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Journal of Power Sources 179 (2008) 27–33
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Electricity generation by a baffle-chamber membraneless microbial fuel cell

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Received 13 November 2007; received in revised form 25 December 2007; accepted 31 December 2007
Available online 4 January 2008

Abstract

Microbial fuel cells (MFCs) for organic waste and wastewater treatment represent innovative technologies for pollution control and energy generation. The research reported here considers the influence of reactor configurations designed to mitigate the impact of oxygen transport on electricity generation by a baffle-chamber membraneless MFC. The reactor was constructed to reduce mixing in the vicinity of the cathode and facilitate thick (>1 mm) biofilm formation on the cathode by adding anaerobic biomass/sludge (4330 ± 410 mg COD L^{-1}), resulting in an overall coulombic efficiency of more than 30% at glucose concentrations ranging from 96 to 960 mg COD L^{-1}, compared to previously reported efficiencies <10% in a completely mixed membraneless MFC. Efficiencies in the absence of anaerobic sludge dropped to 21.2 ± 3.7%, suggesting that the importance of pH buffering provided by the biomass in improving electron transport to the anode. However, the anaerobic sludge itself provided very limited power (approximately 0.3 mW m^{-2}) and power generation was primarily associated with glucose degradation (e.g., 129 ± 15 mW m^{-2}).

Keywords: Biomass; Electricity; Electron transfer; Energy efficiency; Microbial fuel cell; Anaerobic sludge

1. Introduction

Microbial fuel cells (MFCs) represent innovative remediation technologies for waste and wastewater treatment because they have the potential for simultaneous generation of electricity and removal of organic pollutants from waste streams [1–7]. In MFCs, bacteria oxidize organic contaminants in an anaerobic anode chamber, and transfer the electrons through an external circuit; the electrons are typically harvested in an aerobic cathode chamber, where electrons, oxygen and protons are combined to produce water. In essence, by using bacteria as catalysts on possibly both anode and cathode [6–9], MFCs convert the chemical energy released in the oxidation of organic wastes directly to electric energy.

One of the most commonly used components in MFCs is a proton exchange membrane (PEM) that is selective for osmotically transporting protons and other small cations across the membrane, while limiting the crossover of fuel (organic waste) or oxygen gas between the anodic and cathodic chambers [10–13]. However, the high costs of PEMs and their potential for biofouling and associated high internal resistance could restrain the power generation and limit the practical use of MFCs [14]. Consequently, a few research has designed new types of MFCs by omitting the PEM or using low cost polycarbonate nanomaterials [13,15–17]. In one study without PEMs, however, coulombic efficiencies dropped to 9–12% in completely mixed (baffleless) MFCs using glucose as a fuel [16]. This low efficiency was attributed to substantial oxygen mixing in the reactor chamber via its diffusion through the cathode surface [16]. Thus, approaches that focus on restricting O_2 transport through the cathode are needed to improve the efficiency.

One approach to improving the coulombic efficiency when using membraneless MFCs would be via thick biofilm formation on cathode surface to restrict O_2 transport through improved reactor configuration design. Anaerobic sludge or pure bacterial cultures are often used to inoculate MFCs to initiate the growth of a microbial biofilm on the anode [18–20], and sometimes on the cathode [6,9]. Bacteria attached to the anode are thought to directly transfer electrons from organic matter to electrodes through electroactive enzymes such as cytochromes on the outer membrane [1,19] or by producing electrically conductive pilus-like appendages called bacterial nanowires [21,22]. They may

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doi:10.1016/j.jpowsour.2007.12.094

produce pyocyanin to facilitate electron transfer between cells in the solution [23]. These bacteria consist mainly of facultative anaerobes, including *Alcaligens faecalis* [20], *Geobacter sulfurreducens* [19], *Rhodoferax ferrireducens* [10], and *Shewanella oneidensis* [22,24]. Since biofilms are ubiquitous in nature, these facultative bacteria are capable of forming biofilms on the cathode as well. In addition, anaerobic sludge itself may serve as fuel for electricity production. The cell lysis accompanying endogenous decay of anaerobic sludge releases soluble substrates that can potentially support the regrowth of bacteria and electricity generation. However, we currently have limited knowledge of the effect of anaerobic sludge on the electricity generation by MFCs.

Coulombic efficiency in MFCs is affected by many factors, including internal/external resistance [25,26], substrate concentration and the presence of other electron acceptors [4,16,27], bacterial community [28,29], and new electrode or reactor chamber design [6,7,15]. The objective of this research was to improve the coulombic efficiency in membraneless MFCs using a modified reactor configuration for thick cathode biofilm formation to restrict oxygen transfer in MFCs. To this end, we introduced a baffle-chamber membraneless MFC by adding a baffle into the reactor chamber to reduce mixing in the vicinity of the cathode and thus facilitate the thick biofilm formation. Since sludge processing is an important yet challenging issue in wastewater treatment, we also evaluated the feasibility of anaerobic sludge as fuel for electricity generation by MFCs.

2. Materials and methods

2.1. Culture and medium

Both anaerobic biomass and bacteria present in wastewater have been shown to be suitable to inoculate the MFCs as biocatalysts for electricity generation [16,20]. In this work, a mixed microbial culture was taken from a local anaerobic digester. To remove the soluble organic matter, the culture was washed twice with deionized water followed by centrifuging at 10,000 × *g* for 5 min and the pellets were then resuspended in glucose media (described below) for inoculation of the MFCs. Planktonic cells from the MFCs were harvested in a similar way and resuspended in deionized water for microbial decay measurements.

A glucose ($C_6H_{12}O_6$, MW = 180) medium with theoretical chemical oxygen demand (COD) concentrations ranging from 0 to 960 mg L^{-1} was used throughout the investigation period (1 g glucose = 192/180 g COD). The medium also contained per liter: 0.3 g NH_4Cl, 4.8 g NaH_2PO_4, 2.8 g $Na_2HPO_4{\cdot}H_2O$, 0.1 g KCl, 2.5 g $NaHCO_3$, and 0.025 g yeast extract, with final pH adjusted to 7.0 (buffer intensity $\beta = 0.04$ equiv. L^{-1} pH^{-1}) using 0.1 M NaOH or HCl.

2.2. MFC construction

The baffle-chamber membraneless MFC was based on the prototype membrane-free, single chamber microbial fuel cell with an open air-cathode described by Liu and Logan [16]. The MFC was modified by inclusion of a plastic (Plexiglass) baffle to allow fluid mixing in the anode chamber only so that oxygen diffusion adjacent to the cathode surface can be minimized. The modified reactor is illustrated in Fig. 1 and consisted of a cylindrical chamber 4.4 cm long by 2.5 cm in diameter (effective volume of 20 mL including 13 and 7 mL for mixed and quiescent sections, respectively). The baffle was a circular piece of plastic with 0.1 cm smaller diameter than that of the cylindrical chamber and was cut at the bottom so that the dissolved and suspended material could pass between the mixed and quiescent chambers (see Fig. 1). The baffle was designed such that the MFC system mimics traditional wastewater treatment systems with internal settling zones. The anode and cathode were placed on opposite sides of the microbial fuel cell and secured tightly to prevent leaks. The anode was made of carbon paper (effective area of 4.9 cm^2, Toray™ Carbon, E-TEK, NJ, USA). The cathode was similar to the anode in size but was a gas diffusion electrode made of standard carbon cloth (Vulcan XC-72) containing 0.5 mg cm^{-2} of Pt (E-TEK, NJ, USA). Room air in contact with the cathode provided the O_2 used as the electron acceptor. Copper sheets and wires were used to connect the circuit (1400 Ω resistor unless stated otherwise). Sampling ports were provided at the top of each chamber and were sealed with rubber stoppers during operation.

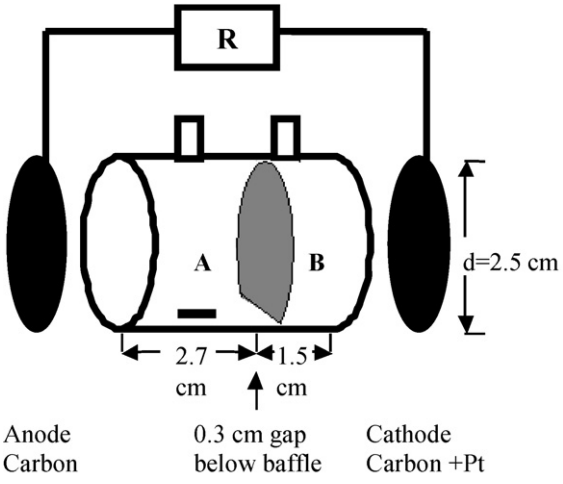

Fig. 1. Schematic of the membraneless microbial fuel cell with magnetically mixed (A)/quiescent (B) chambers.

2.3. MFC operation

The mixed (A) and quiescent (B) sections of the reactor chamber (Fig. 1) were refilled every 3 days until a stable voltage output at an external resistor of 1400 Ω was achieved. Each time, the spent media and planktonic cells from both chambers were removed, and the reactor was filled with fresh medium containing 960 mg L^{-1} COD (equivalent to 5 mM as glucose) and inoculated with the fresh washed anaerobic sludge, prepared as described above, to a final sludge concentration of approximately 4000 mg COD L^{-1}. The chamber adjacent to the anode was mixed at 100 rpm using a micromagnetic stirrer (5/16 in. long and 1/16 in. in diameter) while the anaerobic sludge was allowed to settle without mixing in the vicinity of the cathode to

make a combined mixed/quiescent system. At the end of incubation at room temperature (23 ± 2 °C), thick biofilms were formed on both anode and cathode of the microbial fuel cell. Anaerobic conditions in the cathode chamber were maintained by diffusion restriction layers through biofilm and quiescent liquid film formation within the cathode chamber, as evident by zero readings of dissolved oxygen in the MFC solution.

Once the MFC demonstrated the repeatable electricity generation at an external resistor of 1400 Ω, electricity production was evaluated in the presence (e.g., inoculated with washed anaerobic sludge) and absence (e.g., uninoculated controls) of anaerobic sludge at glucose concentrations ranging from 0 to 960 mg COD L^{-1} in a random order. Three different types of experiments were carried out. To test the role of anaerobic sludge in MFCs, the spent medium along with the suspended cells was removed from both chambers, washed twice by centrifuging at 10,000 *g* for 5 min and reused for another test. Additional fresh and washed anaerobic biomass was occasionally added to maintain constant biomass concentrations at 4330 ± 410 mg L^{-1} ($n = 12$) in the microbial fuel cell to compensate for biomass decay and losses during transfer. Second, a real-time voltage reading was recorded for determining microbial decay coefficients at zero glucose concentrations. Finally, at concentrations of 480 mg L^{-1}, the circuit resistance was varied from 100 to 75,000 Ω over a short period of time (10 min) and the corresponding stable voltages were recorded to determine the maximum voltage and power density in the presence or absence of anaerobic sludge.

At the end of a series of experiments in which a baffle was present for separation between the mixed and quiescent reactor sections, the baffle was removed to create a single chamber baffleless MFC similar to the one reported earlier [16]. Aliquots of substrate (480 mg L^{-1} COD glucose) in the presence and absence of anaerobic sludge were added to the MFC and the voltages were measured over time to evaluate electricity generation. Finally, a PEM (Nafion 117, Dupont) of similar size was attached to the cathode in the single chamber completely mixed MFC providing a reactor configuration equivalent to that described by Liu and Logan [16] to determine the coulombic efficiency in the absence and presence of anaerobic sludge.

Voltage (V, in volts) was continuously recorded at 0.01 Hz using a data acquisition system using LabView™ V 6.1 (National Instruments, Texas) software operating on a personal computer. Current (I, in amps) was calculated as follows:

$$I = \frac{V}{R} = \frac{C}{t} \tag{1}$$

where R, C, and t are resistance (in ohms), charge (in coulombs) and time (in seconds), respectively. The power density of the MFC (P, in watts m^{-2}) was calculated as

$$P = I \times \frac{V}{A} \tag{2}$$

where A (in m^2) is the planar surface area of the anode. The coulombic efficiency was calculated as

$$\eta_C\,(\%) = \frac{C_p}{C_T} \times 100 \tag{3}$$

where C_p is the harvested coulombs calculated by integrating the current over operation time (corrected for the contribution of coulombs generated by anaerobic sludge decay); and C_T is the theoretical value of coulombs from glucose that was added at the beginning of operation of the MFC. C_T is calculated as

$$C_T = \frac{FnSv}{M} \tag{4}$$

where F is Faraday's constant (96,487 C mol^{-1} electron), n is the mol number of electrons produced per mol of substrate (in COD units) oxidation ($n = 4$), S is the substrate (glucose) concentration (in g L^{-1} COD), v is the effective volume of the MFC (L), and M is the molecular weight for oxygen ($M = 32$).

The energy efficiency was calculated as

$$\eta_E\,(\%) = \frac{E_p}{E_T} \times 100 \tag{5}$$

where E_p is the harvested energy (in joules) calculated by integrating the power ($P = I \times V$) over operational time and E_T is the theoretical value of available energy, obtained from the change in Gibbs free energy, ΔG, of 2870 kJ mol^{-1} glucose oxidation with O_2 as the electron acceptor.

2.4. Analytical procedures

Measurements were in duplicate unless otherwise stated. The dissolved oxygen concentrations and pH were measured after all of the MFC solutions were emptied from both anode and cathode chambers. Planktonic cells in the MFCs were harvested at the end of each experiment by centrifuging at 10,000 *g* for 5 min at room temperature. The pellets were resuspended in 20 mL test medium without glucose to determine the biomass concentrations. The supernatants were collected for the measurement of residual substrate concentrations. Both biomass and residual substrate concentrations in the microbial fuel cell were measured as chemical oxygen demand using commercially available reagents (HACH COD vials, Loveland, CO) according to standard methods [30].

The presence of dissolved electron shuttles in the solution of MFCs was analyzed by cyclic voltammetry using a scanning electrochemical microscope (CHI Instruments, Austin, TX). The solution in the presence or absence of anaerobic sludge was harvested when the MFC showed maximum voltage output and was centrifuged (10,000 *g*, 5 min) to collect the supernatant. A voltammetric plot of current versus potential (from −0.5 to 0.5 V) was recorded at a scan rate of 50 mV s^{-1} (minimum of five scans) by inserting a Pt working microelectrode, a Ag/AgCl reference electrode, and a counter electrode in the unstirred supernatant.

3. Results

3.1. Electricity generation in the MFC with mixed/quiescent chambers

Stable electricity generation was observed 7 days after inoculation of mixed liquor containing 960 mg COD L^{-1} glucose and 4330 ± 410 mg COD L^{-1} anaerobic sludge in the MFC. Fig. 2 compares results of the duration of the voltage discharge for an initial glucose concentration of 480 mg COD L^{-1}. A lag period of about 5 h was typically observed before a peak voltage was recorded.

Discharge curves (voltage vs. time) (Fig. 2) showed that adding planktonic cells (e.g., inoculated with washed anaerobic sludge) increased the duration of the voltage discharge. In the absence of anaerobic sludge (e.g., uninoculated controls) the voltage declined more rapidly than those in the presence of anaerobic sludge at a constant resistance of 1400 Ω.

3.2. Electricity generation with anaerobic sludge

In the absence of external substrate ($S_{glucose} = 0$ mg L^{-1}), biomass decay resulted in a slow decline of voltage with relatively constant and small values of 0.050 and 0.035 V in the presence and absence of anaerobic sludge, respectively. Voltage recording was stopped at these values in subsequent experiments with varying glucose concentrations.

3.3. Voltage and power density generated as a function of current

The polarization curve shown in Fig. 3 demonstrated that power generation was a function of circuit resistance in the MFC with mixed/quiescent chambers: the voltage output decreased as the current increased. In the presence of anaerobic sludge, a maximum voltage of 0.55 ± 0.01 V ($R = 75{,}000\ \Omega$) was achieved.

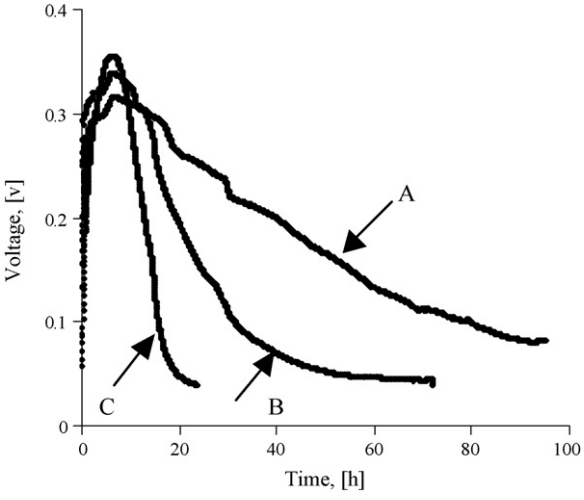

Fig. 2. Discharge curves of glucose (480 mg COD L^{-1}) at an external resistor of 1400 Ω in the presence (A) and absence (B) of anaerobic sludge in the MFC with mixed/quiescent chambers, and absence of anaerobic sludge in the completely mixed flow MFC (C).

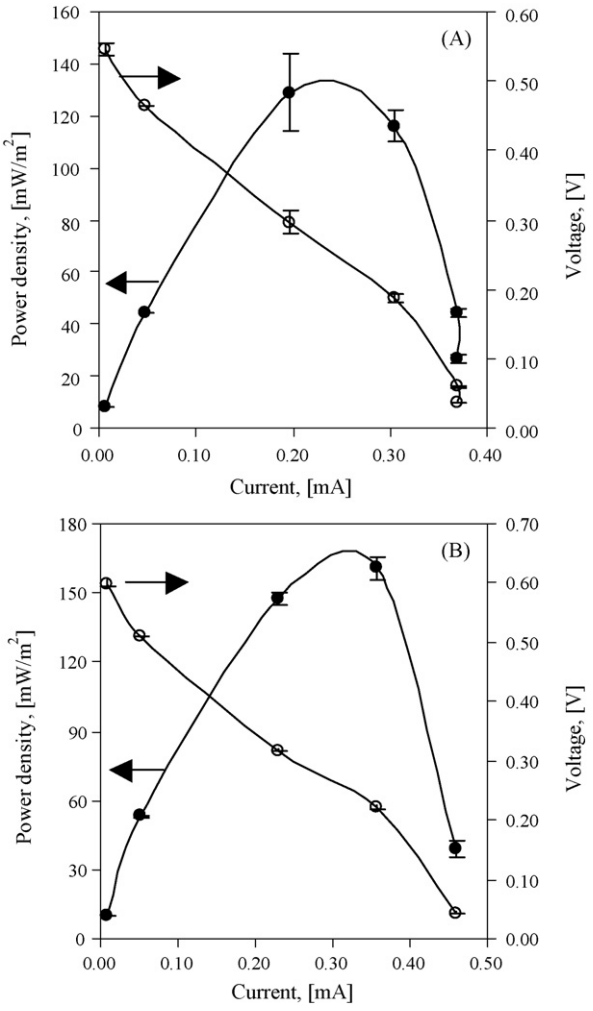

Fig. 3. Steady-state voltage and power density generated as a function of circuit current in the presence (A) and absence (B) of anaerobic sludge in the MFC with mixed/quiescent chambers. Error bars indicate one standard deviation in triplicate measurements.

The maximum power reached 129 ± 15 mW m^{-2} at a current of 0.30 mA. In contrast, without anaerobic sludge in the MFC, the maximum voltage was 0.60 ± 0.00 V and the maximum power of 161 ± 5 mW m^{-2} was generated at a current of 0.36 mA.

3.4. Coulombic efficiency, energy efficiency and residual COD

In the presence of anaerobic sludge, the coulombic efficiencies were fairly constant at a range of glucose concentrations, with an overall average of 31.7 ± 2.7% (Fig. 4 and Table 1). The corresponding energy efficiency varied from 3.4% to 6.7%. A slight decrease in pH (from 7.3 to 7.0) was measured at the end of the test.

In the absence of anaerobic sludge, the coulombic efficiency was 21.2 ± 3.7% at 480 mg COD L^{-1} glucose concentration, which is significantly lower than that in the presence of anaerobic sludge ($t_\alpha = 0.05$, $P < 0.05$). In addition, efficiencies decreased with increased glucose concentration, while the pH

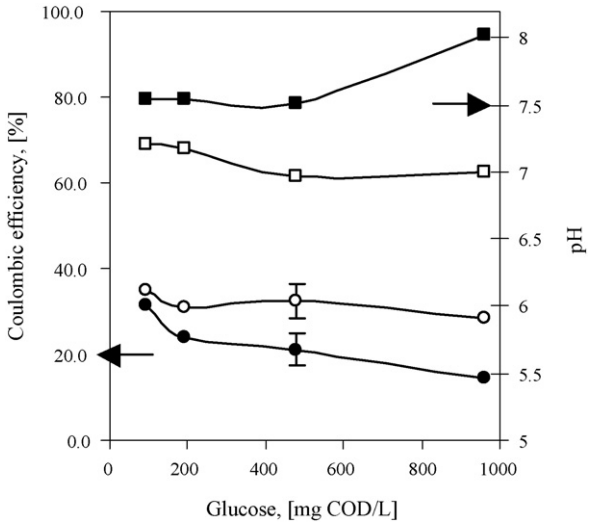

Fig. 4. Coulombic efficiency and final pH of the mixed liquor as a function of glucose concentration in the presence (◯, □) and absence (●, ■) of anaerobic sludge in the MFC with mixing/sedimentation chambers.

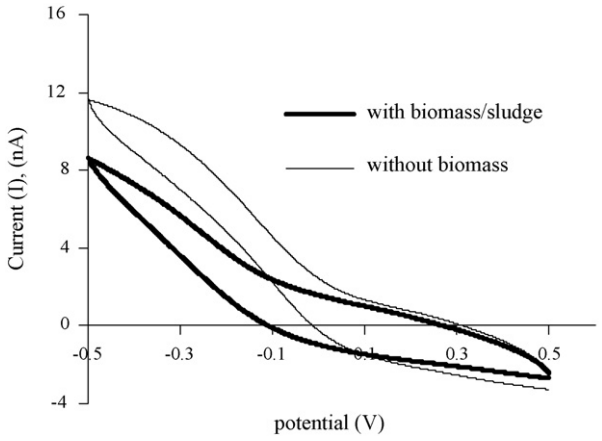

Fig. 5. Cyclic voltammetric scanning (from −0.5 to 0.5 V) of the media in the presence and absence of anaerobic sludge from MFCs showing that no active redox compounds could be detected at a scan rate of 50 mV s^{-1} against a Ag/AgCl reference electrode.

of the medium in MFCs increased to 8 at the end of the test. The corresponding energy efficiency varied from 2.3% to 4.2%.

3.5. Electricity generation in the baffleless MFC

In the baffleless MFC (i.e., without a flow baffle and quiescent chamber), the coulombic efficiencies dropped to 14.0 ± 2.8% (Fig. 2) and 9.0 ± 1.3% in the presence and absence of anaerobic sludge, respectively. These results are consistent with the value reported previously in a completely mixed membraneless MFC under similar conditions with efficiencies of less than 10% [16]. The corresponding energy efficiencies decreased to 2.7% and 2.2%, respectively. These values are significantly lower than those in the MFC with mixed/quiescent chambers ($t_\alpha = 0.05$, $P < 0.03$). In contrast, the maximum voltages with and without anaerobic sludge for the completely mixed MFC were 0.61 ± 0.02 ($n = 4$) and 0.65 ± 0.01 ($n = 4$), respectively, which are significantly higher than those in the MFC with mixed/quiescent chambers ($t_\alpha = 0.05$, $P < 0.04$).

When a PEM was attached to the cathode in the baffleless MFC, the coulombic efficiencies were 26.5 ± 0.2% and 26.8 ± 3.1% in the presence and absence of anaerobic sludge, respectively. These values are not statistically different ($t_\alpha = 0.05$, $P > 0.5$).

3.6. Detection of dissolved redox active components

Anaerobic sludge may involve in electron transfer by excretion of redox components (such as pyocyanin from *Pseudomonas aeruginosa*) in solutions [20]. In this study, however, dissolved redox active components were not detected by cyclic voltammetry in the presence or absence of anaerobic sludge (Fig. 5).

4. Discussion

Changing the MFC configuration from a completely mixed flow mode to one with a baffle separating a mixed anode chamber from a quiescent cathode chamber more than tripled the coulombic efficiency in the absence of anaerobic sludge from 9.0 ± 1.3% to 31.7 ± 2.7% with the addition of suspended anaerobic biomass (Table 1). This increase may be attributed to (1) contribution of additional substrate provided by anaerobic sludge; (2) significant reduction of oxygen transport through the cathode; (3) buffering provided by anaerobic sludge to maintain nearly constant neutral pH in the mixed liquor.

Anaerobic sludge added very limited substrate that can be easily converted into electricity, an indication that anaerobic sludge is not easily convertible to electricity in MFCs. Limited power (0.3 mW m^{-2} or approximately 0.015 V at 4300 mg COD L^{-1} biomass) could be harvested from the anaerobic sludge under endogenous decay conditions, resulting in COD accumulation in the liquids at the end of the tests (data

Table 1
Comparison of power output in the presence and absence of anaerobic sludge in two types of MFCs

MFC configuration	Mixed/quiescent		Completely mixed flow	
	With biomass	Without biomass	With biomass	Without biomass
Coulombic efficiency, η_C (%)	31.7 ± 2.7	21.2 ± 3.7	14.0 ± 2.8	9.0 ± 1.3
Energy efficiency, η_E (%)	3.4–6.7	2.3–4.2	1.7–2.7	1.3–2.2
Maximum voltage observed (V)	0.55 ± 0.01	0.60 ± 0.00	0.61 ± 0.02	0.65 ± 0.01
Maximum power density (mW m^{-2})	129 ± 15	161 ± 5	153	184

not shown). Calculation of the ratio of substrate flux from decay to the electron flux that was harvested indicates that <1% of the sludge were converted to electricity, suggesting that most of the decay products are not suitable for electricity generation in the MFCs. Note that correction for the contribution of coulombs generated by sludge decay has been made during calculation. Hence, the reason of increase of coulombic efficiency in the baffle-chamber membraneless MFCs by additional substrate from anaerobic sludge is excluded.

The baffle-chamber membraneless MFC was effective in restricting fluid mixing within the anode chamber, and inoculation of the anaerobic sludge at a final concentration of approximately 4000 mg COD L^{-1} promoted thick (>1 mm, via COD analysis) biofilm formation on the cathode, both of which could contribute to maintaining anaerobic conditions inside the reactor by minimizing oxygen diffusion through the cathode. Oxygen penetration depth is generally less than 400–760 μm in biofilms [31,32]. It is expected that the penetration depth would be even less because oxygen needs to diffuse through the cathode before it can reach the biofilm inside the MFCs. Although the anaerobic sludge itself will not change the oxygen flux, the thick biofilms on the cathode allow the MFCs to maintain strict anaerobic conditions, which help retain fuel (glucose) that would have been consumed aerobically for prolong electricity generation. The thick biofilms appear to have no interference with the cathode reaction in a long-term operation. Instead, microorganisms in the biofilm could be responsible for catalyzing the oxygen reduction [33].

Other factors such as pH and buffer capacity may contribute to improve the coulombic efficiency as well. For example, in the absence of anaerobic sludge, the observed pH increase (Fig. 4) due to limited solution buffer intensity ($\beta = 0.04$ equiv. L^{-1} pH^{-1}), particularly under high initial glucose concentrations with a long period of operation, might reduce the driving force of reaction in the cathode ($4H^+ + 4e^- + O_2 \rightarrow 2H_2O$) and hence decrease the coulombic efficiency. This can be seen when anaerobic sludge was not added (Fig. 4), but with the sludge added there seems to be less of a drop in coulombic efficiency, perhaps as a result of additional buffer capacity provided by the sludge. The result is consistent with the recent findings that the highest power was generated at pH 7 [12,34]. While the reasons why the observed pH increase at longer time periods remain unknown, pH will increase in the solution if protons consumed at the cathode are not replenished rapidly through the PEMs [12], as may be the case of bacterial cell membranes in the MFCs. It appears the higher initial concentration of glucose results in longer operation and lower coulombic efficiency, but it also remains unclear whether more electron equivalents are shuttled towards microbial growth at longer time periods, thereby reducing the efficiency.

There are two bacterial strategies to efficiently conduct electrons to an anodic electrode [6]: the direct contact by outer membrane cytochromes or conductive pili or pilus-like structures [21,22] and the electron shuttling by mediating molecules [23]. Based on the results from cyclic voltammetry, it is unlikely that the additional increase in electron transfer efficiency can be attributed to generation of electron shuttles by the anaerobic sludge. It is also unlikely that contact of mixed suspended cells with the anode surface may have permitted electron transport because the coulombic efficiencies were not statistically different regardless of the presence of anaerobic sludge when a proton exchange membrane was installed onto the cathode.

Substantially higher coulombic efficiencies (>70%) have been reported for MFCs with PEMs [6,18,35]. Recent studies showed that the power density could be one order of magnitude higher than that of the tested MFCs. However, such systems may require PEMs [9], special coating using a Nafion solution [35], or phosphate buffer and pH correction [6]. In this work, the coulombic efficiencies obtained when a PEM was employed were lower (24.6–29.0%) regardless of the presence of anaerobic sludge. Biofouling of the PEM contributed to the observed low efficiencies. These results indicate that applying a PEM in the design of MFCs may not necessarily translate into increased efficiencies, especially if the MFCs contain a high concentration of biomass in the solution.

The maximum voltage output and associated power density decreased somewhat in the presence of anaerobic sludge. The slopes of the voltage curves given in Fig. 3 indicate the similarity of the electrolytic resistance in the absence or presence of the sludge. Hence, the increased performance of voltage output with no sludge may not be solely attributed to the electrolytic resistances, since the internal resistance in a MFC includes charge-transfer resistance, ohmic resistance, and mass-transfer resistance [25]. Although the overall internal resistance was not measured in this study, we expected that an increase in internal resistance of the bacterial suspension occurred due to the presence of mass transfer resistance [36] and very low or no electrical conductivity of bacteria [37]. The operating voltage (V_{cell}) is defined as follows [38,39]:

$$V_{cell} = E_{cell} - IR_{int} - \eta(I) = \frac{-\Delta G_{rxn}}{nF - IR_{int} - \eta(I)}$$

where E_{cell}, R_{int}, and ΔG_{rxn} are theoretical voltage, internal resistance, and the Gibbs free energy for the aerobic oxidation of glucose, respectively. $\eta(I)$ is the over-potential that must be applied over the reversible potential of the O_2/H_2O half reaction in order to maintain the circuit current (I). The Butler–Volmer equation [40] predicts that the larger the current, the more the over-potential or voltage loss, and this result is confirmed in this work as the operating voltage decreased with increased current. Under the condition of completely mixed flow with no anaerobic sludge in the single chamber MFC, a minimal voltage loss through internal resistance could be achieved with a maximum observed operating output of 0.65 V. This result is consistent with the value reported previously under similar conditions [16].

Implications resulting from this work for design and application of MFCs are as follows: (1) in membraneless MFCs, reactor configurations that reduce O_2 transport can improve the efficiency of electricity generation; (2) addition of anaerobic sludge facilitates the formation of cathode biofilms that may prevent or minimize oxygen diffusion through the cathode into the anode reactor chamber, thus increasing power outputs and overall MFC efficiency. Furthermore, the presence of anaerobic sludge also provides buffering to pH changes and toxic shock

loads. It may also provide a diverse microbial community for enhanced pollutant degradation; (3) additional improvement of coulombic efficiency can be made by reducing the external resistance, which is one of the limiting factors for the MFC operation [34]; and (4) the energy efficiencies observed in this work varied from 2.3–4.2% in the absence of anaerobic sludge to 3.4–6.7% in the presence of anaerobic sludge (Table 1). These values are consistent with those reported recently [11].

It has become apparent in the last few years that MFC optimization must consider both engineering and biological constraints. The baffle-chamber membraneless MFC described in this work improved the overall efficiency by inducing biofilm formation on the cathode to minimize oxygen intrusions to the anode chamber that could otherwise cause loss of electrons transferred to the anode. The cost of MFCs could be decreased significantly by eliminating the need for a PEM, although with some performance loss. While there are potential disadvantages with the baffled MFC design, membraneless tubular air-cathode MFC is one direction to improve the electrochemical performance of the MFCs [25]. By combining both engineering and biological approaches a successful design of MFCs with increased efficiency could be utilized in wastewater treatment with minimal modification.

Acknowledgements

The author thanks Dr. Monroe L. Weber-Shirk for assistance with the data acquisition system and Drs. Leonard W. Lion and Héctor D. Abruña at Cornell University involved in manuscript preparation.

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