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A microfluidic glucose biofuel cell to generate micropower from enzymes at ambient temperature

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ABSTRACT

A Y-shaped microfluidic channel is applied for the first time to the construction of a glucose/O_2 biofuel cell, based on both laminar flow and biological enzyme strategies. During operation, the fuel and oxidant streams flow parallel at gold electrode surfaces without convective mixing. At the anode, the glucose oxidation is performed by the enzyme glucose oxidase whereas at the cathode, the oxygen is reduced by the enzyme laccase, in the presence of specific redox mediators. Such cell design protects the anode from an interfering parasite reaction of O_2 at the anode and offers the advantage of using different streams of oxidant and fuel for optimal performance of the enzymes. Electrochemical characterizations of the device show the influence of the flow rate on the output potential and current density. The maximum power density delivered by the assembled biofuel cell reached 110 μW cm^{-2} at 0.3 V with 10 mM glucose at 23 °C. The microfluidic approach reported here demonstrates the feasibility of advanced microfabrication techniques to build an efficient microfluidic glucose/O_2 biofuel cell device.

1. Introduction

Microfluidic fuel cells can provide an alternative pathway towards miniaturized power supplies. These devices confine all the fundamental components of a fuel cell within a single microstructured network exploiting laminar flow of fluids at a low Reynolds number that to limit convective mixing [1–3]. In such systems, streams of fuel and oxidant flow in parallel within the microchannel eliminating the need for a membrane. The electrochemical reactions take place at the anode and cathode located within the respective streams. Various microfluidic fuel cells working with hydrogen, methanol or formic acid as fuel have recently attracted significant attention [4–7]. The microfluidic approach offers several advantages over macro-scale systems including the use of less reagents and space and less time consumption. Interesting theoretical and experimental works have been published previously describing the effect of flow rate, microchannel geometry, and location of electrodes within microfluidic systems on their performance [8–10].

Enzymatic BioFuel Cells (BFC) convert chemical energy into electrical energy *via* specific enzymes acting as catalysts, and are strong candidates for the supply of power to miniature portable electronic [11] or biomedical devices [12]. Microfluidic enzyme biofuel cells have been developed based on both laminar flow within a microchannel and biological enzyme strategies. Palmore et al. [13] developed a microfluidic fuel cell working from a laccase cathode in the presence of the 2,2′-azinobis (3-ethylbenzothiazoline-6-sulfonate) (ABTS). A transport model was developed to describe the optimal conditions for maximizing both the average current density and the percentage of fuel utilized. The maximum power value reached 26 μW cm^{-2} at 0.4 V at a flow rate of 100 μL min^{-1}. Another device has been developed that generated electrical power from glucose oxidation with a glucose dehydrogenase anode and a bilirubin oxidase-adsorbed O_2 cathode [14]. The originality of this work lay in the electrode-arrangement in a single flow channel. Dissolved O_2 was pre-reduced at an upstream cathode to protect the downstream anode from the oxidative environment. The maximum cell current was 160 μA cm^{-2} at a flow rate of 300 μL min^{-1}.

The objective of this work is to apply advanced microfabrication techniques to build a functional microfluidic glucose/O_2 biofuel cell. At the anode, the glucose is oxidized by the enzyme glucose oxidase (GOD), whereas at the cathode the oxygen is reduced by the enzyme laccase, in the presence of redox mediators. The device is based on a Y-shaped microfluidic channel exploiting the laminar flow of the streams both to protect the anode from interfering parasite reactions of O_2 and to use different media for optimal operation of the enzymes. The dimensions and the operating conditions of this microfluidic device are such that fluid flow is pressure driven and characterized by a Reynolds' number varying from 3.3 to 33.3 [1] in the flow rate range 100–1000 μL min^{-1}. The significant

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performance of the power output is demonstrated by electrochemical characterizations of the device as a function of the flow rate through the microchannel.

2. Experimental

2.1. Chemicals

ABTS, $K_3Fe(CN)_6$, GOD from Aspergillus Niger (198,000 U mg^{-1} solid) and laccase from Trametes Versicolor (20 U mg^{-1} solid) were purchased from Sigma–Aldrich and used without further purification. Buffers were prepared with sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$) and di-sodium hydrogen phosphate (Na_2HPO_4) salts (pH 7.0) from Merck, and with citric acid (Prolabo) and $NaH_2PO_4 \cdot H_2O$ salt (pH 3.0). β-D-glucose (Prolabo) was prepared in phosphate buffer 0.1 M pH 7.0 at least 24 h before its use. The aqueous solutions were prepared using 18.2 MΩ cm MilliQ water (Millipore).

2.2. Fabrication of the microchannel

The microfluidic chip was fabricated using a two-part poly(dimethylsiloxane) (PDMS) elastomer and a standard soft lithography method. Firstly, a master was obtained using an Eertec HQ-6100 negative dry film photoresist [15]. Secondly, the master was replicated in PDMS [16]. Then the PDMS slab was peeled off from the master, and holes were punched using a 1.2 mm diameter tube to provide an access for Teflon tubing. The PDMS slab was then aligned with a glass slide containing the electrodes before sealing. The device consisted of a Y-shaped channel with two inlets and two outlets (Fig. 1). The microchannel dimensions were: 25 mm length, 2 mm wide and 75 μm height.

2.3. Microfluidic cell and electrochemical measurements

The gold electrodes with a planar active area of 0.05 cm^2 (10 mm length and 0.5 mm wide) were deposited by sputtering on a glass substrate (Au: 300 nm thick on a 10 nm thick Cr adhesion layer). The separation between the cathode and the anode was 1 mm.

The catholyte solution consisted of laccase (0.5 mg mL^{-1}) and ABTS (5 mM) in 0.2 M citrate buffer pH 3, saturated with oxygen. The anolyte consisted of GOD (0.5 mg mL^{-1}) and $Fe(CN)_6^{3-}$ (10 mM) in 0.2 M phosphate buffer pH 7, purged with nitrogen gas. A syringe pump (Harvad) was used to pump the solutions into the microchannel at a flow rate varying from 0.1 to 1 mL min^{-1}.

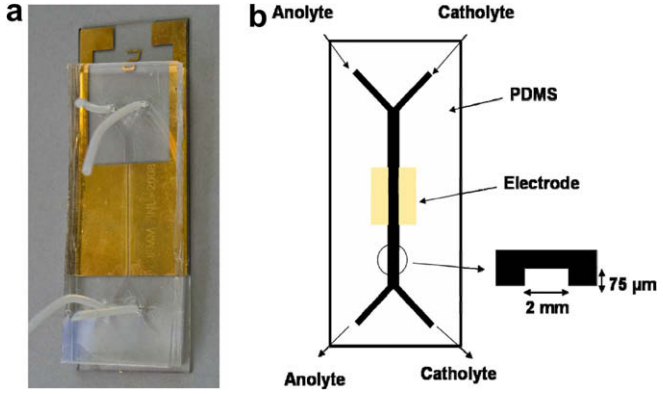

Fig. 1. Glucose/O_2 microfluidic biofuel cell, (a) PDMS-glass device, (b) Scheme of the device consisted in a Y-shaped microfluidic channel with 2 inlets and 2 outlets.

The electrochemical measurements were performed using a potentiostat Autolab (Eco chemie) connected to a computer. The fuel cell performance was evaluated at 23 °C by measuring the cell voltage while varying the current density.

3. Results and discussion

3.1. Physicochemical analysis

In the BFC, the redox reactions are the electro-oxidation of glucose in gluconolactone by the glucose oxidase with $Fe(CN)_6^{3-}$ at the anode, and the electro-reduction of dioxygen in water by the laccase with ABTS at the cathode. The cell voltage is partially controlled by the formal potential of the mediators $Fe(CN)_6^{3-}$ (E'° = 0.12 V vs. SCE) and $ABTS^{\cdot-}$ (E'° = 0.46 V vs. SCE) chosen with a formal potential close to that of GOD (E'° = −0.34 V vs. SCE [17]) and laccase (E'° = 0.535 V vs. SCE [18]), respectively.

In electrochemical laminar flow systems, the mass transport is achieved by both diffusion and convection transport. The ratio of diffusive to convective time scales is denoted as the Peclet number *Pe* (*Pe* = *Uh*/*D*) with *U* the average velocity of the flow, *h* the height of the microchannel and *D* the diffusion coefficient of the molecule [11]. In our system, it varies from 3700 to 37,000 for the flow rates in the range 100 to 1000 μL min^{-1} and the diffusive transport along the microchannel can be thus neglected.

The mixing of the two streams occurs by transverse diffusion only, and is restricted to an interfacial width at the centre of the channel. To check the possibility that the diffusive crossover contributes to the loss of current, we calculated the width of the mixed region δ_{mix}, using Eq. (1) [1]. For the 1 cm-electrode length and the lower flow rate 100 μL min^{-1}, δ_{mix} was 46 μm. As anode and cathode were separated by 1 mm, the diffusive fuel crossover did not affect the performance of the BFC.

$$\delta_{mix} = \left(\frac{Dhx}{U}\right)^{\frac{1}{3}} \quad (1)$$

where *D* is the coefficient diffusion of oxygen and *x* is the downstream distance.

3.2. Performance of the microfluidic biofuel cell

The measured performance characteristics of the microfluidic system based on current density, power density, overall power output and fuel utilization, are affected by the flow rate of the streams that regulates the mass transport limitation. The optimum flow rate would provide little to no fuel crossover while yielding high reactants consumption.

Fig. 2A shows the short-circuit current density delivered by the biofuel cell at the flow rates between 100 and 1000 μL min^{-1}. The maximum current densities increase from 350 to 690 μA cm^{-2} with the flow rate, indicating that the mass transport limitations are thus reduced by enhanced convective transport at high flow rates from the bulk solution to the electrode surface.

The power density was estimated using the oxidant stream saturated with oxygen at pH 3 and the fuel stream purged with nitrogen gas at pH 7 (Fig. 2B). The open circuit voltage (OCV) of the device is 0.55 V. The maximum power density delivered by the biofuel cell is 110 μW cm^{-2} at 0.3 V at 23 °C. This value is higher than previous reported values of 64 μW cm^{-2} at 0.4 V at 23 °C for a miniaturized glucose biofuel cell with immobilized enzymes [19], and of 26 μW cm^{-2} at 0.15 V at 23 °C for a microfluidic cell working from a laccase biocathode [13]. In addition, as observed in Fig. 3A, the dependence of the peak of the delivered power on the flow rate indicates that the power output of the device is primarily controlled by transport characteristics and that the electrochemical reactions are relatively fast.