A novel polyaniline interlayer manganese dioxide composite anode for high-performance microbial fuel cell

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A R T I C L E   I N F O
Article history:
Received 6 December 2016
Revised 3 March 2017
Accepted 7 March 2017
Available online 31 March 2017

Keyword:
Microbial fuel cell
Composite materials
Biocapacitive anode

A B S T R A C T
Sandwich-like structure of manganese dioxide and polyaniline and manganese dioxide (MnO₂/PANI/MnO₂) were deposited on carbon felt anode to improve the power output and storage capacity of microbial fuel cell. This novel structure can significantly increase the active surface area of electrode; provide high interfacial area, short ion diffusion path, and fast electrical pathways. The polyaniline interlayer aims at obtaining a better contact between the manganese dioxide layers and a good electrochemical conductivity of the electrode. The maximum power density of the MFC with a MnO₂/PANI/MnO₂ anode reaches 1124.8 mW m⁻² is 11.6 times higher than that of the bare carbon felt anode (97.6 mW m⁻²). During the chronoamperometric experiment with 120 min of charging and 20 min of discharging, the MnO₂/PANI/ MnO₂ electrode was able to store 27574 C m⁻², whereas the bare carbon felt anode was only able to store 8709 C m⁻². This study suggests that the MFC anode containing MnO₂/PANI/MnO₂ composite materials shows potential for storing energy from waste water and releasing in a short time to the electronic device.

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1. Introduction

Microbial fuel cells are a promising technology that utilizes wastewater as fuel directly to carry out energy recovery and pollution control [1–3]. And recently there are some studies that show the performance of MFCs are enough to some real application [4,5] However the wastewater needs to be treated continuously and the energy which is produced by the MFC might not be consumed continuously. To match the production and demand of this electricity, storage of electricity would be necessary. To fill the gap, some scholars have proposed two techniques for the storage of electricity from MFCs: external and internal capacitors [6–9]. Instead of the use of the external capacitor, internal capacitor (an integrated anode system that contained capacitive material into the bioanode) received more and more attention, leading to the better performance in terms of more charge stored during the charging and discharging experiment. The novel concept makes the anode function as a biocapacitor which can not only generate bioelectricity, but also store and release energy.

MnO₂ received more and more attention as its larger capacitance, its abundance, environmental friendliness and low cost [10]. Zhang and Liang [11] prepared the capacitive anode by electrodepositing MnO₂ on the carbon felt. The addition of MnO₂ increased the capacitance of the anode. However, the poor electronic conductivity of MnO₂, which remains a major challenge and limits the rate capabilities for high power performance. To improve the electrical conductivity, considerable research efforts have been placed on exploring composite structures where MnO₂ in combined with highly conductive materials such as polypyrrole or polyaniline. Conducting polymers are quite attractive because of its low cost, easy and economic synthesis, high energy-storage capacity, and controllable electrical conductivity [12,13]. He and Zhang [14] successfully prepared polypyrrole/MnO₂ composite material for supercapacitor. Xu [15] used polypyrrole as interlayer to synthesize sandwich-like structure of Pt/PtO₂/Pt and which show significantly high electrocatalytic activity. Among the various conducting polymers, PANI has been considered as a promising candidate due to its high capacitance, low cost and environmental stability. Additionally, polyaniline has been studied for use as a MFC anode through modifications. In previous studies, PANI/inorganic composites are also reported to have better conductivity [16–18,22,23]. The PANI-MnO₂ composites have been reported many times in the application of supercapacitors. However, the reports of these kinds of PANI-MnO₂ composites function as a capacitive bioanode in application of MFC are less. Ansari [19] has successfully
prepared PANI-MnO$_2$ composites assessed as a cathode catalyst for improved power generation in MFCs. According to the previous studies, in this work, we focus on investigating the performance of PANI-MnO$_2$ composites function as a capacitive bioanode in application of MFC. We synthesized sandwich-like structure of MnO$_2$/PANI/MnO$_2$ using polyaniline as the interlayer. The incorporation of polyaniline into the interlayer between the manganese oxide layers resulting composite could possess synergic properties from both components, such as enhancement in electronic conductivity.

In this work, we use the sandwich-like structure of MnO$_2$/PANI/MnO$_2$ composite material as the capacitive bioanode to overcome the mismatching of the production and demand of this electricity. We can use this MFC capacitive bioanode containing MnO$_2$/PANI/MnO$_2$ composite materials for production and storage electricity simultaneously, when the small applications do not need electricity, and release the two parts electrons (electronic production and storage) simultaneously when the small applications need electricity. And both biocatalytic and electrocatalytic properties of the composite are improved by the novel structure.

2. Experiment

2.1. Fabrication process of carbon felt @MnO$_2$/PANI/MnO$_2$

The sample preparation included two hydrothermal treatments and an in situ chemical polymerization. The first MnO$_2$ layer was synthesized by a traditional hydrothermal treatment [20]. Then the second polyaniline interlayer was prepared in situ chemical polymerization: First, 10 ml 0.5 mol l$^{-1}$ ammonium persulfate solution was prepared. Then 100 ml mixed solution containing 0.5 mol l$^{-1}$ aniline and 1.5 mol l$^{-1}$ sulfuric acid were prepared. When making the mixed solution, the aniline solution should be slowly added into the sulfuric acid solution with stirring until no white precipitate appeared. Then the electrode was immersed into the aniline and sulfuric acid mixed solution for 1 min under stirring. After that, the carbon felt was put into the ammonium persulfate solution for 90 min under stirring. At this time, the color of solution changed from colorless to pale green. After the completion of the reaction, samples were thoroughly washed with distilled water, and were dried at 60 °C for 6 h. At last, the third MnO$_2$ layer was also prepared with the same hydrothermal method [20].

2.2. MFC configuration

The microbial fuel cell used in this study consisted of two polycarbonate compartments, each with a liquid volume of 100 ml. The sandwich-like structure of MnO$_2$/PANI/MnO$_2$ composite material was employed as the MFC anode. Five graphite rods were used as the MFC cathode. Nafion 117 (Dupont, USA) separated the two compartments. The PEM was pretreated by boiling in H$_2$O$_2$ (10%), then in 0.5 M H$_2$O$_2$, and finally in deionized water each for 1 h. The anodic chamber was initially inoculated using a pre-acclimated cell suspension from MFCs fed with acetate. The anodic compartment was fed with the nutrient buffer solution (NBS) The nutrient buffer solution (NBS) containing the following: 5.97 g l$^{-1}$ NaHPO$_4$ 2H$_2$O, 0.2 g l$^{-1}$ MgSO$_4$, 0.13 g l$^{-1}$ KCl, 2.75 g l$^{-1}$ Na$_2$HPO$_4$ 12H$_2$O, 0.56 g l$^{-1}$ (NH$_4$)$_2$SO$_4$, 0.31 g l$^{-1}$ NH$_4$Cl, 0.015 g l$^{-1}$CaCl$_2$, 0.02 g l$^{-1}$ MnSO$_4$, 0.01 g l$^{-1}$ FeCl$_3$. The medium were refreshed each time when the voltage decreased to less than 50 mV, forming one complete cycle of operation. The cathode chamber of the MFC was fed with 10 g l$^{-1}$ Potassium ferricyanide as the electron acceptor. All MFCs were controlled at a constant temperature of 25 °C. A 20-channel voltage data acquisition instrument was used to obtain the cell voltage.

2.3. Electrochemical measurement and structure characterization

The electrochemical performances of the electrode materials were measured in a three-electrode system by galvanostatic charging-discharging and electrochemical impedance spectroscopy method, using (SP-240, Bio-Logic) French electrochemical workstation. The sandwich structure anodes were used as the working electrodes, an Ag/AgCl was used as the reference electrode (½=197 mV, saturated KCl, corrected to a standard hydrogen electrode; SHE), and the cathode was the counter electrode. The charging-discharging experiments were carried out in a voltage window between −0.5 V and 0.3 V under 2.5 mA cm$^{-2}$. The chronoamperometric experiment polarized −0.1 V. The EIS (inoculation) was studied in the frequency range from 100 kHz to 10 mHz at open circuit voltage by applying 5 mV. The power densities P (mW m$^{-2}$) were calculated using P=IV/A. The surface morphology and microstructure of MnO$_2$/PANI/MnO$_2$ was investigated by means of scan electron microscopy and energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

3.1. Morphological characterization

The morphologies of electrodes were examined by scan electron microscopy. Fig. 1a shows that bare carbon felt exhibits many thin and soft threads. The high magnification SEM (Fig. 1a (insert)) further reveals that the surface of bare carbon felt is very smooth. In Fig. 1b, the skeleton of the carbon felt can be fully covered by the MnO$_2$, with almost no carbon felt exposed to the surface. And the surface of carbon felt was covered by porous mesh MnO$_2$ and became very rough (Fig. 1b (insert)). Fig. 1c presents the SEM images of MnO$_2$/PANI/MnO$_2$. After the MnO$_2$/PANI was subjected to a second hydrothermal treatment, a thin layer of porous mesh MnO$_2$ was observed on their outer-layer surfaces. From Fig. 1c (insert), it can be seen that the PANI interlayer does not change the morphology of the MnO$_2$ grains. And the internal space was remained, thus suggesting that MnO$_2$ grew mainly on the PANI surface rather than the MnO$_2$ inner surface. As shown in Fig. 1d, energy dispersive X-ray spectroscopy (EDX) mapping was performed to determine the Mn, C, O, S, and O distributions in the MnO$_2$/PANI/MnO$_2$ (Au is exclusive of calculating). The EDX showed that these elements were homogenously distributed throughout the electrode, confirming the successful integration of the three layers.

3.2. MFC performance

Fig. 2(a) and (b) showed the power density curves and polarization curves of MFC reactors. The MnO$_2$/PANI/MnO$_2$ modified MFC produced a maximum power density of 1124.8 mW m$^{-2}$, with a value 29% higher than that of the MnO$_2$ modified MFC (872 mW m$^{-2}$) and 11.6 times higher than blank MFC (97.6 mW m$^{-2}$). As calculated from polarization curves, the internal resistance of MnO$_2$/PANI/MnO$_2$ modified MFC was approximately 120 Ω, which was much lower than that of the MnO$_2$ modified MFC (160 Ω). This result indicated that polyaniline interlayer could reduce the transfer resistance of MFCs and improve electrons transferred from microbes to anode surface. Due to the different anode materials, the anode polarization curve has an apparent change. In Fig. 2c, the anode potentials of MnO$_2$/PANI/MnO$_2$ modified anode were more negative than those of MnO$_2$ modified anode and bare anode at the same current density and differences increased with current densities, indicating that the performance of anode was significantly improved after PANI interlayer modification. The addition of biocompatible interlayer PANI could facilitate the adapted bacteria enrichment and contribute significantly to provide more
3.3. Specific capacitance of $\text{MnO}_2$/PANI/$\text{MnO}_2$ modified electrode with inoculation

Fig. 3 represents the typical galvanostatic charging-discharging curves of $\text{MnO}_2$/PANI/$\text{MnO}_2$ at 2.5 mA cm$^{-2}$ between $-0.5$ V and 0.3 V. The specific capacitance of $\text{MnO}_2$/PANI/$\text{MnO}_2$ electrode can achieve a maximum value as high as 2.62 F cm$^{-2}$, which is higher than that of $\text{MnO}_2$ electrode (0.82 F cm$^{-2}$), bare electrode (0.29 F cm$^{-2}$). The specific capacitance could be calculated from the charge-discharge curve according to:

$$ C = \frac{(I_{cd} \times T)}{(U_{cd} \times A)} \quad (1) $$

Where $I_{cd}$ is the charge-discharge current; $T$ is the discharge time(s); $U_{cd}$ is the potential window; and $A$ is the projected anode surface area (cm$^2$). The data illustrated that sandwich structure $\text{MnO}_2$/PANI/$\text{MnO}_2$ electrode exhibit better charge-discharge properties than that of $\text{MnO}_2$. The large specific capacitance is owing to not only the synergic impact of both components of $\text{MnO}_2$ and PANI but also the unique sandwich structure of $\text{MnO}_2$/PANI/$\text{MnO}_2$. In addition, the excellent capacitance of $\text{MnO}_2$/PANI/$\text{MnO}_2$ composite electrode is ascribed to the high conductivity of sandwich structure as a support with the PANI interlayer channel can increase the effective specific surface area and the PANI interlayer can facilitate the electron transportation. Moreover, the PANI interlayer may also access the electrolyte and participate in the reactions with electrolyte and supply an optimal pathway for ion diffusion [24,25].

3.4. The behaviors of capacitive bioanode

The typical current density curves polarized at $-0.1$ V of bare electrode, $\text{MnO}_2$ modified anode and $\text{MnO}_2$/PANI/$\text{MnO}_2$ composite electrode are given in Fig. 4. All the curves exhibited a current peak at the beginning of the discharge, followed by a rapid current decay until it approached a relatively constant value. A peak current far more over that at steady state was showed for the $\text{MnO}_2$/PANI/$\text{MnO}_2$ composite bioanode, suggesting that electrons collected from the metabolism at open circuit state were released to the cathode as soon as the external circuit was connected. The peak current, stable current and cumulative charges were shown in Table 1. As was shown in Table 1, the peak and stable current densities of anodes (exclusive of bare anode) were direct proportion relationship with the charging time (from the beginning to the 120 min). The peak current and stable densities of $\text{MnO}_2$/PANI/$\text{MnO}_2$ bioanode were much higher than that of $\text{MnO}_2$ modified bioanode. The higher peak current and stable produced, the more charge stored during the open circuit period.
The maximum peak current density (charging 120 min) of the MnO$_2$/PANI/MnO$_2$ composite anode was 56.6 mA cm$^{-2}$ and a stable current density 1.52 mA cm$^{-2}$. The maximum peak current density (charging 120 min) of the MnO$_2$ modified anode was 27.1 mA cm$^{-2}$ and a stable current density 0.79 mA cm$^{-2}$. The MnO$_2$/PANI/MnO$_2$ composite bioanode was able to accumulate 35% more charges than that of MnO$_2$ modified bioanode (2049.5 C m$^{-2}$) which was possibly due to the excellent PANI interlayer capacitive performance. It was clearly showed that the accumulate charges, peak and stable current of MnO$_2$/PANI/MnO$_2$ bioanode were all higher than that of MnO$_2$ modified bioanode, demonstrating that the addition of PANI interlayer substantially improved the capacitive performance of anodes. The PANI interlayer can provide electron "superhighways" for charge storage and delivery, which can overcome the limited conductivity of MnO$_2$ itself. The sandwich structure can ensure the high utilization of the electrode materials, facilitating the ion insertion/extraction to obtain a larger specific capacitance. The large specific capacitance is owing not only the unique sandwich structure of MnO$_2$/PANI/MnO$_2$ but also the synergic impact of both components of MnO$_2$ and PANI. Electron transport in the bioanode was affected by the two components of MnO$_2$ and PANI. The mechanism is that under the state of anode charging, biotic and abiotic reactions take place sequentially. Microbial oxidation of organic matter first generates electrons which are then transferred to the solid anode surface. For the MnO$_2$ modified bioanode, the electrons drive the reduction reactions between the oxidation states Mn$^{4+}$ and Mn$^{3+}$ [28]. However for the MnO$_2$/PANI/MnO$_2$ bioanode, both PANI and MnO$_2$ (two parts) can react with the electrons, resulting in the formation of...
two parts reduced products. In comparison to microbial reaction that liberated electrons from organic substrate, the abiotic reactions proceed at a faster rate. Under the state of anode discharging, the stored electrons are then released as a consequence of the two parts reduced products.

3.5. EIS

The Nyquist plots of MnO$_2$/PANI/MnO$_2$ anode, MnO$_2$ anode and bare anode in the MFCs with inoculation obtained using electrochemical impedance spectroscopy at the open circuit potential
were shown in the Fig. 5. In addition, based on the previous study, the interaction between the biofilm and anode surface is the vital for the overall anode performance. All of the Nyquist plots show similar curves containing a small semicircle at high frequency and an inclined line at low frequency. The resistance values contained the solution resistance (Rs) and the charge transfer resistance (Rct) within the electrode materials. As shown in Fig. 5, the Rs of the MnO2/PANI/MnO2 and bare anodes were 39.1 Ω and 49.8 Ω, respectively. However, the MnO2 anode had a large ohmic resistance about 55.8 Ω, due to the relatively low conductivity of MnO2. The MnO2/PANI/MnO2 anode exhibited the smallest value of Rct (67.7 Ω), while MnO2 modified anode showed the largest Rct (161.6Ω). This indicated the MnO2/PANI/MnO2 anode had a better charge transport behavior. The addition of interlayer PANI functionalized the MnO2 and increased the interfacial area and interfacial interactions between the anode surface and the microbial biofilm [29-33]. It suggested that a faster EET of the biofilm on the surface of MnO2/PANI/MnO2 anode than the MnO2 modified anode. Moreover, the MnO2/PANI/MnO2 not only improves the electrode conductivity but also provides more active point, which is owing to the hollow sandwich structure that hosts the microbe for more efficient electrocatalysis.

4. Conclusion

In summary, a sandwich structure MnO2/PANI/MnO2 capacitive bioanode was investigated in an MFC. Polarization curves, charging-discharging experiments, chronoamperometric experiments and the EIS experiments showed that MnO2/PANI/MnO2 bioanode has successfully made MFC function as a biocapacitor, able to store electrons produced organic substrate under the open circuit state and release electrons in a short time to overcome the mismatching of the production and demand of this electricity. The high conductivity polyaniline interlayer could increase more active surface area for microbe attachment and enhance the electron transfer. In this work, a MFC with a sandwich structure MnO2/PANI/MnO2 capacitive electrode it is possible to produce and store energy simultaneously.

Acknowledgment

The project was supported by National Natural Science Foundation of China (No. 21476053 and 51179033), the Doctoral Program of the Ministry of Education (No. 20132304110027).

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