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Microfiltration membrane performance in two-chamber microbial fuel cells

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ABSTRACT

Proton exchange membranes (PEMs) are typically used in two-chamber microbial fuel cells (MFCs) to separate the anode and cathode chambers while allowing protons to pass between the chambers. However, PEMs such as Nafion are not cost-effective. To reduce the cost of MFCs, we examined the performances of cellulose acetate microfiltration membranes in a two-chamber microbial fuel cell using acetate. The internal resistance, the maximum power density and the coulombic efficiency (CE) of the microfiltration membrane MFC (MMMFC) were 263 Ω , 0.831 \pm 0.016 W/m² and 38.5 \pm 3.5%, respectively, in a fed-batch mode, while the corresponding values of the MFC using a PEM were 267 Ω , 0.872 \pm 0.021 W/m² and 74.7 ± 4.6 %, respectively. We further used the MMMFC for poultry wastewater treatment. The maximum power density of 0.746 ± 0.024 W/m² and CE of 35.3 \pm 3.2% were achieved when the poultry wastewater containing 566 mg/L COD was used, removing $81.6 \pm 6.6\%$ of the COD. These results demonstrate microfiltration membranes, compared with PEMs, have a similar internal resistance and reduce pH gradient across the membrane. They parallel PEMs in maximum power density, while CE is much lower due to the oxygen and substrate diffusion. The MMMFC was effective for poultry wastewater treatment with high COD removal.

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1. Introduction

Microbial fuel cells (MFCs) use bacteria to produce electricity from the degradation of organic matter [\[1–3\]. E](#page--1-0)lectrons released by bacteria are transferred from the anode to the cathode through an external circuit and typically combine with oxygen and protons to form water. Two-chamber MFCs consist of an anode and a cathode chamber separated by a membrane, which can prevent the bacteria transfer from the anode to the cathode chamber and reduce the oxygen diffusion to the anode. Most of the reported two-chamber MFCs used PEMs (typically Nafion); a few used anion exchange membranes [\[4–9\]. H](#page--1-0)owever, these membranes are expensive and approximately account for 38% of the capital costs in MFCs [\[10\].](#page--1-0) Therefore, new materials should be explored to make a step forward towards practical implementation of MFCs. Ultrafiltration membranes, J-cloth and Zirfon membranes have been studied in MFCs, and these separators could reduce oxygen diffusion and significantly improve coulombic efficiency [\[7,11,12\]. I](#page--1-0)n this study, we used microfiltration membrane because it has not been previously examined, although it can effectively separate the bacteria from the cathode and reduce the oxygen diffusion to the anode while permitting ion transport. In addition, it can remarkably reduce the capital costs of MFC construction. So, we compared the performance of microfiltration membrane with Nafion membrane when acetate was used in a two-chamber MFC.

Furthermore, since most MFCs used pure compounds such as glucose, acetate, sucrose and an amino acid and it has not been studied previously whether MFCs could be used for chicken farm wastewater treatment, we therefore investigated the effectiveness of the two-chamber MFC with a microfiltration membrane for chicken farm wastewater treatment [\[13–16\]. T](#page--1-0)he performance of the MFC was evaluated in terms of internal resistance, maximum power density, coulombic efficiency and COD removal rate at a constant temperature of 20 ◦C.

2. Materials and methods

2.1. Poultry wastewater and acetate solution

Wastewater was collected from Beijing Deqingyuan Agricultural Technology farm (Beijing, China), and stored at 4° C for 1 week before being used. The wastewater has a COD of 500–600 mg/L and a pH of 6.5. In the tests, 0.1 g KCl, 0.2 g NH₄Cl, 0.6 g NaH₂PO₄, 2.9 g NaCl, $2.5 g$ NaHCO₃, 5 mL vitamin and 10 mL trace mineral solution [\[17\]](#page--1-0) were added per liter wastewater, deionized water and 9 mM acetate solution to obtain the amended wastewater, cathodic electrolyte and acetate medium (COD was 560 mg/L) respectively.

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2.2. MFC construction

MFCs were constructed by joining two Plexiglas cylindrical chambers 18 cm high by 3.8 cm in diameter (empty volume of 200 mL) with a glass tube containing a proton exchange membrane (PEM) (Nafion 117, thickness 0.19 mm, Dupont Co., DE), or a microfiltration membrane (pore diameter 0.45 μ m, film thickness 0.13 mm, Q/IEFJ01, Shanghai Xingya Co., Shanghai), clamped between the flattened ends of the glass tubes (inner diameter 2.0 cm). The PEM was sequentially boiled in H_2O_2 (30%), deionized water, $0.5 M H₂SO₄$, and deionized water (each time for 1 h). Microfiltration membrane was stored in deionized water and gently rinsed prior to use. The anode and the cathode (total electrode spacing of 10 cm) were graphite rod (8 cm high and 2.5 cm in diameter). The cathode was coated with 0.25 mg/cm² Pt. Titanium wire was used for the connection of the external circuit to the electrodes.

2.3. MFC tests

Five MFCs (MFC0-MFC4) were operated in fed-batch mode with the external resistance of 250 Ω (except as indicated) at a fixed temperature of 20° C. The MFCs were inoculated with a mixed bacterial culture from the anode of a two-chamber MFC, which was originally inoculated with domestic wastewater (Gaobeidian Wastewater Treatment Plant, Beijing) and has been operated for more than 2 years. One hundred and fifty milliliter acetate medium was pumped into the anode of MFC1 with PEM, MFC2 with a microfiltration membrane and MFC0 without a membrane; MFC3 and MFC4 with a microfiltration membrane were filled with 150 mL amended wastewater while MFC4 was operated in open circuit mode. All the cathode chambers were filled with cathodic electrolyte. For each batch cycle, the anode chambers were sparged using ultra high purity nitrogen for 20 min before the operation. During operation, the anode chambers were maintained under aseptic anaerobic condition, while the cathode chambers were sparged with air at 120 mL/min to provide oxidant. The system was considered to be stable when the maximum voltage output was reproducible after refilling the reactor with medium more than two times. The medium in the reactors was refilled when the output voltage dropped below 20 mV.

2.4. Calculations and analysis

Microbial growth on the anodic surface of MFCs was investigated by scanning electron microscopy (JSM 6700F, JEOL Ltd.).

Voltage was measured using a data acquisition system (AD8201H, Ribohua Co.,China) every 30 s and converted to power density, $P(W/m^2)$, according to $P = IV/A$, where $I(A)$ is the current, $V(V)$ is the voltage and $A(m^2)$ is the cross-sectional area of the membrane. Polarization curve was obtained by varying the circuit resistance.

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

$$
V = E_{\text{cell}} - IR_{\text{int}} \tag{1}
$$

Coulombic efficiency was calculated as $E_C = C_p/C_{Tj} \times 100\%$. $C_p(C)$ is the total Coulombs calculated by integrating the current over time, calculated as:

$$
C_{\rm p} = \int \frac{V}{R} \mathrm{d}t \tag{2}
$$

where R is the external resistance. C_{Tj} (C) is the theoretical amount of Coulombs that can be produced from either wastewater $(j = w)$ or acetate $(j = a)$, calculated as:

$$
C_{Tj} = Fb_j c_j \nu \tag{3}
$$

Fig. 1. Scanning electron microscopy image of bacteria on the anodic surface of **MFCs**

where F is Faraday's constant (96,500 C/mol of electrons), b_i is the number of mole of electrons produced per mole of substrate $(b_w = 4,$ $b_a = 8$), c_i (mol/L) is the substrate concentration, and ν (L) is the liquid volume (150 mL).

COD was measured according to potassium dichromate method [\[18\]. A](#page--1-0)cetate concentrations were analyzed using a gas chromatograph (Agilent, 6890) equipped with a flame ionization detector and a 30 m \times 0.32 mm \times 0.5 μ m DB-FFAP fused silica capillary column followed the same procedure described by Liu and Logan [\[19\].](#page--1-0)

pH of the anode and cathode chambers were measured by pH meter (PHS-25 pH meter, Shanghai Precision & Scientific Instrument Co., Ltd.) when the system was stable.

Dissolved oxygen analyzer (Model JPSJ-605 D.O. Analyzer, Shanghai Precision & Scientific Instrument Co,. Ltd) was placed in the anode chamber. The mass transfer coefficient of oxygen in the membrane, k_0 , was determined by monitoring the DO concentration over time and using the equation by Kim and co-workers [\[7\]:](#page--1-0)

$$
k_0 = -\frac{V}{At} \ln \left[\frac{c_0 - c_1}{c_0} \right] \tag{4}
$$

where V is the liquid volume in the anode chamber, A is the membrane cross-sectional area, c_0 is the saturated oxygen concentration in the cathode chamber and c_1 is the DO in the anode chamber at time t. The diffusion coefficient D_0 was calculated as $D_0 = K_0 L$, where L is the membrane thickness.

3. Results

3.1. Microbial enrichment

Fig. 1 shows a biofilm was formed on the electrode surface by bacteria in the anode chamber when MFCs were stable. The image clearly demonstrated that bacteria could easily attach to the graphite surface and form a multilayer biofilm, which was considered to play a significant role in electron transfer from bacteria to electrode [\[3,9\].](#page--1-0)

3.2. pH

The pH in the anode and cathode chambers and DO in the anode chambers were measured when the system was stable. The values

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