Electrochimica Acta 106 (2013) 109–113

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Multiwalled carbon nanotubes to improve ethanol/air biofuel cells

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ARTICLE INFO

Article history:
Received 28 March 2013
Received in revised form 8 May 2013
Accepted 10 May 2013
Available online 22 May 2013

Keywords:
Bioanode
Ethanol biofuel cell
Alcohol dehydrogenase
Carbon nanotubes
PAMAM

ABSTRACT

Biofuel cells are important to generate alternative energy. This paper evaluates the electroactivity of a carbon cloth platform containing immobilized multiwalled carbon nanotubes (MWCNTs), a NAD^+-dependent alcohol dehydrogenase enzyme (ADH), poly-methylene green (poly-MG), and an anchoring agent (PAMAM dendrimer, modified NAFION (m-NAFION), or polypyrrole (poly-Pyr)). The PAMAM dendrimer is an excellent medium to achieve ADH immobilization on the carbon nanostructured platform. We obtained power density and open circuit potential (OCP) of $0.278 \pm 0.038\,mW\,cm^{-2}$ and $0.459 \pm 0.025\,V$, respectively, for PAMAM modified with MWCNTs. This new anode configuration is potentially applicable for small energy devices.

1. Introduction

Biocatalyst-based fuel cells, known as biofuel cells, are an alternative energy source that can help sustain the increasing energy demand for application in portable devices requiring batteries with lower power density. Compared with traditional batteries, biofuel cells present the following advantages: they use renewable and non-polluting catalysts; they offer fuel flexibility; they can operate devices at milder temperatures and in physiological pH; and they display excellent reaction selectivity, provided by the biocatalyst. These systems can oxidize organic fuels and reduce oxygen, converting chemical energy into electricity via reactions that involve biochemical steps; i.e., reactions that use microorganisms or enzymes as catalysts [1,2]. The initial studies conducted in the 1960s triggered investigation into immobilized enzymes; researchers have focused on the catalytic mechanism and/or enzymatic electron transfer process, including alcohol oxidation using dehydrogenase enzymes [3,4] such as alcohol dehydrogenase (ADH) [5].

The key point in bioenergy production using NAD^+-dependent enzymes is to regenerate the NAD^+ species and restore the enzymatic cycle. Direct oxidation of NADH at conventional electrodes, such as gold, platinum, and carbon, occurs at considerable overpotential (>1.0 V), with concomitant passivation of the electrode surface [6–8]. Carbon nanotubes (CNTs) can mediate the electrocatalytic oxidation of NAD^+-dependent enzymes [9–15], diminishing the high overpotential for NADH oxidation [9]. The small diameter of CNTs allows the nanotubes to approach the active center of the biomolecules more closely, favoring the electron transfer. Binding at the end of the CNTs takes place via the oxygenated species [9].

Besides decreasing the energy of the NAD^+/NADH system, the immobilization of enzymes on the electrode surface increases the power density and improves the electron transfer kinetics. Many anchoring agents have been proposed to immobilize enzymes; e.g., tetrabutylammonium-modified NAFION (m-NAFION) [16,17], poly(amide amine) dendrimers (PAMAM) [18–20], and conducting polymer polypyrrole (poly-Pyr) [21–23]. The organized structure, large uniformity, narrow molecular weight distribution, and highly functionalized terminal surface of PAMAM dendrimers has led our research group to use them to immobilize the ADH enzyme when preparing nanostructured bioanodes that employ carbon cloth platforms [20,24]. We have already reported the use of PAMAM dendrimers to prepare bioanodes in both single (ADH) and double (ADH and AldDH) enzymatic systems, which has proven an attractive strategy to immobilize dehydrogenase enzymes with major control of enzyme arrangement on the electrode surface. We obtained an electrode containing lower enzyme concentration, which showed that this technique is potentially applicable to the assembly of bioanodes [24].

The advances in the field of the enzymatic biofuel cells based on ethanol (EtOH) show that many literature reports have described how different types of bioanodes behave during EtOH oxidation, in the presence or absence of MWCNTs. The reported bioanodes contained NAD-dependent dehydrogenase

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0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.05.046

[25–30] or pyrroloquinoline quinone (PQQ)-dependent dehydrogenases enzymes [31], such as quino-hemoprotein–alcohol dehydrogenase (QH–ADH) [32], among others. EtOH oxidation in these anodes is improved, and the power density values were satisfactory, attesting to the potential applicability of these bioanodes in low power electronic devices.

In this paper we investigated different bioanode architectures using CNTs deposited on the electrode surface, aiming to enhance the anode performance for application in miniaturized systems. We evaluated how the position of the MWCNTs deposited on the carbon cloth as an electrode surface affected electrode performance. We also studied how the anchoring agents PAMAM, m-NAFION, and poly-Pry affected the immobilization of the ADH enzyme in the presence of MWCNTs.

2. Experimental

2.1. Chemicals

The enzyme ADH (E.C. 1.1.1.1), from *Saccharomyces cerevisiae* lyophilized powder (331 Units mg^{-1}) and the coenzyme nicotinamide adenine dinucleotide hydrate (NAD^+) were purchased from Sigma–Aldrich. All the enzyme and coenzyme solutions were freshly prepared and rapidly used.

Sodium phosphate dibasic (Na_2HPO_4), sodium phosphate monobasic monohydrate ($NaH_2PO_4{\cdot}H_2O$), sodium tetraborate ($Na_2B_4O_7$), sodium nitrate ($NaNO_3$), sodium hydroxide (NaOH), the polyamidoamine generation 4 dendrimer (PAMAM), Pyrrole, ethanol (EtOH), Methylene Green (MG), and NAFION® 117 solution were purchased from Sigma–Aldrich.

Multiwalled carbon nanotubes (MWCNTs) were acquired from Cheap Tubes Inc. (8.0 nm diameter, 10–30 μm length, and >95% purity).

All the reagents were used as received and all the solutions were prepared with high-purity water from a Millipore Milli-Q system. pH was measured using a pH electrode coupled to a Qualxtron model 8010 pH meter.

2.2. Instrumentation

Electrochemical investigations were conducted on a Potentiostat/Galvanostat AUTOLAB PGSTAT 30 (EcoChemie, Netherlands), at room temperature (25 ± 1 °C).

The power density was measured in a cell consisting of two compartments separated by a NAFION® NRE-212 membrane (Sigma–Aldrich), as described elsewhere [3]. A gas diffusion membrane (ELAT) consisting of an E-TEK cathode (2 mg Pt cm^{-2}) hot pressed in a NAFION® NRE-212 membrane was employed as cathodic material. Hot pressing was carried out at 130 °C and 35 kgf cm^{-2}, for 180 s.

The morphology of the bioanodes was examined by scanning electron microscopy (SEM) in a Leica-Zeiss LEO 440 model Scanning electron microscope coupled to an Oxford 7060 model analyzer (Waltham, MA, USA). The MWCNTs thickness was calculated using the software (SmartSEM user interface) of the equipment described above.

All the experimental measurements were performed at least in triplicate.

2.3. Coating the carbon support with MWCNTs

To prepare the MWCNTs ink, a mixture of 1 mg of commercial MWCNTs was dispersed in 395 μL of EtOH, 5 μL of m-NAFION, and 600 μL of 100 mmol L^{-1} phosphate buffer solution (PBS; pH 7.4), followed by sonication for at least 4 h. Then, 50 μL of the MWCNTs ink was dropped onto the carbon cloth platform activated by electrodeposition of poly-MG and different anchoring agents, such as m-NAFION, PAMAM, or poly-Pyr. The resulting electrode was dried overnight, in a desiccator.

2.4. Preparation of the bioanodes

To electropolymerize the MG, a 1 cm^2 carbon cloth (HT 1400 w, Elat CDL-Basf) was immersed into a methylene green (MG) solution as previously described by Zhou et al. (1996) [33]. Briefly, the electropolymerization solution was prepared by dissolving 0.4 mmol L^{-1} MG in 10 mmol L^{-1} $Na_2B_4O_7$ and 100 mmol L^{-1} $NaNO_3$. Twelve successive cycles were performed between −0.3 and 1.3 V (vs. $Ag/AgCl_{sat.}$) to obtain a homogeneous thin film on the carbon support. The electrodeposited poly-MG film was rinsed with high-purity water and dried for 24 h before deposition of further layers. The electrode was further functionalized with an anchoring agent PAMAM, m-NAFION, or poly-Pyr. The PAMAM layer was obtained by pipetting 50 μL of a commercial PAMAM solution (Sigma–Aldrich) directly onto the electrode surface [20]. Also 50 μL of m-NAFION solution obtained as described before [16] was deposited to obtain the NAFION casting configuration. Poly-Pyr was deposited via cyclic voltammetry, by carrying out 12 successive cycles from −0.4 to 0.8 V versus SCE at 50 mV s^{-1} in 50 mL of 100 mmol L^{-1} PBS (pH 7.4) containing 0.25 mol L^{-1} pyrrole monomer [34].

Finally, 50 μL of a solution of ADH and its coenzyme NAD^+ at a 1 mg:1 mL ratio in 100 mmol L^{-1} PBS (pH 7.4) was casted on the prepared electrode platform as described before [20]. Fig. 1 displays the sequences of modified carbon platform that were investigated; MWCNTs were employed in different positions in relation to the anchoring matrixes (PAMAM, m-NAFION and poly-Pry as casting agents) and the enzyme ADH. The following casting sequences were used: carbon cloth/poly-MG/casting agent/MWCNTs/ADH, configuration A; carbon cloth/poly-MG/MWCNTs/casting agent/ADH, configuration B. Table 1 lists the modified carbon cloth platforms investigated herein.

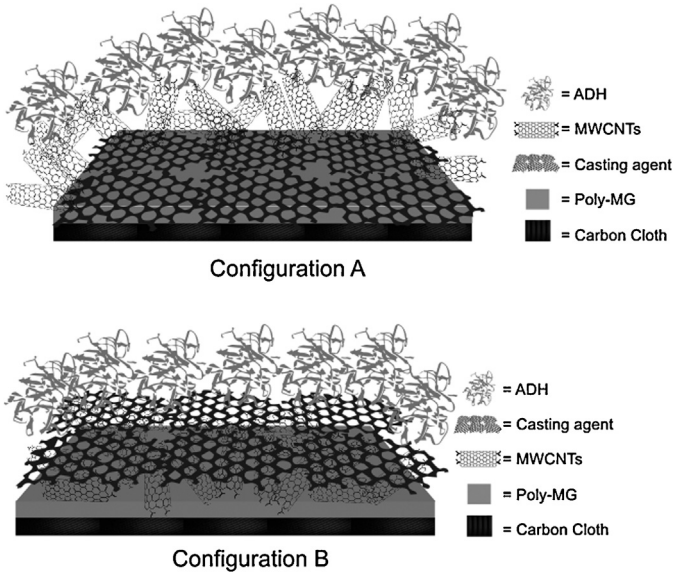

Fig. 1. Schematic representation of electrode preparation: carbon cloth; poly-MG: poly methylene green film; CNTs: MWCNTs; Casting solution: PAMAM, poly-Pyr, or m-NAFION; Enzyme: ADH solution.