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Stability of carbon nanotube yarn biofuel cell in human body fluid

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HIGHLIGHTS

- A yarn-type enzymatic biofuel cell was developed with enhanced long-term (>20 days) stability.
- Enzymatic biofuel cell generates an open circuit voltage of 0.80 V in human blood serum.
- The maximum power density of 1.1 mW cm^{-2} was obtained at an operating voltage of 0.50 V in human blood serum.

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ABSTRACT

High performance with stability, easy-handling electrodes, and biofluid-flow controllable system with mechanical strength of the biofuel cell can be considered as the critical issues for future human body implant. These three challenges are sufficiently considered by using the effective platform regarding the high surface area from multi-walled carbon nanotube-conducting polymer with poly(3,4-ethylenedioxythiophene), and size/shape dependent flexible yarn electrodes for the implantation of biofuel cell. High power biofuel cell of mW cm^{-2} range in physiological condition (low glucose-containing phosphate buffered saline solution and human blood serum) controlling the stirring degree is also first demonstrated for future implantation in this study. Biofuel cells for future implantation in human body vitally require long-term stability and high power outputs. We have demonstrated that a high-surface area yarn-based biofuel cell retained over 70% of its initial power output after an extended 20 days period of continuous operation in human blood serum, while delivering a power density of ~1.0 mW cm^{-2}. Subsequently, our enhanced enzymatic biofuel cell system would be potentially used as an innovative power source for the next generation implantable electronics.

1. Introduction

Biofuel cells (BFCs) are of great interest as power sources for implanted miniaturized biomedical devices since they offer continuous power supply through conversion of biochemical fuels, such as glucose [1]. Implantable electrodes (or devices) need to satisfy many criteria such as biocompatibility, miniaturization, easy-handling, robustness, high power output, high durability, and long-term stability.

To date, the best performing BFCs operating in near physiological conditions have generated a power density of the order of 1 mW cm^{-2}. Kim and Yoo have reported an output of 0.64 mW cm^{-2} in serum condition that operated stably for eight days [2]. In another recent result, a maximum power density of 0.11 mW cm^{-2} was reported in human serum (10 mM glucose solution) [3]. We have recently also reported a BFC operating for 2 days and producing ~1 mW cm^{-2} in both low concentration glucose, 7 mM, in phosphate buffered saline (PBS) and in human blood serum (HBS) [4]. Power generation was even lower in implanted BFC operating in a live cockroach [5]. Under 50 mM trehalose in PBS solution and cockroach hemolymph (ca. 5%) the power outputs were 15 μW cm^{-2} and 55 μW cm^{-2}, respectively.

Enzyme-loaded BFC electrodes tend to suffer degradation due to the presence of chemical species, such as urate, chloride ion, and ascorbic acid which exist at high level in the biological systems like

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HBS [6]. Urate induces remarkable deactivation of bilirubin oxidase as commonly used in the BFC cathode and ascorbic acid decreases the open circuit voltage. As a consequence, BFC performance can deteriorate within hours of operation in physiological conditions. Our enzymatic BFC system was effectively operated with no significant performance loss and stability decline for two days in HBS. The electrodes consist of porous yarns of multi-walled carbon nanotubes (MWNT) coated in poly(3,4-ethylenedioxythiophene) (PEDOT) and incorporating electrode specific enzymes and redox mediators. The high stability and tolerance to antagonistic chemical species was ascribed to the cation-exchange nature of the PEDOT that reduced the rate of degradation without compromising electrode conductivity [4]. These fiber type electrodes have high surface area to volume ratios and can be assembled into compact, robust systems, such as woven textiles [4]. These characteristics favorably compared with film [7] or disk [8] type electrodes that can have relatively low volumetric power density and can be difficult to insert and handle.

BFC power output is dependent on glucose concentration which is also related to blood flow rates in implanted devices. We have shown in our recent study [4] that power output can be doubled by increasing the glucose concentration from 7 mM to 60 mM in PBS. Normal blood flows are very different around major organs such as the heart, liver, or kidney [9]. Yet only a few studies have reported on the effect of biofluid flow on BFC power output [10,11]. In one recent example, an implantable biofuel cell system was used with lobsters [12] to mimic human blood circulation for a resting person (58.9 μl min^{-1}) and a person performing physical activity (235.6 μl min^{-1}). These markedly different flow rates highlight the importance of characterizing BFC performance under different flow conditions, such as by varying stirring speeds.

Here we investigate further the BFC performance in physiological conditions of the MWNT/PEDOT yarn based enzymatic electrodes. In particular, we consider the effect of electrolyte flow rate on BFC power output to determine the likely influence of varying blood flow rates. Secondly, we evaluate the performance of the BFC during continuous operation up to 20 days.

2. Experimental

2.1. Materials

MWNT forests (~400 mm high and consisting of ~12 nm diameter nanotubes) were grown on a Si wafer by chemical vapor deposition. PVA (Mw 146,000–186,000), iron(III) p-toluenesulfonate hexahydrate (Fe(III)PTS), pyridine (anhydrous, 99.8% purity), 1-butanol (~99% purity) and 3,4-ethylenedioxythiophene (EDOT, 97% purity) were from Sigma–Aldrich Corporation and 1 M aqueous sulfuric acid solution was from Daejung Chemicals and Metals Company. The guests of BFC electrode consist of redox mediator, enzyme, and cross-linker. The anodic redox mediator I was PVI-Os(dmo-bpy)$_2$Cl$^{+/2+}$, poly(N-vinylimidazole)-[Os(4,4′-dimethoxy-2,2′-bipyridine)$_2$Cl])$^{+/2+}$, and the cathodic redox mediator II was PAA-PVI-Os(dCl-bpy)$_2$Cl$^{+/2+}$, poly(acryl amide)-poly(N-vinylimidazole)-[Os(4,4′-dichloro-2,2′-bipyridine)$_2$])$^{+/2+}$. Glucose oxidase (GOx) from *aspergillus niger* (219 U mg^{-1}) from Amano Enzyme Inc. (Japan) was used as an anodic enzyme. Bilirubin oxidase (BOD) from *myrothecium verrucaria* (10.5 U mg^{-1}, Sigma Aldrich was used as a cathodic catalyst. Poly(ethylene glycol) diglycidyl ether (PEGDGE) from Polysciences, Inc was used to cross-link each enzymes and redox mediators. Human blood serum (HBS) was purchased from Biological Specialty, USA. Glucose level of HBS was 4 mM–7 mM, as they reported.

2.2. Characterizations and electrochemical measurements

Surface morphologies of BFC electrode were characterized using scanning electron microscopy (Hitachi S4700). For electrochemical measurements, linear sweep voltammetry was obtained using electrochemical analyzing system (CHI 627B from CH Instruments). A three-electrode electrochemical system was used for cyclic voltammetry and chronoamperometry. A biscrolled yarn electrode was used as the working electrode, with Ag/AgCl reference electrode and a Pt mesh counter electrode. The measurements were conducted at 37 °C under the same condition with the human body in an electrochemical cell containing 50 mL PBS solution (20 mM phosphate, 0.14 M NaCl, pH: ~7.4) or HBS.

2.3. Fabrication of BFC biscrolled yarn electrodes

Biscrolled yarn was fabricated with a PEDOT-coated MWNT sheet and guest materials. Guests-filled PEDOT-coated MWNT sheet was slowly twisted using the motor with ~5000 turns per meter of inserted twist per yarn length. After twist insertion, both ends of the biscrolled yarn were fixed to the glass slide using carbon tape and BFC biscrolled yarn was cured at 4 °C for 24 h. Both the anodic yarn electrode (3.5-mm-long, 90-μm-diameter) and the cathodic yarn electrode (4.0-mm-long, 80-μm-diameter) were used and an active external surface area was 1.01 mm^2 for this study.

3. Results and discussion

3.1. Yarn-based anodic and cathodic electrode performance considering the flow of human body fluids

The complete BFC system is introduced in Fig. 1. PEDOT-coated MWNT sheets was used as a host material for our enzymatic BFC system. This PEDOT-coated MWNT sheet was dipped into each guest solution specifically developed for anodic and cathodic electrodes (Fig. 1a). Twisting the sheet (Fig. 1b) completed the fabrication of the biscrolled yarn electrodes for both anode and cathode. Scanning electron microscopy (SEM) image shows BFC electrode surface in Fig. 1c revealing the PEDOT-coated MWNT bundles. Enlarged surface and cross-section images are shown in Fig. 1d,e. The cross-section clearly shows the porous vascular structure that is important for fast mass transport of the fuels, glucose and oxygen, to the reaction centres imbibed within the PEDOT coating.

The electrochemical characterization of the enzymatic BFC electrodes were measured in two buffer conditions, PBS containing low glucose and HBS, and at different stirring rates. Anodic current densities were measured at various glucose concentrations from 0 to 15 mM in PBS (Fig. 2a). Power densities increased almost linearly with glucose concentration over this range. Higher power outputs at a given glucose concentration were achieved with more intense stirring of the buffer solution. Linear sweep voltammetry was conducted at a glucose concentration of 7 mM, which is similar to that of HBS. The linear sweep clearly show the current limited by concentration polarization at potentials above ~0.05 V. The maximum anodic current densities were higher in PBS than in HBS and increased by moderate stirring at 500 rpm. The maximum current density (from the average value of the range between +0.2 V and +0.4 V), as shown in Fig. 2b was 4.7 mA cm^{-2} without any stirring effect and 5.5 mA cm^{-2} with 500 rpm in PBS containing 7 mM glucose fuel, and 4.0 and 5.2 mA cm^{-2} in HBS. These current densities are relatively high compared to the previously reported result of 0.6 mA cm^{-2} under physiological condition (quiescent solution, air, PBS buffer, 15 mM glucose, 37 °C) [13].

Cathodic current density performance is shown in Fig. 3a.