Improving Microbial Fuel Cell Performance Using Porous Capacitive Composite Bioanode Materials with Energy Storage Function

Yuyang Wang *, Guangxu Hu, Jing Dong and Jing Wang

School of Light Industry, Harbin University of Commerce, Harbin 150028, China; hgxu_2020@126.com (G.H.); dongjing03200163.com (J.D.); wangwangmayong@126.com (J.W.)

* Correspondence: wangyuyanglover@163.com; Tel.: +86-45184865185; Fax: +86-45184865185

Abstract: Microbial fuel cells (MFCs) have shown promise in solving energy and environmental problems, but their practical application is limited by their low power output. In this study, carbon nanotubes/polypyrrole composite anode materials were prepared on a porous sponge matrix. By combining the porous characteristics of sponge, the good conductive properties of carbon nanotubes, and the energy storage ability of polypyrrole capacitive materials, the prepared anode exhibited a large specific capacity, high porosity, large specific surface area, good electron transport ability, and good biocompatibility. The results showed that the maximum power density of the modified anode MFC reached 7.46 W m\(^{-3}\), which was 2.53 times higher than that of the control anode. The stored energy \(Q_s\) released by the modified anode was 235.6 C m\(^{-2}\), 6.5 times higher than that of the control electrode. In addition, the transfer impedance \(R_{ct}\) of the S/CNT/PPy electrode (5.5 \(\Omega\)) was much lower than that of the control anode (16.8 \(\Omega\)). The research presented in this paper demonstrates a new approach to improving the power generation ability and energy storage performance of MFCs.

Keywords: energy storage; composite bioanode; porous material

1. Introduction

As a new type of biopower generation technology with great potential, microbial fuel cells (MFCs) provide a new way to address global energy and environmental problems. MFCs provide a cleaner and renewable energy source that has broad application prospects in sewage treatment, environmental protection, and energy development. However, there are still some problems and challenges in the development of MFCs. The power density of MFCs is currently low and cannot meet the needs of practical applications [1–3]. Microbial fuel cells cannot store charge; the generated electrical energy can only be directly consumed or stored by an external device. They rely on the instantaneous electrical energy generated by microorganisms, which cannot provide a large output current.

Therefore, the selection of bioanode materials with excellent performance and energy storage functions is key to improving the output power of MFCs. The list of recently reported anode materials in the MFCs is shown in Table S2. The selected bioanode materials should have a dual identity, functioning as both the anode material of MFCs and the electrode material of supercapacitors.

At present, carbon materials are commonly used as anode materials and mainly include carbon cloth, graphite felt, carbon mesh, carbon paper, carbon fiber, carbon brush, and carbon nanotubes [4–7]. Among these carbon materials, carbon nanotubes (CNTs) have a unique tubular structure, high specific surface area, excellent electronic conductivity, and chemical stability, making them the first choice for microbial fuel cell anodes. Delord et al. [8] used carbon nanotube-modified fiber felt as an anode to improve the performance of the MFCs, achieving an output current density of 7.5 mA cm\(^{-2}\). However, the theoretical specific capacitance of carbon materials is not very high. Although the anode material,
through the composite or modified means, can improve the transfer efficiency of charge on the anode to a certain extent but has not solved the problem that the output current is limited by the amount of charge generated by microorganisms, microbial power production is limited, if it can not effectively accumulate and store the electricity generated, it will be difficult to drive high-power electrical equipment. To further improve the performance of carbon nanotubes in MFCs, scholars have used polymers to modify the carbon nanotubes. Qiao et al. [9] loaded polyaniline onto carbon nanotubes. The resulting carbon nanotube composite anode material with a mass fraction of 20% showed high electrochemical activity. The maximum output power density of the MFC reached 42 mW m$^{-2}$, and the output voltage was 450 mV. Roh et al. [10] coated polypyrrole on carbon nanotubes by in situ chemical polymerization, and the power density of MFCs modified with the polypyrrole composite anode increased by 38%. Lv et al. [11] prepared a polypyrrole/graphene composite MFC anode on a graphite adhesive substrate, and its maximum power density reached 1326 mW m$^{-2}$, which was higher than that of the single polypyrrole-modified MFC anode (1100 mW m$^{-2}$). Zhao et al. [12] prepared an MFC with polypyrrole/carbon nanotube composite anode on a carbon brush by in situ growth, and its maximum power density (1877 mW m$^{-2}$) was 2.63 times higher than that of an unmodified MFC. Although the composite modification of the polymer and carbon materials can improve the performance of MFCs, traditional two-dimensional anodes have low porosity and low specific surface area. This would lead to the serious deterioration of MFC performance over time. Three-dimensional porous sponges have become the focus of research due to their distinctive continuous large pore network structure, high porosity, and high specific surface area. Erbay et al. [13] used porous sponges as the MFC anode substrate, which increased the maximum power density by 40% compared with traditional carbon felt anodes. Wang et al. [14] used a sponge as the anode substrate to improve the power generation and energy storage performance of MFCs.

Therefore, suitable electrode materials should provide their respective advantages while minimizing their shortcomings. In view of this, this paper proposes the preparation of carbon nanotubes and polypyrrole capacitive composite biological anode materials on porous sponges. This material provides a large surface area, high porosity, good conductivity, and high specific capacitance. In addition, it is conducive to electrolyte diffusion, the adhesion of microorganisms, and the transfer of electrons from microorganisms to the electrode surface. Thus, these materials can be used to improve the power generation and energy storage performance of MFCs. In this paper, full name and abbreviation comparison were shown in Table S1.

2. Experimental

The purchased daily sponge was cut to 3 mm $\times$ 2 cm $\times$ 2 cm dimensions and washed in anhydrous ethanol three times. After each cleaning, the sample was ultrasonicated with distilled water for 10 min to remove residual ethanol solution. The sample was then soaked in acetone solution for 5 min to remove the oil, rinsed repeatedly with distilled water, dried, and set aside.

Sodium dodecyl benzene sulfonate (10 g) was added to a 1 L beaker and stirred until evenly dispersed. A volumetric bottle was then used to set the volume for a 10 g/L solution of sodium dodecyl benzene sulfonate. Nitrogen-doped multi-wall carbon nanotubes (0.5 g) with a diameter of 40–60 nm and a length of 5 µm were subsequently added to a 500 mL beaker of sodium dodecyl benzene sulfonate solution. The mixed solution was stirred for 2 h and then ultrasonicated for 1 h. Afterward, the configured carbon nanotube solution was absorbed with a rubber dropper and slowly dropped onto the surface of the sponge. The sponge was put in an oven to dry for 1 h, repeatedly washed with distilled water, and the carbon felt was dripped with the plastic head dropper again. The above process was repeated 20 times to load the carbon nanotubes onto the sponge, and S/CNT was obtained.

Pyrrole (1 mL) was weighed and dissolved in 100 mL of ethanol solution (volume ratio 1:1). The S/CNT prepared in the previous step was added, and the solution was stirred in
an ice water bath until completely dissolved. Then, ammonium persulfate solution (20 mL, 3.2 g ammonium persulfate) was slowly added, reacted for 24 h, repeatedly rinsed with ethanol and water, and vacuum dried at 50 °C for 24 h. Finally, the completed S/CNT/PPy electrode was removed.

The MFC device used in this paper is a two-compartment MFC manufactured by Vente Experimental Vessel Factory with a unilateral volume of 180 mL. The anode was fixed by titanium wire and placed in the anode chamber. Nutrient solution (180 mL) was then added to the anode chamber. The cathode chamber included a solution is potassium ferricyanide solution \((K_3[Fe(CN)]_6, 10 \text{ g L}^{-1})\). Four carbon rods with a diameter of 8 mm and a height of 50 mm were used for the cathode. The surface of the cathode was polished with sandpaper before use, cleaned by ultrasound, and fixed with titanium wire after drying. The MFC device was assembled, the external circuit was connected to the resistor \((1000 \, \Omega)\), and the MFC was placed in a constant temperature oven \((28 \, ^\circ \text{C})\). The anode potential and MFC output voltage were recorded at regular intervals. Sodium acetate \((0.45 \, \text{g}, 2.5 \, \text{g L}^{-1})\) was added to the anodic solution. After the output voltage of the MFC stabilized, the electrochemical tests were carried out. Before the tests, the cathode solution was replaced and the circuit was opened in advance for stabilization.

Before the MFC electrochemical tests, open-circuit treatment was performed and the material was tested after the open-circuit voltage had stabilized. The reference electrode was a saturated calomel electrode \((\text{SCE})\). When the output voltage of the MFC reached a stable level and the circuit was opened for 1 h, the linear sweep voltammetry \((\text{LSV})\) of the MFC was tested using a French BioLogic electrochemical workstation in the 2nd–5th cycle of the two-electrode system. The linear potential sweep was applied between the biological anode and cathode of the MFC, and the corresponding current intensity was recorded by the workstation. The power of the MFC was calculated using Equation (1).

\[
P = \frac{U^2 \times 1000}{R \times V}
\]

where \(P\)—power, \(\text{W m}^{-3}\); \(U\)—Output voltage, \(\text{V}\); \(R\)—External resistance, \(\Omega\); \(V\)—anode chamber volume, \(\text{m}^3\).

Ac impedance spectroscopy \((\text{EIS})\) was used to measure the different components of the internal resistance in an MFC. The test conditions were as follows: Open circuit to stability in a three-electrode system; test frequency range, 100 kHz to 0.01 Hz; disturbance amplitude, 0.005 V. The amount of electricity generated and stored by the capacitive bianodes can be measured through chronocurrent tests. The chronocurrent applies a constant voltage to the MFC; that is, the MFC anode is charged at a constant potential relative to the reference electrode, and the relationship curve between the current and time is obtained. In this study, bichinolinic acid \((\text{BCA})\) was used to calibrate the protein content of the bianodes using a protein concentration determination kit \((\text{Shengong \text{ Biological Company}; \text{Shanghai; China}})\), in which BCA and \(\text{Cu}^+\) formed a blue-purple complex. The concentration of the anode protein was determined by the thrice parallel calibration of samples with different protein content using an ultraviolet spectrophotometer. To demonstrate the performance of the modified electrode, an S/CNT electrode was used as the control electrode.

3. Results and Discussion

3.1. Physicochemical Characterization of the Sponge/Carbon Nanotube/Polypyrrole Electrode

The SEM images of different electrodes are shown in Figure 1, wherein SEM images of the control and S/CNT/PPy electrodes at 50 and 500 times magnification are provided. The porous sponge skeleton can be clearly seen, the CNTs are interwoven and coated on the sponge fibers, and the surface became rough and uneven (Figure 1a,b). Another layer of PPy was added to the CNTs coating, and the active substances loaded on the porous sponge matrix became significantly thicker and increased in quantity (Figure 1c,d). The three-dimensional macroporous structure of the sponge did not change, and many PPy particles were attached to the fiber surface, effectively reducing the electron transfer resistance and
improving the electrode performance. This morphology would be more conducive to the adhesion of microorganisms and improve the electricity generation efficiency of biological anodes.

The infrared spectrum of the S/CNT/PPy electrode is shown in Figure 2. In the S/CNT/PPy spectrum, the peak corresponded to the N–H stretching vibration was observed at 3317 cm$^{-1}$, in-plane bending vibration absorption peaks of the C–H and N–H bonds were found at 1248 and 1014 cm$^{-1}$, and C–N bond expansion vibration and C–H bond out-of-plane bending vibration corresponded to the peaks at 781 and 689 cm$^{-1}$, respectively. These absorption peaks were characteristic absorption peaks of the pyrrole ring of PPy. The recombination of carbon nanotubes did not show significant redshift.

3.2. Performance of Microbial Fuel Cells Equipped with Sponge/Carbon Nanotube/Polypyrrole Anodes

The power density and polarization curves of different materials used as MFC anodes are depicted in Figure 3a,b. The maximum power density of the modified anode MFC reached 7.46 W m$^{-3}$, which was 2.53 times that of the control anode (2.95 W m$^{-3}$, Figure 3a). This indicated the good biocatalytic effect and biocompatibility of polypyrrole, which effectively improved the electrical production performance of the MFC system. The modified anode achieved a higher open circuit voltage, 0.67 V, than the control electrode (0.58 V, Figure 3b). When polarized to 0.2 V, the output current density of the polypyrrole-modified anode (1.75 A m$^{-2}$) was much higher than that of the control anode (0.77 A m$^{-2}$). The modification of the MFC anode with polypyrrole effectively improved the output power of the MFC through its good biocompatibility and large specific surface area. The combination of polypyrrole also promoted the degradation of organic matter on the anode surface.

Figure 1. SEM images of the (a,b) control and (c,d) S/CNT/PPy electrodes at (a,c) 50 and (b,d) 500 times magnification.
biofilm and increased the electrical activity of electricity-producing bacteria on the anode surface, improving the output power of the MFC [15–20].

![Figure 2. FTIR spectra of the S/CNT/PPy electrodes.](image1)

![Figure 3. Performance of MFCs with different anodes: (a) power density curves and (b) polarization curves of the corresponding MFCs.](image2)
The large, permeable porous pores allow the matrix to enter the pores from all directions, which provides convenience for the rapid transmission of substances. The large specific surface area provides several catalytic active points, which is conducive to enhancing the catalytic performance of the electrode, as well as more places for the adhesion and growth of microorganisms.

The anode potential over time when two different anodes are charged for 45 min is shown in Figure 4. When the circuit is disconnected, the electrons generated in the anode are stored on the anode, which is equivalent to charging the MFC. When charging, the charge does not reach the cathode to participate in the reaction but is stored in the anode, so the anode potential becomes negative. When charging begins, the potential of the control anode immediately drops to $-0.36 \text{ V}$ or even more negative values until reaching a stable state. In comparison, the potential of the modified electrode decreases more slowly as a longer charging time is needed to reach a stable potential or electron saturation. The anode is thus able to store more charge and delay this decline in potential.

![Figure 4. Chronopotentiometry of MFCs with two anodes after charging for 45 min.](image)

The discharge curves of two different anodes after charging for 45 min are shown in Figure 5, where $Q_t$ is the stored electricity, $Q_h$ is the total electricity generated, $i_h$ is the peak current density, and $i_s$ is the stationary current density. After charging-discharging for 45 min (C45/D45), $i_h$ and $i_s$ of the S/CNT/PPy anode were 12.71 and 2.73 A m$^{-2}$, respectively, which were much higher than those of the control electrode (1.72 and 1.05 A m$^{-2}$). The total charge $Q_t$ released by the modified anode reached 7607 C m$^{-2}$, which was 4735 C m$^{-2}$ higher than that of the control electrode. The stored energy $Q_s$ released by the modified anode was 235.6 C m$^{-2}$, 6.5 times higher than that of the control electrode. Polypyrrole has good capacitance and can store the electricity produced by the microbes in a capacitive anode. When electricity is needed, a larger current (the sum of the two parts stored and generated) is quickly released, greatly improving its ability to store charge and current output capacity [21–23]. Comparisons between our S/CNT/PPy anode with previous studies are shown in Table 1.
Figure 5. Discharge tests of MFCs with the two anodes after 45 min under −0.1 V voltage in a closed circuit.

Table 1. Comparison of the peak and stable current density of different anode materials in the MFCs.

<table>
<thead>
<tr>
<th>Anodes</th>
<th>Charging Time (min)</th>
<th>Peak Current Density (A m⁻²)</th>
<th>Stable Current Density (A m⁻²)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>10 min</td>
<td>1.7</td>
<td>1.15</td>
<td>[24]</td>
</tr>
<tr>
<td>AcFeM</td>
<td>10 min</td>
<td>5.51</td>
<td>2.65</td>
<td>[25]</td>
</tr>
<tr>
<td>NCNT/S</td>
<td>30 min</td>
<td>7.99</td>
<td>0.77</td>
<td>[26]</td>
</tr>
<tr>
<td>PANI/NCNT/S</td>
<td>30 min</td>
<td>13.27</td>
<td>2.28</td>
<td>[26]</td>
</tr>
<tr>
<td>S/CNT/PPy</td>
<td>45 min</td>
<td>12.71</td>
<td>2.73</td>
<td>This work</td>
</tr>
</tbody>
</table>

The electrochemical impedance diagram of the control and S/CNT/PPy electrodes as MFC anodes is shown in Figure 6. The EIS diagram of the electrodes consists of a semicircle and a straight line. The solution impedance of the control anode (9.2 Ω) was greater than that of the S/CNT/PPy electrode (4.1 Ω), indicating that PPy can effectively improve the electrode performance and accelerate the electron transfer rate. The transfer impedance $R_{ct}$ of the S/CNT/PPy electrode (5.5 Ω) was much lower than that of the control anode (16.8 Ω). This is mainly because the deposition of PPy increased the interface interaction between the electrode surface and the biofilm, reduced the electron transfer impedance of the electrode, and accelerated the extracellular electron transfer of biofilm on the electrode surface with PPy.

A comparison of the protein content between the control and S/CNT/PPy anodes is shown in Figure 7. The content of microorganisms attached to the electrode surface was characterized by its protein content to verify the difference in biocompatibility between different electrode materials. In this experiment, BCA was used to measure the protein content. The protein content of the control and S/CNT/PPy anodes were 54.2 and 10.6 mg cm⁻², respectively (Figure 7). The higher protein content of the modified anode indicated that the addition of PPy effectively improved the biocompatibility of the anode material. This was achieved by attracting more microorganisms to the surface of the biological anode in combination with the three-dimensional porous structure of the sponge matrix. These electrogenic microorganisms could then grow and multiply on the surface and inside of the anode.
The main applications [27–34] of MFCs with capacitive bioanodes were used as hybrid dual-function electric devices. Due to the electricity generation and storage characteristics of capacitive anodes, such MFCs can be used as power sources for low-power-density electrical equipment in intermittent operations. When the power supply and electricity do not match, store the electricity generated by the microorganisms in the capacitive anode.

Figure 6. EIS curves of the control and S/CNT/PPy anodes.

Figure 7. Protein content of MFCs with control and S/CNT/PPy anodes.

4. Conclusions and Prospects

In this paper, a composite MFC anode material consisting of carbon nanotubes and polypyrrole was prepared using a porous sponge as the matrix, and the performance of the composite anode material in MFCs was studied. When polarized to 0.2 V, the output current density of the polypyrrole-modified anode (1.75 A m⁻²) was much higher than that of the control anode (0.77 A m⁻²). The total charge Q released by the modified anode reached 7607 C m⁻², which was 4735 C m⁻² higher than that of the control electrode. The protein content of the S/CNT/PPy anode was also much higher than that of the control. The prepared porous capacitive composite bianodes can simultaneously produce electricity and store energy, providing a new way to improve the power output of MFCs. The main applications [27–34] of MFCs with capacitive bioanodes were used as hybrid dual-function electric devices. Due to the electricity generation and storage characteristics of capacitive anodes, such MFCs can be used as power sources for low-power-density electrical equipment in intermittent operations. When the power supply and electricity do not match, store the electricity generated by the microorganisms in the capacitive anode first. When the need for electricity quickly releases a larger current (the sum of the two parts stored and generated), it greatly improves its current output and further provides
power for high-power electrical equipment; thus, solving the problem of low MFC output power is the main point of this paper.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings13081322/s1, Table S1: Table of full name and abbreviation comparison; Table S2: title List of recently reported anodes materials in the MFCs [35–38].

**Author Contributions:** Y.W. (writing—review and editing): preparation, creation and/or presentation of the published work by those from the original research group, specifically critical review, commentary, or revision—including pre- or post-publication stages. G.H. (resources): provision of study materials, reagents, materials, patients, laboratory samples, animals, instrumentation, computing resources, or other analysis tools. J.D. (conceptualization): ideas; formulation or evolution of overarching research goals and aims. J.W. (formal analysis): application of statistical, mathematical, computational, or other formal techniques to analyze or synthesize study data. All authors have read and agreed to the published version of the manuscript.

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**References**


9. Qiao, Y.; Li, C.M.; Bao, S.; Bao, Q. Carbon nanotube/polyaniline composite as anode material for microbial fuel cells. *J. Power Sources* 2007, 170, 79–84. [CrossRef]


15. He, M.; Zhang, Y.; Du, Q. Three-dimensional polypyrrole/MnO2 composite networks deposited on graphite felt as free-standing electrode for supercapacitors. *Mater. Lett.* 2013, 104, 48–52. [CrossRef]


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