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Structural optimization of contact electrodes in microbial fuel cells for current density enhancements

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ABSTRACT

More than 200% current density enhancement in miniaturized microbial fuel cells (MFCs) has been successfully demonstrated by optimizing the contact electrode structure using micro and nano features. Two fundamental issues are addressed in this work: (1) a methodology to enhance current/power density of MFCs by changing micro and nano structural configurations of contact electrodes and (2) a study on the effectiveness of charge transfer between living cells with organic nanowire-pili and micro/nano interfacial electrodes. This paper details the fabrication and characterization processes of miniaturized MFCs with experimental results, and discusses the prospective power density of MFCs using micro/nano processes. Moreover, a hypothesis for the direct electron transport mechanism from living cells to electrodes is experimentally corroborated. As such, this work represents a step toward higher energy conversion efficiency as well as practical applications of MFCs.

1. Introduction

Compact and highly efficient power sources are integral components for the completion of autonomous sensors and microsystems. A microbial fuel cell (MFC) is a promising candidate for electrical energy harvesting from ubiquitous organic wastes [1]. The breakdown of organic substances to retrieve energy is a naturally occurring process in nature and the possibility to extract electrical charges in the form of MFCs holds great potential in practical applications such as implantable medical sensors and long-term monitoring systems in remote locations.

Recently, μL-scale MFCs fabricated with MEMS technologies were demonstrated using *Geobacteraceae* [2] and *Shewanellaceae* [3] as the organic catalysts that break down reduced carbon molecules during the metabolic process. Previously, our group has also reported miniaturized MFCs which use baker's yeasts [4,5] and *Geobacter sulfurreducens* [6] as the bio-catalysts. A photosynthetic electrochemical cell has also been presented that harnesses the subcellular thylakoid photosystems isolated from spinach cells to convert light energy into electricity [7]. In general, electrons were extracted during these biological processes to provide electricity. Electron mediators have been used to extract electrons and protons from cells or sub-cellular components (to be referred to as "sub-cell" hereafter) in engineering fuel cell systems. Electrons are transported externally via a conducting electrode (anode), and protons are transported through a proton-exchange-membrane (PEM) and reduce the oxidant in the cathode compartment. The efficiencies of these MFCs are low due to many loss mechanisms, particularly during the electron transfer processes. Therefore, various efforts have been conducted to reduce the energy losses in MFCs. One direction to improve the efficiencies is to modify the electrode surfaces with nanostructures such as carbon nanotubes (CNTs). It has been demonstrated that anode electrodes with CNT-doped polyaniline improved the MFC performance [8] and Pt loaded CNTs electrodes increased the power density as high as 6-fold as compared to graphite electrodes [9]. Carbon nanostructures on stainless steel mesh anodes have been shown to increase the power density of MFC by a factor of 60 [10] and CNT powder added to the anode chamber have reduced the anodic resistance [11]. On the other hand, power densities in MFCs are also dependent on the absolute and relative size of their components. The anode to cathode surface area ratio can affect power output, where tripling the surface area of the cathode increased power density by 22% [12].

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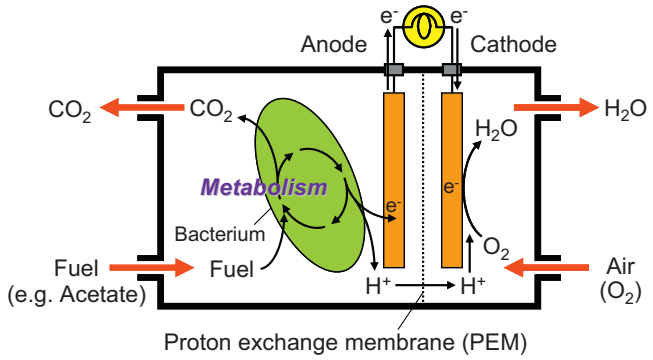

Fig. 1. Schematic diagram showing the operating principle of the microbial fuel cell. Acetate (or other fuel) is fed into the anode chamber and bacteria are used to break down this fuel during metabolism to produce electrical charges.

Furthermore, it has been also demonstrated that the surface area of both electrodes and the PEM in MFCs could affect power density [13]. Our previous work [14,15] also studied and characterized the influences of sub-cell-to-electrode and cell-to-electrode contact structures, respectively, to increase living sub-cell-to-electrode and cell-to-electrode contact areas. These are possible approaches to reduce the loss of electron transfer by using micro- and nano-structured electrodes and to improve the power density of MFCs. This paper details the structural optimization of contact electrodes with experimental characterization to demonstrate current density enhancements with quantitative data to provide design guidelines for future MFCs.

2. Operation principle

Fig. 1 shows the schematic diagram of the operation principle of a MFC. In the anode compartment, organic fuel such as acetate is fed into the system and microorganisms act as bio-catalysts to break down the organic matter. Electrons generated during the metabolic process are transferred to the anode electrode via electron mediators [4,5]. Fig. 2 illustrates the basic operation principle of the MFC by using *G. sulfurreducens* as the catalyst. *G. sulfurreducens* was chosen in this work because their pili have shown to function like "organic nanowires" to directly transfer electrons to the electrodes [16–18]. For our experiments, four different kinds of modified cell-to-electrode contact structures were fabricated as

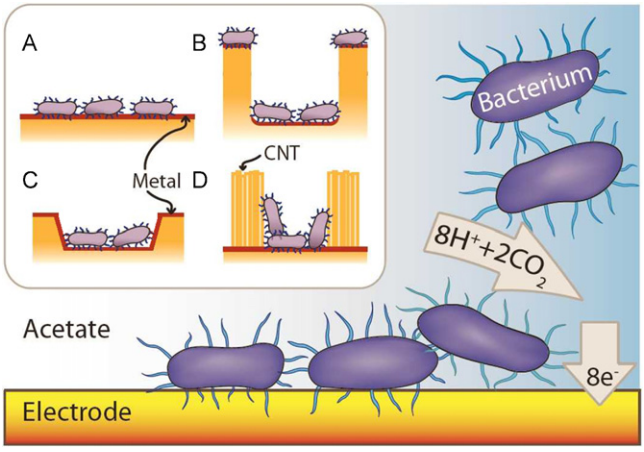

Fig. 2. The basic operating principle of an MFC using *Geobacter sulfurreducens* as the bio-catalyst. The inset shows four different kinds of modified cell-to-electrode contact structures: (A) flat, (B) hole, (C) channel, and (D) vertically aligned CNTs (not drawn to scale). Cell-to-electrode contact structures affect the current/power density of the MFCs.

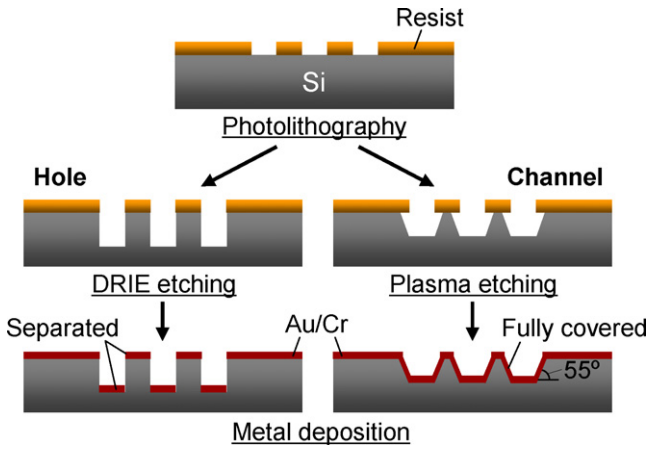

Fig. 3. Fabrication processes of microelectrodes with holes and channels. Two kinds of silicon etching processes were used to make perpendicular and tapered sidewalls.

shown in Fig. 2: (A) flat surface as a reference, (B) surface with micro-holes perpendicularly etched into the substrate, (C) surface with tapered micro-channels, and (D) vertically aligned carbon nanotube (CNT) arrays. These contact structures were used as the basic tools to investigate the current density enhancements and effectiveness of charge transfer between living cells with organic nanowire-pili and micro/nano interfacial electrodes, and to optimize the structural configurations of contact electrodes for current density enhancements.

3. Fabrication

3.1. Micro electrodes

Micro electrodes with (A) flat surfaces, (B) surfaces with 5 μm × 5 μm holes and (C) surfaces with 5-μm-wide, 3.6-μm-deep channels were fabricated. The fabrication processes of micro electrodes with holes and channels are shown in Fig. 3. After patterning photoresist, silicon substrates were etched. The hole-shape patterns were made using DRIE processing, creating 8-μm-deep holes with sidewalls perpendicular to the top surface. Since the metal deposition process was done by the evaporation of Au/Cr (400/200 nm), the sidewalls were not completely covered, making only the 2-μm-wide gaps between the hole patterns active for collecting the charge during MFC operation. The channel-shape patterns were fabricated using an isotropic plasma etching process. The plasma etching process was conducted for 5 min using SF_6 and O_2 with a flow rate of 9:1 applying the RF power of 100 W. The final angle of the sidewalls was 55°, this enabled the entire surface, including the channel sidewalls, to be covered with metal to collect charges. Fig. 4a and b are SEM images of fabricated electrode structures with (a) the hole-pattern and (b) channel-pattern surfaces, respectively. The right-hand images in Fig. 4 show a close-up of the electrode surface. *G. sulfurreducens* have a length of about 1 μm and a diameter of approximately 0.3 μm. Therefore, the dimensions of fabricated holes and channels are large enough to accommodate bacteria. The active metalized areas for the hole and channel patterns are calculated. For the hole-shape patterns, only the gap area between the hole-patterns was measured using the SEM image shown on the right of Fig. 4a. For the channel-shape patterns, the surface area was measured by considering the cross-section of channels as triangles with 2 μm gaps as shown by red lines on the right of Fig. 4b. Consequently, the active metalized areas for hole and channel patterns are calculated as 49% and 154%, respectively, of the flat reference surface area.