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The variation of power generation with organic substrates in single-chamber microbial fuel cells (SCMFCs)

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ABSTRACT

The wastewaters consist of diverse types of organic substrates that can be used as the carbon sources for power generation. To explore the utilization of some of these organics, the electricity generation from three substrates (acetate, ethanol, and glucose) was examined over a concentration range of 0.5–35 mM in single-chamber microbial fuel cells (SCMFCs). The power density generated from glucose was the highest at 401 mW/m^2 followed by acetate and ethanol at 368 mW/m^2 and 302 mW/m^2, respectively. The voltage increased with substrate concentration of 0.5–20 mM, but significantly decreased at high substrate concentrations of 20–35 mM. Kinetic analysis indicated that the inhibition in the ethanol-fed MFCs was the highest at the concentration of 35 mM, while inhibition in glucose-fed MFCs was the lowest at the concentration of 20 mM. These were in accordance with the extents of voltage decrease at high substrate concentration. Moreover, the effect of the distance between anode and cathode on voltage generation was also investigated. The reduction of the electrode distance by 33% in the glucose-fed MFCs reduced the internal resistance by 73% and led to 20% increase in voltage generation.

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1. Introduction

Global warming and spiraling energy prices have added up to burgeoning energy import bill and putting substantial strain on the US economy. In the interest of clean environment, strong economy, and national security, it is imperative to reduce the dependence on imported crude oil. Wastewaters containing a variety of organic substrates hold great potential as an energy source. The microbial fuel cell (MFC) is a promising bio-electrochemical technology, in which anaerobic bacteria convert chemical energy stored in wastewater to electricity (Shukla et al., 2004).

Traditional MFC configuration is the two-chamber MFC (2CMFC) consisting of anaerobic anode and aerobic cathode chambers (Logan et al., 2005, 2006, 2007). In the anode chamber, the anaerobic electrochemically active bacteria growing on the anode surfaces oxidize the organic compounds (i.e. acetate, glucose, protein in wastewater) and produce electrons and protons (Reaction (1)). Electrons and protons then get transferred from the anode to the cathode chamber and react with oxygen to form water (Reaction (2)), thereby generating electricity. The proton exchange membrane (PEM) separates anode and cathode chambers, and was found to be the main source of high internal resistance (R_{in}) in 2CMFCs (Min et al., 2005). The R_{in} of 2CMFCs is normally around 1000 Ohm (Min et al., 2005). The highest power density of 2CMFCs was about 40 mW/m^2 (Logan et al., 2005).

$$C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 8e^+ + 8H^+ \quad (1)$$

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O \quad (2)$$

In recent years, tremendous effort has been made to improve power generation in MFCs. Novel MFC configurations (i.e. single-chamber microbial fuel cell (SCMFC), stacked MFC, and upflow MFC) have been developed by removing PEM to reduce R_{in} and increase power densities (Liu and Logan, 2004; Liu et al., 2005; Logan et al., 2006; He et al., 2006; Logan et al., 2007). Pure cultures (i.e. *Geobacter sulfurreducens* and *Shewanella putrefaciens*) and mixed cultures (i.e. wastewater and activated sludge) have been examined to directly transfer the electrons to the anode surfaces without artificial electron mediators (Kim et al., 2007, 2002; Bond et al., 2002; Chaudhuri and Lovley, 2003; Lovley, 2005). Novel electrode materials (i.e. granulated activated carbon, carbon fiber, carbon cloth, graphite) have been employed to improve biofilm formation for high power generation (Moon et al., 2006; He et al., 2006; Zhao et al., 2005). The operational parameters (i.e. temperature, hydraulic retention time, and substrate concentration) have also been studied to determine the optimal conditions for power generation (Liu and Logan, 2004; He et al., 2006; Mohan et al., 2007).

However, there are two major challenges of power generation in MFCs. Firstly, the high R_{in} of MFCs consumes significant amounts of power generated inside MFCs (Sang et al., 2006; Peng et al.,

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2007). An efficient conversion of chemical energy stored in the organic substrates to electrical energy has not been obtained yet, and thus resulting in low energy recovery in MFCs (Liu et al., 2005). Secondly, the power generation of MFCs increases with substrate concentrations, but high substrate concentrations have been found to inhibit power generation in MFCs (Kim et al., 2007). The threshold concentration for power generation has not been determined in MFCs. Moreover, due to the different substrates present in various concentrations in wastewater, it is imperative to determine the suitability of the substrate types and concentrations for a specific MFC configuration in order to improve power generation.

This study aims at determining the critical values of important operational parameters for increased power generation using both theoretical and experimental approaches. The single-chamber microbial fuel cells (SCMFC) were employed due to its low R_{in} and rapid mass transfer from anode to cathode (Kim et al., 2007). There are three fold objectives of this study. First, three organic substrates, including acetate, ethanol, and glucose were examined at a broad range (0.5–35 mM) to determine the optimal concentration for power generation. Second, an Andrew's inhibition kinetic analysis was performed to evaluate the maximum power density at different substrate concentrations and determine the threshold concentration for substrate inhibition. Third, the R_{in} and power densities were evaluated between two typical MFC configurations (single bottle MFCs-SBMFC, and single-chamber MFCs-SCMFCs) to determine the effects of the electrode distances on MFC performance.

2. Methods

2.1. MFC construction

Single-chamber MFCs (SCMFCs) were reported to have much lower R_{in} than 2CMFCs (Liu and Logan, 2004). Two types of SCMFCs were tested in this study. The first type was made of a glass bottle (Wheaton Scientific, NJ) with an effective volume of 100 mL, termed as single bottle MFC (SBMFC). The anode electrode (surface area: 6 cm^2) was placed inside the bottle, and the cathode (surface area: 6 cm^2) was placed on the extension arm of the bottle with oxygen in the air as the electron acceptor. The distance between two electrodes was 6 cm. The second type MFC consisted of an anode and cathode on opposite sides in a plastic (Plexiglas, PA) cylindrical chamber with a dimension of $4 \times 4 \times 4$ cm (L × W × H) and an effective volume of 30 mL, termed single-chamber MFC (SCMFC). The surface areas of anode and cathode electrodes were 6 cm^2. The distance between the two electrodes was 4 cm. In both types of MFCs, the anode was made of carbon cloth (non wet proofing, E-Tek, FL). The cathode was a carbon cloth (30% wet proofing, E-Tek, FL) containing 0.35 mg/cm^2 platinum on its inner surface facing the media solution. The outer surface of cathode was coated with four layers of polytetrafluoroethane to prevent water evaporation and substrate oxidation by oxygen (Liu et al., 2005). The copper and platinum wires were used to connect the external circuit of MFCs, and the connections on anode and cathode were coated with epoxy (CW 2400, Circuit Specialist Inc., AZ) to prevent the exposure to the media solution inside MFCs. An external resistance (R_{ext}) of 1000 Ohm was used in all MFCs. The MFCs were operated in a 30 °C temperature control room.

2.2. Inocula and media

Domestic wastewater collected from University of Connecticut Wastewater Treatment Plant was used as the inocula in MFCs. The wastewater had a chemical oxygen concentration (COD) of 250–350 mg/L and a pH of 7–8. A growth media containing (per liter) NH_4Cl (310 mg), KCl (130 mg), $NaH_2PO_4 \cdot H_2O$ (4.97 g), $Na_2HPO_4 \cdot H_2O$ (2.75 g), a mineral solution (12.5 mL), and a vitamin solution (12.5 mL) was used to provide suitable nutrients for the growth of anaerobic electrogenic bacteria (Lovley and Phillips, 1988). The wastewater was mixed with the growth media in a ratio of 1:1 for MFC tests.

2.3. Organic substrates

Three types of substrates: acetate, ethanol, and glucose (Fischer Sci., PA) were tested at five concentrations of 0.5, 4, 8, 20, and 35 mM, respectively. A concentrated solution of each substrate was injected into the MFCs and mixed with media solution. The substrate was degraded by electrogenic bacteria inside MFCs during the operational period. A cycle of MFC operation was completed when the voltage became lower than 20 mV, indicating that the substrate was consumed. Upon completion of one cycle, a certain amount of the concentrated solution was injected into the MFC to bring the substrate concentration back to the desirable level. The MFC was operated for four feeding cycles for each concentration.

2.4. Biofilm formation at anode

Before the MFC tests, the domestic wastewater containing a variety of microorganisms such as electrogenic and acidogenic bacteria was inoculated to MFCs for the biofilm formation on the anode. In the acclimation period (normally 5 days) of MFCs, the wastewater was changed daily in MFCs to facilitate the biofilm formation and growth on the anode surfaces (Liu and Logan, 2004). After biofilms fully grew on anode surfaces, the growth media and the organic substrates to be tested were injected to the MFCs for the tests.

2.5. Electrochemical measurement

The voltage (V) over the R_{ext} was recorded every 2-h interval by the Keithly data acquisition system (Liu et al., 2005). The electrochemical characteristics of the anodes were evaluated by the cyclic voltammograms (CV) measurement using a potentiostat (Gamry, PA) and a three-electrode system with Ag/AgCl as the reference electrode, the anode as the working electrode and the cathode as the counter electrode. The voltage was changed from −0.6 V to 0 V in forward and reverse scans at a scan rate of 20 mV/s for a total of five scans (Bard and Faulkner, 2001). The R_{in} of MFCs was measured using the electrochemical impedance spectroscopy (EIS) with a potentiostat (Gamry, PA), in which the anode was used as a working electrode and the cathode as reference and counter electrode. The frequency was changed from 10^5 to 0.1 Hz and the impedance was obtained. The intercept of the EIS curve and x-axis (real impedance, Z_{re}) is the electrolyte resistance (R_{ele}), while the projected length of the EIS curve on x-axis is the sum of kinetic and diffusion resistance ($R_{kin} + R_{diff}$) (Katz and Willner, 2003). The power densities (P) and current densities (I) of MFCs were determined using polarization curve measurement, in which a series of external resistors ranging from 30 to 1500 Ohm were used and the corresponding voltages were recorded using a multimeter (RadioShack, CT). The power density (P) and current density (I) were calculated by $P = V^2/(A \times R)$ and $I = V/(A \times R)$, respectively, where V is the voltage across the external resistors, R is resistance of each external resistor, and A is the surface area of the anode.

2.6. Coulombic efficiency

Coulombic efficiency (CE) is the ratio of the coulombs obtained in a MFC to the theoretical coulombs if all the substrate oxidized