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Performance of sodium bromate as cathodic electron acceptor in microbial fuel cell

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HIGHLIGHTS

- Performance of $NaBrO_3$ as cathodic electron acceptor in MFC was firstly studied.
- The performance of MFC was influenced by $NaBrO_3$ concentration and catholyte pH.
- The open circuit potential could reach 1.635 V at 100 mM $NaBrO_3$ and pH 3.0.

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ABSTRACT

The potential of using sodium bromate as a cathodic electron acceptor in a microbial fuel cell (MFC) was determined in this study. The effects of sodium bromate concentration and initial catholyte pH on the electricity production of the MFC were investigated. The MFC performance improved with increasing sodium bromate concentration and decreasing catholyte pH. The maximum voltage output (0.538 V), power density (1.4908 W m^{-3}), optimal open circuit potential (1.635 V), coulombic efficiency (11.1%), exchange current density (0.538 A m^{-3}) and charge transfer resistance (4274.1 Ω) were obtained at pH 3.0 and 100 mM sodium bromate. This work is the first to confirm that sodium bromate could be used as an electron acceptor in MFCs.

1. Introduction

With decreased availability of fossil fuels and aggravation of global environmental pollution, demands for renewable clean energy considerably increase. A microbial fuel cell (MFC) is a device that can utilise the organic compounds in wastewater to produce electricity. MFCs have attracted increased research attention (Guo et al., 2014; Lv et al., 2014). The cathodic electron acceptor of a MFC is an important factor that influences electricity generation (Wei et al., 2012). The standard potential of a cathodic electron acceptor should be higher than −320 mV (the redox potential of organic matter oxidised by microorganisms in the anode) to generate positive electromotive force (Wang et al., 2011b). Oxygen is a widely studied cathodic electron acceptor because of its high redox potential and unlimited availability (Wang et al., 2011a). However, the poor reduction kinetics of oxygen restricts its application; as such, expensive catalysts are conventionally required (e.g., platinum-based catalysts), thereby limiting the further scale-up of MFCs. Various substances with high oxidation–reduction potentials have been tested as cathode electron acceptors to overcome the limitations of oxygen cathode and increase power output. Oh and Logan (2006) reported that power output can be increased by 1.5 to 1.8-fold by using ferricyanide, instead of oxygen. Jadhav et al. (2014) reported that the maximum power density of a MFC with NaOCl as the catholyte is approximately nine times higher than that when oxygen was used as the electron acceptor. Pandit et al. (2011) compared four cathode electron acceptors, and found that potassium persulfate is the most suitable electron acceptor because of its high open circuit potential (OCP, approximately 1.1 V) and the durability of the voltage output. You et al. (2006) used potassium permanganate as a cathode electron acceptor in a two-chamber MFC; the OCP at pH 3.6 is 1.382 V, which is the highest OCP reported to our knowledge. However, the main cathodic product of the MFC is manganese dioxide (MnO_2) which was deposited on the cathode surface; these

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deposits can increase the internal resistance and reduce the MFC power output.

Given their high oxidisation capacity, bromates are used as oxidants in industrial applications. As illustrated in Eq. (1), the standard electrode potential of BrO_3^-/Br^- is 1.44 V, which is much higher than −320 mV, and also higher than the standard electrode potential of ferricyanide (0.36 V). Therefore, bromate could be used as the cathode electron acceptor in MFCs. However, this approach has currently not been reported to the best of our knowledge.

$$BrO_3^- + 6H^+ + 6e^- = Br^- + 3H_2O \quad E^0 = 1.44\,V \tag{1}$$

In this study, sodium bromate was tested as a possible cathodic electron acceptor in MFCs. The effects of sodium bromate concentrations and initial catholyte pH were analysed by determining OCP and power density. Furthermore, the internal resistance and exchange current density (i_0) of MFCs with catholytes of different pH were also studied.

2. Methods

2.1. MFC configuration

A dual-chamber MFC composed of two glass bottles was used in this study. Two bottles with an operating volume of 90 mL each served as the anode chamber and cathode chamber. These chambers were connected by side-arms, and separated by a cation exchange membrane (4.5 cm^2). Carbon felt (2 cm × 4 cm × 1 cm) and stainless steel mesh (2 cm × 4 cm, Fe, 70.6%; Cr, 18.3%; Ni, 8.5%; Si, 0.8%; Mn, 1.8%; wire diameter 120–150 μm; pore size 450–525 μm) were used as the anode and cathode, respectively. The electrodes were connected with copper wire. An external load resistance (1000 Ω) was linked to the circuit. Both chambers were installed with the Ag/AgCl reference electrode (+0.197 V vs. NHE) to measure the electrode potential.

2.2. MFC inoculation and operation

The electrogenetic microbes of the MFC were obtained from an aeration tank of the Yangjiapu sewage treatment plant. Before inoculation into the MFC, the microbes were anaerobically cultured for 2 d. Subsequently, 20 mL of the inoculum and 60 mL of the nutrient solution were poured into the anode chamber. The 1 L nutrient solution contained 1000 mg of $NaAc{\cdot}3H_2O$, 130 mg of KCl, 310 mg of NH_4Cl, 6640 mg of $NaH_2PO_4{\cdot}2H_2O$, 20,640 mg of $Na_2HPO_4{\cdot}12H_2O$, 2 mg of NaCl, and 20 mL of the trace mineral element solution. During the inoculation, the catholyte was sodium bromate (100 mM $NaBrO_3$ in 100 mM NaCl). The MFC was operated in a batch mode. After each batch was finished, the catholyte was replaced completely, 75% of the anolyte was replaced, and the microbes at the anode chamber bottom were reserved. At the initial operating stage, the current generated by the MFC was low. As the operation continued, the current gradually increased. After the fifth instance of anolyte replacement, the anode potential rapidly decreased to −0.440 ± 0.05 V (vs. Ag/AgCl), thereby demonstrating the maturity of the anode biofilm. When the MFC voltage output was stable, the next series of experiments were proceeded.

The experiments were divided into two parts. First, the sodium bromate concentrations were prepared as 10, 20, 30, 50 and 100 mM, which were designated as M1, M2, M3, M4 and M5, respectively, to study the effect of sodium bromate concentrations on the MFC performance. Second, the catholyte pH (100 mM $NaBrO_3$ in 100 mM NaCl) was adjusted to 7.0, 3.0, 5.0 and 10.0 (labelled as M6, M7, M8 and M9, respectively) to investigate the effects of the initial catholyte pH on the MFC performance. The temperature was maintained at 35 °C for all the tests.

2.3. Measurement

Voltage output (E) and OCP were measured by a multimeter (UNI-T 803; Uni-Trend Electronics Co., Ltd., Shanghai, China). The E values were recorded every 30 min. Current density (I_V) and power density (P) were obtained according to $I_V = E/RV_{Cat}$ and $P = EI/V_{Cat}$, where E is the voltage output, R is the external resistance, I is the current, and V_{Cat} is the working volume of cathode chamber. The influent and effluent NaAc concentrations were determined with a gas chromatograph (model 6890NT, Agilent Inc., USA) equipped with a flame ionisation detector. The concentrations of BrO_3^- and Br^- were measured with an ion chromatograph (IC, ICS-2000, Dionex, USA) equipped with an IonPac AS-19 anion column and an IonPac AG guard column (Mao et al., 2015). Coulombic efficiency (CE) was calculated according to $CE\ (\%) = \frac{M\int_0^{t_0} Idt}{FbV_{An}\Delta c} \times 100$ (Logan et al., 2006), where M is the molecular weight of the substrate (136 g mol^{-1} by $NaAc{\cdot}3H_2O$), t_0 is the time interval of one cycle, F is the Faraday's constant, $b = 8$ is the number of electrons exchanged per mole of NaAc, V_{An} is the volume of liquid in the anode compartment, Δc is the substrate concentration change over the batch cycle (g L^{-1}). The polarisation curves were obtained by changing the external circuit resistances from 10,000 Ω to 20 Ω. Electrochemical impedance spectroscopy (EIS) was used to characterise the electrochemical capability and was performed in an electrochemical workstation with a three-electrode system (Princeton Applied Research, USA). The anode was connected to the working terminal to measure anode impedance. The cathode and Ag/AgCl electrode were connected to the counter terminal and the reference terminal, respectively. When the cathode impedance was measured, the working terminal and counter terminal of the electrochemical workstation were connected to the cathode and anode, respectively (Hosseini and Ahadzadeh, 2012). The EIS tests were conducted under the condition of open circuit voltage with a potential amplitude of 10 mV over the frequency range of 100 kHz to 10 mHz. Tafel analysis was performed using the methods reported by Jadhav et al. (2014) to determine the electrode kinetics.

3. Results and discussion

3.1. Effect of sodium bromate concentration

The effect of sodium bromate concentrations on the performance of the MFC was studied. The corresponding polarisation and power density curves of the MFC are shown in Fig. 1; these curves were used to estimate the maximum power and internal resistance.

The OCP and short circuit current (SCC) of the MFC increased with increasing sodium bromate concentration (Fig. 1A). M1 and M2 showed OCP values of approximately 0.532 and 0.604 V, respectively (the latter was 13.5% higher than the former). M3, M4 and M5 exhibited improved OCP values of 0.621, 0.633 and 0.649 V, respectively. The OCP was significantly influenced at low sodium bromate concentrations (<20 mM) but was not significantly affected at high concentrations (⩾20 mM). Conversely, the SCC was greatly influenced by the sodium bromate concentration. The SCC values of M1, M2, M3, M4 and M5 were 2.049, 3.13, 4.0625, 5.1626 and 6.5375 A m^{-3}, respectively, in the cathode chamber working volume. According to Ohm's law, the total R_{int} of MFC was estimated by the slope of the linear region in the plot of voltage vs. current density (Pinto et al., 2011). Fig. 1A shows that the total R_{int} of the MFC decreased with increasing sodium bromate concentration. Therefore, the increased electron acceptor concentration could increase the OCP and reduce the internal resistance by improving ionic conductivity (Li et al., 2008).