Laccase/AuAg Hybrid Glucose Microfluidic Fuel Cell

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Abstract. In this work a hybrid microfluidic fuel cell was fabricated and evaluated with a AuAg/C bimetallic material for the anode and an enzymatic cathode. The cathodic catalyst was prepared adsorbing laccase and ABTS on Vulcan carbon (Lac-ABTS/C). This material was characterized by FTIR-ATR, the results show the presence of absorption bands corresponding to the amide bounds. The electrochemical evaluation for the materials consisted in cyclic voltammetry (CV). The glucose electrooxidation reaction in AuAg/C occurs around -0.3 V vs. NHE. Both electrocatalytic materials were placed in a microfluidic fuel cell. The fuel cell was fed with PBS pH 5 oxygen saturated solution in the cathodic compartment and 5 mM glucose + 0.3 M KOH in the anodic side. Several polarization curves were performed and the maximum power density obtained was 0.3 mWcm⁻².

1. Introduction

The interest in micro devices has growing in the last years. Microfluidic fuel cells have emerged as an excellent option due to their high efficiencies and energy densities [1]. In this sense, microfluidic biofuel cells are an attractive alternative, because they can operate with enzymatic catalysts. This particularity can be exploited for their use in medical devices as ex vivo or in vivo μTAS o bio MEMS [2]. In this sense, these kinds of devices can operate at high rates with high selectivity [3, 4]. Nevertheless, their main disadvantage is poor stability and low performance [5].

Hybrid biofuel cells, consisting in an enzymatic catalyst with an abiotic one which exhibit higher output power density due to a faster reaction kinetics and a long-term stability [5, 6] resulted from combining the best properties of both kind of catalysts. Gold-based inorganic materials exhibit good catalytic activity for glucose oxidation reaction (GOR). In specific, AuAg/C decrease the oxidation potential of glucose and the associated prime cost [7].

The aim of this work was to develop a hybrid microfluidic fuel cell that combines two of the best electrocatalysts, AuAg/C for the glucose electro-oxidation and Lac-ABTS/C for the oxygen reduction reaction, in order to obtain a microfluidic device with a good performance.

2. Experimental

2.1. Synthesis of catalytic materials
The cathodic material was prepared as follows: ABTS/C (2,2’-azinobis (3-ethylbenzothiazoline-6-sulfonate) (ABTS2−) was prepared adsorbing 800 µL of 5 mM ABTS solution in phosphate buffer solution (PBS pH 5) and dried at room temperature for 24 hours. After that, 800 µL of laccase 1 U mL−1 solution was adsorbed on the ABTS/C, namely Lac/ABTS/C; this material was dried at room temperature.

On the other hand, the AuAg/C was prepared according to previously reported procedure [6]. Briefly, 0.25 mM HAuCl4•3H2O and 0.063 mM AgNO3 (J.T. Baker) aqueous solutions were added to tetra-octyl-ammonium bromide (TOAB, 98% Fluka) in toluene (99.98% Aldrich) as phase-transfer agent. Dodecanethiol (98%, Aldrich) was incorporated to this solution, followed by the addition of NaBH4 in excess. The reaction was maintained at 2 °C for 2.5 h. Finally, a dark brown dispersion was obtained which was purified several times with ethanol (J.T. Baker) and then supported on XC-72 Vulcan carbon.

2.2. Physicochemical characterization

The physicochemical characterization of AuAg/C material was carried out by X-ray diffraction (XRD) on an X-pert MPD Phillips diffractometer and TEM analyses which were conducted on a Jeol JSM – 35CF, transmission electron microscope (TEM) operated at 200 kV. In the case of Lac/ABTS/C, FTIR-ATR experiments were done in a Spectrum 100 (Perkin Elmer) in order to determine the presence of the absorption signals of ABTS and laccase in the cathode. All the experiments were run at room temperature, 16 scans from 4000 to 650 cm−1 were performed with 4 cm−1 resolution for the cathodic catalyst.

2.3. Electrochemical characterization

Electrochemical experiments consisted in cyclic voltammetry (CV) done in a standard three-electrode glass cell using a BAS Epsilon Potenciostat/Galvanostat (Bioanalytical Systems). A Hg/HgO electrode (Radiometer®) and a Pt wire were used as reference and counter electrode respectively.

2.4. Microfluidic hybrid fuel cell evaluation

Microfluidic fuel cell presented in this work consisted in the use of a PVC chip featuring adhesive aluminium electrode collectors and several sheets of polymeric materials. The microfluidic fuel cell geometry is identical to that reported in a previously reported work [7]. An image of the microfluidic fuel cell was showed on figure 1.

The device was assembled for characterization aligning the chip and the several layers of different laminate materials and placing them between two methacrylate pieces that are tighten by screws.
Alkaline solution of 5mM glucose in 0.3M KOH which was previously saturated with nitrogen was passed through the anode with a flow rate of 25 µL min⁻¹. Cathodic compartment was fed with phosphate buffer pH 5 previously saturated with oxygen at the same flow rate. Polarization curves were obtained at 0.02 V s⁻¹.

3. Results and discussion

3.1. Physicochemical characterization

Infrared spectra for the cathodic material Lac/ABTS/C are shown in Figure 2. The composite Lac/ABTS/C presents characteristic peaks attributed to peptide bonds: Amide I (1600–1690 cm⁻¹), Amide II (1480–1575 cm⁻¹) and Amide A (3300 cm⁻¹) which correspond to the enzyme [8]. The Lac/C material exhibited a decrease in transmittance compared to carbon due to presence of organic material adsorbed on the surface of Vulcan carbon. Peaks ascribed to shifts in ABTS was observed: SO₂ symmetrical elongation (1176 cm⁻¹), C = N (2260 – 2240 cm⁻¹) and CH aromatic (3050 – 3150 cm⁻¹). In the case of Vulcan, it is observed C-C and C-O peaks, indicating the presence of acid groups.

On the other hand, figure 3 shows the diffraction pattern and the TEM micrographs for AuAg/C electrocatalyst. The diffraction peaks located at 38.0, 44.2, 64.4, 77.3 and 82° corresponds to the characteristic FCC metals (1 1 1), (2 0 0), (2 2 0) (3 1 1) and (2 2 2) crystallographic planes. The average particle size obtained by TEM is around 10 nm.
The electrochemical behaviour towards glucose electrooxidation reaction is presented in Figure 4. In absence of glucose is possible to observe the typical profile of this material on basic media. The AuAg/C material shows an onset potential for the glucose electrooxidation reaction at -0.45 V, this value is according to already reported results [7].
3.3. Hybrid fuel cell evaluation

Figure 5 shows the polarization and power density curve for the microfluidic hybrid fuel cell. The OCP was around 1.2 V and the maximum current density was 0.3 mWcm$^{-2}$.

![Figure 5 Polarization and power density curves for the microfluidic hybrid fuel cell.](image)

4. Conclusions

Laccase and ABTS were absorbed in Vulcan carbon successfully. This material was evaluated in an alkaline-neutral hybrid fuel cell harvesting 0.3 mW cm$^{-2}$. The use of two different kinds of catalysts allows reach highest power with respect to conventional enzymatic fuel cells.

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