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Anodic current distribution in a liter-scale microbial fuel cell with electrode arrays

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HIGHLIGHTS

- A liter-scale microbial fuel cell with electrode arrays (MFC-EA) was developed.
- A significantly uneven anodic current distribution was found in MFC-EA.
- The electrode spacing influences the ohmic resistance and the biomass distribution.
- The uneven current distribution can be improved by increasing the anolyte conductivity.

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ABSTRACT

A liter-scale microbial fuel cell with graphite rod electrode arrays (MFC-EA) was constructed and its relative anodic current distribution was investigated with 9 groups of anode electrodes. Meanwhile, the influences of COD concentration and ionic strength of anolyte on anodic current distribution were discussed. It is demonstrated that the electrode spacing between the anode segment and cathode significantly influenced the ohmic resistance distribution and the biomass content of each segment, further affected the anodic current distribution. A significantly uneven current distribution was found in MFC-EA, especially at high currents. The further the anode segment was away from the cathode, the smaller the segment current generation contributed to the total current. Consequently, a suitable MFC structure with equidistant electrode spacing will be a necessary consideration for large-scale MFC design. Moreover, for MFC-EA, improvement on the uneven current distribution was achieved by feeding the anolyte with a COD concentration of 1000 mg COD L^{-1} or with 0.2 M KCl.

1. Introduction

Microbial fuel cell (MFC) is a new type of renewable and sustainable technology for electricity generation. In a typical MFC, microorganisms are used as catalysts to oxidize organic and inorganic matter, and electrons produced by the bacteria from the substrates are transferred to the anode electrode and flow to the cathode linked with a load [1–3]. Actually, MFCs have been used to produce electricity and to treat organic wastewater simultaneously. During the past decade, MFC research is a rapidly evolving field, and a mass of works have been contributed to MFC design, materials of construction, fundamentals of voltage generation, methods of electron transfer and key influencing factors [1,4–8]. Hence, it has experienced an increase in power density with a nearly five orders of magnitude (from less than 0.1 m W m^{-2} [9] to over 6.8 W m^{-2} [10] recently). However, many inherent challenges are still faced when MFC technology comes to practical application [4,11–14].

For the practical applications of MFCs, a threshold volumetric power density of 1 kW m^{-3} should be reached after scale-up [2]. One of the traditional ways for scale-up is MFC stacks operated in series or parallel connection [14–18]. Unfortunately, it has been reported that MFC stacks operated in series caused several problems such as voltage reversal and unstable operation [14,16]. Also, the phenomenon of voltage loss was found when two individual MFCs were conducted in series with both electrical and hydraulic connection due to the substrate cross-conduction effect [18]. These severely limited a further improvement in performance of MFC stacks. Another way for the scale-up of MFC is to increase reactor volume [11,12]. However, most of the previous studies on the understanding and progress of MFCs have been achieved with lab-scale (ml-scale) MFCs. When it comes to larger MFCs, the pre-

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vious experiences from the bench-scale MFCs are not satisfactory. There are still many challenges that must be overcome before successful scale-up.

One of the challenges is the difficulty in maintaining the power density at the same order of magnitude as the lab-scale one [12,19,20]. It is generally reported that a liter-scale MFC has a much lower volumetric power density compared with a lab-scale MFC [21–23]. It can be aware from a number of previous studies that the volumetric power density shows a tendency of decreasing with increase in MFC size [21,23,24]. For the treatment of domestic wastewater with a low substrate concentration and a low conductivity, the volumetric power density of MFCs with single chamber air cathode decrease from 8.3 W m^{-3} (28 ml), followed 4.3 W m^{-3} (1 L) and to 3.5 W m^{-3} (1.6 L) with the increasing reactor volume [25]. However, several exceptions were reported [12,23]. Liu et al. harvested a higher volumetric power density (16 W m^{-3}) from a larger MFC (520 ml) with a shorter electrode spacing (2 cm) and a larger anode surface area per volume (150 m^2 m^{-3}) compared with a smaller MFC (28 ml, 14 W m^{-3}, 4 cm, 25 m^2 m^{-3}) [12]. Recently, Fan et al. also reported, compared with their previous MFC reactors (2.5 ml), a doubled volumetric power density of a CEA-MFC was obtained despite the reactor size increased by over ten times mainly due to the high cathode specific area [23]. These suggests that, in the process of MFC scale-up, the power density of MFCs can be maintained or even improved by optimizing some key factors, such as the specific surface area and intervening space of the electrodes [12].

For the enlargement of specific surface areas, an electrode with a three-dimensional structure is an expected choice. Compared with the traditional carbon paper or carbon cloth, the three-dimensional electrode is of a larger surface area based on the same volume of MFC chamber, hence showing an attractive and potential application to the large MFC system in the future [25,26]. Recent studies reported that a three-dimensional electrode would provide a great surface area for microbial attachment and further significantly improve the anodic performance [26,27]. Up to now, several types of three-dimensional electrode have been adopted to increase MFC power, including graphite rods, graphite granules, graphite felt, graphite wool and graphite fiber brush etc.[7,19,20]. It is noted that, among these three-dimensional electrodes, tenuous graphite rods would be more suitable to the scale-up MFCs, not only because they are relatively inexpensive and have a large defined specific surface area but also because they can be easily arranged as designed.

Electrode spacing is another key parameter for MFC due to its significant influence on the internal resistance [4,12,28,29]. Unfortunately, in the scale-up MFCs, the large electrode array gives rise to different intervening spaces between the anode and cathode, hence non-uniform internal resistance distribution in the cell [12]. This will not only influence the biofilm growth on the anodic electrode but also lead to a non-uniform current distribution, whose effect cannot be neglected any more. As a result, the limitations such as poor substrate utilization, low energy generation, and poor utilization of the electrode will be presented in the scale-up MFCs [6]. Therefore, it is valuable to understand the effect of electrode array and to improve the current distribution in scale-up MFCs. To measure the current distribution, graphite rods can be more likely as the electrode because they can be easily designed to separate each anode segments.

The aim of the present work is to investigate the current distribution in the anode chamber of a liter-scale MFC with electrode array (MFC-EA). The segmented anode current collectors were applied and then, the possible reasons for the detected current distribution were analyzed. Furthermore, possible methods are also suggested for the improvement of current distribution in the liter-scale MFC.

2. Materials and methods

2.1. MFC-EA configuration

As shown in Figs. 1 and S1, a liter-scale MFC (1.87 L) was constructed by two polyacrylic plastic chambers with the same volume separated by 90 × 90 mm proton exchange membrane (PEM) (Nafion 117, Dupont). Both the anode and cathode chambers were evenly filled with 225 graphite rods ($\Phi = 2.4$ mm, $L = 140$ mm, Xingyuan, China) in aligned arrangement, serving as the electrodes. The length of the electrodes immersed in the electrolyte was 110 mm. The anode electrode was divided into 9 segments according to Fig. 1a while all the graphite rods in the cathode chamber were interconnected and treated as an electrode. Details of the anode segments are shown in Fig. 1a. The 9 segments were labeled in sequential order as A, B and C rows based on the distance to the cathode and as 1, 2 and 3 lines based on the flow direction of the anolyte. The nine anode segments were connected together to the cathode current collector through an external resistance box. For the independent measurement of the current generated from each anode segment, the wire from each anode segment was electrically isolated from each other. Furthermore, a liquid distributor, which composed of two perforated plates holding a packed bed of glass beads with 4 mm in diameter, was installed at the inlet of the anode and cathode chamber to ensure a uniform flow of the influent electrolyte. Two Ag/AgCl reference electrodes were placed in the anode and cathode compartments, respectively.

2.2. MFC-EA operation

MFC-EA was inoculated with the effluent from a running MFC fed with an artificial wastewater with sodium acetate (500 mg COD L^{-1}; conductivity: 15.12 mS cm^{-1}) [30]. The cathode was continuously supplied with 50 mM fresh potassium ferricyanide solution to minimize its influence on the whole cell performance. The anode were started up in a continuous flow mode at a flow rate of 1 ml min^{-1} (HRT = 15.6 h). During the startup, all the anode segments were connected together to the entire cathode through a resistance of 50 Ω. After successful started up, fresh media was supplied into the anode chamber. All the tests were conducted at a temperature of 25 ± 2 °C.

2.3. Measurements and calculations

For the measurement of anodic current distribution, each segment was connected with a small fixed resistance ($R = 1\ \Omega$) and then connected to the external resistance box (Fig. S1). The measurements were done by varying the external resistance from 5 to $1.0 \times 10^5\ \Omega$ while recording the voltage over the fixed resistances (U_n, V) by an Agilent 34970A data acquisition unit. The current production from each segment (I_n) was calculated by Ohmic law. For each external resistance step, the voltage was measured at a steady state with a voltage drift of less than 5 mV h^{-1}. The relative segment current, i_n, was defined to evaluate the contribution of different anode segments to the total current production and was calculated as:

$$I_n = U_n/R \tag{1}$$

$$i_n = I_n/\sum_{n=1}^{9} I_n \tag{2}$$

where I_n is the segment current, subscript n represents the segment index. The ohmic resistance of each anode segment was measured by HFR (high frequency resistance) method by using a Zennium