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# Behaviour of Ti electrode in the amperometric determination of high concentrations of strong oxidising species

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ABSTRACT

The study of the capabilities of an unusual electrode material, namely, Ti, is presented: the amperometric determination of species showing responses that, on different materials, cannot be often profitably exploited, is proposed. $H_2O_2$ and HClO are successfully analysed, even at high concentrations. In similar conditions, which are quite common in industrial environments, these strong oxidising species are determined by time-consuming, off- or at-line, and multistep procedures. A complex real matrix, such as an industrial detergent, containing high $H_2O_2$ concentrations, has been taken as a meaningful study case to check the effectiveness of the electrode system and procedure proposed.

## 1. Introduction

Electroanalytical methods most commonly pay highest attention to the determination of analytes present in trace. Nonetheless, the determination of certain species at high concentrations is of particular importance in industrial and environmental contexts; dilution, however, often induces undesired or unpredictable shifts of equilibria and is obvious obstacle to in-line operations. In this respect, amperometric sensors appear appropriate to meet with both requirements, the choice of the electrode material constituting a challenging task.

Among the analytes of outmost importance in industry, strong oxidising species are commodity chemicals employed in a number of different applications, such as synthesis of inorganics and organics, treatment of drinking and waste waters and bleaching of cellulose pulp and textile [1]. As a result, strong oxidants need being determined in many different matrices over a wide concentration range, from less than 1 mM to over 10% w/w. However, the protocols for the quantitative evaluation of these chemicals usually require off-line or at-line procedures, such as titrations, which present obvious limitations. On the other hand, as to electroanalytical methods, the most common electrode materials, such as Pt, Au, and glassy carbon (GC), most often do not lead to repeatable and reliable amperometric responses. The main reason lies in the fouling of the electrode surface; in addition, despite the favourable thermodynamics, heavy overvoltages often affect the cathodic reduction of similar species, making the relevant responses even difficult to record. Moreover, a filtering membrane should be added to most of the electrode systems potentially suitable for similar analyses in industrial environments [2]. However, the membrane possesses limited stability over time and only allows a narrow operative temperature range; furthermore, it requires to work under critical flux conditions.

The present study is part of our researches on electrode systems different from the most usual ones, possibly suitable to give answer to analytical problems that are still unsolved. We decided to couple to organic and composite electrode systems [3], an analysis of the capabilities of metals definitely poorly common in electroanalysis. In preliminary experiments, different metals were selected on the basis of inertness, electronic properties and (electro)catalytic behaviour [4]. Ti has been rarely employed in amperometric electroanalysis [5], and in most cases, the use has been limited to low concentrations; we could not find investigations on strong oxidants at high concentrations. Our work is focused on two widely employed strong oxidising species, namely, $H_2O_2$ and HClO, over a wide concentration range.

The actual nature of Ti in contact with similar species deserves a few considerations. The interaction between $H_2O_2$ and Ti, e.g., in the frame of corrosion processes, has been investigated by some authors [6], while literature reports dealing with the effects of other oxidising species are far from being exhaustive [7]. It has been shown that a few nanometer thick layer of $Ti_xO_y$ is spontaneously formed on Ti surface [6]. This layer consists of Ti(II), Ti(III) and Ti(IV) species and is partially amorphous in nature; the density of oxygen atoms progressively decreases with increasing the distance from the interface. It should be evidenced that the nature of crystalline $TiO_2$ [8], widely employed as electrode material in electroanalysis, mainly under the form of particles and nanoparticles, is quite different with respect to Ti oxides spontaneously grown on Ti, constituting the surface of our electrode.

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In addition, $TiO_2$ electrode coatings have been often employed as a part of multicomponent materials, metal nanoparticles or enzymes being anchored to the oxide surface and representing the portion of the electrode system actually in charge of detecting the analytes [9].

Calibration curves with respect to $H_2O_2$ content have been drawn both in 'pure' buffered aqueous solution and in a real matrix, namely, detergent samples. Similar samples have been chosen as meaningful industrial products in which strong oxidising species are key ingredients due to their ability to remove soils. The goal of the study is hence twofold: on the one side, the potentialities of a poorly used metal electrode are studied in the frame of amperometric sensing, and on the other side, the solution to challenging analytical problems is proposed, involving (i) high concentrations of strong oxidants and (ii) effects of potentially heavily interfering species present in a complex real matrix.

## 2. Experimental section

Reagents were from Sigma. $H_2O_2$ was from Carlo Erba (40% w/v). Samples of detergents have been obtained from Officina Naturae (Italy) [11]; in particular, a general purpose detergent for hard surfaces has been employed (trade name: Detersivo universale).

The electrochemical measurements were performed with an Autolab PGSTAT12 (Ecochemie) potentiostat/galvanostat, in single-compartment three-electrode cell, at room temperature. Two-millimetre-diameter Ti disks (grade 1) were the working electrodes. They were polished subsequently with 1, 0.3 and 0.05 μm of alumina powder and then rinsed with Millipore water. An aqueous saturated calomel electrode, KCl sat. (Amel), was the reference electrode; all the potential values given are referred to it. A GC rod was the auxiliary electrode.

Solution media for the electrochemical investigations were 1 M phosphate and citrate buffers at pH 7 and 4 for $H_2O_2$ and at pH 7 for HClO. pH values and concentration range of $H_2O_2$ and HClO have been selected taking into account the most diffused industrial applications [1].

Voltammetric traces have been recorded starting from 0.0 V, at 50 mV $s^{-1}$ potential scan rate; in correspondence to the fourth scan, a steady-state was reached, and the response could be used for analytical purposes. Random additions have been employed for the construction of the calibration curves. Regression of the experimental data is most satisfactory when using a second-order polynomial. Sensitivity is computed as the first derivative of the calibration function calculated in correspondence of the midrange value [11]. All experiments have been carried out in solutions in equilibrium with the atmosphere, i.e., in the presence of dissolved oxygen, to mimic the conditions typical of applicative contexts. However, we could check that the removal of oxygen through deaeration with nitrogen does not lead to significant variation of the electrochemical responses. Lack of sensitivity of Ti electrodes to oxygen reduction, which represents one of the heaviest potentially interfering species, constitutes a further advantage of such a metal electrode.

$H_2O_2$ concentration, both in buffered and in detergent samples, has been determined through standard titration procedure, namely, ASTM D2180 test.

## 3. Results and discussion

The voltammetric responses of the Ti electrode relative to cathodic reduction of $H_2O_2$ (514 mM) and HClO (98 mM) are reported in Fig. 1A–C, respectively. These values represent the highest concentrations explored since the solution pH is not faithfully buffered above them. In the case of $H_2O_2$, two current peaks, located at ca. $-1.1$ and $-1.6$ V, are evident in the forward potential scan at pH 7; at pH 4 they are shifted toward less negative values and that with $Ep \simeq -1.0$ V appears as a shoulder. In the case of HClO, only one peak ($Ep \simeq -1.0$ V) is present at pH 7.

Miah et al. [12] ascribes the two peaks in the forward scan on $H_2O_2$ solutions to the reduction of the analyte and of oxygen species formed as a consequence of its catalytic decomposition and adsorbed on the electrode surface. The current in the backward scan exhibits an odd behaviour: though smaller with respect to the forward scan, cathodic currents are still observed. Actually, the reduction mechanisms of similar species is quite complex and far from being exhaustively clarified, even on noble metal electrodes. Similar behaviour has been previously reported in the case of noble metals in aqueous solvents [13]. Burke et al. [14] proposed a model based on the formation of metal hydrous oxide species on the electrode in correspondence to positive and even slightly negative potentials. These species still survive at surprisingly negative values, giving rise to surface phenomena far from being clear, also leading to persistent cathodic currents.

Sharp current oscillations are evident, past the first portion of the signal, in the voltammetric traces in Fig. 1A–C: the formation of $O_2$ small bubbles at the electrode are visible, which accounts for the oscillations observed.

We could check that Pt and GC electrodes cannot be fruitfully employed in the determination of $H_2O_2$ [13]; in addition, Au could not be employed in the real matrices used in the present communication due to strong fouling of the surface. On the other hand, the

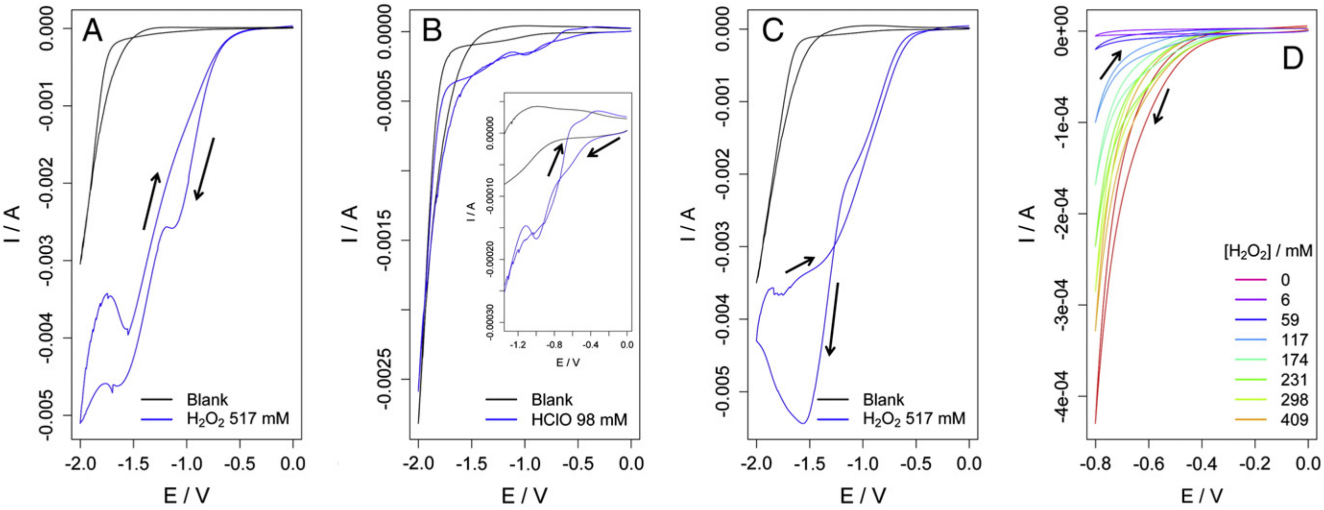

**Fig. 1.** Voltammetric curves on $H_2O_2$ (A, C) and HClO (B) aqueous solutions at pH 7 (A, B) and 4 (C)—fourth scans. Representative voltammetric traces recorded in the presence of different $H_2O_2$ concentrations at pH 7—fourth scans (D).