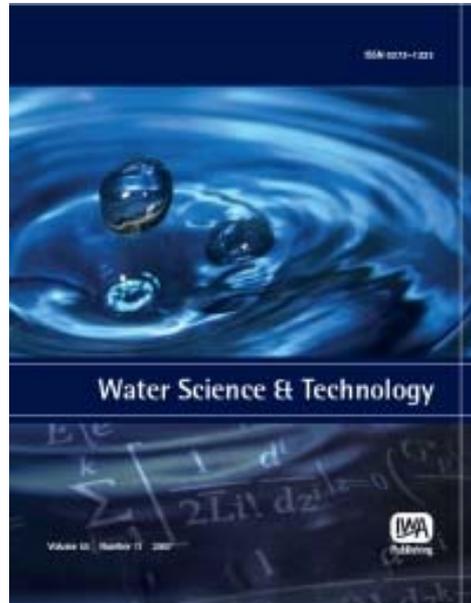


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Production of electricity from surplus sludge using a single chamber floating-cathode microbial fuel cell

Zhihua Liu, Xiaoming Li, Bin Jia, Yao Zheng, Li Fang, Qi Yang, Dongbo Wang and Guangming Zeng

ABSTRACT

A single-chamber, membrane-less and floating-cathode microbial fuel cells (MFC) was successfully started up using surplus sludge as fuel without adding carbohydrate after 20 days. The electricity generation of the MFC was investigated. The results showed that the obtained maximum voltage was 440.7 mV when external resistance was 1,000 Ω . There were four phases (rapid fall phase, stationary phase, fall phase and stationary phase of low voltage) in the periodic time of MFC, and the output voltage range of 150–300 mV lasted for 107 hours during stationary phase. In addition, the obtained maximum power density was 220.7 mW m^{-2} and internal resistance was 368.13 Ω in the MFC. Consequently, surplus sludge could be used to generate electricity in MFC, which could provide a novel process for sludge recycling.

Key words | floating cathode, microbial fuel cell, surplus sludge

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INTRODUCTION

Microbial fuel cells (MFCs) are being developed as a new method for both renewable energy production and wastewater treatment (Heilmann & Logan 2006). Electrically active bacteria at the method of an MFC oxidize substrates under anaerobic conditions. This oxidation by the bacteria releases protons and electrons. The electrons are transferred to the anode and travelled through a circuit to the cathode. The protons move directly to the cathode through solution. At the cathode, oxygen, protons and electrons are combined to produce water (Logan *et al.* 2006). Electricity has been generated in MFCs from various organic compounds, including sugars, starch, cellulose, domestic wastewater, industrial and animal waste streams (Min & Logan 2004; Rodrigo *et al.* 2006; Zhang *et al.* 2006; Ren *et al.* 2007; Tunc *et al.* 2008). However, compared to chemical fuel cells, MFCs are low power density. The power density in MFCs could be enhanced by improving the operating conditions. In air-cathode MFC, the maximum power density was 2,400 mW m^{-2} (normalized to the cathode projected

surface area) using graphite fiber brush anodes at 9,600 $\text{m}^2 \text{m}^{-3}$ reactor volume (Logan *et al.* 2007). The cathode catalysts such as Pt, CoTMPP are main means to reduce cathode overvoltage in MFC (Cheng *et al.* 2006a). However, the recent research shows the non-catalyzed cathode MFCs can be operated efficiently using high surface graphite as cathode material (Freguia *et al.* 2007). In addition, the power density could be enhanced by improving reactor structure, such as square MFC, cylinder MFC, rotating cathode MFC, cassette-electrode MFC and graphite-granule membrane-less tubular air-cathode MFC (Liu & Logan 2004; He *et al.* 2007; Kim *et al.* 2007; You *et al.* 2007; Shimoyama *et al.* 2008).

With handling capacity of wastewater increasing in the city, the quantity of surplus sludge would be increased in municipal sewage plant and it would become an important problem to deal with surplus sludge. Up to 2008, there are 1470 urban sewage treatment plants that were operated in China. The projected processing capacity was

$9.038 \times 10^7 \text{ t d}^{-1}$ and the practical handling capacity was $6.639 \times 10^7 \text{ t d}^{-1}$. As a result, the unsettled amount of sludge was $1.822 \times 10^7 \text{ t}$ in 2008 and it would be increasing. The sludge disposal not only consumes large amount of energy and cost but also generates the secondary pollution. So it is the research emphasis to sludge recycling, such as bio-hydrogen production and composting (Yin & Tang 2005; Xie *et al.* 2008). The previous study shows electricity can be generated directly from sludge (Dentel *et al.* 2004), but the power density was very low. Because there are abundant organic matters (protein, carbohydrate, fats etc.) in the sludge, it is an important research directions to improve the power density by fully using the organic matters in surplus sludge. Therefore, it is of great interest to develop new the reactor structure and operating conditions that can improve power density.

Since the power output of MFCs is low relative to other types of fuel cell, it will be essential to reduce their cost if power generation using this technology is to be an economical method of energy production (Liu & Logan 2004). The use of air-cathode can reduce MFC costs because passive oxygen transferring to the cathode does not require energy intensive air sparging of the water. Proton exchange membranes (PEMs) such as Nafion are quite expensive. Moreover, the catalysts in the cathode such as Pt are quite expensive. So we wondered if these materials were essential for power production in an MFC.

In this study, we designed and constructed the single-chamber, membrane-less and floating-cathode MFC using surplus sludge. The performance and characteristics of the MFC was investigated in terms of electrode potential and power density from surplus sludge without adding carbohydrate.

MATERIALS AND METHODS

MFC construction and operation

The single-chamber, membrane-less and floating-cathode MFC was designed and constructed, which consisted of an anode placed on the bottom and a floating cathode placed on the top in a glass cylindrical chamber (empty bed volume of 200 mL) (Figure 1). The anode was made of

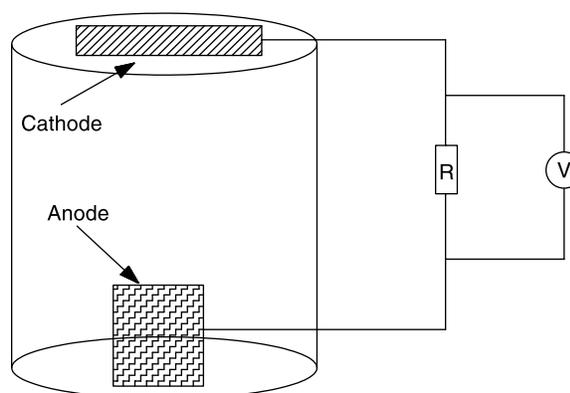


Figure 1 | Schematic of single-chamber, membrane-less and floating-cathode MFC used to generate electricity from surplus sludge.

rough graphite (its superficial area was 6 cm^2) and did not contain a catalyst. The cathode used in the absence of the catalyst was the rough graphite and was floated with 1/2 of the electrode being exposed to the air. Copper wire was used to connect the circuit ($1,000 \Omega$ resistor unless stated otherwise). The system was considered to be operating under steady conditions when the voltage output was reproducible after refilling the reactor with medium at least two times.

Experimental conditions

The fuel used in the experiment came from the desilter of the municipal sewage treatment plant (Changsha, China). The reactor was repeatedly filled with sludge without adding carbohydrate until bacteria in the sludge colonized the electrodes and produced electricity. The chamber was refilled when the voltage decreased to less than 20 mV ($1,000 \Omega$ resistor). Experiments were conducted at a constant temperature ($30^\circ\text{C} \pm 1^\circ\text{C}$).

Analytics and calculation

COD were measured using a standard method (CEPA 2002). The data were collected automatically using a multimeter with a data acquisition system (UT803, China) and a personal computer. Following a stable power generation, the external resistor was varied over the range of 0–5,000 Ω to obtain a polarization curve.

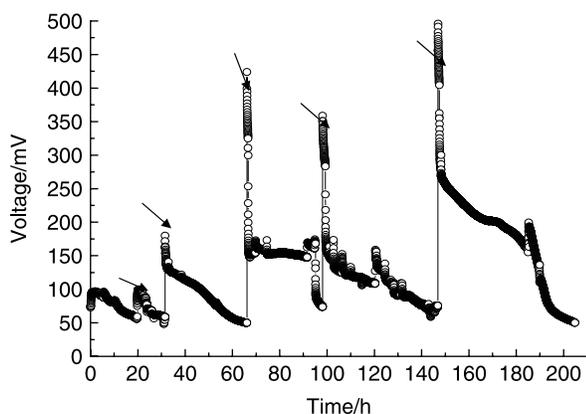


Figure 2 | Startup of MFC using sludge without adding carbohydrate (arrowhead indicates substrate change).

Electric current (I) was calculated by ohm's law,

$$I = \frac{U}{R_e} \quad (1)$$

where U was the voltage and R_e the external resistance.

Power density (P) was calculated as

$$P = \frac{UI}{A} = \frac{U^2}{RA} \quad (2)$$

where A was the anode superficial area.

The internal resistance of MFCs (r_{int}) was calculated from the slope of plots of voltage (V) versus current (I) using

$$U = -Ir + \varepsilon \quad (3)$$

When R_e equal to r , the power density was maximal,

$$P_{max} = \frac{\varepsilon^2}{4rA} \quad (4)$$

where ε was generated voltage and r internal resistance.

RESULTS AND DISCUSSION

Startup of MFC using surplus sludge

A repeatable cycle of power generation was sustained by surplus sludge after an acclimated period of approximately 20 days. The startup of MFC in latter 10 days was shown (Figure 2). The voltage generation decreased gradually when the new substrate (surplus sludge) was added to the reactor. When the voltage decreased to less than 50 mV,

one cycle was over and then the 3/4 sludge of reactor was replaced with new one. In addition, the maximum voltage increased from 100 mV to 455.9 mV when running time from 20 hours to 60 hours.

These experiments indicated that electricity production at relatively high power densities could be sustained using surplus sludge. So the single-chamber, membrane-less and floating-cathode MFC with the sludge as fuel could supply a new path for sludge recycling.

Power generation using surplus sludge

The system developed here was able to continuously generate electricity from the organic matter in the surplus sludge while accomplishing sludge treatment. When the system was stably operated during the batch cycle after 2 months, the electricity generation over time under steady state was presented in Figure 3. It showed that the maximal voltage output was 440.7 mV and the working time of the cycle was 175 hours. There were four phases in the Figure 3. Phase I was the rapidly falling phase, where the voltage output quickly decreased from 440.7 mV to 300 mV at the beginning of system operated for 2.9 hours. Phase II was the stable phase, where the voltage putout was 150–300 mV for 107 hours. Phase III was the falling phase, where the voltage decreased from 150 mV to 20 mV in 22 hours. Phase IV was the stable phase of low voltage, where the voltage was approximately 220 mV for 43 hours.

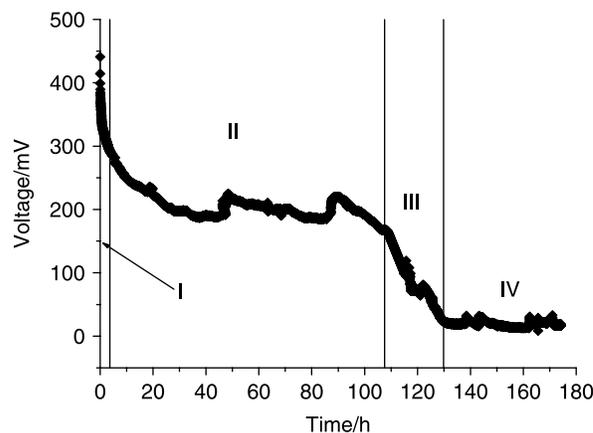


Figure 3 | Electricity generation over time under steady state.

The experiments were adopted a single-chamber, membrane-less and floating-cathode MFC. A periodic time of MFC was divided four phases (Figure 3). In the voltage stale phase, the voltage could maintain higher value (150–300 mV) for a long time, which was a feature of MFC with surplus sludge as fuel without Plus carbohydrate. This result was different with the previous one of MFC investigations (Dentel *et al.* 2004). About this new phenomenon, we would give a detailed illustration.

SCOD concentration of substrate and voltage as a function of time were presented in Figure 4. The voltage output was changed with the changing of SCOD, which indicated that the voltage output was correlated with the SCOD concentration of substrate. At the beginning of the periodicity, there were a mass of biodegradation matter (volatile fatty acid, VFA) (Hu 1998), and the rapid decomposition of such matter was the vital reason that the voltage decreased rapidly in the first phase. In the second phase, the SCOD concentration of substrate kept stable which resulted in the stable voltage output. At the end of periodicity, the concentration of SCOD still was high (555 mgL⁻¹), but the voltage output was low (only 82.4 mV). This result was different with the previous one of MFC investigations (Dentel *et al.* 2004; Liu & Logan 2004). The result showed that there were large numbers of soluble proteins and total sugar in the system at the end of periodicity (data not show). These matters could be also used as fuel in MFC, but it remains unclear how to make full use of the usable matter in the surplus sludge, thereby increasing the power output.

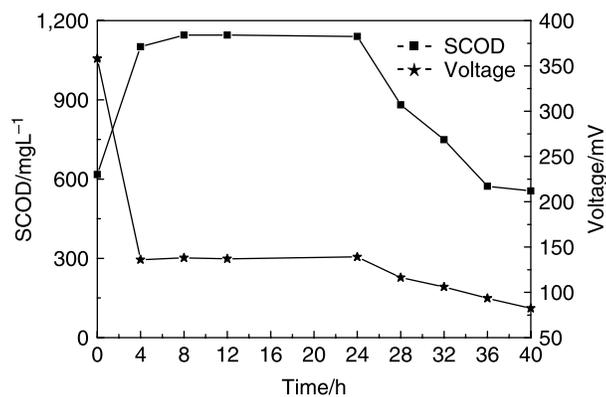


Figure 4 | SCOD concentration and voltage as a function of time.

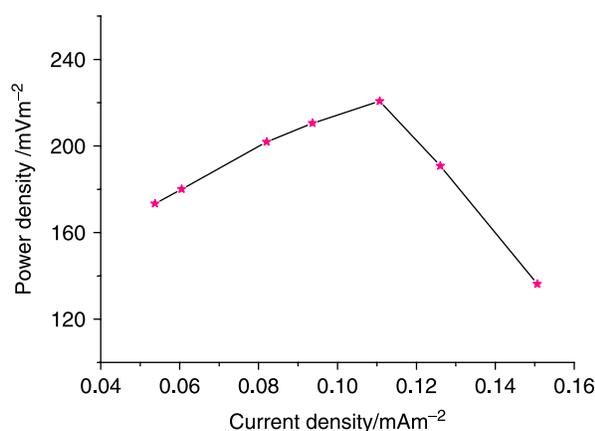


Figure 5 | Power density as a function of current density.

Polarization curve

The maximum power density of MFC using surplus sludge as fuel was determined by varying the circuit resistance from 5,000 Ω to 0 Ω (Figure 5). From Figure 5, it was found that the maximum power density was 220.7 mW m⁻² when the current density was 0.11 mA cm⁻² and the external resistance was 350 Ω.

Figure 6 plots cell voltage versus current. The result of the fitted line showed that the generated voltage was 431.18 mV and internal resistance was 368.13 Ω which was coincident with the experiment result (350 Ω). According to the Equation (4), we could calculate the maximum power density that was 210.4 mW m⁻². The calculation result was in agreement with the experiment result (220.7 mW m⁻²).

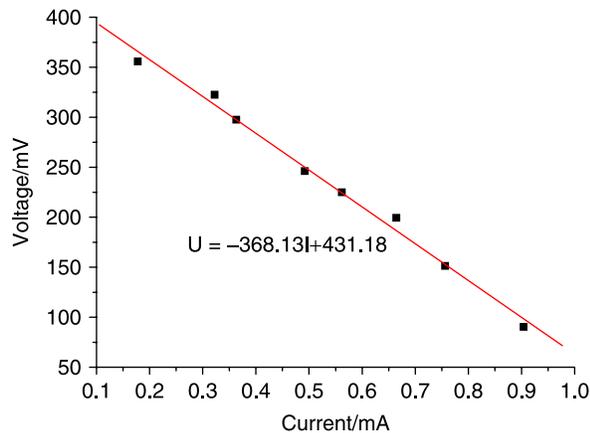


Figure 6 | Voltage as a function of current.

Table 1 | Power generation and catalyst of cathode reported in the literature versus those obtained in this study

Substrate	Description	Catalyst of cathode	P_{\max} (mW m^{-2})	Reference
Defined	Glucose	Pt	494	Liu & Logan (2004)
	Glucose	CoTMPP	403	Zuo <i>et al.</i> (2007)
	Bovine serum albumin	Pt	354	Heilmann & Logan (2006)
	Acetate	FePC	2,011	Yu <i>et al.</i> (2007)
	Glucose	None	101	Zuo <i>et al.</i> (2007)
Complex	Meat packing wastewater	Pt	80	Heilmann & Logan (2006)
	Domestic wastewater	Pt	146	Liu & Logan (2004)
	Surplus sludge	None	220.7	This study

Table 2 | Power generation and internal resistant reported in the literature versus those obtained in this study

Substrate	Internal resistant (Ω)	P_{\max} (mW m^{-2})	Reference
Acetate	281.28	146.56	You <i>et al.</i> (2006)
Glucose	317.21	192.04	You <i>et al.</i> (2006)
Acetate	320	76	Min & Logan (2004)
Surplus sludge	368.13	220.7	This study
Acetate	77	1,210	Liu <i>et al.</i> (2005)
Glucose	89	403	Zuo <i>et al.</i> (2007)
Glucose	35	811	Cheng <i>et al.</i> (2006b)

The maximum power output (220.7 mW m^{-2}) in the MFC using surplus sludge is 1.6–2.8 times higher than the values (range of $80\text{--}146 \text{ mW m}^{-2}$) obtained in MFCs using meat packing wastewater, domestic wastewater and glucose without catalyst in the cathode, respectively (Table 1). However, this power generation was lower in comparison with MFC using glucose, acetate and protein showing the maximum power density of $4,032,011,354 \text{ mW m}^{-2}$, respectively. The possible explanations for the lower power output could be due to the cathode overvoltage compared to the MFCs with the cathode catalyst (Pt, CoTMPP *et al.*).

The internal resistance was an important data to judge the performance of MFC. In the membrane-less MFC, the internal resistance was 281.28Ω with acetate and 317.21Ω with glucose, and the power density was 146.56 and 192.04 mW m^{-2} , respectively (Table 2). Our experimental results (368.13Ω , 220.7 mW m^{-2}) were comparable to the above results. Improving the operating conditions of MFC (increasing anode surface area, increasing electric

conductivity *et al.*) the internal resistance could reduce to 35Ω and the power density could increase to 811 mW m^{-2} using glucose, while that reduce to 77Ω and increased to $1,210 \text{ mW m}^{-2}$ using acetate, indicating that further decrease the internal resistances in MFC using surplus sludge could improve the power density.

CONCLUSION

- (1) A single-chamber, membrane-less and floating-cathode microbial fuel cell was successfully started up using surplus sludge as fuel without adding carbohydrate after 20 days.
- (2) There were four phases (rapid fall phase, stationary phase, fall phase and stationary phase of low voltage) in the periodic time of microbial fuel cell. The putout of voltage range of $150\text{--}300 \text{ mV}$ was lasted for 107 hours during stationary phase.

- (3) The obtained maximum power density are 220.7 mW m^{-2} and internal resistance was 368.13Ω in the microbial fuel cell using surplus sludge as fuel.

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REFERENCES

- Cheng, S., Liu, H. & Logan, B. E. 2006a Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells. *Environ. Sci. Technol.* **40**(1), 364–369.
- Cheng, S., Liu, H. & Logan, B. E. 2006b Increased power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing. *Environ. Sci. Technol.* **40**(7), 2426–2432.
- China Environmental Protection Agency 2002 *Water and Wastewater Monitoring Analysis Method*, 4th edition. China Environmental Sciences Press, Beijing.
- Dentel, S. K., Strogen, B. & Chlu, P. 2004 Direct generation of electricity from sludges and other liquid wastes. *Water Sci. Technol.* **50**(9), 161–168.
- Freguia, S., Rabaey, K., Yuan, Z. & Keller, J. 2007 Non-catalyzed cathodic oxygen reduction at graphite granules in microbial fuel cells. *Electrochimica Acta* **53**, 598–603.
- He, Z., Shao, H. & Angenent, L. T. 2007 Increased power production from a sediment microbial fuel cell with a rotating cathode. *Biosens. Bioelectron.* **22**, 3252–3255.
- Heilmann, J. & Logan, B. E. 2006 Production of electricity from proteins using a microbial fuel cell. *Water Environ. Res.* **78**(5), 531–537.
- Hu, Y. 1998 Organic matter concentration and biodegradation of liquid from sludge storage. *Shanghai Environ. Sci.* **17**(8), 12–15.
- Kim, J. R., Chen, S., Oh, S.-E. & Logan, B. E. 2007 Power generation using different cation, anion, and ultrafiltration membranes in microbial fuel cells. *Environ. Sci. Technol.* **41**(3), 1004–1009.
- Liu, H. & Logan, B. E. 2004 Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environ. Sci. Technol.* **38**(14), 4040–4046.
- Liu, H., Cheng, S. & Logan, B. E. 2005 Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature, and reactor configuration. *Environ. Sci. Technol.* **39**(14), 5488–5493.
- Logan, B. E., Hamelers, B., Rozendal, R., Schroder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W. & Rabaey, K. 2006 Microbial fuel cell: methodology and technology. *Environ. Sci. Technol.* **40**(17), 5181–5192.
- Logan, B., Shaoan, C., Watson, V. & Estadt, G. 2007 Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. *Environ. Sci. Technol.* **41**(9), 3341–3346.
- Min, B. & Logan, B. E. 2004 Continuous electricity generation from domestic wastewater in a flat plate microbial fuel cell. *Environ. Sci. Technol.* **38**(21), 5809–5814.
- Ren, Z., Ward, T. E. & Regan, J. M. 2007 Electricity production from cellulose in a microbial fuel cell using a defined binary culture. *Environ. Sci. Technol.* **41**(13), 4781–4786.
- Rodrigo, M. A., Canizares, P., Lobato, J., Paz, R., Saez, C. & Linares, J. J. 2006 Production of electricity from the treatment of urban waste water using a microbial fuel cell. *J. Power Sources* **169**, 198–204.
- Takefumi, S., Shoko, K., Akira, Y., Yoshiyuki, U., Logan, B. E. & Kazuya, W. 2008 Electricity generation from model organic wastewater in a cassette-electrode microbial fuel cell. *Appl. Microbiol. Biotechnol.* **80**, 325–330.
- Tunc, C., Kaichang, L., Hakan, B. & Hong, L. 2008 Electricity production from twelve monosaccharides using microbial fuel cells. *J. Power Sources* **175**, 196–200.
- Xie, B., Guo, L., Li, X., Yang, Q., Zhang, Y., Yang, Y., Zeng, G., Liu, J. & Yang, Z. 2008 Bio-hydrogen production from different pretreated sludge by *Pseudomonas sp* GL1 and changes in the liquid phases. *Environ. Sci.* **29**(4), 996–1001.
- Yin, J. & Tang, X. 2005 *Sewage Sludge Disposal and Recycling*. Chemical Industry Press, Beijing.
- You, S., Zhao, Q. & Jiang, J. 2006 Biological wastewater treatment and simultaneous generating electricity from organic wastewater by microbial fuel cell. *Environ. Sci.* **27**(9), 1786–1790.
- You, S., Zhao, Q., Zhang, J., Jiang, J., Wan, C., Dua, M. & Zhao, S. 2007 A graphite-granule membrane-less tubular air-cathode microbial fuel cell for power generation under continuously operational conditions. *J. Power Sources* **173**, 172–177.
- Yu, E. H., Cheng, S., Scott, K. & Logan, B. 2007 Microbial fuel cell performance with non-Pt cathode catalysts. *J. Power Sources* **171**, 275–281.
- Zhang, E., Xu, W., Diao, G. & Shuang, C. 2006 Electricity generation from acetate and glucose by sedimentary bacterium attached to electrode in microbial-anode fuel cells. *J. Power Sources* **161**, 820–825.
- Zuo, Y., Cheng, S., Call, D. & Logan, B. E. 2007 Tubular membrane cathodes for scalable power generation in microbial fuel cells. *Environ. Sci. Technol.* **41**(9), 3347–3353.