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Original Research Article

BIOELECTRICITY GENERATION IN A MICROBIAL FUEL CELL USING NON-PRECIOUS METAL CATHODES

Paweł P. WŁODARCZYK *, BARBARA WŁODARCZYK
Institute of Environmental Engineering and Biotechnology, University of Opole, Opole, Poland

A b s t r a c t

The development of microbial fuel cell (MFC) technologies represents a key direction in improving wastewater treatment methods. This approach allows for simultaneous wastewater pre-treatment and energy recovery in the form of bioelectricity. However, one of the primary obstacles to the broader application of MFCs is their limited electricity output. As a result, increasing the efficiency of this process remains a central research objective. In this study, a carbon-based electrode (carbon felt, CF) was used as the anode in MFCs. For the cathode, copper mesh modified with various non-precious metal catalysts (CF, stainless steel, Cu-B, Ni-Co) was employed. The experiments were conducted in glass MFC reactors, with sintered glass serving as the chamber separator. Several electrode configurations were tested: CF/CF, CF/SS, CF/Ni-Co, and CF/Cu-B. Experiments were conducted using a glass reactor (glass MFC) equipped with carbon-based electrodes. To reduce costs, a foamed glass membrane was used as the separator. Bioelectricity generation was observed in all tested configurations. Among them, the CF/Ni-Co system demonstrated the best overall performance, providing faster start-up, higher power density.

Keywords: bioelectricity, microbial fuel cell, cathode, non-precious metals, by-product

1. INTRODUCTION

Wastewater is predominantly treated in centralized treatment facilities, a process that entails considerable operational and disposal costs [1–3]. Consequently, researchers are continuously seeking new strategies not only to improve treatment efficiency but also to repurpose wastewater as a valuable resource [4–8]. Since wastewater contains substantial amounts of stored energy, particularly in the form of organic compounds, it represents an underutilized energy source. In fact, it has been estimated that the energy embedded in wastewater is nearly nine times greater than the amount required for its treatment [9]. Given the vast quantities of municipal and industrial wastewater generated annually, technologies that enable energy recovery from these streams are becoming increasingly essential [10–

* Institute of Environmental Engineering and Biotechnology, University of Opole, ul. Kard. B. Kominka 6a, 45-032 Opole, Poland, pawel.wlodarczyk@uni.opole.pl, +48 77 401 60 48

12]. Even partial recovery of this energy could contribute meaningfully to global energy sustainability [9–13].

The urgent challenge is to develop new energy platforms that can produce sufficient power while mitigating the environmental burdens of energy generation. Achieving carbon neutrality by 2050, while still meeting growing energy demands, requires not only a transformation of energy infrastructure but also a shift in consumption patterns [14–16]. Greater reliance on electricity during periods of surplus and reduced use during shortages will be indispensable. This means that it will generally be necessary to change the people lifestyle [9]. To address future needs, every feasible energy source must be exploited, with a particular focus on renewable options. Within this context, wastewater emerges as a promising renewable-like resource.

Microbial fuel cells (MFCs) are one of the most promising technologies for harnessing energy from wastewater [9,17–19]. These bioelectrochemical systems simultaneously generate electricity and treat wastewater (or contaminated water) by oxidizing substrates via anodic biofilms [20]. Microorganisms commonly forming such biofilms include bacteria, as well as fungi [21–25]. However, the microbial communities in the anodic chamber are far more diverse than currently characterized, and many of their functional roles remain to be clarified. Sources of microorganisms for MFCs typically include soil, sediments, activated sludge from wastewater treatment plants, or inocula from previously operated MFCs [26–33]. In these systems, the anodic biofilm acts as the anode catalyst, with its performance determined by microbial metabolic activity. Because microbial metabolism is inherently slow, both electricity production and wastewater purification rates are limited. Nonetheless, these microorganisms are indispensable for converting organic substrates present in wastewater. For this reason, anodes are fabricated from biocompatible materials such as carbon, carbon felt, or carbon fibers [9,18,33]. In contrast, cathodes can be constructed from non-biocompatible materials, since their catalytic activity does not depend on microorganisms [34–36]. When purely chemical reactions occur at the cathode, the oxygen reduction reaction proceeds more efficiently than in biologically mediated systems. Cathodes can therefore be made from a wide range of materials, including carbon-based substrates, metallic electrodes, or metals coated with catalytic layers.

Platinum is considered the most effective cathodic catalyst [37] but is prohibitively expensive, driving the search for alternative, non-noble metal catalysts [36,38–42]. Nickel, for instance, offers promising catalytic properties, yet pure forms such as Raney Ni present handling challenges. Raney Ni should not be exposed to air due to its instability; even post-preparation it retains residual hydrogen, making it susceptible to spontaneous ignition upon contact with oxygen [43]. Consequently, alloy-based electrodes are preferred, as they offer greater safety and cost advantages.

In the present study, several non-noble metal cathodes - including carbon felt (CF), stainless steel (SS), Cu-B alloy, and Ni-Co alloy - were evaluated in MFCs equipped with CF anodes. The investigation focused on both bioelectricity generation (mainly cell voltage) and the reduction of chemical oxygen demand (COD).

2. MATERIALS AND METHODS

A glass MFC with a foamed glass membrane was employed to reduce construction costs. The system comprised two vertically arranged chambers, with the anode at the bottom and the cathode above. This configuration limited oxygen diffusion into the anode. Although the foamed glass membrane did not provide complete chamber separation, the vertical arrangement minimized oxygen transfer to the anode. A schematic and photograph of the MFC are shown in Figure 1.

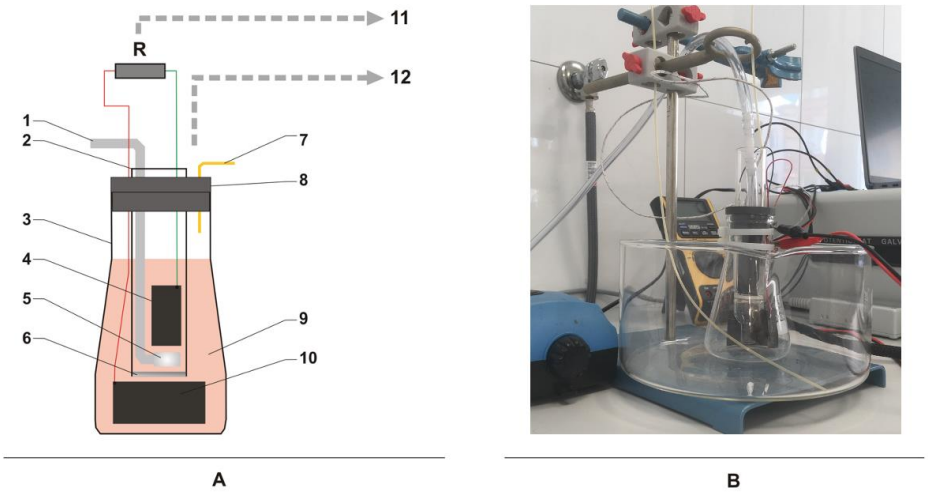

Fig. 1. Scheme (A) and view (B) of microbial fuel cell used in experiment: 1 – air inflow; 2 – cathode chamber; 3 – anode chamber; 4 – cathode; 5 – stone air bubbler; 6 – foamed glass; 7 – CO_2 outflow; 8 – 3D printed sealing plug; 9 – molasses decoction (MD); 10 – anode; 11 – electrical measurements; 15 – COD measurements

The anode chamber was sealed with a plug (8 in Figure 1). Carbon dioxide generated during operation was vented through an outflow pipe (7 in Figure 1) into a water trap to ensure gas collection and system tightness. The cathode was continuously oxygenated (5 $L \cdot h^{-1}$) using a stone air bubbler (5 in Figure 1) [36]. The MFC circuit was connected to a 100 Ω resistor (R in Figure 1) [44–47]. The inoculum originated from a previously operating MFC.

Carbon felt (CF) was employed as the anode material, while several cathode materials were tested: carbon felt (CF), stainless steel (SS), and copper mesh electrodes modified with Cu–B and Ni–Co catalysts (4 in Figure 1). CF and SS were obtained as commercial products, whereas the catalyst-coated electrodes were prepared by electrochemical deposition on copper mesh. The SS cathode was in the form of a mesh fabricated from AISI 304 alloy. The parameters of the CF and SS electrodes are summarized in the Appendix (Table 1). The Cu–B alloy was deposited from an electrolyte primarily composed of $NaBH_4$ and $CuSO_4$ [42,48–52], and the Ni–Co alloy from an electrolyte containing mainly $NiSO_4$ and $CoSO_4$ [49,53–56]. The mixtures for catalysts deposition were summarized in Appendix (Table 2). The measurements were performed in the MFC using the four electrode systems investigated in this study (CF/CF, CF/SS, CF/Cu-B, and CF/Ni-Co). The CF/CF system served as the reference for evaluating metal electrodes that did not contain precious metals.

The cathode undergoes continuous oxidation during MFC operation, which makes pre-oxidation necessary to prevent changes in its catalytic properties. Because, under MFC cathode operating conditions, the cathode is continuously exposed to dissolved oxygen. Without pre-oxidation, progressive oxidation during operation could change the surface properties of the catalyst and reduce the repeatability of the measurements. Therefore, pre-oxidation was used to obtain a more stable and predictable catalytic surface before electrochemical testing. This approach was intended to minimize changes in cathode properties during MFC operation and improve comparability between the tested cathode materials. For the measurements, the cathodes were pre-oxidized at 673 K for 6 h in a laboratory furnace [42,53]. A by-product, orange pomace juice (OPJ), was used as the substrate in the anode chamber to feed the microorganisms. The OPJ was obtained from orange pomace remaining after juice production. The pomace was homogenized using a blender and subsequently filtered to obtain a clear

OPJ free of solid particles. Due to the high concentration of components, the OPJ was diluted at a ratio of 1:5 prior to use [58].

During the measurements, the cell voltage (both at start-up and during MFC operation), polarization curves, power density curves. First, the MFC start-up process was conducted and repeated several times until a stable voltage was reached. This period corresponded to the formation of a stable biofilm on the anode, which ensured consistent cell performance. Only after stable anode operation had been established was it possible to compare the effects of different cathode materials, specifically those not containing precious metals. Diluted OPJ was periodically supplied to the anode chamber when a significant drop in cell voltage was observed, which clearly indicated the depletion of nutrients available to microorganisms in the current batch of input (diluted OPJ).

Polarization and power density curves were recorded after completion of the MFC start-up stage, when a stable anodic biofilm had been formed and repeatable cell voltage values were obtained. The measurements were therefore performed during stable MFC operation, in a representative feeding cycle after substrate addition and voltage stabilization.

Electrodeposition was performed using a regulated power supply (PowerLab 305D-II, China). The sealing plug was fabricated with an M200 3D printer equipped with Z-Suite software (Zortrax S.A., Olsztyn, Poland). Electrode oxidation was conducted in an LAC LH06/12 furnace (LAC s.r.o., Židlochovice, Czech Republic). pH and conductivity were measured with a HI 5522 meter (HANNA Instruments, Woonsocket, RI, USA). Molasses decoction (MD) was mixed in an external tank using a CAT R17 mechanical stirrer (Ingenieurbüro CAT M. Zipperer GmbH, Staufen, Germany). Electrical measurements of the MFC were carried out with a PGSTAT302N potentiostat (Metrohm-Autolab BV, Utrecht, Holland) and a Fluke 8840A multimeter (Fluke Corporation, Everett, WA, USA). Temperature was monitored with a UNI-T UT33C multimeter (UNI-Technology, Hong Kong). The equipment and instruments used in the study were summarized in Appendix (Table 3).

3. RESULTS AND DISCUSSION

In the first step, the MFC start-up process was analyzed. The procedures were carried out for the four electrode systems examined in this study (CF/CF, CF/SS, CF/Cu-B, and CF/Ni-Co). Voltage values were measured during MFC operation, with diluted OPJ periodically supplied to the anode chamber. Figure 2 shows the cell voltage profiles obtained during successive start-up cycles.

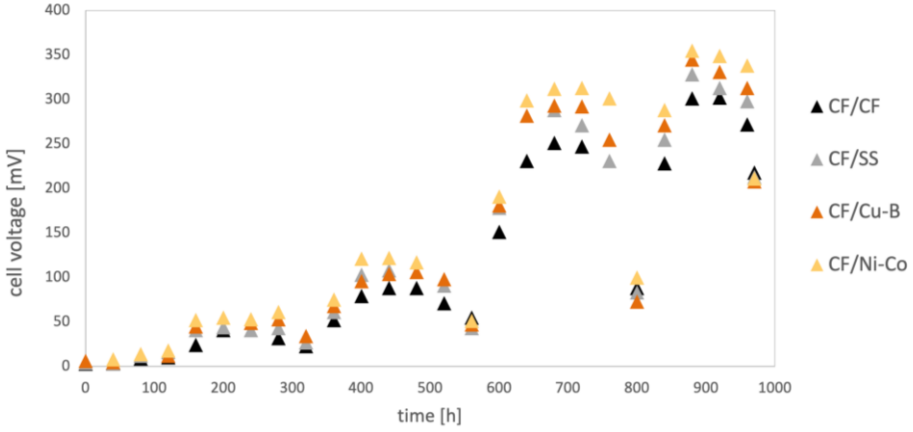

Fig. 2. Cell voltage profiles recorded during MFC start-up
for the four electrode systems: CF/CF, CF/SS, CF/Cu-B, and CF/Ni-Co

First, the MFC start-up process was carried out. These procedures were repeated several times until a stable voltage was obtained. This period corresponds to the formation of a stable anode biofilm, enabling reliable MFC operation. Assuming the anode is operating stably, we can proceed to the next step: a comparison of cathode materials without precious metals. Before each start-up cycle, the diluted OPJ solution in the anode chamber was replaced. According to the obtained data (Figure 2), all analyzed electrode systems (CF/CF, CF/SS, CF/Cu-B, and CF/Ni-Co) successfully initiated MFC operation, as evidenced by the measurable cell voltage. During the first start-up, the cell voltage for all electrode systems remained negligible for approximately 100 hours. After this period, it began to increase, reaching values in the range of 35–52 mV, depending on the electrode system. In the second start-up, the voltage increased further to 96–122 mV, with the highest value observed for the CF/Ni-Co electrode system. After the third start-up, the voltage reached 311–355 mV for all electrode systems, again with the CF/Ni-Co system showing the best performance. Subsequent start-ups did not result in any further voltage increase. After the start-up process, when the cell voltage stabilized, the CF/Ni-Co electrode system achieved a 14% higher cell voltage compared to the CF/CF system, 7% higher than the CF/SS system, and 3% higher than the CF/Cu-B system. Overall, the relatively low voltages obtained can be attributed primarily to the MFC design, which employed a foamed glass membrane to reduce costs. Nevertheless, despite these low values, the data provide a basis for assessing how the electrode material influences cell voltage in the systems analyzed in this study.

The performance of the MFCs, expressed as cell voltage, was evaluated for the four electrode systems (CF/CF, CF/SS, CF/Cu-B, and CF/Ni-Co) during a single cycle and across six successive cycles with diluted OPJ feeding. The results are presented in Figure 3.

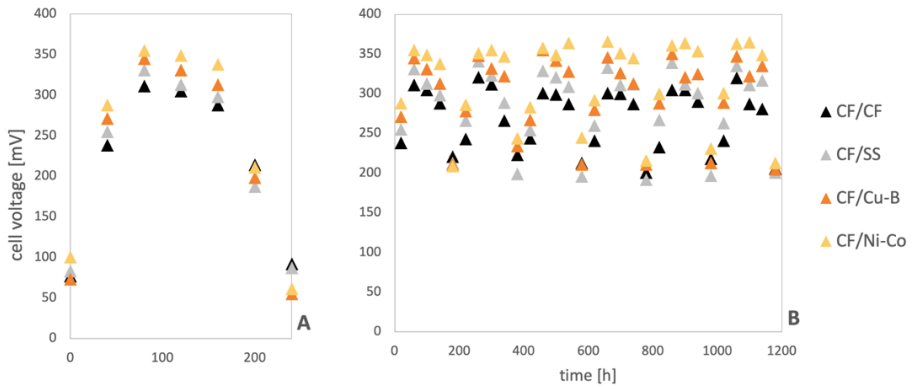

Fig. 3. Cell voltage of MFCs with CF/CF, CF/SS, CF/Cu-B, and CF/Ni-Co electrode systems during one (A) and six (B) feeding cycles with diluted OPJ

The analysis of cell voltage after biofilm stabilization (Figure 3A) showed that, within a single cycle, the CF/CF electrode system exhibited the lowest activity, while the CF/Ni-Co system achieved the highest performance. Subsequently, the effect of cyclic addition of diluted OPJ was examined. During cyclic MFC operation, the cell voltage declined by 80–90% over approximately 260 h, depending on the electrode type, reflecting substrate utilization by the microorganisms. To maintain voltage stability, fresh diluted OPJ was supplied whenever the voltage dropped by 60%. Consequently, in the feeding cycle experiments (Figure 3B), the biofilm was replenished roughly every 200 h, with the interval dependent on the electrode system. The voltage fluctuations observed in MFC performance resulted from the cyclic feeding strategy applied in this study. For practical applications, however, continuous substrate supply (such as by constant circulation) would be required.

A trend comparable to that observed in the single cycle was also noted across six consecutive cycles (Figure 3B). The CF/CF electrode system again exhibited the lowest maximum cell voltage (~310 mV), whereas the CF/Ni-Co system achieved the highest (~365 mV). With cyclic addition of diluted OPJ, the CF/Ni-Co electrode system demonstrated a 18% increase in cell voltage.

In summary, after six cycles the CF/Ni-Co electrode system achieved an 18% higher cell voltage compared to the CF/CF system, the CF/Cu-B system showed a 15% increase, and the CF/SS system a 9% increase relative to the CF/CF system. This indicates that, under the applied conditions, the cathodic process was improved most effectively by the Ni-Co catalytic layer, most likely due to its higher activity toward oxygen reduction and lower cathodic polarization.

Subsequently, polarization and power density characteristics were evaluated for the electrode systems CF/CF, CF/SS, CF/Cu-B, and CF/Ni-Co. The corresponding curves are presented in Figure 4 (A – power density, B – polarization).

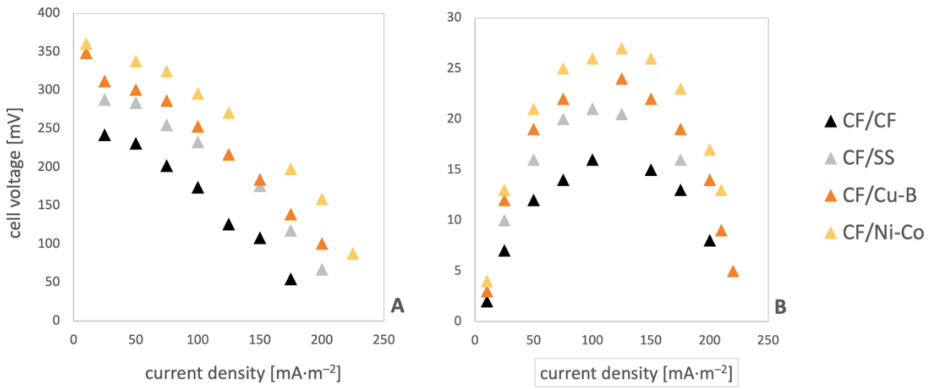

Fig. 4. Polarization (A) and power density (B) curves for CF/CF, CF/SS, CF/Cu-B, and CF/Ni-Co electrode systems

Independent of the electrode system applied (CF/CF, CF/SS, CF/Cu-B, and CF/Ni-Co), the MFC functioned properly and generated bioelectricity. The highest power density (27 $mW \cdot m^{-2}$) was obtained with the CF/Ni-Co system, while the lowest (16 $mW \cdot m^{-2}$) was recorded for the CF/CF system. The CF/SS and CF/Cu-B systems yielded intermediate values of 21 $mW \cdot m^{-2}$ and 24 $mW \cdot m^{-2}$, respectively. Importantly, the CF/Ni-Co system consistently maintained the highest power density across the entire range of current densities, whereas the CF/CF system showed the lowest values throughout the measurements.

The superior performance of the CF/Ni-Co system can be attributed to the higher catalytic activity of the Ni-Co alloy toward the cathodic oxygen reduction process under the tested MFC conditions. The Ni-Co cathode probably reduced cathodic activation losses more effectively than the reference CF, SS, and Cu-B cathodes, which resulted in higher cell voltage and higher current density. In addition, the alloy-type catalytic layer may provide more favorable electrochemical properties and a more stable active surface after pre-oxidation.

4. CONCLUSIONS

In this work, the feasibility of using cathodes without precious metals (SS, Cu-B, and Ni-Co) was evaluated. The Cu-B and Ni-Co cathodes were prepared by electrochemical deposition on a copper mesh, while the SS electrode was purchased as a finished product. The CF cathode served as the

reference. Among the tested systems, the CF/Ni-Co electrode consistently exhibited the best performance in terms of both cell voltage and power density. Across six feeding cycles with diluted OPJ, the CF/Ni-Co system achieved an 18% increase in cell voltage and over a 60% increase in power compared with the CF/CF reference. It should be emphasized, however, that these results were obtained during short-term MFC operation. Therefore, additional analyses, including long-term electrode stability tests, are required.

The development of low-cost electrode materials that combine durability with high bioelectrocatalytic activity remains crucial for the broader implementation of MFC technology. This study demonstrates that electrodes not containing precious metals, such as Ni-Co, can be effectively applied as MFC cathodes. It should be noted that the measurements refer to MFC fed with OPJ. The findings support the adopted research approach and highlight the potential for further investigations aimed at developing cost-effective electrodes for large-scale MFC applications.

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APPENDIX

Table 1. Parameters of the electrode materials used in the study: CF (carbon felt) and SS (stainless steel)

Electrode	Parameters	Manufacturer
CF	100 % carbon fiber 99% carbon content density 0.12-0.14 g·cm^{-3}	Ningbo VET Energy Technology Co., Ltd China
SS	18% chromium 8% nickel 0.08% carbon	Pracownia Metaloplastyczna, Wołomin, Poland

Table 2. Composition of the solutions applied for Cu–B and Ni–Co catalyst deposition

Alloy	Component	Volume [mol·L^{-1}]
Cu-B	NaOH	1.00
	Trilon B	0.12
	$CuSO_4 \cdot 7H_2O$	0.05
	$NaBH_4$	0.02
Ni-Co	H_3BO_3	1.03
	$NiSO_4$ x $7H_2O$	0.92
	NaCl	0.25
	$CoSO_4$ x $7H_2O$	0.07

Table 3. Equipment and instruments used in the study

Model	Manufacturer
PowerLab 305D-II	(N/A), China
M200 3D printer with Z-Suite software	Zortrax S.A., Olsztyn, Poland
LAC LH06/12 furnace	LAC s.r.o., Židlochovice, Czech Republic
HI 5522 meter	HANNA Instruments, Woonsocket, RI, USA
CAT R17 mechanical stirrer	Ingenieurbüro CAT M. Zipperer GmbH, Staufen, Germany
PGSTAT302N potentiostat	Metrohm-Autolab BV, Utrecht, Holland
Fluke 8840A multimeter	Fluke Corporation, Everett, WA, USA
UNI-T UT33C multimeter	UNI-Technology, Hong Kong

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