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Full Length Article

Effect of in-situ immobilized anode on performance of the microbial fuel cell with high concentration of sodium acetate

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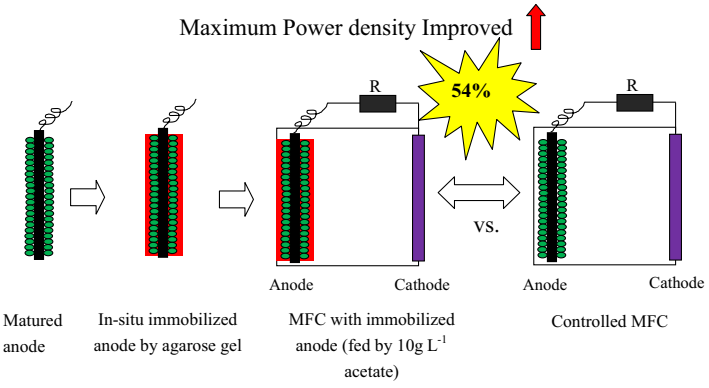
HIGHLIGHTS

- An efficient in-situ immobilization method was developed for anode of the MFC.
- The MFC with immobilized anode generated higher voltages than the control MFC.
- The MFC with immobilized anode produced higher power densities than the control MFC.
- The Geobacter abundance in the MFC with immobilized anode was higher.

GRAPHICAL ABSTRACT



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ABSTRACT

To improve performance of the microbial fuel cell (MFC) with high concentration of organics, a procedure for in-situ immobilized anode with agarose gel was proposed in this study. The performance of power generation, electrochemical activity, and microbial community of the MFC with immobilized anode (i-MFC) was investigated using different concentrations (i.e., 1, 5, 10, and 20 g/L) of sodium acetate. The i-MFC could generate electricity within one hour after refreshing substrate. With 5 g/L acetate, the maximum voltages were 560 and 460 mV in the i-MFC and controlled MFC (c-MFC), respectively. With 10 g/L acetate, the maximum voltage of the i-MFC was much higher than that of the c-MFC (500 vs. 300 mV). With the acetate concentrations of 5 and 10 g/L, the maximum power densities in the i-MFC were 610 ± 50 and 370 ± 40 mW/m^2, respectively, while the maximum power densities in the c-MFC were 343 ± 30 and 240 ± 20 mW/m^2, respectively. Cyclic voltammetry measurements indicated that microbial activity of the i-MFC anode was higher than that of the c-MFC anode under the high acetate concentration (3.00 vs. 2.19 mA). The relative abundance of *Geobacter* on the i-MFC anode was much higher than that on the c-MFC anode (62% vs. 40%). The in-situ immobilization strategy provided an easily performed and efficient way to keep the activity of exoelectrogens, resulting in the improvement of MFC performance.

1. Introduction

High concentrations of organics were often detected in many types of industrial wastewater, such as wastewater from process-

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ing plants of brewery, wine, and potato. Values of chemical oxygen demand (COD) of such wastewater change from 700 to 8000 mg/L [1,2]. Microbial fuel cell (MFC) was a kind of bioelectrochemical system (BES) that can generate electricity via organic biodegradation by electrochemically active bacteria [1]. Therefore, the MFC could be a promising approach to treat wastewater containing high COD concentrations, which should consume little energy or even generate electricity output (i.e., energy harvesting) [3]. However, the performance of MFC was affected by many factors, such as anode and cathode materials, reactor structure, substrates, exoelectrogens, and others [1]. High concentrations of substrates could inhibit activity of exoelectrogens in the MFC. It had been shown that in a dual-chamber MFC constructed with *Geobacter sulfurreducens*, the maximum power densities decrease from 16 to 13 mW/m^3, and coulumbic efficiency (CE) from 46% to 23% with acetate concentrations from 5 to 20 mM [4]. In an MFC inoculated with *Shewanella putrefaciens*, the maximum current could not increase further as the initial concentration of lactate exceeded 200 mM [5]. Sharma and Li [6] demonstrated that the maximum voltages generated by a single-chamber air-cathode MFC inoculated with domestic wastewater increased with concentrations of acetate, ethanol, and glucose from 0.5 to 20 mM, but significantly decreased with concentrations of 20–35 mM. Therefore, under high organic concentrations, it should be necessary to improve the MFC performance for its potential applications in industrial wastewater treatment.

Cell immobilization methods, such as adsorption, covalent binding, and entrapment, had been shown to reduce the environmental pressure (e.g., high salinity, toxicity) to microbes and to keep high cell densities in the biofuel cells [7,8]. The entrapment method, in which polymers or inorganics were utilized to form a framework with cells, had the advantages of good mechanical strength and stability, tunable porosity, and others. Using the entrapment method to immobilize exoelectrogens on the anode could stabilize the MFC performance under severe environmental conditions. *Shewanella oneidensis* MR-1 had been immobilized with graphite and alginate granules in the MFC, resulting in 0.8–1.7 times higher CE than the control [9]. A method of one-step vapor deposition of silica had been used to immobilize *S. oneidensis* to form an aqueous sol-gel in the anode of MFC [10], which improved the maximum power density of MFC. A culture mixture in an air-cathode MFC had been immobilized using the polyvinyl alcohol and powdered active carbon to treat distillery wastewater [11]. The immobilized MFC could produce electricity of 72 mW/m^2 with the influent COD concentration of 3600 mg/L. The entrapment methods for the immobilized anode of MFC above included the following steps: mixing exoelectrogens with polymers and attaching the mixture to the electrode. Such methods may cause some problems, such as damage of exoelectrogens due to violently mixing between bacteria and polymers, and delay of electricity generation because of the time needed for the attachment. Therefore, an in-situ immobilization strategy should be more attractive in the MFC.

As a natural organic polymer (i.e., a linear polyscaccharide), which can be produced from marine red aglae [12], agarose has higher biocompatibility with lower cost than some of artificial polymers, such as polyvinyl alcohol. Compared with alignate and silica, agarose is more sensitive to temperature, thus easier to form gel for immobilization [13,14]. The objectives of this study were to develop an in-situ agarose immobilized procedure and to investigate the effect of in-situ immobilized exoelectrogens on the MFC performance under high substrate (acetate) concentration. The characteristics of immobilized and control MFCs, including power density, internal resistance, CE, and bacteria community, were determined and compared.

2. Materials and methods

2.1. Reactor construction and operation

The base anode of MFC was made of carbon cloth (W0S 1002, CeTech., Taiwan, China). Characteristics of the carbon cloth included 125 g/m^2, thickness of 360 μm, and effective area of 16 cm^2 (L × W = 8 cm × 2 cm) [15]. The carbon cloth was treated with 450 °C in a muffle furnace for 30 min before use. Plain carbon cloth was rolled into a cylindrical shape (diameter of 1 cm and height of 2 cm) with a plastic mesh (grid: 3 mm × 3 mm, thickness: 0.1 mm) as a separator to keep inner tunnels for bacterium growth. Platinum-catalyst air-cathode was made as previously described [16]. The perspex reactor had an effective volume of 28 mL with a diameter of 3 cm and a length of 4 cm. The anode and cathode were connected with an external resistance of 1000 Ω via titanium wire.

The inoculum was from effluent of a grit chamber in a municipal wastewater treatment plant (Datansha, Guangzhou, China). During the startup stage, when the voltage was lower than 20 mV, the reactors were refreshed with a solution including 1 g/L sodium acetate, 50 mM phosphate buffer, and vitamins [16]. After the reactors could generate the maximum voltage >500 mV for at least three cycles, the matured anodes in the MFCs were used for immobilization of exoelectrogens as follows.

2.2. Immobilization of exoelectrogens on the anode

A schematic diagram of the procedure for anode immobilization was shown in Fig. 1. One gram of agar was dissolved into 100 mL phosphate buffer solution by heating at 100 °C. After the agar gel was cooled down to 40 °C, the matured anode was quickly put into the solution. A sterilized knife was used to cut the immobilized anode to a cubic size of 2.5 cm × 1.5 cm (H × d) after the agar gel was totally solidified at 30 °C. The immobilized anode was washed several times with distilled water and then refilled into the reactor (i-MFC). Reactors with the matured anodes without the immobilization procedure were used as the control (c-MFC). The reactors were operated with 1, 5, 10, and 20 g/L of sodium acetate as the substrate. All tests were duplicated at 30 ± 2 °C.

2.3. Analysis and calculations

Voltages were measured across the external resistor every 15 min using a data electronic multimeter (DataTaker 85, Australia). The current in the circuit was calculated using Ohm's law, which was normalized with the cathode projected surface area

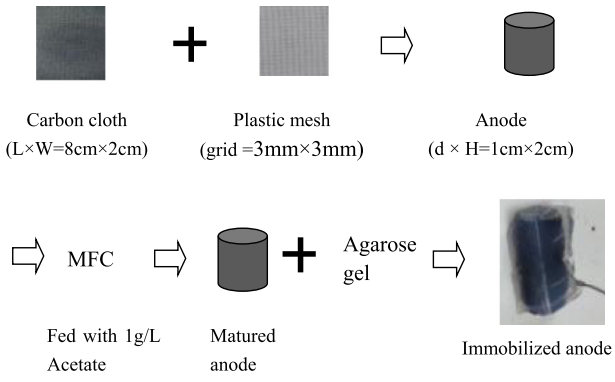

Fig. 1. The schematic diagram of the procedure to the anode immobilization in the microbial fuel cell.