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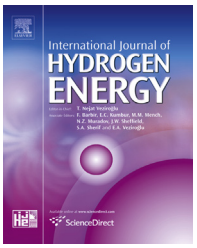

Biofilm distribution and performance of microfluidic microbial fuel cells with different microchannel geometries

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ABSTRACT

Laminar-flow controlled microfluidic microbial fuel cells (MMFCs) with three different microchannel geometries, including the converging channel, the straight channel and the diverging channel, are presented and investigated. The biofilm distribution along the microchannel is visualized and compared. The effects of microchannel geometry on the start-up process and cell performance are also evaluated. The results show that the MMFC with the diverging channel (MMFC-D) begins to generate current in the shortest time compared with MFCs with the converging channel (MMFC-C) and the straight channel (MMFC-S). Moreover, the maximum power density (2447.7 ± 38.9 mW cm^{-2}) of MMFC-D is 429% and 24% higher than that of MMFC-C (462.7 ± 17.5 mW cm^{-2}) and MMFC-S (1980.1 ± 27.5 mW cm^{-2}), respectively. The high performance of MMFC-D can be explained by the combined effect of the good and uniform attached biofilm and the low anode resistance, which significantly depends on the microchannel geometry.

Introduction

Microbial fuel cells (MFCs) are bioelectrochemical devices that convert chemical energy of organic substrates to electrical energy via microorganism metabolism [1]. Recently, benefited from microfabrication and lab-on-chip technology, MFCs are successfully scaled down to (sub)microliter. Compared with other micro fuel cells, microfluidic microbial fuel cells (MMFCs) have been demonstrated as promising platforms for fundamental MFC researches due to eliminating noble metal catalysts and specified reactants, enabling low cost, high autonomy and biocompatible power supply [2–5]. More importantly, because of the unique advantages of the natural small size and precise control, MMFCs have been used as biosensors [6] and the power resource for portable electronics [7,8].

However, the performance of MMFCs is limited by many technical challenges including high internal resistance [9–11], oxygen intrusion [12,13] and nonuniform biofilm formation in

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the microchannel [14]. For most miniaturized MFCs, the internal resistance can reach as high as several thousand ohms resulting from the commonly used gold electrodes. It has been demonstrated that the poor contact between the gold electrode and exoelectrogenic bacteria leads to high internal resistance of the micro MFCs [7]. Thus, carbon-based high surface-to-volume ratio electrodes have been applied in the MMFCs to reduce internal resistances [12,15,16]. In addition, most miniaturized MFCs are fabricated based on the polydimethylsiloxane (PDMS) material which is highly oxygen permeable. In this case, oxygen intrusion would induce a poor cell performance due to the considerably small amount of the biomass at the MMFC anode. Adding oxygen scavengers and using non-PDMS materials could alleviate oxygen permeation and improve microbial electrogenesis [9,17]. The anode biofilm also plays an essential role in the performance of MMFC. Choi et al. [14] demonstrated that the cell performance of the micro MFC is significantly limited when the growth space for the microorganisms is less than 55 μm thick. The sparsely distributed biofilm was observed in a 10 μm-thick space, resulting in a high internal resistance and further a poor performance. Besides, a high shear rate is a typical characteristic in microfluidic environment facilitating the dense biofilm [10], which will further affect the performance of MMFCs.

Unlike a traditional MMFC with a proton exchange membrane, membraneless MMFCs utilize co-laminar flow to separate the anolyte and catholyte without a physical barrier [18,19]. A liquid–liquid interface acting as the virtual membrane is developed by co-laminar parallel streams of liquid fuel and oxidant in a microchannel. In 2011, Li et al. [20] firstly reported a membraneless MMFC with a total volume of 0.3 μL. The maximum current density was 25.42 mA cm^{-2} produced by *Shewanella oneidensis*. Recently, bioelectrochemical systems (BES) based on co-laminar flow microfluidic control were developed to analyze the influence of certain chemical stimulant to microbial electrochemical activity [21] and identify microorganism electroactivity [22]. Unfortunately, because of the undesired inherent crossover effect in the laminar flow fuel cells and the microbial metabolism at the anode may be restricted by the catholyte (e.g. ferricyanide). Moreover, it is found from the previous studies that the distribution of the anode biofilm in the membraneless MMFC is nonuniform along the microchannel [15,23], which will result in a decreased electrode utilization and a low cell performance. Therefore, it is expected that the biofilm along the microchannel could be well-distributed and the performance would be improved through changing the geometry of the microchannel.

In the present work, three membraneless MMFCs with different microchannel geometries are presented and compared. The influence of channel structure on start-up process of membraneless MMFCs is investigated. In order to evaluate the effect of different channel geometries on MMFC, the distribution of biofilm through the microchannel is observed and corresponding biofilm thickness is obtained. Then, electrochemical impedance spectroscope (EIS) is performed at the anode to obtain anode resistances. Finally, cell performances at different flow rates are discussed.

Materials and methods

Device fabrication

Graphite plates (EDM Supplies Inc., poco grade EDM-3) were served as electrodes and machining to different microchannel structures through changing the angle of the microchannel by spark-erosion wire cutting technology (Sodick AQ400LS, Japan). Three membraneless MMFCs were constructed as reported before [15]. Prior to assemble into the fuel cell, the anode electrode surface where microorganism grows was rinsed by 70% alcohol and deionized water, then polished slightly to obtain a rough substrate. Fig. 1 shows the schematic illustration of MMFCs with three types of microchannels. Membraneless MMFCs with the converging channel, straight channel and diverging channel were denoted as MMFC-C, MMFC-S and MMFC-D, respectively. All of the width of the microchannel inlet is equal to 2 mm and length of the microchannel is 30 mm. The difference of the microchannel is the outlet width which is 1 mm for MMFC-C, 2 mm for MMFC-S and 4 mm for MMFC-D, respectively. The effective electrode surface area of the three cases is equal to 40 mm^2.

Inoculation

The anode was injected 3.39 g L^{-1} (COD of 1500 mg L^{-1}) sodium acetate diluted in the mineral medium by a syringe pump (Longer LSP02-1B, China) for continuous flow. The mineral medium contained 15.3 g L^{-1} $Na_2HPO_4 \cdot 12H_2O$, 3 g L^{-1} KH_2PO_4, 0.5 g L^{-1} NaCl, 0.1 g L^{-1} $MgSO_4 \cdot 7H_2O$, 11 mg L^{-1} $CaCl_2$ and 1.0 mL L^{-1} trace elements solution. The composition of trace elements solution were: 1.0 g L^{-1} $FeSO_4 \cdot 7H_2O$, 70 mg L^{-1} $ZnCl_2$, 100 mg L^{-1} $MnCl_2 \cdot 4H_2O$, 6 mg L^{-1} H_3BO_3, 130 mg L^{-1} $CaCl_2 \cdot 6H_2O$, 2 mg L^{-1} $CuCl_2 \cdot 2H_2O$, 24 mg L^{-1} $NiCl_2 \cdot 6H_2O$,

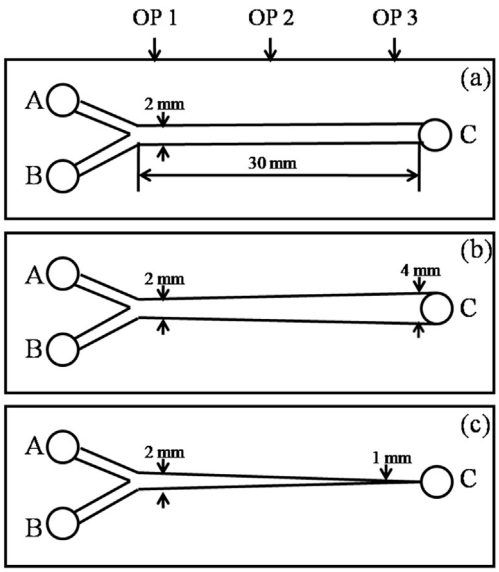

Fig. 1 – Schematic illustration of (a) MMFC-S (b) MMFC-D and (c) MMFC-C.

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