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Sensors and Actuators B 106 (2005) 803–809

SENSORS AND ACTUATORS B CHEMICAL

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Electrochemical sensor for sulfite determination based on iron hexacyanoferrate film modified electrodes

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Received 21 July 2004; received in revised form 23 September 2004; accepted 30 September 2004
Available online 10 November 2004

Abstract

The development of a sulfite sensor and its application to wine analysis is described. The method for the determination of sulfite is based on the use of glassy carbon electrodes modified with films of Prussian Blue [iron(III,II) hexacyanoferrate(II,III)]. The resulting modified electrodes exhibit a reversible redox response ascribed to the oxidation/reduction of iron atoms present in the electrodeposited film. These films have a potent and persistent electrocatalytic activity towards the oxidation of sulfite with a detection limit of 80 μM and a good linear relationship (0.999) between the catalytic current and sulfite concentrations. According to these results, the described modified electrodes have been used as sensors for the determination of sulfite in various types of wine samples and the results obtained are in agreement with those obtained by the standard iodometric method.

Keywords: Sulfite; Iron(III,II) hexacyanoferrate(II,III) films; Modified electrodes; Sensors; Wine

1. Introduction

During the last years great attention has been drawn to the development of methods for sulfite determination. Sulfite is used as a preservative in the food industry because its addition to several products (vegetables, fruits, and several beverages) prevents oxidation, inhibits bacterial growth and assists in preserving vitamin C [1]. Despite these great advantages, the sulfite content in foods and beverages should be strictly limited due to its potential toxicity and products containing more than the established threshold level must be adequately labelled. Therefore, the existence of methods allowing an accurate measurement of sulfite is very important for food industry in order to control product quality. Among the methods available for the measurement of this analyte we can highlight spectrofluorometry [2], chemiluminiscence [3,4], phosphorimetry [5], spectrophotometry [6], flow injection analysis (FIA) [7] and enzymatic techniques [8]. However, the majority of these methods need extensive sample pre-treatment and reagent preparation. In this sense, the development of sensors for sulfite determination is of considerable interest because its use involves several advantages such as rapid response, high specificity, low cost and no need of sample preparation. In the recent years several chemically modified electrodes for sulfite sensing based on polyaniline [9], poly[Ni-(protoporphyrin IX)] [10], [Ru(bpy)(tpy)Cl]PF$_6$ [11], metal pentacyanonitrosylferrate [12,13], and copper hydroxide [14] have been designed. Nowadays, it continues to be a great deal of interest in the development of new materials capable to be incorporated to electrode surfaces in order to obtain electrochemical sulfite sensors with better analytical properties. In this way, electrodes modified with films derived from inorganic polymeric microstructures containing atoms of transition metals with different oxidation states (mixed valence compounds) have been extensively investigated. An important class of the insoluble mixed valence compounds is formed by the polynuclear transition metal cyanides and particularly by the transition metal hexacyanoferrates. According with several studies [15–19], the transition metal hexa-

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doi:10.1016/j.snb.2004.09.033

cyanides have the general formula $M_x[N_y(CN)6]_z$, where M and N are transition metals with different oxidation states and can be generated by electrodeposition from solutions containing hexacyanoferrate(III), a metal cation and a potassium electrolyte. Indeed, the electrocatalytic activity exhibited by hexacyanometallate films towards the oxidation of several analytes such as, hydrazine [20], NADH [21,22], dopamine [23], SO_2 [24] and catecholamine [25] have been studied.

During the past years our efforts have been drawn to design electrochemical sensors based on chemically modified electrodes, in particular hexacyanoferrates derivatives. As part of our research goals we have recently developed a sensor for the determination of nitric oxide based on indium hexacyanoferrate film modified electrodes [26]. In this paper, as a continuation of this topic, we describe the electrocatalytic oxidation of sulfite on carbon electrodes modified with films derived from electrodeposition of iron hexacyanoferrate colloidal solutions and the possibility to use this type of modified electrodes as sensors for sulfite determination in wines.

2. Experimental

2.1. Materials and reagents

Reagents grade potassium hexacyanoferrate(III) ($K_3[Fe(CN)_6]$) and iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) were obtained from Scharlau Chemie SA. Iodine volumetric standard solution (0.0513 N), and starch were purchased from Aldrich SA. Other chemicals used in this work, such as, potassium phosphate, sulfuric acid, sodium sulfite, sodium hydroxide, ethylenediaminetetraacetic acid disodium salt and potassium chloride were reagent grade quality and used as received without additional purification steps. All solutions were prepared just prior to use. The measurements were carried out at room temperature. Water was purified with a Millipore Milli-Q system.

2.2. Electrochemical measurements

Cyclic voltammetric and amperometric studies were carried out with a BAS CV-27 potentiostat connected to a BAS X-Y recorder and with an Autolab/PGSTAT10 potentiostat FROM Eco-Chemie. The electrochemical experiments were carried out in a three-compartment electrochemical cell with standard taper joints so that all compartments could be hermetically sealed with Teflon adapters. A glassy carbon (GC) disk electrode (geometric area: 0.2 cm^2) was used as working electrode. Prior to each experiment, glassy carbon electrodes were polished with 1 μm diamond paste (Buehler) and rinsed with water. A coiled platinum wire served as auxiliary electrode. All potentials are reported against a sodium-saturated calomel electrode (SSCE) without taking into account the liquid junction.

2.3. Real samples

Three different samples of Spanish wines were analyzed: (i) two white commercial wines, one from Comunidad de Madrid (wine 1) and the other from Castilla-León (wine 2) and (ii) a red wine kindly supplied by a wine cellar in El Perdigón, Zamora (wine 3). Bottles were opened just before analysis.

3. Results and discussion

3.1. Iron hexacyanoferrate films: electrodeposition and characterization

Iron hexacyanoferrate (abbreviated as FeHCF hereafter) films can be electrochemically deposited onto a number of conducting substrates such as platinum, gold, glassy carbon, and transparent electrodes. The electrochemical behaviour of these films has been previously described by others authors [27–29], but since the response depends on the aqueous solution electrolyte and on the synthesis conditions a brief description will be given in order to characterize the system. Fig. 1A shows a series of consecutive cyclic voltammograms for a glassy carbon electrode in contact with a solution containing 1.0 mM $Fe(NO_3)_3$, 1.0 mM $K_3[Fe(CN)_6]$ in KCl 0.1 M. The increase in the peak currents with the repeated scanning indicates that electrodeposition on the electrode surface is taking place. The voltammograms obtained exhibit two groups of redox couples at formal potentials around +0.16 and +0.82 V ascribed to [Fe(II)–CN–Fe(III)/Fe(II)–CN–Fe(II)] and [Fe(II)–CN–Fe(III)/Fe(III)–CN–Fe(III)] process respectively [30]. These oxidation/reduction electrochemical processes are accompanied by a flux of cations from the electrolyte solution in order to maintain electroneutrality [31]. In this sense, it is necessary to pay close attention to the choice of the supporting electrolyte, for example in the case of FeHCF films, several studies [32] reported the effectivity of potassium ions to support the redox reactions. This choice plays a key role in the voltammetric response, i.e., when the potassium salt is replaced by other cation, the mentioned waves are less well-defined, because the transport across the film is impeded. When the modified electrode is removed from the electropolymerization solution, rinsed with water, and placed in 0.1 M potassium chloride, the voltammetric response shown in Fig. 1B is obtained. As one would expect two well-defined redox couples ascribed to [Fe(II)–CN–Fe(III)/Fe(II)–CN–Fe(II)] and [Fe(II)–CN–Fe(III)/Fe(III)–CN–Fe(III)] processes are observed. Their formal potential, evaluated as the mean of the anodic and cathodic peak potentials, are quite similar to that observed during the electrodeposition step. Our attention will be focused on the wave centered at +0.82 V, because this peak exhibits high electrocatalytic activity for the oxidation of sulfite. The voltammetric behaviour of this wave is that