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RDE study of thiosulfate oxidation on gold

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ABSTRACT

Gold rotation disk electrode was used to study thiosulfate oxidation processes. The values of current in anode voltammograms measured on the fresh electrode surface are independent of the electrode rotation speed. This means that the rate of the process under study is limited by slow (in comparison with diffusion) heterogeneous reactions. The probable mechanisms of these reactions were analyzed. Voltammograms have a maximum of current and depend on the voltammetric scan rate. The reason of these effects is connected with electrode passivation.

1. Introduction

Thiosulfate leaching and electrochemical dissolution of gold in non-toxic thiosulfate solutions are promising for use in gold hydrometallurgy for the purpose of gold recovery from ores and scrap of non-ferrous metals [1]. Gold dissolution in thiosulfate solutions proceeds with the formation of a complex compound of monovalent gold $Au(S_2O_3)_2^{3-}$. This compound is well soluble and fairly stable in neutral and alkaline media [2]:

$$Au(S_2O_3)_2^{3-} \rightleftarrows Au^+ + 2S_2O_3^{2-} \quad (1)$$

$$K = [Au(S_2O_3)_2^{3-}]/[Au^+][S_2O_3^{2-}]^2 = 10^{26} \quad (2)$$

Other soluble forms of the complex compounds of gold(I) with thiosulfate are unknown. In spite of favorable thermodynamic possibilities, gold is poorly soluble in thiosulfate solution. The rate of gold dissolution in this system is very slow and varies within the range 5 $\mu A\ cm^{-2}$ [3] to 25 $\mu A\ cm^{-2}$ [4]. Kinetic limitations of gold dissolution rate in these solutions are explained by passivation of metal surface. Oxide coatings are not usually considered as a reason of electrode passivation in the system under study. It is considered more probable (and confirmed experimentally [5]) that the passive layer is composed of polysulfides. According to [6], polysulfide passive layer is formed as a result of electrooxidation of thiosulfate ions proceeding on gold electrode simultaneously with gold dissolution. Because of this, investigation of thiosulfate electrooxidation can promote better understanding of the processes of gold dissolution and passivation in thiosulfate solutions.

Previously thiosulfate oxidation on indifferent glassy carbon electrode was studied in [7]. It was discovered that thiosulfate is oxidized to sulfate without production of elemental sulfur by a two-step anodic process. The first step is the transformation of thiosulfate into tetrathionate; the second step is the transformation of tetrathionate into sulfate. The anode voltammograms on RDE (rotation disk electrode) of this material have two characteristic plateaus of current; the height of them depends on the electrode rotation speed. This fact provides evidence that the process rate is to a substantial extent controlled by diffusion of thiosulfate ions. No signs of the passivation of glassy carbon electrode can be observed. However, thiosulfate oxidation on gold electrode proceeds in a different manner. The first step is the transformation of thiosulfate into tetrathionate; the second step is the transformation of tetrathionate into sulfate and elemental sulfur [6]. Voltammograms of thiosulfate electrooxidation on gold electrode differ from voltammograms on indifferent electrode. They do not have a diffusion plateau of current but they have a maximum of current within the potential range 0.7–0.8 V (SHE). Current falloff after this potential is explained by gold surface blocking by the film of elemental sulfur produced from the oxidation of thiosulfate [8].

Comparisons between these data indicate that the electrode material plays a substantial part in thiosulfate electrooxidation. The mechanism and kinetics of this process on gold electrode differ from those on indifferent electrode. Meanwhile, electrode processes that take place on gold anode in thiosulfate solutions remain poorly studied. In the present work we study the features of the anode behavior of gold in thiosulfate solutions by means of

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voltammetry on a fresh surface of gold rotating disk electrode (RDE). Ascertainment of these features can contribute to better understanding of the processes that take place during gold dissolution in thiosulfate solutions.

2. Experimental

Studies were carried out in the aqueous solutions of 0.1 M $Na_2S_2O_3$ + 0.5 M Na_2SO_4 (pH $\approx$ 10). The salts of 'pure for analysis' grade and twice distilled water were used to prepare solutions. The solutions were prepared directly before experiments to prevent possible decomposition of solutions.

Voltammograms were measured using the RDE within rotation speed range from 0.0 to 1890 rpm. The electrode was an end of gold wire 0.8 mm in diameter with the side surface insulated by Teflon. Measurements were carried out in a three-electrode cell with the help of an IPC-compact potentiostate (Inst. Phys. Chem. RAS) using a Pt counter electrode and an Ag/AgCl reference electrode. The potentials are given in the scale of the saturated hydrogen electrode (SHE). The electrode surface was renewed directly before measurement in the solution under study by cutting off a thin ($\approx$5 μ) metal layer. This method of electrode surface preparation ensures the fresh and reproducible metal surface for each voltammogram [9].

3. Results and discussion

3.1. The maximum of anode current

Voltammograms measured in the solution of 0.1 M $Na_2S_2O_3$ + 0.5 M Na_2SO_4 with different RDE rotation speeds and the voltammogram recorded in the solution of base electrolyte are shown in Fig. 1. Currents in the base electrolyte are small in comparison with the currents in the solution under investigation. The measurement procedure used to record the curves shown in Fig. 1 included the following operations. At first, the electrode was immersed in the solution under study and rotated at the necessary speed. Then its surface was renewed by cutting off metal layer at OCP, then electrode potential was scanned from the initial level (0.0 V) to 1.3 V and back. Only the currents of the first direct and reverse scans were recorded. Then the procedure of voltammogram measurement was repeated at another electrode rotation speed.

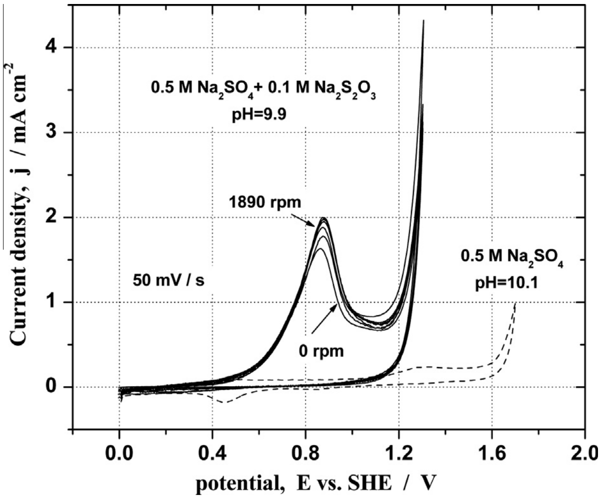

Fig. 1. Dependences of current density on potential and electrode rotation speed in the solution of 0.1 M $Na_2S_2O_3$ + 0.5 M Na_2SO_4 and in the base electrolyte.

Fig. 1 shows that the first direct scan has the maximum of current at the potential approximately equal to 0.8 V. The current at the reverse scan is close to zero. During the cyclic scanning of electrode potential without renewal of its surface, the maximum of current is observed only in the first cycle, while the current is close to zero during the second and next following cycles. This behavior of current is independent of the speed of electrode rotation and similar to that observed with the stationary gold electrode [8,10]. These results provide evidence that the drop of current at the first scan after approximately 0.8 V is connected with the formation of the passive layer which prevents current passing through the electrode–solution interface. The composition of the passive layer depending on the potential of the gold electrode was studied in [5,6] using surface enhanced Raman scattering spectroscopy. It was discovered that at potential close to 0.7 V the recorded spectra contain the bands that are characteristic of polysulfide (*cyclo*-octasulfur, S_8). Because of this, there are reasons to suppose that the passive layer on the gold anode is a polysulfide film. The formation of elemental sulfur and the formation of polysulfides was linked with the overall reaction of thiosulfate oxidation [6]:

$$S_2O_3^{2-} + H_2O \rightarrow S^0 + SO_4^{2-} + 2H^+ + 2e^- \tag{3}$$

It should be noted that electrode passivation is not observed during thiosulfate oxidation on graphite, glassy carbon, platinum and silver. So, the formation of polysulfide layer and subsequent electrode passivation are specific features of gold surface.

Changes at gold-solution interface also take place during long-term (about 60–420 min) exposure of gold under thiosulfate-based leaching conditions. Under these conditions the SERS spectra reveal the presence of sulfide ions or elemental sulfur, tetrathionate, $Au(S_2O_3)_2^{3-}$, and possibly adsorbed sulfite ions as a product of thiosulfate decomposition [11]. However, it should be noted that the changes in the composition of the gold surface layer observed under the indicated conditions seem unable to explain the current drop on the curves shown in Fig. 1. Indeed, the maximum of current on the curves shown in Fig. 1 is observed on the fresh gold surface. Moreover, we determined in our experiments that voltammograms measured on the fresh electrode surface and on the surface kept in thiosulfate solution for 60 min after cutting off are identical. The above-mentioned facts indicate that the passive layer on gold (under our experimental conditions) is formed not as a result of the decomposition of thiosulfate in the region of OCP but as a result of the anodic Faraday process taking place on its surface. Within the potential range under study, this process includes at least two electrode reactions.

3.2. Electrode reactions

One of the electrode reactions that take place in the anode region of potential at the gold electrode is thiosulfate electrooxidation:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \quad E^0 = 0.08\ \mathrm{V\,(SHE)} \tag{4}$$

The product of this electrode reaction is tetrathionate; it can be transformed on the surface of gold electrode through a series of successive chemical rearrangement reactions participated by higher polythionates into sulfate and elemental sulfur (reaction (3)) [5]. The mechanism of this transformation has not been studied in detail, but the results of SERS measurements taken at a gold nanorod array electrode in [12,13] confirm that the possible participants of this process—tetrathionate, trithionate, sulfite, and thiosulfate—decompose to cyclo-S_8, polymeric sulfur, and monoatomic sulfur at the gold surface. It should be stressed that in the case of indifferent electrode (for example, glassy carbon electrode) the formed tetrathionate gets oxidized to sulfate without the formation of elemental sulfur [7]. This means that the reactions of thiosulfate