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Review

Microbial Fuel Cell Performance Boost through the Use of Graphene and Its Modifications—Review

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Abstract: The conversion of chemical energy contained in organic matter into electricity has become an object of interest for many scientists worldwide. This technology is used in microbial fuel cells (MFC). Apart from generating electrical energy, these cells can be used simultaneously for wastewater treatment. Although the technology is constantly being improved, currently functioning microbial fuel cells cannot provide appropriate output parameters to use on an industrial scale. One of the barriers is so-called extracellular electron transfer, which in turn depends on the electrode type used, its material, shape, and size. According to current literature, carbon, graphite, stainless steel, and ceramics are the most frequently used electrode materials. However, more and more often, scientists are turning to other, unusual materials, the production of which uses the newest technologies, and one of them is graphene. This material is modified in different ways and connected with other materials, and the results of this seem to be very promising. Scientists manage to get a higher level of extracellular electron transfer and, hence, higher output parameters of the whole system. This article describes chosen technologies and attempts made by scientists worldwide to use graphene in MFC and their results.

Keywords: alternative energy; microbial fuel cells; graphene; electrodes; micro-organisms; electrochemistry

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1. Introduction

Microbial fuel cells are increasingly an object of interest due to the possibility of simultaneous electrical energy production and wastewater treatment, and connecting them with other technologies [1,2]. In addition, this technology is used to recover different resources such as nutrients, e.g., nitrogen and phosphorus or critical metals, and for desalination and biodetection [3]. One of the essential aspects on which intensive works are in progress is the material used to build electrodes. In recent years, there has been considerable development in materials for electrodes used in microbial fuel cells [4]. More and more often, scientists reach for materials based on the most recent achievements of technology, and one of them is graphene. This material is increasingly used in industry and science, including microbial fuel cells. Graphene is connected with other materials and modified in numerous ways, and it seems to be a perfect alternative for standard carbon or stainless steel electrodes. Much of the research conducted gives excellent results, which have been described in this article.

2. Methodology

There is a vast amount of data in the current literature about microbial fuel cells themselves, as well as the structure and materials for electrodes used. More often, scientists reach for the newest material-engineering solutions using such materials as graphene. The criteria for creating this article and searching for the described articles were the year of publication, the accuracy of the search, and the number of citations. The newest articles were searched for and written no later than 2017. Due to this, the included data are current,

and state the latest achievements of the world of science. Articles had to be about graphene as a material for electrodes or used in a cathode chamber as a catalyst additive, which has been described in a different part of the article. The impact factor of the magazine has also been taken into account, which led to choosing the most valuable and adequate works. From a search in Google Scholar, of 18,300 results of the phrase "graphene microbial fuel cell", 60 most relevant ones have been chosen, and based on them, the article has been written. This type of methodology resulted in a review article about the most interesting and the newest and most appropriate scientific achievements in the field of graphene used in microbial fuel cells.

3. Graphene as Material

In 2004, a group of researchers from the University of Manchester conducted by A. Geim and K. Novoselov reported on the discovery of stable in-free-state graphene. This material is considered to be one of the most outstanding achievements in the field of science and technology. Graphene is a hexagonal crystalline single layer of graphite, which is the simplest form and one of the essential crystalline allotropes of carbon atoms with a C-C bond distance of 0.142 nm [5]. It is of great interest in the field of sensors, biomedicine, composite materials, and microelectronics [6]. A wide range of applications, such as transparent conductive films, ultra-sensitive chemical sensors, thin film transistors, quantum dots, and anti-corrosion coatings, have been extensively tested and recognized by the scientific world. Attempts are being made to introduce this still expensive material for use on an industrial scale, and the results seem to be very promising.

Graphene is the only carbon allotrope in which each carbon atom is tightly bound to its neighbors through a unique electron cloud [7,8]. However, it raises several particular questions for quantum physics. Along with the quantum Hall effect, graphene comes in several forms, such as graphene nanoribbons, nanosheets, nanoplates, and three-dimensional graphene [9]. Each of these characters can have fantastic application possibilities. Graphene is most commonly used in the form of graphene oxide (GO) and reduced graphene oxide (rGO), and the diagrams of these compounds are presented below (Figure 1).

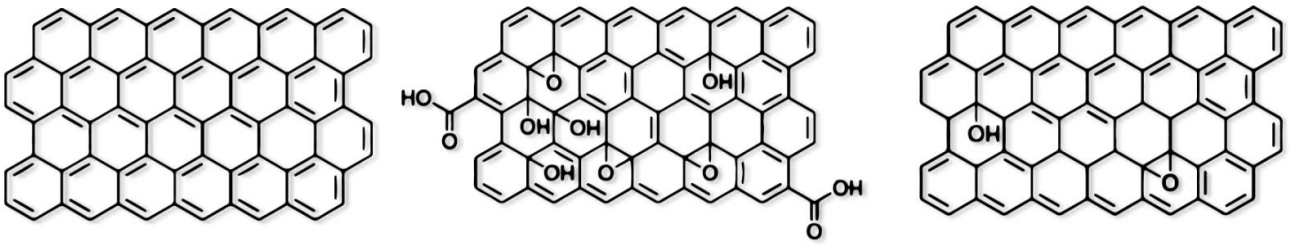

Figure 1. Graphene (G), graphene oxygen (GO), and reduced graphene oxygen (rGO).

3.1. Graphene Properties

A strong interest in graphene and the possibility of introducing it into mass production results directly from its unique properties. Graphene is a two-dimensional layer of single-atomic thickness [10]. This layer is made of carbon atoms with sp^2 hybridization, creating a tightly packed crystal lattice, which in its structure resembles a honeycomb. Scientists believe that graphene is the only known two-dimensional material found in nature. Numerous studies on the properties of this material show that it is a very stable material and, at the same time, attractive because of its potential application in electronics, where silicon has been used so far. Examples include single-electron transistors or field emitters.

Graphene has unique properties that are directly related to its structure, including very high mechanical strength and flexibility, and excellent electrical conductivity [8,11]. The possibilities of creating new composite materials with the participation of graphene, which take advantage of its strength and a large variety of chemical interactions, also seem to be very interesting. The very high mobility of electrons in graphene can reach up to 2×10^5 cm^2/Vs at room temperature, while, by comparison, in silicon, the mobility is at

the level 1.4 × 10^3 cm^2/Vs [12]. This feature significantly affects the conductive properties of solids, which is of great importance in terms of the use of this material in electronics. The maximum electrical conductivity was determined at the level of 6000 S/cm for a single graphene layer [13]. A very high thermal conductivity also characterizes it at the level of approx. 5000 W/mK [14] and excellent mechanical strength, approx. 200 times higher for GO than for steel [15]. Young's modulus of elasticity is higher than 1 TPa [16], with strength up to 130 GPa [17].

Based on these results, graphene has been recognized as the most durable material discovered, obtained, and characterized so far. The specific capacitance of graphene is 550 F/g [18], and it is a material impermeable to gases and very flexible. The graphene flake is light and transparent—it absorbs only about 2% of the light. Graphene has an extensive specific surface area, which is theoretically 2630 m^2/g [19]. These properties turn out to be excellent in terms of the construction and use of microbial elements of fuel cells, the results of which are described in the following chapters.

3.2. Preparation of Graphene Methods

Graphene is produced by several techniques, each with different potential applications in science and industry. Mechanical stripping using an adhesive tape made of high-quality graphite is mainly used for pure research applications. Graphene obtained in this way has very high mobility parameters [20], but it cannot be mass-produced due to its enormous cost. Until recently, graphene obtained in this way was even the most expensive material in the world. However, large sample sizes are unnecessary in science, and this type of graphene can be produced in any laboratory.

Another technique for producing graphene is chemical vapor deposition (CVD) on metals [21,22]. This process was pioneered by Korean scientists and is now used in many laboratories worldwide. Graphene has become a much cheaper material due to this method—the cost of producing graphene on copper is significantly lower than graphene obtained from graphite. At the same time, graphene on copper has a significantly lower quality than graphene obtained from graphite and cannot be used to produce electronic devices. However, it can be used to build touch screens, where the quality (number of defects, domain size, and homogeneity) is less critical.

Graphene can be produced as well on silicon carbide [23]. The method of producing carbon by thermal decomposition of SiC makes it possible to obtain large areas of high-quality graphene. However, the cost of the SiC substrate is very high. The first graphene integrated circuit was fabricated on graphene grown on SiC.

In 2011, the Institute of Electronic Materials Technology and the Department of Physics at the University of Warsaw announced the joint development of a technology for obtaining large fragments of graphene with the best quality to date [24]. Polish scientists used a chemical deposition technique from a gas layer on a silicon carbide substrate. Due to this, the obtained graphene is less sensitive to imperfections in the carbide, provides high electron mobility of 1500 cm^2/Vs [25], and makes it possible to determine the number of layers one wants to obtain and the degree of enrichment with another material. Studies have shown not only better properties of graphene obtained in this way but also the existence of an energy gap in it.

In 2015, the Technical University of Lodz unveiled a liquid-phase graphene device that can produce large-area graphene sheets with near-theoretical properties [26]. Scientists named their product HSMG (High Strength Metallurgical Graphene). In 2016, the HSMG method received patent protection in the European Union and the United States of America.

4. Microbial Fuel Cell Principles of Operation

4.1. Constructrion of a Microbial Fuel Cell

Electricity production in a microbial fuel cell results from the direct process of converting chemical energy into electricity. Micro-organisms oxidize organic matter such as municipal wastewater [27], simultaneously releasing protons, electrons, and carbon

dioxide. The external circuit transports electrons from the anode, the electron acceptor, to the cathode. A typical microbial fuel cell is built from an anodic and cathodic chamber separated by an ion-exchange membrane. The ions are moved from the anodic chamber to the cathodic through this membrane. In the cathodic section, oxygen reduction to water occurs [4]. This is a so-called two-chamber microbial fuel cell. In the first chamber, there are anaerobic conditions, while an oxygen presence is necessary for the second due to the reduction reaction. Microbial fuel cells can also operate as a single-chamber system [28]. In this type of MFC, an ion-exchange membrane is not necessary. On one side, they have open access to oxygen and, on the other direct, contact with ions produced in the anodic chamber [29]. Both one- and two-chamber MFC can operate in series and parallel connections. The two types of systems are shown in Figure 2.

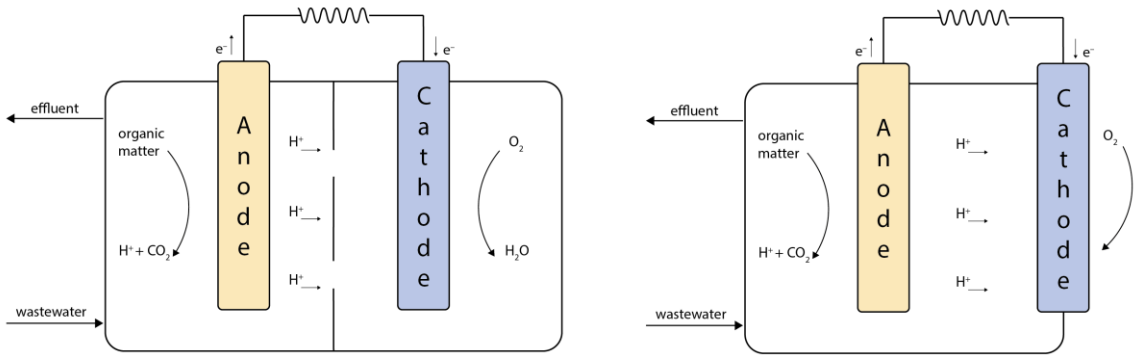

Figure 2. Two types of MFC—one- and two-chamber.

4.2. Extracellular Electron Transfer

One of the main elements of the respiration process and metabolism ways of various forms of life, including micro-organisms, is extracellular electron transfer [30,31]. In order to maximize energy yield, micro-organisms use the ultimate electron acceptor with the highest available potential to transfer electrons from the donor and adjust their electron transfer pathways accordingly. If the availability of electron acceptors in the environment is limited, they pass to fermentative metabolism or utilize insoluble solid electron acceptors [32]. In this case, micro-organisms transport electrons outside the cells to achieve a final reduction reaction through the mechanism of extracellular electron transfer. In the natural environment, micro-organisms use solid minerals or organic substances as electron acceptors and donors. In laboratory conditions, such as in MFC, the anode and cathode work as electron acceptors and donors, respectively.

Electrons produced during micro-organism metabolism can be transported to an anode through indirect or direct electron transfer, depending on the catalysts used. In the case of direct transfer, close physical contact between bacteria cells and the anode is essential. Certain types of bacteria, e.g., *Geobacter sulfurreducens* or *Shewanella oneidensis* MR-1, use this type of electrochemical communication with an anode [32]. Micro-organisms, which cannot use the direct path of electron transfer or do not have direct contact with an anode, can use indirect mechanisms using the participation of mediators. The direct and indirect electron transfer mechanisms are shown in Figure 3.

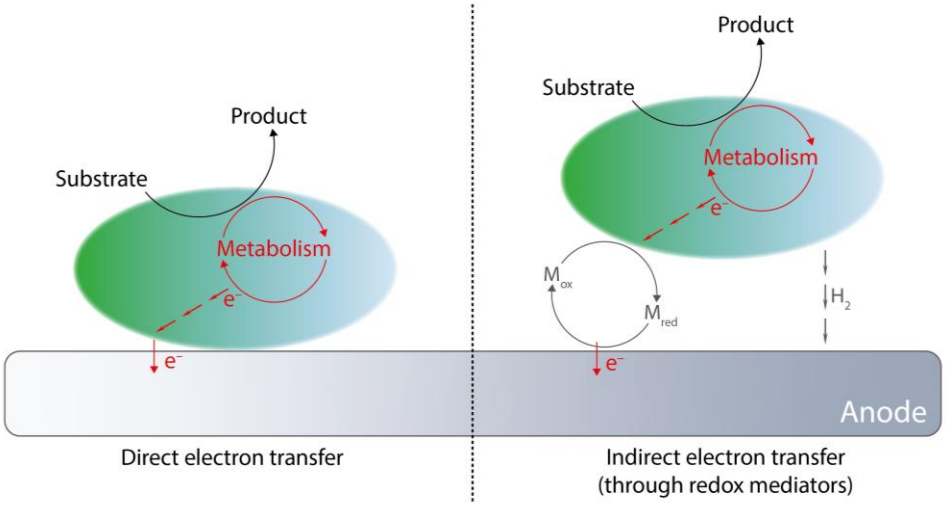

Figure 3. Mechanisms of electron transfer between micro-organisms and anode in MFCs.

5. Graphene Applications in Microbial Fuel Cells

Since the first discovery of the two-dimensional nanomaterial graphene, there has been high interest in its potential applications according to its excellent conductivity, tremendous surface, and outstanding mechanical strength [33–35]. One of the promising solutions is a microbial fuel cell. The limited performance of MFC compared with other fuel cell technologies and the high cost of its components are two main barriers to its commercialization. Graphene, if technological developments make it cheaper to obtain, seems to offer a solution to this problem. Graphene can be used to build anodes in terms of increasing the efficiency of transporting electrons, to build cathodes, and used in a cathode chamber to efficiently catalyze the oxygen reduction reaction.

5.1. Anodes Based on Graphene Used in MFC

Graphene is considered a suitable additive for anodes due to its advanced properties, such as high conductivity, and good thermal and mechanical strength. Graphene has non-linear and also higher diamagnetism compared to graphite [36]. Used in anode, it ensures brilliant energy efficiency in comparison with other carbon-based materials. Graphene has no toxic effect on bacterial growth during MFC operation [37]. Its modifications or connection with metals or conductive polymers can minimize the toxicity of other materials, such as copper [38]. With its properties and application in MFCs, graphene can bring a kind of revolution in energy and wastewater treatment. Different forms of graphene, such as graphene oxide (GO), single/multilayered graphene, 2D/3D graphene, and reduced graphene (rGO), were used as anode materials in MFC.

In order to build a functional MFC system, bacteria must form dense biofilms on the surface of the anode to ensure efficient charge transfer from the individual bacteria to the external electrode, which is the source of the current and output of the MFC. Additions of certain substances can increase, and others decrease this process. Based on previous studies, it can be concluded that graphene is one of the materials whose addition significantly improves MFC efficiency. The method of chemical vapor deposition was used for three-dimensional graphene (3D) integration with an anode of a miniaturized microbial fuel cell (mini-MFC) (56-µL anode chamber). The structure of graphene showed fewer defects in layers, and the framework showed high REDOX peak current density. 3D graphene anode facilitated efficient mass transfer and effective electron transport, by forming denser biofilm [39]. The graphene oxide was incorporated on the carbon brush using an electrophoretic technique. Sayed et al. (2021) [40] used a modified hummer's method to exploit a thin layer of graphene oxide on the anode. The authors used real wastewater in MFCs and obtained the power density increased more than 10 times compared to pure carbon brush (from 33 mW/m^2 to 381 mW/m^2), although the COD removal was nearly similar

for the two MFCs. The authors proved by the electrochemical impedance spectroscopy measurements that the graphene improved the electron transfer from the micro-organism to the anode surface. To improve the efficiency of MFCs, researchers are experimenting with various types of bacteria that thrive in low-oxygen environments, such as *Shewanella oneidensis* and *Geobacter* [41]. The problem with MFC efficiency often comes down to the bacterial biofilm, through which electrons have difficulties getting through. Researchers at the University of California Los Angeles (UCLA) solved this problem by growing bacteria on electrodes made of graphene oxide with silver ions embedded in it. The bacteria began to reduce the ions to nanoparticles, which in turn went into their cells and thus helped more electrons escape outside. During the study, it was shown that with these improvements, the bacteria began transferring up to 81% of the electrons they produced to the electrode, an unprecedented figure at this time [42]. In terms of testing the compactness and thickness of the biofilms formed, they used three different materials for anode electrodes—carbon paper, carbon paper with reduced graphene oxide (rGO), and carbon paper with reduced graphene oxide and silver nanoparticles added (rGO/Ag). It turned out that the maximum power density from the rGO/Ag electrode reached 6600 $\pm$ 300 mW/m^2, which was a much higher value than for carbon paper anodes (500 mW/m^2) or anodes of rGO (1300 mW/m^2). In addition, due to utilizing a composite built from carbon paper with the addition of graphene and silver nanoparticles, a very high coulombic efficiency was achieved at the previously mentioned level of 81% [42]. The fabrication of the anode with graphene and adding metal oxides (ZnO and TiO_2) was tested in terms of electron transfer and cobalt remediation efficiency through microbial fuel cells (MFCs). The highest current density was obtained in the GO-ZnO composite anode (75.43 mA/m^2) and the lowest in GO anode (39.47 mA/m^2). The maximum remediation efficiency of cobalt (II) was noted in MFC with the GO-ZnO composite anode 91% on day 45 [43]. In addition, very high-power density through the use of graphene was achieved by using a three-dimensional (3D) macroporous graphene foam core/satellite structure with the addition of a nanocomposite Fe_3O_4/Au (Fe_3O_4/Au NCs-3DGF) to build anode [44]. It was found that nanocomposites Fe_3O_4/Au improve anode–bacteria interaction, according to the high biological affinity between the Fe_3O_4/Au core and *Shewanella oneidensis* MR-1. Due to the three-dimensional incorporation of macroporous graphene foam, the surface of the anode on which bacteria could settle expanded, and bacterial penetration into the anode also occurred. Taking advantage of these properties, the anode Fe_3O_4/Au NCs-3DGF showed enhanced bacterial carrying capacity and highly efficient extracellular electron transfer, which together contributed to a 71-fold increase in volumetric power density compared to the graphite counterpart (2980 $\pm$ 54 mW/m^2 in comparison with 41 $\pm$ 4 mW/m^2). In addition to the obtained graphene-based foams, the gels can also be used. Yu et al. (2018) [45] used graphene aerogel (GA) as bioanode via the hydrothermal reduction method. Authors obtained 36 times more electricity generation than that of pure carbon paper as anode (maximum power density of 5 mW/m^3 and electrode potential of 488 mV). Graphene anode coated with iron (II) persulfide nanoparticles (FeS_2) is another example of the use and modification of this material in the MFC [46]. The nanoparticles FeS_2, by which the graphene anode is coated, not only have a positive effect on bacteria adhesion and enrichment of electrochemically active species of *Geobacter* on the electrode surface but also promote efficient extracellular electron transfer, thus giving a fast start-up time of 2 days, and a very high-power density of 3220 mW/m^2. Chen et al. [47] in their study developed a three-dimensional composite hydrogel with reduced graphene oxide and polyacrylamide (rGO/PAM) in combination with graphite brush (GB) and used it to build an MFC anode. The rGO/PAM material was produced by in situ polymerization of acrylamide in a graphene oxide dispersion, followed by reduction with ascorbic acid. The researchers found that the resulting porous scaffold with a large surface area and biocompatibility provided measurable benefits for both strong diffusions of the culture medium, bacterial colonization, and electron transfer. As a result, the GB/rGO/PAM anode also produced a high maximum power density of 758 mW/m^2 during a steady power generation state. In addition, they found that specially oriented

rGO/PAM (O-rGO/PAM) with increased conductivity can, even more, improve maximal MFC power density, achieving 782 mW/m^2. These results appeared to be much higher than in the case of traditional graphite brush, typical carbon anode, or control electrodes based on GB/GO/PAM and CC (plain carbon cloth)/rGO/PAM tested in the same conditions. Another solution, which markedly increased surface area and enhanced bacterial adhesion, was modification of carbon felt anode with graphene oxide-zeolite, which resulted in a maximum power density of 280.56 mW/m^2 [48]. Jawaharraj et al. [49] used a 3D nickel (Ni) foam modified with plasma-grown graphene as anode, nitrate mineral salts media (NMS) supplemented with 0.1% CH_3OH as anolyte, carbon brush as cathode, and 50 mM ferricyanide as catholyte. The study showed that minimal coating of graphene layers improved the bioelectrochemical interactions of *Rhodobacter sphaeroides* cells with underlying ferromagnetic nickel surfaces.

As described above, graphene is combined with elements or chemical compounds that can also modify other properties of the overall system. One of these elements was silver, often regarded as exhibiting antibacterial properties against bacteria such as *Escherichia coli*. However, in the case of the *Shewanella* sp., it did not significantly affect their viability. Researchers at UCLA [42] supported this with a biocompatibility assessment study using a laser scanning microscope. Silver did not reduce the viability of *Shewanella* sp. (93% viability for rGO/Ag versus 95% for carbon paper and 92% for rGO). With the addition of silver, the maximum output current density from the rGO/Ag electrode reached as high as 9200 mA/m^2, which was much higher than the carbon paper electrode (600 mA/m^2) or rGO without this addition (1200 mA/m^2). The pyrite (FeS_2) addition, an iron mineral from the sulfide cluster, resulted in an output current density of 3060 mA/m^2 in MFC powered by acetate [46]. In order to improve the electron transfer rate, a study focusing on the fabrication of graphene-polyaniline composite anodes (GO-PANI) was also conducted [50]. The construction of this type of anode based on graphene and polyanilines in the so-called benthonic microbial fuel cell (BMFC) resulted in a maximum current density of 87.71 mA/m^2. The modified graphene anode showed four times higher efficiency than the unmodified anode. Similarly, the GO-PANI remediation efficiency was 65.51% for cadmium (II) and 60.33% for lead (II), which was also higher than that of the unmodified graphene anode. Anodes based on polyaniline and graphene were also combined with titanium sub-oxides (TS) and compared to carbon cloth [51]. The authors observed an enhanced voltage of 980 mV and the power density of 2073 mW/m^2. The combination of rGO-PANI/carbon cloth compared to pure carbon cloth increased power density twice and accelerated the growth of electrogenic biofilm [52]. Li et al. [53] used rGO modified with polydopamine as an anode and achieved power density of 2047 mW/m^2, which exceeded six-times the power density obtained by using pure carbon cloth.

5.2. Graphene Used in the Cathode Chamber of MFC

In addition to the characteristics of anodes, cathodes must have a catalytic capacity, enabling efficient reduction of terminal electron acceptors. The catalytic activity can be improved if the cathodes are modified with nanomaterials. The most common cathode catalyst is the expensive precious metal platinum (Pt). Cathode catalysts account for more than 50% of the total cost of MFCs, which is considered the most expensive component [54]. Therefore, exploring other stable and simple materials that can be effectively used to build MFC electrodes is crucial. Graphene-based materials are among the attractive non-precious oxygen reduction reaction (ORR) catalysts due to their low cost compared to Pt and their unique properties.

Graphene in the cathode space can be used in various forms and, when used properly, can effectively increase the efficiency of the entire cell. High power densities have been achieved using three-dimensional graphene nanosheets (3D-GNS). Such sheets were used as cathode catalysts in MFCs operating under inert conditions. Compared to activated carbon, the 3D-GNS catalysts showed high efficiency [55]. Researchers tested graphene nanosheets using alternating current with three loads—2, 6, and 10 mg/cm^2. The use of

3D-GNS yielded the highest power density values: 2059 ± 3 mW/m^2, 1855 ± 7 mW/m^2, and 1503 ± 5 mW/m^2, respectively, for a load of 10, 6, and 2 mg/cm^2. The addition of 3D-GNS also lowered ohmic losses at a level of 14–25%, letting the 3D-GNS-based microbial fuel cell achieve maximal power P_{max} = 5746 ± 186 mW/m^2. Yang et al. [56] tested nanocomposites based on cobalt and zinc oxygen nanoparticles on a carrier covered by graphene oxygen (GO-Zn/Co). They were synthesized by hydrothermal treatment of graphene oxide and cobalt and zinc acetates, followed by pyrolysis at controlled temperatures. The porosity of the obtained nanocomposites changed with pyrolysis temperature and Zn/Co molar ratios. The resulting GO-Zn/Co nanocomposites exhibited apparent antibacterial activity, inhibiting the formation of biofilms on the cathode surface. MFCs using GO-Zn/Co prepared in this way as a cathode catalyst achieved a maximum power density of 773 mW/m^2, which was even higher than the most advanced Pt/C catalyst, 744 mW/m^2, and the output power remained unchanged during constant operation for one month. Improving the performance of MFCs with graphene-based nanocomposites can also be achieved by combining them with other materials, such as titanium dioxide (TiO_2). By synthesizing sulfonated graphene oxide (SGO) as a potential conductive matrix and using titanium dioxide nanoparticles and polyaniline (PANI) anchored on SGO, nanocomposites SGO-TiO_2-PANI can be obtained and used as a potential cathode catalyst in MFCs. Papiya et al. [57] tested such a catalyst by comparing it with a catalyst GO-TiO_2-PANI and TiO_2-PANI. Titanium dioxide nanoparticles bridged PANI and SGO via hydrogen bonding/electrostatic interaction and improved the thermal stability of the SGO-TiO_2-PANI catalyst. The electrochemical characteristics of these nanocatalysts suggested that SGO-TiO_2-PANI exhibited a higher reduction current (−0.46 mA), better stability, and lower internal resistance (46.2 Ω) compared to GO-TiO_2-PANI and TiO_2-PANI. Consequently, the MFC using SGO-TiO_2-PANI showed a maximum power density of 904.18 mW/m^2—higher than GO-TiO_2-PANI (734.12 mW/m^2), TiO_2-PANI (561.5 mW/m^2), and Pt/C (483.5 mW/m^2). The researchers attributed the enhanced catalytic activity of the SGO-TiO_2-PANI catalyst to the nanocomposite's high electronic conductivity and durability. Increased MFC performance was also achieved by using in situ polymerization of pyrrole (Py) on reduced graphene oxide (rGO), formed as a nanocomposite support matrix for deposition of nickel-nickel oxide (Ni-NiO) nanoparticles. Pattanayak et al. [58] established that in the presence of an oxidant, pyrrole monomers were electrostatically adsorbed on the negatively charged rGO layer, where π-π interactions between Py monomers caused its polymerization as polypyrrole (PPy). The synergistic action of the support matrix components resulted in sustained electrocatalytic activity during the oxygen reduction reaction of the prepared Ni-NiO/PPy-rGO composite in an inert environment. Better stability and electrocatalytic activity of Ni-NiO/PPy-rGO (reduction potential of 0.535 V at −0.235 mA) was observed compared to the conventional Pt/C catalyst (reduction potential of 0.521 V at −0.204 mA). The Ni-NiO/PPy-rGO nanocatalyst showed a higher current density of 2135 mA/m^2 and power density ∼ of 679 ± 34 mW/m^2 compared to commercial Pt/C (1788 mA/m^2 and ∼ 481 ± 24 mW/m^2). Adding copper (I) oxide (Cu_2O) nanoparticles to reduced graphene oxide also increases microbial fuel cell efficiency. Xin et al. [59] examined the output voltage, coulombic efficiency, and microbial population in a single-cell MFC with a cathode catalyst made of copper (I) oxide nanoparticles and reduced graphene oxide (Cu_2O/rGO). They compared this voltage with a commercial platinum/carbon (Pt/C) catalyst. The study showed that MFCs with the Cu_2O/rGO cathode catalyst exhibited higher output voltage (0.223 V) and coulombic efficiency (92.5%) compared to commercial Pt/C (0.206 V, 90.3%, respectively). Moreover, the Cu_2O/rGO cathode catalyst exhibited excellent catalytic activity in the oxygen reduction reaction and promoted O_2 diffusion to the cathode surface. Interestingly, the relative abundance of *Geobacter* electrogenic micro-organisms in the MFC anode biofilm with Cu_2O/rGO cathode catalyst (49.28%) was higher than that of commercial Pt/C (32.33%). The total abundance and diversity of the MFC cathode biofilm with Cu_2O/rGO catalyst was lower than that of commercial Pt/C due to the antibacterial properties of Cu_2O/rGO. However, according to the researchers, this phenomenon may

have exposed more active catalytic sites on the cathode and further improved the power generation efficiency of the MFC. Table 1 presents the results of MFC performance with an anode or cathode made from graphene.

Table 1. MFC performance with anode or cathode made from graphene.

Graphene Type	Type of Electrode	MFC Type	Bacteria Type	Substrate Type	MFC Performance	Ref.
Graphene-coated carbon brush (RGO-CB)	Anode	Double chamber	-	Real industrial wastewater	381 mW/m^2	[40]
Reduced graphene oxide (rGO)	Anode	Double chamber	*Shewanella*	-	1300 mW/m^2	[42]
Carbon paper with silver nanoparticles added (rGO/Ag)	Anode	Double chamber	*Shewanella*	-	6600 ± 300 mW/m^2	[42]
Lignin-derived graphene oxide GO-ZnO composite	Anode	Double chamber	Biofilm with majority of *Klebsiella pneumoniae* sp. and *Enterobacter* sp.	Wastewater with cobalt addition	1.214 mW/m^2	[43]
Lignin-derived graphene oxide GO-TiO_2 composite	Anode	Double chamber	Biofilm with majority of *Klebsiella pneumoniae* sp. and *Enterobacter* sp.	Wastewater with cobalt addition	0.784 mW/m^2	[43]
Lignin-derived graphene oxide (GO)	Anode	Double chamber	Biofilm with majority of *Klebsiella pneumoniae* sp. and *Enterobacter* sp.	Wastewater with cobalt addition	0.148 mW/m^2	[43]
Three-dimensional (3D) macroporous graphene foam core/satellite structure with the addition of a nanocomposite Fe_3O_4/Au (Fe_3O_4/Au NCs-3DGF)	Anode	Double chamber	*Shewanella oneidensis* MR-1	-	2980 ± 54 mW/m^2	[44]
Graphene aerogel (GA)	Anode	Double chamber	Anaerobic sludge	Acetate solution	2381.44 mW/m^3	[45]
Graphene anode coated with iron (II) persulfide nanoparticles (FeS_2)	Anode	Double chamber	Mixed-bacteria with *Geobacter*	Acetate solution	3220 mW/m^2	[46]
Graphene anode coated with iron (II) persulfide nanoparticles (FeS_2)	Anode	Double chamber	Mixed-bacteria with *Geobacter*	Beer factory wastewater	310 mW/m^2	[46]
Three-dimensional composite hydrogel with reduced graphene oxide and polyacrylamide (rGO/PAM) in combination with graphite brush (GB) GB/rGO/PAM	Anode	Double chamber	Mixed bacteria	Culture medium	758 mW/m^2	[47]
Carbon felt anode with graphene oxide-zeolite	Anode	Single chamber	Pre-treated mixed anaerobic sludge	Synthetic wastewater with sodium acetate	280.56 mW/m^2	[48]
Carbon felt anode with graphene oxide	Anode	Single chamber	Pre-treated mixed anaerobic sludge	Synthetic wastewater with sodium acetate	77.82 mW/m^2	[48]
3D nickel (Ni) foam modified with plasma-grown graphene	Anode	Double chamber	Rhodobacter sphaeroides	Nitrate mineral salts media (NMS) supplemented with 0.1% CH_3OH	141 mW/m^2	[49]
Graphene oxide-polyaniline composite (GO-PANI)	Anode	Double chamber benthic MFC	-	Synthetic wastewater	1.1 mW/m^2	[50]
Graphene oxide (GO)	Anode	Double chamber benthic MFC	-	Synthetic wastewater	0.11 mW/m^2	[50]
Graphene polyaniline combined with titanium sub-oxides (GO-PANI-TS)	Anode	Double chamber	-	-	2073 mW/m^2	[51]
Carbon cloth modified with polyaniline and reduced graphene oxide (CC/rGO-PANI)	Anode	Double chamber	Biofilm with Geobacter predomination	Wastewater	1.9 times higher than CC anode	[52]
Carbon cloth with polydopamine–reduced graphene oxide (CC/rGO-PDA)	Anode	Double chamber	Mixed culture	Acetate solution	2047 mW/m^2	[53]
Carbon cloth reduced graphene oxide (CC/rGO)	Anode	Double chamber	Mixed culture	Acetate solution	1062 mW/m^2	[53]
Three-dimensional graphene nanosheets (3D-GNS)	Cathode	Double chamber	Activated sludge	Acetate solution	2059 ± 3 mW/m^2	[55]
Graphene oxide-supported zinc cobalt oxides	Cathode	Double chamber	Anaerobic digester sludge	Acetate solution	773 mW/m^2	[56]
Sulfonated graphene oxide (SGO) with TiO_2 and Polyaniline (PAni) nanoparticles	Cathode	Single chamber	Prepared inoculum	-	904.18 mW/m^2	[57]
Graphene oxide (GO) with TiO_2 and Polyaniline (PAni) nanoparticles	Cathode	Single chamber	Prepared inoculum	-	734.12 mW/m^2	[57]
Pyrrole (Py) on reduced graphene oxide (rGO) with nickel–nickel oxide (Ni–NiO) nanoparticles (Ni-NiO/PPy-rGO)	Cathode	Single chamber	Mixed bacterial culture	-	679 ± 34 mW/m^2	[58]

Table 1. *Cont.*

Graphene Type	Type of Electrode	MFC Type	Bacteria Type	Substrate Type	MFC Performance	Ref.
Reduced graphene oxide with copper (I) oxide nanoparticles (Cu_2O/rGO)	Cathode	Single chamber	Biofilm with *Geobacter* dominance	-	Output voltage of 0.223 V	[59]

5.3. Graphene Advantages in Terms of Microbial Fuel Cells

Graphene is a next-generation material with excellent physical and chemical properties. Due to these properties, the functioning of microbial fuel cells can be improved in several aspects compared to traditional materials. Anodes based on graphene can increase electron transfer efficiency [53]. They also have a larger specific surface area compared to typical electrodes and promote more active microbe–electrode–electrolyte interaction. When it comes to processes in the cathodic chamber, the oxygen reduction reaction is effectively catalyzed by graphene-based materials due to the clear pathway and increased active sites and conductivity of the material [60]. Of course, there are many challenges, such as synthesis complexity and property degeneration. However, despite them, graphene-based electrodes hold promise in developing microbial fuel cells and other bioelectrochemical systems to achieve sustainable wastewater treatment and bioenergy production.

6. Summary and Conclusions

Graphene derivatives and combining them into nanocomposites with other materials can be successfully used in both the anode and cathode chambers of microbial single- and two-chamber fuel cells. In the case of the anode, it can be observed that graphene and its modifications, as well as combining it with other materials, significantly increases the efficiency of MFCs. Combining graphene with pyrite, polyanilines, or polyacrylamide, or the construction of graphene-based three-dimensional hydrogel electrodes seem very promising for improving power generation. As mentioned earlier, graphene modifications also yield tangible results in the cathode space of microbial fuel cells. The results presented here indicate that nanocomposites based on cobalt and zinc oxide nanoparticles on a graphene oxide-coated support or titanium dioxide and polyaniline anchored on sulfonated graphene oxide can serve as a viable alternative to commercial platinum-based cathode catalysts in microbial fuel cells. Similar conclusions are suggested by using copper (I) oxide nanoparticles in combination with reduced graphene oxide as a highly catalytic active and antibacterial cathode catalyst that could replace commercial catalysts for power generation in MFCs. The efficiency and electroactive stability of a nanocomposite support matrix for the deposition of nickel nanoparticles and nickel oxide and the use of in situ polymerization of pyrrole on reduced graphene oxide as a nanohybrid catalyst in single-chamber microbial fuel cells were also demonstrated. These results are achieved due to the unique properties exhibited by the material graphene. The mobility of charge carriers in the suspension of monolayer graphene is impressively high, as a consequence of which electrons move in graphene at tremendous speed without scattering, which in turn leads to an increase in the efficiency of the entire cell. After analyzing the described studies, further development of material engineering in the field of graphene-based nanocomposites and combining this material with others seem to be most appropriate, as these results encourage the development of microbial fuel cells. Also worthy of attention is research into the very acquisition of the still relatively expensive material graphene and attempts to reduce its price so that it can be used on an industrial scale.

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