

RESEARCH PAPER

Effect of membrane on power density of ethanol/O₂ biofuel cell

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ABSTRACT

A biofuel cell is a device for converting chemical energy to electrical energy by a simple way. A high-impact anode is prepared in this research. Here, carboxylated multiwall carbon nanotube (COOH-MWCNT), polydiallyldimethyl ammonium chloride (PDDA) and alcohol dehydrogenase were cast on modified glassy carbon with polymethylene green to construct the bioanode for biofuel cell. The polymethylene green is used as an electron mediator for NAD⁺ that is coenzyme for alcohol dehydrogenase. This new bioanode construction has a good storage and operational stability. The modified electrode was characterized by cyclic voltammetry. The biofuel cell was made with bioanode and carbon-platinum cathode, with and without membrane, and characterized by linear sweep voltammetry to obtain polarization curve for biofuel cell assembly. The biofuel cells had power density 350 $\mu\text{W}\cdot\text{cm}^{-2}$ and 1713 $\mu\text{W}\cdot\text{cm}^{-2}$, with membrane and membraneless, respectively. The open circuit voltage of both biofuel cells was 0.28V for more than 1 hour. The anode easy construction and simple cell design make it useful for implant medical instruments.

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INTRODUCTION

Worldwide energy demands continue to increase yearly. Petroleum products presently provide much of this demand, however, the problems such as pollution and weather warming are acting as a major propellant for research about other renewable energy technologies [1]. Fuel cells are devices that convert chemical energy into electrical energy. Biofuel cells offer a potential solution for this problem, they need simple materials for fuels such as sugars and alcohols [2-3]. Biofuel cells have been usually classified as both microbial and enzymatic fuel cells according to whether the enzymes are located inside of microorganisms or outside of living cells [4]. Of the main advantages of the enzymatic fuel cells are their ability to

produce biofuel cells orders of magnitude smaller than microbial cells, and allowing operation takes place nearer to the redox potential of the enzyme itself. For a well-organized operation of an enzyme-based biofuel cell a number of conditions must be provided. The enzyme should have high catalytic activity, stability but they are expensive [5]. Enzyme-based fuel cells are still a valuable challenge, because of their high turnover rates related to enzymes. Because enzymes have high biocatalytic rate [6]. In recent years, there has been a growing interest in biofuel cell. However, a major problem with biofuel cells is membrane. So far, membrane has been a controversial topic among scientists. Membrane has a key role in designing biofuel cell. This paper will give an account of

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membrane in biofuel cell. The experimental data are rather controversial, and there is no general agreement on the role of membrane in biofuel cell design. This work takes the form of a case-study of the membrane. Recent evidence suggests that biofuel cell may use membrane (7, 8). Some of the biofuel cells are composed of two separate parts. In a two-chamber design, the anode and the cathode compartments are separated by an ion-selective membrane, allowing proton transfer from the anode to the cathode and preventing oxygen diffusion in the anode chamber from the cathode compartment. The membrane must have a good capability for exchanging protons [9, 10]. In fuel cells, the main task of membranes is to separate the anode and the cathode and to stop the passage of the anode electrolyte to the cathode compartment, and also to prevent moving the air purged in cathode partition to the anode section, [11]. In the biofuel cell, the Nafion membrane equilibrates the cation species present in the anolyte and catholyte [12]. In addition, other cation species have a higher concentration in the anolyte than protons causing to slightly reduce the contribution of proton transport compared to the transport of other cations, that consequently decreases the performance of the biofuel cells. The diffusion coefficient of protons in Nafion is relatively higher than other cations. Currently, the most available PEM for biofuel cells is Nafion from DuPont. Working in an ambient temperature is a favorite condition for biofuel cells. In the present work, we used polydiallyldimethylammonium chloride (PDDA), carboxylated multiwall carbon nanotube (HOOC-MWCNT), alcohol dehydrogenase (ADH) and polymethylenegreen (PMG) for construction bioanode PDDA/ADH/PDDA/HOOC-MWCNT/PMG/GC in the preparation of biofuel cell with platinum-carbon (Pt/C) cathode, with and without membrane, to consider the membrane effect in our biofuel cells.

EXPERIMENTALS

Materials

ADH (E.C. 1.1.1.1), from *Saccharomyces cerevisiae* lyophilized powder (> 300 Units mg⁻¹), (stored at -20° C) and NAD⁺ were purchased from Sigma-Aldrich. The sodium phosphate dibasic (Na₂HPO₄), sodium phosphate monobasic monohydrate (NaH₂PO₄·H₂O), sodium tetraborate (Na₂B₄O₇), sodium nitrate (NaNO₃), PDDA, ethanol (EtOH) and methylene green (MG) were

obtained from Merck. All the enzyme and coenzyme solutions were freshly prepared and rapidly used. HOOC-MWCNTs (Content of -COOH: 0.49 wt %, Outside diameter: 50- 80 nm, Inside diameter: 5- 15 nm, Length: 10- 20 nm, and Purity: > 95%) were acquired from US Research Nanomaterials Inc. Nafion[®] N117 membranes (DuPont) were pre-treated at 80°C with 5 wt % H₂O₂ and 2 M H₂SO₄ solutions for 1 h, then rinsed and stored in deionized water. All the solutions were prepared with double distilled deionized water.

Instrumentation

Cyclic voltammetry (CVs) and linear sweep voltammetry (LSV) were performed in an analytical system model EG&G 263A potentiostat/galvanostat (controlled by a Power Suite software package and a GPIB interface). A usual three-electrode cell assembly consisting of an Ag/AgCl reference electrode and a Pt rode counter electrode were used for the electrochemical measurements. The working electrode (anode) was glassy carbon electrode (GCE; area 0.07 cm²) from Azar Electrode (Uromia, Iran); cathode of electrode was Pt/C electrode (Pt; area 1 cm²). In these experiments, all the potentials have been reported versus the Ag/AgCl reference electrode. The morphological characterizations of anode surfaces were examined by means of Hitachi S4160 field emission scanning electron microscope (FESEM) with 10-20 nm gold deposition layer thickness and 30 kV voltages. All the solutions for CVs were purged with high purity nitrogen gas for about 20 min before performing electrochemical experiments. Also, a continuous flow of nitrogen over the aqueous solution was maintained during CVs measurements. All the experiments were carried out at room temperature (25 °C). pH was measured using a pH electrode coupled to a Metrohm model 691 pH meter.

Preparation of electrodes

Preparation of polymethylene green modified electrode

As explained in our previous work [13], the first step for electrode preparation is electropolymerization of methylene green on GCE surface with cyclic voltammetry in a solution containing 0.4 mM methylene green and 0.1 M sodium nitrate in 10 mM sodium tetraborate by performing cyclic voltammetry from -0.5 to 1.3 V versus Ag/AgCl for 20 sweep segments at a scan rate of 50 mV.s⁻¹. This method is the same as Zhou method [14].

Preparation of the modified electrode

For electrode preparation, using an ultrasonic bath, 1 mg of HOOC-MWCNTs was dispersed in 1 mL of ethanol to give a black suspension. The modified GCE with polymethylene green (PMG) was treated by dropping HOOC-MWCNT suspension, and then dried in air. 2% PDDA solution was dropped on HOOC-MWCNTs/PMG/GC electrode and left to dry in air. Alcohol dehydrogenase solution (10 mg. mL⁻¹, pH 7.5, 0.1 M PBS) dropped on the HOOC-MWCNTs/PMG/GC electrode. Finally, the dried ADH /HOOC-MWCNTs/PMG/GC electrode was covered by 2% PDDA to obtain the designed electrode (PDDA/ADH/PDDA/HOOC-MWCNT/PMG/GC).

Enzymatic biofuel cell construction

As shown in Scheme 1, in the BFC, the PDDA/ADH/PDDA/HOOC-MWCNTs/PMG/GC electrode is used as bioanode and Pt/C is used as cathode. The BFC was assembled by immersing ADH modified electrode and cathode in one compartment cell with volume of 1 mL. The cell is filled with oxygen saturated phosphate buffer (pH 7.5, 0.1 M) containing 1.0 mM NAD⁺ and 1.0 mM ethanol. In membrane –containing cell, nafion membrane was applied between anode and cathode. The cell was equilibrated for 2-6 h before working. The open circuit voltage was monitored for 1-3 h; Cell polarization was carried out at a scan rate of 1 mVs⁻¹ with two electrodes. The power density was obtained using the geometric surface area of the anode and cathode (Scheme 1).

RESULT AND DISCUSSION

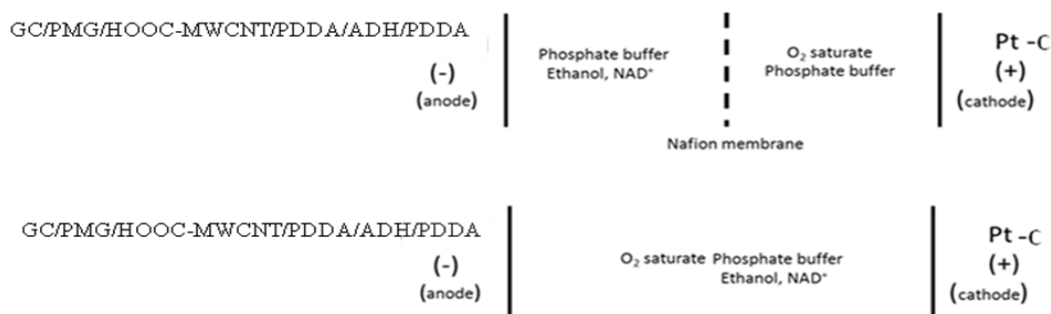
Electrochemical characterizations of GC/PMG/HOOC-MWCNTs/PDDA/ADH/PDDA

In the following experiments, each newly prepared film on GCE is washed carefully in deionized water to remove the loosely bound PDDA

on the modified electrode. It is then transferred to pH 7.5 PBS for the other electrochemical characterizations. These optimized pH solutions have been chosen to maintain the higher stability (pH = 7.5). The cyclic voltammeteries of the modified electrode is shown in our previously published results. The CV of the modified anode is shown in our previous work [13]. On the basis of the results, modification of electrode and immobilization of ADH do not affect on enzyme function, and enzyme functionality can be saved for long time.

Biofuel cell performance of PDDA/ADH/PDDA/HOOC-MWCNT/PMG/GC modified anode

The BFC is characterized while PDDA/ADH/PDDA/HOOC-MWCNTs/PMG/GC and Pt-C are used as anode and cathode, respectively, and the voltage is measured in oxygen saturated PBS (0.1 M, pH 7.5) containing 1 mM ethanol and 1 mM NAD⁺. Membraneless and with membrane biofuel cells the PDDA/ADH/PDDA/HOOC-MWCNT/PMG/GC modified electrode was applied as anode together with a Pt/C electrode as cathode in a 1 mM solution of ethanol in pH 7.5 PBS containing 1 mM NAD⁺. The application of the PDDA/ADH/PDDA/HOOC-MWCNT/PMG/GC modified electrode for the biofuel cell has been demonstrated during ADH electrode testing in galvanostatic regime (Fig. 1). Analysis has shown that the catalytic electrooxidation current of ethanol appears at 0.28 V with a current density of 0.002 A/cm² and reaches 4 A/cm² at 0 V vs. Ag/AgCl. Current density was calculated versus geometric electrode area, giving 0.07 cm². The open circuit potential (OCV) (0.28V) of the cell with ADH modified electrode is close to the mediated redox potential of the NAD⁺/NADH cofactor of the enzyme. Thus, PDDA/ADH/PDDA/HOOC-MWCNT/PMG/GC electrodes based on membraneless electron



Scheme 1: Schematic representation of cell design with membrane (top), membraneless (down).

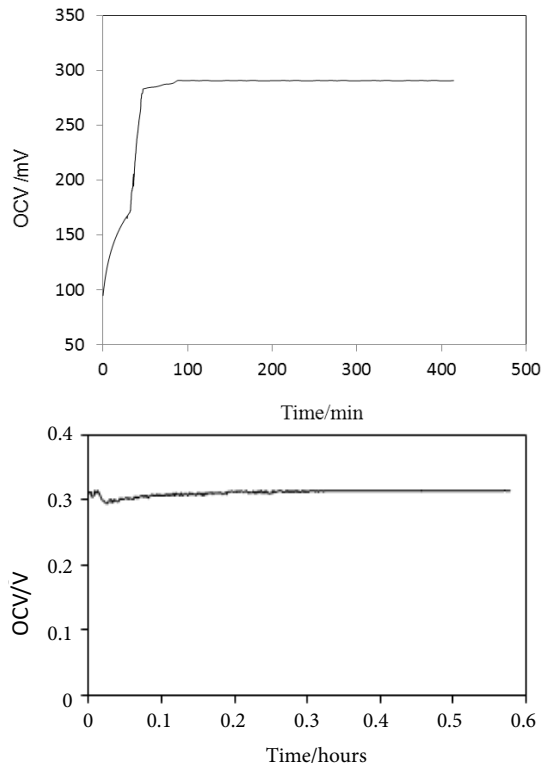


Fig. 1: OCV of BFC with bioanode GC/PMG/HOOC-MWCNT/PDDA/ADH/PDDA and Pt/C cathode in oxygen saturated PBS (pH 7.5, 0.1M), 28°C, 1mM ethanol and 1mM NAD⁺ membraneless(top) and with membrane(down).

transfer between the active site of the enzyme and MWCNTs offer promising composites for generation of biofuel cells. Before the polarization experiments, the anodes were kept in the cell solution for 1 h for the OCV measurements. The

OCV data provide a measure of the maximum voltage associated with a fuel cell [15]. The OCV values as well as the power density and current maxima obtained for the different cell designs. Furthermore, after each recorded linear scan, the OCV value is restored spontaneously in the cell in ca. 120 min, showing the reversibility and stability of the immobilized enzymes. As the current is produced, the cell voltage starts to decrease, the cell voltage drops faster and becomes 0 V at 4 A/cm² of the short circuit current (SCC). From the measured I–V curves (polarization curves), maximum power densities are calculated 350 and 1713 W/cm² for membrane and membraneless biofuel cells, respectively. The results are shown in Fig. 1. Power tests were performed by varying cell design (with or without membrane). The results showed that in a cell with membrane, the power density diminishes. This can be explained by the fact that low diffusion rate of proton in membrane can be diminished, so electron transfer, NAD⁺ diffusion to the mediator and substrate arrival are less effective in this situation. The power density curves of the cells as a function of cell design are depicted in Fig. 2. The power density values in Fig. 2 demonstrate a straight relationship between the cell design and power values. As the membrane is used in the cell, a proportional decrease in power density is achieved. The power density values of membrane and membraneless biofuel cell range from 0.00035 to 1.713 mW. Cm⁻², respectively. The highest power density is achieved with the membraneless cell, which provides a power density of 1.713 mW.Cm⁻² at 0.281 V.

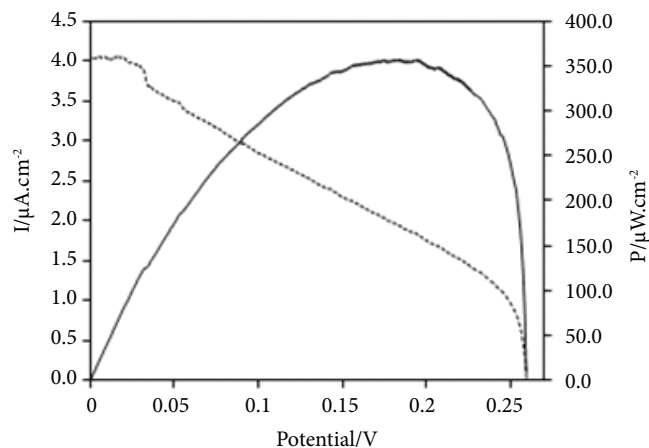


Fig. 2: Polarization curve of BFC with bioanode GC/PMG/HOOC-MWCNT/PDDA/ADH/PDDA and Pt –C cathode in oxygen saturated PBS (pH 7.5, 0.1M), 28°C, 1mM ethanol and 1mM NAD⁺ in scan rate of 1mV.S membraneless (top) and with membrane(down).

CONCLUSION

A modified glassy carbon anode based on alcohol dehydrogenase was successfully prepared by means of an immobilization in a nanocomposite network. The immobilized enzyme displayed a good and stable catalytic activity towards the ethanol oxidation reaction. The anode was then assembled in an ethanol-feed enzymatic fuel cell device, equipped with or without a Nafion 117 membrane as membrane and a Pt/C electrode immersed in 0.1 M oxygen saturated phosphate buffer solution as cathode. The proton transport features of the electrolyte membrane were investigated by means of polarization test, revealing the unsuitability of membrane in the operative conditions of the enzymatic fuel cell device. Once assembled the BFC device, polarization and power density curves were acquired, demonstrating the applicability of the ADH-modified electrode as a promising anode for BFC applications, and that it can work in membraneless conditions better than BFC with membrane. The latter is good for building nanosize devices working as implanted BFC.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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