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Production of Electricity from Acetate or Butyrate Using a Single-Chamber Microbial Fuel Cell

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Hydrogen can be recovered by fermentation of organic material rich in carbohydrates, but much of the organic matter remains in the form of acetate and butyrate. An alternative to methane production from this organic matter is the direct generation of electricity in a microbial fuel cell (MFC). Electricity generation using a single-chambered MFC was examined using acetate or butyrate. Power generated with acetate (800 mg/L) (506 mW/m^2 or 12.7 mW/L) was up to 66% higher than that fed with butyrate (1000 mg/L) (305 mW/m^2 or 7.6 mW/L), demonstrating that acetate is a preferred aqueous substrate for electricity generation in MFCs. Power output as a function of substrate concentration was well described by saturation kinetics, although maximum power densities varied with the circuit load. Maximum power densities and half-saturation constants were $P_{max} = 661$ mW/m^2 and $K_s = 141$ mg/L for acetate (218 Ω) and $P_{max} = 349$ mW/m^2 and $K_s = 93$ mg/L for butyrate (1000 Ω). Similar open circuit potentials were obtained in using acetate (798 mV) or butyrate (795 mV). Current densities measured for stable power output were higher for acetate (2.2 A/m^2) than those measured in MFCs using butyrate (0.77 A/m^2). Cyclic voltammograms suggested that the main mechanism of power production in these batch tests was by direct transfer of electrons to the electrode by bacteria growing on the electrode and not by bacteria-produced mediators. Coulombic efficiencies and overall energy recovery were 10–31 and 3–7% for acetate and 8–15 and 2–5% for butyrate, indicating substantial electron and energy losses to processes other than electricity generation. These results demonstrate that electricity generation is possible from soluble fermentation end products such as acetate and butyrate, but energy recoveries should be increased to improve the overall process performance.

Introduction

Harvesting products from wastewater in order to make the process more economical and sustainable is the next frontier in wastewater treatment (*1, 2*). Hydrogen production from wastewater by biological fermentation has drawn much attention as a method of producing a valuable product during treatment of wastewaters containing high concentrations of carbohydrates (*3–7*). One mole of glucose can theoretically be converted into 12 mol of hydrogen, but the maximum yield via known fermentation routes is only 4 mol of hydrogen when acetate is the sole byproduct. While the maximum efficiency of hydrogen production is therefore 33%, typically only 15% of the energy is recovered as hydrogen (*2, 8*) with the remainder of the organic matter present as fatty acids and alcohols.

To improve the economics of hydrogen production from wastewater, additional processes are needed to recovery the remaining energy. One approach is to link hydrogen production with methane production by using a two-stage process (*2*). Although two-stage anaerobic treatments have been used to make methane, it has not yet been proven outside of the laboratory that hydrogen can be recovered at high concentrations from the first stage using actual wastewaters. A second approach is to use phototrophic bacteria to recover additional hydrogen from the byproducts of hydrogen fermentation (*9, 10*). Although solar energy is free, the availability of sufficient land area and the instability of sufficient solar energy at the plant would make such a process difficult for wastewater treatment applications. A third approach is to recover the remaining energy directly as electricity in a microbial fuel cell (MFC). While electricity production has been shown in MFCs using glucose or acetate, much remains to be done in order to use this technology for wastewater treatment.

Bacteria present in wastewater, anaerobic reactor sludges, and marine sediments have been shown to produce electricity in a MFC (*11–14*). Bacteria that have been identified to be capable of making electricity in fuel cells, most of which are metal-reducing bacteria, include *Geobacter sulfurreducens* (*15, 16*), *Geobacter metallireducens* (*13, 16*), *Shewanella putrefaciens* (*17, 18*), *Clostridium butyricum* (*19*), *Rhodoferax ferrireducens* (*20*), and *Aeromonas hydrophila* (*15*). It has also been recently shown that electricity generation in an MFC resulted in large part from the production of mediators, or electron shuttles, by a microbial community consisting of primarily three bacteria: *Alcaligenes faecalis*, *Enterococcus faecium*, and *Pseudomonas aeruginosa* (*12*).

Many MFCs contain two chambers (*16–18, 20*). One chamber contains electrochemically active bacteria growing under anaerobic conditions that grow as a biofilm attached to the anode. The other chamber is kept aerobic by sparging water with air and contains the cathode. The two chambers are typically separated by a proton exchange membrane (PEM), which allows the transfer of protons from the anode to cathode chamber and that helps to physically block oxygen diffusion into the anode chamber. Recently, single-chamber MFCs have been developed that use a cathode exposed directly to air instead of air-sparged water (*11, 21, 22*). There are several advantages of using a single-chamber MFC versus a two-chambered system: increased mass transfer to the cathode; decreased operating costs, because it is not necessary to sparge the water; an overall decrease in reactor volume; and a simplified design. Power output can further be increased in a single-chamber MFC by removing the PEM (*11*). Although there is increased oxygen diffusion into the anode chamber in the absence of the PEM, the formation of an aerobic biofilm on the cathode inner surface (facing the anode) removes any oxygen that diffuses into the chamber, preventing the loss of anaerobic conditions in the anode chamber. The lack of a PEM also substantially decreases the cost of the materials needed to make a MFC.

The primary fermentation end products during biohydrogen production are acetic and butyric acids. Thus, to link

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a MFC to biohydrogen production it must be shown that power can be generated from degradation of these compounds. However, there are no previous studies on electricity production from butyrate, which can account for up to 70% of the aqueous byproducts of hydrogen production from sugar fermentation (*8*). Power generation from acetate in two-chambered MFCs is well known, but there have been no previous reports of power generation using acetate in single-chambered systems. Here we demonstrate that electricity can be generated from butyrate in a single-chambered MFC, and we compare power densities obtained from acetate and butyrate with those previously obtained in the same system using glucose (*11*).

Methods

MFC Construction and Operation. The membrane-free single-chamber MFCs consisted of an anode and cathode placed on opposite sides in a plastic (Plexiglas) cylindrical chamber 4 cm long by 3 cm in diameter (empty bed volume of 28 mL) as previously reported (*11*). The anode electrode was made of toray carbon paper (without wet proofing; E-Tek). The cathode was carbon paper containing 0.35 mg/cm² Pt (E-Tek). Platinum wire was used to connect the circuit.

Following inoculation and stable power generation using domestic wastewater (after four transfers of wastewater into the reactor, 140 h), a nutrient medium containing acetate or butyrate was added to the anode chamber. Acetate (80–800 mg/L) and butyrate (75–1000 mg/L) concentrations were varied to determine power output as a function of substrate concentration. No precautions were taken to remove dissolved oxygen from the medium or to maintain anaerobic conditions in the anode chamber. Experiments were conducted at least in duplicate, in a constant-temperature room (30 °C).

Calculations. Voltage (V) was measured using a multimeter with a data acquisition system (2700, Keithly) and used to calculate the power (P) according to $P = IV$. Power was normalized by either the cross-sectional area (projected) of the anode, A, or by the liquid volume, v. The Coulombic efficiency was calculated as, $E = C_p/C_{Ti} \times 100\%$, where C_p is the total coulombs calculated by integrating the current over time. C_{Ti} is the theoretical amount of coulombs that can be produced from either sodium acetate ($i = a$) or sodium butyrate ($i = b$), calculated as

$$C_{Ti} = Fb_iS_iv/M_i \qquad (1)$$

where F is Faraday's constant (96 485 C/mol·electrons), b_i the number of moles of electrons produced per mole of substrate ($b_a = 8$, $b_b = 20$), S_i the substrate concentration, and M_i the molecular weight of the substrate ($M_a = 82$, $M_b = 110$). Overall energy recovery was calculated as, $E_E = E_p/E_{Ti} \times 100\%$, where E_p (J), is the total energy calculated by integrating the power over time. E_{Ti} (J) is the theoretical amount of energy that can be produced from the substrate, calculated as

$$E_{Ti} = \Delta HS_iv/M_i \qquad (2)$$

where ΔH is the enthalpy change of the following reaction under standard conditions:

$$C_2H_4O_2 + 2O_2 \rightarrow 2CO_2\ (g) + 2H_2O\ (l) \qquad (3)$$

$$C_4H_8O_2 + 5O_2 \rightarrow 4CO_2\ (g) + 4H_2O\ (l) \qquad (4)$$

Power was modeled as a function of substrate concentration (S) using an empirical Monod-type equation as

$$P = P_{max}S/(K_s + S) \qquad (5)$$

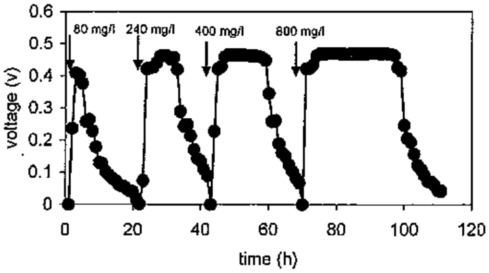

FIGURE 1. Voltages generated using acetate at different concentrations.

P_{max} the maximum power and K_s the half-saturation constant were determined using the Solver function in Microsoft Excel 2002.

Analysis. Acetate and butyrate concentrations were analyzed using a gas chromatograph (Agilent, 6890) equipped with a flame ionization detector and a 30 m × 0.32 mm × 0.5 μm DB-FFAP fused-silica capillary column followed the same procedure described previously (*11*). Electrode open circuit potentials (OCP) and working potentials were measured using a multimeter (83 III, Fluke) with Ag/AgCl reference electrode (RE-5B, Bioanalytical Systems).

Cyclic Voltammetry (CV). Cyclic voltammetry (PC 4/750 potentiostat, Gamry) was used to characterize the oxidation–reduction reactions on the electrode surface by measuring the current response at an electrode surface to a specific range of potentials in an unstirred solution at a scan rate of 20 mV/s (minimum of 5 scans). The anode was the working electrode, and the counter electrode was the MFC cathode with a Ag/AgCl reference electrode. The potentials were originally in the range of −800 to 200 mV, but since peaks were only found in the range of −500 to 0 mV, this smaller range was used in the latter experiments.

Results

Power Generation as a Function of Substrate Concentration. Following inoculation and stable power generation of the reactor with wastewater, a stable voltage was generated after three additional transfers (~60 h) using a medium containing acetate (80 mg/L) or butyrate (75 mg/L) into the anode chamber. An example of the cycle of power generation for reactors fed different initial acetate concentrations (80–800 mg/L) is shown in Figure 1. A plot of the maximum power output at each initial substrate concentration demonstrated saturation kinetics at three different circuit loads of 218, 1000, and 5000 Ω (Figure 2A). A maximum power density of $P_{max} = 661$ mW/m² and half-saturation constant of $K_s = 141$ mg/L ($R^2 = 0.997$) was obtained using a 218 Ω resistor, while those using 1000 and 5000 Ω resistors were $P_{max} = 343$ mW/m² and $K_s = 43$ mg/L ($R^2 = 0.999$) and $P_{max} = 86$ mW/m² and $K_s = 9$ mg/L ($R^2 = 0.999$), respectively. For the butyrate-fed MFC and a 1000 Ω resistor, the maximum power was approximately the same with $P_{max} = 349$ mW/m² and a half-saturation constant of $K_s = 93$ mg/L ($R^2 = 0.887$) (Figure 2B).

Power as a Function of Current Density. By varying the circuit resistance from 70 to 5000 Ω (current densities of 0.2–2.2 A/m²) with acetate (800 mg/L) as the substrate, a maximum power of 506 mW/m² (12.7 mW/L) was obtained at a current density of 1.8 A/m² (218Ω) (Figure 3). The MFC using butyrate (1000 mg/L) as substrate generated a maximum power of 305 mW/m² (7.6 mW/L) at a current density of 0.65 A/m² (1000 Ω).

Electrode Potential. Electrode open circuit potentials and working potentials were measured for each substrate by varying the circuit load. With acetate (800 mg/L) as the substrate, the anode and cathode open circuit potentials were −480 ± 15 and 318 ± 10 mV (Ag/AgCl reference electrode),