Using cathode spacers to minimize reactor size in air cathode microbial fuel cells

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Scaling up microbial fuel cells (MFCs) will require more compact reactor designs. Spacers can be used to minimize the reactor size without adversely affecting performance. A single 1.5 mm expanded plastic spacer (S1.5) produced a maximum power density (973 ± 26 mW m⁻²) that was similar to that of an MFC with the cathode exposed directly to air (no spacer). However, a very thin spacer (1.3 mm) reduced power by 33%. Completely covering the air cathode with a solid plate did not eliminate power generation, indicating oxygen leakage into the reactor. The S1.5 spacer slightly increased columbic efficiencies (from 20% to 24%) as a result of reduced oxygen transfer into the system. Based on operating conditions (1000 Ω, CE = 20%), it was estimated that 0.9 L h⁻¹ of air would be needed for 1 m² of cathode area suggesting active air flow may be needed for larger scale MFCs.

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1. Introduction

Microbial fuel cells (MFCs) can be used to convert organic and some inorganic matter directly into electricity (Kim et al., 2002; Logan et al., 2006). Certain types of bacteria, called exoelectrogens, can oxidize organic matter and transfer electrons outside the cell, producing an electrical current. Air cathodes are commonly used in MFCs, where oxygen and protons combine with electrons to produce electrical power. One of the primary applications of MFCs will likely be wastewater treatment, as a single process can be used to simultaneously accomplish both wastewater treatment and power generation (Feng et al., 2008, 2011; Liu et al., 2004; Min et al., 2005). MFCs are also being examined as biosensors (Di Lorenzo et al., 2009; Kim et al., 1999, 2003), and recently it has been shown that power densities can be increased through the incorporation of reverse electrodialysis stacks into the system (Kim and Logan, 2011). Through modification of MFCs, it is possible to accomplish additional goals, such as salt water desalination (Cao et al., 2009; Jacobson et al., 2011; Mehanna et al., 2010).

One of the challenges for scaling up MFCs and other bioelectrochemical systems is the development of compact reactors. So far, there have only been a few studies that describe larger scale reactors using multiple electrodes or chambers in MFCs (Dekker et al., 2009; Zhang et al., 2010), or microbial electrolysis cells (Cusick et al., 2011; Rader and Logan, 2010). In typical laboratory reactors, most researchers report only the liquid volume used for the reactor design, with little consideration given to the reactor volume needed for the cathode. When larger MFCs are made, it will be necessary to provide an additional cathode compartment to allow air flow past the cathode and oxygen transfer sufficient to avoid adverse effects on power production. The overall reactor size can be minimized by using closely spaced electrodes and by using as little space as possible for providing air to the cathode. To further minimize the reactor volume, cathodes can be arranged so that they face a common air chamber, but the volume of used for this chamber could still affect electrode packing density. For example, if the anode chamber is ~2 cm wide (typically used in our air-cathode MFCs), then the anode specific surface area could at best be 50 m² m⁻³ (no space used for the cathode). However, if the cathode chamber occupied another 1 cm, this would reduce the number of electrodes that could be placed in the module, and decrease the anode specific surface area to 33 m² m⁻³. It is therefore important to minimize the thickness of the air chamber in order to increase electrode surface area per volume of reactor. The effect of spacing between the cathodes on performance and the amount of air needed for the cathode, have not previously been addressed in MFC designs.

A suitable spacer used between the cathodes can minimize the multiple chamber reactor size and as long as there is no negative significant change in the microbial fuel cell performance, such as power density and columbic efficiency. In order to more efficiently design cathode chambers for large scale MFCs, we examined the use of plastic spacers between adjacent cathodes on MFC performance in terms of power production and coulombic efficiency (CE). Spacers were first added on top of a single cathode to determine if their presence, through a reduced area for air transfer, had any
effect on power generation. Next, the cathodes were placed together on either side of the spacers to evaluate the efficiency of air flow based on performance. We also examined power production when the cathode was fully sealed off. These tests allowed examination of reactor architectures that could result in the design of more compact MFCs.

2. Methods

2.1. Reactor construction

MFCs were constructed from a solid block of Lexan drilled with a 3 cm diameter hole as previously described (Liu and Logan, 2004; Logan, 2008). The anode end was covered by a solid plate on one side, and the cathode end contained a flat plate with a 3 cm diameter hole to allow direct air contact. Cathodes contained a Pt catalyst (0.35 mg m\(^{-2}\)) on the water side and four diffusion layers on the air side as previously described (Cheng et al., 2006). Heat treated (Feng et al., 2010) carbon brushes were used as anodes.

Three different expanded plastic spacers were used (Dexmet Corp.) that had thicknesses of 1.50 mm (S1.5, 30PTFE50-625P), 1.3 mm (S1.3, 20PE25-285P) and 0.40 mm (S0.4, 5PTFE10-100P) (Fig. 1C). When a spacer was used, it was placed between two MFC reactors with the cathodes facing each other. In some tests, the cathode plates remained on and the reactors were bolted together using long screws (Fig. 1A). In some other tests, the cathode plates were removed so the cathode cloth was pressed directly against the spacer. The open structure of these expanded plastic materials allowed air to passively diffuse to the cathodes. When a solid plate was placed between two reactors (P), the cathodes were closed. In additional tests to better examine the effect of a lack of air flow on power generation, the ends of the MFCs were sealed off from air using a rubberized fabric wrapped around the ends of the two reactors (SP) (Fig. 1B). In another test to reduce air transfer to the cathode, two MFCs with regular open-air cathodes were fed with CE, so that the maximum oxygen utilization rate could be calculated from moles of electrons to moles of oxygen, assuming only oxygen reduction by protons and electrons, according to

\[ W = \frac{10^3RT}{bFP} \]

where \( I \) is the current density (A m\(^{-2}\)), \( R \) the gas constant (0.0821 L atm mol\(^{-1}\) K\(^{-1}\)), \( T \) the temperature (303 K), \( b \), the conversion factor from moles of electrons to moles of oxygen, \( F \) Faraday's constant (96,480 C per mol e\(^{-}\)), \( P \) the pressure (1 atm), and 1000 is for unit conversion. This oxygen utilization rate is based only on the measured current. Thus, the oxygen utilization rate will increase with CE, so that the maximum oxygen utilization rate could be \( W_{\text{max}} = W \times 100\% / CE \). For example, if the measured CE is 20\%, then the maximum possible oxygen utilization rate if all substrate went into current generation (CE = 100\%) would be \( 5 \times W \). Note that this calculation does not account for oxygen that may be used by bacteria that does not result in power generation.

2.2. Reactor operation

MFCs (duplicate reactors) were inoculated using effluent from another operating MFC. The medium consisted of 1 g L\(^{-1}\) sodium acetate, 50 mM phosphate buffer solution (PBS), 310 mg L\(^{-1}\) NH\(_4\)Cl, 130 mg L\(^{-1}\) KCl (Liu and Logan, 2004), 5 mL L\(^{-1}\) vitamins and 12.5 mL L\(^{-1}\) trace elements (Cheng et al., 2009). Reactors were operated in fed-batch mode in a constant temperature room (30 °C). Following cycles of reproducible cycles of voltage generation, coulombic efficiencies (CEs) and power densities were obtained as previously described (Liu and Logan, 2004) using the single-cycle method, with the external resistor varied every 20 min (Logan et al., 2006). Following operation as individual reactors (with no spacer plate, NS), two reactors were combined and operated with one (S1.5) or two spacers (2S1.5) between the two cathodes, or with a solid plate placed over the cathode to reduce oxygen transfer (P or SP). After cathode plates were removed (no CP), the reactors were operated with one spacer (S1.5 no CP; S1.3 no CP; S0.4 no CP) or with two spacers (2S1.5 no CP).

2.3. Oxygen calculations

The oxygen flowrate needed for the measured current generation, \( W \) (mL m\(^{-2}\) s\(^{-1}\)) was calculated from the current density assuming only oxygen reduction by protons and electrons, according to

\[ W = \frac{10^3RT}{bFP} \]

3. Results and discussion

3.1. Power generation of MFC reactors with spacers

Power generation was not affected solely by the presence of the spacer on the surface of the cathode during operation at a fixed external resistance (1000 Ω). When one or two S1.5 spacers were placed over the cathode, the power densities were similar, with 973 ± 26 mW m\(^{-2}\) (S1.5) and 990 ± 21 mW m\(^{-2}\) (2S1.5) (Fig. 2A). These power densities were the same as that obtained when the air cathode of the MFC was exposed directly to air in the absence of a spacer (999 ± 4 mW m\(^{-2}\)). Thus, all polarization and power density curves were the same for these three conditions (NS, S1.5 and S1.5), demonstrating that the use of the S1.5 and 2S1.5 spacers did not adversely affect oxygen transfer to the cathode, and the performance of the MFC. Therefore, passive oxygen transfer to the cathodes in these MFCs through the spacer S1.5 was sufficient to avoid oxygen limitations at the cathode under these conditions. In addition, examination of the cathode potentials for these two spacers (2S1.5 and S1.5) shows that they were very similar to that of the cathode lacking a spacer (NS) at the lower current densities (Fig. 2B).

It was found that when a solid plastic plate was placed over the cathode to try to eliminate oxygen transfer to the cathode that voltage generation was sustained (Fig. 3A). Polarization data collected after the solid plastic plate was placed on the end of the cathode still indicated a maximum power density of 484 ± 74 mW m\(^{-2}\), which is only 52% less than that obtained with the
in the water and in the space surrounding and within the porous water seal, there was still sufficient residual oxygen (presumably decreased less than 50 mV in 2 h. This shows that even with the oxygen in air. When this water seal was used, the output voltage possible oxygen flux in water is much less than that possible from air using water. This operational condition created a water seal around the reactor (as typically done on the tops of BOD bottles), and substantially reduced oxygen transfer into the system as the reactors were filled with fresh medium and then immersed in a beaker of water, thus sealing off all edges and the cathode from the air chamber between the cathodes. With one or two layers of the S1.5 spacer, the reactor performance was not adversely affected, with 1021 ± 22 mW m\(^{-2}\) (S1.5) and 1026 ± 16 mW m\(^{-2}\) (2S1.5). However, when the thinner spacers were used, power densities decreased to 680 ± 56 mW m\(^{-2}\) (S1.3) and 464 ± 36 mW m\(^{-2}\) (S0.4) (Fig. 4). This shows that the thinner spacers reduced the space too much between the cathodes, and inhibited air flow to the cathodes, resulting in decreased power generation (33% or more). Based on these tests, it was concluded that the S1.5 spacer provided a suitable minimum spacing between the cathodes. Using a thin spacer therefore can reduce the distance open plate. Placing additional rubberized fabric around the cathode to better seal the cathode from the air further reduced power to 369 ± 35 mW m\(^{-2}\) (Fig. 2A). These results show that a better seal on the cathode, using a solid plate, reduces but does not eliminate power. The best seal was obtained with the plate and the rubberized fabric. However, even under this condition there was still power generation. Taken together, these results indicated that there was relatively large amount of oxygen leaking into the reactor, likely through the septa, sides of the cathode, and the gaskets. Since power was generated, it seems most likely that the oxygen leakage occurred through or near to the cathode, and not the anode. Unaccounted for oxygen leakage into this system (not directly through the cathode face) may help to explain why CE are not effectively, if we assume 0.4 mL air remained dissolved in 28 mL of media (30 °C), this would be sufficient to result in a loss of 0.5% of the substrate when CE = 100%, and 2.7% of the substrate with CE = 20% (assuming the oxygen is used, but substrate removal is less efficient in current generation). When the MFC was removed from the water and again exposed to air, the voltage quickly (within 1 h) returned to normal levels (Fig. 3B).

In the above tests with spacers placed between the cathodes, there was space between the cathodes due to the thickness of the cathode plate (5 mm) holding down the cathode (Fig. 1A). To eliminate this extra space, the cathode plates (CP) were then removed, and the reactor was operated with only the spacer between the two flat carbon cloth cathodes, minimizing the reactor volume needed for the air chamber between the cathodes. With one or two layers of the S1.5 spacer, the reactor performance was not adversely affected, with 1021 ± 22 mW m\(^{-2}\) (S1.5) and 1026 ± 16 mW m\(^{-2}\) (2S1.5). When this water seal was used, the output voltage decreased less than 50 mV in 2 h. This shows that even with the water seal, there was still sufficient residual oxygen (presumably in the water and in the space surrounding and within the porous cathode) to produce a small amount of current. The amount of coulombs transferred in this immersed water experiment is 3% of all coulombs transferred over a complete cycle. To put this in perspective, if we assume 0.4 mL air remained dissolved in 28 mL of media (30 °C), this would be sufficient to result in a loss of 0.5% of the substrate when CE = 100%, and 2.7% of the substrate with CE = 20% (assuming the oxygen is used, but substrate removal is less efficient in current generation). When the MFC was removed from the water and again exposed to air, the voltage quickly (within 1 h) returned to normal levels (Fig. 3B).

Fig. 2. (A) Power densities and whole cell voltages, and (B) electrode potential (A = anode, and C = cathode) curves for reactors set up with different spacers: NS, no spacer; P, cathode covered by a solid plate; SP, cathode covered by a solid plate and sealed with fabric; S1.5, one single 1.5 mm spacer; 2S1.5, two pieces of 1.5 mm spacers.

Fig. 3. (A) Voltages of one batch cycle for MFCs setup with different spacers or solid plate: NS, no spacer; P, cathode covered by a solid plate; SP, cathode covered by a solid plate and sealed with fabric; S1.5, one single 1.5 mm spacer; 2S1.5, two pieces of 1.5 mm spacers; (B) voltage over one batch cycle when the control reactors (no spacers) were exposed to water and then air.
of two cathodes, and thus reduce the reactor size. Spacers could also be used in between more than just two reactors. For example, using two spacers to connect the four cathodes of four reactors. Tests with this four reactor condition successfully generated voltage as expected based on results using two reactors (data not shown).

### 3.2. Coulombic efficiencies

The CEs ranged from 20% to 28% in all tests in the presence and absence of the different spacers (1000 \( \Omega \) resistance) (Fig. 5). The CE was lowest for the MFC exposed to air (no spacer, NS), with CE = 20 ± 1%. In the presence of the spacers, the CEs increased to 21 ± 1% (2S1.5) and 24 ± 0% (S1.5) when the cathode was covered with a plastic solid plate, the CE was 26 ± 1%. The highest CE was obtained for the thinnest spacer (S0.4, 28 ± 1%) after removing cathode plate.

### 3.3. Oxygen demand in air cathode MFC

The stoichiometric oxygen demand for 28 mL of anode solution (containing 1 g L\(^{-1}\) of sodium acetate) is 15 mL of pure oxygen or 73 mL of air (CE = 100%). However, actual CEs are much lower, and therefore less air is needed. For example, at a CE of 20%, only 15 mL of air would be needed for the generated current.

If the MFC is operated at a resistance of 1000 \( \Omega \), the oxygen flow required would be 0.05 mL m\(^{-2}\) s\(^{-1}\) (0.19 L h\(^{-1}\) m\(^{-2}\) oxygen flow or 0.9 L h\(^{-1}\) m\(^{-2}\) airflow; CE = 20%). However, the rate of oxygen consumption varies inversely with resistance due to an increase in the current. For the maximum power density of 1000 mW m\(^{-2}\) (80 \( \Omega \)), the current is 4.2 A m\(^{-2}\), the oxygen consumption rate would be 0.27 mL s\(^{-1}\) (1.0 L h\(^{-1}\) m\(^{-2}\)) per square meter of cathode area (Fig. 6), indicating that 1.3 mL m\(^{-2}\) s\(^{-1}\) (4.7 L h\(^{-1}\) m\(^{-2}\)) of air would be needed for the maximum power generation. In contrast, at high resistances, the current is relatively low and thus there is little change in the required air flow rate with resistance.

### 4. Conclusions

Spacers can be placed between cathodes to reduce reactor size. One (973 ± 26 mW m\(^{-2}\)) or more 1.5 mm spacers (990 ± 21 mW m\(^{-2}\)) did not affect power production compared to an MFC exposed to air. Thinner spacers (1.3 or 0.4 mm) reduced power by 33% or more. The S1.5 spacer slightly increased coulombic efficiencies. It was estimated that air flow rates of 4.7 L h\(^{-1}\) m\(^{-2}\) cathode area were needed for a power density of 1 W m\(^{-2}\) (CE = 20%). This suggests that pressure driven air flow may be needed for larger-scale MFCs, and that the use of spacers can help reduce reactor volume and therefore cost.

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