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Which determines power generation of microbial fuel cell based on carbon anode, surface morphology or oxygen-containing group?

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ABSTRACT

To clarify the role of carbon surface nature in the power generation of microbial fuel cell (MFC) based on carbon anode, three carbon felt samples, obtained by simple water cleaning (CCF), heating (HCF) and oxidation with ammonium persulfate (ACF), were characterized with SEM, BET, FTIR, cyclic voltammetry and acid titration, and their performances as anode of MFC were investigated with polarization curve measurement, chronoamperometry and chronopotentiometry. It is found that the power output of MFC depends on the morphology rather than the oxygen-containing group concentration of the carbon felt surface. CCF, HCF and ACF have their surface oxygen-containing groups of 1.52, 0.8 and 0.45 mM m^{-2} and specific surface areas of 0.33, 0.65 and 1.19 m^2 g^{-1}, but yield their maximal power densities of 606, 858 and 990 mW m^{-2}, respectively. This study suggests that intensive attention should be paid to the design of surface morphology in order to improve power generation of MFC.

Introduction

Microbial fuel cell (MFC) has attracted much attention because it generates electricity using organic wastes [1]. In a MFC, electrons are produced at anode from the oxidation of organic matters, transferred via the external circuit and consumed at cathode [2]. Unlike small organic molecules-based fuel cell, in which noble metals such as platinum are necessary as anodic electrocatalysts [3,4], MFCs can generate electricity using non-noble metals [5–8]. MFCs generate electricity through several mechanisms, among which the mechanism involving direct electron transfer between anode and bacteria mainly contributes to the power output [9–11]. Therefore, improving the physical contact between anode and bacteria favors the power generation of MFCs.

Carbon materials are attractive as MFC anodes because of their biocompatibility and electronic conductivity [12–17].

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Some researchers believed that increasing the specific surface area of carbon materials improved the power output of MFCs due to the more space available for bacterium adherence on carbon [12,15,16], while others ascribed the improved MFC performance to the oxygen-containing groups on carbon surface, which adsorbs bacteria and favors the physical contact between carbon and bacteria [14,18–20]. It is understandable that carbon surface natures, including specific surface area and concentration of oxygen-containing groups, affect the power generation of MFCs based on carbon anodes. However, the carbon materials having large specific surface area do not mean they have large concentration of surface oxygen-containing groups. Therefore, the problem should be clarified: which determines the power generation of MFCs based on carbon anodes, specific surface area or surface oxygen-containing groups?

To clarify the role of carbon surface nature in the power generation of MFCs based on carbon anode, three carbon felt samples with various specific surface area and surface oxygen-containing group concentration were obtained by simple water cleaning, heating and oxidation with ammonium persulfate in this work, remarked as CCF, HCF and ACF, respectively. The resulting samples were characterized with SEM, BET, FTIR, cyclic voltammetry and acid titration and their performances as anode of MFC were investigated with polarization curve measurement, chronoamperometry and chronopotentiometry. *Escherichia coli*, which has been generally believed to catalyze the glucose oxidation in microbial fuel cell in the absence of any artificial electron mediators [10,21,22], was used as the bacteria for power generation.

Experimental

Anode treatment

Carbon felts (Beijing Carbonsci Tech. Co. Ltd) were cut to pieces with 3 cm × 3 cm to act as anodes. CCF was obtained by soaking the carbon felt pieces in methanol and distilled water for 12 h successively to remove possible organic and biomass contamination. HCF was obtained by heating CCF at 200 °C for 48 h. ACF was obtained by immersing CCF in 0.8 M ammonium persulfate solution (APS, 2 M H_2SO_4) for 24 h at ambient temperature. All the samples were rinsed with sterile water several times, as described in Ref. [23], before each experiment.

Bacterial cultivation

The *E. coli* DH5α was cultivated aerobically at 37 °C in a conical flask containing 250 mL standard Luria–Bertani medium (LB) for 12 h and then harvested by centrifugation at 4 °C (6000 rpm, 5 min). The resulting bacteria were washed several times and then suspended in 50 mM anaerobic phosphate buffer (pH 7.0) solution containing 2 g L^{-1} glucose [24].

MFC construction

A cube MFC was used, which consisted of a polymethyl methacrylate chamber (5.0 cm × 4.0 cm × 5.0 cm) and a membrane cathode assemble (MCA) on one side (3.0 cm × 3.0 cm). The MCA was made with carbon cloth hot-pressed on one side of a cation exchange membrane (CEM). 0.5 mg cm^{-2} commercial 20% Pt/C as cathode catalyst and polyvinylidene fluorine (PVDF) as binder were mixed by a weight ratio of 15:65 in 0.8 mL N-methyl-2-pyrrolidone to serve as cathode paint on the carbon cloth, as described in our previous report [25].

2 g L^{-1} glucose as electron donor in phosphate-buffered basal medium (PBBM), which consists of (per liter of deionized water): 5.8 g NaCl, 0.1 g KCl, 0.25 g NH_4Cl, 10 mL vitamin solution, 10 mL trace mineral solution and phosphate buffer (50 mM, pH 7.0), was added into anode chamber. To initiate the MFC experiment, the single chamber was inoculated with 10 mL cell suspension at 37 °C in a constant temperature incubator (HPG-280H, China), as described in Ref. [24].

Measurement and characterization

Electrochemical measurements were carried out on Solartron 1480. The polarization curve measurement, chronoamperometry and chronopotentiometry were performed in MFC with the carbon felt anode as working electrode, air cathode as counter electrode and Ag/AgCl (saturated with KCl) as reference electrode. Cyclic voltammetry was performed in a three electrode cell with the carbon felt as the working electrode, An Ag/AgCl (saturated with KCl) as the reference electrode and a platinum plate as the counter electrode.

Titration methods were used to determine the concentrations of surface oxygen-containing groups [26–31]. Typically, 30 mg carbon felt was shattered and soaked in 25 mL of 10^{-3} M NaOH solution for 16 h, and then 20 mL filter effluent was titrated with 10^{-3} M HCl solution.

The surface morphologies were observed by the Field-emission-type scanning electron microscopy (FESEM; ZESISS ULTRA 55) and specific surface area of the samples was determined using Brunauer–Emmett–Teller (BET) method on the Carlo Erba Sorptometer, in which N_2 adsorption at 77 K was applied. FTIR was performed on Perkin–Elmer Spectrum RX-1, USA.

Results and discussion

Power generation of MFCs

Fig. 1 presents the polarization curves (Fig. 1(A)) and power outputs (Fig. 1(B)) of MFCs with different anodes. It can been seen from Fig. 1 that the treatment conditions of carbon felt anodes affect significantly the anodic activity or the power generation of MFC. The MFC using ACF anode delivers a power density of 990 mW m^{-2}, about 1.6 times that of the MFC using CCF anode (606 mW m^{-2}), 13% larger than that of the MFC using HCF anode (858 mW m^{-2}), as shown in Table 1. The power densities reported in this paper were on the base of apparent areas of the electrodes. This result suggests that the anodic activity is in the order of ACF, HCF and CCF.

To confirm the different anodic activity of carbon felt treated under different conditions, chronoamperometry and