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

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ABSTRACT

Sandwich-like structure of manganese dioxide and polyanilline and manganese dioxide (MnO_2/PANI/MnO_2) 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 polyanilline 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 MnO_2/PANI/MnO_2 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 MnO_2/PANI/ MnO_2 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 MnO_2/PANI/MnO_2 composite materials shows potential for storing energy from waste water and releasing in a short time to the electronic device.

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.

MnO_2 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 MnO_2 on the carbon felt. The addition of MnO_2 increased the capacitance of the anode. However, the poor electronic conductivity of MnO_2, 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 MnO_2 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/MnO_2 composite material for supercapacitor. Xu[15] used polypyrrole as interlayer to synthesize sandwich like structure of PtPd/PPy/PtPd, 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 studies 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-MnO_2 composites have been reported many times in the application of supercapacitors. However, the reports of these kinds of PANI-MnO_2 composites function as a capacitive bioanode in application of MFC are less. Ansari [19] has successfully

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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-likes 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 persulphate 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 persulphate 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-likes 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_2O_2 (10%), then in 0.5 M H_2SO_4, 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} $NaH_2PO_4.2H_2O$, 0.2 g l^{-1} $MgSO_4$, 0.13 g l^{-1} KCl, 2.75 g l^{-1} $Na_2HPO_4.12H_2O$, 0.56 g l^{-1} $(NH4)_2SO_4$, 0.31 g l^{-1} NH_4Cl, 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 spectra measurement, 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 (+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

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