Research Article

Carbon Nanotubes Modified Carbon Cloth Cathode Electrode for Self-Pumping Enzymatic Biofuel Cell

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A self-pumping enzymatic biofuel cell (self-pumping EBC) with a new cathodic catalyst which was modified by coating the mixture of carbon nanotubes/cafeic acid (CNTs/CA) on a carbon cloth (CC) to form a CNTs/CA/CC cathode electrode was fabricated. By using UV spectrophotometer, the absorbance of CA, CNTs, and the CNTs/CA composite was observed. To evaluate how the CNTs/CA/CC cathodic electrode improves the electrochemical performance of the self-pumping EBC, the measurement of the redox reaction current peak by cyclic voltammetry (CV) was implemented. In accordance with CV measurement, the utilization of the modified CNTs/CA/CC cathodic electrode exhibited a higher oxygen reduction current peak at 319.1 μA under the saturated oxygen. The anode and cathode flow rates were 0.416 $\mu\text{L s}^{-1}$ and 0.844 $\mu\text{L s}^{-1}$ which contribute to obtaining the capillary driven liquid efficiency as 30% for the former and 59% for the latter. Moreover, the self-pumping EBC performance tests showed that the maximum power density (MPD) of the self-pumping EBC with the modified cathodic electrode achieved 0.592 mW cm^{-2} which improved 10% in the performance compared with the bare CC electrode, 0.534 mW cm^{-2} .

1. Introduction

Biofuel cell converts chemical energy into electrical energy through a series of biochemical reactions by utilizing biocatalyst. Compared to many traditional environment-friendly energy sources, such as wind power, solar power, and geothermal power generation, the biofuel cell (BFC) is a growing alternative energy source. According to the type of catalyst, the biofuel cell can be separated into the fuel cell as microbial biofuel cell (MBC) that uses micro bacteria to react for electricity and enzymatic biofuel cell (EBC) that employs enzymes as a catalyst to separate electrons from parent molecule and force it to go around an electrolyte barrier through a wire to generate an electric current. This study is focusing on the EBC type that produces higher electrochemical performance and more simple structure compared to the MBC [1, 2].

The unique characteristic of the EBCs is that enzymes are used as biocatalysts in the redox reaction such as glucose

dehydrogenase [3, 4], glucose oxidase [5–7], laccase [8, 9], and alcohol dehydrogenase [10]. The mechanism for oxidizing GOx is described in Figure 1. The GOx immobilized on the anode surface reacts with glucose to produce protons and electrons while the incoming electrons moving from the anode to the cathode electrode via the external circuit decrease the ferricyanide ($\text{Fe}[\text{CN}]_6^{3-}$) to ferrocyanide ($\text{Fe}[\text{CN}]_6^{4-}$). Simultaneously, protons that migrate through the Nafion⁵ 117 membrane to the cathode compartment reduce oxygen to water and reoxidize ferrocyanide to ferricyanide.

Chitosan (CS) is a physicochemical biopolymer for enzyme immobilization with the attractive properties such as an excellent film-forming ability and a good adhesion, non-toxicity, and biocompatibility [11]. Y. Zhang and coworkers [12] developed a new glucose biosensor by coating CS as a protection film on the surface of GOx. B. K. Shrestha et al. [13] succeeded in fabricating the electrode immobilized

FIGURE 1: Enzymatic biofuel cell schematic showed the major components and its basic operation.

CS-GOx on its surface to achieve a high-performance glucose biosensor.

Carbon nanotubes (CNTs) electrode and modified carbon electrode, the prominent materials for their application in bioanalytical devices, are particularly appropriate to establish an efficient electrical communication between enzymes and electrode [5–7, 14]. The research of A.B. Moghaddam and coauthors [15] indicated that SWCNT with graphite-based electrode offered an improvement in the CA electrochemical behavior and investigated the influence of the scan rate in the CA oxidation by CV measurement. With the presence of CA, the anodic and cathodic peak was 17-fold higher than that of a bare GCE [16].

Based on the fuel delivery mechanism, the fuel cell system is divided into an active system and passive system using an extra pump and capillary effect, respectively. The input power of the pump in the active ones is sometimes much larger than that of their output power. On the other hand, the delivered fuel in the passive system works through the capillary effect [17]; the fuel concentration gradient diffuses into the anode component [18]; the cohesion and adhesion pressure causes the liquid fuel to work against the gravity [19]. In our previous research, Y.F. Tsai and H. Yang [20] successfully turned out a new research direction that their fabricated EBC can drive fuel by itself through the capillary effect named self-pumping enzymatic fuel cell whose maximum power density was quite low.

With the above information, in this study, the self-pumping EBC is with a modified CC at the cathode and anode electrode CNTs/CA/CC and GOx[TPP/CS/CC], respectively, to enhance the self-pumping EBC's electricity. The GOx[TPP/CS/CC] electrode was prepared by the same method in the previous study [20], where CS solution was coated on the surface of the anodic electrode as an adhesion film to ensure the stability and biocompatibility of the enzyme GOx on the electrode surface. The fabricating process of the new catalyst attached to the cathode electrode CNTs/CA/CC is described in Section 2.3. Whether the CNTs/CA can improve the redox current as well as the power output of the self-pumping EBC through several methods such as UV

spectrophotometer, CV measurement, and polarization test (Tafel test) was evaluated, and the performances of the self-pumping EBC were successfully investigated.

2. Experimental

2.1. Materials. Glucose oxidase from *Aspergillus niger* (Gluzyme Mono® 10.000 BG) was obtained from Novo Nordisk Bioindustrials Inc. (Copenhagen, Denmark). Carbon cloth was obtained from CeTech Co. (domestic company). MWCNTs were purchased from Carbon Science and Technology (Taiwan). Caffeic acid (CA) powder was obtained from Sigma-Aldrich. CS powder (MW 140000 dal/mol) with 90% deacetylation and sodium tripolyphosphate (TPP) were purchased from Shin ERA Technology Co., Ltd. (Taiwan). Potassium hexacyanoferrate(III) ($\text{K}_3[\text{Fe(CN)}_6]$) was obtained from Wako Chemicals (USA). Nafion 117 membranes (DuPont) were pretreated before being applied to the electrode.

2.2. Preparation of Anodic Electrode Immobilized GOx Enzyme. The fabricating process of anodic electrode GOx(TPP/CS/CC) was described previously [20]; however, a short summary will be given for convenience. There were three separate steps in the fabrication process of the anodic electrode. (1) The first step is the preparation of CS carrier acidic solution: dissolving 1 g of CS in 100 ml of 1% (v/v) acetic acid under magnetic stirring is to make the acidic aqueous solution. Simultaneously, 25 mg TPP was added to 25 ml of deionized water (D.I. water) to prepare a 50 wt% TPP cross-linker aqueous solution, followed by adding the cross-linking agent aqueous solution to the preprepared CS solution and thoroughly stirring the mixture. (2) The second step is the preparation of alkaline solution: 4g of NaOH was added to 100 ml of deionized water to create 1 M NaOH solution. A small piece of the acidic pretreated carbon cloth ($2 \times 3 \text{ cm}^2$) was first immersed in the CS carrier/cross-linking reagent solution and sonicated for 10 min to coat the CS/TPP cross-linked on CC surface followed by transferring the cross-linked CC into the NaOH solution

FIGURE 2: EDC, NHS, and GOx reaction mechanism for activated and stabilized enzyme.

to precipitate the coated CS. The washing procedure was repeated 3 times to remove the residue from the NaOH solution on the surface of the modified CC which was stored in D.I. water for usage. (3) The third step is the immobilization of enzyme GOx (Figure 2): 40 mg GOx was added to the prepared phosphate buffer solution (PBS, pH 6, 50 mM) and stirred until it was completely dissolved. The GOx solution was continuously mixed with NHS aqueous solution (4 mg/ml, stirred at 110rpm for 1 h) and EDC aqueous solution (2.4 mg/ml, stirred at 110rpm for 1 h) for enzyme activation and stabilization [21]. The CS/TPP coated CC was finally immersed in the activated GOx solution.

2.3. Preparation of Cathodic Electrode. For preparing the cathodic electrode CNTs/CA/CC, after CNTs was purified by the acidic treatment that was the mixture of the sulfuric acid (H_2SO_4) and nitric acid (HNO_3) at the concentration of 3:1, 10 mM CA was combined with 10 mg/ml purified CNTs dissolved in 5 ml of ethanol solution and shaken by ultrasonic bath for 16 h. As shown in Figure 3, the bottle on the left side is the CNTs/CA catalyst and bare CNTs on the right side. After dispersion for 16 h, the CNTs/CA were completely mixed with each other in the ethanol solution, whereas the CNTs in the bottle with the absence of CA precipitated at the bottom. The CC was then immersed in the CNTs/CA solution and sonicated for 10 min so that the CC surface was completely coated with CNTs/CA. Because the reduction reaction at the cathode requires a large reduction current, the employment of the new catalyst CNTs/CA/CC supports increasing the reduction reaction current peak.

2.4. Fabrication of Self-Pumping EBC. The whole EBC stack and its components were shown in Figure 4, which consists of top and bottom end plates, PDMS gasket, cathode and anode flow field plate, current collectors, rubber gasket, the modified cathode and anode electrodes, and Nafion 117 membrane located in between the two electrodes composed as a sandwich structure. The cathode electrode is modified by CNTs/CA/CC, while the anode electrode was covered by GOx[TPP/CS/CC]. The fuel used as an anolyte is the mixed solution of 0.1 M glucose, 0.1 M NaCl, and 0.1 M PBS, pH7, whereas the mixture of 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M PBS pH7 was used as catholyte.

There are three reservoirs in both top and bottom plate structures as shown in Figure 5. Reservoir 1 is the fuel supply and reservoirs 2 and 3 installed a well wettability cotton to intrigue the self-pumping structures. The fuel was added to reservoir 1 and transported to reservoir 2 by capillary force. By the end, the fuel was transported to the flow field. Sufficient fuel filling can be observed in the wettability of reservoir 3. Then the flow rate was determined by collecting the 500 mm³ fuel each time based on the elapsed time. The fuel eventually flowed through the anode flow field, where the oxidation reaction occurred and was then transported to the outlet reservoir 3 (Figure 5).

3. Results and Discussion

3.1. Electrode Hydrophilic Modification. For the self-pumping EBC, the capillary force requires higher hydrophilic properties of the anode and cathode electrodes. By using Optical Contact Angle Meter Model 100SB, the original carbon

FIGURE 3: CNTs and CNTs/CA dissolved in ethanol. (a) 0 h. (b) 4 h. (c) 8 h. (d) 16 h.

clothes used as anode and cathode sides of the self-pumping EBC were hydrophobic with the surface contact angle of 138.80° (Figure 6). To modify the surface of CC electrode being hydrophilic, the CC was immersed in the mixture of acids (H_2SO_4 : $\text{HNO}_3 = 3:1$) and then sonicated for 5 min to produce hydrophilic carboxyl functional group (COOH) [22]. The contact angle measurement of the treated carbon materials was then observed to be nearly 0° (Figure 6).

3.2. Electrode Structural Characterization. The chemical structures of GOx (curve a), CS/CC (curve b), and GOx[CS/CC] (curve c) were characterized by FTIR spectroscopy shown in Figure 7. The appearance of the characteristic absorption peak of the tested electrode (c) at 2873 cm^{-1} was different from (a) and (b) that represented the GOx enzyme successfully immobilized on the CS/CC electrode. In FTIR spectra of native GOx (curve a), the strong absorption peak at 3300 cm^{-1} is prescribed to the N-H stretching as well as the typical peaks observed at 1650 and 1526 cm^{-1} which are characterized by amide I ($\text{C}=\text{O}$) stretching vibrations and amide II (N-H and C-N

stretching) bands of native GOx. The FTIR spectrum showed the CS/CC electrode as curve b; the major peaks have $\text{C}=\text{O}$ and amide NH_2 stretching vibration (1080 and 1597 cm^{-1} , resp.).

UV spectrophotometric method was developed in this study for quantification of the interaction ability of CA and CNTs in the CNTs/CA solution that was coated on the cathode electrode CNTs/CA/CC. Figure 8 showed the UV spectra of the supernatants of CNTs/CA adduct (curve a), free CA (b), and CNTs (c). The spectrum of CA in aqueous solution displayed a maximum absorption peak at 325 nm . The UV spectra of the CNTs dispersed in aqueous solution exhibited strong absorbance at 210 nm . It is obvious that the chemical absorption of the CNTs/CA composite displayed two strong peaks at 210 nm and 325 nm (curve a).

3.3. Electrochemical Characterization. To estimate the effect of the CNTs/CA composite on the electrochemical properties of the self-pumping EBC and to know whether the CNTs could enhance the redox current peak, CV curves of

FIGURE 4: Single self-pumping EBC assembly as a sandwich structure and related components.

the CNTs/CC, CA/CC, and CNTs/CA/CC were measured under the saturated oxygen condition (Figure 9). The CVs of the catalysts were performed by using a 3-electrode system (Zennium E Electrochemical Workstation) with an Ag/AgCl reference electrode, a Pt wire counter electrode, and the working electrode of the CNTs/CC, CA/CC, and CNTs/CA/CC submerged in the 20 ml solution of 0.1 M $K_3Fe(CN)_6$ and 0.1 M KCl at the potential range of +0.7V~0.3V and the scan rate of 0.1 V.s⁻¹. The working electrode was prepared by loading catalyst (CNTs, CA, and CNTs/CA) on glassy carbon electrode (GCE, 3 mm in diameter). According to Figure 9, there was no current signal of the electrode with free CA (curve a) caused by no catalytic reaction of oxygen, while a small current peak of 30.9 μA was found in the electrode with CNTs (curve b). However, when CNTs/CA/CC was tested under the same condition, the peak current was significantly higher than those of the CNTs/CC or CA/CC. Curve (c) showed the reduction reaction current peak of 139.1 μA at the potential of 0.12 V. This phenomenon was the evidence of the effectiveness of coating CNTs/CA on the cathode electrode which enhanced the oxygen reduction reaction peak.

To further study the electrochemical reaction, the CV tests of the CNTs/CA/CC under different types of gases such as saturated argon, air, and saturated oxygen were measured (Figure 10). It is noted that the polarization curve of the CNTs/CA/CC electrode under the saturated oxygen

TABLE 1: The capillary driven fluid efficiency.

Flow rate (Q)/efficiency(μ)	Anode	Cathode
$Q_{ideal} (\mu l.s^{-1})$	1.40	1.43
EBC without modified CNTs/CA/CC		
$Q_{actual} (\mu l.s^{-1})$	0.499	0.764
$\mu_{capillary} (\%)$	35	53
EBC with modified CNTs/CA/CC		
$Q_{actual} (\mu l.s^{-1})$	0.416	0.844
$\mu_{capillary} (\%)$	30	59

condition (curve c) showed the highest current peak (321.5 μA) compared with the other two cases.

3.4. Performance of Self-Pumping EBC. In the electrical performance tests of the whole cell, the 0.1 M glucose mixed 0.1 M NaCl solution and 0.1 M $K_3Fe(CN)_6$ solution were fed into the anode and cathode, respectively, by the capillary force at different flow rates for both types of EBC (Table 1).

Theoretically, the ideal flow field solutions of cathode and anode were 1.43 and 1.40 $\mu l.s^{-1}$, respectively. The measurement of the flow rate in the self-pumping EBC with modified CNTs/CA/CC electrode showed that the

FIGURE 5: The schematic of the distributed fluid by the capillary effect.

FIGURE 6: Contact angle measurement of carbon cloth for anodic and cathodic electrodes before and after modification.

flows in the cathode and anode flow field were 0.844 and $0.416 \mu\text{s}^{-1}$, respectively. The actual value is divided by the theoretical value; the capillary driven liquid efficiency for cathode flow field is 59% and that for the anode flow field is 30%. The performance of the self-pumping EBC with and without CNTs/CA/CC modified cathode electrode was evaluated by measuring their polarization curve and power density curve (Figure 11). The MPD of the EBC with the modified cathodic electrode was 0.592

Wcm^{-2} at 0.44 V , which improved by 10% compared to the EBC with the unmodified cathode (0.534mWcm^{-2} at 0.42 V).

Figure 12 showed the electric current recorded over a time interval of 20 min at the constant voltage. In this experiment, Reservoir 1 was continuously refilled when it ran out of fuel. The transient peak current fell to the steady state as the external circuit connected. After 75 sec discharge, the current density maintained a steady state and was recorded every 3

FIGURE 7: The FTIR spectrum of GOx (a), CC coated chitosan (b), and GOx immobilized CS/CC (c).

FIGURE 10: The polarization curves of the CNTs/CA/CC cathodic electrode. (a) Saturated argon. (b) Air. (c) Saturated oxygen.

FIGURE 8: The absorbance peaks of the catalyst measured by UV spectrophotometer. (a) CNTs/CA. (b) CA. (c) CNTs.

FIGURE 11: The polarization curve for self-pumping EBC with and without cathodic electrode CNTs/CA/CC.

FIGURE 9: The CV curves of the electrode. (a) CA/CC. (b) CNTs/CC. (c) CNTs/CA/CC.

min, which obtained an average value of $1.125 \pm 0.12 \text{ mA} \cdot \text{cm}^{-2}$ and indicated the self-pumping EBS stability.

FIGURE 12: The current density versus elapsed time for the stability examination of the self-pumping EBC.

4. Conclusion

A self-pumping EBC with the CNTs/CA/CC modified cathodic electrode for improving its performance was fabricated. According to the electrochemical evaluation, the CNTs/CA/CC electrode executed an excellent catalytic activity of the oxygen reduction reaction that contributed to increasing the current peak at $139.1 \mu\text{A}$. Under different gases saturated $0.1 \text{ M K}_3\text{Fe}(\text{CN})_6$ and 0.1 M KCl solutions, the highest current peak was observed in the presence of oxygen. Moreover, the MPD of the EBC with the CNTs/CA/CC cathodic catalyst was 10% higher than that of the EBC with the unmodified electrode with 0.592 mWcm^{-2} at 0.44 V compared to 0.534 mWcm^{-2} at 0.42 V , respectively. By the EBC stability examination, the output current and power density were stable after 75 sec discharge; the measured current density was $1.125 \pm 0.12 \text{ mA/cm}^2$ as the fuel was continuously pumped by the capillary force.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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