Increasing power generation for scaling up single-chamber air cathode microbial fuel cells

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1. Introduction

Microbial fuel cells (MFCs) are devices that use microorganisms to catalyze the conversion of chemical energy in organic compounds into electrical power. They have great potential as a technology for sustainable bioenergy production due to their ability to generate electricity from wastewater while simultaneously treating wastewater (Logan and Regan, 2006). Several types of MFCs have been developed, including two-chamber (Oh and Logan, 2006), single-chamber (Liu et al., 2005a), upflow (He et al., 2006), flat (Min and Logan, 2004), and tubular (Zuo et al., 2007) designs. Most of these systems have been studied in the laboratory using high substrate concentrations and well buffered solutions (Liu et al., 2005a; Park and Zeikus, 2002). Electricity generation has also been demonstrated with different types of wastewaters, including domestic, food processing, and animal wastewaters (Liu et al., 2004; Rozendal et al., 2008). Among the different types of MFCs that have been developed, the air cathode MFC is the most likely configuration to be scaled up for wastewater treatment due to its high power output, simple structure, and relatively low cost. Solution conditions such as pH (Raghavulu et al., 2009), temperature, ionic strength (Liu et al., 2005b), and substrate concentration (Liu et al., 2004) can also affect power generation.

Through optimization of MFC architecture and solution chemistry, the maximum power densities of MFCs with oxygen have reached 6.9 W/m\textsuperscript{2} (power normalized to the anode area) (Fan et al., 2008), or 1.55 kW/m\textsuperscript{3} (power normalized to the reactor volume) (Fan et al., 2007). With a ferricyanide as catholyte, a maximum power density of 2.15 kW/m\textsuperscript{3} was produced using a small liquid volume (0.336 mL anode volume) (Nevin et al., 2008). These achievements indicate the MFC technology could advance to conventional anaerobic digesters in the term of power density, under optimized conditions (Rabaey and Verstraete, 2005). High power densities have only been achieved using laboratory-scale MFCs and liquid volumes less than 30 mL (Zhang et al., 2010a,b,c). When MFCs sizes have been tested at the scale of several liters or more, reported volumetric power densities generally have been lower, and typically less 35 W/m\textsuperscript{3} (Dekker et al., 2009; Liu et al., 2008). This suggests that scaling factors have not been well understood or controlled. In most cases the main reason for low power densities is a high internal resistance which can be due to anode and cathode overpotentials, substrate concentration, membrane resistance, and solution resistance (Clauwaert et al., 2008). To minimize internal resistance, electrodes should be designed to reduce electrode overpotential. High surface area materials and different surface treatments have been used to increase anode performance (Cheng and Logan, 2007; Logan et al., 2007). Increasing the anode surface area can significantly increase power density in smaller (28 mL) reactors (Logan et al., 2007), but it did not appear to increase power in a larger (520 mL) MFC of a similar...
design (Liu et al., 2008). Changing the solution composition can improve power densities in both larger and smaller systems, especially when solution conductivity is initially low. Increasing the ionic strength of larger MFC from 100 to 300 mM, for example, increased power by 25% (Liu et al., 2008). In a 20 L stacked, two-chamber MFC, cathode performance was improved by decreasing the pH, sparging with pure oxygen instead of air, and increasing the flow rate, resulting in a volumetric resistivity decrease to 1.2 mΩ/m² and a power density increase to 144 W/m³ (Dekker et al., 2009). Balancing pH by using completing the liquid loop over cathode and anode (Clauwaeert et al., 2009), or adding CO₂ to cathode to minimize pH imbalance in both anode and cathode chamber of two-chamber MFCs (Fornero et al., 2010) also increased power generation, but the additional energy demands for recycling the flow and the need for a membrane are detrimental aspects of these approaches.

It is generally thought that the cathode surface area limits power production, but this is based on laboratory studies with highly optimized solution conditions of feed strength (acetate concentration) and solution conductivity (buffer concentration). In addition, most previous studies have focused on a single type of reactor with acetate and buffer solutions, and not wastewater. Thus, little has been done to examine the importance of electrode surface areas, cathode performance and reactor geometry relative to solution conditions such as conductivity and substrate concentration relative to both idealized and actual wastewaters. Such information is needed in order to scale up MFCs and achieve high power densities with wastewater treatment systems. In this paper, we systematically varied substrate concentration using acetate, and conductivity, and then examined the effects on power using different cathode specific surface areas. We examined trends in cathode sizes using the acetate and wastewater solutions based on the data obtained here, combined with results from others. We show that cathode surface area is always important for increasing power, but that the cathode size has a much less appreciable impact on power generation with an actual wastewater due to limiting factors of wastewater strength (COD) and solution conductivity.

2. Methods

2.1. Microbial fuel cells

Single-chamber air cathode microbial fuel cells (MFCs) with four different liquid volumes having varied cathode specific surfaces areas were used in this study (Fig. 1). All reactors used the same type of anode brushes consisting of graphite fibers and a titanium core as previously described (Logan et al., 2007), but the brush size varied with the scale of the reactor. All cathodes contained a Pt catalyst and four diffusion layers prepared as previously described (Cheng et al., 2006a) in order to optimize cathode performance in these comparisons.

A 28-mL MFC was constructed as previously described (Logan et al., 2007) and used to study the effect of substrate concentration and solution conductivity on the electrode performance and power density. The specific surface area of the cathode for this MFC was 25 m²/m³.

A 250-mL MFC was constructed from a rectangular plastic container by cutting a 4 cm × 6 cm hole on each of the four sides, and placing air cathodes over each hole (sealed with Aquarium Sealant). A single graphite brush anode (5 cm in diameter, 7 cm in length) was suspended in the middle of the container. This 250-mL MFC was used to investigate the effect of cathode surface area on power generation. Cathode surface area was increased from 24 to 48, 72 and 96 cm² by connecting the additional cathodes in series, resulting in the cathode specific surface areas of 9.6, 19, 29 and 38 m²/m³.

Two larger but differently shaped MFCs were used to study the effect of reactor shape and cathode surface area on power generation, in order to see which design resulted in higher power densities. A 1-L MFC was made from a cylindrical container by cutting two holes on the side of bottle covering them with an air cathode. The cathode active area was 132 cm², producing a cathode specific surface area of 13 m²/m³. A single graphite brush anode (5 cm in diameter, 14 cm in length) was suspended in the middle of the bottle.

A larger 1.6-L MFC was constructed in the same plate-shaped arrangement as the 28 mL reactor, using four brush anodes [each 5 cm in diameter, 7 cm in length (Logan et al., 2007)] and one or two cathodes (one on each side). The cathode surface area with both cathodes was 290 cm², resulting in the cathode specific surface area of 9.1 m²/m³ with one cathode, or 18 m²/m³ (using two cathodes).

2.2. Inoculation and operation of MFCs

All MFCs were inoculated with a suspension of bacteria from an existing MFC fed operated for approximately two years, and enriched with an external resistor of 1000 Ω. After inoculation with a 50:50 mixture of inoculum and medium, the MFCs were fed only the 100 mM phosphate buffer solution containing 1 g/L (except as noted) sodium acetate and nutrient medium containing 0.31 g/L NH₄Cl, 0.13 g/L KCl, 12.5 mL/L mineral solution, and 5 mL/L vitamin solution (Liu et al., 2005a). The feed solution was replaced when the voltage dropped below 20 mV, forming one complete cycle of operation.

The maximum power densities were calculated from polarization curves obtained either using linear sweep voltammetry (LSV) or by varying the external resistance (1000–50 Ω). LSV curves were obtained using a potentiostat (PC4/750 potentiostat, Gamry Instrument Inc., PA) from the open circuit voltage (OCV).
to 50 mV at a slow scan rate (0.1 mV/s) shown to produce good agreement with the multiple resistor method (Velásquez-Orta et al., 2009). A two-electrode system was used with the cathode as the working electrode and the anode as both the counter electrode and the reference electrode.

Acetate concentrations in the medium were varied (0.15, 0.25, 0.5, 1.0 and 2.0 g/L) to investigate the effect of substrate concentration on the electrode performance and power production in 28-mL MFCs with 100 mM phosphate buffer solution. Solution conductivity was varied from 1.7 to 20 mS/cm by using different concentrations of phosphate buffer (from 10 to 200 mM). Some tests were conducted with unamended domestic wastewater (TCOD = 420 mg/L, SCOD = 190 mg/L, pH = 7.2, conductivity = 1.3 mS/cm) collected from the primary clarifier overflow of Penn State University Wastewater Treatment Plant using 28-mL, 1 L and 1.6 L MFCs. Experiments were conducted twice at each solution conductivity, and the results averaged. All experiments were conducted in a constant temperature room at 30°C.

2.3. Analyses

The voltage (V) across an external resistance (1000 Ω except as noted) in the MFC circuit was monitored at 20 min intervals using a multimeter (Keithley Instruments, OH) connected to a personal computer. Current (I) and power (P = IV) was calculated as previously described (Kim et al., 2005), and normalized by the cathode surface area or the volume of liquid media. An Ag/AgCl reference electrode was set into the reactor closed to the cathode and used to record the cathode potential. The anode potential was obtained by subtracting cell voltage from cathode potential.

3. Results and discussion

3.1. Effect of substrate concentration on power generation and electrode potentials

The maximum power density was increased with the substrate concentration in 28 mL MFCs (Fig. 2A). At 0.15 g/L, the power density was 27 W/m³. When the substrate concentration increased, power increased by 33% to 36 W/m³ (0.5 g/L), and by 56% to 42 W/m³ at 1 g/L. Further increases in the acetate concentration to 2 g/L did not appreciably affect power density. Measurements of the electrode potentials show that the anode performance was significantly affected by substrate concentrations below 1 g/L, but that the cathode performance was not (Fig. 2B). For example, at current density of 3 A/m², increasing the substrate concentration from 0.15 to 1 g/L made the anode potential more negative by 0.115 V, decreasing it from −0.331 to −0.446 V (vs Ag/AgCl). This reduction in anode potential increased the power density by 36%. This result indicates that at low substrate concentrations power can be hindered by the anode, not the cathode.

3.2. Effect of solution conductivity on power generation and electrode potentials

The maximum power densities were increased with solution conductivity (by varying concentration of phosphate buffer) (Fig. 3A). At the solution conductivity of 1.7 mS/cm (10 mM PBS), which is typical for domestic wastewater, the power density was only 16 W/m³ with a current density of 2.8 A/m². Power density
increased by 107% to 33 W/m³ when the solution conductivity increased to 7.8 mS/cm (50 mM), a value typical of many laboratory studies. Further increases in conductivity to 20 mS/cm (200 mM PBS) increased the power to 60 W/m³, an increase similar to that previously reported for this reactor with carbon cloth anode (Liu et al., 2005b).

The main impact of solution conductivity was the cathode performance when the solution conductivity was below 20 mS/cm (200 mM PBS) (Fig. 3B). There was no appreciable impact on anode performance. For example, when the conductivity increased from 1.7 to 20 mS/cm, cathode potential increased by 0.27 V while the anode performance varied by less than 0.04 V. This shows that increase in power production was due only to the cathode performance.

3.3. Prediction of power generation with increasing electrode size

Domestic wastewater has both a low substrate concentration (COD) and a low conductivity. The maximum power density of MFC fed with domestic wastewater was only 8.3 W/m² in this 28 mL MFC. This is much lower than that obtained with 1 g/L acetate in a solution of similar conductivity, indicating that both the type of substrate and its concentration affected power production. As a result of the above studies, we can infer that when wastewater was used the anode performance was reduced due to the low COD of the wastewater, and the cathode performance was reduced due to the low conductivity compared to laboratory solutions (7.8 or 18.6 mS/cm).

![Fig. 4. Predicted power as function of current for (A) different cathode sizes and (B) different anode sizes in 28-mL MFCs with domestic wastewater. Numbers show the increasing rate of size (surface area for cathode, brush length for anode), numbers 1 refer to 7 cm² for cathode (A), and 25 mm diameter by 25 mm length brush for anode (B).](image)

By fitting the polarization curves obtained for the electrodes in the 28 mL MFC with domestic wastewater, equations were obtained for the cathode and anode potentials as a function of current density (Fig. 3B). Using these equations, we could predict the effect of the electrode size on the power generation. For the MFC fed with domestic wastewater, the equations were $E = -0.489i + 0.23 (R^2 = 0.98)$ for the cathode, and $E_a = 0.147i - 0.514 (R^2 = 0.99)$ for the anode. If the cathode size was increased and the anode size was unchanged, at same circuit current the anode potential would not be changed (same anode polarization), but the cathode potential would be increased as the cathode polarization decreased (cathode current density decreased). Thus the cell voltage is increased and the volumetric power density increased. Power generation was predicted to significantly increase with cathode surface area (from 7 to 28 cm²) not with anode size (length of a brush 25 mm in diameter that was varied from 25 to 100 mm) (Fig. 4). For example, doubling the cathode surface area was predicted to increase power by 62%, while the power was predicted to only increase by 12% by doubling the anode size. This showed that increasing cathode size was a more effective approach for increasing power production with brush anodes than anode surface area.

3.4. Effect of varying cathode surface area on power density

The 250-mL MFC (1 g/L acetate in 100 mM PBS) was used to investigate the effect cathode area on power density (using LSV). The power increased by a factor of 5, or from 15 to 78 W/m³, when the cathode surface area was increased from 24 to 96 cm² by increasing the number of cathodes from 1 to 4 (Fig. 5). For the 1, 2 and 3 cathode arrangements, as the voltage was scanned from the OCV ~800 to 50 mV, the power increased and symmetrically decreased except for the case with four cathodes (96 cm²). In this case the reactor exhibited “power overshoot”, whereby the power density dropped off faster than expected past the maximum power output. It has recently been shown that this is due to how long the reactor is acclimated to a specific resistance (Watson and Logan, 2011). Thus, power overshoot will result from insufficient time for bacteria to adjust to a different resistance. With longer acclimation times, it is likely that the power could be slightly increased to higher levels (Watson and Logan, 2011).

3.5. Performance of the larger MFCs

With domestic wastewater, 1.6 L plate-shape MFC produced a maximum power density of 3.5 W/m² with 1 cathode (9.1 m²/m³), and 6.8 W/m² with 2 cathodes (18.1 m²/m³), while the 1 L
Power production with MFCs having several different configurations, sizes and operation conditions was examined to better understand factors affecting scale up of these systems. Increasing the cathode size was one of the most efficient ways to increase volumetric power density of air cathode MFC, although the extent of the change in power was greater for laboratory solutions than a wastewater. For example, doubling the cathode size should increase power by 62%, but it only increased power by 12% by doubling the anode size. Experimental results obtained here (and in other studies) showed that the volumetric power density of MFC was linearly related to the cathode specific surface area and independent of MFC size, reactor configuration. The increasing rate (the slope of the line) of power density with cathode specific surface area depended on the solution composition, with the effect of cathode size much greater for acetate than for domestic wastewater. However, in all cases these results suggest that designing MFC with high specific surface area is a key factor for increasing power density when scaling up systems.

High cathode specific surface areas require that we use large cathodes with relatively less liquid per cathode surface area, and thus a smaller electrode spacing. For the cylinder-shaped MFC in which the anode was placed in the centre of the cylinder cathode, the cathode specific area is \( A_s = \frac{2}{r} \), where \( r \) is the radius of cylinder MFC (cathode specific area \( 13.2 \text{ m}^2/\text{m}^3 \)) produced 4.3 W/m\(^3\). Those volumetric power densities seem to be much lower than that previously obtained with ml-scale MFCs [8.3 W/m\(^3\) here, compared to 12.8 W/m\(^3\) by Ahn and Logan (2009) and 15.5 W/m\(^3\) by Cheng et al. (2006b)], all with a cathode specific area of 25 m\(^2\)/m\(^3\). However, if we analyze all data on the basis of the cathode specific surface area, we can see that the volumetric power density was a linear function of cathode specific surface area (slope of 0.348) (Fig. 6). Thus, we conclude that the configuration of the MFC (i.e., plate or cylinder) was less important than that the cathode specific surface area for power generation in tests with wastewater.

With higher substrate concentrations and solution conductivity using acetate and PBS, the maximum power density (Fig. 6) is also a linear function of the cathode specific surface area, although the slope of the line is much higher in this case (2.23; \( R^2 = 0.998 \)). This indicates that an increase in the cathode surface area produces much larger gains in power production with high substrate and high conductivity solutions than with actual wastewaters.

3.6. Implications for scaling-up MFCs

Power production with MFCs having several different configurations, sizes and operation conditions was examined to better understand factors affecting scale up of these systems. Increasing the cathode size was one of the most efficient ways to increase volumetric power density of air cathode MFC, although the extent of the change in power was greater for laboratory solutions than a wastewater. For example, doubling the cathode size should increase power by 62%, but only increased power by 12% by doubling the anode size. Experimental results obtained here (and in other studies) showed that the volumetric power density of MFC was linearly related to the cathode specific surface area and independent of MFC size, reactor configuration. The increasing rate (the slope of the line) of power density with cathode specific surface area depended on the solution composition, with the effect of cathode size much greater for acetate than for domestic wastewater. However, in all cases these results suggest that designing MFC with high specific surface area is a key factor for increasing power density when scaling up systems.

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Reducing costs while increasing large cathode specific surface areas is the main challenge for scaling-up MFCs that are capable of producing high power densities. Pt or other metal based catalysts, which are the common cathode catalysts for oxygen reaction in small MFCs, will likely not be feasible for large-scale MFCs. Using a biocathode to increase current densities shows great promise, but these systems so far have required dissolved oxygen rather than air at the cathode (Clauwaert et al., 2007; He and Angenent, 2006). Therefore, the use of these biocathodes would be costly due to the need to aerate water. It has been recently reported that an air cathode made of the activated carbon and a metal mesh as current collector had an oxygen reduction performance only slightly less than that of a Pt cathode, suggesting that it is possible to use much less expensive cathodes (Zhang et al., 2009). Taken together, these findings indicate that scaling-up MFCs is feasible, but additional work needs to be done on increasing the cathode specific surface area while controlling oxygen cross over so that MFCs can be used in practical applications.

4. Conclusions

Increasing the cathode specific surface area is the most important factor in scaling-up MFCs for wastewater treatment. Doubling the cathode size was predicted to increase power by 62%, while only 12% for the anode with domestic wastewater. The goal of producing 400 W/m\(^3\) of MFC (to be competitive with anaerobic digestion) is possible if the reactor is designed to have relatively small liquid volumes and thus a smaller electrode spacing.

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