A BIOLOGICAL FUEL CELL MICROFABRICATED WITHIN A SINGLE SHEET OF PAPER

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ABSTRACT

We report a novel technique for fabricating microbial fuel cells (MFCs) within a single sheet of paper, which greatly (i) reduces fabrication cost/processes of the fuel cell devices and (ii) revolutionizes their mass production for the potential use as a disposable battery in resource limited settings. A number of device units were simply batch-fabricated on a flexible/scalable single sheet of paper by spraying/screen-printing electrode materials and forming hydrophilic regions with hydrophobic wax. A 3-D MFC structure was created by forming four functional layers of an anode, a hydrophilic reservoir, a hydrophobic wax-based ion exchange membrane, and an air-cathode in a single sheet of chromatography paper. Upon adding one drop of bacteria-containing liquid onto the device, the hydrophilic reservoir allowed for rapid bacterial cell attachment to the electrode, where bacterial respiration then transferred electrons from the organic liquid to the electrode, generating power to an external load.

INTRODUCTION

Recently, paper-based microbial fuel cells (MFCs) have attracted a great deal of research interest as a disposable and accessible power source in resource-limited regions [1-7]. The paper-based device can generate electricity from bacteria-containing liquid derived from renewable and sustainable wastewater which is readily accessible in the local environment [7]. Moreover, the intrinsic feature of paper allows for rapid adsorption of bacteria-containing solution through capillary force of paper without external pump/tubing and promotes immediate microbial cell attachment to the electrode, leading to a rapid power generation using a small amount of the liquid [8, 9]. However, the promise of this technology has not yet been translated as practical power applications, because their device configuration is complicated with necessary multifunctional parts such as the anode, cathode, and ion exchange membrane, demanding manual assembly of the device and hampering batch fabrication. In addition, there are potential issues during device fabrication such as misalignment of paper layers and vertical discontinuity between layers, which ultimately decrease power generation. Even newly developed origami MFCs suffer from lack of clamping methods for mechanically maintaining the stacked layers [7].

In this work, we microfabricated the MFC in a single sheet of paper, eliminating the aforementioned major technical hurdles. A 3-D MFC structure was developed by incorporating four functional layers of a nickel and polypyrrole/carbon black (Ppy/CB) anode, a hydrophilic reservoir, a hydrophobic wax-based ion exchange membrane, and an activated carbon based air-cathode in a single sheet of chromatography paper (Fig 1). Since the configuration of the microfluidic reservoir and anode has a great influence on bacterial cells' distribution through the paper matrix, their attachment over the anode, and electron transfer efficiency [10], different shapes of anodes over the reservoir were thoroughly explored in terms of device performance and sample injection efficiency. The device developed in this work greatly reduced fabrication time/cost of the fuel cells and revolutionized their mass production for the potential use as a disposable power source in remote and resource limited regions.

Figure 1. (a), (b) & (c) Photo-images of the biological fuel cell fabricated in a single sheet of paper with different anode/reservoir configurations, (d) a schematic diagram of the device and (e) a microscopic image of the cross section of the MFC.

MATERIALS AND EXPERIMENTAL SET-UP

Device Fabrication

All functional layers for the MFC configuration were constructed in a single large sheet of Whatman 3MM chromatography paper (20cm x 20cm), where 25 individual devices were simultaneously batch-fabricated (Fig. 1 & 2). The hydrophobic wax melted into the paper substrate strengthened the paper fiber matrix while retaining its flexibility. The wax was also used as the ion exchange membrane as it provided hydrophobic property of the paper, separating the anode part from the air-cathode and allowing protons to pass through efficiently [1]. The penetration depth of the melted wax printed on the bottom side of a paper was carefully controlled by adjusting the heating time (Fig 1e). The anode was prepared on one side of the paper while the air-cathode was manufactured on the other side of the paper, exposing the cathode to the air for MFC cathodic reactions.

Figure 2: Schematic illustration of the process employed to create the microbial fuel cell in a single sheet of paper

Hydrophobic wax boundary and ion exchange membrane (Step (1)~(5))

The wax boundary, first printed on both sides of the paper (Xerox phaser printer), was formed into the paper substrate by baking in the oven at 130°C for 2.5min (Fig 2 (1)~(3)). Then another film of wax was printed on bottom side of the paper and subsequently baked for 45s at 130°C to form the ion exchange membrane (Fig 2 (4) & (5)). As the penetration depth of wax is proportional to the heating time, different ion exchange membrane thicknesses can be achieved to optimize the device performance.

Air-cathode preparation on paper (Step (6) ~ (8))

Activated carbon (AC)-based air-cathode was constructed over the ion exchange membrane prepared on the bottom side of the paper. The air-cathode was prepared by applying the AC catalysts (CABOT Corporation) (560mg) with a blinder solution (Fig 2 (6)). The blinder solution was prepared by adding a mixture of (i) 1200μL of 5 wt% Nafion solution, (ii) 150μL of DI water, and (iii) 600μL of isopropanol into a beaker, followed by ultrasonication for 1 min. Then, the conductive nickel was sprayed on top of the AC-based cathode to provide stronger structural support and to function as a current collector (Fig 2 (7)), which was subsequently air-dried for 2h (Fig 2 (8)).

Anode preparation on paper (Step (9) ~ (13))

The anode consists of two parts; (i) a bottom Ppy/CB film to improve the bacterial adhesion/biofilm formation and the electron transfer efficiencies [11], and (ii) a highly conductive nickel film for efficient electron collection. The reservoir was filled with deionized (DI) water and frozen in -20 °C for 2 h (Fig 2 (9)) so that the hydrophilic reservoir region was secured from the top side of the paper during the anode preparation. The Ppy/CB solution was

prepared by suspending 83.5mg of Ppy/CB mixture (Ppy 20wt%, Sigma-Aldrich) in 25mL of 70% v/v ethanol. After we sprayed the Ppy/CB liquid through the patterned mask, the device was air-dried at room temperature for 8 minutes to evaporate the excessive solvent prior to forming nickel film (Super Shield™ Nickel Conductive Coating, MG Chemical) (Fig 2 (10) & (11)). The device was then air-dried for 24h to remove the residual moisture in the anode reservoir and fully solidify the anodic films (Fig 2 (12) & (13)).

Inoculum

Wild-type *Shewanella oneidensis* MR-1 cultivated in L-broth medium (10.0g triptone, 5.0g yeast extract and 5.0g NaCl per liter) at 35°C for 24 hours was subsequently centrifuged and suspended in fresh L-broth medium. The optical density (600 nm, OD₆₀₀) of the bacteria suspension was 2.606Å. Since the centrifugal process removed the shuttle-molecules for extracellular electron transfer (EET), the direct contact of bacteria to the anode is considered to be the major method for EET in this application [12, 13].

Operating principle and measurement setup

When the inoculum was added into the inlet of the device, it was transported throughout the reservoir. The rapid adsorption of the paper promoted bacterial cell attachment to the anode, where bacterial respiration transferred electrons from the organic matter to the anode and flow through an external load while the anode was connected to the cathode. The protons were transferred through the ion exchange membrane and reduced with the oxygen and electrons travelled from the anode. Data acquisition system (NI, USB-6212) with a customized LabVIEW interface were used to measure the potential between anode and cathode (Fig. 3). To determine the current generated by the device, external resistors (10kΩ and 1kΩ) were used to connect the anode and cathode, and current flow through the resistor was calculated by Ohm's law.

Figure 3: Schematic diagram of the device operating principle and test setup (a), and the photo-image of the device measurement (b).

RESULTS AND DISCUSSION

80μL of bacterial inoculum was slowly and carefully dropped on the centers of all the device samples. Upon dropping, the liquid simultaneously spread along the microfluidic inlet channels formed by different anodic configurations and infiltrated underneath the anode. The device samples were first left open-circuit, and then 10kΩ resistors and 1kΩ resistors were subsequently connected to the devices (Fig 4). Once the inoculum was added to the device,

Figure 4: Voltages measured from (a) the devices with different anode coverage, and same microfluidic channel length. And (b) devices with same anode coverage, but different microfluidic channel length.

open circuit voltages (OCVs) and currents with resistors were generated. To maximize the device performance of the device, various anode/reservoir configurations with different microfluidic channel lengths and anode areas were explored in this work [14]. We prepared nine device samples with different anode shapes for two experimental sets. One experimental set had five device samples with the different anode surface areas (or exposed inlet reservoir areas) and the same microfluidic channel lengths (Fig 1b). Another set included five other samples with different channel lengths and the same anode area (Fig 1c). The sample #AP was used for both experimental sets as a reference.

For the first experimental set with the different anode areas (or exposed inlet reservoir areas), the OCVs significantly varied with samples (Fig 5a). The sample #A1 with the smallest exposed inlet area (or the largest anode area) generated the highest OCV while the values decreased with the increase of the inlet areas or the decrease of the anode areas. These results indicate that the larger anode areas provide a greater accessible area for bacteria to attach [15] while the consequently reduced inlet areas decrease the oxygen invasion into the reservoir, ultimately increasing the OCV [16]. In particular, the oxygen penetration into the anode abiotically and biotically reacts with the anode and reduces the OCVs.

When external resistors were connected to the device samples, the higher current densities with the larger anode areas (or smaller exposed inlets) were obtained in the same way as the OCVs (Fig

Figure 5: (a) Open circuit voltages (OCVs) were measured for the first 7 minutes and then all devices were connected to (b) 10 kΩ and (c) 1 kΩ external loads and the currents were calculated. (d) The current density increased with higher anode area coverage under different load conditions.

5b & 5c). The highest current density of $0.87\mu\text{A}/\text{cm}^2$ and power density of $55.2\mu\text{W}/\text{m}^2$ under the 1kΩ was obtained from the device with the largest anode coverage (#A1) (Fig 5c & 5d).

On the other hand, the second experimental set exhibited the similar current densities from the devices with the same anode area (Fig 6) even though there was a significant change in the microfluidic channel lengths. The results indicate that the anode area or exposed inlet region is a more critical factor for the device performance than the microfluidic channel architecture. However, it should be noted that the minor variations in the current generation were observed with the microfluidic geometry of the device inlet, showing that the sample #P1 provided more efficient bacteria cell transportation to the anode than the sample #P5.

The single sheet paper-based MFC showed great potential in terms of device fabrication and cost. For higher performance toward the practical applications, the device array can be readily prepared in a large sheet of paper and a series or parallel

Figure 6: Similar current densities were observed on shapes with same anode coverage under (a) 10 kΩ and (b) 1 kΩ load.

connection can be achieved by folding the sheet or by piling up the several sheets of papers.

CONCLUSION

In this work, we demonstrated a novel and practical technique for manufacturing a bio-fuel cell in a single sheet of paper. The single sheet device platform solved the intrinsic issues generated from the conventional paper-based fuel cell devices such as discontinuity between vertical layers, inconsistent connections between different layers, and complicated fabrication procedure. Furthermore, the proposed design provided an inexpensive, time-saving, and user-friendly device platform that would facilitate studies on the fundamental MFC studies such as effects of different anode materials, MFC device architecture and bacterial cells' transportation on its performance. Although further research has to be done to more accurately characterize and improve the proposed design, the current work shows the great potential of the single sheet paper-based MFC as a novel power source.

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