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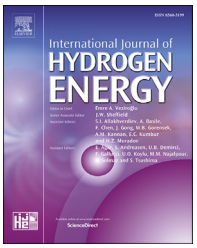

Voltage reversal causes bioanode corrosion in microbial fuel cell stacks

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ABSTRACT

A better understanding of voltage reversal phenomenon and its long-term effects on power generation are crucial to efficiently improve the voltage of microbial fuel cell (MFC) stacks. In this study, six MFCs with imbalanced performances were connected in series. After over 100 h of operation under voltage reversal conditions, increased turbidity and color were observed in the anolyte of the reversed MFC. In addition, the cyclic voltammogram of the anode changed form a typical catalytic current to a capacitance current. The scanning electron microscopy (SEM) showed that biofilm was dissociated from the anode surface, indicating that long-term operation under voltage reversal could damage the biofilm and ultimately resulted in the failure of MFC stacks. X-ray diffraction (XRD) and SEM equipped with energy dispersive X-ray spectrometry (EDX) analyses showed that the black particles in the anolyte was mostly carbon exfoliated from the anode, suggesting that carbon corrosion caused the biofilm failure.

Introduction

Microbial fuel cell (MFC) is a promising energy-harvesting system that generates electricity from organic matters in wastewater, allowing for the integration of renewable energy production and wastewater treatment [1–3]. A typical MFC consists of two electrode chambers separated by a proton exchange membrane, each harboring an anode and a cathode. At the anode, exoelectrogenic bacteria attached on the surface are capable of degrading organic matters, and simultaneously transferring electrons to the electrode via direct or indirect pathways [4–6]. At the cathode, the electrons came from the anode and the protons permeated from the anode chamber are combined with oxygen, thereby generating electricity. In addition to wastewater treatment, MFCs have wide potential applications on biosensors, bioelectronics, and bioremediation [7–9].

Currently, the implementation of MFCs is largely limited due to the low working voltage. The theoretical maximum voltage that a MFC can create is around 1.1 V with oxygen as

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electron acceptor and acetate as organic matter [4]. In practice, the working voltage of a MFC at the maximum power density ranges from 0.2 to 0.5 V owing to energy losses (i.e. ohmic loss, activation loss, and mass transfer loss) [10,11]. Such low working voltage has been an obstacle for the application of MFCs, as the voltage required as power sources for electronic devices are usually higher than 1.5 V [12]. Therefore, effective approaches to boost the voltage of MFCs are urgently required.

Various approaches have been reported to enhance the voltage of MFCs, including using power management systems equipped with capacitors and inductors [13–15]. Gong et al. used a power management system to increase the voltage of benthic fuel cell to 7 V, which was used as power source of an acoustic modem and a seawater oxygen/temperature sensor system [13]. Donovan et al. used a power management system that enabled a sediment microbial fuel cell to power a remote sensor [15]. However, the system efficiencies were reportedly low in those systems, indicating substantial energy losses. Moreover, the relative complex electronic systems and intermittent operation were also bottlenecks of this approach.

Fuel cell "stack", in which multiple cell units are connected in series, is another approach to boost the voltage and has been widely used in proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) [16,17]. It has been reported that a series connection can boost the voltage of MFCs to the level directly usable as power sources of electronic devices [18–20]. However, the performance of MFC stacks is often severely hindered by the "voltage reversal", in which the voltage of one MFC in the stack reversed from a positive to a negative value, whereas the voltages of other MFCs maintained at positive values [10,12]. Voltage reversal often occurs in serially stacked MFCs, especially when the MFC stack operated at a high current density [21,22], and can cause a significant reduction of output voltage of the MFC stack, as well as the lifetime of the reversed MFC unit [23].

The imbalanced performance of MFC units in the stack can be magnified by the heterogeneity of reactions on the bioanode of MFC, and is therefore considered as a main reason of voltage reversal [10,24,25]. It has been reported that the heterogeneity of the MFC-units performances could be caused by different anodic reaction rates, and the slow reaction rate on the anode of the MFC with lower performance was responsible for the voltage reversal [12]. Moreover, substrate depletion in the anode chamber could cause a loss of bacterial activity, resulting in voltage reversal [22]. To avoid the voltage reversal, several approaches have been reported, e.g. manipulating critical current density and applying an assistance current with an assistance electrode [10,26].

It has been reported that, upon the voltage reversal, the reversed MFC unit changes from a galvanic cell to an electrolysis cell (i.e. microbial electrolysis cell) [10]. Because a part of energy is used for electrolysis, the energy output of the MFC stack largely reduced. At the anode of the reversed MFC, oxygen production is usually considered as the main reaction [27]. In addition, the positive potential range is also suitable for carbon oxidation, which is a common phenomenon in serially stacked DMFCs and PEMFCs [28,29]. Carbon oxidation (Eq. (1)) was also reported on the anode of a three-electrode bio-electrosynthesis system, which simultaneously produce H_2 and organic compounds on the cathode [30]. However, carbon oxidation has never been reported during the voltage reversal of stacked MFC in series.

$$C + 2H_2O \leftrightarrow CO_2 + 4H^+ + 4e^-;\ E = 0.118\ V\ vs.\ SHE \quad (1)$$

The scope of this study is to investigate the bio-electrochemical reactions occurred in the reversed MFC unit upon voltage reversal, as well as its long-term effects on the power generation of MFC stack. We firstly started up six MFC units with different external ohmic resistances to construct MFCs with imbalanced performances. Then the six MFC units were stacked in series and operated at a high current density to cause voltage reversal. The bio-electrochemical properties and surface morphology of the anode of the reversed MFC were analyzed before and after voltage reversal. Moreover, black particles accumulated in the anolyte were analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. This study provides useful information on the long-term effects of voltage reversal on MFC stacks performance, which will be beneficial to efficiently increase voltage production.

Methods and materials

Experimental setups

Six MFCs with the same configuration as described in previous study were used in this study [31]. Each MFC consists of an anode and a cathode, which are separated by a cation exchange membrane (Ande Membrane INC., China), and two plexiglass plates with a serpentine channel as the frame (Supplemental material, Fig. S1). The effective volume of the serpentine channel in each plexiglass plate is 2.7 mL. Both anode and cathode chambers were equipped with Ag/AgCl reference electrodes. All the electrodes were made of carbon cloth (HCP330, Hesen Co. Ltd., China) with an effective surface area of 25 cm^2. To reduce the ohmic resistance of electrodes, carbon clothes were connected to titanium sheet.

Inoculation and operation

The effluent of anode chamber in a MFC (working volume of anode chamber: 1.4 L) that has been producing electricity for more than two years in our lab was used as the inoculum. During the start-up process, the inoculum containing suspended exoelectrogenic bacteria and residual anaerobic culture medium (0.68 g CH_3COONa, 6.0 g Na_2HPO_4, 3 g KH_2PO_4, 0.1 g NH_4Cl, 0.5 g NaCl, 0.1 g $MgSO_4 \cdot 7H_2O$, 15 mg $CaCl_2 \cdot 2H_2O$, and 1.0 mL trace elemental solution per liter) continuously flowed through the anode channels of six MFCs in a flow rate of 0.5 mL min^{-1} [32]. 50 mM $K_3[Fe(CN)_6]$ was used as electron acceptor in the cathode chamber. After the MFCs were successfully started up (i.e., when the current density of all the MFCs become relatively stable), the influent were changed to pre-sterilized anaerobic culture medium as mentioned above. The medium was pre-sterilized at 121 °C for 20 min to avoid possible contamination by other unknown bacteria and purged with high concentration N_2 (99.99%) to maintain an

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