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Anode Modification with Reduced Graphene Oxide–Iron Oxide Improves Electricity Generation in Microbial Fuel Cell

Dawid Nosek[1*], Agnieszka Cydzik-Kwiatkowska[1]

[1] Department of Environmental Biotechnology, University of Warmia and Mazury in Olsztyn, ul. Słoneczna 45G, 10-709 Olsztyn, Poland

* Corresponding author's e-mail: dawid.nosek@uwm.edu.pl

ABSTRACT

In recent years, much research has focused on energy recovery from biomass as an alternative to fossil fuel usage. Microbial fuel cells (MFCs), which produce electricity via microbial decomposition of organic matter, are of great interest. The performance of an MFC depends on the electrode material; most often, carbon materials with good electrical conductivity and durability are used. To increase the power output of an MFC, the anode material can be modified to reduce the internal resistance and increase the anode surface area. Therefore, this study determined how modifying a carbon felt anode with reduced graphene oxide (rGO) and a combination of rGO with iron (III) oxide (rGO-Fe) affected electricity generation in an MFC fueled with wastewater. A mixed microbial consortium was used as the anode biocatalyst. The MFC-rGO-Fe produced significantly higher voltages than other cells (average 109.4 ± 75.1 mV in the cycle). Power density curves indicated that modifying the anode with rGO-Fe increased the power of the MFC to 4.5 mW/m^2, 9.3- and 3.9-times higher than that of the control MFC and the MFC-rGO, respectively. Anode modification reduced the internal resistance of the cells from 1029 Ω in the control MFC to 370 and 290 Ω in the MFC-rGO and MFC-rGO-Fe, respectively. These results show that a mixture of rGO with iron (III) oxide positively affects electricity production and can be successfully used for anode modification in the MFCs fueled with wastewater.

Keywords: MFC, reduced graphene oxide, iron(III) oxide, electricity generation, wastewater.

INTRODUCTION

Although fossil fuels continue to be the primary source of energy, clean energy sources, such as wind, solar power, or biomass, are used more and more frequently to meet energy needs while preventing the depletion of natural deposits and reducing environmental pollution. One promising technology for energy recovery is microbial fuel cells (MFCs), in which bacterial chemical energy is converted into electricity [Mohan et al. 2008]. The mechanism of energy production in an MFC is based on the bacterial decomposition of organic compounds at the anode under anaerobic conditions, which is accompanied by the release of protons and the transfer of electrons to the anode. The produced protons pass into the cathode chamber by the membrane separator, whereas the electrons flow through the external circuit to the cathode, and as a result, electricity is generated [Ghasemi et al. 2013].

However, the energy production of these devices remains too low for full-scale implementation, so scientists have begun to take steps toward increasing the efficiency of MFCs. One such method involves modifying the anode by increasing its specific surface area and improving its electrical conductivity. The anode can be modified electrochemically, chemically, thermally, and by using nanocomposites [Nosek et al. 2020]. One promising nanocomposite is graphene (G).

G is a nanomaterial that has a planar structure, is composed of carbon atoms bonded to each other via sp^2-hybridized orbitals, and is characterized by a high mechanical strength, high environmental compatibility, and a large specific surface

[Li et al. 2016]. The electrons in graphene seem to be almost insensitive to disorder and electron-electron interactions and have very long mean free paths. G and graphene oxide (GO) show good electrical, mechanical, and thermal properties due to their specific morphological and structural features, such as the Hall effect, bipolar electric field effect, high thermal conductivity, tunneling effect, high Young's modulus, and high visible light transmittance [Yu et al. 2020].

The properties of GO differ significantly from common metals and semiconductors [Castro Neto et al. 2009]. GO has a very high resistance due to the presence of alkoxy (C-O-C), hydroxyl (-OH), carboxyl (-COOH), carbonyl (C=O), and other oxygen functional groups [Pendolino and Armata 2017]. As GO is a two-dimensional carbon material, it has a single atomic layer, and the size of its sheets is dispersed. Due to a large number of functional groups, the structure of GO is more complex than that of G, and its properties depend on it. Compared to G, GO has lower large-scale production costs and is easier to process [Yu et al. 2020]. High-quality GO is produced in graphite flake dispersions using well-known chemical or electrochemical methods. Due to the fact that most of these methods use strong oxidants (e.g., potassium permanganate), GO has a substantial number of defects in its crystal lattice. Therefore, the conductive properties of GO are much weaker than those of graphene, although its optical and mechanical properties are less affected by these defects [Tarcan et al. 2020]. To overcome the disadvantages of GO, the interest in using reduced graphene oxide (rGO) has been growing. It is produced by chemical, thermal, microwave, photochemical, photothermal, and microbiological methods. Its electrochemical activity is determined by residual functional groups and various types of defects in varying proportions – GO reduction results in materials with typical C/O ratios of 12/1 [Báez et al. 2017].

G and its derivatives have been used as anode surface modifiers in MFC. Pareek et al. [2019] used GO and electrochemically reduced GO (ErGO) to modify carbon cloth anodes (CC). After modification of the anode with ErGO, the power density increased 17.5 and 8.75 times, respectively, in comparison with MFC with unmodified and GO-modified anode. The high open circuit potential in the MFC with ErGO (0.75 V) suggested that the electrogenic activity and rate of reaction at the anode were higher. After modification of the anode in the MFC with ErGO, cyclic voltammetry showed more intense redox peaks, indicating higher catalytic activity and rapid electron transfer. MFC with ErGO removed more COD (72%) than those with the anodes modified with GO (59%) and CC (51%). The high efficiency of ErGO electrodes was due to their large specific surface area and the efficiency of charge transfer.

To further increase the efficiency of MFCs, a combination of metal nanocomposites and rGO can be used for anode modification. An additional advantage of using metals like iron is the fact that they can stimulate the growth of electroactive bacteria such as *Geobacter* sp. [Liu et al. 2018; Zheng et al. 2022]. Ma et al. [2020] tested the mixtures of Fe_3O_4 nanospheres (Fe_3O_4-NS) and rGO at different weight fractions for anode modification. The use of Fe_3O_4-NS/rGO resulted in improved extracellular electron transfer performance and better biocompatibility of the anode surface. The authors showed that the maximum power density obtained with an MFC with Fe_3O_4-NS/rGO-modified anodes was significantly higher than that obtained with unmodified carbon paper anodes or the anodes modified with either Fe_3O_4-NS or rGO. In the study, it was observed that the content of Fe_3O_4-NS in the modifying mixture was important. An MFC with the anode modified with Fe_3O_4-NS/rGO at a ratio of 1.5:1 showed the best electron transfer capacity, a large electroactive region, and low charge transfer resistance. The power density was also highest in this MFC, reaching over 1837.4 mW/m^2. However, these very good results were produced by an MFC inoculated with pure cultures of *Escherichia coli* strains and fueled by a synthetic medium containing optimized carbon sources and 2-hydroxy-1,4-naphthoquinone as an electron mediator.

To the best of the authors' knowledge, there are no studies that have assessed the potential of a mixture of Fe and rGO for anode modification in an MFC fueled with waste materials like wastewater and in which a mixed microbial consortium is used as the anode biocatalyst. Therefore, this study investigated the possibility of using a mixture of rGO and Fe_2O_3 to modify a carbon cloth anode in an MFC via a simple deposition method during the purification of municipal wastewater.

MATERIALS AND METHODS

The dual-chamber MFCs were made of plexiglass. The active volumes of the anode and cathode chambers were 2 L. A Nafion 117 proton-exchange membrane (PEM) (Dupont) with dimensions of 8 cm x 8 cm was used as a separator between the chambers. Cathodes were made of 10 cm x 20 cm x 0.3 cm graphite felt (GF) applied to a stainless wire. Before use, the GF was sonicated in an ultrasonic bath (InterSonic, 15 min) to remove impurities. An MFC with an unmodified anode was used as a control (MFC-control). In the remaining MFCs, rGO and rGO/Fe_2O_3 were deposited on the anodes at doses of 0.2 g rGO (MFC-rGO) and 0.2 g rGO, and 0.05 g Fe_2O_3 (MFC-rGO-Fe). For this purpose, appropriate amounts of Fe_2O_3 (Chempur, Poland) and rGO (Sigma Aldrich) were suspended in 100 mL of distilled water in an ultrasonic bath for 15 min. The anodes were placed in a crystallizer, quenched with an rGO and rGO/Fe_2O_3 slurry (each anode separately), as well as autoclaved (121°C, 1.1 Bar, Classic Prestige Medical 210001). After autoclaving, the electrode was dried at 80°C.

The anode chamber in each MFC was inoculated with 100 mL of fermentation sludge. MFCs were supplied with synthetic municipal wastewater [Coelho et al., 2000], and sodium acetate in the amount of 400 mg COD/L was used as a source of organic carbon. The anode chamber was sealed against air access, and the chamber contents were mixed at a speed of 100 rpm. The cathode chamber was constantly aerated by an air diffuser (20 mL/min). The composition of the catholyte was as follows: 75 mL of phosphate buffer and 3 g of NaCl in 2 L of distilled water; the catholyte was replaced once a week. Initially, the MFCs were left for 5 days for open circuit incubation. After 5 days, the content of the anode chamber was replaced with a fresh portion of wastewater, and the MFCs were operated on an external resistance of 1200 Ω. The operation cycle of the MFC was 48 hours, and after this time, half of the anode chamber volume was replaced. The experiment was conducted for 7 stable cycles.

The polarization and power curves were determined according to Watson and Logan [2011] using a True-RMS multimeter, varying the external resistance of the cell from 75 to 7200 Ω. Voltage changes were recorded every minute using a 6600 Counts PC-LINK data acquisition unit. The current was calculated from the external resistance using Ohm's law. All calculations were performed according to Watson and Logan [2011].

The data were analyzed statistically using Statistica 13.3 (StatSoft). The data from the last 5 cycles of MFC operation were taken for the analysis. One-way analysis of variance (ANOVA) was used, followed by Tukey's HSD test.

RESULTS AND DISCUSSION

Three MFC reactors, with an unmodified GF anode and with anodes modified with rGO and rGO-Fe_2O_3, were tested. In all tested MFCs, the voltage was generated from the first cycle of operation. The highest voltages were obtained immediately after the addition of the substrate, which may have resulted from proton flow through the membrane, but during the first 2–5 hours, the voltages dropped rapidly.

In the MFC-control, the voltages were quite stable from the 10th h (17.7 ± 14.3 mV, Fig 1a). In MFC-rGO, from the 10th h of the measurement, the mean voltage was 29.1 ± 83.6 mV and there was no statistical difference in voltage between MFC-control and MFC-rGO (Fig. 2). The observed voltages were not very stable, due to the reverse voltage recorded during some cycles (Fig. 1b). The voltage reversals could have resulted from the increases in pH during MFC operation or insufficient current generation by the anode consortium [An et al., 2015]. The significantly highest voltages were obtained in MFC-rGO-Fe. In this cell (Fig. 1c) a similar situation can be observed as in the previous reactors – a sharp drop in voltage in the first hours, while an increase in voltage was noticed from about 30th h of the cycle. The average voltage in this MFC was 109.4 ± 75.1 mV. The improvement of parameters in the case of the modified rGO-Fe electrode was related to the role of graphene and iron in the improvement of electron transfer from microorganisms to the anode surface [Sayed et al. 2021]. Despite better electricity generation in MFCs with modified anodes, the efficiency of COD removal was similar in all tested MFCs (Fig. 3).

This study proved that modification of anode with G combined with metal oxides can improve electricity generation in MFCs. The highest power was achieved in MFC-rGO-Fe (4.5 mW/m^2) – it was 9.3 and 3.9 times higher in comparison with the control and the MFC-rGO, respectively (Fig. 4). The higher power obtained in MFC-rGO

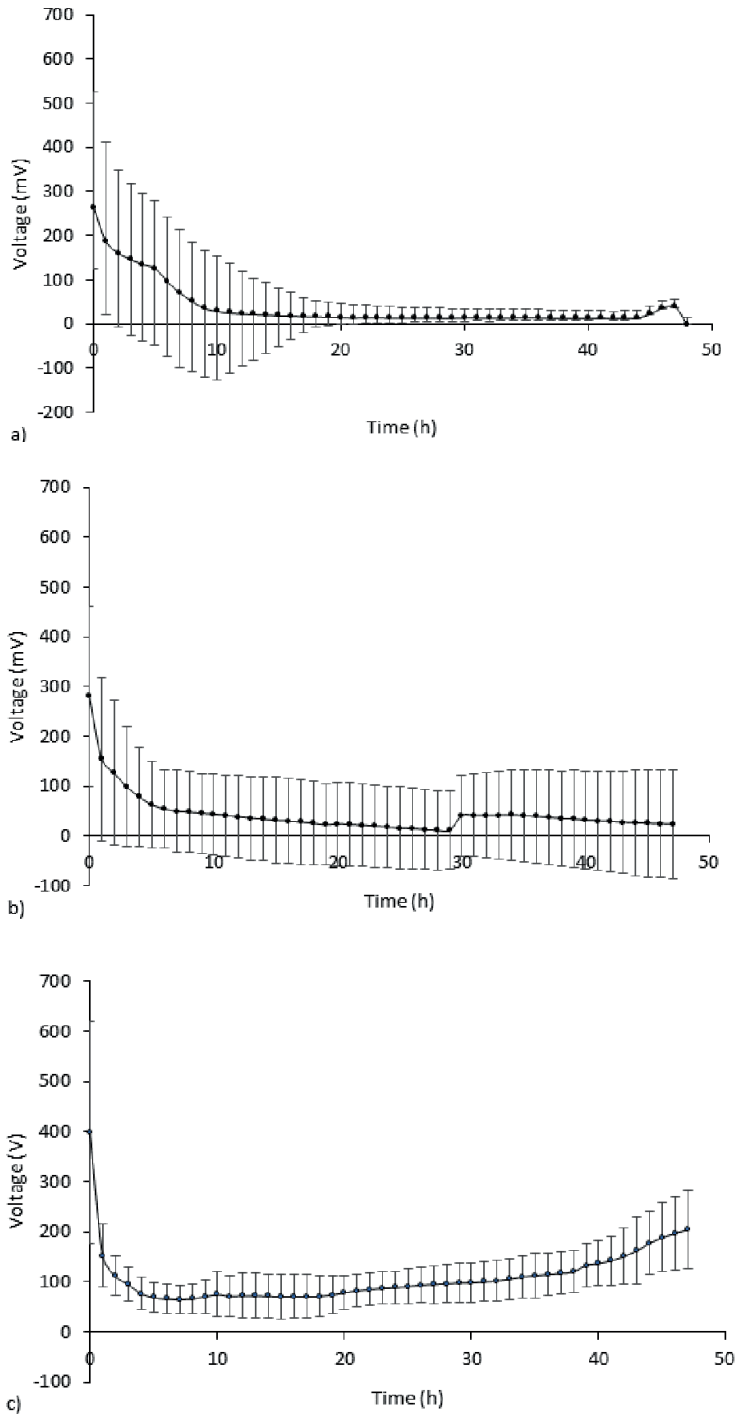

Figure 1. Voltage changes during the operation cycle of the reactors a) MFC-control, b) MFC-rGO, c) MFC-rGO-Fe (n = 7, the error bars mean standard deviation)

and MFC-rGO-Fe was due to the better conductivity of the anode and the larger surface area for the electroactive biofilm due to the presence of graphene and iron. Yaqoob et al. [2021] used oil palm biomass waste-derived graphene derivatives (L-GO) as an anode in the MFC dual-chamber to remove Pb^{2+} from wastewater. The MFC with the L-GO anode produced a power density of $20 \cdot 10^{-3}$ mW/m^2 and a current density of 17.54 mA/m^2 and provided 85% Pb^{2+} removal efficiency. However, the identical anode modified with zinc oxide increased the power density to $1350 \cdot 10^{-3}$ mW/m^2, the current density to 142.98 mA/m^2, and the Pb^{2+} removal efficiency to 91%.

The polarization curves (Fig. 5) show that the MFC-control was characterized by the highest internal resistance (1118 Ω). Modification of the anode with rGO reduced the internal resistance

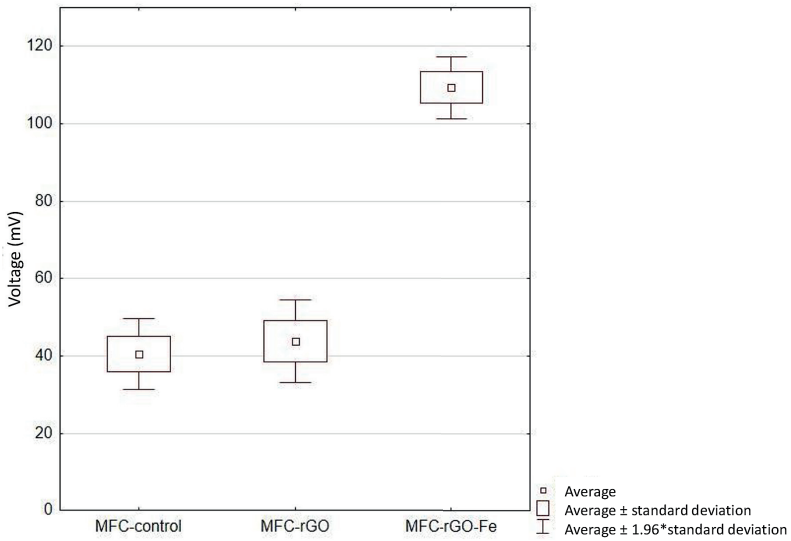

Figure 2. Statistical differences in the voltages obtained in the individual reactors (ANOVA – Tukey's HSD post-hoc test), $p<0.05$

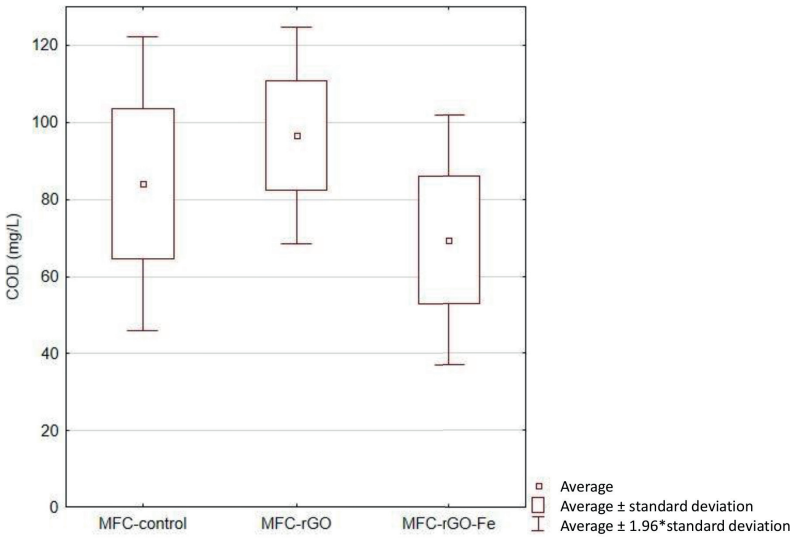

Figure 3. Lack of statistical differences in the COD effluent concentration obtained in the individual reactors (ANOVA – Tukey's HSD post-hoc test), $p<0.05$

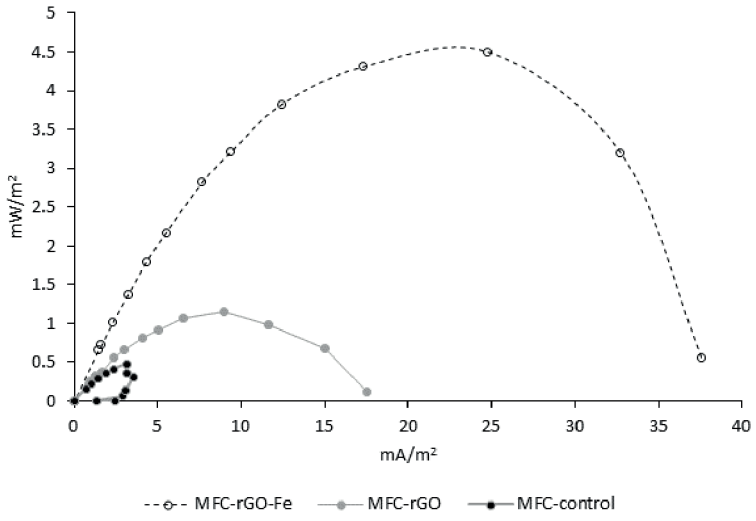

Figure 4. Power curves for all tested MFCs

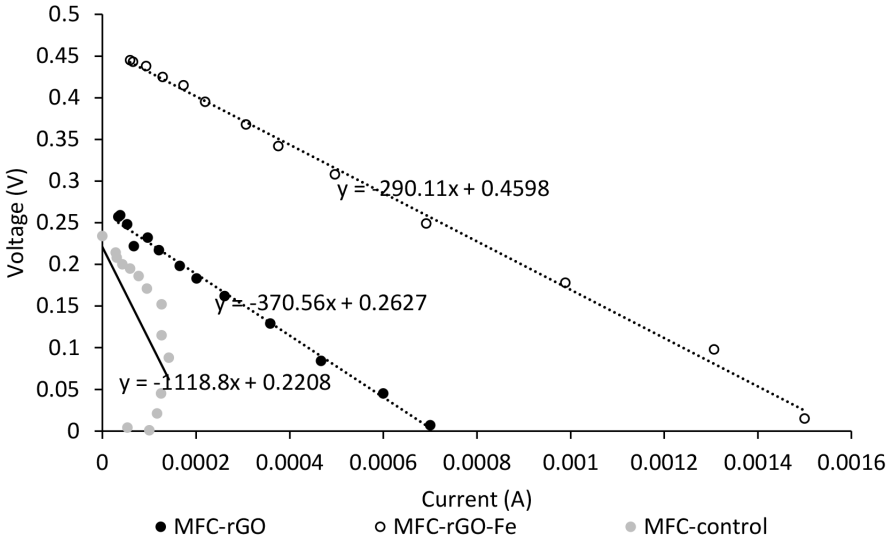

Figure 5. Polarization curves for all tested MFCs

by 66.9%. The best effect was achieved by modifying the anode with both rGO and Fe – the internal resistance was reduced to 290 Ω (by about 74.1% in comparison with the MFC-control). The lower internal resistance of the rGO cell could be related to a decrease in the mass transfer resistance, due to the high conductivity of rGO, an increase in the specific surface area, as well as the possibility of using the graphene layer as nanowires for the extracellular electron transfer [Huang et al. 2011; Abdelkareem et al. 2018]. Additionally, Fe compounds can act as electron mediators, accelerating the transfer of electrons. For example, zero-valent iron, through its strong reducibility on the anode, induced anaerobic conditions, leading to the non-use of electrons for other processes and creating a strong electrochemical activity of the biofilm [Yu et al. 2019]. In a study of Gana Kumar et al. [2014], the use of the carbon cloth (CC) anode modified with rGO-SnO_2 reduced the electron transfer resistance between the electrode and the electrolyte which resulted in a faster electrochemical reaction in comparison with MFCs with the CC and rGO-CC anodes. It was also observed that SnO_2 has a positive effect on the rate of charge transfer compared to the graphene sheets alone.

CONCLUSIONS

The presented study shows that the composite electrodes based on rGO and metal oxides have a great potential to increase the power of MFC. Modification of the anode with rGO in combination with iron improves the stability of the generated voltage and increases the anode conductivity as well as the power obtained by the cell. The highest power was obtained for the MFC-rGO-Fe, which was 9.3- and 3.9-times higher than that of the control and the MFC-rGO, respectively. Additionally, the lower internal resistance of the cell in MFC-rGO-Fe was observed, by about 74% than MFC-control. Modification of the anode with rGO and iron did not affect organics removal from wastewater.

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