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Characterization of carbon paste electrodes modified with manganese based perovskites-type oxides from the amperometric determination of hydrogen peroxide

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ABSTRACT

This work proposes the amperometric determination of hydrogen peroxide reduction and oxidation as a tool for the characterization of $La_{1-x}A_xMnO_3$ perovskites dispersed in a graphite composite electrode (carbon paste electrode, CPE). The catalytic activity of perovskites towards the oxidation and reduction of hydrogen peroxide is highly dependent on the nature of the A cation and on the temperature and time of calcination employed during the synthesis. Therefore, the selection of the optimal synthesis conditions to obtain the best catalytic activity towards hydrogen peroxide can be performed from amperometric determinations.

We also report the analytical application of the perovskite modified CPE through the quantification of hydrogen peroxide in two real samples. Some preliminary results about the usefulness of $La_{0.66}Sr_{0.33}MnO_3$–CPE to develop a glucose biosensor by incorporation of the enzyme glucose oxidase (GOx) within the electrode are also reported. The difference in sensitivity to glucose at CPE–GOx and CPE–$La_{0.66}Sr_{0.33}MnO_3$–GOx (11.9 μA mol^{-1} L and 158.1 μA mol^{-1} L, respectively), clearly demonstrate the advantages of the association of the biocatalytic activity of GOx and the catalytic activity of perovskites towards hydrogen peroxide oxidation/reduction, and opens the doors to the development of new sensors for other important bioanalytes.

1. Introduction

Perovskite-type oxides have received great attention in the last years due to their catalytic activity in different processes like waste gas purification and catalytic combustion [1,2]. The high electronic conductivity, the mobility of the oxide ions within the crystal, and the variations on the oxygen content, have made the perovskites-type oxides attractive materials for their application in electrochemical sensors, fuel cells, and as catalysts in oxidation and reduction processes [2,3]. Perovskites containing transition metals like Mn, Fe, Co or Ni are the best oxidant catalysts. Among these perovskite-type oxides, manganites of general formula $AMnO_3$, are the most active thermally stable catalysts, and represent an interesting alternative for the decomposition of pollutants like CO [4], hydrocarbons and nitrogen oxides [2].

Perovskite-type oxides with general formula ABO_3 usually contain a rare earth cation in position A and a transition metal in position B [2]. The partial substitution of A cation with other cations of different oxidation states such as an alkaline-earth element, produces changes in the oxidation state of B-site cations to maintain the electroneutrality of the compound [5]. This change in the oxidation state of B can result in the formation of structural defects. In the case of Mn perovskites, for instance, these changes produce excess of oxygen that strongly affects their catalytic activity [4–9]. The partial substitution of the cation B by another cation, B′, of similar oxidation state and ionic radius, can improve the stability of the perovskite and enhance their redox efficiency [10]. For example, $LaMnO_3$ perovskites and their derivatives $La_{1-x}A_xMn_{1-y}M_yO_3$ (where A is a lanthanide, actinide, alkaline, or alkaline-earth metal, and M is a transition metal like Co, Fe or Ni) show interesting properties for reactions with hydrogen peroxide due to the possibility of having Mn in different oxidation states Mn(II), Mn(III) and Mn(IV) and a flexible oxygen stoichiometry [9].

Ponce et al. [11] and Ciambelli et al. [12] have studied $A_{1-x}Sr_xMnO_3$ (A = La [11], and A = La, Sm and Nd [12]) and found interesting differences in the oxygen forms in the coordination spheres of Mn (IV). $La_{1-x}Sr_xCoO_{3-\delta}$ perovskites possess oxygen deficiencies, whereas $La_{1-x}Sr_xMnO_{3+\delta}$ samples show oxygen overstoichiometry [10]. Anh et al. [13] have reported that the catalytic properties of $La_{1-x}Sr_xCoO_{3-\delta}$ for hydrogen peroxide decomposition

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depends on the oxygen vacancies and proposed the use of this material deposited on a Pt electrode for the potentiometric determination of hydrogen peroxide. Carbonio et al. [14] have studied the catalysis of hydrogen peroxide decomposition using Ni containing perovskite oxides such as $ANiO_3$ (A: La, Pr, Eu), and $La_{1-x}A_xNiO_3$ (A: Sr, Th), among others. They confirmed that the active sites for hydrogen peroxide decomposition are the highly oxidized Ni (in oxidation states III and IV).

Differences in the perovskite structure are associated with differences in their catalytic activity. Indeed, for $LaMnO_3$, it has been reported that the structure can be modified during the synthesis, depending on the oxygen pressure. $LaMnO_{3-\delta}$ is highly active for hydrogen peroxide decomposition due to the presence of Mn in high oxidation state (Mn(IV)) and oxygen vacancies on the perovskite surface [15].

Shimizu et al. [16] have evaluated the potentiometric and amperometric response of hydrogen peroxide at carbon-based electrodes containing different perovskite-type oxides. They have reported that the electrodes loaded with large surface area $La_{0.6}Ca_{0.4}BO_3$ perovskites (B: Cr, Mn, Fe, Co, Ni, $Ni_{0.7}Fe_{0.3}$), present an important activity towards the electrooxidation of hydrogen peroxide, and that the most reactive was the one containing Mn. The electrode modified with the selected perovskite, $La_{0.6}Ca_{0.4}MnO_3$ showed a relatively good analytical performance for hydrogen peroxide quantification.

In this work we propose the amperometric determination of the catalytic activity of different $La_{1-x}A_xMnO_3$ perovskites incorporated in a composite graphite electrode (carbon paste electrode, CPE) towards the oxidation and reduction of hydrogen peroxide as an additional tool for the characterization of perovskites. Hydrogen peroxide is a redox marker of vast importance in the industrial, environmental and clinical research [17]. Since the first report of Adams, more than 50 years ago, the CPEs have been used for a large number of electroanalytical applications [18], most of them also including interesting developments for the quantification of hydrogen peroxide. Different strategies have been proposed to improve the sensitivity and selectivity of the electrochemical quantification of this analyte. Carbon electrodes modified with metals [19–24], metal oxides [25–29] and Prussian blue [30–34] have been successfully used for this task. Among metal oxides, MnO_2 has demonstrated an important catalytic activity towards the oxidation and reduction of hydrogen peroxide [27–29].

We discuss in the following sections the influence of A cation and the temperature and calcination time used during the synthesis of the perovskites present in the CPE on the catalytic activity towards hydrogen peroxide. The analytical usefulness of the CPE modified with $La_{1-x}A_xMnO_3$ is also evaluated from the determination of hydrogen peroxide concentration in two commercial products. We also report some preliminary results about the use, for the first time, of the $La_{0.66}Sr_{0.33}MnO_3$-modified CPE containing glucose oxidase (GOx) as a sensor for glucose biosensing.

2. Experimental

2.1. Reagents

Hydrogen peroxide (30% (v/v) aqueous solution) was purchased from Baker. Glucose oxidase (GOx) (Type X-S, *Aspergillus niger*, EC 1.1.3.4, 157,500 Units per gram of solid, Catalog number G-7141) was obtained from Sigma. Glucose was acquired from Merck, graphite powder was from Fisher (#38) and the mineral oil was from Aldrich. Other chemicals were reagent grade and used without further purification.

Single phase manganese based perovskites were obtained from nitric solutions by a denitration process under microwave irradiation. Aqueous solutions (0.5 mol L^{-1}) of metal nitrates with the corresponding cationic stoichiometric proportions were prepared using anhydrous or hydrated metal nitrates from Merck.

Ultrapure water (ρ = 18 MΩ cm) from a Millipore-MilliQ system was used for preparing all the solutions. A 0.050 mol L^{-1} phosphate buffer solution pH 7.40 was employed as supporting electrolyte.

2.2. Apparatus

Electrochemical measurements were performed with a TEQ_02 potentiostat. The electrodes were inserted into the cell (BAS, Model MF-1084) through holes in its Teflon cover. A platinum wire and Ag/AgCl, 3 M KCl (BAS, Model RE-5B) were used as counter and reference electrodes, respectively. All potentials are referred to the latter. A magnetic stirrer provided the convective transport during the amperometric measurements.

The carbon paste electrode (CPE) was prepared in a regular way by mixing in an agate mortar graphite powder (70.0%, w/w) and mineral oil (30.0% w/w) for 30 min. CPE containing perovskites were prepared in a similar way, mixing first the perovskites nanoparticles with mineral oil for 1 min, followed by the incorporation of the graphite powder and mixing for additional 30 min. A portion of the resulting pastes was packed firmly into a Teflon tube cavity (3 mm diameter). The electric contact was established through a stainless steel screw. The surface was smoothed onto a weighing paper every new experiment.

The structural characterization of the perovskites and electrodes was carried out by X-ray powder diffraction using a Philips PW3710 X-ray diffractometer. Lattice parameters were refined by Fullprof version 3.5 code. The average crystallite sizes were determined by the Scherer formula using the mean high wide peak of single reflections.

Morphological observations of the samples were performed by scanning electronic microscopy (SEM) using a SEI Company Model Quanta 200 with EDS detector EDAX DX-4.

The specific surface areas were estimated from the analysis of the adsorption isotherms by the Brunauer–Emmett–Teller (BET) method using an ASAP 2020 Micromeritics equipment.

2.3. Procedure

Amperometric measurements were conducted in a stirred 0.050 mol L^{-1} phosphate buffer solution pH 7.40 by applying the desired working potential and allowing the transient currents to decay to a steady-state value prior to the addition of the analyte and subsequent current monitoring. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1A displays a SEM image of CPE containing 5.0% (w/w) of the ferromagnetic and metal conductor phase $La_{0.66}Sr_{0.33}MnO_3$ (LSM). The picture shows the typical structure of the graphite composite, suggesting that the presence of the perovskite does not modify its pattern. The distribution of La and Mn in the picture section (Fig. 1B and C, respectively) obtained by EDS, indicates that the perovskite is homogeneously dispersed within the CPE and at the electrode surface.

Fig. 2 shows hydrodynamic voltammograms for 0.020 mol L^{-1} hydrogen peroxide obtained at different electrodes: CPE (a), CPE–LSM (2.0% w/w) (b), and CPE–LSM (5.0% w/w) (c). At variance with CPE, at CPE modified with LSM there is an important decrease in the overvoltage for the oxidation of hydrogen peroxide (300 mV) while the reduction starts at −0.050 V. It is important to remark that the reduction of this compound at bare CPE is