Power Generation in Fed-Batch Microbial Fuel Cells as a Function of Ionic Strength, Temperature, and Reactor Configuration

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Power density, electrode potential, coulombic efficiency, and energy recovery in single-chamber microbial fuel cells (MFCs) were examined as a function of solution ionic strength, electrode spacing and composition, and temperature. Increasing the solution ionic strength from 100 to 400 mM by adding NaCl increased power output from 720 to 1330 mW/m². Power generation was also increased from 720 to 1210 mW/m² by decreasing the distance between the anode and cathode from 4 to 2 cm. The power increases due to ionic strength and electrode spacing resulted from a decrease in the internal resistance. Power output was also increased by 68% by replacing the cathode (purchased from a manufacturer) with our own carbon cloth cathode containing the same Pt loading. The performance of conventional anaerobic treatment processes, such as anaerobic digestion, are adversely affected by temperatures below 30 °C. However, decreasing the temperature from 32 to 20 °C reduced power output by only 9%, primarily as a result of the reduction of the cathode potential. Coulombic efficiencies and overall energy recovery varied as a function of operating conditions, but were a maximum of 61.4 and 15.1% (operating conditions of 32 °C, carbon paper cathode, and the solution amended with 300 mM NaCl). These results, which demonstrate that power densities can be increased to over 1 W/m² by changing the operating conditions or electrode spacing, should lead to further improvements in power generation and energy recovery in single-chamber, air—cathode MFCs.

Introduction

Electricity generation using microbial fuel cells (MFCs) has drawn much attention recently as a new form of renewable energy production (1–5). Bacteria that have been identified as capable of making electricity in fuel cells include a wealth of genera of Geobacter (3, 6), Shewanella (2, 7), Pseudomonas (4), and others (1, 8–9). Electricity can be generated in MFCs using mixed cultures enriched from domestic wastewater (4), ocean sediments (10), animal wastes (11), and anaerobic sewage sludge (5, 12). Virtually any form of biodegradable organic matter can be used, including carbohydrates such as glucose (13) and starch (11), fatty acids (14), amino acids (15–16), and animal and human wastewaters (4, 11). In addition to electricity generation, the process can be used to treat wastewaters. However, in order for this technology to be a viable wastewater treatment method, further improvements in MFC performance are needed.

Factors that affect MFC performance include the following: rate of substrate degradation, rate of electron transfer from bacteria to anode, circuit resistance, proton mass transfer in the liquid, and performance of the cathode. Most MFCs are operated at neutral pH in order to optimize bacterial growth conditions. However, the low concentration of protons at this pH makes the internal resistance of the cell relatively high compared to chemical fuel cells that use acid or alkaline electrolytes. There are two ways to decrease the internal resistance without changing the bulk solution pH. One is to increase the solution conductivity by increasing the ionic strength (IS), and the other is to decrease the electrode spacing. Up to now, these two factors have not been systematically examined in MFCs for their effect on power generation. MFC performance can also be affected by temperature as a result of its effect on bacterial kinetics, oxygen reaction rates catalyzed by Pt on the cathode, and the rate of mass transfer of protons through the liquid. MFC studies are normally conducted at elevated temperatures of 30–37 °C. However, operating the reactor at lower temperatures may reduce operational costs, especially if the reactor is used for wastewater treatment. Thus, more information is needed on the performance of MFCs as a function of temperature.

The cathode electrode materials and methods of construction can also affect MFC performance. Oh et al. (17) have shown that the relative size of the anode and cathode electrodes affects power output. High Pt loading rates (0.5 mg cm⁻²) are usually used in MFCs in order to ensure that a lack of sufficient catalyst does not limit power generation. However, Cheng et al. (18) found that Pt loadings on a carbon cloth electrode as low as 0.1 mg cm⁻² did not significantly affect performance. They also found that the cathodes prepared with Nafion as the bonding agent achieved higher power densities than those using PTFE. Both carbon paper and cloth have been used in MFC systems (13, 18), but the effect of these carbon materials on power generation in air—cathode MFCs has not been examined.

In this study, we examined the effect of solution ionic strength, electrode spacing, and temperature on electricity generation using a single chamber, membrane-free MFC. Two different cathode materials were evaluated in order to ascertain the effect of these materials on power generation.

Methods

MFC Construction. The single-chamber MFC consisted of an anode and cathode placed in a plastic (Plexiglas) cylindrical chamber with a length of 4 cm and a diameter of 3 cm (empty bed volume of 28 mL) as previously reported (13). The anode electrode was made of plain toray carbon paper (without wet-proofing; E-Tek, USA), and was pierced in several places, forming holes ~1 mm in diameter, so that water motion in the chamber was not blocked when the anode was placed at the far end of the chamber or moved to within 2 cm of the cathode. Unless stated otherwise, the cathode was made of carbon paper containing 0.5 mg/cm² of Pt (10% of Pt/C catalyst, 30% wet-proofing; E-TEK, USA). In some tests, a carbon cloth (50% wet-proofing; E-TEK) cathode was used. A Pt/C paste was prepared by mixing a chemical binder (5% Nafion solution) and catalyst (20% Pt; E-TEK) to form a paste (final Pt content of 0.5 mg/cm²) that was applied to one side.
of the carbon cloth electrode. The electrode was then dried at room temperature for 24 h before use.

**MFC Tests.** All MFCs were inoculated with domestic wastewater (14 mL, ~300 mg-COD/L) and nutrient medium (14 mL; 15) amended with sodium acetate (1 g/L). After replacement of this solution twice over 2 days, the system was then operated using only the nutrient medium and acetate. The system was considered to be operating under steady conditions when the maximum voltage output was reproducible after refilling the reactor with medium at least two times. Power density curves were obtained by changing the circuit resistor, measuring the maximum power generated over a complete batch cycle of operation. The medium in the reactor was refilled when the voltage dropped below ~30 mV.

A series of experiments were conducted to study the individual effects of solution ionic strength, electrode spacing, temperature, and cathode materials on MFC performance. In one set of tests, the conductivity of the solution was increased by adding 100 (final IS = 200 mM), 200 (IS = 300 mM), or 300 mM NaCl (IS = 400 mM) to the medium in order to investigate the effect of ionic strength on power generation. At the highest (400 mM) and lowest (100 mM) solution ionic strength, the electrode spacing was changed from 4 to 2 cm. Temperature was reduced from 32 to 20 °C, and the cathode material was changed from the carbon paper to the carbon cloth electrode.

**Calculations and Analysis.** Voltage (V) was measured using a multimeter with a data acquisition system (2700, Keithly, USA), and used to calculate the power (P) according to $P = IV$. Power was normalized by the cross sectional area (projected) of the anode. Electrode potentials were measured by using a multimeter (83 III, Fluka, USA) and a reference electrode (Ag/AgCl; RE-5B, Bioanalytical systems, USA) located in the middle of the fuel cell chamber.

Coulombic efficiency was calculated as $E = (C_n/C_t) \times 100\%$, where $C_n$ is the total coulombs calculated by integrating the current over time, and $C_t$ is the theoretical amount of coulombs that can be produced from acetate, calculated as

$$C_t = \frac{FbSv}{M}$$

where $F$ is Faraday’s constant (96,485 C/mol-electrons), $b$ represents the number of moles of electrons produced per mole of acetate, $S$ stands for the substrate concentration, $v$ is the liquid volume, and $M$ represents the molecular weight of sodium acetate. Overall energy recovery was calculated as $E_o = (E_0/E_t) \times 100\%$, where $E_0$ is the total energy calculated by integrating the power over time. $E_t$ is the theoretical amount of energy that can be produced from acetate, calculated as

$$E_t = \frac{\Delta HSv}{M}$$

where $\Delta H$ is the enthalpy change of the following reaction under standard conditions:

$$C_2H_4O_2 + 2O_2 \rightarrow 2CO_2(g) + 2H_2O(l)$$

The internal resistance of the cell, $R_{int}$, was calculated from the slope of plots of $V$ and $I$ using

$$V = E_{cell} - IR_{int}$$

where $E_{cell}$ is the electromotive force of the cell.

**Results.**

**Effect of Ionic Strength.** A maximum power of 720 mW/m² was obtained at a current density of 0.26 mA/cm² using the medium with a solution ionic strength of 100 mM (Figure 1). The power generated here is higher than that previously reported using a similar system (506 mW/m²) (14), possibly because of the increased access of fluid in the chamber to both sides of the anode electrode due to the holes in the electrode. While it is also possible that the maximum power was due to a higher Pt content on the cathode (0.5 mg Pt/cm² versus 0.35 mg Pt/cm² in a previous study), Pt loadings as low as 0.1 mg/cm² did not significantly affect maximum power densities in this system performance (carbon cloth cathode; 1B). The maximum power density was increased when the solution ionic strength was increased, reaching a maximum of 1330 mW/m² (0.44 mA/cm²) at an IS = 400 mM (Figure 1). This power density was 85% larger than that obtained using the plain medium at an IS of 100 mM.

The effect of IS on anode and cathode performance was examined by placing a reference electrode into the anode chamber. The anode working potential decreased with the ionic strength (Figure 2A) while the cathode working potential increased with the ionic strength, producing a greater overall circuit voltage (Figure 2B). This improvement in both anode and cathode potentials may have been due to the decrease in internal resistance as a result of an increase in IS. On the basis of the voltage and current curves, the internal resistance of the cell using only the medium (IS = 100 mM) was 161 Ω, decreasing to 91 Ω with the addition of 100 mM NaCl (IS = 200 mM). However, further increasing the ionic strength only slightly reduced the internal resistance to 83 Ω (IS = 300 mM) and 79 Ω (IS = 400 mM).

The overall coulombic efficiency, defined as the recovery of total electrons in acetate as current, increased with current...
density for all runs at different ionic strengths, or from 25 to 46% (0.15–0.39 mA/cm²; IS = 100 mM) and from 39 to 61% (0.20–0.51 mA/cm²; IS = 400 mM) (Figure 3A). This increase was likely a consequence of a decrease in the operation time due to faster substrate utilization, resulting in less oxygen transfer into the chamber before exhaustion of the substrate. Coulombic efficiency also increased slightly with NaCl addition, reaching a maximum of 61% at a current density of 0.51 mA/cm² (IS = 400 mM). The overall energy recovery, which represents the energy harvested as electricity from bacteria versus that lost to other processes, also increased with ionic strength from 6.9–9.6% (0.11–0.36 mA/cm²; IS = 100 mM) to 12.9–15.1% (0.20–0.51 mA/cm²; IS = 400 mM) (Figure 3B).

Effect of Electrode Spacing. The effect of electrode spacing on MFC performance was investigated by reducing the distance between the anode and cathode from 4 to 2 cm. The maximum power density increased from 720 to 1210 mW/m² when the electrode distance was decreased to 2 cm (IS = 100 mM) (Figure 4). This increase in power density corresponded to a decrease of internal resistance from 161 to 77 Ω when the electrode spacing was reduced from 4 to 2 cm. No further improvement in power generation was observed if the medium IS was increased to 400 mM (Figure 4). Bacterial activities are well-known to be affected by temperature, with biological processes often modeled as an empirical function of temperature as $ı = T^{\theta - 30}$, where $ı$ is microbial growth under anoxic conditions and 1.2 for heterotrophs, and $T$ is the temperature in Celsius (19). The observed difference by a factor of 1.1, versus factors of 2.9 to 8.9 predicted by this equation (relative to 20 °C), suggests that either the bacteria were not growing under optimal conditions at the higher temperature or that factors
other than bacterial growth, such as the diffusion of substrate or products, limited electricity generation.

Decreasing the temperature did not affect the anode working potential over a current range of 0.11 to 0.36 mA/cm² (Figure 7B). The cathode working potential of MFC operated at 20 °C was also comparable to that operated at 32 °C for current densities in the range of 0.11–0.23 mA/cm². However, at higher current densities (>0.24 mA/cm²), the cathode potential at 20 °C was lower than that at 32 °C (Figure 7B). Thus, this suggests that the performance of the cathode was the main factor affecting power generation at higher current density.

The overall coulombic efficiencies at the two different temperatures were comparable, ranging from 17–45% (0.10 to 0.36 mA/cm²) at 20 °C to 25–46% (0.15–0.39 mA/cm²) at 32 °C (Figure 8). The overall energy recovery decreased from 9.6% to 6.9% when the current density increased from 0.23 to 0.39 mA/cm², for the MFC operated at 32 °C. For the MFC operated at 20 °C, the recovery decreased from 9.2% at a current density of 0.22 mA/cm² to 4.6% at a current density of 0.36 mA/cm².

Effect of Cathode Material. By replacing the carbon paper with a carbon cloth electrode, the maximum power density was increased from 660 mW/m² (0.22 mA/cm²) to 1114 mW/m² (0.33 mA/cm²), or an overall increase of 69% at 20 °C (Figure 9A). This increase in power production was reflected by a significant increase in the cathode potential using the carbon cloth, while the anode potentials were essentially unchanged in the current density range of 0.07–0.39 mA/cm² (Figure 9B).

Coulombic efficiency increased with current density for both cathode materials, similar to that found in previous tests but under different conditions, ranging from 17 to 45% (0.10–0.36 mA/cm²) using the carbon paper cathode, and from 22 to 52% (0.09–0.50 mA/cm²) with the carbon cloth cathode (Figure 10). A similar energy recovery (9.2%) was observed at a current density of 0.21 mA/cm² for both materials. However, at a higher current density of 0.27 to 0.50 mA/cm², energy recovery was greater (6.8–9.0%) using the carbon cloth cathode than with the carbon paper cathode (4.6–8.8%).

Discussion
It is clear that there are still many ways that power densities can increased in microbial fuel cells through changes in the solution chemistry as well as in construction and operation. We obtained a maximum power density of 1330 mW/m², which to our knowledge is the highest value yet obtained for a direct-air–cathode MFC with acetate. Higher values have only been reported for MFCs that use ferricyanide at the
cathode or polymers bound to an electrode (20–21). Ferricyanide must be chemically replaced or regenerated, while charged polymers (polyaniline) could be degraded by bacteria over time. To achieve the high power densities reported here, we altered relatively simple characteristics of the system that had carbon electrodes and oxygen as an electron acceptor. With small changes in electrode spacing or solution chemistry, the maximum power density achieved here was up to 163% larger than that previously achieved using this system (506 mW/m²; 13).

Some of the ways that operational parameters and construction can increase power generation are expected on the basis of our knowledge of hydrogen fuel cells, while others are not. For example, power generation in PEM hydrogen fuel cells is strongly a function of the performance of the membrane, but the MFC used here did not contain a membrane. In our MFC the protons are transported in the solution between the electrodes, and therefore the membrane is not needed (13). The neutral pH limits the proton concentration in the solution, but the conductivity of the solution is important. Power was increased by up to 85% by adding NaCl (300 mM) to the solution in the anode chamber. However, solution conductivities can only be increased within the limits suitable for bacterial growth. Nonhalophile bacteria enriched from freshwater and wastewater environments typically have optimal growth at salt concentration < 1.2% (220 mM NaCl; 22) with little growth above 3% (23). Our previous work has demonstrated that electricity can be generated with the simultaneous treatment of domestic wastewater (4, 11). It would not be practical to increase the IS of a wastewater in order to increase the performance of a MFC used for wastewater treatment. However, results on the effects of IS do suggest that MFCs may be highly effective when used with saline industrial wastewaters or in conjunction with wastewater treatment systems using seawater, using bacteria that can grow in seawater (6). In some cities around the world, seawater is used in waste treatment systems for toilets and other gray water municipal systems (for example, Hong Kong; 24).

It was determined that changing the cathode from a carbon paper to a carbon cloth increased the cathode potential and the resulting power density. These results could be due to several factors. First, although the two cathodes have the same Pt content (0.5 mg/cm² Pt), differences in their thickness, porosity, and hydrophilicity could affect rates of oxygen diffusion into the anode chamber. Second, it is possible that the Pt/C catalyst binder used to make the cloth cathode was more efficient than the one in the commercially produced cathode. Cheng et al. (16) recently found that the cathode performance was a function of the binder chemical, with the MFC using Nafion producing more power than the one using poly(tetrafluoroethylene) (PTFE). While Nafion was used as the binder for the carbon cloth cathode, the binder material used in the carbon paper cathode was not specified by the manufacturer. Third, the biofilm that develops on the two different cathode materials could affect overall power generation. We have observed that a biofilm will grow on the inner surface of the cathode (facing the solution) in the single-chamber, membrane-free MFC, likely supported by oxygen diffusion through the cathode (13). It has been observed in long-term tests that the development of this biofilm can affect power generation (18).

Fourth, the different thickness of catalyst layer on cathode might affect oxygen diffusion or the cathode reaction rate, as the Pt catalyst concentration used in our catalyst mixture was different from that reported for the commercial cathode (20% Pt in the carbon cloth and 10% Pt in the manufactured carbon paper).

It was also shown here that just by moving the anode closer to the cathode (to within 2 cm), power density could be increased by 67%. This effect of increased power generation with decreased electrode spacing has also been found by Cheng et al. (23) in a similar type of reactor where the flow is directed to flow through a porous anode. It is not known how close the electrodes could be placed to each other as several factors are important in electrode spacing. First, a high void volume (greater electrode spacing) is needed to prevent clogging and fouling of the system due to buildup of bacteria in the system. At the same time, a large surface area per volume is desired in order to increase power densities per unit volume of reactor. Second, placing the electrodes too closely could increase the potential for short circuiting. Third, oxygen diffusion through the cathode could affect bacteria on the anode, reducing the power output. In a recent test, a MFC was operated with the anode and cathode placed directly on opposite sides of a proton exchange membrane that was permeable to oxygen (11). Despite the close proximity of the two electrodes, the MFC produced electricity, although at lower power densities than achieved here.

The effect of temperature on MFC performance was surprising as there was only a slight reduction in power density (9%) when the temperature was reduced from 32 to 20 °C. Typically, chemical reaction rate coefficients are doubled with each 10 °C increase in temperature. The fact that the power density decreased only slightly when the temperature was changed to room temperature is encouraging, as this characteristic may aid in the development of MFCs used for wastewater treatment. Operation of MFC systems at lower temperatures would be a great benefit for treating many different wastewaters under anaerobic conditions. Additional research, however, is needed to more fully investigate MFC operation across different temperatures and to determine how temperature fluctuations affect MFC performance.

It is clear from this and other studies that the efficiency of the cathode can substantially affect maximum power densities in MFCs (17, 20–21). Hydrogen fuel cells are operated at much higher temperatures, and generally the cathode, if operated under optimal conditions of humidity, can achieve orders-of-magnitude greater power densities than these same electrodes when used in MFCs. Low temperatures and proton concentrations, combined with the nature of the cathode material and its interaction with water, results in maximum power densities in MFCs that limit cathode performance. It was shown here that replacement of the carbon paper cathode with a carbon cloth cathode resulted in 69% greater power density even though the two cathodes had the same Pt content (0.5 mg/cm²). The reasons for this increase could be due to differences in thickness, porosity, hydrophilicity, and catalyst binder, but these factors were not individually examined here. Further investigation is needed into which of these factors can be changed to optimize the cathode materials and boost power generation. We also need to create cathodes that increase coulombic efficiency and energy recovery by limiting oxygen diffusion through the cathode. It has been estimated that 21–50% of the substrate can be lost to oxygen diffusion through a carbon paper cathode (13). Although the coulombic efficiency (up to 61%) and energy recovery (up to 15.1%) were improved in this study compared to our previous study (less than 30% of CE and 7% of ER) (13–14), further improvements are needed. Such improvements must be made to the cathode, while also limiting the potential for cathode flooding due to water accumulation on the air side of the cathode, or even water leakage through the fibrous material. Simultaneously achieving these goals will produce greater power densities and energy recoveries, increasing the potential for MFCs to be used for wastewater treatment and renewable energy production.
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