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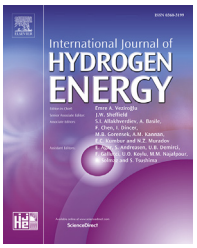

Evaluation of hybrid and enzymatic nanofluidic fuel cells using 3D carbon structures

R.A. Escalona-Villalpando [a], A.C. Martínez-Maciel [b], J.C. Espinosa-Ángeles [b], E. Ortiz-Ortega [a], N. Arjona [a], L.G. Arriaga [a], J. Ledesma-García [b,*]

[a] Centro de Investigación y Desarrollo Tecnológico en Electroquímica, 76703, Querétaro, Mexico
[b] División de Investigación y Posgrado, Facultad de Ingeniería, Universidad Autónoma de Querétaro, 76010, Mexico

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ABSTRACT

Membraneless nanofluidic fuel cells are devices that utilize fluid flow through nanoporous media which serve as three-dimensional electrodes. In the case of hybrid fuel cells (HFC) an enzymatic and an abiotic catalyst are incorporated on the electrodes. Here we compared two different HFC. In the first one (HFC-1), glucose oxidase- and Pt-based electrodes were used as bioanode and cathode respectively. This cell reached an open circuit voltage (OCV) of 0.55 V and a maximum power density of 5.7 $mWcm^{-2}$. In the second one (HFC-2), AuAg- and laccase-based electrodes were used as anode and biocathode respectively. This cell exhibited an OCV of 0.91 V and a maximum power density of 17 $mWcm^{-2}$. Finally, enzymatic electrodes were used to develop a high performance biofuel cell (3.2 $mWcm^{-2}$) that exhibited high stability over 4 days. These preliminary results indicate that the incorporation of enzymes into the 3D carbon structures is an efficient alternative for miniaturized nanofluidic power sources.

Introduction

Glucose biofuel cells (GBFCs) based on three-dimensional "3-D" electrode nanostructures are promising due their unique physico-chemical properties, good electrical conductivity (interconnected network) and high area/volume ratio electrodes. These properties allow for an increased quantity of immobilized enzyme that results in enhanced current density and minimizes the resistance to mass transport by diffusion through the pores [1,2]. There are a few studies that exploit 3-D electrodes applied to GBFCs: carbonaceous foam materials on the meso- and macroporous scales were used to immobilize glucose oxidase (GOx) with an Os redox polymer (for mediated electron transfer, MET) coupled with a bilirubin oxidase biocathode reported a maximum open circuit voltage (OCV) and power density of 0.55 V and 202 μW cm^{-2}, respectively [3]. Other materials that have been continuously published to increase the overall performance of the GBFC are multiwalled carbon nanotubes (MWCNTs), due to their high electrical conductivity, nanometric scale dimension, electrochemical stability and good compatibility with enzymes [4,5]. On other hand, a sub-type of fuel cell called hybrid fuel cells (HFCs) have been studied, which are devices that integrate an abiotic catalyst and an enzymatic either in the cathode or

* Corresponding author.
E-mail address: janet.ledesma@uaq.mx (J. Ledesma-García).
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anode, depending of the case. The purpose of this strategy is to combine the catalytic properties in the glucose oxidation and oxygen reduction, in this way, decrease their disadvantages and improve the overall performance of the device [6]. Recently, nanofluidic flow-through pores using a vanadium redox electrolyte in a membraneless cell were studied. A high power and current density was obtained compared to other microfluidic cells [7]; here, we report the development of nanofluidic flow-through pores in two glucose/O_2 air-breathing hybrid fuel cells (HFCs). The first of these cells uses glucose oxidase (GOx) and Pt/C as the bioanode and cathode, respectively; the second uses laccase (Lc) and AuAg/C as the biocathode and anode. Finally, both bioelectrodes was also evaluated in a glucose/O_2 air-breathing GBFC (Scheme 1).

Experimental

Materials

Glucose oxidase (GOx) from *Aspergillus Niger* (100,000–120,000 U/g) type X–S, laccase (Lc) from *Trametes versicolor* (0.5 U/mg), D-(+)-glucose ACS reagent, ferrocene methanol and glutaraldehyde solution (GA) 50% were purchased from Sigma-Aldrich. KOH pellets, H_2SO_4, HNO_3 and isopropyl alcohol were supplied by J.T.Baker. Nafion® 5% solution was acquired from Electrochem Inc. A phosphate buffer solution (PBS) was prepared using Na_2HPO_4 and KH_2PO_4 (pH 7.1), and the acetate buffer solution (HAc-NaAc) was prepared from acetic acid and sodium acetate (pH 5) (J. T. Baker). All aqueous solutions were prepared using deionized water ($\rho \geq 18$ MΩ cm).

Preparation of the hybrid and bioelectrodes

The electrodes were prepared using a commercial carbon nanofoam (Marketech Inc.) that was 20 mm long and 1 mm wide. The enzymatic electrodes were prepared as previously reported [8]: briefly a sheet of carbon nanofoam (3 cm × 0.5 cm) was submerged in a solution based on GOx or Lc (5 mg mL^{-1}) in 0.1 M PBS or HAc-NaAc with multiwalled carbon nanotubes MWCNTs (2 mg mL^{-1}), and glutaraldehyde (GA) 1% in a volumetric ratio of 1/1/0.1 for approximately 1 h. The abiotic electrodes were prepared by spray coating at 3.5 mg Pt/C (ETEK, 30 % wt) for the cathode or AuAg/C for the anode with 49 μL of Nafion® 5% and 315 μL of isopropanol [9].

Evaluation of the nanofluidic fuel cell: hybrid and enzymatic

The fuel cell design for this study was slightly modified from the previous designs of our group [10]. The air-breathing nanofluidic fuel cell consisted of two poly(methylmethaclylate) caps (PMMA) with a window (9.5 mm × 2 mm) in the cathode tap as an air intake for the catholyte stream. This was fabricated using a CNC micro-milling system; both taps were separated using a silicone polymer film cut using a cutter plotter (Graphtec America Inc.). The co-laminar flow paths of the anolyte and catholyte solutions through the fuel cell were driven by two syringe pumps (Kd Scientific). HFC with MWCNT-GA/GOx as the bioanode and Pt/C as the cathode (HFC-1) was used PBS for the anolyte and 0.3 M KOH as the catholyte. In the case of HFC-2 with MWCNT-GA/Lc as biocathode and AuAg/C as anode, HAc-NaAc and 0.3 M KOH were used as the catholyte and anolyte, respectively. For the GBFC, GOx- (Anode) and Lc-based (cathode) bioelectrodes were used. PBS and HAc-NaAc was used as the anolyte and catholyte, respectively. For HFC-1 and HFC-2 the anolyte solution consisted in 5 mM glucose N_2-saturated, while the catholyte solution was saturated with O_2. The current density measurements were normalized by the cross-sectional area of the electrode perpendicular to the flow of the reactants (0.02 cm^2). Linear polarization was performed at 5 mV s^{-1} from open circuit voltage to 0 V with triplicate experiment.

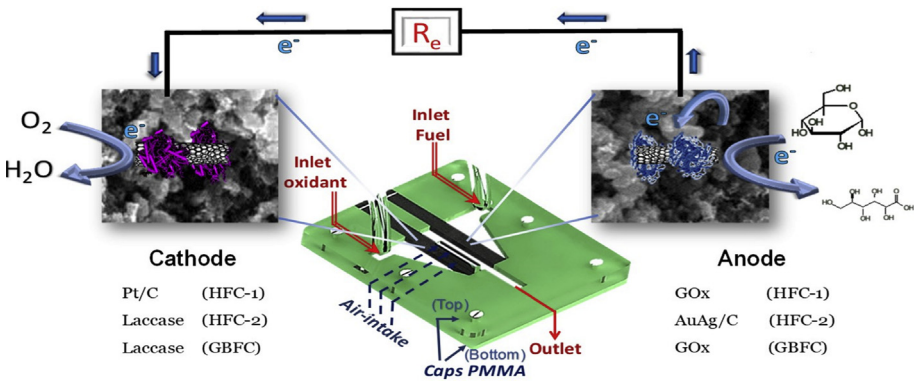
Electrochemical measurements

The electrochemical tests consisted of cyclic voltammetry (CV) performed using a potentiostat/galvanostat (BioLogic SAS Science Instrument VSP-300). A standard three-electrode cell was used with an Ag/AgCl and Pt wire as the reference and counter electrode, respectively. MWCNT-GA/GOx and MWCNT-GA/Lc electrodes were used as working electrodes in 0.1 M PBS (pH 7.1) and 0.1 M HAc-NaAc (pH 5), respectively.

Results and discussion

Electrochemical characterization of MWCNT-GA/GOx and MWCNTA-GA/Lc

Glucose electrooxidation was evaluated directly at a GOx-based electrode. Fig. 1, shows an initial increase in the



Scheme 1 – Schematic representation of the nanofluidic hybrid and biofuel cell components.

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