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ORIGINAL RESEARCH PAPER

Effect of carbon nanotube modified cathode by electrophoretic deposition method on the performance of sediment microbial fuel cells

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Abstract A multi-walled, carbon nanotube (MWNT)-modified graphite felt (GF) cathode was fabricated to improve the performance of sediment microbial fuel cells (SMFC). Three types of MWNT-modified GF cathodes were prepared by different electrophoretic deposition (EPD) times. Maximum power density of SMFC with MWNT-GF*** cathode at 60 min EPD was 215 ± 9.9 mW m^{-2}. This was 1.6 times that of SMFC with a bare GF cathode. Cyclic voltammetry and the amount of biomass showed that biomass density and electrochemical activity increased as the electrophoretic deposition time extended. Therefore the electrode possesses the highest catalytic behavior toward O_2 reduction reaction. This simple process of carbon nanotube modification of a cathode by EPD can serve as an effective technique to improve the performance of SMFC.

Keywords Carbon nanotube · Cathode · Electricity production · Electrophoretic deposition · Fuel cell · Sediment microbial fuel cell

Introduction

Microbial fuel cells (MFCs) utilize anode-respiring microorganisms (Logan and Regan 2006) as catalysts. They can generate electricity from the oxidation of organic or inorganic matter. The sediment microbial fuel cell (SMFC), with its anode embedded in the anaerobic sediment and its cathode suspended in

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aerobic water, is an adaptation of reactor-type MFCs (Reimers et al. 2001; Bond et al. 2002). SMFC could be utilized as power production for wireless sensor (Donovan et al. 2008, 2013) and sediment bioremediation (Hong et al. 2010; Song et al. 2010). However, several important challenges need to be resolved for its practical application.

A low O_2 reduction rate in the cathode is an important limiting factor for SMFC. An obvious resolution method is to apply a catalyst at the cathode. Platinum was used as catalyst for cathode to increase the rate of O_2 reduction (Reimers et al. 2001; Rezaei et al. 2007). However, Pt is too expensive (Cheng et al. 2006) and is easily poisoned by reacting with sulfide and organics making it unsuitable for large-scale applications. Biocathodes are good alternatives (De Schamphelaire et al. 2010; Song and Jiang 2011) compared to chemical cathodes. In a biocathode SMFC, O_2 can be effectively reduced via the catalysis of electrochemically-active microorganisms. Therefore, bicathodes have the important advantage of low cost, resistant to poisons and are continuously self-renewed. The characteristics and configuration of biocathode materials can affect extracellular electron transfer on the biocathode. Thus, modification of biocathodes surface can affect SMFC performance.

Carbon nanotubes (CNTs) have been evaluated as possible electrodes in MFCs (Liang et al. 2011; Sharma et al. 2008) due to their unique properties, such as higher active surface area, excellent conductivity, good adhesion for bacteria. However, few studies have focused on CNT-modified electrodes in SMFCs. In order to increase its limited output power, SMFCs require a larger electrode surface. Therefore, the uniformity of the electrode catalyst and simplicity of the process become key factors to judge CNT modifications of the electrode in SMFCs. Electrophoretic deposition (EPD), which has the advantage of process simplicity and thickness control, is an effective technique in the deposition of CNTs on to the desired electrode surface (Boccaccini et al. 2006).

In this study, CNTs were deposited on cathode by the EPD technique and the impact of EPD time was evaluated on the performances of SMFCs. The morphological structure of the electrode was characterized by scanning electron microscope (SEM). In addition, electrochemical properties of electrode were deeply analyzed to explain the differences in SMFC performance.

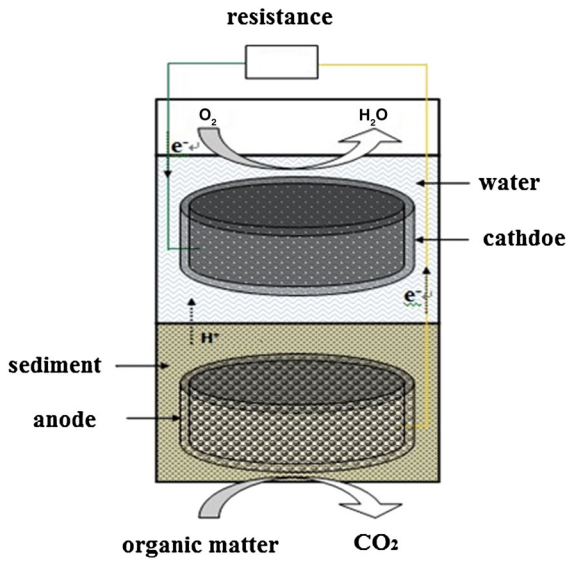

Fig. 1 Schematic detail of configure of SMFC in this study

Materials and methods

Electrode preparation

Multi-walled carbon nanotubes (MWNTs) purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen China) were refluxed by sonicating in a mixture of concentrated 16 M HNO_3 and 18 M H_2SO_4 (1:3, v/v) at 80 °C for 1 h. Then MWNTs were then washed with deionized water until the filtrate was neutral. They were dried under a vacuum. The 0.5 g acid-treated MWNTs were ultrasonically dispersed in 500 ml water (1 mg MWNTs ml^{-1}) for 0.5 h at 25 °C. Two pieces of graphite felt (GF) (200 mm × 50 mm × 30 mm), wherein one was used as the cathode and the other was used as the anode, were immersed into the suspension of MWNTs in parallel. The distance between two electrodes was 30 mm. A DC power supply of 32 V was applied to the two electrodes for 10–60 min. The MWNTs began to deposit on the GF of anode. Then GF-MWNTs electrode was taken from the suspension and dried in a vacuum before using as the cathode in SMFCs. Cathodes with the different EPD deposition times, GM10 (10 min), GM30 (30 min) and GM60 (60 min) were tested. In addition, bare GF was used as control.

SMFCs construction and operation

The sediments (0–10 cm below the sediment–water interface) were obtained from Jinchuan River in

Nanjing, China and passed through a 0.5 cm sieve to remove coarse debris. The loss on ignition (LOI) of the sediment was 3.2 % (w/w). SMFCs were constructed in glass beakers, 11 cm diam. 15 cm ht (Fig. 1). The GF anode was buried below the sediment–water interface and the cathode was suspended in overlying water. SMFCs were operated at a fixed external resistance of 1,000 Ω and maintained at 25 °C. The 0.5 % (w/w sediment) *Acorus calamus* leaves were added to the sediment to improve the mass transfer rate in the anode region (Song et al. 2014). The SMFCs were operated in duplicate under each experimental condition.

Analysis

Cyclic voltammetry (CV) was performed on a potentiostat (CH Instruments, Chenhua Instrument Co., China) with Ag/AgCl as a reference electrode, the cathode as a working electrode and the anode as a counter electrode. The potentials were shifted from −600 to 600 mV at a scan rate of 10 mV s^{-1}. The output voltage of SMFCs was automatically recorded using a precision multimeter and a data acquisition system (Keithley Instruments 2700, USA). The external resistor was varied from 50 to 2,000 Ω to obtain the polarization curves (Logan et al. 2006). Voltage was converted to power density based on the foot print area of the anode (Reimers et al. 2001). The morphologies of the electrode surfaces were studied by using a scanning electron microscope (SEM). The LOI of the sediment was determined by weighing the sample before and after combustion at 550 °C for 4 h (Song et al. 2010). The biomass of the cathode biofilms was measured using phospholipids analysis by modified Lowry method (Findlay et al. 1989) and the biomass concentration was expressed as the mass of phosphrous per cathode surface area.

Results and discussion

Electrode characterization

SEM images (Fig. 2) of GFs, which were coated with MWNTs by EPD with various processing times (10–60 min), confirmed the formation of the uniform MWNTs nanoporous network on the surface of GFs, while the control cathode had a smooth and clean surface. The optimum time for deposition was 60 min.

To verify the MWNTs had been attached to the GF, the electrodes were weighed before and after the electrophoretic deposition (Table 1). The result confirmed that the amount of MWNTs coated on the GF increased with the electrophoretic deposition time. The increased weight of GF coated by EPD for 60 min was much higher than others; it was approximately 2.4 times than that coated for 10 min.

SMFC performance

The variation of SMFC voltage outputs with various cathodes are shown in Fig. 3. The voltage from all applied SMFCs was low during the first 3 days of operation, and then voltage outputs of SMFC with GM60 cathode sharply increased and stabilized at about 580 mV on day 12. A slightly lower voltage of 540 mV was obtained in SMFC with GM30 cathode and SMFC with GM10 cathode reached maximum voltage of 502 mV on day 18. The SMFC with control cathode had a much slower increasing in voltage and produced the lowest maximum voltage (450 mV). These results indicated that the GF with MWNTs decorated can effectively improve the SMFC performance.

O_2 reduction is a combination of chemical and biological catalytic process in cathode of SMFC. In order to distinguish the effect of each process, the maximum power density (P_{max}) of each SMFC was measured with and without biomass attachment by two methods described previously (Song and Jiang 2011) at the end of the experiment (Fig. 4). In the first method, the effects of both chemical and biological catalytic processes were obtained. P_{max} was measured by a biocathode that have been operated in each SMFC for 30 days. Clearly, the SMFC with the control cathode produced a lower P_{max} (135.4 ± 10.9 mW m^{-2}), followed by SMFC with GM10 cathode (159.9 ± 10.5 mW m^{-2}) and with GM30 cathode (186.2 ± 3.9 mW m^{-2}). The highest P_{max} of 214.7 ± 9.9 mW m^{-2} was produced by SMFC with the GM60 cathode, which was approx. 1.6 times that of SMFC with control cathode.

In the second method, the cathode in each SMFC for a 30 days run was sterilized and then used for P_{max} determination. Therefore, only the chemical catalytic effect was reflected in the P_{max} value. Compared with

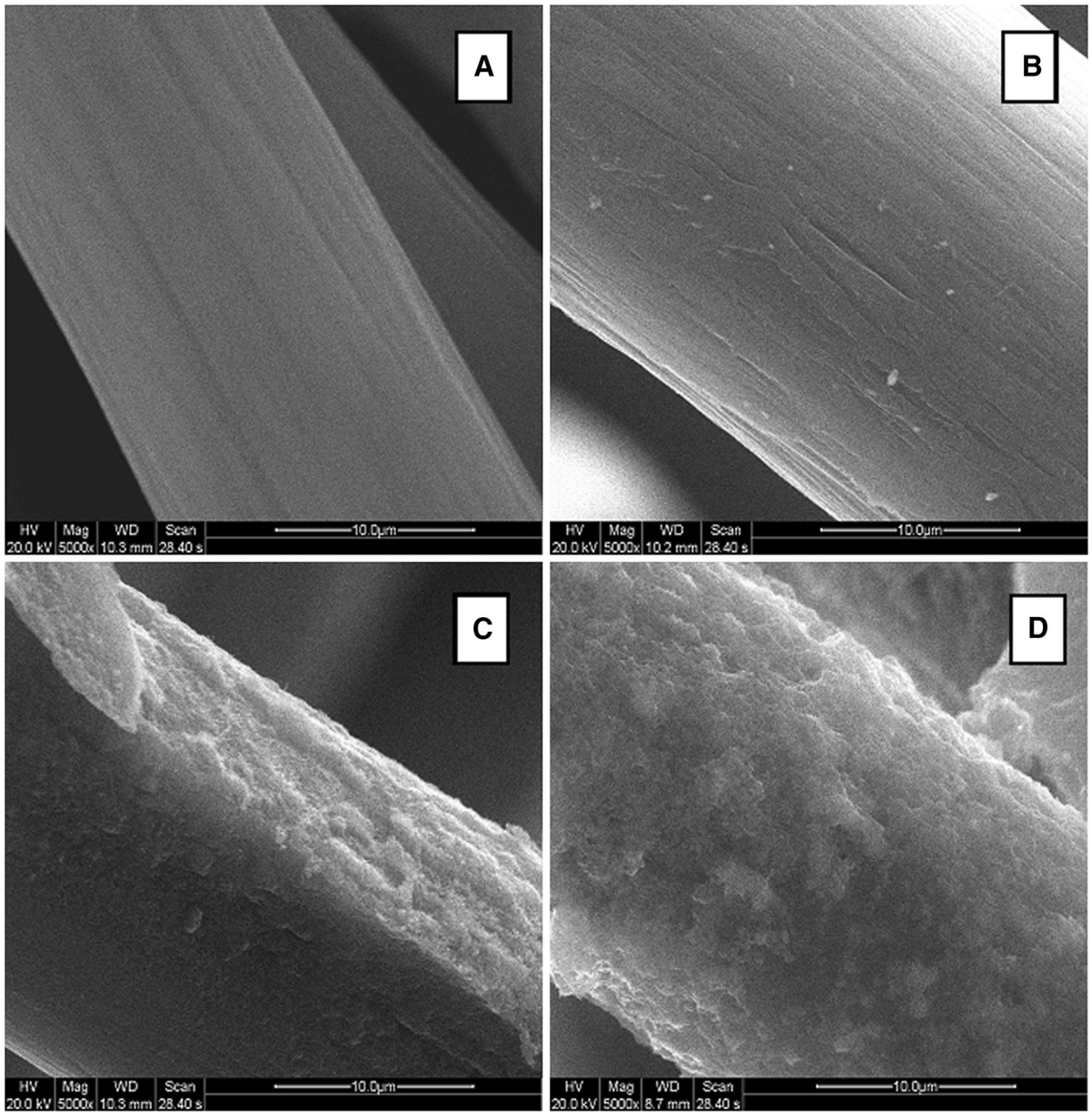

Fig. 2 SEM images of the different cathodes. **a** Control, **b** GM10, **c** GM30, **d** GM60

Table 1 MWNT content on cathode under different electrophoretic deposition time

Electrophoretic deposition time (min)	10	30	60
MWNT loading amount (%)	0.69 ± 0.05	1.24 ± 0.08	1.68 ± 0.1

the biocathode SMFCs, the P_{max} of abiotic cathode SMFCs decreased about 50 %, implying that bacteria in cathode were carrying out O_2 reduction. The highest P_{max} (100.8 ± 4.0 mW m^{-2}) and the lowest P_{max} (68.4 ± 9.3 mW m^{-2}) was still produced by SMFC with the GM60 cathode and SMFC with control cathode, respectively. The former is 1.5 times than that of the latter. The results showed that MWNT modified

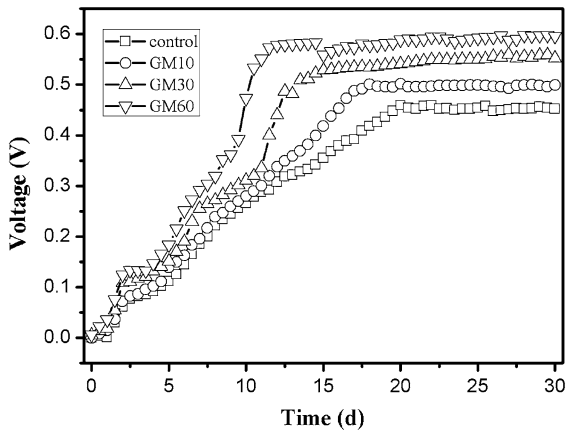

Fig. 3 Voltage generation of SMFCs produced by different electrode configurations during the 30 days of operation

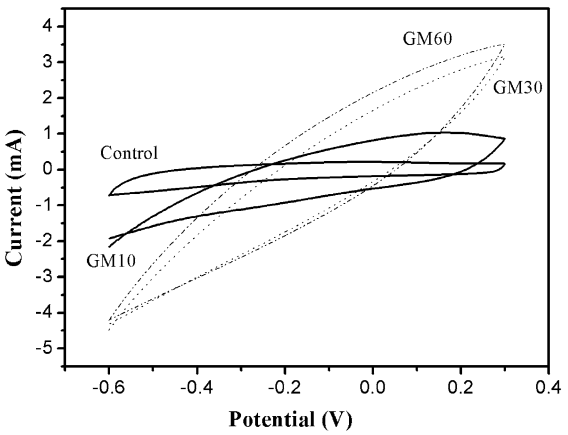

Fig. 5 Cyclic voltammograms of the different cathode

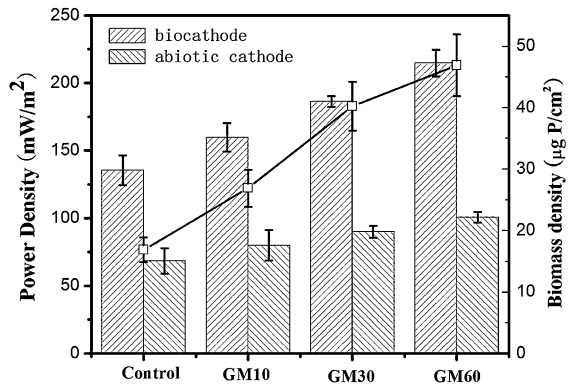

Fig. 4 Biomass densities in the compartments of biocathode and maximum power densities of SMFC with biocathode and abiotic cathode

cathodes were improved the performance of SMFC by enhancing chemical/biological catalysis of O_2 reduction.

To analyze the effect of biomass on cathode performance, the biomass densities were also calculated (Fig. 4). The highest amount of biofilm on the GM60 cathode was 46.9 ± 5 μg P cm^{-2}, which was more than that of the control. In addition, the relationships between P_{max} and biomass densities for the SMFCs with different cathode were evaluated through linear regression (data not shown). The power density had positive correlations ($r^2 = 0.99$) with biomass densities. The results indicated that an increased amount of biomass densities would improve the P_{max} of SMFCs. In addition, the biomass densities increased as the electrophoretic deposition time extended. It implied that electrophoretic deposition of MWNTs on GF electrode was in favor of microbial adsorption, thereby increased the effect of biological O_2 reduction.

Characterization of cathode biofilm

CV was used to evaluate the catalytic behavior of the biocathodes. As shown in Fig. 5, SMFC with the GM60 cathode gave maximum current in both the forward scan (3.4 mA) and reverse scan (−4.2 mA), followed by SMFC with the cathode GM30 (3.1, −4 mA) and GM10 (1, −2.1 mA). Relatively lower current output (0.9, −0.7 mA) was recorded in SMFC with the control cathode. This result indicated that the GM60 cathode possessed the highest catalytic behavior toward O_2 reduction reaction than that of the control, which was consistent with the power generation. Therefore, the electrochemical activity of the cathode biofilm is promoted by MWNTs and the electrochemical activity is enhanced as the electrophoretic deposition time extended. Combined with SEM and biomass densities calculation, the results implied that the three-dimensional nanostructure facilitated the attachment of microorganisms to the MWNTs coated GF electrode, thus enhanced the O_2 reduction reaction of cathode.

Significance and potential of MWNT-GF biocathode in SMFCs

The P_{max} of SMFCs is usually 10–20 mW m^{-2} of anode electrode surface (Lowy et al. 2006) and the

higher P_{max} of SMFCs can be obtained in the marine environment (Tender et al. 2002; Reimers et al. 2006). Output power can be increased by enhancing mass transfer rate in the anode region (Rezaei et al. 2007; De Schamphelaire et al. 2008). De Schamphelaire et al. (2014), proposed that the addition of biomass can increase organic matter and enhance cellulase activity, thus increasing SMFC output power. In this study, the biomass was added to the anode region in SMFC in order to keep a high mass transfer rate, while cathode was modified by MWNTs to enhance O_2 reduction rate. The P_{max} of SMFC increased to 214.7 mW m^{-2} of electrode footprint area. This was 1.6 times relative to that of the SMFC with the control cathode. Furthermore, the results also indicate that the electrophoretic deposition of MWNTs on GF is a simple and efficient method to modify cathode in SMFCs for large scales. MWNT has high specific surface areas and high electrical conductivity, so it can be used as an excellent catalyst for electrode. By alteration of the EPD process time, high performance biocathode can be obtained.

Conclusion

As a novel electrode-modifying method, electrophoretic deposition of MWNTs on GF, was employed to the biocathode in SMFCs. The SMFC with MWNT-GF biocathode exhibited better SMFC performance than that of the SMFC with bare GF cathode. When the electrophoretic deposition time was 60 min, the maximum power density of SMFC was 214.7 ± 9.9 mW m^{-2}, which was approx. 1.6 times that of SMFC with bare GF cathode. In addition, MWNT coating GF offers a good prospect for biocathode application in SMFC. Further studies are necessary to optimize the type of catalyst used in EPD process and to examine the synergy mechanism between microorganisms and catalyst on the cathode.

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