



Bioelectrodes based on pseudocapacitive cellulose/polypyrrole composite improve performance of biofuel cell



Michał Kizling^a, Krzysztof Stolarczyk^b, Petter Tammela^c, Zhaohui Wang^d, Leif Nyholm^d, Jerzy Golimowski^b, Renata Bilewicz^{b,*}

^a College of Inter-Faculty Individual Studies in Mathematic and Natural Sciences (MISMaP), Stefana Banacha 2C, 02-097 Warsaw, Poland

^b Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

^c Nanotechnology and Functional Materials, Department of Engineering – The Ångström Laboratory, Uppsala University, Box 534, 751 21 Uppsala, Sweden

^d Department of Chemistry – The Ångström Laboratory, Uppsala University, Box 538, 751 21 Uppsala, Sweden

ARTICLE INFO

Article history:

Received 16 October 2015

Received in revised form 13 January 2016

Accepted 26 January 2016

Available online 27 January 2016

Keywords:

Supercapacitor

Biofuel cell

Laccase

Fructose dehydrogenase

Polypyrrole

Nanocellulose

ABSTRACT

Enzymatic electrodes with high internal capacitance, based on cellulose/polypyrrole composite were optimized and utilized to design improved enzymatic fuel cell. Fructose dehydrogenase *Gluconobacter* sp. specifically adsorbed on the cellulose/polypyrrole matrix and electrophoretically immobilized and electrochemically entrapped Laccase *Trametes versicolor*, were used as the anode and cathode bioelectrocatalysts, respectively. The cellulose/polypyrrole composite film exhibited pseudocapacitive properties under mild pH conditions. Following modification with carboxylic groups the composite material enabled highly efficient adsorption of enzyme and provided good electrical contact between the enzymatic active sites and the electrode surface. The modified cellulose/polypyrrole composite based electrode was used for the anode leading to mediatorless fructose oxidation giving large catalytic current density, 12.8 mA cm⁻². Laccase and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) as the mediator entrapped in the cellulose/polypyrrole composite film generated dioxygen reduction current density of 2 mA cm⁻². Application of pseudocapacitive matrix and decreasing the distance between electrodes to 1 mm lead to improvement of the biofuel cell power output and its regeneration ability. The power of the cell was found to increase by introduction of a preconditioning step during which the cell was kept at open circuit voltage under fuel flow. After 24 h of preconditioning the matrix was recharged and the device output reached the power, 2.1 mW cm⁻² and OCV, 0.59 V.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The interest in energy harvesting devices based on alternative fuels has exponentially increased during the last two decades [1]. The biological fuel cells (biofuel cells) attract now special interest of electrochemists, who notice that while conventional fuel cell technologies are approaching mass production, these still have several important limitations. The reasons for the increased interest in biofuel cells stem from their unique conditions of operation that cannot be met by conventional fuel cells; low-temperature operation (20–40 °C) activity near neutral pH, the selectivity and specificity of enzymes and the decreasing price of the biocatalysts. Moreover, biofuel cells can utilize a wide diversity of fuels and a multitude of biocatalysts and also offer low costs of operation and maintenance in comparison with conventional fuel cells [2–5].

Although great progress has been made in this field during the last few years, there are still significant difficulties to overcome. One problem is the rapid voltage drop often seen when turning biofuel cell powered devices on. As the latter is associated with the power limitations of the systems, the approaches based on the utilization of electrical capacitance are currently discussed in the literature [6]. The latter types of systems are of particular importance when high power has to be delivered or stored within a very short time. Adding to the efficiency issues, storage of the electric energy produced by the biofuel cell is, in fact, also acquired, directly or indirectly, i.e. electrostatically or via electrochemical reactions, which by no means straightforward. Conventional capacitors and batteries, which are commonly used for storage purposes, are inefficient and quite expensive devices, riddled with limiting fundamental and practical issues such as self-discharge processes.

Supercapacitors (SCs) [7], batteries [8], and combinations thereof [9] are rechargeable devices which can store significantly higher amounts of electric energy than conventional devices. Similar to state-of-the-art fuel cells, energy storage devices are currently designed using advanced, almost exclusively carbon based nanomaterials [9] such as carbon nanotubes (CNTs) and graphene. As such, carbon based SCs are regarded as

* Corresponding author at: Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02093 Warsaw, Poland.

E-mail address: bilewicz@chem.uw.edu.pl (R. Bilewicz).

important energy storage devices owing to their excellent properties, including high power densities and sufficient electrical conductivity, in addition to being relatively inexpensive and inert. Moreover, conducting organic polymers e.g. polyaniline (PANI) [10], polypyrrole (PPy) [11], etc. are also very promising and widely used electrode materials for electrodes in SCs owing to their availability and high specific capacitance, i.e. up to about 3000 F g^{-1} [12]. However, SCs or batteries cannot produce electric energy by themselves and hence need to be externally charged. The enzymatic fuel cell (EFC) on the other hand, converts chemical energy into electric energy and similar to state-of-the-art electrochemical capacitors, nanostructured electrodes based on carbon and metals, for example, CNTs and gold nanoparticles modified electrodes, are currently used to design very efficient EFCs [13]. Nevertheless, the current and power densities achieved for biodevices containing even most advanced nano-biostructures, are still much lower than those of commercially available fuel cells. Consequently, external capacitors are used to enhance the applicability of the EFCs [14].

Several combinations of fuel cells and a capacitor in a hybrid device can be found in the literature, including the combination of EFCs with conventional capacitors [15], conventional FCs with an SC [16] and EFC/SC hybrid. [17] It is important to emphasize that in all the previous reports two discrete modules, that is, a fuel cell and a capacitor, were electrically wired to each other and tested as a new device. The very first work with a singular module, that is, one and invisible, simultaneously functioning as a supercapacitor and a fuel cell was shown by Pankratov with co-workers [18,19]. Soon after the authors also fabricated and characterized an enzymatic self-charging supercapacitor using biological catalysts [20]. However, in the biodevice pseudocapacitive and charging components were located on the opposite sides of the electrodes. Agnes with co-workers showed reloading effect capacitor – like of enzymatic fuel cell based on carbon nanotubes [21]. First single electrode surface containing current generating enzyme together with charge collecting matrix was shown in our recent reports [22,23].

In this paper, we describe the manufacturing of bioelectrodes based on pseudocapacitive cellulose/polypyrrole matrix. It is shown that the power of the biofuel cell can be increased by adding carboxylic groups to the cellulose/polypyrrole composite in order to enable more efficient and oriented fructose dehydrogenase adsorption [24]. To increase the stability of the laccase-based cathode the enzyme was electrophoretically immobilized on the matrix structure and entrapped in a layer of electropolymerized polypyrrole [25]. The influence of internal capacitance of the hybrid material on the power output of BFC is described.

2. Experimental

2.1. Materials and chemicals

Citric acid ($\text{C}_6\text{H}_8\text{O}_7$), disodium hydrogen phosphate (Na_2HPO_4), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and fructose ($\text{C}_6\text{H}_{12}\text{O}_6$) were purchased from PO-Ch. Multi-walled carbon nanotubes (MWCNTs) were obtained from Nanocyl (Belgium) and modified with naphthalene groups as previously described [26]. The inorganic reagents from POCh (Gliwice, Poland) and the organic reagents from Aldrich were used without further purification. The water was distilled and had passed through a Milli-Q purification system.

Fructose dehydrogenase (FDH) from *Gluconobacter* sp. was purchased from Sorachim whereas Laccase *Trametes versicolor* (activity $\geq 10 \text{ U/mg}$) was obtained from Sigma Aldrich. The enzymes were used without further purification.

Pyrrole (Merck), pyrrole-2-carboxylic acid (Sigma-Aldrich) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (BDH Prolabo), Tween-80 (Merck), 37% HCl (Merck), and NaCl (BDH Prolabo) were used as received and were mixed with deionized water to the desired concentrations. The cellulose from the *Cladophora* sp. algae was obtained as previously described [28].

2.2. Material preparation and characterization

The preparation of the cellulose/polypyrrole composite (CPPy) has been thoroughly described in our recent papers [27–29]. To functionalize the composite surface with carboxylic group, the prepared material (100 mg CPPy) was dispersed in 10 ml 0.5 M HCl and sonicated for 60 min, to obtain stable a homogeneous solution. Next, 10 ml of 0.5 M HCl solution containing 0.01 M pyrrole-2 carboxylic acid and 0.01 M FeCl_3 . The polymerization was allowed to continue for 30 min under stirring, after which the product was collected in a Buchner funnel and washed with 0.5 M HCl, and 0.1 M NaCl solutions.

To obtain the bioanode for the biofuel cell, the composite (CPPy) or the $-\text{COOH}$ modified composite (CPPy-COOH), was mixed with acetylene black in proportion 95:5 in an agate mortar. The respective mixture was then dispersed in 96% ethanol (to yield a concentration 20 mg ml^{-1}) via high-energy ultrasonication and $80 \mu\text{l}$ of suspension was dropped on the surface of a glassy carbon electrode (GCE, BAS) with a surface area of 0.071 cm^2 . The thickness of the obtained layer was 1.5 mm. Subsequently $60 \mu\text{l}$ of FDH solution containing 20 mg ml^{-1} of enzyme was dropped onto the surface of the GCE and electrodes was kept in a fridge overnight to evaporate the solvent.

Two CPPy based cathodes were examined: one with laccase adsorbed on the composite surface (denoted CPPy-Lac) and another with immobilized laccase and the mediator – 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (denoted CPPy-ABTS-Lac). To obtain the CPPy-Lac electrode, $20 \mu\text{l}$ of CPPy suspension was dropped on the GCE surface, which then was immersed in a laccase solution (30 mg in 1 ml 1:1 ethanol – McIlvaine buffer mixture, overnight). The mediator containing system, (CPPy-ABTS-Lac) was prepared by trapping the mediator and the enzyme in an electropolymerised polypyrrole layer. To obtain the CPPy-ABTS-Lac electrode, a CPPy modified GCE was immersed in a solution containing laccase (50 mg ml^{-1}) 10 mM of pyrrole and 10 mM of ABTS. To better disperse the enzyme within the polymer matrix DC pulse signals (4 V for 10 s, and next, 0.5 V for 3 s) were applied to the electrode 180 times. The electrode was subsequently thoroughly washed with deionized water to remove any weakly adsorbed molecules.

To obtain the carbon nanotube (MWCNT) – nanostructured electrode surface, naphthylated MWCNT were used. The covalent modification of the carbon nanotubes with naphthyl groups has been described elsewhere [26]. In this process 8 mg of naphthylated nanotubes were dispersed in 12 ml of ethanol and sonicated thoroughly for 30 min. Subsequently $40 \mu\text{l}$ of MWCNT suspension was dropped onto the GCE surface and the electrode was allowed to dry. The MWCNT covered electrode was then immersed in a laccase solution (30 mg ml^{-1}) and kept in the fridge overnight to allow adsorption of the enzyme.

All electrochemical measurements were done in a Swagelok® type compartment designed and constructed by J. Golimowski, (Fig. 1). This stationary, open type device consists of a plexiglass tube containing two opposing glassy carbon electrodes each 0.8 cm diameter, and an optional slot for a Ag/AgCl reference electrode. The transparent tube enabled accurate control of the distance between the electrodes.

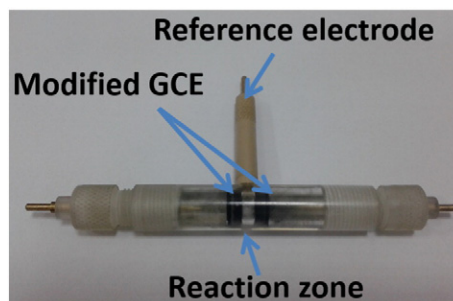


Fig. 1. The cell used for the electrochemical measurements.

Download English Version:

<https://daneshyari.com/en/article/1267778>

Download Persian Version:

<https://daneshyari.com/article/1267778>

[Daneshyari.com](https://daneshyari.com)