Electrochimica Acta 63 (2012) 64–68

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

A novel hydrogen peroxide sensor based on LaB_6 electrode

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ARTICLE INFO

Article history:
Received 22 September 2011
Received in revised form 7 November 2011
Accepted 12 December 2011
Available online 29 December 2011

Keywords:
LaB_6 electrode
γ-Fe_2O_3 nanoparticles
Hydrogen peroxide sensor

ABSTRACT

This article reports a novel simple and low-cost LaB_6 electrode using the catalysis of the γ-Fe_2O_3 nanoparticles, fabricated the γ-Fe_2O_3–LaB_6 sensor for the determination of hydrogen peroxide (H_2O_2). The performance of the sensor was initially assessed by cyclic voltammetry (CV) and amperometric *i–t* curve methods. In phosphate buffer (pH7.0, 0.1 M), the γ-Fe_2O_3–LaB_6 sensor exhibits a good linear dependence ($R = 0.9997$) on the concentration of H_2O_2 from 2.0×10^{-7} M to 6.0×10^{-4} M, a high sensitivity of 2.01×10^7 μA M^{-1} cm^{-2} and a detection limit of 6.34×10^{-8} M (signal/noise = 3). Furthermore, the sensor is also good resistant towards typical inorganic salts and some biomolecules. Our developed electrochemical sensor provides an attractive alternative choice for the determination of H_2O_2 in field applications.

1. Introduction

Hydrogen peroxide (H_2O_2) is an important intermediate in environmental and biological reactions [1,2]. It is also a raw material in chemical production. H_2O_2 can be used as antimicrobial, decolourant, oxidant and so on. The determination of H_2O_2 is vital in biopharmaceutical, biochemical analysis and environmental analysis. Currently, a variety of methods for detecting H_2O_2, such as titrimetry [3], chemiluminescence [4], fluorometric [5] and spectrophotometry [6,7] have been developed. However, these traditional methods are complicated to operate and have lower detection sensitivity. Electrochemical sensors have attracted much attention due to its high sensitivity, good linear range, fast and stable response signal. The conventional electrochemistry analytical technique for the detection of H_2O_2 was developed using enzymes or proteins [8–10]. Unfortunately, the instability and high-cost of the enzyme may be the biggest barrier in these sensors. Thus, the nonenzymatic electrode for H_2O_2 detection was considered. It is mainly focus on the modification of the electrode surface, such as carbon nanotubes [11,12], metal nanoparticles [13–15], and other composites [16–18].

Lanthanum hexaboride (LaB_6) is an extremely hard inorganic compound with high melting point. It is widely used in modern technology as an excellent thermionic electron emission source because of its preeminent physical and chemical properties [19]. The known refractory binary compounds of boron with transition elements have attractive properties from an electrochemical standpoint. As a class, these materials are extremely hard, chemically insert, and have high electrical conductivity. LaB_6 has been studied as an electrode for electrochemical applications. Curran and Fletcher [20] had fabricated the Lanthanum hexaboride electrode successfully.

Gligor et al. [21] had found the iron-enriched natural zeolite modified carbon paste electrode can be used for the detection of H_2O_2. The Fe_2O_3 nanoparticles are stable in a wide pH range, and easy to prepare. Although the Fe_2O_3 nanoparticles have three crystal forms: α, γ and amorphous as a result of the different preparation process, the γ-Fe_2O_3 is the main traditional high-temperature shift catalyst and is good for improving the activity of low-temperature catalyst [22].

In this paper, we fabricated a novel γ-Fe_2O_3–LaB_6 electrode for electrochemical determination of H_2O_2. All of these are based on the catalytic oxidation of γ-Fe_2O_3 nanoparticles and high electrical conductivity of LaB_6. This electrochemical sensor is easy to fabricate and low-cost, with high sensitivity, good linear dependence, strong mechanical stability, good resistant and immunity to contamination. We expect our electrochemical sensor can provide a simple and convenient method for the determination of H_2O_2 in many fields.

2. Experimental

2.1. Reagents and apparatus

H_2O_2 solution (30%, Beijing Chemical Works). LaB_6 powder (99.9%, 500 mesh) was purchased from Jiangyan QS Chemical Co. Ltd., (Jiangyan, China). γ-Fe_2O_3 nanoparticles (99.5%, spherical, 20 nm) was obtained from Shanghai jingchun industrial Co. Ltd.,

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doi:10.1016/j.electacta.2011.12.046

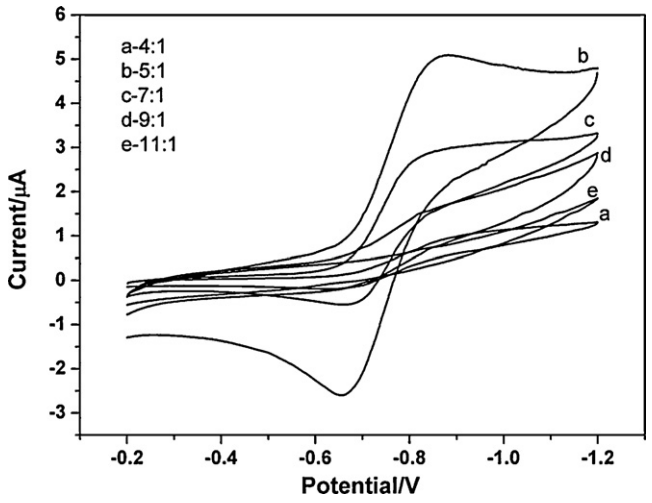

Fig. 1. The cyclic voltammetric response of 10 mM Eu^{3+} (in 0.2 M pH5.5 HAc-NaAc buffer) with the LaB_6 electrode in the different quality ratios (LaB_6:paraffin).

(Shanghai, China). Conductive adhesive was from Shanghai RS Components Co. Ltd., (Shanghai, China). Medical paraffin was purchased from Beijing zhongpu Chemical Plant (Beijing, China). All other reagents were of analytical grade and used without further purification. All aqueous solutions were prepared with doubly distilled water.

Electrochemical experiments were performed on a CHI660B electrochemical workstation (Shanghai Chenhua Instrument, Shanghai, China). A three electrode configuration was employed with the LaB_6 electrode or γ-Fe_2O_3–LaB_6 nanocomposite electrode as a working electrode. The Pt wire and saturated calomel electrode acted as the counter and reference electrodes. KQ118-Ultrasonic cleaning (Kunshan Ultrasonic instruments Co. Ltd., Kunshan, China).

2.2. Preparation of the LaB_6 electrode and the γ-Fe_2O_3–LaB_6 electrode

It has been reported that the carbon paste electroactive electrode with paraffin as a binder [23], this kind of electrode has a good voltammetric response, and is suitable for investigating the mechanism of electrochemical processes of oxide powders. Based on of these, we fabricated the LaB_6 electrode with paraffin as a binder. Taking into account the tightness of adhesion, and the electrochemical current response, we tried many different quality ratios of these two substances to detect Eu^{3+} as the reference of an electrode performance. Fig. 1 shows the cyclic voltammetric responses of Eu^{3+} with the LaB_6 electrode in the different quality ratios, demonstrating that the quality ratio of 5:1 (LaB_6:paraffin) was the best for the electrode response signal. So, the first step for fabricating the LaB_6 electrode was mixed these two substances evenly in this quality ratio, and then heat the mixture, when the wax melted, removed the mixture to cool at room temperature. At last, the LaB_6 electrode with a geometric area 0.108 cm^2 was sealed tightly in the Teflon holder with insulation adhesive to prevent any liquid sweeping. One side of LaB_6 was connected to a 10 cm long Cu rod by conductive adhesive as the electrode connector, and the other side was exposed as the working surface for the electrochemical experiment. The electrode surface was mechanically smoothed on sandpaper and washed with doubly distilled water before use. The γ-Fe_2O_3–LaB_6 electrode (geometric area 0.1224 cm^2) was prepared by the same method, excepting the quality ratio (LaB_6:paraffin:γ-Fe_2O_3 nanoparticles) was 5:1:1. The ratio is fixed to ensure that the amount of the catalyst (γ-Fe_2O_3) is steady for each electrode. The

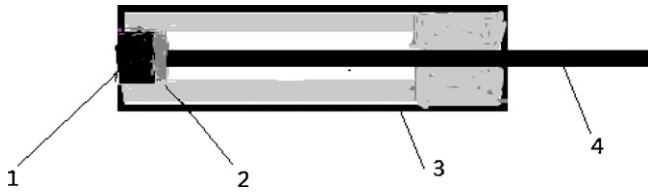

Fig. 2. The schematic diagram of the γ-Fe_2O_3–LaB_6 electrode: (1) γ-Fe_2O_3–LaB_6. (2) Conductive adhesive. (3) Teflon tube. (4) Cu rod.

schematic diagram of the γ-Fe_2O_3–LaB_6 electrode is displayed in Fig. 2.

2.3. Electrochemical measurement

CV and amperometric *i–t* curve were carried out in the electrochemical cell with 0.1 M pH7.0 PBS (phosphate buffer) as the buffer, and H_2O_2 solutions were added into the cell for CV and amperometric *i–t* curve measurements. Magnetic stirring was used before CV measurements and throughout amperometric measurements to ensure the homogeneity of the solutions. The solutions were purged with highly purified nitrogen gas throughout the electrochemical experiments. The electrode was refreshed in doubly distilled water successively, and then dried at room temperature before each use. All experiments were carried out at the room temperature.

3. Results and discussion

3.1. The cyclic voltammograms of H_2O_2 at the LaB_6 electrode and γ-Fe_2O_3–LaB_6 electrode

Fig. 3 shows the cyclic voltammograms of LaB_6 electrode in the absence (a) and presence of 0.01 M H_2O_2 (b) in the 0.1 M PBS (pH7.0) solution. No obvious oxidation and reduction peaks of H_2O_2 were obtained in the potential range of 0.8 to −0.4 V. Fig. 4 displays the CVs of the γ-Fe_2O_3–LaB_6 electrodes in the absence (a) and presence of 0.08 μM H_2O_2 (b); 0.5 μM H_2O_2 (c); 0.05 mM H_2O_2 (d); 1 mM H_2O_2 (e) in the 0.1 M PBS (pH7.0). A couple of reductive and oxidative peaks are observed (curve a) in the potential range of 0.6 to −0.4 V, which are assignable to the reduction of Fe(III) and oxidation of Fe(II) species in the absence of H_2O_2.When the H_2O_2 was added in the PBS buffer, the current of the reductive and

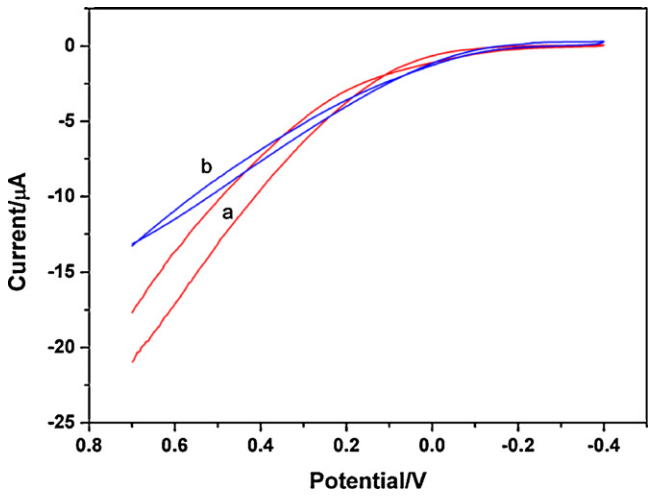

Fig. 3. The cyclic voltammograms of LaB_6 electrode in the absence (a) and presence of 0.01 M H_2O_2 (b) in the 0.1 M PBS (pH7.0) solution at the scan rate of 100 mV s^{-1}.