

# ELECTRICAL POWER GENERATION FROM BIOCHEMICAL ENERGY USING LAMINAR BIOFUEL CELLS

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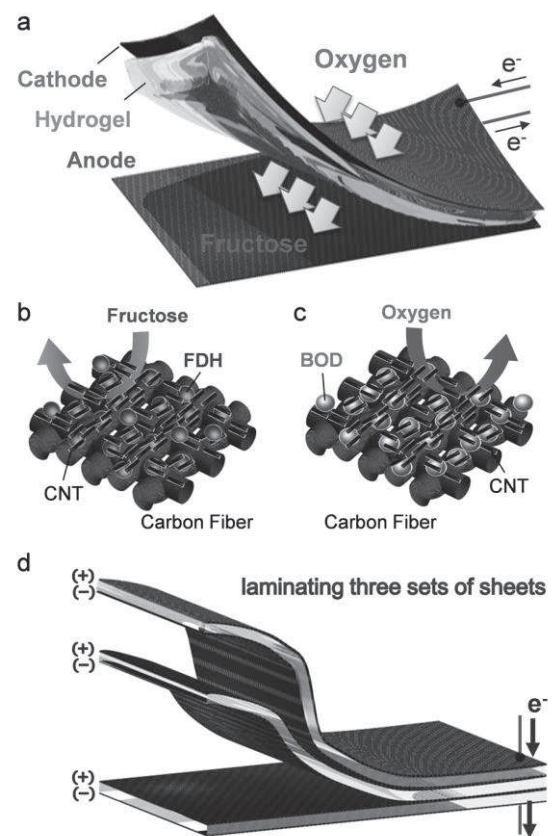
**Abstract:** Similar to conventional electrolyte batteries, biofuel cells often need to be stacked in order to boost their single cell voltage ( $<1$  V) up to a practical level. Here, we report a laminated stack of biofuel cells that is composed of bioanode fabrics for fructose oxidation, hydrogel sheets containing electrolyte and fuel (fructose), and  $O_2$ -diffusion biocathode fabrics. The anode and cathode fabrics were prepared by modifying fructose dehydrogenase and bilirubin oxidase, respectively, on carbon nanotubes-decorated carbon fiber fabrics. The total thickness of the single set of anode/gel/cathode sheets is just 1.1 mm. The laminated triple-layer stack produces an open-circuit voltage of 2.09 V, which is a 2.8-fold increase over that of a single set cell (0.74 V). The present layered cell ( $5\text{ mm} \times 5\text{ mm}$ ) produces a maximum power of 0.64 mW at 1.21 V, a level that is sufficient to drive light-emitting diodes.

**Keywords:** biofuel cell, series-connection, carbon fabric bioelectrode, gas-diffusion biocathode, enzyme-nanotube hybrid

## INTRODUCTION

Enzyme-based biofuel cells (BFCs) that generate electricity through enzymatic oxidation of biological fuels like sugars and alcohols have attracted attention as ubiquitous, safe power sources [1-4]. In this decade, the output current of enzymatic BFCs have been dramatically improved from  $\mu\text{A}$  to mA level [5-8]. In contrast, the cell voltage is determined by the coupling of redox reactions at anode and cathode, and is typically limited around 1.0 V, a value that is insufficient for many practical applications; for example, a single light-emitting diode (LED) requires a voltage larger than 1.6 V. Therefore, in a similar manner to electrolyte batteries, BFCs are often stacked for boosting the output voltage [5, 9-11]. When stacking with series-connections, each BFC should be isolated by proper packaging to prevent short-circuits via ion-conductive fuel solutions, and these packages are then interconnected electrically with metal lead. Such requirements, however, are often troublesome from the standpoint of exploiting the BFC's simplicity and disposability.

In this manuscript, we describe a layered biofuel cell constructed by laminating enzyme-modified carbon fabric (CF) strips and hydrogel film containing electrolyte and fuel as shown in Figure 1. The hydrogel sheets ensure ion-conduction between anode/cathode fabrics, and also serve as the fuel tank that could eliminate the necessity of packaging. A BFC sheet using a conventional agarose [12] was thick and weak due to the fragile nature of agarose. In the present work, we employ a heavy-duty "double



*Fig.1 (a) Schematic illustration of a biofuel cell sheet constructed by laminating enzyme-modified nanoengineered carbon fabric strips with a hydrogel film that retains electrolyte solutions and fructose fuel. (b) Schemes of fructose oxidation at the enzymatic anode. (c) Schemes of oxygen reduction at the enzymatic gas-diffusion cathode. (d) Schematic illustration of multi-lamination for boosting power.*

network (DN) hydrogel”, resulting in a very flexible, thinner BFC (~ 1 mm thickness). The pre-modification of CF with carbon nanotubes (CNTs) was effective to improve the performances of both bioanode and biocathode. The laminated stack of the improved bioelectrodes was practical for LED lighting.

## RESULTS AND DISCUSSION

### Performance of FDH/CNT/CF bioanodes

Figure 2a shows cyclic voltammograms of the FDH/CNT/CF electrodes (solid plots) at  $10 \text{ mV s}^{-1}$  in a stirred buffer solution containing 500 mM fructose. In comparison with the FDH/CF electrode prepared without CNTs (broken line plot), the increased specific surface area produced by CNT-modification obviously increased the current density by at least an order of magnitude. In fact, the measured double-layer capacitance of the CNT-modified electrodes has a 2 orders larger value (ca.  $6.7 \text{ mF cm}^{-2}$ ) than that of the original CF ( $0.07 \text{ mF cm}^{-2}$ ). The oxidation current density depended on the concentration of the Triton

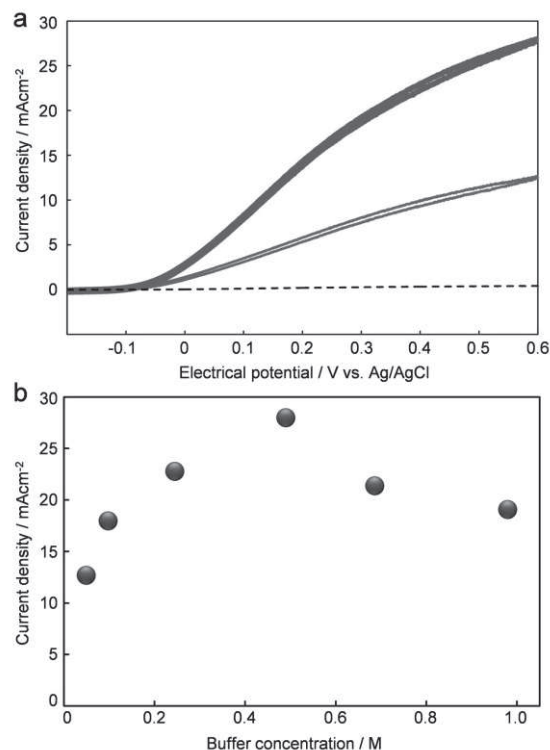


Fig.2 (a) Cyclic voltammograms of fructose oxidation at  $10 \text{ mV s}^{-1}$  in a stirred 50 mM buffer solution (pH 5) containing 500 mM fructose. The CF strip electrodes were modified with only  $10 \text{ mg ml}^{-1}$  FDH (broken line) or with both  $10 \text{ mg ml}^{-1}$  CNT and  $10 \text{ mg ml}^{-1}$  FDH (line). The activity of the bioanode fabric was enhanced by optimizing the buffer concentration to 0.5 M (bold line). (b) Current density at 0.6 V vs Ag/AgCl of the FDH anode measured in different buffer concentration.

X-100 surfactant used for the CNT dispersion [12]. The CNT dispersion with 0.5 % surfactant is capable of entirely penetrating into the CF strip. This uniform modification with CNT would be a reason of the enhanced anode performance. In addition, the electrode performance was drastically enhanced by increasing the buffer concentration in the measurement solutions from 50 mM to 0.5 M (bold line). This is made possible by the existence of adequate buffer capacities that prevent local pH changes caused by oxidation products. Excess buffer concentration, however, lead to a low current density (see Figure 2b). This is probably due to lowering of the enzyme activity because the enzyme is exposed by a high ionic strength solution. The maximum current of the optimized bioanode produced  $15.8 \text{ mA cm}^{-2}$  at 0.6 V using a 500 mM buffer. Even in quiescent conditions, the current reached  $5.8 \text{ mA cm}^{-2}$  at 0.6 V, being equivalent to that in DN hydrogel made with 500 mM McIlvaine buffer solution (pH 5.0) containing 500 mM fructose.

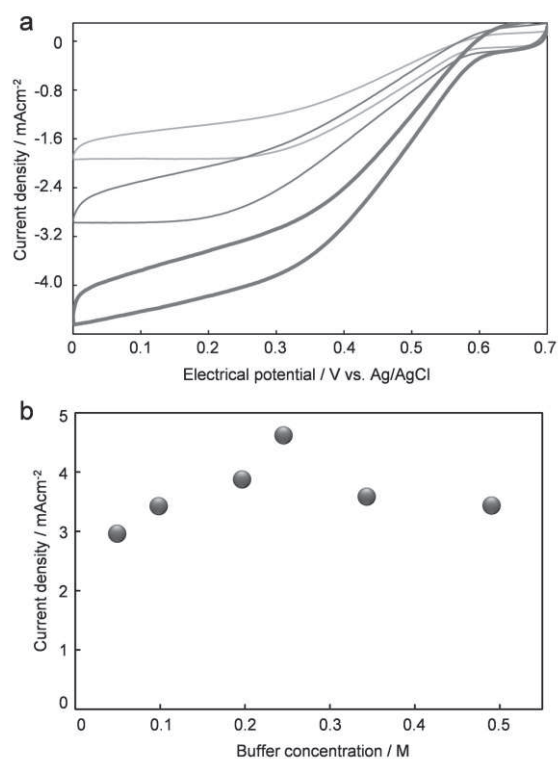


Fig.3 (a) Cyclic voltammograms of  $\text{O}_2$  reduction at a BOD/CNT-modified CF strip measured at  $10 \text{ mV s}^{-1}$  on the solution. The activity of the CF electrode was enhanced by further modification with CNT after the BOD immobilization (line) and by subsequent optimization of buffer concentration (bold line). (b) Current density at 0 V vs Ag/AgCl of the BOD cathode fabric with different buffer concentration.

### Performance of gas-diffusion biocathodes

Figure 3a shows cyclic voltammograms of a BOD-modified CF cathode at  $10 \text{ mV s}^{-1}$ . The electrode strip was put on an oxygenic pH 5.0 buffer solution so as to contact the solution by the BOD-modified face. The reduction current density reaches  $\sim 1.9 \text{ mA cm}^{-2}$  (at 0 V) by utilizing an oxygen supply from the ambient air through the CF. Moreover, an additional CNT coating onto the BOD-modified face of the CF strip enhanced the performance further to  $2.9 \text{ mA cm}^{-2}$ . Presumably, the hydrophobic nature of that coating controls excess penetration of solution into the CF electrodes [12-13]. In addition to optimizing the performance of the bioanode fabric, the cathodic performance can be optimized by changing the buffer concentration (Figure 3b); the maximum current was  $4.6 \text{ mA cm}^{-2}$  at 0 V using a 250 mM buffer condition.

### Performance of the laminated biofuel cell sheets

The FDH/CNT-modified CF anode and the CNT/BOD/CNT-modified gas-diffusion CF cathode were laminated to the opposite faces of a DN hydrogel sheet (0.5 mm thick) made with 250 mM McIlvaine buffer solution (pH 5.0) containing 500 mM fructose. The enzyme-modified hydrophilic anode appeared to become moistened by blotting of the solution from the hydrogel layer. On the other hand, the  $\text{O}_2$  reduction at the hydrophobic cathode proceeded at the three-phase boundary of the hydrogel-electrode interface. Figure 4a shows typical examples of the cell performance. The open-circuit voltage of the cell was 0.74 V, which is similar to the difference between the potentials at which fructose oxidation and oxygen reduction start to occur in cyclic

voltammograms ( $-0.14 \text{ V}$  in Fig. 2a and  $0.60 \text{ V}$  in Fig. 3a, respectively). The maximum

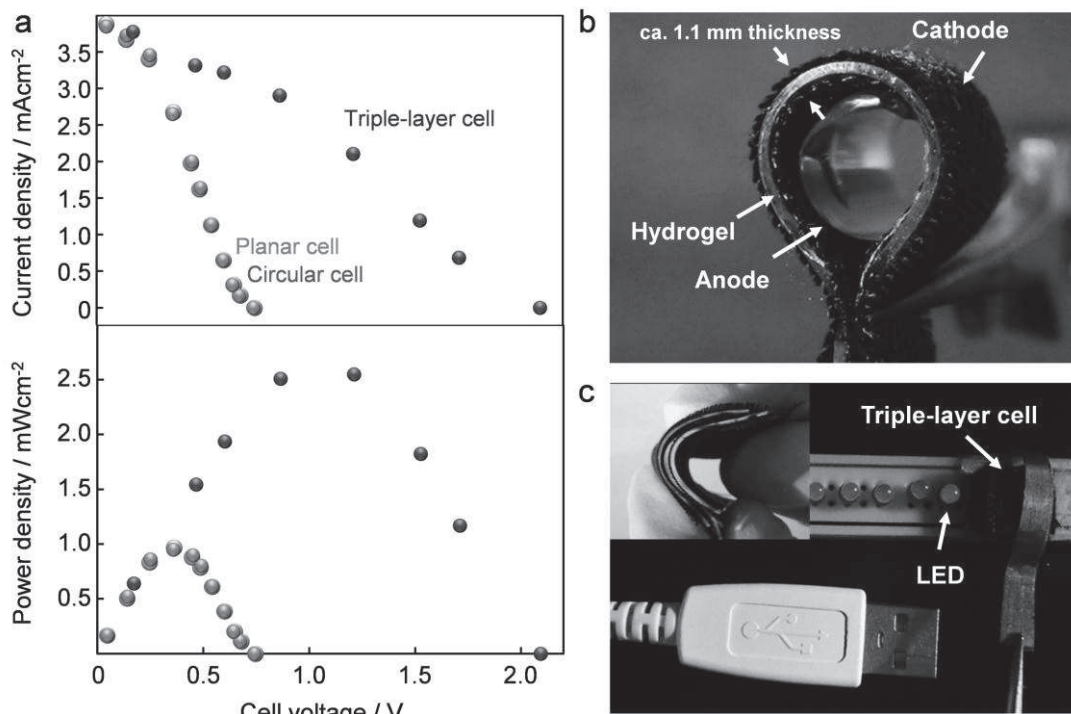


Fig.4 (a) Performance of the biofuel cell ( $1 \text{ cm} \times 0.2 \text{ cm} \times 1.1 \text{ mm}$ ) with and without bending. The internal hydrogel layer was made with 250 mM McIlvaine buffer solution (pH 5.0) containing 500 mM fructose. The performance of a triple-layer cell is also shown. (b) Photograph of the biofuel cell sheet bend into a circle. (c) Photograph of the emission from LEDs connected with the triple-layer cell (inset).

power density reached  $0.95 \text{ mW cm}^{-2}$  at  $0.36 \text{ V}$ , which was determined by the BOD-cathode fabric because of its comparatively inferior activity compared to the FDH-anode fabric. The internal resistance of the cells was negligible small, being  $10 \Omega$  hydrogel resistance and  $26 \Omega$  cell resistance measured by AC impedance spectroscopy ( $\pm 5 \text{ mV}$ ,  $1 \sim 100000 \text{ Hz}$ ). The stability of the cells decreased extremely for few hours. Since the bioelectrodes maintained 85 % performance in 500 mM fructose buffer solution (pH 5.0) for 24 h, the shorter stability is due to drying of the hydrogel.

Importantly, the performance of the cell bent into an circle is almost identical to that of a cell that was not bent. Such high flexibility originates in the superior mechanical strength of both the fabric bioelectrodes and the DN hydrogel. As shown in Figure 4b, the present laminar cell is thin, being only 1.12 mm thick, which also leads to a flexible character. Moreover, owing to the characteristic properties of the hydrogel, the laminar cell requires no sealing frame. Such important cell characteristics confer attractive advantage from a practical viewpoint. The application of such a laminar cell for boosting the output voltage is demonstrated in Figure 4. The booster cell was fabricated simply by lamination of anode/hydrogel/cathode sheets (see Figure 1d). As

shown in Figure 4a, the open-circuit voltage of the laminated cell was 2.09 V, which is 2.8-fold that of a single cell. The maximum current was quite similar to that of the single cell. These results indicate that layered cells can be connected in series without suffering from short-circuit, even without packaging. Ionic isolation between the cells could be avoided by the hydrophobicity of gas-diffusion cathodes and the solid-like property of hydrogels. The laminated cell produced a maximum power of 0.64 mW at 1.21 V ( $2.55 \text{ mW cm}^{-2}$ ,  $6.28 \text{ mW cm}^{-3}$ ); using this level of power, we were able to light the LEDs, as demonstrated in Figure 4c.

## CONCLUSIONS

We have developed layered biofuel cells constructed by laminating FDH/CNT-modified CF strips, fuel-containing DN hydrogel films, and CNT/BOD/CNT-modified gas-diffusion CF strips. A single-layer cell of anode/hydrogel/cathode sheets was very thin (1.1 mm thickness), and exhibited high flexibility, being resistant to a circular bending stress. A triple-layer cell produced a higher open circuit voltage of 2.09 V corresponding to a 2.8-fold improvement over the single cell voltage (0.74 V) and a maximum power of 0.64 mW ( $2.55 \text{ mW cm}^{-2}$ ) at 1.21 V, indicating a successful series-connection even without packaging of each cell. It is important to note the output voltage can easily be tuned by changing the number of layers. Such a flexible, tunable, totally organic power source could be combined in the future with wearable electronics.

## ACKNOWLEDGEMENT

The carbon fabric and carbon nanotubes were kindly donated from Toho Tenax Co. and Bayer Co., respectively. This work was partly supported by the Noguchi Institute and Grant-in-Aid for Young Scientists (B).

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