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Integration of cantilevered porous electrodes into microfluidic co-laminar enzymatic biofuel cells: Toward higher enzyme loadings for enhanced performance

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ABSTRACT

This paper introduces a novel design of co-laminar microfluidic biofuel cell that incorporates three-dimensional (3D) porous electrodes containing immobilized enzymes. An innovative characteristic of the microfluidic configuration presented here is the presence of cantilevered bioelectrodes protruding along the internal walls of the miniature electrochemical chamber. Such suspended-like electrodes can maximize the penetration depth of the reactants inside the porous medium. As a first proof-of-concept, we demonstrate the integration of a bioanode and a biocathode into a lamination-based ethanol/O_2 microfluidic biofuel cell fabricated via rapid prototyping. With enzymes deposited into the 3D fibrous structure of 25 mm long, 1 mm wide and 0.11 mm thick carbon paper electrodes, the volumetric current density reached ≈2.9 mA cm^{-3} at 0.43 V under a flow rate of 50 μL min^{-1}. A major advantage of the presented microfluidic cell is that it can be adapted to include a larger active electrode volume via the vertical stacking of multiple thin bioelectrodes. We therefore envision that our design would be amenable to reach the level of net power required to supply energy to a plurality of low-consumption electronic devices.

1. Introduction

Employing enzymes as catalysts to convert the chemical energy of biofuels into electrical energy is today envisioned as an attractive option for supplying power to low-consumption electronic devices [1,2]. Co-laminar enzymatic fuel cells (CL-EFCs) are a subtype of biofuel cells in which the main electrochemical chamber is a micrometer-sized fluidic channel with low Reynolds number and high Peclet number. Viscous forces are hence dominant over inertia forces and laminar flow conditions dominate. This means that fuel and oxydant streams can flow in parallel (i.e., side by side) without mixing, except by diffusion. In the meantime, ionic transport is permitted across the co-laminar interface formed along the microchannel. As a direct consequence, CL-EFCs offer the advantage of disposing the proton exchange membrane conventionally used to separate the anodic and cathodic compartments. Although the absence of physical membrane favors miniaturization and reduces fabrication costs, the practical deployment of CL-EFCs is still hindered by limited low power yields. A promising mean to alleviate this hindrance is to employ three-dimensional porous electrodes (3D-PEs). Compared to two-dimensional (2D) electrodes, notable performance improvements were indeed reported for co-laminar fuel cells exploiting chemical reactants and the enlarged reactive surface of 3D-PEs [3,4]. Similarly, the possibility to utilize the internal surface area of 3D-PEs in CL-EFCs would allow for higher enzyme loading and enhanced performance [5–10]. Despite such potential advantages, most designs of CL-EFCs still rely either on soluble enzyme catalysts flowing over bare 2D electrodes (e.g., patterns of thin gold layers) [11–13] or enzymes immobilized on modified flat surfaces [14–17]. In this study, we introduce and evaluate a novel lamination-based CL-EFC that integrates cantilevered 3D-PEs with the aim to reach higher enzyme loadings and enhanced performance.

2. Materials and methods

2.1. Preparation of bioelectrodes

This section only summarizes the preparation of the bioelectrodes (see supplementary information for details regarding the fabrication method and the enzyme immobilization protocols). Briefly, Toray carbon paper (TCP) was used as the electrode material. TCP sheets purchased were 110 μm thick (TGP-H-030, Toray). Electrodes were cut from the TCP sheets using a cutting plotter (CE 6000-40, Graphtec). An example of electrode pattern obtained after the cutting process is shown in Fig. 1B. Enzymes were subsequently immobilized onto hydrophilic rectangular zones having a volume of ≈0.0028 cm^3 (see dashed

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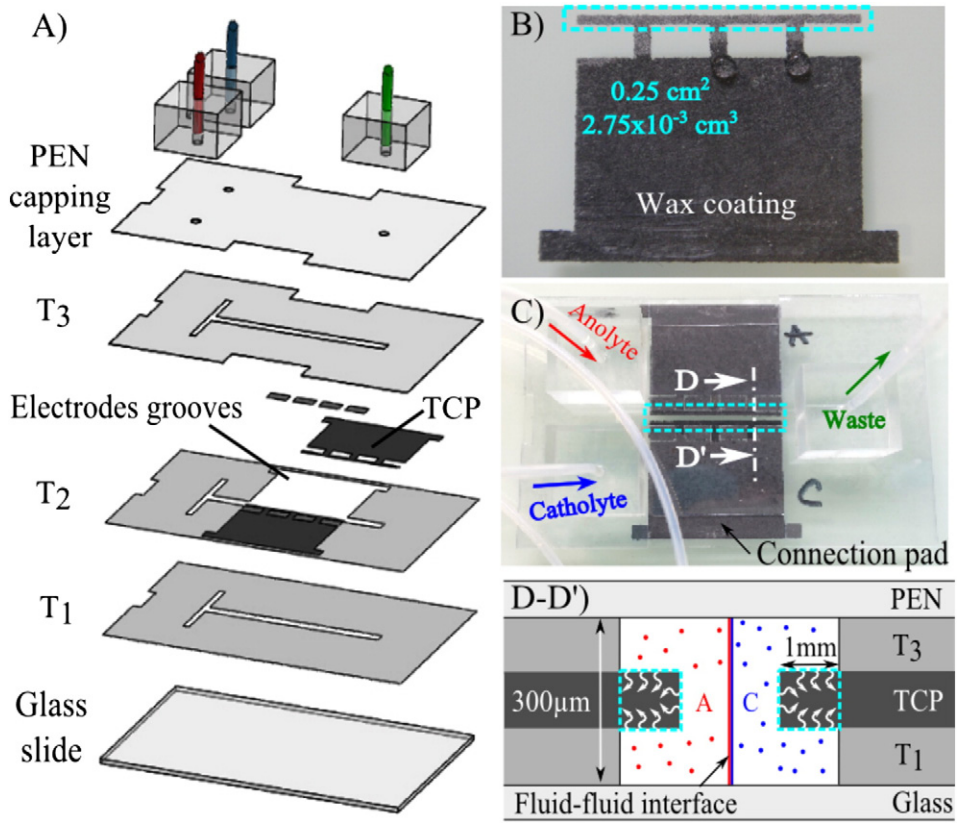

Fig. 1. A) Expanded view illustrating the lamination-based design of the microfluidic biofuel cell. B) Enlarged view of a patterned electrode after cutting: the hydrophilic zone intended for enzyme immobilization is indicated by the dashed lines. The remaining of the electrode is coated with wax. C) Overview of the final cell. D–D′) Cross sectional view showing the central position of the porous cantilevered electrode inside the main microchannel. The white arrows illustrate the penetration of the reactants along the three exposed sides of the *suspended* electrodes.

lines in Fig. 1B). To oxidize ethanol at the anode, we employed the enzyme alcohol dehydrogenase in presence of β-nicotinamide adenine dinucleotide sodium salt. Prior to enzyme immobilization, a first electropolymerized poly(methylene green) film was used as an electrocatalyst. A phosphate buffer solution containing the enzymes was subsequently pipetted onto the poly(methylene green) film and dried at room temperature. To reduce oxygen at the cathode, a droplet of solution containing a mixture of laccase and carbon nanoparticles was first deposited onto the TCP. After drying at room temperature, this first layer was entrapped along with 2,2-azinobis(3-ethylbenzothiazoline-6-sulfonate) diammonium salt in a electropolymerized polypyrrole film.

2.2. Design and fabrication of the CL-EFC

The CL-EFC containing both bioelectrodes is based on a T-shaped laminated structure composed of double sided pressure adhesive (DSPA) films sandwiched between a glass slide and a polyethylene naphthalate (PEN) capping layer (see Fig. 1). The DSPA layers (labeled $T_{j=1,3}$ in Fig. 1) were 100 µm thick (Montex-DX 1, X-Film) whereas the PEN layer was 75 µm thick (ES361075, Goodfellow). DSPA and PEN layers were also prepared using a cutting plotter. This rapid prototyping technique offered two main advantages: i) access to a cleanroom was not required; ii) the assembly of CL-EFC could be completed within minutes once the bioelectrodes were ready.

To facilitate handling, all layers were 75 mm long, 50 mm wide. The T-branches were 12 mm long, 1.5 mm wide whereas the main microchannel was 45 mm long, 3 mm wide. For the assembly of the entire structure, we used a CNC-machined mechanical guide enabling a manual alignment with sufficient accuracy ($\pm$ 100 µm). First, T_1 was aligned and taped on a glass substrate. Each subsequent layer was sequentially taped above the previous one. The bioelectrodes were placed in specific grooves patterned in T_2. In this way, the bioelectrodes were centered in the middle of the microchannel (see cross section D–D′ in Fig. 1). For this study, we intentionally favored such cantilevered (i.e., protruding) electrodes rather than electrodes conventionally placed at the bottom of the microchannel. Indeed, when fluids flow over bottom 3D-PEs, the penetration depth of the reactants inside the porous medium may be limited [3]. In fact, reactants may solely interact with the top portion of the 3D-PEs [3]. For the delivery and removal of fluids, polytetrafluoroethylene (PTFE) tubing was firmly inserted into the holes of three access ports made of Plexiglas. The three cubic ports were then fixed to the top PEN layer E_3 by using two square layers of DSPA film (not shown in Fig. 1-A).

3. Results and discussion

3.1. Bioelectrodes

First, the enzymes immobilized onto the 3D-PEs were visually inspected via scanning electron microscopy (SEM). Top and cross sectional views of an enzyme-modified anode are shown in Fig. 2. As can be viewed from Fig. 2A, the overall surface of the TCP is well covered by the enzyme layer. Nevertheless, when observing the thickness of the enzyme-modified TCP, it appears that the enzymes do not fully penetrate into the fibrous electrode structure (see comparison to bare TCP in Fig. 2B). Similar observations were made for the biocathode (data not shown). This suggests that our current immobilization protocols should be improved prior to be used with thicker TCP electrodes. As a viable alternative, however, our CL-EFC could be adapted to increase the amount of enzymes exposed to the reactants by stacking multiple bioelectrodes such as the ones used here. The bioelectrodes were also