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Sequencing polarity-inverting microbial fuel cell for wastewater treatment

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ABSTRACT

A novel sequential polarity-inverting microbial fuel cell (MFC) is developed to neutralize anodic acidification and cathodic alkalinization and treat wastewater. The same electrode sequentially experiences anaerobic anode, aerobic cathode and anoxic cathode phases like a SBR (Sequencing Batch Reactor Activated Sludge process), and such two SBR half cells with opposite electrode polarities consist of a complete MFC. The system successfully buffers electrolyte and generates electricity with a maximum power density of $623 \pm 4\,mW/m^3$. Chemical oxygen demand is completely removed. Three bacteria, *Arthrobacter* sp., *Stenotrophomonas* sp. and *Sphingobacterium* sp., are found on the polarity-inverting electrode, and *Arthrobacter* sp. is believed to be capable of transferring electrons both to and from electrode. The proof-of-principle of a polarity-inverting MFC described here may offer an opportunity of integrating MFCs into the practical wastewater treating process.

1. Introduction

Microbial fuel cells (MFCs) can convert organic matters in wastewaters into electrical energy using electrochemical active bacteria (EAB) as biocatalyst [1]. However, few practical applications with this technology have been implemented up to date. Limitations to the performance of MFCs mainly lie in high overpotentials with anode acidification and cathode alkalinization, as well as the lack of cost-effective catalyst for oxygen reduction [2,3].

Cheng et al. demonstrated that an electroactive biofilm could alternatively catalyze anodic and cathodic reactions (polarity inversion) in a half cell, which partly addressed pH drifting and poor electrode reaction kinetics [4–6]. Hartline and Call investigated the effects of substrate and electrode potential on electrotrophic activity of inverted bioanodes, but it is unclear howor if communities shift once these communities are inverted into biocathodes [7]. Some EAB are optional and remain active in aerobic environment, such as *Shewanella* [8]. Oxygen exposure during medium replenishment in anode is believed to be helpful for electrogenesis, because of the inhibition to methanogenesis [9]. Effects of anode aeration on power generation and microbial community were investigated and a measurable voltage output was observed within a wide range of oxygen concentration (0.1–4 mg/L) [10]. Overall, electricity-producing communities have high tolerance for oxygen, and even can catalyze both anodic and cathodic reactions, which is helpful to buffer electrolyte and regulate pH.

MFCs may not be sufficient as a stand-alone wastewater treatment technology to achieve high effluent quality. The idea of combining MFCs with other treatment technologies has recently been proposed [11]. Sequencing batch reactors (SBRs) have become a primary treatment process used for industrial and domestic wastewater in medium and small towns, due to its advantages that include reduced land use, low cost, operational flexibility and ease of control [12]. Normally, a full scale SBR plant has at least two tanks and each tank employs a time-oriented operational mode instead of space-oriented mode in continuous activated sludge processes. Specifically, in one SBR cycle the bacteria may experience anaerobic, aerobic and anoxic phases, which are exactly identical to anode, oxygen-cathode and denitrification-biocathode conditions. Considering that anodic biofilm can catalyze both anodic and cathodic reactions, we proposed a novel two-chamber polarity-inverting MFC running like two parallel SBRs, where anaerobic phase (anode) of one chamber corresponds to aerobic and anoxic phases (cathode) of the other chamber and vice versa. Electricity generation would be triggered by the differences of redox potentials between the two chambers. A previous SBR-MFC systems have

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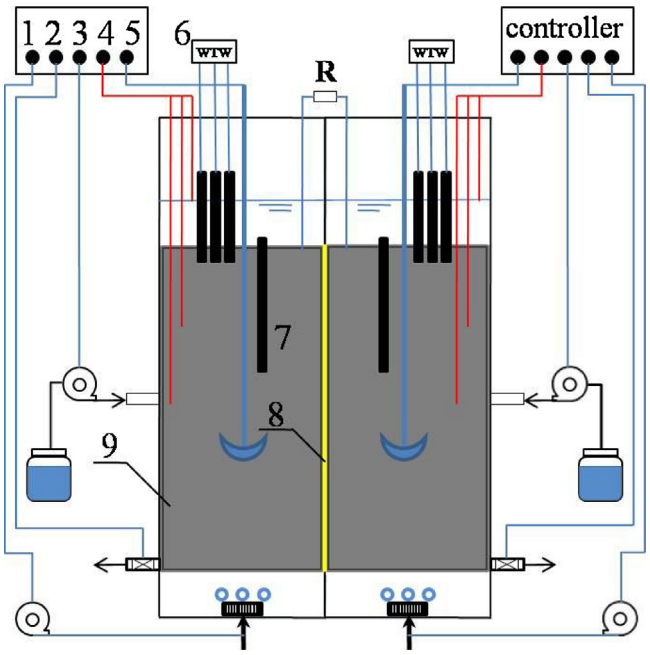

Fig. 1. Schematic of the sequencing polarity-inverting MFC. (1) air pump controller; (2) magnetic valve controller; (3) feeding pump controller; (4) liquid level controller; (5) mechanic stir controller; (6) portable multiline meter; (7) reference electrode; (8) Nafion membrane; (9) carbon felt.

been proposed by mechanically submerging a biocathode MFC into a SBR [13,14] or feeding the outlet of SBR into subsequent MFC [15], which was completely different from the concept here.

A novel bioreactor combining MFC and SBR was designed for treating wastewater and recovering energy. The two SBR chambers as half cells alternatively acted as anode and cathode. The same biofilms sequentially catalyzed anodic and cathodic reactions to lower overpotential and avoid pH splitting. In practice, this design can be applied to upgrade the existing SBRs plants. The system was preliminarily investigated in terms of pollutants removal, electrochemical performance, catalytic behaviors and community structures.

2. Materials and methods

2.1. Construction of the MFC reactor

The MFC reactor was symmetrically constructed, as detailed in Fig. 1. The size of each chamber was 8[L] × 8[W] × 30[H], 1920 cm^3. The liquid level was 25 cm high and the net solution volume was about 1200 cm^3. The two chambers were separated by Nafion membrane (Nafion 117, Dupont) after pretreatment [16]. Two 0.5 cm thick carbon felts (Dalian Xingke Carbon Fiber Co., Ltd., Dalian, China) were rolled up in the chambers as anode/cathode electrodes (20 cm × 25 cm) without any pretreatment. The electrodes were connected with an external resistor *via* titanium wire (Suntec titanium Ltd., Dalian, China). In each chamber, a gas diffuser was placed at the bottom, three wires with different length were fixed on the walls for controlling the solution level, and three holes were set on the top for pH, redox potential (Eh) and dissolved oxygen (DO) probes.

2.2. Acclimation and operation

The electrochemically active biofilms to sequentially catalyze anode and cathode reactions were enriched in a three-chamber MFC. Two anodes shared one cathode in the middle for similar running conditions, and further for similar enriched anodic biofilms. The anodic inoculum was taken from the existing MFC, which was initially inoculated with the sludge from a plant with CAST process. After the acclimation for ~30 days, the system reached a steady state (Fig. S1), then, the middle cathode chamber was removed and the two anode chambers were reassembled to be a polarity-inverting MFC.

Table 1
Time setting and the corresponding electrode polarity in a typical cycle.

SBR1			SBR2		
anode	12 h	anaerobic phase	aerobic phase anoxic phase settling discharging feeding	8 h 3.8 h 10 min 1 min 1 min	cathode
cathode	8 h 3.8 h 10 min 1 min 1 min	aerobic phase anoxic phase settling discharging feeding	anaerobic phase	12 h	anode

The feeding medium contained (per L of tap water): 0.235 g $C_6H_{12}O_6$, 0.19 g NH_4Cl, 0.09 g KH_2PO_4, 0.5 g NaCl, 0.1 g $MgSO_4{\cdot}7H_2O$, 0.015 g $CaCl_2$, and 1 mL trace nutrient solution [17]. The feeding medium had a final pH of around 7.0 and a conductivity of 1.15–1.20 mS/cm. The pH was not controlled throughout the experiments.

During each cycle, 0.6 L of feeding medium was added, *i.e.*, 50% volumetric exchange ratio. One typical operation cycle was approximately 24 h and consisted of six phases as described in Table 1. After influent filling, an anaerobic phase (12 h) began, corresponding to anode. In next phase, aeration was supplied for 8 h, defined as aerobic cathode using oxygen as electron acceptor. The periods without air flushing, including stirring phase for 3.8 h, settling for 10 min discharging for 1 min and filling for 1 min, acted as anoxic cathode phase because of insufficient oxygen. Each phase was automatically controlled by timers.

2.3. Electrochemical and chemical measurements

The voltages generated in the experiment were collected using a data acquisition system (PISO–813, ICP–DAS) [18]. Power density (P, mW/m^3) was normalized by the working volume according to $P = E_{cell}^2/(R_{ex}V_r)$, where E_{cell} (V), R_{ex} (Ω) and V_r (m^3) were the cell voltage, external resistance and working volume, respectively. Coulombic efficiencie (CE) was calculated according to the previous method [19]. A stepwise change of R_{ex} was performed to obtain polarization and power curves using a three-electrode system. At the beginning, opening circuit for 60 min was performed for the open circuit voltage (OCV), and then voltages over R_{ex} at 30 min interval per resistor were recorded. Cyclic voltammograms (CVs, 5 mV/s) were carried out using a CHI760E electrochemical workstation (CH Instruments, Chenhua Instrument Co., China). At least 2 cycles were performed and the last cycle was shown. $Hg/HgCl_2$ reference electrode (+0.242 V vs. SHE) was employed in all electrochemical tests.

The concentrations of COD and nitrogen compounds were measured according to standard methods [20]. Samples were filtered through a 0.45 μm membrane before analysis. The standard parameters pH, conductivity, Eh and DO were determined potentiometrically with a digital, portable multiline meter (Multi 3430, SET F, WTW, Germany).