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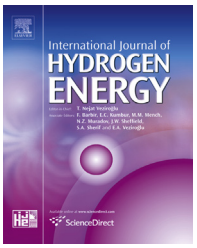

Appropriate mechanical strength of carbon black-decorated loofah sponge as anode material in microbial fuel cells

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ABSTRACT

A new composite anode material, possessing an appropriate mechanical strength, was fabricated by depositing carbon black on the loofah sponge matrix surface. Carbon black was oxidized in nitric acid (HNO_3) and hydrogen peroxide (H_2O_2), respectively, to increase electrochemical properties before starting deposition. Microbial fuel cell (MFC) with the H_2O_2 treated carbon black anode achieved the maximum power density of 61.7 ± 0.6 W/m^3, which was higher than one decorated with the HNO_3 treated or untreated carbon black. Scanning electron microscopy (SEM) observation showed a compact bacterial attachment on the H_2O_2 treated carbon black surface. Results of electrochemical impedance spectroscopy (EIS) and Tafel plots indicated a fast electron transfer rate between the H_2O_2 pre-treatment of carbon black and electrochemically active bacteria (EAB). Therefore, the H_2O_2 treated carbon black-loofah sponge anode was promising for MFC application in terms of its superior performance, straightforward fabrication method and ultra-low cost.

Introduction

The characteristic of electricity production and simultaneous wastewater treatment for microbial fuel cells (MFC) has drawn much research attention recently [1,2]. MFC is a promising technology, in which microbial oxidation of organic matter and biomass can directly convert chemical energy into electricity energy. However, low power density has been one of the bottlenecks for the MFC application. The anode performances play a crucial role on the overall performance of MFCs. Among many anode performance-limiting issues, the anode material is a one of the significant factor, which can affect bacterial growth, electron transfer and substrate supply. Therefore, high-performance anode materials are highly desired.

For this purpose, many efforts were made to develop a new three-dimensional (3D) anode material. Several 3D anode materials with good biocompatibility and large surface area were prepared for the promotion of bacterial growth. The carbon nanofiber mats with layered architecture were used for anode material to enhance biofilm growth [3]. A vitreous carbon foam acted as the anode showed a strong affinity for bacterial development and a steady power output [4]. The 3D nanocomposite anode was fabricated by the ice-segregation method and offered the hierarchical structure for bacterial colonization, thus resulting in a high power density [5]. In addition, some 3D electrode materials were also was synthesized to provide more catalytic site for enhancement of anodic electron transfer. The nickel-coated sponge was applied as the anode to encapsulate microbial

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cells producing excellent electrochemical activity and stabilized power output [6]. Owing to the more catalytic site, the MFC with the carbon nanotube-sponge electrode achieved the higher volumetric power density [7]. Overall, above-mentioned 3D anode materials electrodes provided a larger surface area for the bacterial attachment and anodic electron transfer compared with the commercial two-dimensional electrodes, such as carbon cloth [8] and graphite paper [9]. However, the high surface areas of those 3D electrodes were not fully used to current generation due to the micropore architecture inside the electrode materials, which hindered bacterial growth and substrate supply [10]. Furthermore, the high costs of material and fabrication for those electrodes limited practical application of MFCs. As a consequence, the macroporous and low-cost electrodes could be potentially promising anode materials.

In recent years, the macroporous structure electrodes could be fabricated by the carbonization of the materials with the natural porous architecture. The layered corrugated carbon (LCC) deriving from the carbonization of corrugated cardboard was served as electrode material [11]. As a typical macroporous structure electrode, the loofah sponge (LS) anode resulting from the cocarbonization of the polyaniline and LS was synthesized [12]. As compared to the traditional 3D anode, the macroporous structure of the carbonized LS anode allowed an unhindered substrate supply and product removal, thereby inducing a significant improvement of the anode performance. Whereas, it should be pointed out that carbonization technology can give rise to a decrease in the material's mechanical strength. Therefore, the mechanical fragility of the carbonized electrodes with macroporous structure was still technical challenges for the MFC application.

Carbon black deposition that give initial material's mechanical strength, good electronic conductivity, high specific surface area and low cost, was widely used as electrode decoration [6,7,13–15]. For the previous report, various carbon black coated material served as anode in MFCs showed good biocompatibility, high surface area and superior performance [16,17]. However, the most commonly applied carbon black Vulcan XC72 exhibited insufficient properties for bacterial oxidation due to its low electrocatalytic activity [18]. In conventional fuel cells, to overcome this problem, several studies of oxidative treated carbon black by nitric acid (HNO_3) or hydrogen peroxide (H_2O_2) displayed the higher electrocatalytic activity compared with the untreated carbon black [19,20].

In the present study, due to the inherent homogeneous macroporous structure and appropriate mechanical strength, a combination of LS and the high electrocatalytic activity of carbon deposition strategy would be proposed in MFCs. It is expected that the treated carbon black decorated LS, which possessed appropriate mechanical strength and a high electrocatalytic activity, might be applied to the anode material of the MFC. The performance of the MFCs with HNO_3/H_2O_2 treated carbon black decorated LS anode was investigated in terms of surface functional groups, the morphologies of the biofilm, electrochemical properties of the anodes and the power generation of MFCs.

Materials and methods

Anode material

The carbon black-coated LS were employed as anodes. The mature and naturally dry LS obtained from Hubei province in China were cut into cube shape (4 × 4 × 1 cm) and 0.5 g in weight (Fig. 1a). A commercial carbon black Vulcan XC72 (Cabot Co.) was treated with 100 mL of 65% (V/V) HNO_3 solution and 100 mL of 30% (V/V) H_2O_2, respectively, stirred for 24 h. The treated carbon black was subjected to filter/wash until water reached pH neutral and dried at 95 °C for 2 h. The treated and untreated carbon black was again heat treated under a nitrogen atmosphere using a high temperature furnace (JQF1100-30, China) with the following protocol: heating up to 300 °C at the rate of 5 °C/min and then heating up to 900 °C at a rate of 10 °C/min and annealing for 2 h. After heat-treatment, all carbon black was cooled under a nitrogen atmosphere until a temperature of 100 °C was achieved. Carbon black aqueous solution was prepared by adding 0.3 g carbon black and 8 mL isopropanol into 32 mL deionized water. The suspension could be well-dispersed by alternate stir and ultrasonication for 15 min at ambient temperature. The carbon black-coated LS were produced by alternately dipping the LS into carbon black aqueous solution for 2 min each. Between each immersing operation, the anode material was dried by thermolamp. A total carbon black loading on LS surface reached 0.4 g/g (Fig. 1b). The carbon black-LS composite anode exhibited outstanding mechanical properties (Fig. 1c).

MFC configuration and operation

Two-chamber MFCs were fabricated with plexiglass plates, separated by a cation exchange membrane (CEM, CMI-7000, Membrane International, USA). The volume of anode compartment was 25 mL (5 × 5 × 1 cm) and the cathode chamber had a serpentine flow channel with 2.7 mL. The MFC anodes modified with the untreated, the HNO_3 treated and the H_2O_2 treated carbon black were denoted as MFC-C, MFC-HNO_3 and MFC- H_2O_2, respectively. Carbon cloth (E-TEK, B-1A, America) with a working area of 25 cm^2 (5 × 5 cm) served as cathode electrodes. Titanium wires were used for electron collection.

The MFC anode chambers were inoculated with the effluent from an active acetate-fed MFC operated for over 2 year. The culture medium solution in the anodic chamber composed of 0.68 g/L sodium acetate, 6.0 g/L Na_2HPO_4, 3.0 g/L KH_2PO_4, 0.1 g/L NH_4Cl, 0.5 g/L NaCl, 0.1 g/L $MgSO_4 \cdot 7H_2O$, 15.0 mg/L $CaCl_2 \cdot 2H_2O$ and 1.0 mL/L trace elements solution. The cathode chambers were continuously provided 50 mM potassium ferricyanide served as electron acceptors at 1.5 mL/min, the same to the anolyte. All MFCs were operated with the external resistances of 50 Ω at 30 ± 2 °C in an environmental chamber.

Data calculation and analyses

The electrochemical impedance spectroscopy (EIS) and Tafel tests were performed with a Zennium electrochemical

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