Enhanced performance of microbial fuel cell using carbon microspheres modified graphite anode

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Abstract

In the present work, dual-chamber microbial fuel cell (MFC) was constructed, in which anaerobic sludge was used as the inoculum and potassium ferricyanide as the electron acceptor. We have investigated the untapped potential of carbon microspheres modified graphite anode (CGA) fabricated by hydrothermal and calcinations method in the MFCs operation. The results showed that the CGA could be utilized as a novel and efficient MFC anode. The output power of the MFC involved with CGA is approximately 358 mW·m⁻², which is 3.1 times of the counterpart MFC with graphite anode (GA). Furthermore, this MFC showed a 68% chemical oxygen demand (COD) removal rate of the wastewater. Through further analysis, the CGA could improve the specific surface area and enhance the adsorption of microorganism, which could efficiently favor the electron transfer rate between the microorganism and external circuit, resulting in the increase of the electrochemical activity of MFC.

Introduction

Microbial fuel cell (MFC) plays an important role in solving the energy crisis and environmental problems. It can not only treat wastewater, but also generate electricity from organic matter present in wastewater [1–4]. A dual-chamber MFC consists of anode, cathode, and proton exchange membrane. Among these accessories, anode can affect the location of electroactive bacteria attachment, the electron transfer rate from microorganism to external circuit, and the oxidation rate of anode substrate in the overall cell [3, 5–7]. Therefore, the performance of MFC enormously depends on the properties of anode in the operation.

At present, graphite electrodes are commonly applied in MFC due to their enormous surface area, good mechanical strength, excellent chemical stability and electron transfer rate [8–10]. However, they have weak electro-catalytic activities, and the few pores on them cannot provide sufficient adhesion sites for bacteria. Furthermore, some volatile compounds exist on the surface of the graphite anode, resulting in the hindering of the electron transfer rate between bacteria and electrode [11]. Therefore, enhancing the catalytic activity of graphite anode is a key role to improve the performance of MFC. In recent years, various chemical and physical modification methods have been explored in order to improve the performance of MFCs [12–14]. Platinum (Pt) is widely used as anode modification material because of its high oxidation rate of hydrogen and small organic molecules. However, large-scale application has been restricted due to its high price [4, 15]. To decrease the modification cost, Xie et al., fabricated carbon nanotubes (CNTs)-sponge anode, showing good prospects for the application of MFC.
The special surface morphology provided a large specific surface area that was favorable for microbial colonization and catalytic decoration. Zhou et al., employed simple electrochemical method to treat the graphite anode, and achieved superior MFC performance [17]. They revealed that the surface morphology, internal resistance, and anode potential were changed by electrochemical oxidation method, which was beneficial for the microbial attachment and electron transfer on the anode surface, resulting in the performance improvement of the MFCs. The rougher surface and deeper cracks of the modified anodes could enhance the microbial adhesion on the anodes. The lower internal resistance and lower anode potential was beneficial to improve the power generation and the COD removal efficiency. Therefore, using a low-cost electrode material with further modification to improve the performance of the MFCs is of great significance.

In the present work, the graphite anode (GA) was first modified by hydrothermal method with aqueous glucose solutions. After the hydrothermal process, the carbon microspheres could be synthesized on the surface of GA [18]. With further calcination treatment under nitrogen, the surface states of the anode could change [19, 20] and the carbon microspheres modified graphite anode (CGA) was prepared for the exploration in the MFC operation. Carbon microspheres synthesized by hydrothermal method can provide a protective effect to reduce the loss of GA in the calcination treatment; on the other hand, the specific surface area of GA will increase with the carbon microspheres modification and some surface impurities will be removed under the calcinations effect which is beneficial to increase the specific surface area and enhance microbial attachment of GA. The properties of MFCs with the GA and CGA were integrated in this work, and the results could provide theoretical support for improving the production capacity of MFCs.

**Materials and Methods**

**Preparation of GA and CGA**

In the experiment, two anodes were prepared for the potential investigation of MFC. One was GA (Sanjie, Nantong) as the comparison, while the other was CGA. The size of the two anodes was 20 mm × 10 mm × 3 mm. The CGA was prepared as follows: the GA was put into 80 mL glucose solution with the concentration of 1.5 mol·L⁻¹. Subsequently, the GA and the glucose solution were transferred into a Teflon-lined stainless steel autoclave, and were then hydrothermally reacted at 200°C for 16 h. The obtained electrode with the hydrothermal treatment was washed with methanol, acetone, and deionized water for three times, respectively. The obtained electrode was then dried at 80°C for 2 h. Finally, the dried electrode was put into porcelain boat sealed with aluminum foil and sintered at 300°C for 1 h and 800°C for 2 h with the ramp rate of 5°C·min⁻¹ to generate the CGA.

**Characterization of anodes**

Surface microscopic characterization of GA and CGA was examined by scanning electronic microscopy (SEM, xl-30, Philips Company, Amsterdam, The Netherlands). Contact angle (JC0000C1, Shanghai Zhongchen Digital Equipment Co. LTD, Zhejiang, China) was measured utilizing ultrapure water at room temperature in order to quantify the wettability of the two anodes. The specific surface area of each anode was measured by multipoint BET method (high purity nitrogen gas was adsorbate, liquid nitrogen temperature was 77.35 K). X-ray diffractometer (XRD, Macscience-M18XHF) was used to observe the degree of its graphitization. The two anodes were characterized by Fourier transform infrared (FT-IR) spectra (FTIR-8400S, SHIMADZU, Wolverton, Milton Keynes, UK) to analyze the information of bonds between atoms.

**MFC construction and operation**

Dual-chamber MFC was assembled with the single chamber volume of 220 mL, in which the anaerobic sludge, the sodium acetate of the concentration of 1 g·L⁻¹, 0.5 M potassium ferricyanide (K₃[Fe(CN)₆]) and proton exchange membrane (PEM, nafion, 117) were used as inoculum, anode substrate, cathode substrate, and partition of the two chambers, respectively. The GA and CGA were placed in the anode chamber with a titanium wire (the diameter was 0.8 mm) to be the connection of the external circuit to electrodes. The two MFCs were operated in a batch mode with the external resistance 1000 Ω, and voltages were obtained from data acquisition card. The MFCs device showed as Figure 1.
**Enhanced Performance of Modified Graphite Anode**

**J. Liu et al.**

**Electrochemical characterization**

After inoculation of microorganisms, the polarization and power density were obtained by changing external resistance from 1000 Ω to 9000 Ω. Before the test, the circuit was opened for 12 h and then recorded corresponding to the resistance of the voltage. In the course of each test, the MFCs are resting for half an hour to ensure the stability of voltage. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tested by the electrochemical workstation (CH760e, Chen Hua, Shanghai, China) could characterize the internal resistance and electron transfer rate of MFCs. MFCs discharge current with time changing ($I_t$) was also measured with the discharge time of 400 s. CV, EIS, and $I_t$ measurements were all conducted in a three-electrode configuration with the anode as the working electrode, the cathode as the counter electrode and the calomel electrode as reference. To measure the chemical oxygen demand (COD) removal rate, samples were collected from the beginning to the end of MFC circle. In order to characterize the recovery rate of electrons, the columbic efficiency (CE) was calculated in the operation circle of MFC by dividing the theoretical power with the actual power.

**Results and Discussion**

The surface morphologies of GA and CGA are analyzed by SEM measurements. The SEM images clearly show the differences of surfaces between GA and CGA. As shown in Figure 2A, the surface of the GA was smooth and showed flaky structure before inoculation of microorganisms. While, obvious changes occurred and carbon microspheres with the average diameter of 1 μm formed and coated on the surface of the anode for the CGA due to the hydrothermal and calcinations treatment as shown in Figure 2B. The illustration in Figure 2B shows the results of the specific surface area of the two anodes and their respective surface morphologies. The SEM images clearly show the differences of surfaces between GA and CGA.
N₂ adsorption-desorption isotherms. As can be found, the specific surface areas of GA and CGA are 3.614 m²·g⁻¹ and 4.120 m²·g⁻¹, respectively. At a relative pressure from 0 to 0.7, the adsorption amount of GA and CGA are similar. While near a $P/P_0$ of 0.7–1.0, the adsorption amount suddenly increases for the CGA, which may be due to the formation of carbon microspheres.

Figure 2C, D are SEM images of the GA and CGA after attachment of microorganisms after the MFC working. From Figure 2C, only small amounts of bacteria and some anode substrate can be observed on the surface of the GA, which may be due to the smooth surface. However, for the post-inoculated CGA as shown in Figure 2D, the microorganisms groups and anode substrate are significantly observed to be attached to the CGA. It is generally known that the interesting groups of microorganisms play a key role in the electron transfer from bacteria to the electrode [7, 21], which means more electrons were produced by microorganisms due to large number of microorganisms attaching on electrode. The results indicate that the CGA with larger amounts of microorganisms is beneficial to the electrochemical activity of MFCs. The surface wettability is further investigated by the water contact angles. The results illustrate that the water contact angles of GA and CGA are about 127° and 14°, respectively, as shown in Figure 2E,F. The GA exhibits a higher value of contact angle, which indicates its lower wettability. While for the CGA, the lower contact angle exhibits a higher wettability due to the hydrothermal and calcinations treatment. As can be known from Figure 2, the microorganisms can easily grow on the surface of CGA due to the enhancement of specific surface area and higher wettability, which suggests that the MFC with CGA may hold excellent performance than that with GA in the process of MFC.

The XRD patterns and FT-IR spectra are further characterized to analyze the crystal structures and the information of chemical groups of GA and CGA. As shown in Figure 3A, before modification, a peak of GA exists at $2\theta = 26.6^\circ$, which is the characteristic peak of graphite carbon. While compared with that of GA at 26.6°, the characteristic peak of CGA shows a slight shift. The shift may be caused by the surface changes of CGA with the carbon microspheres modification and following calcinations treatment. The FT-IR spectra are used to deeply determine the surface information of chemical groups in the GA and CGA from Figure 3B. As can be found, the FT-IR spectra of the GA and CGA exhibit obvious differences, which are due to the changes on the surfaces of electrodes. A lot of impurity peaks appear on the surface of GA in the range of 1300–1900 cm⁻¹, indicating that the surface of GA possessed some exceeded groups which are different from that of the CGA. However, for CGA, the impurity peaks obviously decrease, which means the CGA has been optimized because of hydrothermal carbonization and high temperature calcinations. With further analysis, the peaks observed on the surface of CGA are some oxidation groups [22–26]. The above results showed that some exceeded groups on the surface of GA could be removed under the process of hydrothermal and calcinations. During the process of modification, some volatile organic compounds and part of oxygen-containing functional groups can be reduced, while some functional groups still existed. The surface optimization of the anode makes it easier for the microorganisms to adhere to the anode surface as observed from Figure 2D, which may be beneficial to strengthening the output power of MFC.
The electro-catalytic characterization of GA and CGA is measured by EIS, which is an effective method to explore the interfacial properties of anodes [27]. The x-intercept gives the electrolyte resistance ($R_s$) in the high-frequency region and the diameter of semicircle represents the charge transfer resistance ($R_{ct}$) [28], a straight line following the semicircle. As shown in Figure 4A, the semicircle of CGA is smaller than that of GA, suggesting a lower $R_{ct}$ of CGA. The two electrodes show basically consistent results in $R_s$, which are 3.52 Ω (GA) and 3.02 Ω (CGA), respectively. $R_{ct}$ is estimated to be 37.2 Ω and 13.7 Ω for the GA and CGA. Figure 4B shows the CV curves of the GA and CGA without inoculation bacteria at the scanning rate of 0.05 V/s in NaCl solution. From the results, we can find that CGA presented a much higher redox current than that of GA, indicating a higher electro-catalytic activity of the CGA. The results may be induced by the improvement of the surface area and electron transfer capacity of CGA after modification.

The anode significantly affects the biological properties of MFC reactors and it was a key factor of electron transfer from microbes to anode in the working process of MFC. When the output voltage is stable, typical voltage generation profiles can be recorded for the MFC with anodes after inoculating bacteria. Figure 5 clearly presents one circle voltage export of MFC in the working process of MFC. As can be seen, the MFC with CGA generates a higher maximum voltage than that with GA and the maximum voltage of MFCs with GA and CGA can reach approximately 620 mV and 790 mV, respectively. The results show an excellent performance of the MFC with CGA. Twelve hours later, with the external resistance gradually decreasing, the voltage gradually decreases, and this is mainly to obtain the polarization curves, power density curves, and electrochemistry test results during the time. The drop of voltage at ~18 h is because of the external resistance reduced to the minimum before the end of the tests. After the end of the period and the external resistance was adjusted to 1000 Ω, the output voltage of MFC with CGA is also 2-3 times higher than that with GA. When the voltage of MFC is lower than 0.05 V, the test can be ended. As can been found from Figure 5, the operation cycle of MFC with CGA is approximately 72 h, while that with GA is approximately 49 h. Therefore, the operation cycle of MFC is greatly extended with CGA, instead of GA.
The output power density can reflect the stand or fall of MFCs production performance, so it is a kind of index for evaluation of MFCs performance. The output power density of MFCs with GA and CGA are measured and the results are shown in Figure 6A. As can be known, with the external resistance varying from 100 Ω to 9000 Ω, a maximum power density of 358 mW·m−2 for the MFC with CGA occurred at the current density of 667 mA·m−2. The maximum power density value is 3.1 times that of the MFC with GA (113 mA·m−2), which suggests that the power density of the MFC with CGA significantly increase, compared with that with GA, and the CGA are more conducive to the power output of MFC than GA.

Two liner parts of different slopes could be distinguished in the polarization curves as shown in Figure 6B. Based on that, the slope of voltage versus the current is the actual internal resistance of electrode [29]. As can be found from Figure 6B, the open circuit voltage and the polarization curves can intersect with the vertical axis, and the open circuit voltage for the MFC with CGA is approximately 800 mV. While for the MFC with GA, the open circuit voltage is only 630 mV, which is about 170 mV less than that of the MFC with CGA. Through further calculating from the polarization curves, the internal resistance of the MFC with CGA is about 0.95 KΩ, which is about 2.6 times lower than that of the MFC with GA (~2.6 KΩ), indicating that the resistance of CGA significantly decreases after the modification by GA.

Electrochemical impendence spectroscopy is a powerful tool for depth analysis of MFCs. A typical spectrum is composed of a high-frequency main arc and a low-frequency side arc, which is related to the charge transfer at the oxide/electrolyte interface and the diffusion of species, respectively. The diameter of the semicircle represents the $R_{ct}$, which is affected by the kinetics of the electrode reactions [14, 30]. And the Warburg impedance is mainly caused by the diffusion. The $R_{ohm}$ can be calculated from the x-intercept at real part ($Z'$) at a very high frequency, which represents the intrinsic resistance of electrode materials, the contact resistance at the active material or current collector interface and ionic resistance of electrolyte [31]. In the experiments, EIS tests were further measured when MFCs output voltage stabilized with the maximum power generating at open circuit. From the EIS curves shown in Figure 7A, a preceding well-defined semicircle can be observed clearly. As can be found, the semicircle of CGA is much smaller than that of GA, suggesting lower interfacial $R_{ct}$ for CGA and a faster electron transfer rate between CGA and electrolyte [32]. $R_{ct}$ are calculated to be 25.68 Ω and 200.5 Ω for the CGA and GA, respectively. Because of the similar MFC configurations and electrolyte compositions, there are no significant differences in the corresponding $R_{ohm}$, which are calculated to be approximately 9.12 Ω and 12.5 Ω. The reduction of impedance can be attributed to the increased specific surface area and microbial active sites of CGA with the hydrothermal and calcinations treatment, which makes electrical activity of CGA enhanced in the working process of MFC.

Cyclic voltammetry clearly indicated the electron transfer properties during MFC operation. When the anodes inoculate with bacteria, the generated electrons transferred from bacteria to electrode. The redox activities of the MFCs were investigated with a calomel reference electrode and a Pt counter electrode. Figure 7B shows that no obvious oxidation/reduction peak is observed for the CVs of the two MFCs with GA and CGA. A much higher redox current can be observed for the MFC with CGA, compared with that with GA, indicating that the CGA improved the electron transfer properties of MFC. Both the GA and

![Figure 6. Power-current (A) and polarization curves (B) of MFCs with GA (a) and CGA (b).]
CGA inoculated with bacteria show higher redox current compared with bare electrode shown in Figure 4B, which may be caused by that the GA and CGA with bacteria improve the rate of electron generation and transfer.

The discharge current could reflect the MFC electricity generation performance. As the parameters of reactors and cathodes are same, the differences of power generation for the two MFC reactors are mainly determined by electron transfer rate in anode chambers [33]. In this work, discharge current is measured by electrochemical workstation with a three-electrode system to investigate the electricity generation performance of MFCs with GA and CGA. As is generally known, for one MFC reactor, a high current can be obtained when the MFC holds a high voltage and a low resistance. As shown in Figure 8, the highest current of 9 mA is obtained at the beginning of MFC with CGA, and it is gradually decreased until stability with the current of about 4 mA. The current is significantly larger than that of MFC with GA. The result considered is that the prepared CGA offers a suitable nanostructure environment for bacterial growth and a better electron transfer from bacterial to electrode compared with GA, resulting in the production of higher current by the catalytic activity of bacteria.

Sodium acetate solution is prepared to simulate higher concentrations of COD wastewater to investigate the removal performance of MFC with GA and CGA. The microorganisms in anode chamber could not only consume carbon source but also produce electricity. Therefore, COD removal rate can reflect consumption level of carbon source and electogenesis capacity of MFC. Figure 9 shows the
COD removal rate and CE of MFC with GA and CGA. The MFC with GA can degrade 58% of COD, while that with CGA could remove 68% of COD. The results indicate that the MFC can effectively reduce the concentration of COD. As can be seen in Figure 9, except the excellent COD removal performance, MFC with CGA has a higher CE (~ 16.7%) than that with GA (~ 7.2%). As described previously, it is mainly caused by the lower internal resistance and better adhesion of bacteria for the CGA which conducted the process for producing higher electricity in an anaerobic way [29].

**Conclusion**

In summary, we successfully prepared a novel CGA material by hydrothermal and calcinations methods for the application of MFC. The results of SEM, BET, the water contact angle, XRD, and FT-IR indicated that the CGA had a good morphology and a higher wettability with larger specific surface area and less surface impurities than GA, which is beneficial for the attachment of microorganism groups and electronic transmissions. Electrochemical test results showed that the CGA held a lower $R_c$ which facilitates the transfer of electrons from microorganisms to the outer circuit. Besides, a much higher redox current from the CV curves indicated higher electron-catalytic activity of the CGA than GA. The test results in the MFC operation process showed that the performance of MFC with CGA was obviously enhanced, which exhibited a better catalytic performance with power density of 358 mW·m⁻² and the value is 3.1 times of that of the MFC with GA. The operation circle of MFC with CGA had been extended to 72 h, while that of MFC with GA was only 49 h. Through further analysis of the electrodes of inoculated microorganisms, a fast and efficient electron transfer from bacterial to electrode could be achieved for the MFC with CGA, resulting in the improvement of electrochemical activity of MFC. The results of wastewater treatment showed that the COD removal rate and CE of MFC with CGA could reach 68% and ~16.7%, respectively. While that of MFC with GA could only reach 58% and ~7.2%, respectively. The MFC with CGA exhibited a better effect on the treatment of wastewater than that with GA. These conclusions provide important prospects for developing a new kind of anode modification method.

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**Conflict of Interest**

None declared.

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