



Features of Sulfite Oxidation on Gold Anode

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ABSTRACT

Electrochemical oxidation of sulfite ions on gold was studied by means of voltammetry with the electrode renewed by cutting off a thin layer. It was demonstrated that two different kinds of voltammograms can be recorded on gold, depending on experimental conditions. Voltammograms of the first kind, with current maximum at 0.8 V, is typical for the fresh gold surface. The second one, with current maximum at 0.6 V, is observed on gold surface modified during sulfite oxidation. Modification of gold surface is likely to be due to the formation of “sulfur adlayer” in the reduction of adsorbed products of sulfite oxidation. Attention is attracted to the fact that the characteristics of the oxidation of sulfite and sulfur dioxide on gold have many common features.

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1. Introduction

Electrochemical oxidation of oxygen-containing compounds of tetravalent sulfur S(IV) ($\text{SO}_2(\text{aq})$, HSO_3^- , SO_3^{2-}) attracts permanent attention because this process is used in industrial technological schemes. Anodic oxidation of sulfur dioxide is a constituent of the hybrid sulfur cycle for hydrogen production; it is used for flue gas desulfurisation, etc. [1]. The application of thiosulfate-sulfite electrolyte in technologies utilizing the trough-mask plating technique for microelectronic and microsystem application [2] stimulates investigation of the anodic process in sulfite solutions.

The composition and concentrations of the indicated compounds of S(IV) in aqueous solutions depend on pH. In solutions with $\text{pH} < 1.85$ sulfur dioxide dominates, while in solutions with $\text{pH} > 7.2$ mainly sulfite ions are present in solution [3]. The electrochemical oxidation of S(IV) was studied most thoroughly in acid solutions. It was discovered that the rate of oxidation at the anodes made of noble metals is limited mainly by the diffusion of discharging ions. However, it was also found that oxidation rate is strongly dependent on the nature of electrode material, on prehistory of electrode surface, on the state of metal surface, potential range within which the current of oxidation is measured. These effects are explained by the influence of adsorption of sulfur species [3]. The features of anode current in alkaline solutions in which mainly sulfite ions are present have not been studied so

thoroughly, and above-mentioned effects were not discussed. In the present work we describe the results of voltammetric studies of sulfite oxidation on gold anode.

2. Experimental

Voltammograms were measured in the solutions of 0.1 M $\text{Na}_2\text{SO}_3 + 0.5 \text{ M Na}_2\text{SO}_4$ (analytical grade) prepared using twice distilled water, $\text{pH} \approx 10$. Solutions were prepared directly before measurements to decrease the probability of their decomposition before experiment. Measurements were carried out using an IPC-compact potentiostat (Inst. Phys. Chem. RAS) and an electrode cell with Pt counter-electrode and Ag/AgCl reference electrode. The counter electrode (surface area of about 20 cm^2) was located separately from the volume of the cell with a working electrode. The sample of tested solution was 50 mL in volume. Potential values are presented in the SHE scale.

To provide reproducible initial state of electrode surface, the method and instrumentation for voltammetry on electrode with renewable surface were used [4]. The working electrode is the end of gold wire 0.5 mm in diameter. The side surface of the wire is insulated by epoxy resin. The surface is renewed directly in solution at a given potential value by cutting off a thin ($5 \mu\text{m}$) layer of the metal of working electrode. This method ensures rapid preparation of fresh and reproducible metal surface. The algorithms of electrode potential variation used to reveal the features of the behavior of sulfite oxidation current will be described in the corresponding paragraphs of the text.

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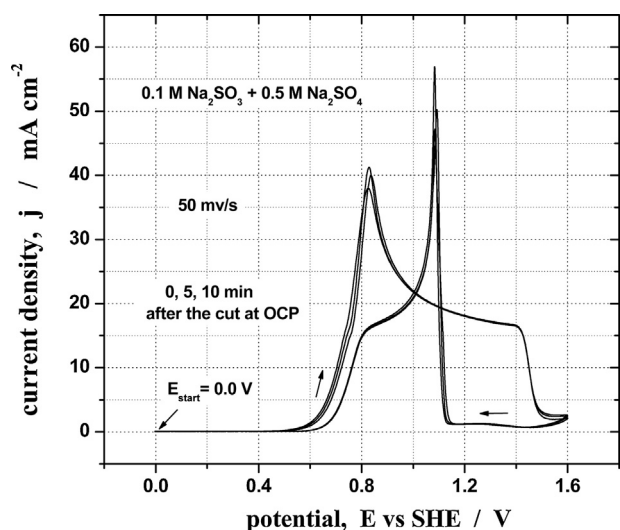


Fig. 1. j-E curves measured after different time intervals between electrode cutting and the start of potential scanning. Scanning algorithm: $E_{\text{start}} = 0.0 \rightarrow 1.6 \rightarrow 0.0\text{V}$ (50 mV/s).

3. Results and discussion

3.1. “Fresh” surface of gold electrode

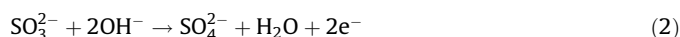
The dependences of current density (j) on potential (E), recorded during single cycling of electrode potential from 0.0V to 1.6V and back, are shown in Fig. 1. Electrode surface was renewed before measurement by cutting off a thin layer at the open circuit potential (OCP). The electrode after cutting was kept in solution for a given time interval, and then its potential was varied within the indicated potential range with the constant rate 50 mV/s. One can see in the data presented in Fig. 1 that long-term exposure of renewed electrode surface with the solution under investigation does not lead to changes of the appearance of voltammograms. Voltammograms measured immediately after electrode surface renewal and 10 min later are reproduced quantitatively. This points to the absence of micro-impurities able to affect sulfite oxidation process in solution.

The data presented in Fig. 1 also show that the shapes of voltammograms measured during the direct and inverse periods of potential sweep are different. For direct scans, very small current is observed within the range from 0.0V to approximately $E = 0.6\text{V}$, then a sharp increase in sulfite oxidation current occurs, with the maximum near 0.8V. Then, up to 1.4V, the current is only weakly dependent on electrode potential, which depicts delayed diffusion of discharging particles. In the region more positive than 1.4V, a sharp decrease of the current of sulfite ion oxidation is observed. This decrease in current is explained by the fact that intense formation of one or several forms of gold oxides starts on electrode surface when the potential is more positive than the indicated potential value [5]. The formation of oxides on gold surface leads to the “oxygen” passivation of the electrode with respect to sulfite oxidation reaction. This fact is confirmed by the behavior of current during the inverse scan (from 1.6V to 0.0V). One can see that during the inverse potential sweep this passive layer slows down sulfite oxidation until 1.1V. However, when this potential value is achieved, metal surface gets free from the passive layer in a jump, and becomes accessible for sulfite oxidation.

It should be noted that the voltammograms of the oxidation of SO_3^{2-} ions in 0.5M Na_2SO_4 ($\text{pH} \approx 10$) shown in Fig. 1 and the voltammograms of oxidation of SO_2 molecules in the solutions of 0.5M H_2SO_4 presented in [6–8] have the same shape and almost

coincide in potential values. For example, according to [8] SO_2 oxidation starts at the potential of $\approx 0.6\text{V}$, current peak is situated between 0.75 and 0.85V, and a sharp decrease in current due to gold oxidation is observed at the potential of 1.4V. Coincidence between results of measurements in media of so different acidities is not an ordinary effect. Therefore, to confirm the results, we took additional measurements of voltammograms for sulfite oxidation in 1.0M sulfuric acid and in the Britton–Robinson buffer ($\text{pH} = 9.2$). It was found that the shape and positioning of the direct scans of the cyclic voltammogram for these solutions are virtually the same as those in Fig. 1. This effect suggests that the processes of electrochemical oxidation of the above-mentioned oxygen-containing compounds of S(IV) at a gold electrode are of similar nature.

The dependences of current on potential, measured with gold electrode in the solutions of sodium sulfite with different concentrations, are shown in Fig. 2. Before measuring the j-E curve, the working electrode was cut at the OCP, then electrode potential was changed linearly with the rate of 50 mV/s from the starting potential $E_{\text{start}} = 0.0\text{V}$ to 1.6V. Then measurements were carried out in solution with another sulfite concentration. One can see (insert in Fig. 2) that current is directly proportional to sulfite concentration in solution. Because of this, there are reasons to state that the anode current in the system under study is due to sulfite ion oxidation. The electrochemical oxidation of sulfite produces a sulfate–dithionate mixture in solution in accordance with the overall reactions



The total current efficiency of these reactions is close to 100%, but the current efficiency of partial reactions depends on the electrode material. For example, SO_3^{2-} converted into $\text{S}_2\text{O}_6^{2-}$ makes up 3% for graphite and ~ 30 [9] or 45% [10] for gold. This suggests difference between the mechanisms of sulfite oxidation at anodes of different metals. The specifics of the mechanism of electrode Reactions (1) and (2) at a gold electrode call for further studies.

Voltammograms measured with the gold electrode in the solution of 0.1M Na_2SO_3 for different potential sweep rates are shown in Fig. 3. Measurement algorithm is the same as that used

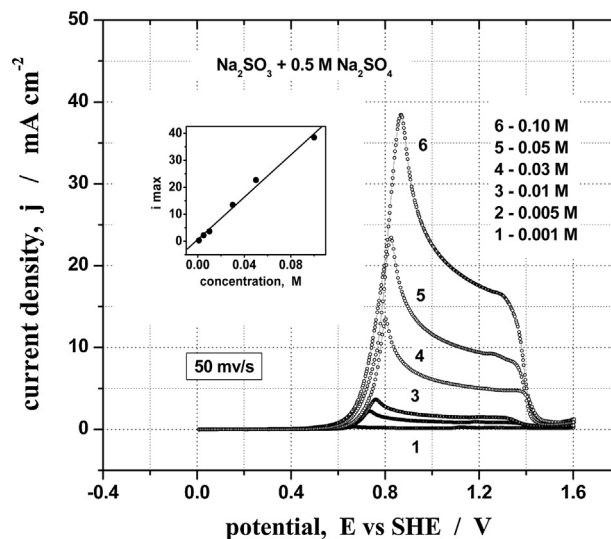


Fig. 2. j-E curves measured with different sulfite concentrations in solution. Scanning algorithm: $E_{\text{start}} = 0.0 \rightarrow 1.6\text{V}$ (50 mV/s). Insert shows the dependence of current in the maximum of j-E curve on sulfite concentration.

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