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Enhanced performance of microbial fuel cells using electrochemically treated carbon felt anode

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ABSTRACT

The microbial fuel cell (MFC) technology is emerging as an effective technology for wastewater treatment to remove and detect many pollutants and simultaneously generate power. The anode is an essential component for bacterial attachment and extracellular electron transfer (EET). Thus, anode performance is critical for improving an MFC system's overall performance. Materials that are electronically conductive and provide favorable conditions for creating biofilm are good candidates for the anode. Carbon paper and carbon felt are the most used anode materials. However, the characteristics of these materials can be modified to increase their performance. This paper presents a modification of the conventional carbon anode by electrolyzing the carbon felt in a phosphate buffer and an experimental evaluation of the impact of the treatment. The tests were performed using an air cathode MFC, electrogenic bacteria Shewanella Baltica 20 fed on lactose-rich L-B. The treatment with phosphate buffer generates functional groups on the surface of the carbon felt, which establishes robust biofilm on the anode and offers lower charge-transfer resistance compared to the untreated carbon felt. This facilitates electron transfer from exoelectrogens to the anode, increasing the current density and power density output. Three times higher power density was observed in the cell with a modified anode than in an untreated carbon-felt anode.

1. Introduction

Microbial fuel cells (MFCs) have emerged as promising technologies that harness the metabolic activity of exoelectrogens to convert chemical energy into electrical energy. In MFCs, the anode, cathode, and membrane are the fundamental components, with the anode chamber playing a critical role in the biochemical reaction. The performance of MFCs relies on the efficient formation of a biofilm on the anode surface, which influences the rate and kinetics of the reaction. While previous research focused on expanding the anode surface area to accommodate more biofilm, scaling up MFC systems requires addressing additional considerations [1].

One of the rate-limiting steps in MFCs is the mechanism through which bacteria transfer electrons to the electrode. The anaerobic environment in the anodic chamber promotes microbial growth and biofilm formation on the anode's surface [2,3]. Anode conductivity is also crucial for facilitating effective electron transport. While certain metals or alloys exhibit excellent electrochemical activity, they may not be conducive to optimal microbiological activity. Expensive materials like platinum and titanium have demonstrated long-term electron transport capabilities but pose cost challenges, necessitating research into alternative, cost-effective materials [4].

The search for suitable anode materials that are inexpensive, biocompatible, and electrically conductive remains an ongoing challenge. Although commercially available graphene oxides have shown effectiveness, their high cost hinders practical implementation. Natural carbon-based materials offer a more economically viable option, potentially reducing power costs in MFCs. However, there is limited knowledge of converting waste into carbonized anode materials, and concerns regarding stability, compatibility, and scalability persist [5,6].

Given these challenges, electrochemical oxidation emerges as an eco-friendly, cost-effective, and straightforward technique for modifying carbon-based anodes [6–10]. This approach aims to increase the anode's surface area and change its surface chemistry, facilitating biofilm adherence. Electrochemically treated anodes exhibit remarkable stability, as the treatment alters the anode surface by creating functional groups. These modified anodes do not experience film detachment during MFC operation, making them suitable for long-term and large-

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scale MFC applications.

In this study, we propose a simple, rapid, and cost-effective electrochemical approach for modifying carbon felt anodes at ambient temperature. Our modification is the optimized modification of a previously reported method [7,8]. We electrochemically treated carbon felt in phosphate buffer to enhance its performance as an MFC anode. Additionally, we investigated the internal resistance of the modified and unmodified anodes, as reducing internal resistance is crucial for improving power generation in MFCs [11,12].

To summarize, the objectives of this study are to (i) investigate the performance of electrochemically modified carbon felt as an MFC anode, (ii) evaluate the anode's ohmic resistance using electrochemical impedance spectroscopy (EIS), and (iii) assess the internal resistance through linear sweep voltammetry and varying circuit resistance (VCR) analysis. By addressing these aspects, we aim to contribute to the understanding and advancement of MFC technology for sustainable energy generation and wastewater treatment applications.

2. Materials and method

A small-scale air cathode MFC design was used to conduct experiments with the electrochemically active microorganism *Shewanella baltica 20*. The following sections describe the various components of MFC, microbial growth conditions, and experimental procedures for evaluating the performance of the MFC.

2.1. MFC assembly

An experimental MFC was manufactured using Plexiglas. The anode and cathode chambers were both of size 30 mm × 40 mm × 7.5 mm, resulting in a working volume of 9 mL. The anode chamber was designed with inlet and outlet ports to allow wastewater to flow in and out. Carbon felt with a dimension of 40 mm × 50 mm × 0.2 mm was chosen as the electrode material for both the anode and cathode. A proton exchange membrane (PEM; NAFION 117, Sigma-Aldrich) was used to separate the two compartments. 1 mm rubber gaskets were used on both the anode and cathode sides to prevent leakage. When the microbial fuel cell was not in use, the anode and cathode compartments were filled with deionized water to maintain membrane conductivity.

2.2. Bacterial culture condition

Shewanella baltica 20, an exoelectrogen gram-negative bacteria strain provided by the medical microbiology and immunology department at the University of Pécs in Hungary, was used in the experiments. *Shewanella baltica 20* demonstrated effective biofilm growth in our preliminary experiments on carbon felt and carbon cloths.

2.3. Experimental procedure

A facultative anaerobe named *Shewanella baltica 20* was cultured in Luria Bertani (LB) media at 25 °C for 48 h. Then, cultured microbes with an optical density of 0.3 (at 600 nm) were added to lactate-rich LB media and fed to the microbial fuel cell to enrich the microbial population in the anode chamber and promote biofilm growth on the anode surface.

The two electrodes were linked to a Picolog voltage data recorder to log the voltage output data on a computer. The open-circuit voltage was monitored for seven days before the MFC produced a stable voltage output. After attaining a stable open-circuit voltage, the MFC was continually fed with lactate-containing LB media without bacterial strain. Resistance was connected between the anode and the cathode to obtain the power output. Experiments were repeated with various lactate concentrations in the LB media, and the current output was noted.

Similarly, the MFC was operated using synthetic wastewater simulating dairy wastewater of the following compositions.

a) NH_4Cl, 40 mg/L; $MgCl_2$, 10 mg/L; $CuSO_4$, 0.1 mg/L; $CaCl_2$, 5 mg/L; $MnSO_4$, 0.1 mg/L; $ZnCl_2$, 0.1 mg/L; and phosphate buffer L.
b) NH_4Cl, 40 mg/L; $MgCl_2$, 10 mg/L; $CuSO_4$, 0.1 mg/L; $CaCl_2$, 5 mg/L; $MnSO_4$, 0.1 mg/L; and $ZnCl_2$, 0.1 mg/L. The lactate concentrations were also adjusted.

The flow rate of both the synthetic wastewaters and LB medium was 0.1 mL/min. At each change in lactate content, samples were taken from the anode chamber's outlet to determine the MFC's ability to remove chemical oxygen demand (COD) and consume lactate.

2.4. Modification of anode

For electrochemical modification, carbon felt electrodes were first soaked in acetone for 24 hours to remove organic impurities, then soaked in distilled water for 24 hours, and then rinsed thrice with distilled water. After rinsing, carbon felt was left in the oven at 50°C to dry. After drying, the electrode (working electrode) was immersed in phosphate buffer solutions (0.1 M, pH = 7.2). Another carbon felt was immersed in the same solution as a counter electrode. Then, a constant current of 20 mA was applied to the electrode for 3 h using chronopotentiometry techniques [7,8]. After this treatment, the working electrode was transferred to the oven to dry.

2.5. Electrochemical measurements

The microbial growth of *Shewanella baltica 20's* was characterized by measuring the biomass concentrations at 600 nm with a spectrophotometer. The colony count was multiplied by the dilution multiple to determine the obtained viable microbial population in CFU/mL. The D-Lactate Assay kit from Megazyme was used to measure the lactate concentrations quickly. The (COD) of influent and effluent streams of the anode chamber of the MFC was measured using a DR3900 Laboratory spectrophotometer.

The collected samples underwent filtration using a 45-μm filter before conducting COD testing. To mitigate the risk of contamination, the specimens were procured using sterile and non-reactive receptacles and transported to the laboratory following proper labeling and sealing procedures. Conventional sulfuric acid injections effectively decreased the pH and maintained the chemical oxygen demand (COD) level in wastewater until the analysis time. To maintain the composition of wastewater, measures were taken.

Samples were held at low temperatures, namely refrigerated or frozen, depending on the duration required for the study. The materials utilized in the study were accurately prepared in accordance with the approved methodology and afterward analyzed using the Hach Lange DR3800 spectrophotometer. The preparation process may have encompassed dilution and digestion using suitable reagents, as outlined in the procedure for COD determination. The accuracy and reliability of COD measurements were ensured by meticulous handling and preparation techniques.

The high-resolution data recorder PicoLog was used to record the online voltage and current. The polarization curve was created by applying external Resistance ranging from 5 KΩ to 100 Ω after getting a steady current for each variation in COD in synthetic wastewater. The output currents were computed, the output voltages were measured using Ohm's law, and the polarization curves were acquired. The electrochemical investigations included linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and classical varying circuit resistance (VCR) methods. LSV and EIS were performed with a PalmSens4 potentiostat (Utrecht, Netherlands). The LSV was carried out for the whole cell in the two-electrode configuration, with the anode as the working electrode and the cathode as the counter and reference electrode [11]. This configuration allows for the identification of the total internal resistances that are required for operation optimization. The MFC was initially disconnected from the external Resistance until

the potential was stabilized. Subsequently, the current response resulting from the potential scanning was recorded at a scan rate of 0.1 mV s^{-1} starting from open circuit voltage (OCV). This scan rate was chosen to compare with the results of the VCR method.

Similar to LSV, a VCR, the MFC was disconnected from the external electrical Resistance (R_{load}) and then gradually increased the external load from 10 Ω to 220 KΩ (stabilization time between each change was 6–10 min), and the cell voltage was recorded at the load resistance.

Electrochemical impedance spectroscopy (EIS) was performed separately on the anode, cathode, and whole cell. The AC amplitude was kept at 10 mV, the frequency varied from 100 kHz to 5 mHz with 5 steps per decade, and the external Resistance of 1000 Ω was applied. Two electrode experiments were performed on the whole cell with the anode as the working electrode and the cathode as the counter and reference electrode.

3. Results and discussion

3.1. Optimization of anode modification

Fig. 1 shows the cyclic voltammograms of the anode without biofilm. Although no pronounced oxidation/reduction peaks appeared, higher redox currents indicate better surface modification upon electrolysis of carbon felt. This shows that the modified anodes displayed much better electron transfer properties than the unmodified ones. This substantial alteration in electrochemical properties may contribute to the performance improvement of the MFCs. Therefore, carbon felt (anode) was electrolyzed at 20 mA for different durations to achieve the highest current for the observed redox peak. As can be seen in Fig. 1, the current is increasing up to two hours, but after two hours, the current intensity remains the same. Two hours of electrolysis was chosen as an optimum time to modify the anode.

3.2. MFC performance

Experiments were conducted with artificial wastewater having COD of 2000 mg/L, 3500 mg/L, and 5000 mg/L using MFC with untreated and treated anode. In this present study, simulated wastewater resembling dairy effluent was employed, with particular emphasis on measuring chemical oxygen demand (COD) levels. The Chemical Oxygen Demand (COD) of dairy effluent in practical scenarios exhibits a wide range, spanning from 100 to 50,000 mg/L [12], which depends upon the effluent's composition and the procedures employed for its treatment. Dairy effluent frequently contains proteins and lipids. The performance of both MFC types in terms of output voltage and power generation is shown in Fig. 2, Fig. 3, and Fig. 4.Fig. 5..

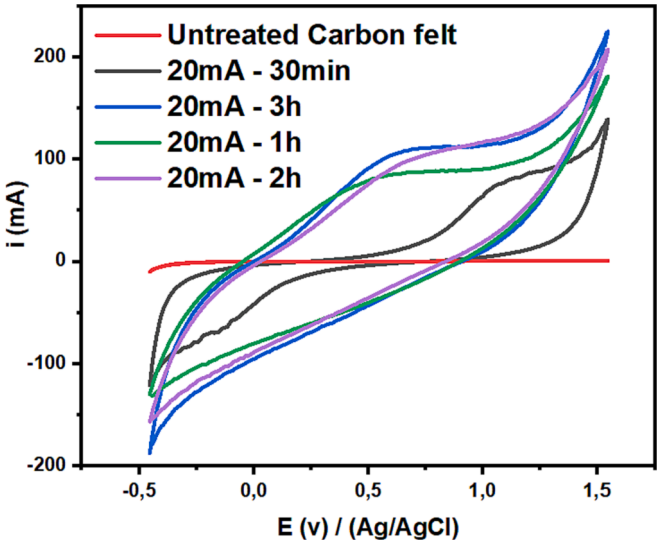

Fig. 1. Cyclic voltammograms of untreated and treated carbon felt at 20 mA at different duration.

The maximum power output for untreated electrodes is 0.0192 mW (Fig. 2). The power generated in the MFC shows how effectively the MFC converts the COD in the influent into electrical energy. The maximum power density increased with the treated electrode to 0.059 mW, suggesting that the electrode treatment enhanced the anode functionality, yielding higher power output than the simple carbon-felt anode.

Fig. 3 and Fig. 4 show the maximum power output for two COD values of 3500 mg/L and 5000 mg/L, respectively. The maximum power output obtained for the untreated electrode is 0.011 mW and 0.014 mW, and 0.039 mW and 0.054 mW with the treated electrode for 3500 mg/L and 5000 mg/L COD, respectively.

The open-circuit voltage (OCV) was also measured in both scenarios. Without electrode treatment in the first case, the OCV was measured at 276 mV, which increased dramatically to 405 mV after the electrode treatment.

An increase in OCV indicates an improvement in the electrochemical potential difference produced by the MFC and enhanced microbial activities taking place. Altering the COD of wastewater showed no significant changes in power or voltage output.

3.3. Internal and ohmic Resistance

The internal and ohmic resistance was obtained using linear sweep voltammetry (LSV), classical varying circuit resistance (VCR), and electrochemical impedance spectroscopy (EIS) techniques. Since there is some confusion in the literature regarding the ohmic loss (Resistance) and internal Resistance, we first delineate the difference between the two mentioned resistances. Due to several losses, the measured MFC voltage is always considerably lower than its theoretically achievable value (emf) (Eq.1).

$$E_{cell} = E_{emf} - \left(\sum h_a + \left|\sum h_c\right| + IR\right) \quad (1)$$

In general, overvoltage is defined as the difference between the measured cell voltage and the cell emf and the sum of the overpotentials of the anode and the cathode, and the ohmic loss of the system. where the $\sum h_a$ and $\sum h_c$ are the overpotentials of the anode and the cathode respectively, and IRΩ is the sum of all ohmic losses which are proportional to the generated current (I) and ohmic Resistance of the system (R_Ω). The overpotentials of the electrodes are current-dependent. In an MFC, they can be categorized as follows: (i) activation losses, (ii) bacterial metabolic losses, and (iii) mass transport or concentration losses [13]. In MFCs, the measured cell voltage is usually a linear function of the current and can be described simply as:

$$E_{cell} = OCV - IR_{int} \quad (2)$$

where IR_{int} is the sum of all internal losses of the MFC, which are proportional to the generated current (I) and internal Resistance of the system (R_{int}). A comparison of Eqs (1) and (2) shows that the overpotentials of the anode and the cathode that occur under open circuit conditions are included in the value of OCV in Eq. (2), while the current-dependent overpotentials of the electrodes and ohmic losses of the system are captured in IR_{int}.

R_{int} includes more than just ohmic Resistance (R_Ω); both terms are often used interchangeably, but MFC researchers should be aware of the differences between these two terms. Based on various techniques, MFC performance can be assessed in terms of overpotentials and ohmic losses or OCV and internal losses.

Here, in this work, the internal Resistance of both modified and unmodified cells was assessed using LSV and VCR methods (Table 1). The results obtained with VCR and LSV are in good agreement. Moreover, the ohmic Resistance for both modified and unmodified cells was

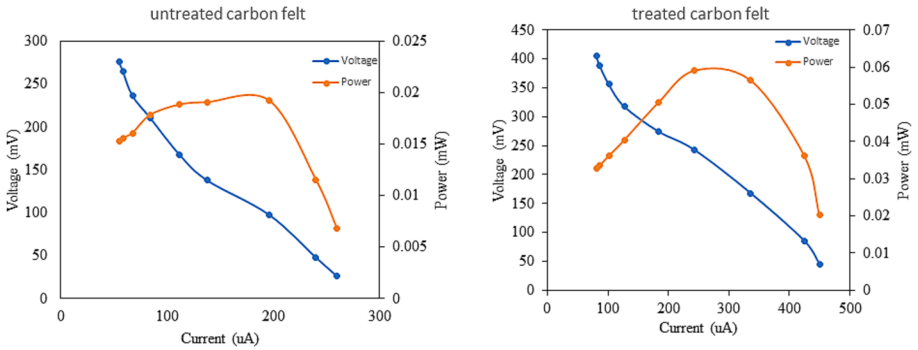

Fig. 2. Polarization Curve determining power out at COD 2000 mg/L for both untreated and treated anodes.

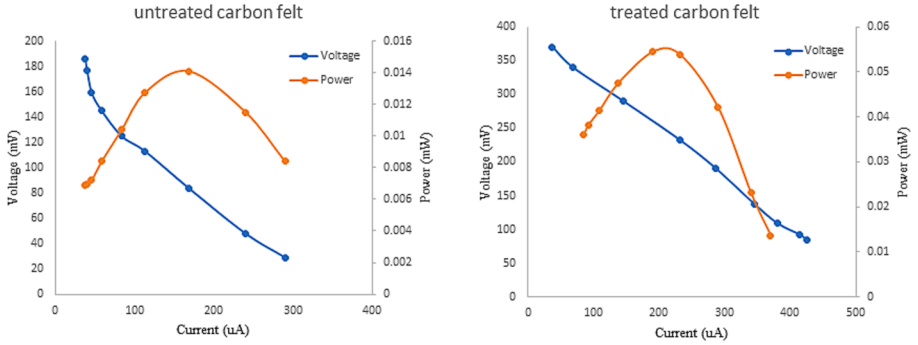

Fig. 3. Polarization Curve determining power out at COD 3500 mg/L for both untreated and treated anodes.

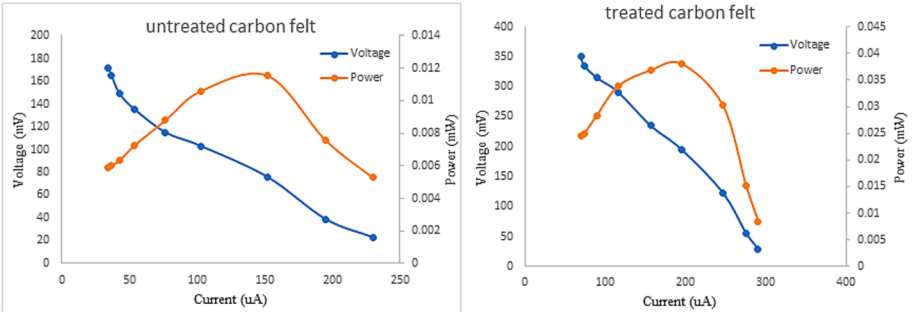

Fig. 4. Polarization Curve determining power out at COD 5000 mg/L for both untreated and treated anodes.

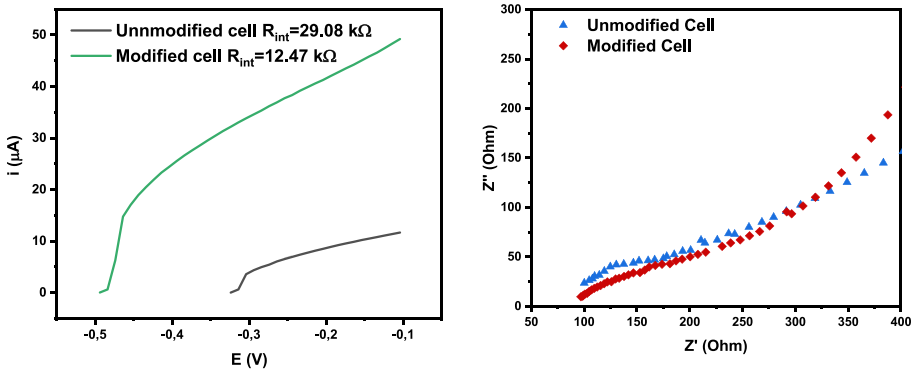

Fig. 5. (a) Linear sweep voltammograms (b) Nyquist plan plots of modified and unmodified cell.

obtained using the EIS technique (Fig. 1). As expected, the ohmic Resistance is quite the same for both modified and unmodified cells as it is related to the conductivity of the fed solution. Nevertheless, the internal Resistance is significantly lower for the modified cells (the cell containing treated anode).

Table 1
Internal Resistance and ohmic Resistance of modified cells in comparison with unmodified cell.

MFC	Internal Resistance (kΩ) (LSV)	Internal Resistance (kΩ) (VCR)	Ohmic Resistance (Ω) (EIS)
Unmodified	29.08	31	97
Modified	12.47	13.5	94

4. Conclusions

The findings of this research demonstrated that utilizing the electrochemical oxidation of anode is a viable and efficient technique to enhance the functioning of MFCs, leading to better performance in terms of COD removal and power generation. These results suggest that this approach holds considerable potential for practical implementation. In summary, the following deductions can be made:

(i) The maximum power densities of the MFC with the treated anode (0.059 mW) were almost three times larger than that of the untreated anode (0.19 mW).
(ii) Applying electrochemical oxidation to the anodes altered their electrochemical characteristics. The MFC's internal Resistance reduced significantly to 12.5 kW when the anode was treated, less than half for the untreated anode of the same material.
(iii) The obtained cyclic voltammograms confirmed the increasing surface area and current response because of additional functional groups created on the surface.

CRediT authorship contribution statement

Fatemeh Poureshghi: Conceptualization, Methodology, Formal analysis, Data curation, Investigation, Writing – original draft, Writing – review & editing. **Rajnish Kaur Calay:** Project administration, Funding acquisition, Writing – review & editing. **Subhashis Das:** Formal analysis, Data curation, Methodology, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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