

Short communication

## Increased sustainable electricity generation in up-flow air-cathode microbial fuel cells

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### Abstract

Sustainable electricity was generated from glucose in up-flow air-cathode microbial fuel cells (MFCs) with carbon cloth cathode and carbon granular anode. Plastic sieves rather than membrane were used to separate the anode and cathode. Based on 1 g/l glucose as substrate, a maximum volumetric power density of  $25 \pm 4 \text{ W/m}^3$  ( $89 \text{ A/m}^3$ ) was obtained for the MFC with a sieve area of  $30 \text{ cm}^2$  and  $49 \pm 3 \text{ W/m}^3$  ( $215 \text{ A/m}^3$ ) for the MFC with a sieve area of  $60 \text{ cm}^2$ . The increased power density with larger sieve area was mainly due to the decrease of internal resistance according to the electrochemistry impedance spectroscopy analysis. Increasing the sieve area from  $30 \text{ cm}^2$  to  $60 \text{ cm}^2$  resulted in a decrease of overall internal resistance from  $41 \Omega$  to  $27.5 \Omega$  and a decrease of ohmic resistance from  $24.3 \Omega$  to  $14 \Omega$ . While increasing operational recirculation ratio (RR) decreased internal resistance and increased power output at low substrate concentration, the effect of RR on cell performance was negligible at higher substrate concentration.

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### 1. Introduction

Depletion of energy reserves, global warming and the concern of environmental pollution are inspiring the search for new environment-friendly and sustainable energy production methods. Microbial fuel cells (MFCs) utilize bio-electrochemical processes of bacteria so that electrical energy is directly recovered from biodegradable compounds. Particularly, if organic wastewater is used as anodic fuel, chemical oxygen demand (COD) present in wastewater is decomposed while electrical current is generated. This gives rise to the potential for MFCs to be applied in wastewater treatment.

In a MFC system, internal energy loss accounts for a significant element that inherently determines the scales of magnitude in power generation (Logan et al., 2006). The sources of energy loss occurring in a MFC generally stem from the resistance to electron transport in terms of charge-transfer resistance, ohmic resistance and diffusion resistance, of which ohmic resistance is often the key performance driver of a fuel cell (Barbir, 2005). Such portion of inherent resistance is greatly dependent upon MFC design configuration other than anodic microorganisms (Logan and Regan, 2006). One of the most effective manners for reducing ohmic resistance is to reduce the electrode spacing (Cheng et al., 2006a; Liu et al., 2005). Another approach to this problem is to construct an up-flow anode, in which substrates flow through the biofilms. This modified design, in combination with continuous operation, has resulted in a relatively low internal resistance and increased power (Rabaey et al., 2005; He et al., 2006). However, MFCs with up-flow design often utilize potassium ferricyanide as the catholyte, and unsustainable liquid-state catholyte may be impractical for large systems.

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Although air-cathode MFCs that use free air as the electron acceptor has several inherent advantages (Liu et al., 2004; Liu and Logan, 2004), power generation from air-cathode MFC still remains lower than that from liquid-state-catholyte MFCs (Rabaey et al., 2005; You et al., 2006). Therefore, a great emphasis should be placed on further improvements of an air-cathode MFC to increase power yields by reducing design- or operation-dependent internal resistance without losing productivity and sustainability.

The authors herein show that an up-flow air-cathode microbial fuel cell can continuously generate an increased power from glucose solution based on sieve area of the MFC for ion transport. An examination of electrochemical polarization behavior and internal resistance characterization of MFC was carried out, followed by an investigation on the influence of recirculation on power and internal resistance of the cell.

## 2. Materials and methods

### 2.1. MFC setup

Both the MFC-1 and MFC-2 were built with a 0.2 cm-thick cylindrical Plexiglas tube with inner diameter of 3 cm and total height of 13.5 cm (overall volume of 95 ml). A coniform-shaped cover was placed on the top of the MFCs to collect effluent streams, and an influent port was set at the bottom of the reactor for feeding substrate. Homogeneous sieves (diameter of 2.0 mm for each) were carefully drilled on the wall of the anode bed and these sieves with the total area of 30 cm<sup>2</sup> for the MFC-1 and 60 cm<sup>2</sup> for the MFC-2 were available for internal electrolyte ion and conduction. Graphite granules (diameter of 3–5 mm; Jiangsu Province, China) were screened and filled in the anode zone, producing an anodic bed with wet volume of 55 ml. The external electrical connections were created using copper wires with one end connected to a 1 cm-diameter and 5 cm-length graphite rod inserted into the granules and the other end connected to the cathode. The cathode was made of flexible carbon cloth (E-TEK, 30% wet proofing; 10 cm × 10 cm; projected area of 90 cm<sup>2</sup>) that was tightly bound outside the anode wall. This ensured a close electrode spacing and low internal resistance. The inside surface of the carbon cloth was loaded with carbon/platinum catalysts (E-TEK, 20% Pt; 0.8 mg Pt/cm<sup>2</sup>). The preparation for the cathode was performed according to the methods as described by Cheng et al. (2006b). The photos of the MFC reactor can be referred to S. 1.

### 2.2. MFC operations

Both MFC reactors were initially started up with anaerobic sludge that was collected from the thickening tank in Wenchang Wastewater Treatment Plant (WWTP), Harbin, China. Anaerobic sludge was filtered through 0.15 mm-pore mesh to remove coarse particles before uses. During the operational phases, anaerobic sludge was diluted by distilled water to seed sludge that contained mixed liquid suspended solid (MLSS) of 500 mg/l. The mixture of seed sludge and nutrient solution was continuously fed into the MFCs until the electrochemically

active bacteria were cultivated and current was produced. The anode-fed chemicals consisted of (per liter of deionized water): glucose (0.6 g), NaHCO<sub>3</sub> (3.13 g), KCl (0.13 g), NaH<sub>2</sub>PO<sub>4</sub> (4.22 g), Na<sub>2</sub>HPO<sub>4</sub> (2.75 g), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (0.56 g), MgSO<sub>4</sub>·7H<sub>2</sub>O (0.2 g), CaCl<sub>2</sub> (15 mg), FeCl<sub>3</sub>·6H<sub>2</sub>O (1 mg) and MnSO<sub>4</sub>·H<sub>2</sub>O (20 mg). Trace metals were also added to the solution for growth support of microorganisms (Lovley and Phillips, 1988). During the experiments, substrates were continuously fed into the reactors at a constant flow rate of 0.4 ml/min and recirculated from the upper port back to the bottom with two separated peristaltic pumps (type BT100-1Z, China) as shown in S. 1. The recirculation ratio (RR) here is defined as the relative ratio of recirculation rates (ml/min) to influent flow rate (ml/min).

### 2.3. Electrochemical analysis

Voltage yields from the two MFCs for long-term operation were sampled every 60 s by using a dual-channel digital voltage collection instrument (12 bit A/D conversion chips, US) connected with a personal computer. Voltage obtained was then converted to power density that was normalized by wet anodic volume in unit of Watts per cubic meter (W/m<sup>3</sup>). After the MFCs generated power stably, external resistance ( $R_{ex}$ ) was in turn shifted in the range of 1  $\Omega$  to 10<sup>4</sup>  $\Omega$  to demonstrate electrochemical polarization and power curves. Open circuit voltage (OCV) of the cell was obtained after the circuit was disconnected for 10 h. Data for each resistance was collected after the cell was operated stably for a minimum time of 5 h.

In order to examine internal resistance in the cells, electrochemistry impedance spectrometer (Eis) measurements of the cells was taken after the cell was operated at an open-circuit condition for 5 h. The impedance measurements were done from 100 kHz to 5 mHz by applying a sine wave of rms of 10 mV on top of the bias potentials with the potentiostat Parstat 263A (Princeton Applied Research). Scanning data were fitted and simulated by ZSimpWin3.10 software (Echem., US). The internal resistance of the cells were read from the  $x$ -intercept in the Nyquist plots (i.e. imaginary impedance of zero) (Cooper and Smith, 2006).

## 3. Results and discussion

After a lag period of about 377 h, there was a stable power production with voltages of 0.309 V and 0.385 V across the external resistor ( $R_{ex} = 50 \Omega$ ) in the MFC-1 and MFC-2 (data not shown). Thereafter, voltage and power output as function of current density in two MFCs were examined. As illustrated in Fig. 1, the open circuit voltage (OCV) of both MFCs were quite similar (approximately 0.7 V), and the maximum volumetric power reached was  $25 \pm 4 \text{ W/m}^3$  ( $89 \text{ A/m}^3$ ) for MFC-1 and  $49 \pm 3 \text{ W/m}^3$  ( $215 \text{ A/m}^3$ ) for MFC-2. It can be seen from polarization curves that such differences in power observed here should be attributed to the different internal resistance of the two cells. It was noticed that, for both MFCs, the maximum power point (MPP) occurred at the linear region of polarization curve, in which voltage dropped linearly with electrical current (Fig. 1). Power of  $49 \pm 3 \text{ W/m}^3$  generated from MFC-2 was shown sim-

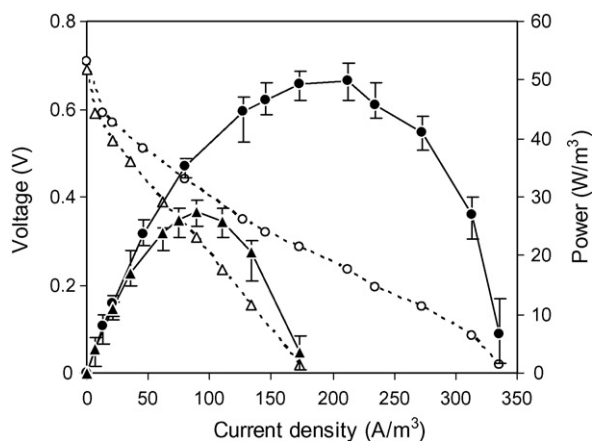


Fig. 1. Polarization (dash line) and volumetric power (solid line) curves of MFC-1 (triangles) and MFC-2 (circles) with glucose (1 g/l) as substrate. Error bars  $\pm$  S.D. indicates performance tests in triplicate.

ilar as the reported value of  $51 \text{ W/m}^3$  from air-cathode MFC under continuous operation (Cheng et al., 2006a).

By fitting impedance spectra data to equivalent electrical circuit, Nyquist plots were obtained as shown in Fig. 2. MFC-1 and MFC-2 had an overall resistance of  $41 \Omega$  and  $27.5 \Omega$ , including charge-transfer resistance of  $7.7 \Omega$  (18.78%) and  $6.1 \Omega$  (22.2%), ohmic resistance of  $24.6 \Omega$  (60%) and  $14 \Omega$  (51%) as well as diffusion resistance of  $8.7 \Omega$  (21.22%) and  $7.4 \Omega$  (26.8%), respectively. Impedance responses to low frequency sine waves indicated lines with slopes of 0.24 (MFC-1) and 1.48 (MFC-2), implying that the diffusion resistance was not caused by typical Warburg infinite diffusion layer (slope of 1). Ohmic resistance in the MFC-1 was observed  $10.5 \Omega$  greater than that in the MFC-2 (Fig. 2) and the most possible reason for this discrimination appears to be larger sieve area in the MFC-2 for more efficient ion transport in the electrolytes. These results indicate that internal resistance is inversely proportional to sieve area and that it will be possible to further decrease internal resistance of the cell by designing a reactor with larger sieve area than those tested here.

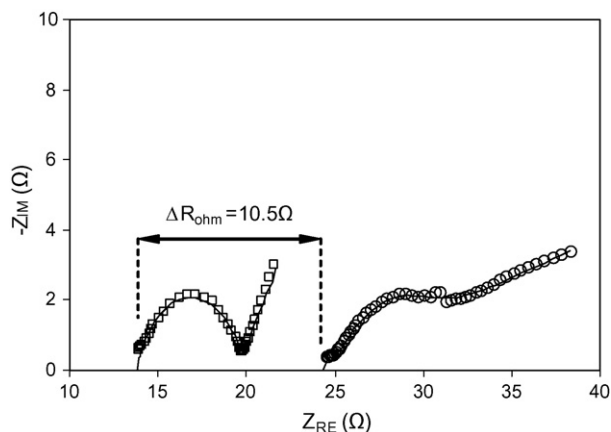


Fig. 2. Nyquist plots of impedance spectra of MFC-1 (circles) and MFC-2 (squares). The cell was disconnected for 5 h before measurements.

The large ohmic resistance in both MFCs was shown to be consistent with that obtained from polarization analysis and comparable to that of 50.3% in the internal-cathode MFC by He et al. (2006). On the contrary, diffusion resistance (21.22% and 26.8%) was much higher than the literature value of 8.5% (He et al., 2006), which seems likely to result from a limitation to oxygen mass transfer onto catalyst layer at the open-air cathode. Additionally, internal resistance (ohmic resistance) of  $14 \Omega$  in MFC-2 is much lower than that of previously reported values from two-chamber aerated-cathode MFCs (Min et al., 2005; Oh et al., 2004; Oh and Logan, 2006) and single chamber air-cathode MFCs (Liu and Logan, 2004; Liu et al., 2005). Relatively lower internal resistance observed here may result from the larger cross-section area, closer distance between the electrodes, membrane-free design and flow-through operation, which produces less resistance for ion transports from the anode to the cathode.

Further effects of hydraulic conditions (recirculation) in the anode bed on the cell performance were explored using MFC-2 with larger sieve area of  $60 \text{ cm}^2$ . Fig. 3 shows a corresponding correlation between power output and internal resistance at various recirculation ratios (RR) and glucose concentrations. For the MFC-2 operated under high glucose concentration (2 g/l), increasing RR from 0 to 120 only increased volumetric power by 8.8% ( $P = 0.027 \times \text{RR} + 36.83$ ,  $R^2 = 0.986$ ), corresponding to a slight decrease of internal resistance by 7.86% ( $R_{\text{int}} = -0.018 \times \text{RR} + 27.74$ ,  $R^2 = 0.926$ ). This suggested a minor effect of RR on power yields. For low glucose concentration (0.4 g/l), power output was linearly increased from  $2.8 \pm 2 \text{ W/m}^3$  to  $35.1 \pm 1 \text{ W/m}^3$  ( $P = 0.268 \times \text{RR} + 4.04$ ,  $R^2 = 0.981$ ) when RR was increased from 0 to 120. In this case, internal resistance of for RR=0 was found to be 53.7% higher than that for RR=120 ( $R_{\text{int}} = -0.119 \times \text{RR} + 39.96$ ,  $R^2 = 0.963$ ), implying a strong dependence of internal resistance on hydraulic conditions in the anode at low substrate concentration.

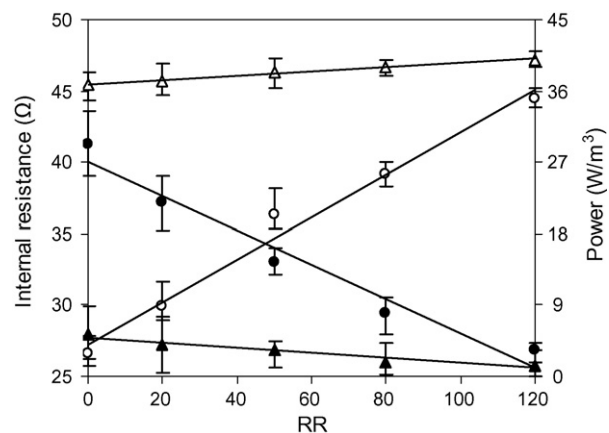


Fig. 3. Effects of recirculation ratio (RR) on power output (open symbols) and cell internal resistance (solid symbols, read from the  $x$ -intercept of Nyquist plots) at glucose concentration of 2 g/l (triangles) and 0.4 g/l (circles) in MFC-2. Power were measured at a fixed resistor of  $50 \Omega$  and error bars  $\pm$  S.D. represent power and internal resistance tests in triplicate.

One of the possible reasons for the improved performance may be that recirculation changes the working pattern of the reactor. At high recirculation ratio, the MFC behaves as a completely mixed system with all areas of the granules under the same substrate concentration. While in the absence of recirculation, the MFC would approach a plug flow reactor such that the substrate was gradually depleted along the height of the anode. Therefore, when electrical energy recovery is the ultimate goal, the MFC is better operated at high substrate concentration to maintain a high level of power yield and to reduce operational costs for recirculation.

#### 4. Conclusions

An up-flow air-cathode MFC system was developed for sustainable power generation from glucose. Increasing sieve area from 30 cm<sup>2</sup> to 60 cm<sup>2</sup> decreased overall internal resistance of the cell from 41 Ω to 27.5 Ω, and increased volumetric power density from 25 ± 4 W/m<sup>3</sup> to 49 ± 3 W/m<sup>3</sup>. The decrease of overall internal resistance and increase of power mainly resulted from the decrease of ohmic resistance. The impacts of recirculation on power and internal resistance of the cell depended on anodic substrate concentrations. Using an up-flow air-cathode MFC to generate electricity from organic substances provides a new method and insight toward air-cathode MFC design and operation for applications in wastewater treatment. On the other hand, it is also seen that platinum catalysts applied for the air cathode are quite expensive; hence, alternative materials such as biologically catalyzed cathode are required for further optimizations of air-cathode MFC performance and costs.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bios.2007.10.010.

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