Characterization of glucose biofuel cell based on electrodes modified by carbon nano horns

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Abstract. In this study, a film-like biofuel cell (BFC) using carbon nano-horn (CNH) as an electrode material was fabricated using micro-electro-mechanical systems (MEMS) technology. The cell was fabricated on a flexible polyimide (PI) substrate, and a porous carbon-coated aluminum (Al) electrode with a width of 3.0 mm and a length of 10 mm was formed using photolithography and screen-printing techniques. The BFC investigated consists of a porous carbon anode (area of 30 mm$^2$) modified by glucose oxidase and ferrocene, and a cathode (area of 30 mm$^2$) modified by bilirubin oxidase. The constructed BFC was able to produce a power density of 18.0 μW/cm$^2$ in phosphate buffer wherein 100 mM glucose was dissolved at room temperature, and this value was at least 10 times that of the BFC reported by Y. Fukushi et al. Furthermore, by examining the temperature-dependence of the BFC’s power density, it was possible to attain a maximum power density of 39.9 μW/cm$^2$ in a phosphate buffer solution wherein 100 mM glucose was dissolved at 40 °C.

1. Introduction

Enzymatic biofuel cells (BFCs) that utilize enzymes as electrocatalysts instead of metals have attracted attention as ubiquitous sustainable power devices that can generate electricity directly from the blood or bodily fluids [1–3]. A characteristic feature of BFCs is their ability to generate power using various kinds of fuels, such as glucose, lipids, and hydrogen. In addition, they function under mild conditions, from room temperature to human body temperature under neutral pH conditions.

Y. Fukushi et al. reported a flexible biofuel cell equipped with a microchannel that mimicked the blood vessels in the human body [3]. Although a BFC fabricated by MEMS technology using ketjenblack (KB) as an electrode material has been reported by Y. Fukushi et al., its power density was only 1.45 μW/cm$^2$, and further improvement in the output was necessary for practical use. The use of KB as an electrode material presents some challenges: the enzyme used as the catalyst is easy to peel off, and the reaction area is small. Therefore, we endeavored to use a carbon nano-horn (CNH) with a specific surface area larger than that of the KB electrode and a structure that is thought to be less susceptible to enzyme peel-off.

CNH has been extensively studied as a catalyst support in hydrogen fuel cells, solar cells, capacitors, and so on, and it is thought to be highly suitable for use as an electrode material in BFCs, since it provides high conductivity and specific surface area, while simultaneously exhibiting high dispersibility. In a previous study of BFCs based on CNH, the CNH was modified by carbon-fiber microelectrodes.
(CFMEs), and the performance was evaluated [4]. There has been no report on the creation of a film-like BFC using CNH to date. In this study, a film-like BFC using CNH as an electrode material was investigated to determine whether flexible glucose BFCs with a high power density could be realized.

2. Experimental

2.1. Power Generation Mechanism

The BFC investigated in this study consists of a porous carbon anode modified by glucose oxidase (GOD) and ferrocene, and a cathode modified by bilirubin oxidase (BOD). Figure 1 shows the power generation principle. Electrons removed from glucose by GOD are transferred to the anode through the ferrocene mediator, and protons are released from glucose at the same time. The electrons flow through the resistance and are delivered to the cathode, where oxygen is reduced by these electrons and protons. The power thus generated can be diverted through an external circuit connected between the anode and the cathode.

2.2. Design of glucose fuel cells with CNH electrode

Figure 2 shows the layout of the cathode and anode. These electrodes were fabricated by photolithography on a polyimide (PI) sheet, coated with aluminum (Al) and then modified by carbon black and respective enzymes. Both the anode and cathode had a width of 3 mm and a length of 10 mm. The gap between the anode and cathode was 1 mm. The anode and cathode were deposited on Al with a width of 3 mm and length of 30 mm. The areas of the anode and the cathode were $3 \times 10$ mm$^2$.

2.3. Fabrication processes of carbon-modified electrodes

Figure 3 (a) First, a layer of Al was deposited on the surface of a PI sheet by thermal vacuum deposition. (b) Then, the photoresist (S1818) was spin coated on the Al film. (c) The electrode pattern was optically defined by photolithography. (d) The Al film was partially removed by wet chemical etching using a solution mixture (dihydrogen phosphate ($H_2PO_3$) : nitric acid ($HNO_3$) : acetic acid ($CH_3COOH$) : $H_2O$ = 2 : 1 : 1 : 1). (e) The photoresist was removed with acetone. After this, carbon-modified electrodes were formed on the surfaces of Al film by screen printing with carbon paste (MRX-713J-A, TAMURA Corporation), which was then cured at 150 °C for 20 min. (f) Finally, the surface of the carbon paste film was coated by screen printing with an ink mixture of carbon nano-horn (CNH, SIGMA-ALDRICH Inc.), and polyvinylidene fluoride (PVDF, KUREHA Inc.), which was subsequently cured at 100 °C for 20 min.
2.4. Fabrication of the enzyme-modified electrodes

A small amount of GOD (0.05 mg) was mixed with 30 μl of phosphate buffer solution (PBS, 50 mM, pH 7.0). Then, 0.05 mg of the ferrocene mediator was mixed with 30 μl of PBS. Subsequently, 10 μl of the resulting solutions was dropped onto the porous carbon anode and left to dry for 90 min. Similarly, 0.05 mg of BOD was mixed with 30 μl of PBS. Then, 10 μl of the resulting solution was dropped onto the porous carbon cathode and left to dry for 90 min. As a reference, carbon electrodes were also fabricated using similar conditions to those previously reported.

2.5. Measurements

Electrochemical measurements were performed in an air-saturated, 0-mM, 50-mM, 100-mM and 200-mM PBS of glucose, at room temperature. Measurements were also performed over a range of temperatures, from 20 to 70 °C, in 100-mM PBSs of glucose. The power generated was evaluated by measuring the cell voltage while varying the external load resistance between 0 and 3 MΩ. W was calculated using the equation \( W = \frac{V^2}{R} \), where R is the load resistance, and V is the generated voltage measured between the terminals of the BFC. The power density was calculated by dividing W by the area of the anode or cathode, which was 30 mm².

3. Results and discussion

Figures 4 and 5 show the measured CV curves of the CNH and KB anodes and cathodes immersed in PBSs with glucose concentrations of 0, 50, 100 and 200 mM. The glucose oxidation current started to rise above 0.1 V for the CNH and KB anodes in 50, 100, and 200 mM glucose and showed the maximum values at 0.4 V. Depending on the concentration, the maximum current density increased and the maximum current density of the CNH anode was 2.50 μA/cm² with 200 mM glucose solutions.
Moreover, the maximum current density of the CNH cathode was 0.89 μA/cm² with 200 mM glucose solutions.

Figure 6 shows a comparison of the relationships between the power density and voltage for the BFCs with CNH and KB electrodes immersed in fuels with different glucose concentrations (0, 50, 100 and 200 mM). The maximum power for the BFC with CNH electrodes was 18.0 μW/cm² at 37 mV for the 100-mM glucose solution, while that for the BFC with KB electrodes was 8.9 μW/cm² at 233 mV for the 100-mM glucose solution. Therefore, the power generation amount of the CNH electrode is twice or more than that of the KB electrode. This is probably due to the fact that the physical adsorption of the enzyme to CNH is superior than that to KB due to the three-dimensional structure.

Figure 7 shows the relationships between the power density and output voltage of the BFCs with CNH and KB electrodes in 100 mM glucose solutions over the temperature range 20–70 °C. An output 2.2 times better than that obtained at room temperature (20 °C) could be confirmed. Below 60 °C, the output was lower than that at room temperature, and at 70 °C, almost no power generation could be confirmed. Since the enzyme is a protein, it is thought that thermal degeneration began at or above 60 °C, resulting in enzyme inactivation.

4. Conclusion

In this study, a film-like biofuel cell (BFC) using carbon nano-horn (CNH) as an electrode material was fabricated using MEMS technology. This BFC was able to produce a power density of 18.0 μW/cm² in a phosphate buffer, wherein 100 mM glucose was dissolved at room temperature. Furthermore, by examining the temperature-dependence of the BFC’s power density, it was possible to attain a maximum power density of 39.9 μW/cm² in a phosphate buffer solution, wherein 100 mM glucose was dissolved at 40 °C.

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