



# Electricity generation and bivalent copper reduction as a function of operation time and cathode electrode material in microbial fuel cells



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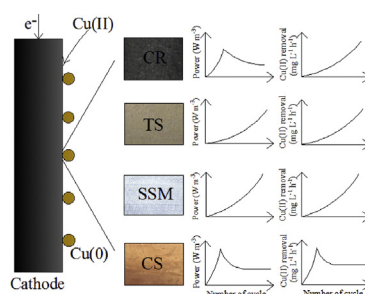
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## HIGHLIGHTS

- TS and SSM cathodes showed increased power production and Cu(II) removal over time.
- CR exhibited decreased power production and increased Cu(II) removal over time.
- TS and SSM cathodes exhibited a reduction of ohmic resistance over time.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 9 December 2015

Received in revised form

5 January 2016

Accepted 6 January 2016

Available online 1 February 2016

### Keywords:

Microbial fuel cell  
Cu(II) reduction  
Electricity generation  
Cathode electrode  
Deposited copper

## ABSTRACT

The performance of carbon rod (CR), titanium sheet (TS), stainless steel woven mesh (SSM) and copper sheet (CS) cathode materials are investigated in microbial fuel cells (MFCs) for simultaneous electricity generation and Cu(II) reduction, in multiple batch cycle operations. After 12 cycles, the MFC with CR exhibits 55% reduction in the maximum power density and 76% increase in Cu(II) removal. In contrast, the TS and SSM cathodes at cycle 12 show maximum power densities of 1.7 (TS) and 3.4 (SSM) times, and Cu(II) removal of 1.2 (TS) and 1.3 (SSM) times higher than those observed during the first cycle. Diffusional resistance in the TS and SSM cathodes is found to appreciably decrease over time due to the copper deposition. In contrast to CR, TS and SSM, the cathode made with CS is heavily corroded in the first cycle, exhibiting significant reduction in both the maximum power density and Cu(II) removal at cycle 2, after which the performance stabilizes. These results demonstrate that the initial deposition of copper on the cathodes of MFCs is crucial for efficient and continuous Cu(II) reduction and electricity generation over prolonged time. This effect is closely associated with the nature of the cathode material. Among the materials examined, the SSM is the most effective and inexpensive cathode for practical use in MFCs.

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## 1. Introduction

Bioelectrochemical systems (BESs) including microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are regarded as new, sustainable and effective technologies for the recovery of metals from wastes and wastewaters [1]. Among the variety of heavy

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metals that can be recovered by BESs from wastes and wastewaters, the recovery of Cu(II) has attracted significant attention due to its wide presence in acid mine drainage wastewaters [2,3]. The reduction of Cu(II) can be achieved on the abiotic cathodes of two-chamber MFCs, since this metal has a relatively high redox potential (+0.286 V vs. standard hydrogen electrode, SHE) relative to the redox potential of the organic matter (ca.  $-0.30$  V for acetate under standard conditions vs. SHE) in the anolyte [4]. MFCs with various operating volumes and experimental conditions, as well as different architectures, have been explored for more efficient Cu(II) reduction and higher electricity generation with varying degrees of success, as shown in Table 1 [3–13]. However, these studies do not investigate the performance of the cell in multiple batch cycles, and the long-term stability of MFCs for Cu(II) reduction, even though the longevity of the MFCs is crucial for its commercial application.

Non-corrosive, carbon-based materials such as carbon cloth, carbon rod, graphite felt, graphite foil, graphite rod, graphite plate, as well as, metals of titanium wire and copper plate have been used as cathodes in MFCs for Cu(II) reduction [3–13]. In view of a practical environmental application, the prolonged operation of MFCs results in increasing amount of copper deposited on the surface of the cathodes, and as a result, the interaction of the cathode material with the deposited copper becomes crucial for determining the long-term performance of the cell. Copper is an excellent conductor that interacts with various materials. It promotes enhanced electrocatalytic activity towards oxygen and hydrogen peroxide reduction reactions in conventional electrochemical processes, due to the enlarged surface roughness and to the presence of new active sites [14–16]. Films of CuO on stainless steel mesh also exhibit efficient catalytic activities for propene oxidation [17] while copper phthalocyanine performs as platinum catalysis for oxygen reduction reaction in MFCs [18]. With regards to the capacitance of the electrodes, nanocrystals of copper can function with mesoporous activated carbons similarly as noble metals such as Pt and Pd, giving rise to substantial enhancement of the capacitance of carbonaceous electrodes [15]. Based on the intrinsic excellent characteristics of copper, Motos et al. [10] successfully decreased the internal resistance of MFCs, by coupling a copper plate cathode with an anion exchange membrane and a carbon felt anode. Using a short distance between the electrodes, the copper reduction rate was  $75 \text{ mg L}^{-1} \text{ h}^{-1}$  and the maximum power production was  $5.5 \text{ W m}^{-3}$  at a high initial Cu(II) concentration of  $2000 \text{ mg L}^{-1}$  [10] (Table 1). The metal reduction rates and power production would be reasonably expected to increase in proportion to the concentration of Cu(II) in the water. However, the performance of the electrode materials commonly used in MFCs, including carbon rod (CR), titanium sheet (TS) and stainless steel woven mesh (SSM), is significantly influenced by the deposited copper, which with its excellent physico-chemical characteristics may alter the electrochemical behaviour of the cathode and, as a result, the overall performance of MFCs. This effect has not been systematically investigated in literature.

In this study, specimens of CR, TS and SSM are investigated as cathode materials in MFCs for simultaneous electricity generation and Cu(II) reduction, in multiple batch cycle operations. Furthermore, copper sheet (CS) is additionally used as one further cathode material to assess the MFC system performance. The effect of the deposited copper on system performance is elucidated by linear sweep voltammetry (LSV), scanning electronic microscopy (SEM), energy dispersive X-ray spectrometry (EDS), X-ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS). The maximum power density and Cu(II) reduction in the MFCs were compared with those obtained with different batch cycle operations under otherwise identical conditions. The circuit current, the anodic coulombic efficiency (CE) and the cathodic CE were

employed to assess system performance.

## 2. Materials and methods

### 2.1. Reactor setup

Two-chamber MFCs (duplicates) were used in all experiments, with the chambers separated by a cation exchange membrane (CMI-7000 Membranes International, Glen Rock, NJ). The anodes were made with porous graphite felt ( $1.5 \times 1.5 \times 1.0$  cm, Sanye Co., Beijing, China). The working volumes of the anode and cathode compartments were 20 mL each. The cathodes were made with CR (Chijiu Duratight Carbon Co., China), TS, SSM and CS (Qingyuan Co., China) and were all exposing the same surface area of  $8 \text{ cm}^2$ . The compositions of cathode electrodes is listed in Table S1. The cathode materials were first mechanically polished with abrasive papers and then cleaned with ethanol and deionized water before their installation in the MFCs [19,20].

### 2.2. Inoculation and operation

The anodes were inoculated from the anodes of previous operating MFCs running on acetate for faster anodic biofilm acclimation [3,11,19,20]. The composite of anolyte was as previously described [21]. The anolyte was sparged with ultrapure  $\text{N}_2$  gas for 15 min, prior to transfer into the reactors. For anode acclimation, deionized water was used as catholyte and CR as cathode electrodes, with an external resistor of  $510 \Omega$ . After six-cycle anolyte refreshments with each lasting 2–3 days, the catholyte was replaced by aqueous  $\text{CuCl}_2$  at a Cu(II) concentration of  $50 \text{ mg L}^{-1}$ . Prior to adding the Cu(II)-catholyte into the cathode chambers, the catholyte was thoroughly sparged with ultrapure  $\text{N}_2$  gas for 15 min in order to exclude the effect of dissolved oxygen on Cu(II) reduction [4]. The acclimation period was completed after another 2–3 refreshments with stable and repeatable voltage output. New electrodes of CR, TS, SSM and CS were then alternatively installed in the cathode chambers for multiple batch cycle operations with each cycle (defined as each refreshment in catholyte) lasting 6 h. Unless otherwise stated, the same cathodes were always used for multiple batch cycle operations. All reactors were operated in fed-batch mode and all experiments were run in duplicate and at room temperature ( $20 \pm 3^\circ \text{C}$ ). The inoculation and solution replacements were performed in an anaerobic glove box (YQX-II, Xinmiao, Shanghai).

### 2.3. Measurements and analyses

Total chemical oxygen demand (COD) was measured using standard methods. Cu(II) species were analyzed by an atomic absorption spectrophotometer (AAnalyst 700, PerkinElmer). A SEM (QUANTA450, FEI company, USA) equipped with an EDS (X-MAX  $20 \text{ mm}^2$ – $50 \text{ mm}^2$ , Oxford Instruments, UK), and XRD (XRD-6000, Shimadzu LabX, Japan) measurements were used to examine the morphologies of the electrodes after Cu(II) reduction, as well as the crystal products. The sample preparation was strictly performed at  $\text{N}_2$  atmosphere [22]. The cathode and anode potentials were monitored by a data logger using an automatic data acquisition system (PISO-813, Hongge Co., Taiwan). Power density was normalized to the cathode chamber working volume ( $\text{W m}^{-3}$ ). LSV was conducted using a potentiostat (CHI 760C, Chenhua, Shanghai), with two electrode system of a working electrode (cathode electrode) and a counter electrode (anode electrode). The LSV was performed from open circuit potential (OCP) to  $0.0 \text{ V}$  at a scan rate of  $0.1 \text{ mV s}^{-1}$ . Cathodic LSV and EIS were performed using the same potentiostat with three electrode system consisted of a working electrode (cathode electrode) in the cathode, an Ag/AgCl reference

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