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Parylene C-coated PDMS-based microfluidic microbial fuel cells with low oxygen permeability

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HIGHLIGHTS

- A parylene C coating is proposed to reduce the oxygen permeability of a PDMS-based micro MFC.
- The power density and sustained time of the MFC were improved by coating PDMS with parylene C.
- The structured electrode shows better cell performance than a flat electrode.
- There is an optimal electrolyte flow rate that generates the best co-laminar MFC performance.
- The optimal flow rate depends on the biofilm, which is affected by the shear stress of the stream.

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ABSTRACT

Oxygen invasion is the main bottleneck in developing microscale microbial fuel cells as an efficient power source. This study reports for the first time the development of a polydimethylsiloxane -based co-laminar microbial fuel cell utilizing a parylene C coating to lower the oxygen permeability. In addition, the surface of the Au electrode is micropillar-structured to reduce the internal resistance of the microbial fuel cell. The performance of this novel microfluidic microbial fuel cell is investigated under various flow rates of electrolytes. The shear stress simulation shows that shear stress, induced by increasing flow rates, strongly impacts the biofilm electrode performance. To the best of our knowledge, the measured peak power density ($71.89 \pm 5.13\,\mu W\,cm^{-2}$) and maximum current density ($182.0 \pm 4.82\,\mu A\,cm^{-2}$) with the structured electrode are higher than those of any other reported polydimethylsiloxane-based microscale microbial fuel cells. The proposed microbial fuel cell appears to be a promising power supply that can be easily integrated with portable or implantable biomedical devices.

1. Introduction

The importance of microsystems has been rapidly spreading to the fields of wireless parts, optical parts, biochips, and portable devices, as well as airbag sensors and inkjet heads. In order to utilize these microsystems, a micro-sized portable power source is a vital component [1]. Micro fuel cells, currently being developed by researchers, mainly use a metal catalyst [2]. In contrast to this, microbial fuel cells (MFCs) have the merit of converting chemical energy into electrical energy using electrochemically active microorganisms as a catalyst [3]. The microorganisms used in MFCs as self-renewal catalysts oxidize organic matter under pH neutral conditions at temperatures close to body temperature. Compared with bio fuel cells using special enzymes as a catalyst, an MFC can ideally completely oxidize organic fuels to carbon dioxide and water by various endozoic enzymes for the perfect extrusion of energy [4]. Furthermore, MFCs do not require operations such as enzyme separation and purification, and the reproduction of the bacterial cells leads to a biocatalyst regeneration and thus great long-term stability. Therefore, micro MFCs could be an interesting option for use as a power source for portable medical and electronic instruments, and relevant research is necessary and critical [5].

The micro MFCs studied to date have typically utilized a Nafion 117 proton exchange membrane (PEM) or cation exchange membrane [6–12]. Recently, by applying a membrane-less laminar flow-based microfluidic MFC structure, research to enhance the performance of MFCs has been conducted [13–18]. The development of a membrane-less microfluidic MFC is meaningful to demonstrate the possibility of commercialization of power sources of lab-on-a-chip type micro

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medical devices requiring biocompatibility [19]. Lab-on-a-chip devices are usually fabricated based on micromachining of microelectromechanical systems (MEMS). Thus, the configuration of the micro MFC, which is fairly easy to integrate with these devices because of the use of similar fabrication techniques, is a polydimethylsiloxane (PDMS)-glass hybrid chip with Au electrodes [20,21].

Gold electrodes often show the disadvantage that the internal fuel cell resistance is large because of a poor charge transfer resistance between the biofilms and the gold electrodes [22]. In membrane MFCs, this demerit has been supplemented by forming a micro or nano scale structure on the Au electrode surface. Improvement of the cell performance by such surface modification has been reported by Inoue et al. [23] and Kano et al. [24]. PDMS is a cheap material with a simple fabrication process. Furthermore, there are no significant problems, manufacturing PDMS-based MFCs integrated with biochips. PDMS, however, has a disadvantage of high oxygen permeability. In micro-sized MFCs, even if a small amount of oxygen exists in the anode chamber, a loss of electron flow to the oxidation electrode can occur, and the metabolic activity of the anaerobic microbe cell can be hindered [22]. More severely, strictly anaerobic bacteria, such as *Geobacter suflurreducens* – one of the most prominent electroactive bacteria – may not survive the presence of oxygen traces. Thus, in microscale MFCs, oxygen invasion into the anode chamber is very fatal even at minute amounts [20]. Therefore, improved cell performance has been reported in microfluidic MFCs where the anode chamber was made of polymethyl-methacrylate (PMMA), which has a low oxygen permeability, and carbon-based electrodes [25,26]. However, when PMMA and a general carbon electrode are used, micromachining-based hermetic bonding is impossible, and there are many difficulties in integrating manufacturing with a bio lab-on-a-chip because manual operations are needed in the fabrication processes.

In this study, a simple way to lower the oxygen intrusion rate into the chip of a PDMS-based membrane-less microfluidic MFC with a gold electrode, of which the fabrication process can be smoothly combined with microfluidic bio devices, was developed for the first time. Despite this characteristic, PDMS, which generally serves as a channel material in microfluidic devices but has high oxygen permeability (52,531 cm^3 mm/m^2·day·atm), has been used frequently in previously reported micro MFCs because of its other many merits. In this study, to solve this problem, parylene was used as it can provide a good environment for electrochemical bacterial metabolism and can be fabricated using MEMS micromachining. Parylene has several advantages: It is inexpensive, has as low oxygen permeability and good chemical resistance and can be fabricated simply by chemical vapor deposition (CVD). This material is also biofriendly, so it is commonly used in medical devices. The oxygen intrusion protection effect due to the parylene C coating on PDMS was evaluated. The Au electrode surface also was micropillar-structured to effectively augment the reaction area between the electrode and microorganisms. To maximize the performance of the fuel cells developed by this process, the flow rate conditions to provide optimum biofilms on the structured electrodes in co-laminar flows within the microchannel were investigated and shear stress simulations were conducted.

2. Materials and methods

2.1. Microbial fuel cell design and fabrication

The proposed proof-of-concept MFCs were fabricated by coating parylene C onto the PDMS surface by low pressure CVD. Parylene C, which has very low oxygen permeability (2.8 cm^3 mm/m^2·day·atm), was selected among various parylene candidates. The surface of the electrode must be as large as possible compared to the volume in order to reduce the internal resistance, which is the drawback of a gold electrode in microfluidic MFCs [27]. Hence, as shown in Fig. 1, the electrode surface of the micro MFC was structured by an array of micropillars to increase the surface area. The diameter of the pillars is 20 μm with a height of 7.5 μm. The gap between the pillars is 20 μm. Compared to an unstructured surface, the surface area of the micropillar decorated gold electrode increased by 30.62%. The widths of the anode and cathode were determined to be 200 μm, and the space between these electrodes was 250 μm. Considering the machining error, a 25 μm clearance was allowed between the electrode and channel wall. The volume of the anode channel chamber is 0.3 μL; thus, the MFC was designed on the submicron scale, which has rarely been reported.

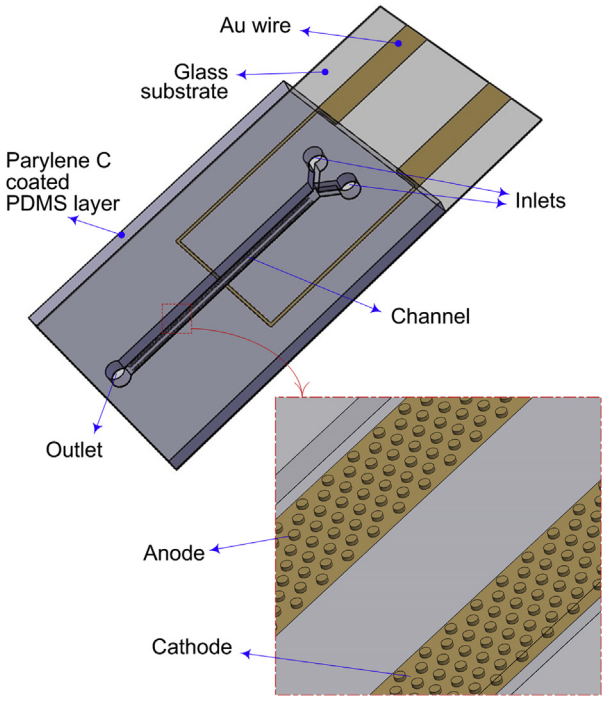

Fig. 1. Schematic diagram of the proposed microbial fuel cell.

The MFCs proposed in this work were fabricated based on MEMS micromachining techniques that are used in the manufacturing of existing microfluidic biochip devices [28]. The MFC was designed such that a gold electrode was formed on the glass wafer, and the PDMS layer, on which the microchannel was made, was combined with it. A microchannel 55 μm deep was made by soft lithography on a PDMS slab used as a cover. After using polyvinyl chloride tape to cover the part that will be bonded with the glass wafer, the microchannel surface of the PDMS slab was coated with about 1-μm-thick parylene C by low-pressure CVD. Two inlets and an outlet were mechanically punched in the coated PDMS slab. In order to arrange the anode and cathode side by side inside the microchannel, 50-nm-thick Cr and 200-nm Au were deposited sequentially on the glass wafer by sputtering, followed by patterning using photolithography. In the case of the structured electrode, gold microstructures with a cylindrical shape were electroplated on the deposited electrode using a LIGA-like process. Last, the glass wafer and the parylene-uncoated part of PDMS were hermetically bonded by O_2 plasma surface treatment. The completed microfluidic MFC is shown in Fig. S1.

2.2. Preparation of electroactive biofilms

In this work, a *Geobacteraceae*-enriched culture was used as a biocatalyst. The inoculum was cultured from primary waste water obtained from a waste water treatment plant. The bacterial growth medium was a mixture of buffer solution (200 mL), primary waste water (10 mL), vitamin solution (2.5 mL), and mineral solution (2.5 mL). The buffer solution contained (per liter) 2.69 g $NaH_2PO_4·H_2O$, 4.33 g Na_2HPO_4, 0.31 g NH_4Cl, and 0.13 g KCl. The mineral solution