Stretchable glucose biofuel cell with wirings made of multiwall carbon nanotubes

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Abstract. In this study, we fabricated a flexible and stretchable glucose-biofuel cell with wirings made of multi wall carbon nanotube (MWCNTs) on a polydimethylsiloxane substrate. The biofuel cell 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 anode and the cathode were connected with the MWCNT wirings. The maximum power of 0.31 μW at 76.6 mV, which corresponds to a power density of 1.04 μW/cm$^2$, was realized by immersing the biofuel cell in a phosphate buffer solution with a glucose concentration of 100 mM, at room temperature.

1. Introduction
Recently, enzymatic biofuel cells (BFCs) that use glucose in a human body to produce electricity have been of special interest. This is because they work under mild conditions (room temperature, neutral pH and atmospheric pressure), which make them amenable to use in the human body [1-12]. However, when these devices are used in the human body, the flexibility and stretchability of BFCs are among their most important features. Recently, as a potential candidate for a flexible BFC to be used in vivo, Fukushi et al. reported a flexible glucose BFC on a polyimide (PI) sheet because PI offers good biocompatibility, with high thermal stability and flexibility [13]. In addition, Miyake et al. fabricated flexible BFCs with a structure of sandwiched d-fructose dehydrogenase in carbon fabric (CF) [14, 15]. Although these devices were flexible, they were not stretchable. The fabrication of stretchable electrodes and wiring is as necessary as bending flexibility to realize wearable BFCs. Fujimagari et al. recently reported a stretchable glucose BFC using wirings made of silver nanowires [16].

In contrast, carbon nanotube (CNTs) have drawn much attention because they are both electrically conductive and stretchable [17-26]. Polydimethylsiloxane (PDMS) is a material that has been extensively investigated for use in many bidevices because it is biocompatible, flexible, and stretchable [27-30]. For example, Lu et al. fabricated a strain sensor using metal wiring patterns transferred on a stretchable PDMS substrate [31]. We considered that a stretchable wiring for flexible and stretchable BFCs can be realized by utilizing CNTs embedded in a PDMS substrate. However, there has been no report on creation of a stretchable glucose BFC using CNT wirings. In this study, we fabricated a glucose BFC with flexible, stretchable wirings made of multi wall carbon nanotube (MWCNT) on a PDMS substrate.
2. Experimental

2.1. Power Generation Mechanism
The BFC investigated in this research 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 electron flow though the resistance, and are delivered to the cathode where oxygen is reduced by these electrons and protons. The generated power can be diverted through an external circuit connected between the anode and the cathode.

2.2. Design of wiring and electrodes
Figure 2 shows the layout of the cathode, anode and MWCNT wirings. 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 MWCNTs with a width of 3 mm and length of 25 mm. The areas of the anode and the cathode were 3 x 10 mm².

2.3 Wiring fabrication processes
Figure 3 shows the MWCNT wiring fabrication processes. At first, a PI film (Du Pont-Toray Co., Ltd.) with a thickness of 50 μm was cleaned by acetone and ethanol, and place a mask made of polyethylene-terephthalate film with the wiring patterns with the areas of 3 x 30 mm² and the depth of 100 μm [Fig. 3(a)]. 10 mg of MWCNT (Nanocyl) and 136.4 mg of a PDMS precursor (Dow Corning Toray Co. Ltd.) was mixed with the addition of 13.6 mg of a curing agent (Dow Corning Toray Co. Ltd.), and the resultant paste was filed in the wiring patterns of the mask using a screen printing technique. The mask was removed after the solidification of the MWCNT/PDMS mixture. The wiring patterns were cured at 100 °C for 20 min. Another PDMS layer was formed on the top of the wiring patterns on the PI sheet, and the PDMS layer was solidified at 100 °C for 20 min to form the MWCNT wiring embedded in the PDMS substrate [Fig. 3(b)]. Finally, the PI sheet was peeled off [Fig. 3(c)]. A similar stretchable wiring using carbon black was also fabricated using a similar processes using a mixture of carbon black and PDMS. The thickness of the resultant porous carbon electrode was approximately 100 μm.
2.4 Fabrication of the carbon-modified electrodes
The surfaces of the MWCNT wirings film were coated by screen-printing with carbon paste (carbon black) and polyvinylidene fluoride (PVDF, KUREHA, Inc.) mixed ink, which was then cured at 80 °C for 1 h.

![Figure 3. Wiring fabrication processes.](image)

2.5 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. Then, 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 120 min. As a reference, carbon electrodes were also fabricated using similar conditions to those previously reported.

2.6 Measurements
Changes in resistance of the MWCNT or carbon black wirings were measured by stretching the wirings. Each wire was stretched in 2-mm intervals using a jig until it broke. Electrochemical measurements were performed in an air-saturated, 50 mM, 100 mM and 200 mM phosphate buffer solution (PBS) of glucose, at room temperature. The power measurement was performed with the wiring part stretched and the porous carbon electrodes unstretched. The power $W$ generated was evaluated by measuring the cell voltage while varying the external load resistance between 0 and 2.7 MΩ using a source meter (Keithley 2400, Source Meter). The following equation was used to calculate $W$:

$$ W = V^2 / R \quad (1) $$

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 mm$^2$.

3. Results and discussion
Figure 4 shows the resistance change of the wirings with a length of 30 mm, a width of 3 mm and a thickness of 100 μ as a function of elongation. The resistance of a carbon black wiring was also shown as a reference. The resistance change of a carbon black wiring was also shown as a reference. The maximum elongations of MWCNT and carbon black were 10 mm and 30 mm, respectively. The resistance of the MWCNT wirings increased from 267 Ω to 601 Ω, and that of the carbon black wiring increased from 44 kΩ to 55 kΩ at the elongation of 10 mm. The smaller resistance of the MWCNT
wiring compared to that of the carbon black wiring may be due to the wired structure of MWCNTs [26].

Figure 5 shows the relationship between the power density and the output voltage of the BFCs with different wirings. The smaller power density of the BFC with the carbon black wirings was considered due to the larger resistance of the wirings. The power density of the glucose BFC with the MWCNT wirings exhibited the maximum of 1.04 μW/cm² at 76.6 mV, and that of the porous carbon wiring exhibited 0.123 μW/cm² at 44.3 mV.

Figure 4. Change of resistance of MWCNT and porous carbon wirings as a function of elongation.

Figure 5. Relationships between power density and output voltage for BFCs with MWCNT and porous carbon wirings.

Figure 6 shows the relationships between the power density and the output voltage for the BFC measured in glucose solutions with different glucose concentrations of 50, 100, and 200 mM. The power densities for the BFCs in 50, 100, and 200 mM were 0.70 μW/cm² at 65 mV, 1.04 μW/cm² at 76.6 mV, and 1.07 μW/cm² at 80 mV, respectively. The power density was saturated above 100 mM, and this may suggest that the rate of glucose oxidation at the anode was limited by electron transfer processes at the anode.

Figure 6. Relationships between power density and output voltage for BFCs in glucose solutions of 50, 100, and 200 mM.

Figure 7. Relationships between power density and output voltages for BFCs without elongation and with elongation of 2.5 mm in 100 mM glucose solution.
Figure 7 shows a comparison of the relationships between the power density and the output voltage without stretching and being stretched at the elongation of 2.5 mm measured in the glucose solution of 100 mM. The power density without elongation was 0.26 $\mu$W/cm$^2$ at 44.2 mV, and that with the elongation of 2.5 mm was 0.12 $\mu$W/cm$^2$ at 15.7 mV. This reduction of the power density under elongation was due to the increased resistance. The power density without elongation in Fig. 8 was smaller than that of Fig. 7. This is due to the fact the resistance was increased by the contact resistance between the jig and the BFC electrodes.

4. Conclusion
In this study, we fabricated a flexible, stretchable glucose BFC with the MWCNT wirings on a PDMS substrate. The BFC investigated consists of a porous carbon anode (area of 30 mm$^2$) modified by GOD and ferrocene, and a cathode (area of 30 mm$^2$) modified by BOD. The anode and the cathode were connected with the MWCNT wirings. The maximum power of 0.31 $\mu$W at 76.6 mV (corresponding with a power density of 1.04 $\mu$W/cm$^2$) was realized by immersing the BFC in a PBS with a glucose concentration of 100 mM, at room temperature.

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