes can produce higher current density than bacteria that form thin biofilms [33,34]. On the other hand, thick biofilm can also hinder electron transfer. Since the anode surface plays a significant role in promoting and maintaining bio-catalytic activity, this surface can be modified to become a more favorable habitat for microorganisms enhancing electron transfer from the bacteria to the anode surface. Generally, greater bacterial adhesion enables the generation of more power with minimum electricity loss [35].

The aim of the literature review is to present possible methods of increasing the efficiency of electricity production by modifying the anode materials, and the effect that these modifications have on the structure of the microbiological community inhabiting the anode surface. This review summarizes the advantages and disadvantages of individual materials and the possibilities for their use in the production of environmentally friendly electricity in MFCs.

2. Electrode Materials

The anode material and its structure can directly affect bacteria attachment, electron transfer, and substrate oxidation. Anode materials must be corrosion-resistant, have a high specific surface area and electrical conductivity, and have a low electrical resistance and a low cost. The anode must also be made of a chemically stable material that can operate in an environment where highly diverse organic and inorganic constituents are present, which can react with some anode materials and reduce MFCs performance [36]. To ensure electron transfer, the anode material should be biocompatible [37]. In this review, the most frequently used electrode materials are presented, along with possible methods of modifying them, which can change the structure of the microbial communities on the anode and improve electricity generation in the MFCs.

2.1. Carbon Electrodes

Carbon-based electrodes are commonly used in various types of MFCs (Table 1) because they are chemically stable, resistant to environmental conditions in MFCs, have a high electrical conductivity, and a high specific surface area, which creates good conditions for biofilm development [38]. Carbon-based electrodes can be made of carbon/graphite felt (CF/GF), CC, carbon paper (CP), graphite paper (GP), and activated carbon (AC) [2,39]. The most commonly used CF and CC are characterized by a high porosity, electrical conductivity, and a specific surface area; however, CF shows better chemical and mechanical stability and is cheaper [40]. Despite the many advantages of carbon materials, they also have some disadvantages, such as a high hydrophobicity, which does not favor the adhesion of microorganisms and thus translates to a lower electron transfer capacity [41]. For hydrophilic surfaces, an instantaneous bacterial attachment is observed—the planktonic bacterial cells simultaneously attach and form colonies that increase and cover the whole surface. For hydrophobic surfaces, a progressive bacterial attachment is observed—only a limited number of bacteria attach to the surface and form colonies decreasing the surface hydrophobicity. Decreased surface hydrophobicity allows for immobilization of new bacteria [42]. On the other hand, a hydrophobic surface will be easily colonized by bacteria with a high cell surface hydrophobicity or bacteria that switched from hydrophilic to hydrophobic phenotypes in response to environmental conditions [43].

Although carbon materials generally exhibit good electrical conductivity, MFCs power generation efficiency can differ depending on which material is used. For example, cell voltage was higher when CF was used as the anode in a dual-chamber MFC than when CC or CP were used. For CF, the maximum power density of MFC was 420 mW/m^2, while for CC and CP, the power density was two log units (0.76 mW/m^2) and three log units ($8.37 \cdot 10^{-6}$ mW/m^2) lower, respectively, than that of CF [44]. Similar results were obtained by using anodes of various carbon-based materials in the soil MFC. The highest voltage and power were obtained in the MFC with a GF anode (346 ± 5 mV and 24.0 mW/m^2, respectively). The values obtained for GP were much lower (130 ± 5 mV and 4.5 mW/m^2, respectively). The type of carbon material affects also the charge transfer resistance (Rct). After a comparison of anodes made of aluminum sheet, GF and CC showed that the lowest Rct was observed for GF [45].

Table 1. Summary of carbon anode properties.

Anode (Non-Modification)	Reactor Configuration	Substrate	Power Density	Anode Surface Characterization	Reference
GF	dual chamber	sodium acetate trihydrate	0.48 A/m^2	disorganized web of fibers with a diameter of 10 to 14 µm	[46]
Porous graphite	single chamber	glucose	2.6 W/m^2	large number of pores with a diameter of 0 to 300 nm	[47]

Table 1. *Cont.*

Anode (Non-Modification)	Reactor Configuration	Substrate	Power Density	Anode Surface Characterization	Reference
CP	dual chamber	distillery wastewater	110 mW/m^2	water contact angle 126° (medium hydrophobicity)	[48]
GF	dual chamber	glucose	388 mW/m^2	water contact angle >120° (medium hydrophobicity)	[49]
CC	single chamber	wastewater	40 mW/m^2	smooth fibers of around 7 µm diameter	[50]
CF	singe chamber	glucose	680 mW/m^2	smooth surface	[51]
Graphitized mesophase pitch-based carbon foam			1800 mW/m^2	a well-developed macropore structure with a single hole diameter of around 300 µm	
Mesophase pitch-based carbon brush (CBr)			1350 mW/m^2	smooth surface	

The surface morphology of anode materials should be improved with respect to anode-bacteria interactions [52]. To increase the surface area of an anode, electrochemical oxidation [53,54], chemical [55], and heat treatment can be used [56], increasing the adhesion of microorganisms and the output power of the cell. In recent years, carbon microfiber (CMF) paper and carbon nanofiber (CNF) mats have been tested as anode materials in MFC. The use of thinner carbon materials for CNF electrodes resulted in a larger specific surface area and a better morphology of the electrode surface, which promoted adhesion of bacteria and formation of a dense and stable biofilm, increasing energy production. Compared to CMF, CNF showed a 10-fold increase in current [57], better electron transfer kinetics, and high electrical conductivity [58–60]. Activation of CNF in a tube furnace (creating activated carbon nanofiber nonwoven, ACNFN) increased the specific surface area of CNF from 25.31 to 1158.75 m^2/g [61]. The porous structure of ACNFN favored the active colonization of the anode by bacteria, resulting in a high and stable energy production. Biofilm growth on the ACNFN anode was about 3.2–4.2 times thicker than that on the CC anode. Highly conductive anodes with increased biocompatibility can be obtained using the polymer 3D printing technique and the carbonation process. The obtained materials have over 95% porosity; thus, the surface area (internal and external) for biofilm growth is high. The maximum voltages of the 3D anodes were about 33.7–138.4% higher than the voltage obtained with the CC anode and depended on the pore size in 3D anodes. The maximum power densities decreased in the order: 300 µm > 200 µm > 400 µm > 100 µm > 500 µm > CC. The unexpectedly low maximum power density of 100 µm anode with the largest specific surface area indicated that 3D printing technology can increase the power of the MFC, but the pore size in anodes should be optimized. The solution resistance of the MFC with the 3D anodes averaged 24.2 Ω and was approximately 8.6 Ω lower compared to the CC anode, while the Rct of the CC anode was slightly lower than that of the 3D anodes [62].

The configuration of the electrodes has evolved from a planar to a three-dimensional structure; however, the power generation and cost of the electrode so far discussed have not reached commercial levels. Therefore, in recent years, modifications with the use of carbon compounds and nanostructures have attracted much interest.

2.2. Metal Electrodes

Electrodes made of metals such as silver, SS, aluminum, nickel, molybdenum, titanium, gold, and copper ensure high performance in MFCs due to their good electrical conductivity.

Stainless steel is a commercially available industrial material with a high mechanical and corrosion resistance, high conductivity, and low cost [63], and it is regarded as a good electrode material for MFC anodes [64]. The macroporosity of SS anodes enables attachment of carbon nanoparticles, which improves the anode biocompatibility and also favors internal colonization by bacteria that could enhance electrode reactions [65]. To increase the specific surface area of SS anodes, the surface can be etched with, e.g., sulfuric acid (VI) [65].

When using copper wires, an increase in the anode surface from 2.5 to 20.1 cm^2 increased the maximum power density from 0.3 to 0.67 mW/m^2. It was also shown that an increase in the initial COD concentration from 1000 to 6000 mg COD/L with an anode area of 20.1 cm^2 further increased the maximum power density to 2.9 mW/m^2 [66]. It should be remembered that copper is toxic to microorganisms [2]; therefore, copper is more often used as a cathode in MFCs [67–70]. Baudler et al. [71] tested gold, silver, copper, nickel, cobalt, and titanium as anode materials in comparison to a graphite electrode. On gold, silver, copper, and nickel anodes, a homogeneous and optically dense red biofilm was formed, indicating predominance of *Geobacter* sp. The electrodes made of gold, silver, and copper had a current density higher than that made of graphite. Active biofilm did not form on the cobalt and titanium anodes. In the study, no toxic effects of copper were observed on electrochemically active bacteria.

The use of nickel foam improved electricity generation in a single-chamber MFC. The maximum output power with nickel foam was about 45 mW/m^2 higher than with a CC anode. It was observed that, although nickel foam increased electricity production, it also underwent anodic corrosion to form nickel phosphate [72]. In another study, using nickel foam as an anode in MFC ensured a maximum power density of 8.29 W/m^3, a Coulomb efficiency of 6.95%, and an internal resistance of 116 Ω. Modification of nickel foam using chitosan, polyaniline, and titanium carbide increased the power and Coulomb efficiency more than two-fold and reduced the internal resistance 2.5-fold. Epifluorescence and scanning electron microscope (SEM) analysis of microbial colonies on a nickel foam anode indicated that the adhesion of bacteria was less stable and that the colonies were not firmly attached to the anode surface [73].

These reports indicate that metal anodes, although they are good electron conductors, have low chemical resistance because they dissolve in contact with the anolyte, and their relatively flat surface may have lower biocompatibility than the surface of carbon anodes. Therefore, most experiments in MFCs with metal anodes indicate the necessity of modification of the anode surface.

3. Anode Modification

The main limitations in up-scaling of MFCs include low power density and expensive electrode materials. Power density can be increased by ensuring that the anode is hydrophilic and has a high specific surface area.

The surface roughness is of great importance for energy production in the MFCs as the anode morphology should facilitate the adherence of bacteria and subsequent biofilm formation. Electrochemical oxidation of CC anodes with ammonium bicarbonate, at different voltage densities, contributed to the removal of impurities from the CC surface, and the degree of etching increased with increasing current density, causing the formation of grooves increasing the specific surface of the anode [74]. Electrochemical modification of the surface of the nano-rough gold deposited on silicon wafers showed that at lower current densities, randomly distributed deposits appeared on the anode surface, covering about 50–70% of the surface. The use of higher current densities resulted in the formation of gas bubbles that shaped round micro-craters with a diameter of about 10 μm, increasing the density of the generated current 6.7 times compared to the unmodified anode [75].

Hydrophobicity of surface often determines the adhesion of the biofilm to the anode. Guo et al. [76] modified a glassy carbon anode with different functional groups such as $-OH$, $-CH_3$, $-SO_3^-$, $-N^+(CH_3)_3$. The anode modified with $-OH$ group showed the highest surface hydrophobicity. The best results were achieved for the anode modified by $-N^+(CH_3)_3$—the water contact angle of 15°

was reduced 4 times compared to the unmodified anode, and the amount of biomass produced on the electrode surface was the highest. The percentage of Geobacter sp. on the $-CH_3$-modified anode was about 40% lower than that on the anodes with modified with $-N^+(CH_3)_3$, $-OH$, and $-SO_3^-$ [76].

The literature indicates that, to overcome the problem of low power density, modification of anode materials, especially with high porosity nano-structured materials, is a good approach.

3.1. Metal Compounds

An improvement in MFC performance can be obtained by modification of the anode with iron compounds. Iron-reducing bacteria such as *Geobacter* sp. and *Shewanella* sp. are important electrogenes in MFCs [77,78]. Due to the insolubility of iron compounds in the pH range of 7 to 8, Fe-reducing bacteria reduce this metal either via direct contact with their outer membrane cytochromes or by using conductive pili [79]. The use of Fe-modified electrodes in a bio-electrochemical coagulation system increases the activity of denitrification enzymes [80]. The addition of iron also prevents methane production under low redox potential [81], which is a common problem in MFCs. In an MFC with a CF anode modified with graphene oxide (GO) and Fe_2O_3 and powered with pure acetate, the maximum stable voltage was 590 ± 5 mV [82], and the presence of iron stimulated the growth of exoelectrogens belonging to *Desulfovibrio* sp. Fe_3O_4 and bentonite-Fe were used as GF anode modifiers, significantly decreasing the internal resistance of MFC and increasing the maximum power densities to 18.28 and 29.98 mW/m^2, respectively, compared to 10.6 mW/m^2 obtained in an MFC with a GF anode. Modifications contributed to the enrichment of exoelectrogens from the genera *Proteiniphilum* and *Geobacter* in the anode biofilm [83]. The dose of iron for modification should be carefully chosen, because overdosing may result in lowered energy production [84].

MnO_2, Pd, or Fe_3O_4 nanoparticles mixed with carbon black (CB) were used for the modification of a CC anode in an MFC designed for removal of pharmaceutically active compounds. Nanoparticles of MnO_2, Pd, or Fe_3O_4 were loaded to the anode surface by using 5% Nafion reagent as a binder. In MFCs with modified anodes, efficient removal of carbamazepine (over 80%) and, to a lesser extent, ibuprofen (up to 20%) was noted. The maximum power density increased by 21, 15, and 10%, respectively, in MFCs with Pd−, MnO_2−, and Fe_3O_4−modified CB/CC anodes compared to the MFC with a CB/CC anode. The anodic biofilm on anodes modified with MnO_2 and Fe_3O_4 was enriched with *Geobacter* sp., while modification of the anode with Pd promoted the occurrence of both *Geobacter* sp. and *Sphaerochaeta* sp. [85].

Electricity generation in MFCs can also be increased by co-modification with active substances. Co-modification of MoO_2 nanoparticles highly dispersed on nitrogen-doped carbon nanorods with Co increasing the electron conductivity of carbon. The biofilm from an MFC with an anode co-modified with Co had fewer *Geobacter* sp., but it provided a higher power density in comparison to an anode without Co. This indicates that Co is toxic for exoelectrogens but improves electrocatalytic activity and increases power density [86]. Such an observation was confirmed by Alhamadi et al. [87] who showed that Co/cellulose nanocomposites had antibacterial properties regarding both G+ and G- pathogens such as *Staphylococcus aureus, Escherichia coli, Acinetobacter baumannii*, and *Pseudomonas aeruginosa*. On the other hand, Kooti et al. [88] reported that $CoFe_2O_4$ (10 mg/mL) did not affect the growth of *E. coli, P. aeruginosa, S. aureus*, and *Bacillus subtilis.* In another experiment, Co oxide synthesized from cobalt (II) nitrate increased the voltage in an MFC and electron transfer by almost two-fold compared to an MFC with an unmodified anode [89].

The anode surface can also be modified by adding a modifying substance to the substrate inoculated to an MFCs. The addition of Fe and S to the substrate resulted in the maintenance of a stable voltage in the reactor and reduced the charge-transfer resistance of the anode. The power density curves showed that, in the presence of Fe and S, the maximum power density of the MFC was 1.92 times greater than in the control MFC [90]. Iron sulfides are capable of acting as naturally occurring electrical conductors and electrocatalysts, which, due to their metallic and semiconductor properties, facilitate extracellular electron transfer [34]. Many ferric reducing bacteria and sulfur

reducing bacteria in anode biofilms are classified as exoelectrogens [91]. Sulphur reducing bacteria can transfer electrons through four possible pathways, which are (I) syntrophic interaction with sulfur oxidizing bacteria; (II) via cytochromes when there is a direct contact of the cell with the electrode; (III) synthesis of electron-conducting pili produced by bacteria attached to the electrode surface; and (IV) nanoparticles of metal sulfides, such as FeS, that transfer electrons via the external membrane of the microbial cells [92–95]. The group of microorganisms involved in the biosynthesis of iron sulfide nanoparticles, and thus, in biochemical processes generating electricity, include *Shewanella putrefaciens* [96], *Desulfobulbus* sp. [97] *Desulfovibrio vulgaris*, and *Acidiphilium cryputum* [98]. The increase in the share of sulfur metabolizing microorganisms belonging to *Desulfobulbus* sp. positively correlated with the production of electric current in a powered with waste volatile fatty acids [99]. Modification of the anode with iron sulfide nanomaterials promoted the growth of sulfur reducing bacteria belonging to *Enterobacteriaceae*, *Desulfovibrio* sp., and *Geobacter* sp., which increased the electricity production in MFC [90].

3.2. Carbon Composities

MFCs performance can be improved by anode modifications with allotrope varieties of carbon (e.g., graphene), carbon compounds (e.g., graphene oxide—GO), or other carbon composites (e.g., carbon black—CB or carbon nanotubes—CNT). Carbon modifiers increase the specific surface area of the anode, which creates more space for the attachment of microorganisms and increases the number of electrochemically active sites for the electron transfer. Many of the carbon compounds are also good conductors. For these reasons, carbon modifiers are commonly used in MFCs (Table 2), although the antibacterial activity of some carbon compounds such as, e.g., graphene has been reported [100]. The antimicrobial activity of GO surface coatings increased four-fold when GO sheet area decreased from 0.65 to 0.01 μm^2. The higher antimicrobial effect of smaller GO sheets was attributed to oxidative mechanisms associated with the higher defect density of smaller sheets [101].

Previous studies indicate that an attractive option for anode modification is graphene, made of carbon atoms with sp^2 hybridization, which form a tightly packed crystal lattice resembling a honeycomb [102]. The structure of graphene gives it mechanical strength, flexibility, and excellent electrical conductivity [82,103]. Modification of a CF anode using GO (GO was deposited by immersing CF in a suspension of GO in ethylene glycol and heating at 200 °C) in an MFC powered with sodium acetate increased the maximum stable voltage to about 13% higher than in MFC with an unmodified anode [82]. Even better results were obtained by using reduced GO (rGO). Wu et al. [104] showed that cathode modification with rGO in a membrane-less MFC improved energy recovery due to the improved structure of cathode and electron transfer, and better biocompatibility of functional bacteria related to electron transfer in comparison to a GO-modified anode. The modification of CF with zeolite clay/GO increased the power density and corresponding Coulomb efficiency by 3.6 and 2.75 times compared to an MFC with an unmodified CF anode. The high specific surface area of GO facilitated the coating of the anode with zeolite. Zeolite adheres well to bacterial cells, which increased the anodic biocompatibility [105]. Microbiological studies of biofilm on anodes covered with rGO and GO showed that rGO favored the growth of exoelectrogens from *Geobacter* sp., which predominated in the microbial community. The presence of rGO also promoted the growth of *Ignavibacterium* sp., which both transfer electrons to the anode and degrade organic pollutants [104].

Another type of carbon compounds for anode modifications are CNTs, which are graphene foils rolled into cylindrical nanotubes. The tube diameter can vary considerably and ranges from less than 1 nm to over 100 nm [106]. CNT, depending on the type of arrangement of hexagonal rings, can show metallic or semiconductor properties. CNTs are characterized by high flexibility and excellent thermal conductivity [107]. Liang et al. [108] observed that anode modification with GO, graphene, and CNT increased the electrochemically active surface and the number of microbes in the anode biofilm, and improved electricity generation in MFC. Depending on the modifying factor, after 110

days, from 0.49 to 0.98 kJ of energy was obtained. In an MFC with a CNT-modified anode, the highest phenanthrene removal efficiency (78%) was obtained.

In MFC with a CNT/SS anode, the maximum power density was in the range of 69.8–164.9 W/m^3, and it was 7 to 21 times higher than in the control MFC with a GF anode. The energy recovery was at a level of 0.15–0.60 kWh/kg COD [29]. It was also shown that multi-walled CNT with OH hydroxyl group produced the higher current in comparison with CNT due to surface roughness and looser network dispersion, which allowed for better bacterial adhesion [109]. Modification of GF anode with CNTs increased the abundance of *Deltaproteobacteria*, *Alphaproteobacteria*, and *Geobacter* sp. in comparison to unmodified anode [110]. In another study, similar conclusions were reached, because the abundance of *Desulfomonas* sp. and *Geobacter* sp. on the GF anode modified with nitrogen-doped CNT/polyaniline/MnO_2 was 1.33 times higher than in the biofilm of unmodified GF anode [111].

CB is a low-cost conductive nanomaterial, produced in the process of burning petroleum products, that is used in electrochemical devices or sensors [112]. CB showed exceptional mechanical properties, biocompatibility, and good electrochemical properties; therefore, it has been used to produce electrodes with thin layers of composites. CB can be activated with chemical compounds. Study of Zheng et al. [113] indicated that in MFC operated on LS matrix modified with CB with H_2O_2 treatment produced more power compared to identically operated MFC but with CB with HNO_3 treatment and a control MFC without chemical treatment of CB. The integration of conductive coke with a relatively high specific surface area to which microorganisms readily adhere to a conductive CB, which has a low electrical resistance at a ratio of 2:1, increased in power density by a factor of 2.3 in comparison with control. The complementary advantages of both carbon materials enhanced the performance of the MFC [114].

Table 2. Performance of MFCs with an anode modified with carbon nanocomposites.

Anode Modification	Reactor Configuration	Substrate	Power Density	Inoculum	Reference
LS/CB/H_2O_2	Dual chamber	Sodium acetate	62 W/m^3	MFC effluent	[113]
CVe/ACP	MFC stack	Urine	21 W/m^3	Anaerobic activated sludge	[115]
CC/CB	-	Sodium acetate	12 A/m^2	MFC effluent	[116]
CC/MWCNT-COOH	Single chamber	Glucose	560 mW/m^2	Activated sludge	[117]
Carbon fiber brush/MWCNT	Dual chamber	Wastewater	1278 mW/m^3	Wastewater	[118]
SS/AC SS/CNT SS/SWCNhorns	Single chamber	Acetate	244 mW/m^2 261 mW/m^2 327 mW/m^2	MFC effluent	[119]
Sponge/nitrogen-doped CNT	Dual chamber	Sodium acetate	2.8 W/m^3	-	[120]
3D G/MWCNTs/SS	Dual chamber	Lactate	502 W/m^3	*Shewanella oneidensis*	[121]
GOA-GFB graphite fiber brush/graphene oxide aerogel	Dual chamber	Sodium lactate	54 W/m^3	*Shewanella oneidensis* MR-1	[122]
Nitrogen-doped CNS/CC	Dual chamber	Sodium acetate	1122 mW/m^2	anaerobic sludge	[123]

3.3. Polymers

In recent years, much research has focused on the modification of anodes in MFCs using semiconductor polymers such as polydopamine (PDA), polypyroles (PPy), and polyaniline (PANI). Modification of the anode with polymers increased capacitive properties, biocompatibility, and an

active surface of the anode [124]. Polymers are quite stable and are not quickly consumed in the reactor. The literature review shows that, in MFCs with polymer-modified anodes, the power density was in the range of 17–3317 mW/m^2 (Table 3). The use of polymers and additional modifiers, such as graphene or metal nanoparticles, allows us to obtain more electrochemically active sites on the anode [41].

The use of PANI as a modifier increases the electrochemical activity and roughness of the anode, reduces the anode potential, and also gives higher reproducibility of the results than in the case of unmodified anode [125]. PANI is a hydrophilic compound, therefore PANI coating can enhance the transfer of nutrients to the anode biofilm [126]. For anode modifications, PANI together with nanocomposites, e.g., Au, can be used to increase the low biocompatibility of pure metal nanoparticles. The Au/PANI-modified CC anode showed higher electrochemical activity due to increased specific surface area and electrical conductivity. The power density generated at the Au/PANI/CC anode was 2.42, 1.45, and 3.72 times higher than that of the unmodified anode, PANI-modified, and Au-modified CC anode, respectively [127]. Mashkour et al. [126] investigated the effect of modification of an anode from bacterial cellulose-carbon nanotubes (BC/CNT) with polyaniline (BC/CNT/PANI). Before colonization, Rct for the BC/CNT-modified anode was 14.52 Ω and for the BC/CNT/PANI-modified anode was 41.28 Ω. The higher Rct of BC/CNT/PANI anode compared to the BC/CNT anode can be explained by a low conductivity of PANI in neutral pH. However, after biofilm formation, the Rct of the electrodes demonstrated an opposite trend. Biofilm density on the BC/CNT/PANI-modified anode was higher than on the BC/CNT anode. Image analysis indicated that PANI increased the biocompatibility of the anode and microbial growth—the average diameter of bacteria in biofilm from the BC/CNT/PANI-modified anode was more than two times higher than in the biofilm from the BC/CNT-modified anode.

The method used for anode modification also affects the efficiency of energy generation in the MFC. The use of pulsed electropolymerization allowed to obtain a brush-like structure on the surface of PANI-modified CC anode. The obtained maximum power density of an MFC with an anode modified with pulsed electropolymerization was 36% higher than that of an MFC with an anode modified with PANI at a constant voltage and 58% higher than in an MFC with an unmodified anode. In addition, over 50% reduction in Rct was obtained if pulsed electropolymerization was applied during the anode modification in comparison with other anodes [128].

Modification of an anode with PDA causes that the anode surface is more hydrophilic and a cell power density in MFC is higher [129]. PDA was used to modify Mo_2C/MoO_2 nanoparticles on a CF anode, increasing the current density by 4.96 times compared to the unmodified FC anode and 1.38 times compared to an the MFC with the Mo_2C/MoO_2-modified anode. Modification of nanoparticles with PDA also lowers the Rct of MFC [130]. The promising results were obtained by modifying a CC anode simultaneously with PDA and rGO. The use of both modifications of CC anode increased the power density 2.2 and 1.9 times compared to the PDA-modified and rGO-modified anodes, respectively. The presence of PDA increased hydrophilicity of the anode surface and adhesion of bacterial cells, while the rGO provided more electrochemically active sites on the anode surface [131].

The beneficial effect of a simultaneous modification of an anode with polymer and other substances was also reported for PPy. The modification of CBr with PPy, carboxymethylcellulose and CNTs allowed us to obtain a macroporous 3D structure with a high specific surface area on the anode that promoted adhesion and growth of microorganisms. This modification increased the working time of MFCs due to long-term maintenance of an electrochemical activity of microbial cells. CNTs increased the anode conductivity, and PPy provided a high capacity and biocompatibility of the anode [120]. Modification of SS anode with PPy increased the corrosion resistance, biocompatibility, and power density of the anode compared to an unmodified stainless-steel anode [132]. Modification of anodes with CNT and PPy was reported as an attractive and inexpensive alternative to the use of Pt in MFCs [133]. There are also reports on the use of more niche modifiers, such as poly(3-aminophenylboronic acid). The use of poly(3-aminophenylboronic acid) to modify the CC anode shortened the growth time of the bacterial

biofilm on the electrodes by two times, while the power density was 928 ± 20 mW/m^2 and was about 4.5 times higher than in the MFC with an unmodified anode [134].

In many cases, the modification of anodes with polymers contributed to the improvement of the hydrophilicity and specific surface of the anode. PANI electroplating introduced a rough layer on the graphite fiber. SEM analysis showed that the PANI membrane was rough and loose, containing a lot of nano-cilia. Bare GF had a strongly hydrophobic surface (water contact angle of 113–120°), but after modification with PANI, the water droplet was completely and rapidly adsorbed by the anode [135]

On the other hand, the sponge made of polyvinyl formaldehyde and graphite nanopowder showed a hyperhydrophilic character—regardless of the share of the graphite nanopowder, the anode contact angle was <10° [136]. In another study, the PDA/rGO coating improved biocompatibility of the CC membrane—the water contact angle was close to 0° (superhydrophilicity). Superhydrophilicity contributed to the rapid adherence of microorganisms and increased bacterial stability on the anodes [137]. Polymers also reduce the corrosivity of metals. The bare SS plate was smooth with only some scratches. In contrast, the PPy-coated SS plate surface was covered with particles with a diameter of 1 to 2.5 µm, and the electrode surface was rough and porous. The corrosion potential decreased from −553.6 to −382.2 mV after the modification of the SS plate with PPy [132].

Table 3. Performance of MFCs with anodes modified with polymers.

Anode Modification	Reactor Configuration	Substrate	Power Density	Inoculum	Reference
PPy-CMC-CNTs/CBr	Dual chamber	Sodium acetate	2970 mW/m^2	Mixed culture	[138]
PPy-CMC-TiN/CBr hydrogel anode	Dual chamber	Sodium acetate	14 W/m^3	Anaerobic mixed culture	[139]
SS/PPy-W	Single chamber	Sodium acetate	1870 mW/m^2	Landfill leachate	[140]
PPy/MWNT/graphite rods	Single chamber	Saccharose	201 mW/m^2	Anaerobic sludge	[141]
magnetic PPy/nanofibers/$SrFe_{12}O_{19}$/nonwoven textile	Dual chamber	Glucose	3317 mW/m^2	MFC effluent	[142]
PPy/SAC/SS	Dual chamber	Sodium acetate	45 W/m^3	*Geobacter sulfurreducens*	[143]
Ti_4O_7/GO/PANI	Single chamber	Oil-containing restaurant wastewater	2073 mW/m^2	mixed bacterial culture	[144]
PANI/GF	Dual chamber	Sodium acetate	216 mW/m^2	Anaerobic sludge with *Chaetoceros*	[145]
Au/PANI/CC	Dual chamber	Glucose	804 mW/m^2	*Escherichia coli* ATCC 27325	[127]
TiO_2-20 *PANI/CP	Dual chamber	$NaHCO_3$	813 mW/m^2	*Shewanella loihica PV-4*	[146]
rGO/PANI/CBr	Single chamber	Glucose	862 mW/m^2	Sludge	[147]
PANI/Fe/GF	Bentos MFC	Seawater and marine sediment	17 mW/m^2	Marine sediment	[148]
PANI nanoflower/CC	Dual chamber	Mixed medium containing M9 salt medium, 5% LB broth, and 10 mM sodium lactate	389 mW/m^2	*Shewanella oneidensis* MR-1	[149]
PDA/rGO/CC	Dual chamber	Sodium acetate	2047 mW/m^2	Activated anaerobic sludge	[131]
PDA/Mo_2C-MoO_2/GF	Single chamber	Glucose	1640 mW/m^2	*E. coli*	[130]
PDA **/AC/SS	Single chamber	Wastewater with acetate	803 mW/m^2	Wastewater	[129]

* 20 cycles of cyclic voltammetry polymerization. ** With 50% (wt.) polydopamine (PDA) added.

In research on modifications of the anode with polymers or co-modification with other metal or carbon compounds, pure cultures of microorganisms such as *Escherichia coli* [127] or *Shewanella* sp. [150, 151] are most often used to inoculate the reactors. There are few studies on the influence of anode modifications with polymers on multispecies microbial community of anode. They indicate that the modifications increase the number of *Proteobacteria*, *Deltaproteobacteria*, and the genus *Geobacter* [110,152]. The presence of polydiallyldimethylammonium (PDDA) on the CF electrode accelerated the attachment of exoelectrogens to the surface through electrostatic attraction—*Geobacter* sp. and *Pseudomonas* sp. were about nine and three times higher, respectively, on PDDA-modified CF anode than on the unmodified anode [152]. On the other hand, the share of exoelectrogens from genera *Acinetobacter*, *Brucella*, and *Bacillus* was about 1.4 times lower on PDDA-modified CC anode than on the unmodified anode [153]. Chen and Wang [154] showed that *E. coli* cells grown in PDDA microcarriers had the same viability as those grown in suspension, as evidenced by an increase in optical density and cell number. However, *Chlorella vulgaris* cells showed extremely poor viability inside PDDA microcarriers, possibly due to blockage of nutrient uptake by the diallyldimethylammonium quaternary ammonium cation. At anodes modified with 50% PDA, an approximate twofold increase in the percentage of *Proteobacteria* (up to 33%) and *Firmicutes* (up to 3%) biomass was observed compared to unmodified anode [129]. Modification of the CC anode with PANI stimulated the participation of *Geobacter* sp. in the biofilm, while the simultaneous use of PDA with rGO on the CC anode caused that *Geobacter* sp. accounted for over 80% of the microorganisms identified in the biofilm. The anode modifications could select for the growth of bacteria from the anolyte. Changes in the properties of the anode surface may also affect a transcriptomic profile of microorganisms in MFC; in the cells of microorganisms inhabiting the PDA/rGO modified anode, electrogenesis related to outer-surface octaheme *c*-type cytochrome *omcZ* was highly expressed [155].

4. Conclusions

To increase the production of electricity in MFCs, a holistic approach should be applied that connects operational parameters of the reactor with environmental conditions and microbial structure of the biomass. The literature review shows that the most promising solutions for MFCs are modification of anodes from highly conductive carbon nanomaterials with polymers (e.g., PDA or PANI) and carbon-derived materials (e.g., GO or CNT). Such modifications increased hydrophilicity and the specific surface of anodes, resulting in a higher electricity production. Anode modifications affect the composition of exoelectrogenic bacteria in the anode biofilm, and sulfur-reducing bacteria are regarded as microorganisms mostly responsible for the efficient production of electricity. Although technological research indicates an improvement in the efficiency of energy generation as a result of modification, there is little data showing the effect of modification on microbial metabolism. Therefore, future research should focus on metatranscriptomic analysis to indicate factors that determine the activity of exoelectrogens in MFCs.

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Abbreviations

AC	active carbon
ACNFN	activated carbon nanofiber nonwoven
ACP	activated carbon powder
BC	bacterial cellulose
CB	carbon black
CBr	carbon brush
CC	carbon cloth
CF/GF	carbon/graphite felt
CMC	carboxymethylcellulose
CMF	carbon microfiber
CNF	carbon nanofiber
CNS	caron nanosheet
CNT	carbon nanotubes
COD	chemical oxygen demand
CP	carbon paper
CVe	carbon veil
GFB	graphite fiber brush
GO	graphene oxide
GOA	graphene oxide aerogel
GP	graphite paper
kWh	kilowatt hour
LS	loofah sponge
MFC	microbial fuel cell
MWCNT	multi-walled carbon nanotube
PANI	polyaniline
PDA	polydopamine
PDDA	polydiallyldimethylammonium
PEM	proton exchange membrane
PPy	polypyroles
Rct	charge transfer resistance
rGO	reduced graphene oxide
SAC	sargassum activated carbon
SS	stainless-steel
SWCNhorns	single-walled carbon nanohorns
TiN	titanium nanoparticle

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