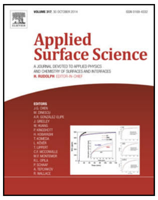
Applied Surface Science 317 (2014) 84–89

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc



Graphite coated with manganese oxide/multiwall carbon nanotubes composites as anodes in marine benthic microbial fuel cells

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ARTICLE INFO

Article history:
Received 19 June 2014
Received in revised form 22 July 2014
Accepted 8 August 2014
Available online 19 August 2014

Keywords:
Manganese oxide
Modified anodes
Kinetic activity
Electron transfer mechanism

ABSTRACT

Improving anode performance is of great significance to scale up benthic microbial fuel cells (BMFCs) for its marine application to drive oceanography instruments. In this study, manganese oxide (MnO_2)/multiwall carbon nanotubes (MWCNTs) composites are prepared to be as novel anodes in the BMFCs via a direct redox reaction between permanganate ions (MnO_4^-) and MWCNTs. The results indicate that the MnO_2/MWCNTs anode has a better wettability, greater kinetic activity and higher power density than that of the plain graphite (PG) anode. It is noted that the MnO_2 (50% weight percent)/MWCNTs anode shows the highest electrochemical performance among them and will be a promising material for improving bioelectricity production of the BMFCs. Finally, a synergistic mechanism of electron transfer shuttle of Mn ions and their redox reactions in the interface between modified anode and bacteria biofilm are proposed to explain its excellent electrochemical performance.

1. Introduction

Since microbial fuel cells (MFCs) are well-known as bioelectrochemical devices that harvest electrical energy from organic or inorganic matter via the catalyzation of some bacteria, which makes it obtain considerable attention from microbiological, environmental, and material researchers [1–3]. Reimers et al. [4] developed the novel concept of using marine benthic MFCs (BMFCs) as a remote source of power to drive instruments work for a long term. In general, the BMFCs consists of an anode which is buried under marine sediment (an anoxic zone), and connect by an electrical circuit to the cathode which is immersed in seawater (an oxic zone) [5–7].

Recently, many researchers have studied different methods and various types of materials for enhancing MFCs anode performance. Whereby (i) electroactive species such as anthraquinone-1,6-disulfonic acid (AQDS) [8], or (ii) highly conductive species such as conducting polymers [9] and metal particles [10] have achieved excellent performance. However, most of these methods are costly, time impractical and usually produce large amounts of contaminants that can add other environmental problems. Owing to the electro-catalytic ability of MnO_2 toward the oxygen reduction reaction (ORR), it is considered to be one of the most promising materials for the fabrication of MFCs cathode [11,12]. Carbon nanotubes (CNTs) are an excellent conducting additive or support template of MnO_2 for offering the advantage of low resistance, which is important for the fabrication of efficient electrode. To date, only few studies of applying MnO_2/CNTs composites in MFCs have been reported. Zhang et al. [13] used the MnO_2/CNTs cathode in MFC, and achieved a maximum power density of 210 mW m^{-2}. Similar results are reported by Chen et al. [14] also using MnO_2/CNTs cathode but coated on stainless steel mesh. To the best of my knowledge, few researches have been done on the performance of MnO_2/CNTs as anode material.

In this study, MnO_2/MWCNTs nanocomposites with different MnO_2 contents (25%, 50% and 75 wt %) were characterized and utilized as the BMFCs anode materials respectively. The performance of the as-prepared anodes was evaluated through comparison with that of the PG and MWCNTs. Scanning electron microscopy (SEM), contact angle measurement and Tafel plots were applied to characterize their structural and electrical properties. Furthermore, a possible mechanism was presented for the explanation of this work.

2. Materials and methods

2.1. MnO_2/MWCNTs nanocomposites preparation

The MWCNTs (30–50 nm in diameter, Shenzhen Nanotech Port Co., Ltd.) supported MnO_2 nanocomposites were prepared by the redox method as previously described [14–16]. The

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http://dx.doi.org/10.1016/j.apsusc.2014.08.044
0169-4332/

MnO_2/MWCNTs composites with different percentage of MnO_2 were obtained by changing the concentrations of $KMnO_4$. Firstly, 1 g of MWCNTs were added into the 400 mL $KMnO_4$ solution with different concentrations (0.009, 0.0287 and 0.086 M), and then stirred continuously at 70 °C for 6 h. During the synthesis, the pH of the solution was controlled at 1 by using 1 M HCl solution. The resulting colorless suspension was then filtered, washed several times using distilled water, and vacuum-dried at 100 °C overnight for further analysis. Assuming that MnO_4^- was completely reduced to MnO_2 in all cases, the desired MnO_2/MWCNTs with loading levels of 25, 50 and 75 wt.% should be correspond to the initial $KMnO_4$ solution of 0.009, 0.0287 and 0.086 M, respectively.

2.2. Electrode preparation

Four types (MWCNTs, MnO_2 (25%)/MWCNTs, MnO_2 (50%)/MWCNTs and MnO_2 (75%)/MWCNTs) of anodes (4 cm × 4 cm) were prepared by the following procedures. Firstly, 0.2 g of as-prepared powders was mixed with 5 mL Nafion solution to prepare pastes, then pasting on the surface of plain graphite (PG) to produce uniform films, finally pressing to fabricate electrodes. The control was the PG anode.

2.3. BMFCs construction

Five separate cells were constructed by using MWCNTs, MnO_2 (25%)/MWCNTs, MnO_2 (50%)/MWCNTs, MnO_2 (75%)/MWCNTs and PG anode respectively, each fitted with the same graphite cathode (4 cm × 4 cm, 2 cm thickness). In this setup, the cell was of cylindrical shape and made of plexiglass (7 cm in diameter, 20 cm in height). The natural seawater and marine sediment utilized here were fetched from the Jiaozhou Bay, Qingdao, China (36°10.3′ N, 120°18.1′ E). The anode was buried 5 cm below the sediment surface, with the cathode 10 cm above the anode. Each cell experiment was conducted in three parallels to obtain average values.

2.4. Analysis and calculation

The nanocomposite samples were structurally characterized by X-ray diffraction (XRD), using a Macscience-M18XHF Advance X-ray diffractometer. The morphologies of samples were compared with a scanning electron microscope (SEM, Hitachi S-4800). The water contact angle was measured by a contact angle meter (KRUSS DSA100).

Tafel plots were performed with an Electrochemical Workstation (Model LK2005A, TianJin Lanlike Co., Ltd.) at scan rate of 1 mV s^{-1} from $\eta = 0$–100 mV, where $\eta = 0$ is the open circuit potential (OCP) of the anode versus the reference electrode. Tafel plots were conducted in a conventional three electrode configuration: a saturated calomel electrode (SCE) served as the reference, the anode as the working and the cathode as the counter electrode [8]. When obtaining a steady voltage, the polarization curves and the power density curves were monitored by varying external resistances (40–7000 Ω). Anode potentials (vs. SCE) were measured using a digital multimeter (Shenzhen Huayi Instrument Co., Ltd.). Power (mW) was calculated by using the equation: $P = IV$, where I and V represent current (A) and voltage (V) respectively. Power density (mW m^{-2}) and current density (mA m^{-2}) were calculated by the anode projected surface area (1.6×10^{-3} m^2) [17].

3. Results and discussion

3.1. Structure characterization

XRD was first employed to confirm the successful fabrication of the MnO_2/MWCNTs composite. Fig. 1 shows the XRD patterns of the pristine MWCNTs and the MnO_2/MWCNTs composites. In the pattern of the pristine MWCNTs sample, two well-defined peaks are observed at around $2\theta = 26°$ and 44° associated with the (0 0 2) and (1 0 0) diffractions of the graphite (Fig. 1 (a)) [14]. From Fig. 1d, characteristic peak at $2\theta = 44°$ is also observed in both patterns of the MnO_2/MWCNTs composites, indicating the MWCNTs combined into MnO_2 have XRD signal nearly identical to the pristine. The intense diffraction peaks at $2\theta = 12°$, 37° and 66° in the pattern of the MnO_2/MWCNTs composite are matched well with the crystal planes of (0 0 1), (1 1 1) and (0 2 0) in MnO_2 (JCPDS 42-1317, MnO_2) respectively. This result indicates that birnessite-type MnO_2 has been successfully incorporated on the MnO_2/MWCNTs composites [15,16]. Additionally, it is noted that with the increasing of the MnO_2 contents, the peak at $2\theta = 44°$ is gradually decreasing. It also indicates the successful formation of MnO_2/MWCNTs composite.

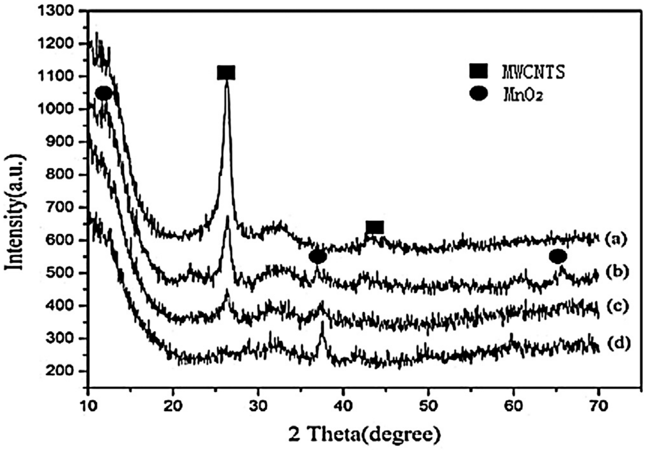

Fig. 1. X-ray diffraction patterns of (a) MWCNTs and MnO_2/MWCNTs nanocomposites with different MnO_2 contents: (b) 25%, (c) 50% and (d) 75%.

SEM was used to monitor the morphological characteristics of the MnO_2/MWCNTs composite. Fig. 2 presents the SEM images of the MWCNTs before and after MnO_2 deposition. From Fig. 2, it can be seen that the unmodified MWCNTs are in the form of the small bundles with a diameter of 30–50 nm. Upon reaction with $KMnO_4$, the MWCNTs are uniformly decorated with the particles on their surfaces, as shown in Fig. 2b–d, indicating the deposited MnO_2 on the MWCNTs are in the form of particles. However, it is noted that there is no obvious change of the surface morphology of the MWCNTs upon the incorporation of MnO_2 particle. Also, with the increasing of the contents of MnO_2 from 25% to 75%, the surface coverage of the MnO_2 particles is enhanced.

3.2. Wettability of the anode surface

Water contact angle measurements were used to investigate the wettability of the MnO_2/MWCNTs modified anode surface [18,19]. In Fig. 3, photographs are shown of the water droplets on a variety of the different modified electrode surfaces. Compared to that of the bare PG electrode (145°) and the MWCNTs modified electrode (137°), the contact angles of the MnO_2/MWCNTs modified electrode surfaces are greatly decreased (49° for 25% MnO_2/MWCNTs, 55° for 50%MnO_2/MWCNTs, 65° for 75%MnO_2/MWCNTs). This suggests that the modification method can lead to the formation of a hydrophilic surface. It should result from the hydrophilic functional group (i.e., —OH) introduced by the modification layer of MnO_2 on MWCNTs. The MWCNTs surface may have a little amount of hydrophilic oxidative group [20], but from Fig. 3, its contact angles still