Short communication

Increased performance of a tubular microbial fuel cell with a rotating carbon-brush anode

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A B S T R A C T

A novel method was proposed to improve the power output of microbial fuel cells (MFCs) by rotating the carbon-brush anode. The MFC with a rotating anode produced a peak power density of $210 \pm 3 \text{ W/m}^3$ and a maximum current density of $945 \pm 43 \text{ A/m}^3$, 1.4 and 2.7 times higher than those of the non-rotating case, respectively. The difference of the electrochemical impedance spectroscopy and cyclic voltammetry before and after anode rotation clearly suggested that the mass transfer to the spiral space was enhanced by the rotating anode. Furthermore, Tafel plots analysis also revealed that the rotating anode can improve the electrochemical activity of the biofilm.

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1. Introduction

Microbial fuel cells (MFCs) are renewable bioenergy technologies that have been investigated for producing electricity from organic matters (Logan et al., 2006; Du et al., 2007). In MFCs, the electrochemically active bacteria (EAB) attached on the anode can directly convert chemical energy into electric energy through the bioelectrochemical oxidation of organic matters. Hence, MFCs are promising for simultaneous wastewater treatment and power generation. At the present stage, however, the low power output inherently hinders their practical application. The substrate transport (Torres et al., 2008; Moon et al., 2005; Ieropoulos et al., 2010; Picoreanu et al., 2010), electrochemically active bacteria community composition (Aelterman et al., 2008; Srikanth and Mohan, 2012), operation conditions (Gil et al., 2003) and reactor architectures (Feng et al., 2010; Antonopoulo et al., 2010; Kim et al., 2010; Zuo et al., 2010) have been identified as the crucial factors for further improving the MFC performance.

It was well demonstrated that three-dimensional spiral anode usually leads to a significant increase in power output because of the enhanced mass transfer of substrates and mediators. Kim et al. (2012) claimed that a 2-fold increase in power output can be achieved by the flow regime driven mass transfer in an air-cathode MFC with a helical flow channels anode. As a typical spiral type electrode, carbon-brush electrodes comprise multiple strands of carbon fibers distributed along a spiral-shape in a twisted titanium wire backbone, and thus enable more compact architecture. However, the surface area of the carbon-brush anode was not sufficiently used for electricity generation because of the insufficient substrate supply in the inner space of the spiral structure (Liu et al., 2013). To alleviate this limitation, spiral spacers were inserted to the carbon-brush anode to create a helical flow for enhancing the ions and mediators transport in a vertical-oriented tubular MFC (Zhang et al., 2013). These studies demonstrated that the spiral flow pattern was promising for improving the MFC power output. Nevertheless, the complicated manufacturing procedures for the helical flow channels anode are still technical challenges that must be solved before commercial success can be announced.

It has been proved that the substrate supply can be greatly enhanced by rotating the electrodes. Cheng et al. (2012) reported that the chemical oxygen demand (COD) removal can be greatly improved in a rotatable bio-electrochemical contactor (RBEC). He et al. (2007) proposed a rotating cathode to supply additional oxygen to accelerate the breakdown of organic materials in sediment microbial fuel cell (SMFC). Due to the inherent spiral structure, a combination of the carbon-brush anode and the rotation strategy would provide the additively induced elevation or descent fluid flow in the anode chamber, leading to an extra enhancement for the mass transport of substrate and products inside the inner space of the spiral structure, and thereby the enhanced performance.

In this study, the rotating carbon-brush anode was used to enhance the substrate supply and product removal for improving
the MFC power output. It was expected to propose a simple and effective method to recover more energy by the MFCs.

2. Materials and methods

2.1. MFC configuration

A tubular MFC was fabricated using plexiglass cylinders as shown in Fig. 1. The 4.0 cm in diameter and 4.0 cm in high inner cylindrical chamber with 60 through-holes (0.5 cm in diameter) was served as the anode compartment, which volume was 50 mL. A cation exchange membrane (CMI-7000, Membrane International, USA) was wrapped outside the anode chamber to separate the catholyte and anolyte. The carbon-brush anode was 3.0 cm in outer diameter and 4.0 cm in length (Liu et al., 2013) and a carbon cloth (15.0 cm × 4.0 cm) was used as the cathode. Two twisted titanium wires for fixing carbon fibers and collecting current were mounted on a vertical-shaft, with which the carbon-brush anode was rotated by a variable speed motor (PK545-NA, China) (Fig. 1).

2.2. MFC operation

The tubular MFC was inoculated with the effluent containing amounts of mixed bacterial from an acetate-fed MFC in a continuous-flow mode. Fresh anolyte containing 0.68 g/L CH₃COONa, 6.0 g/L Na₂HPO₄, 3.0 g/L KH₂PO₄, 0.1 g/L NH₄Cl, 0.5 g/L NaCl, 0.1 g/L MgSO₄·7 H₂O, 15.0 mg/L CaCl₂·2 H₂O and 1.0 mL/L trace elements solution was pumped into the anode chamber at 3 mL/min. To exclude the possibility of the cathodic performance limitation, the anolyte was replaced when the cell voltage reached relatively steady-state (< 1 mV/5 min). The volumetric power densities were calculated by equation: $P = UI/V$, where $V$ is the volume of the anode chamber, $I$ and $U$ are the sustainable current and cell voltage after the MFC reached steady-state, respectively.

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Tafel tests were conducted before and after anode rotation using an electrochemical workstation (Zahner Zennium, Germany) with the carbon-brush anode as the working electrode, the carbon cloth as the counter-electrode and an Ag/AgCl electrode as the reference electrode. CV measurements were conducted at 1 mV/s in the potential window from −0.4 to +0.6 V vs. SHE, while Tafel plots were carried out from −0.8 to +0.2 V vs. SHE at the same scan rate. EIS tests were performed with a frequency ranging from 100 KHz to 10 mHz and a perturbation amplitude of 10 mV. Before the impedance measurement, the MFC was operated at 1000 Ω for at least 2 h to achieve the steady state. COD was measured using the fast digestion-spectrophotometric method (Lianhua 5B-3C, China) (Logan et al., 2006).

3. Results and discussions

3.1. MFCs performance

After inoculation for 200 h, the tubular MFC reached a stable voltage of 0.54 ± 0.01 V at 50 Ω with the immobile carbon-brush anode. Subsequently, the MFC was operated by rotating the anode at 3 rpm. As a result, the cell voltage rapidly increased ~30 mV and stabilized at 0.57 ± 0.01 V in continuous-flow mode (Fig. S1). As shown in Fig. 2A, a similar improvement of the MFC voltage before and after anode rotation was also obtained in fed-batch mode. This phenomenon can be attributed to the enhanced substrate supply and product removal in the spiral space of the carbon-brush anode. Furthermore, it was noted from Fig. 2A that the duration of electricity generation was slightly affected by the anode rotation. For example, compared with the immobile anode, a slight increase from 17 to 20 h in the duration of electricity generation was obtained for the MFC with a rotating anode.

During the MFC operation, both the substrate consumption and proton accumulation would gradually deteriorate the cell performance. In order to distinguish these two effects, COD measurements were carried out to determine the substrate consumed by EAB. In the fed-batch model, the COD removal efficiency was estimated to be 51.6 ± 1.9% and 51.1 ± 1.2% for non-rotating and rotating anodes, respectively. The nearly identical and insufficient COD remove efficiency revealed that the electricity production was dominated by the proton accumulation rather than the substrate depletion.

To further confirm this point, the MFC performance with rotating and non-rotating anodes was compared in continuous flow mode. From Fig. 2B, the MFC with a rotating anode produced a peak power density of 210 ± 3 W/m³, 40% higher than with a non-rotating anode (150 ± 3 W/m³). Correspondingly, the maximum current density increased from 349 ± 11 to 945 ± 43 A/m² (Fig. 2C). In addition, the MFC voltage variation as a function of external resistances from open circuit to 3 and then to 2501 Ω is shown in Fig. 2D. It was clear that a remarkable promotion was obtained for the rotating anode when the external resistance was lower than 21 Ω. These results suggested that severe mass transfer limitation at high current densities was migrated by rotating the anode, implying that anode rotation was an effective method to enhance the MFC power output. For non-rotating anode, the substrate supply and product removal were mainly diffusion-dominated at the biofilm/bulk solution interfaces. In contrast, the rotating anode can enhance the mass transport between the inner spiral space and bulk solution by vigorous convection.

Fig. 1. Schematic diagram of the MFC with a rotating spiral carbon-brush anode.
Consequently, a favorable microenvironment, i.e., stable pH, sufficient substrate supply and continuous metabolic product removal, inside the spiral space was maintained, therefore leading to an improved electricity generation.

3.2. Electrochemical properties of the anode biofilm

To further verify and quantify the influence of anode rotation on the mass transfer of substrate and products in the anode, EIS measurements were conducted in continuous flow mode and the acquired data were fitted to the equivalent circuit model (Fig. S2) (Sun et al., 2010). As shown in Fig. 3A, the dramatically reduced diffusion resistance \( R_d \) implied the enhanced mass transfer within the spiral space of the carbon-brush anode (Table 1). From Fig. 3B, it was also clear that the non-rotating showed an oxidation peak current of 0.044 A at 0.212 V vs. SHE resulting from the combined effect of the limited substrate supply and inhibitory metabolic products accumulation in the biofilm. However, in the case of the rotating carbon-brush anode, the oxidation peak was positively...
shifted to 0.396 V vs. SHE and the oxidation peak current was increased to 0.069 A due to the improved substrate supply and microbial product removal at the biofilm/bulk solution interfaces.

It was also noted that the MFC with the rotating anode not only exhibited the enhanced substrate supply at spiral space but also showed the promoted metabolic activity of the EAB. Fig. 3C and Table 1 compared the Tafel plots fitting results of the MFC with rotating and non-rotating anodes. From the results, it is clear that the MFC with a rotating anode showed a higher exchange current density \( i_0 \) of 0.14 mA/cm² and a lower anodic Tafel slope \( \beta_a \) of 192.68 mV/decade. These results confirmed that the rotating anode enabled a faster electron-transfer kinetics as compared to the non-rotating anode.

4. Conclusions

In this work, the anode rotation was proved to be an effective method to enhance the mass transport within the carbon-brush anode. The results indicated that rotating the carbon-brush anode not only led to the enhanced substrate supply and product removal, but resulted in the promoted electrochemical activity of bacteria. These beneficial effects were responsible for the significantly improved electricity generation. Based on the modeling and empirical analysis (Fig. 53), the power consumption of the rotation was negligible as compared to the performance increment resulting from anode rotation. This result suggested that anode rotation is a promising method to improve the MFC performance. In addition, anode rotation can be further warranted for future applications when natural river currents or ocean tides were used to replace the driving motor.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.bios.2014.08.014.

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