



Flexible, layered 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 mm \times 5 mm) produces a maximum power of 0.64 mW at 1.21 V, a level that is sufficient to drive light-emitting diodes.

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1. 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 (Heller, 2004; Barton et al., 2004; Cooney et al., 2008; Willner et al., 2009). In this decade, the output current of enzymatic BFCs have been dramatically improved from μ A to mA level (Sakai et al., 2009; Gao et al., 2010; Zebda et al., 2011; Miyake et al., 2011a). 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 (Ferrigno et al., 2002; Sakai et al., 2009; Gullett et al., 2010; Holzinger et al., in press). 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 Fig. 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 (Haneda et al., in press) was thick and weak due to the fragile nature of agarose. In the present work, we employ a heavy-duty "double 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.

2. Experimental section

2.1. Preparation of carbon fabric anodes

A 5 mm \times 5 mm strip (0.3 mm thickness) of carbon fabric (CF) (TCC-3250, donated from Toho Tenax Co.) was first modified with multiwalled carbon nanotubes (CNTs) (Baytubes, donated from Bayer Material Science Co.) to increase the specific surface area (Supplementary Fig. 1). The CNTs were pretreated by heating at 400 °C for 11 h and by immersing in mixed acid ($H_2SO_4 + HNO_3$ in a 1:3 ratio) for 5 h. The treated CNT were dispersed in water containing 0.5% Triton X-100 surfactant. A 40 μ l aliquot of the 10 mg ml⁻¹ CNT dispersion was dropped on a CF strip and dried in air. After degassing the CNT-modified strip by immersion in a stirred McIlvaine buffer solution for more than 1 h under vacuum

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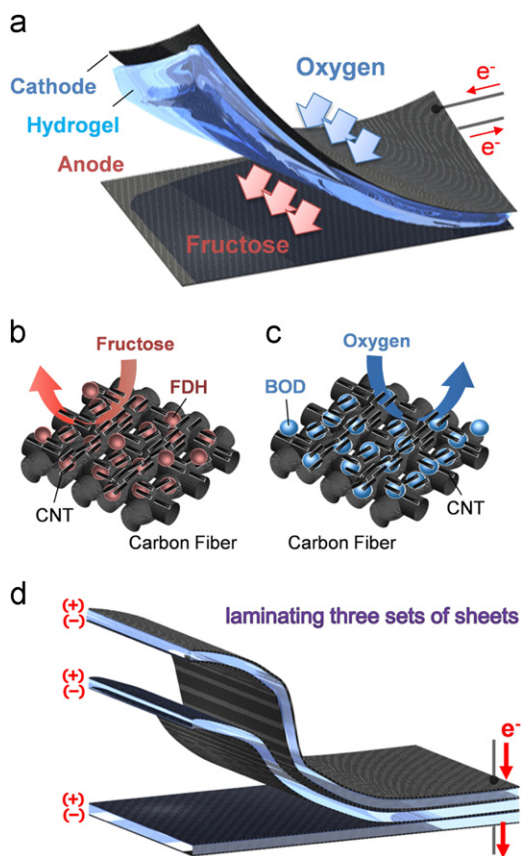


Fig. 1. (a) Schematic illustration of a biofuel cell sheet constructed by laminating enzyme-modified nanoengineered carbon fabric strips with a hydrogel film that retains electrolyte solutions and fructose fuel. (b) Schemes of fructose oxidation at the enzymatic anode. (c) Schemes of oxygen reduction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

(0.09 MPa), the CNT-modified strip shows hydrophilic property. Then, the CNT-modified CF strip was immersed in a stirred solution of D-fructose dehydrogenase (FDH) (EC1.1.99.11, 169.9 U mg⁻¹, ca. 140 kDa, from Gluconobacter, purchased from Toyobo Enzyme Co.) for FDH immobilization (Tominaga et al., 2009; Tsujimura et al., 2010; Miyake et al., 2011b). It has been reported that FDH works as an electrocatalyst for two-electron oxidation of fructose (Tominaga et al., 2007; Murata et al., 2009). The flavin-containing subunit of FDH accepts electrons from fructose, and transfers these electrons to the heme c-containing subunit that can electrically communicate with electrode. A geometric area of 0.564 cm² was utilized for calculation of the current density in cyclic voltammetry (CV).

2.2. Preparation of gas-diffusion carbon fabric cathodes

The preparation of the cathode basically followed the procedures used for our previous carbon particle (ketjenblack)-based BOD cathode (Miyake et al., 2011b; Haneda et al., in press). BOD is one of the multi-copper oxidases that can directly catalyze the four-electron reduction of O₂ to H₂O even without electron transfer mediators (Tsujimura et al., 2007; Wen et al., 2011). The type 1 Cu site of BOD accepts electrons from fabric electrode, and transfers these electrons to the type 2–3 cluster of BOD for O₂ reduction. A 40 μl aliquot of a 10 mg ml⁻¹ CNT solution was put on a CF strip and dried in air, followed by thoroughly washing out the surfactant by soaking in an ethanol solution for more than 1 h with stirring. The surface of the CNT-modified CF electrode was

further modified with a 0.1 ml solution of 5 mg ml⁻¹ bilirubin oxidase (BOD, EC 1.3.3.5, 2.5 U/mg, from Myrothecium) in vacuum oven (AVO-205N, purchased from AS ONE, 0.09 MPa, 35 °C). The strip was additionally coated with the CNT solution to make the surface hydrophobic. A surface area of 0.25 cm² was utilized for calculation of the current density in cyclic voltammetry (CV).

2.3. Preparation of the hydrogel films

The fructose-containing double-network (DN) hydrogel films were prepared by a three-step process (Gong, 2010; Wu and Gong, 2011): (1) single network hydrogel formation, (2) second network formation into the single network hydrogel and (3) loading of 500 mM fructose. We used stock solutions A, B and C. Solution A contains 2-acrylamido-2-methylpropane (AMPS, 1 M), N,N-methylenebisacrylamide (MBAA, 40 mM), 2-oxoglutaric acid (OA, 1 mM) and ammonium persulfate (APS, 19 mM). Solution B was a mixture of acrylamide (AAM, 4 M), OA (1 mM), NaCl (80 mM) and APS (19 mM). Solution C contains AAm (2 M), OA (1 mM) and APS (19 mM). At first, the solution A was poured into a silicone mold, and preliminarily crosslinked by UV exposure (265 nm, 8 W) for 5 h. The formed soft gel was then immersed in solution B for 14 h to prevent dramatic swelling and further irradiated with the UV lamp for 5 h to reinforce the gel in order to become a sheet. After washing with water for 24 h, the gel sheet was immersed in solution C for 14 h followed by UV irradiation (5 h) to form a DN network. Finally, the DN gel sheet was immersed in 500 mM fructose solution for 24 h.

2.4. Electrochemical measurements

The performance of the CF electrodes was analyzed by a three-electrode system (BSA, 730C electrochemical analyzer) in solution using a Ag/AgCl reference and a platinum counter electrode. The FDH-modified anodes were evaluated in stirred McIlvaine buffer (pH 5.0) containing 500 mM fructose, while the BOD-modified cathodes were used in air-saturated McIlvaine buffer (pH 5.0). The performance of a biofuel cell sheet constructed using the fructose-containing DN hydrogel film (0.5 mm thick) was evaluated from the cell voltage upon connecting with a variable external resistance between 180 Ω and 10 kΩ. The current and the power were derived from the cell voltage and the resistance. Unless otherwise indicated, the electrochemical measurements were carried out at room temperature, around 25 °C.

3. Results and discussion

3.1. Performance of FDH/CNT/CF bioanodes

Fig. 2a shows cyclic voltammograms of the FDH/CNT/CF electrodes (solid plots) at 10 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 mF cm⁻²) than that of the original CF (0.07 mF cm⁻²). The oxidation current density depended on the concentration of the Triton X-100 surfactant used for the CNT dispersion (Haneda et al., in press). The CNT dispersion with 0.5% surfactant is capable of entirely penetrating into the CF strip (see Supplementary Fig. 1b). This uniform modification with CNT would be a reason for the enhanced anode performance. In addition, the electrode

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