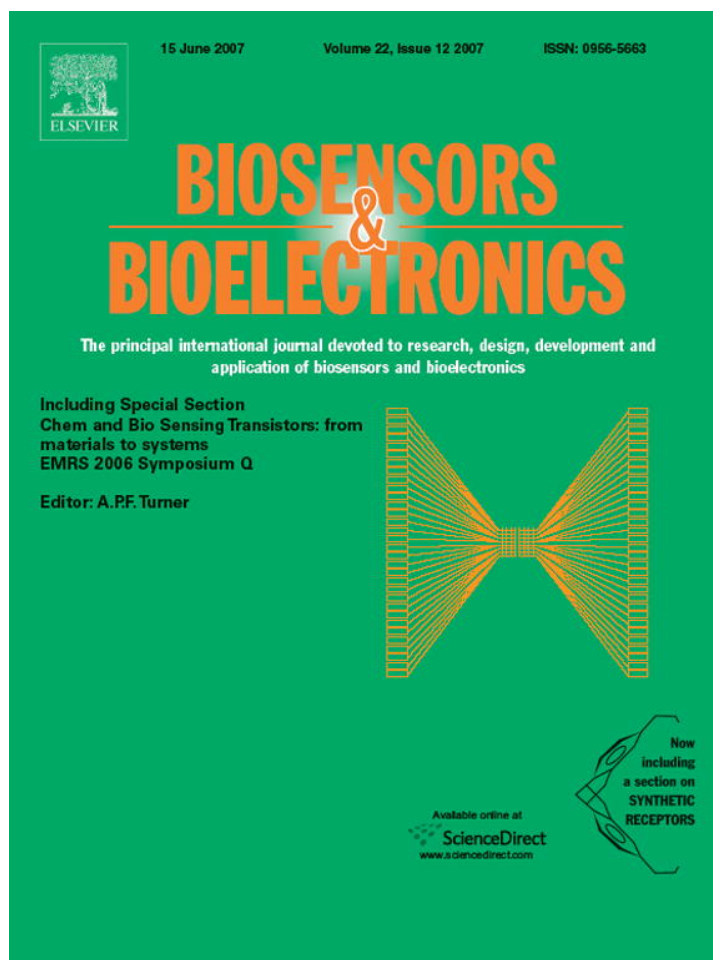


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Short communication

## Increased power production from a sediment microbial fuel cell with a rotating cathode

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### Abstract

The application of a rotating cathode in a river sediment microbial fuel cell increased the oxygen availability to the cathode, and therefore improved the cathode reaction rate, resulting in a higher power production (49 mW/m<sup>2</sup>) compared to a nonrotating cathode system (29 mW/m<sup>2</sup>). The increased dissolved oxygen in the water of our lab-scale sediment MFC, however, resulted in a less negative anode potential and a higher anodic charge transfer resistance, which constrained the maximum power density. Thus, an optimum balance between the superior cathode reaction rates and the inferior anode reaction rates due to higher dissolved oxygen levels must be ascertained.

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**Keywords:** Microbial fuel cell; Rotating cathode; Internal resistance; Impedance spectroscopy

### 1. Introduction

A likely application of microbial fuel cell (MFC) technology is in remote bodies of water where electric energy can be extracted from organic-rich aquatic sediments (Lovley, 2006b). For this purpose, researchers have developed sediment MFCs that consist of an anode electrode embedded in the anaerobic sediment and a cathode electrode suspended in the aerobic water column above the anode electrode (Reimers et al., 2001). Electricigenic bacteria in the sediment transfer electrons produced during the oxidation of organic or inorganic matter to the anode electrode; while oxygen is reduced in the water column by accepting electrons from the cathode electrode. As a result, an electric current is generated. Classically, H-type MFCs have been used to study microbial respiration in the anode (Rabaey and Verstraete, 2005). Such MFCs contain a cation exchange membrane to separate the anaerobic anode from the aerobic cathode. A cation exchange membrane is not necessary in sediment MFCs, because the decreasing oxygen gradient over the depth of water and sediment columns creates the necessary potential difference naturally.

Most sediment MFCs have been tested in marine environments, and only a few in rivers (Bond et al., 2002; Shantaram et al., 2005; Lovley, 2006a). Seawater has a higher electrical conductivity than river water (~50,000 vs. ~500  $\mu$ S/cm at 20 °C). Therefore, seawater sediment MFCs are expected to produce greater electric power than river-water MFCs due to a lower electrolyte resistance. In addition to the water conductivity, the electric power from a sediment MFC also depends on the type of cathode catalyst and electrode material used, and the distance between electrodes. A typical maximum power density found with sediment MFCs is ~10–20 mW/m<sup>2</sup> of anode surface area (Lowy et al., 2006); however, both Tender et al. (2002) and Reimers et al. (2006) have reported a maximum power density higher than 30 mW/m<sup>2</sup> in marine environments.

In H-type MFCs, oxygen is supplied by forced aeration (Angenent et al., 2004). Sediment MFCs, however, utilize the dissolved oxygen that is naturally present in water. Dissolved oxygen is essential for the cathodic reaction, and therefore sediment MFCs are typically installed in shallow waters with the cathode close to the water surface; or they are installed in deep ocean locations where relatively high oxygen levels (dissolved oxygen ~0.5 mg/L) are present in cold seeps (Reimers et al., 2006).

Rotating biological contactors (RBC), as used in wastewater treatment, consist of vertical disks that are mounted on a

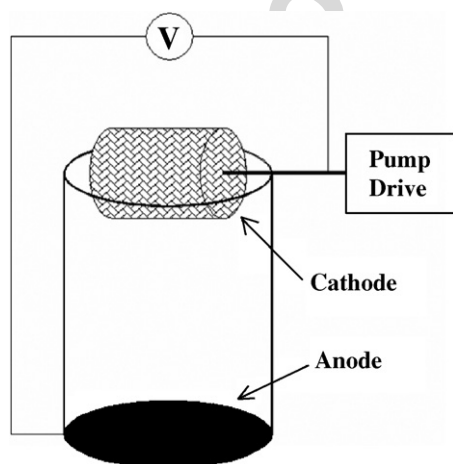
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horizontal shaft and are partially immersed in the wastewater while rotating continuously. The intermittent exposure of the rotating disks to air provides oxygen to the attached biofilms for aerobic bacterial metabolism of organic material in the wastewater (Masters, 1998). Rotation of the disks also increases the dissolved oxygen in the wastewater. We show herein that the RBC concept was also beneficial for sediment MFCs by increasing the oxygen availability to a rotating cathode electrode. No external energy input is necessary when the rotating disks are driven by natural river currents or ocean tides.

## 2. Experimental

### 2.1. Sediment MFC setup and operation

A river sediment MFC was constructed in the laboratory as described previously (Reimers et al., 2001; Tender et al., 2002) except that a platinum-coated cathode was used (Scheme 1). Carbon cloth (apparent surface area of 100 cm<sup>2</sup>, E-Tek, Somerset, NJ) was placed on the bottom of a plastic bottle (working volume of 1.3 L) as the anode electrode and covered by a 0.5-cm layer of fresh sediment from the Mississippi river (St. Louis, MO). A horizontal shaft was placed in a cylindrical cathode that was made of reticulated vitreous carbon (RVC, 10 PPI, ERG, Oakland, CA). The shaft and cathode were rotated by a Masterflex pump (Cole-Parmer Instrument Company, Vernon Hill, IL). The cathode was 50% submerged in the river water at a distance of 12 cm from the bottom of the cathode to the top of the anode. The cathode electrode had a diameter of 6 cm, a length of 6 cm and a surface area of 86 cm<sup>2</sup>. Platinum was coated on the cathode electrode (<0.5 mg Pt/cm<sup>2</sup>) by chemical deposition (Gharibi et al., 2005). The anode and cathode electrodes were connected to an external electric circuit via a carbon fiber (Zoltek Companies Inc., St. Louis, MO) and a copper wire, respectively. The operation was conducted at room temperature (~21 °C). The sucrose solution consisted of (per litre of deionized water): sucrose, 2.16 g; NH<sub>4</sub>Cl, 0.08 g; CaCl<sub>2</sub>·2H<sub>2</sub>O, 0.08 g; KCl, 0.08 g; NaCl, 0.40 g; MgCl<sub>2</sub>, 0.08 g; K<sub>2</sub>HPO<sub>4</sub>, 0.72 g; KH<sub>2</sub>PO<sub>4</sub>, 0.32 g; FeCl<sub>2</sub>, 0.04 g;



Scheme 1. Schematic of a lab-scale sediment MFC with a rotating cathode made of carbon foam.

K<sub>2</sub>SO<sub>4</sub>, 0.02 g; iron citrate, 0.01 g; yeast extract, 0.002 g; and trace metals (1.6 mL) (He et al., 2005).

### 2.2. Chemical and electrochemical analyses

The chemical and electrochemical measurements followed the procedures described previously (He et al., 2005). The dissolved oxygen was measured using a DO meter (Model 50B, YSI Incorporated, Yellow Springs, Ohio, USA). We used an equivalent circuit (EC) for the analysis of the anodic impedance spectroscopy (S. 1).  $R_s$  and  $R_c$  represent the electrolyte and electric resistance of the anode, while  $R_t$  is the anodic charge transfer resistance.  $Q_{dl}$ ,  $Q_c$ , and  $Q$  represent the double layer capacitance and other capacitors. A constant phase element (CPE), instead of a capacitor element, was employed during simulation (not shown in the EC) because of a serious dispersion effect, which relates to a rough electrode surface. The diffusion characteristic appears at the low frequency; however, the slope of the diffusion characteristic line is much lower than 1, indicating that it is not a typical Warburg infinite length diffusion. Therefore, a CPE was employed to represent this diffusion characteristic. Impedance spectroscopy measurement for the rotating cathode produced chaotic data and could not be utilized for analysis.

## 3. Results and discussion

Initially, the river sediment MFC was operated without cathode rotation. After operating for 30 h with an immobile cathode, the sediment MFC produced a maximum potential of 0.19 V at an external resistance of 1000 Ω (data not shown). Subsequently, this peak potential decreased to 0.06 V in the following 65 h due to consumption of easily degradable organic materials in the sediment. The potential of the sediment MFC temporarily increased to 0.09 V within 1 h after beginning cathode rotation (0.5 rpm), but it then dropped to zero volts within 22 h due to the accelerated breakdown of the remaining organic material in the sediment.

Upon the addition of an exogenous electron donor (sucrose solution) to the sediment at a 0.5-rpm rotational cathode speed, the potential increased from zero to 0.36 V within 27 h and remained constant for 40 h (1000 Ω—data not shown). We fed a synthetic solution containing sucrose and phosphate buffer with a conductivity of ~10,000 μS/cm (estimated at 20 °C) at a 10-day hydraulic retention time. When the rotational speed of the cathode was increased from 0.5 to 2 rpm after 7 days of feeding the sucrose solution, the potential increased further to 0.50 V within 12 h and remained constant for 25 h. Discontinuation of sucrose addition to the sediment decreased the potential from 0.50 V to below 0.10 V (Fig. 1). When sucrose addition was reestablished, the potential returned to ~0.50 V (Fig. 1), indicating that an ample supply of easily degradable organic material is crucial for electricity generation. The slow increase in water conductivity of the MFC electrolyte over a period of 10 days (one hydraulic retention time) by replacing river water with the sucrose solution (containing phosphate buffer) did not increase the potential considerably.

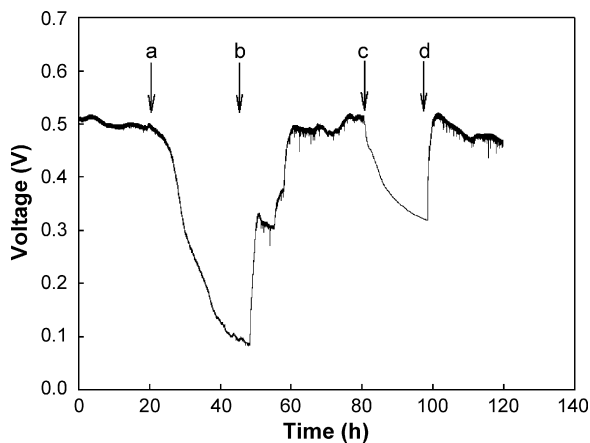


Fig. 1. Voltage production at an external resistor of  $1000 \Omega$  with a rotating speed of 2 rpm. A sucrose solution was fed when the feeding pump was switched on: (a) the feeding pump was switched off; (b) the feeding pump was switched on; (c) the rotating cathode was switched off; (d) the rotating cathode was switched on.

The beneficial effect of the rotating cathode was demonstrated by stopping and then restarting cathode rotation during sucrose addition (Fig. 1) and investigated further by constructing polarization curves after varying the external resistor between open circuit and  $40 \Omega$  (Fig. 2A). The maximum power density

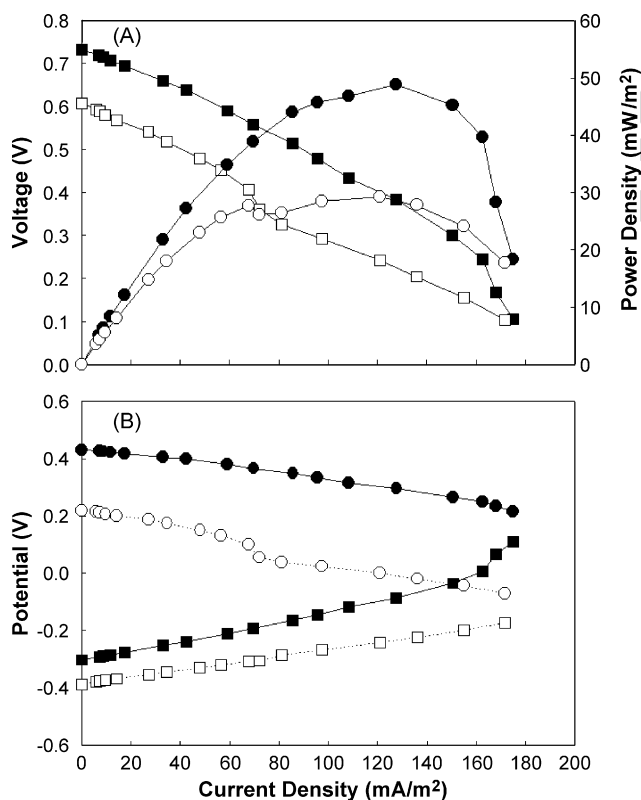


Fig. 2. Comparison of sediment MFCs performance with and without a rotating cathode: (A) polarization curves of the sediment MFC with (black) and without (white) a 2-rpm rotating cathode when the sucrose solution was continuously fed: voltage (square) and power density (circle); (B) anode (square) and cathode (circle) potentials (vs. Ag/AgCl, 205 mV vs. SHE) as a function of current density: with (black) and without (white) a 2-rpm rotating cathode.

with a nonrotating cathode was  $29 \text{ mW/m}^2$ . When the cathode was rotating, the maximum power density was  $49 \text{ mW/m}^2$ , which is a 69% improvement over the nonrotating cathode. We found higher power densities than have been reported for other sediment MFC studies. Besides the rotating cathode, these high densities were obtained in part because platinum was used as the cathode catalyst, and in part due to the addition of a steady supply of easily degradable organic material, which mimicked the natural replenishment of Mississippi sediments.

Cathode rotation increased the dissolved oxygen concentration from 0.4 to 1.6 mg/L in the bulk liquid adjacent to the cathode. This resulted in a higher cathode potential (vs. an Ag/AgCl reference electrode) regardless of the current density (Fig. 2B), and thus improved overall performance compared to the nonrotating cathode. At open circuit, the cathode potential with and without a rotating cathode was 0.43 and 0.22 V, respectively (Fig. 2B). As a result, the overall open-circuit potential was 0.73 and 0.61 V, respectively (Fig. 2A).

The rotating cathode also produced a consistently higher (less negative) anode potential than the nonrotating cathode (Fig. 2B), which has a negative effect on the overall performance. This negative effect of the higher dissolved oxygen (the dissolved oxygen level at the sediment/liquid interface was 1.5 mg/L during rotation) on the anode potential was more severe at the higher current densities  $>160 \text{ mA/m}^2$  during which the overall voltage decreased faster over the current density with rotation compared to without rotation, resulting in a similar overall voltage at the highest current density of 172–175  $\text{mA/m}^2$  (Fig. 2B). The accelerated decline in overall voltage (and thus the power density) was likely caused by the insufficient supply of protons/cations from the anode to match the increased demand from the cathode reaction. Indeed, the rotating cathode increased the pH from  $6.90 \pm 0.16$  to  $7.43 \pm 0.08$  due to a faster consumption of protons (Rozendal et al., 2006; Zhao et al., 2006).

We investigated differences of the anodic resistances using impedance spectroscopy (IS). This electrochemical technique has recently been used to study the internal resistance of MFCs, which is a key factor limiting their power output (He et al., 2006). By fitting experimental data into equivalent circuits (S. 1) and performing simulations (Fig. 3), we found that the total anodic resistance (including anodic electrolyte resistance and anodic charge transfer resistance) was 105.5 and  $78.0 \Omega$  for the rotating and nonrotating cathode, respectively. This difference was due to the higher anodic charge transfer resistance of the rotating cathode ( $65.1 \Omega$ ) compared to the nonrotating cathode ( $28.0 \Omega$ ), demonstrating the negative effect of the higher dissolved oxygen level in the sediment on the capacity of the electrogenic bacteria. These bacteria are often strictly anaerobic, and traces of oxygen will slow the electron transfer rate from the biofilm to the anode. The anodic electrolyte resistances, which are the x-axis intercepts in Fig. 3, were only slightly different ( $40.4$  and  $50.0 \Omega$  for the rotating and nonrotating cathode, respectively), probably due to minor improvement in ion transport caused by mixing of water during cathode



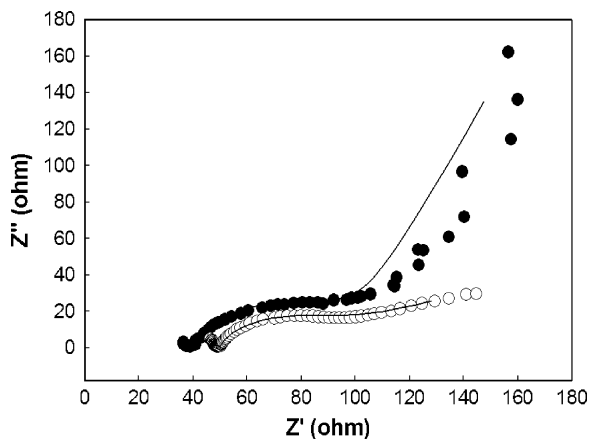


Fig. 3. Nyquist plot of impedance spectroscopy for anode electrodes with (black) and without (white) a 2-rpm rotating cathode when the sucrose solution was continuously fed. Both solid lines represent simulated data with equivalent circuits.

rotation. Thus, an optimum balance between the improvement of the cathode reaction and the deterioration of the anode reaction due to higher dissolved oxygen levels must be established.

#### 4. Conclusion

In this paper, we have shown an improved performance of a river-water sediment MFC by rotating the cathode to supply additional oxygen. Compared to an immobile cathode, the maximum power density was improved from 29 to 49 mW/m<sup>2</sup> (a 69% improvement) when the cathode rotated. The rotating cathode is promising when natural water currents or ocean tides are available to drive the rotating cathode. However, excess oxygen in the bulk liquid of the MFC increased the anodic charge transfer resistance, ultimately limiting the power density at the highest current. Thus, an optimum rotational speed of the cathode is required. The improvement of the sediment MFC system could become pertinent for the bioremediation of contaminated sediments in rivers, because a higher electric current demonstrated the accelerated breakdown of organic materials at the anode due to the indirect addition of a free electron acceptor (O<sub>2</sub>) through the fuel cell.

#### Supplementary material

The figure of equivalent circuit (S. 1) is available free of charge via the Internet at <http://www.sciencedirect.com>.

#### Acknowledgement

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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.2007.01.010.

#### References

- Angenent, L.T., Karim, K., Al-Dahhan, M.H., Wrenn, B.A., Domiguez-Espinosa, R., 2004. Trends Biotechnol. 22 (9), 477–485.
- Bond, D.R., Holmes, D.E., Tender, L.M., Lovley, D.R., 2002. Science 295, 483–485.
- Gharibi, H., Mirzaie, R.A., Shams, E., Zhiani, M., Khairmand, M., 2005. J. Power Sources 139, 61–66.
- He, Z., Minteer, S.D., Angenent, L.T., 2005. Environ. Sci. Technol. 39 (14), 5262–5267.
- He, Z., Wager, N., Minteer, S.D., Angenent, L.T., 2006. Environ. Sci. Technol. 40 (17), 5212–5217.
- Lovley, D.R., 2006a. Nat. Rev. Microbiol. 4, 497–508.
- Lovley, D.R., 2006b. Curr. Opin. Biotechnol. 17 (3), 327–332.
- Lowy, D.A., Tender, L.M., Zeikus, J.G., Park, D.H., Lovley, D.R., 2006. Biosens. Bioelectron. 21, 2058–2063.
- Masters, G.M., 1998. Introduction to Environmental Engineering and Science, second ed. Prentice-Hall, Inc., Upper Saddle River, New Jersey.
- Rabaey, K., Verstraete, W., 2005. Trends Biotechnol. 23 (6), 291–298.
- Reimers, C.E., Tender, L.M., Fertig, S., Wang, W., 2001. Environ. Sci. Technol. 35, 192–195.
- Reimers, C.E., Girguis, P., Stecher III, H.A., Tender, L.M., Ryckelynck, N., Whaling, P., 2006. Geobiology 4, 123–136.
- Rozendal, R.A., Hamelers, H.V.M., Buisman, C.J.N., 2006. Environ. Sci. Technol. 40 (17), 5206–5211.
- Shantaram, A., Beyenal, H., Veluchamy, R.R.A., Lewandowski, Z., 2005. Environ. Sci. Technol. 39 (13), 5037–5042.
- Tender, L.M., Reimers, C.E., Stecher III, H.A., Holmes, D.E., Bond, D.R., Lowy, D.A., Pilobello, K., Fertig, S.J., Lovley, D.R., 2002. Nat. Biotechnol. 20, 821–825.
- Zhao, F., Hamisch, F., Schroder, U., Scholz, F., Bogdanoff, P., Hermann, I., 2006. Environ. Sci. Technol. 40 (17), 5193–5199.