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Short communication

A polypyrrole/anthraquinone-2,6-disulphonic disodium salt (PPy/AQDS)-modified anode to improve performance of microbial fuel cells

Chunhua Feng[a,*], Le Ma[a], Fangbai Li[b], Hongjian Mai[a], Xuemei Lang[a], Shuanshi Fan[a]

[a] *The Key Lab of Enhanced Heat Transfer and Energy Conservation, Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China*

[b] *Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, PR China*

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ABSTRACT

This study reports a new approach of improving performance of microbial fuel cells (MFCs) by using a polypyrrole/anthraquinone-2,6-disulphonic disodium salt (PPy/AQDS)-modified anode. The immobilization of AQDS on a carbon felt anode was accomplished by electropolymerization of pyrrole while using AQDS as the dopant. The dual-chamber MFC operated with this modified anode in the presence of *Shewanella decolorationis* S12 showed the maximum power density of 1303 mW m^{-2}, which was 13 times larger than that obtained from the MFC equipped with an unmodified anode. Evidence from cyclic voltammerty (CV) and scanning electron microscopy (SEM) results indicated that the increase in power generation was assigned to the increased surface area of anode, the enhanced electron-transfer efficiency from the bacteria to the anode via immobilized AQDS, and an increase in the number of bacteria attached to anode.

1. Introduction

Microbial fuel cells (MFCs), known as the environmentally friendly and sustainable power sources, have attracted great interest of researchers in the disciplines of microbiology, electrochemistry, material science and chemical engineering (Reguera et al., 2005; Richter et al., 2008; Gorby et al., 2006). Being in infancy stage of its development, the MFC delivers much lower power output when compared to the well-developed chemical fuel cell (CFC). One of the significant issues contributing to low performance is the "inefficiencies" of the anodic processes (Rinaldi et al., 2008) that involve the interaction between bacteria and electron acceptors (i.e., anode).

The immobilization of an electron redox mediator on the anode surface demonstrates to be a useful method to improve the efficiency of extracellular electron transport and hence to boost power output (Lowy et al., 2006; Park and Zeikus, 2002, 2003; Adachi et al., 2008). Previous report (Lowy et al., 2006) has shown that the MFC equipped with an anthraquinone-2,6-disulphonic disodium salt (AQDS)-modified graphite electrode generated 5 times larger power density than the untreated counterpart. However, the method of AQDS adsorption onto the graphite surface resulted in a poorly adhered AQDS film (Adachi et al., 2008). To improve the stability of the treated electrode, a modification was made to the coating process in which a polyethyleneimine middle layer was employed to crosslink AQDS and the underlying anode substrate (Adachi et al., 2008). This modified approach, despite the advantage of further improving bioelectricity generation, was time-consuming (e.g., at least 48 h required) and involved the utilization of a non-conductive polymer (e.g., polyethyleneimine) which may cause an increase in electronic resistance of the anode.

Our strategy is to immobilize AQDS on the carbon felt electrode surface by electropolymerization of pyrrole while using AQDS as the dopant. This allows the formation of a highly conductive polypyrrole (PPy)/AQDS composite film within a few minutes. We then evaluate the performance of a dual-chamber MFC operated with the PPy/AQDS-modified anode. The electrocatalytic property and the surface morphology of this electrode in the presence and absence of *Shewanella decolorationis* S12 are also examined by using cyclic voltammerty (CV) and scanning electron microscopy (SEM) techniques.

* Corresponding author. Tel.: +86 20 22236581; fax: +86 20 22236581.
E-mail address: chfeng@scut.edu.cn (C. Feng).

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2. Materials and methods

2.1. Anode preparation

The starting anode substrate was a piece of carbon felt (4.4 cm × 4.4 cm × 0.5 cm) which was purchased from Liaoyang Jingu Carbon Fiber Sci-Tech Co., Ltd. (China). A Ti wire (1 mm in diameter) was inserted inside the carbon felt to allow the external circuit connection. The electropolymerization of PPy/AQDS composite film on the carbon felt surface was performed in a three-electrode electrochemical cell, with a saturated calomel electrode (SCE) as reference electrode and a Pt mesh (4 cm × 4 cm) as counter electrode. All the potentials reported throughout this paper were referred to SCE. An Autolab potentiostat (PGSTAT30, Eco Chemie) was used to control the working potential of the carbon felt electrode. The electrolyte contained 0.1 M pyrrole (Aldrich) and 5 mM AQDS (Aldrich). Pyrrole was purified by distillation prior to use. Upon a constant potential of 0.8 V applied, the PPy/AQDS composite film was formed and the total charge density passed was 0.08 C cm^{-2} (per geometric anode area). The time required for the electropolymerization process was 6 min. The freshly prepared PPy/AQDS-modified carbon felt was then thoroughly rinsed with a 0.1 M phosphate buffered solution (PBS, pH 8.0) before further use. For comparison, the PPy/AQDS composite film was also electrodeposited on a glass carbon (GC, 3 mm in diameter) electrode with the same charge density.

2.2. Bacteria and medium in the anode chamber

S. decolorationis S12 (Hong et al., 2007) was used as the biocatalyst in the anode chamber. It was isolated from activated sludge in a textile printing wastewater treatment in Guangzhou, China and was cultured in LB medium (10 g L^{-1} peptone, 5 g L^{-1} yeast extract and 5 g L^{-1} NaCl) at 30 °C. For MFC inoculation, 1 mL of the above bacteria was transferred to the sterilized anode chamber. The medium added to the anode chamber contained 10 mM lactic acid and 0.1 M PBS-based nutrient solution (pH 8.0) consisting of 5.84 g L^{-1} NaCl, 0.10 g L^{-1} KCl, 0.25 g L^{-1} NH_4Cl, 10 mL of vitamin solution (Lovley and Phillips, 1988) and 10 mL of mineral solution (Lovley and Phillips, 1988).

2.3. MFC operation and electrochemical tests

A dual-chamber microbial fuel cell was constructed, separated by a cation exchange membrane (Zhejiang Qianqiu Group Co., Ltd. China). Each cell chamber made of polycarbonate has an effective volume of 75 mL. The anode was a piece of PPy/AQDS-modified carbon felt or an unmodified one with the identical size (4.4 cm × 4.4 cm × 0.5 cm). For MFC operation, the bacteria and medium were added to the sterilized anode chamber in which the anaerobic respiration of bacteria occurs; the PBS solution (0.1 M, pH 7.0) with or without 45 mM potassium hexacyanoferrate was added to the cathode chamber. The cathode was a bare carbon felt electrode (4.4 cm × 4.4 cm × 0.5 cm). In the absence of hexacyanoferrate, the MFC was run by bubbling air to the cathode. Cell voltages were recorded by a 16-channel voltage collection instrument (AD8223, China) under the conditions of a 1000 Ω external resistance and a controlled temperature of 30 °C. The anode and cathode polarization curves and the cell power density curves were obtained by varying the external resistor over the range from 5 to 5000 Ω when the performance of MFC approached steady state. Current density (I) was calculated as $I = V$ (cell voltage)/R (external resistance), and power density (P) was calculated as $P = V \times I$. Both I and P were normalized to the projected area of anode surface. The anode potentials were measured by inserting a sterilized SCE electrode into the anode chamber; the cathode potentials were calculated as the sum of the anode potential and the cell voltage. Coulombic efficiency (η) was calculated as $\eta = C_p/C_{th} \times 100\%$, where C_p is the Coulombs obtained by integrating the current over time, and C_{th} is the theoretical Coulombs calculated based on the consumption of lactic acid. CV tests were performed by using the anode as the working electrode, the cathode as the counter electrode, and a SCE as the reference electrode. The electrochemical behaviors of PPy/AQDS modified on the GC electrode were also examined by CV.

2.4. SEM tests

The surface morphologies of the unmodified, PPy/AQDS-modified carbon felt electrodes before and after incubation were examined by a LEO 1530 VP scanning electron microscope. A thin layer of gold was sputtered to these samples before mounted on the aluminum stab. The preparation of the inoculated sample was referred to the procedures described elsewhere (Park and Zeikus, 2003). Briefly, to stabilize the bacteria attached to the anode, the sample (cut from the anode) was immersed in 4% glutaraldehyde solution for 5 h. It was then rinsed with a PBS solution (pH 7.0) for 3 times, followed by dehydration with increasing concentration of ethanol (34%, 50%, 75%, and 95%) for 10 min each and further rinses in isoamyl acetate twice (10 min each time). The sample was then dried at CO_2-critical point for 3 h.

3. Results and discussion

3.1. Power generation

The bioelectricity generation behavior of a dual-chamber MFC is significantly influenced by the anode material used. Fig. 1 shows the cell voltage curves, anode and cathode polarization curves, and power density curves of two individual MFC reactors operated with a PPy/AQDS-modified anode (MFC-A) and an unmodified anode (MFC-B). When their anode chambers were fed with 10 mM lactic acid in the presence of *S. decolorationis* S12 and cathode chambers were bubbled with air, both MFCs exhibited a typical voltage-generation profile as reported by others (Qiao et al., 2008; Cheng and Logan, 2007). As shown in Fig. 1a, there is a starting-up period followed by a rapid increase in voltage output, then voltage rises to a plateau. After lasting for a long period, it begins to drop due to substrate depletion. During the first feeding cycle, the MFC-A required 23 h to reach a steady cell voltage of about 0.62 V; in contrast, a lag time of 46 h was observed for the MFC-B. The MFC-B delivered a steady cell voltage of 0.36 V which was only 58% of the MFC-A. Four reproducible cycles of voltage generation (corresponding to an operation time of 580 h) were obtained for the MFC-A (data not shown), indicating the stability of the modified anode. In addition, the coulombic efficiency of the MFC-A was calculated to be 32% that was 2.7 times larger than the value (12%) of the MFC-B. All these data indicate that the PPy/AQDS-modified anode substantially improves performance of MFCs.

Performance comparison of the MFC-A and MFC-B was also conducted by using a potassium hexacyanoferrate (45 mM)-feeding cathode instead of the aerated cathode. The use of ferricyanide as the electron acceptor is preferable to fundamental laboratory studies owing to its facile reaction rate (Oh et al., 2004; Zhang et al., 2008). Fig. 1b shows a comparison of the anode and cathode polarization curves between the MFC-A and the MFC-B. We can see that the two MFCs exhibit negligible difference in their cathode potentials because of the identical cathode used in both samples. The anode potentials, however, are highly dependent on modification of the carbon felt with PPy/AQDS. The anode open circuit potential (OCP) of the MFC-A was −0.53 mV, increased by 71% as compared with the MFC-B. In addition, for the MFC-B, increasing