Journal of Power Sources 272 (2014) 277–282

Contents lists available at ScienceDirect

Journal of Power Sources

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

Tubular bamboo charcoal for anode in microbial fuel cells

Jun Zhang [a, b], Jun Li [a, b, *], Dingding Ye [a, b], Xun Zhu [a, b], Qiang Liao [a, b], Biao Zhang [a, b]

[a] Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400030, China
[b] Institute of Engineering Thermophysics, Chongqing University, Chongqing 400030, China

HIGHLIGHTS

- Bamboo charcoal tube as the anode material was firstly applied in MFCs.
- The C–N and C=O bonds on the bamboo charcoal surface were detected.
- The bamboo charcoal anode showed better biocompatibility and performance.
- The laboratory scale-up of the bamboo charcoal tube anode was demonstrated.

ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form
6 August 2014
Accepted 26 August 2014
Available online 4 September 2014

Keywords:
Microbial fuel cells
Bamboo charcoal tube
Carbonization
Scale-up

ABSTRACT

The anode material plays a significant role in determining the performance of microbial fuel cells (MFCs). In this study, the bamboo charcoal tube is proposed as a novel anode substrate by carbonizing the natural bamboo. Its surface functional groups, biocompatibility and internal resistance are thoroughly investigated. Performance of the MFCs with a conventional graphite tube anode and a bamboo charcoal tube anode is also compared. The results indicate that the tubular bamboo charcoal anode exhibits advantages over the graphite tube anode in terms of rougher surface, superior biocompatibility and smaller total internal resistance. Moreover, the X-ray photoelectron spectroscopy (XPS) analysis for the bamboo charcoal reveals that the introduced C–N bonds facilitate the electron transfer between the biofilm and electrodes. As a result, the MFC with a bamboo charcoal tube anode achieves a 50% improvement in the maximum power density over the graphite tube case. Furthermore, scale-up of the bamboo charcoal tube anode is demonstrated by employing a bundle of tubular bamboo charcoal to reach higher power output.

1. Introduction

Microbial fuel cells (MFCs) are novel devices that use bacteria as a biological catalyst to directly convert the chemical energy to electrical energy from organic wastes [1–3]. However, the major limitation for widespread practical applications lies in the relatively low power density [4–8]. In MFCs, the anode characteristics (material, structure and arrangement) play a key role in determination of the bacteria attachment, biofilm enrichment, substrate oxidation and electron transfer between the microorganisms and the electrode, thus significantly affecting the MFC power output.

Over the past decades, several types of commercially available carbon-based porous materials have been used as the anode, such as carbon cloth, carbon paper, carbon foam, granule graphite and graphite fiber brush [9–11]. These anodes achieved good performances due to their high electrical conductivity, strong biocompatibility and appropriate mechanical strength [12]. However, further improvement in the performance is limited by the micropore architecture (pore diameter less than 10 μm) inside the material, which hinders the bacterial colonization due to the confined space. More importantly, even the attached bacteria may die off due to substrate undersupply within the micropores, further decreasing the electro–catalytic activities of the biofilm. In addition, it was also reported that the small pores inside manganese modified kaolin electrodes can be clogged easily by rapid microbial growth [13]. To avoid this limitation, numerous open macro-scale porous anode materials, including nanoweb–reticulated vitreous carbon (RVC) [14], polyurethane-sponges [15] and carbon nanotube (CNT)-sponges [16] have been proposed. These macroporous scaffolds conduced to the uniform biofilm coverage without the clogging problem and good mass transfer between the solution and the biofilm, therefore promoting the MFC power output.

* Corresponding author. Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400030, China.
Tel./fax: +86 23 6510 2474.
E-mail addresses: lijun@cqu.edu.cn, junli.cqu@gmail.com (J. Li).

http://dx.doi.org/10.1016/j.jpowsour.2014.08.115
0378-7753/

In recent years, researchers have paid an increasing attention to the eco-friendly and straightforward porous electrode material fabricated by carbonization of natural resources, due to their inherent porous architecture, economic sustainability. Chen et al. [17] demonstrated that the three-dimensional macroporous kenaf anode showed higher electrochemical activity and better performance than the graphite rod. They also described that the anode carbonized with layered corrugated carbon boosted the anode performance and current generation for microbial bioelectrochemical systems (BES) [18], clearly suggesting that the carbonization of natural materials is an effective way to develop novel porous anode materials.

Bamboo is a tribe of flowering perennial evergreen plants and is also the fastest-growing plants in the world. It is native in China (especially in south of China) and is widely distributed in the Asian-Pacific region. Bamboo charcoal, carbonized from bamboos, has been employed in filtration and purification of toxic gas for a long time due to its high specific surface area and strong adsorption capacity. More importantly, it was noted that these features also fulfill the requirement of the MFC anode, implying the bamboo charcoal can be a potentially promising anode material. However, little attention has been paid towards its application. Yang et al. [19] firstly used the bamboo charcoal as the anode in a membrane-less and single-chamber MFC, but they only studied the cathodic Pt loading rather than the anode. Moqsud et al. [20] investigated the bioelectricity generation with various electrode materials, and suggested that the bamboo charcoal was comparable with the carbon fiber. Nevertheless, the potential advantage of the bamboo charcoal as an anode material has not been demonstrated.

In the present study, considering the hierarchical structure of macropore to micropores, a bamboo charcoal tube carbonized from a natural bamboo tube was used as the anode material in a two chambered MFC. A series studies including scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), colony-forming units (CFU), electrochemical impedance spectroscopy (EIS), start-up process and MFC performance were carried out. The corresponding results were also compared with the graphite tube anode. Furthermore, a scale-up experiment of the bamboo charcoal tube anode was conducted by employing a bundle of tubular bamboo charcoal as the MFC anode.

2. Materials and methods

2.1. Electrode material

A bamboo charcoal tube anode with 2 mm in internal diameter, 3 mm in external diameter and 24 mm in height was obtained through carbonization of bamboo tube which was collected from Chongqing University. Carbonization was conducted in a high temperature furnace (JQF1100-30, China) at 1000 °C for 2 h under a flow rate of N_2 atmosphere about 300 cm^3 min^{-1} [18]. For comparison, a conventional graphite tube with the same dimensions was also adopted as the anode in the same MFC. Additionally, the electrical conductivity of graphite tube and bamboo charcoal tube were tested using a two-point method. The graphite tube and bamboo charcoal tube showed a resistance of 16 and 25 Ω, respectively. A carbon cloth (E-TEK, B-1A, USA) with 50 mm in width and 164 mm in length was used as the cathode.

2.2. MFC configuration and operation

A tubular two-chamber MFC was manufactured using two cylindrical plexoglas tubes with 50 mm in height and 40 and 80 mm in internal diameter, respectively. The internal cylinder was drilled with well-distributed through-holes (5 lines × 11 rows, 0.50 cm in diameter) and was served as the anode chamber. To separate the anode and cathode, the outside of the internal cylinder was covered by a cation exchange membrane (CEM, CMI-7000, Membrane International, USA). A carbon cloth was fixed against to CEM. The volume of the anodic and cathodic compartment was 63 and 153 mL, respectively. An Ag/AgCl reference electrode (saturated with KCl, 0.198 V vs. SHE) was placed in the anode compartments. The graphite and bamboo charcoal tube anodes were fixed against to the inner wall of the anode chamber (Fig. 1a and b). To obtain reliable and reproducible results, two groups of graphite and bamboo charcoal tube anodes (each group had one graphite and bamboo charcoal tube anode with the same size) were synchronously fixed around the wall of anode chamber with angular separation of 90° (Fig. 1c) and this experiment was also repeated three times. To evaluate the individual performance of graphite and bamboo charcoal tube anodes, the titanium wire from the graphite and bamboo charcoal tube anodes were electrically isolated from each other, and were connected to the common carbon cloth cathode through separate resistors. Additionally, for scale-up of the anode, each bundle of bamboo charcoal tube was placed with an electrode center spacing of 4 mm.

The tubular MFC was inoculated with the effluent from an MFC which have been operated for over two years. The anolyte containing 0.68 g L^{-1} sodium acetate and 6 g L^{-1} Na_2HPO_4, 3 g L^{-1} KH_2PO_4, 0.1 g L^{-1} NH_4Cl, 0.5 g L^{-1} NaCl, 0.1 g L^{-1} $MgSO_4 \cdot 7H_2O$, 15 mg L^{-1} $CaCl_2 \cdot 2H_2O$, and 1.0 mL L^{-1} trace elements solution were fed and a 50 mM potassium ferricyanide [$K_3[Fe(CN)_6]$] solution was provide as the catholyte. Both the anolyte and catholyte were pumped at a flow rate of 3 ml min^{-1} under continuous-flow condition. The external resistance of every anode was fixed at 3000 Ω during the start-up and operation process. All tests were performed at a temperature of 30 ± 1 °C.

2.3. Data acquisition and calculation

The morphologies of the anode surfaces were analyzed by a TESCAN VEGA3 SBH SEM. The relative percentage of surface elements were obtained by XPS (XSAM800, Kratos Co, UK) and XPS peak was fitted using XPSPEAK v3.1 software.

The total number of active bacteria was estimated by CFUs [21,22]. The effluent from a running MFC fed by acetate was used as the bacterial suspension. The graphite and bamboo charcoal tube electrodes were suspended in the anode chamber filled with the bacterial suspension for 48 h. Then the electrodes were taken out and washed by phosphate buffer to remove loosely adhering cells. Subsequently, the bacterial cells on the electrodes were dispersed into 1 mL sterile phosphate buffer by ultrasonication for 10 min. The total viable counts were obtained using an inverted fluorescence microscope (IX81, Olimpus) to observe bacterial colonies in the phosphate buffer.

Electrochemical impedance spectroscopy (EIS) measurements were conducted using a Zennium electrochemical workstation (Zahner, Germany) with graphite and bamboo charcoal tube anode acted as the working electrode, the carbon cloth as the counter electrode and an Ag/AgCl as the reference electrode. EIS tests were performed with a frequency range from 10^5 Hz to 10^{-2} Hz over perturbation amplitude of 10 mV and the external resistances were 3000 Ω.

The primary voltages of the MFC were recorded using a data acquisition system every 10 s (Agilent 34970 A, The Netherlands). Polarization and power densities curves were plotted through adjusting external resistance from 10000 to 300 Ω. The cell voltage was recorded when the MFC reached a relatively steady-state (<1 mV min^{-1}) for at least 30 min. The areal power density of the MFC was calculated as $P = UI/A$, where A is surface area of the