



Anode current on gold in mixed thiosulfate-sulfite electrolytes



A.G. Zelinsky*

Institute of Solid-State Chemistry, Siberian Branch of Russian Academy of Sciences, Kutateladze Street 18, Novosibirsk, 630128, Russia

ARTICLE INFO

Article history:

Received 13 September 2014

Received in revised form 15 December 2014

Accepted 15 December 2014

Available online 17 December 2014

Keywords:

gold
thiosulfate-sulfite electrolyte
RDE
passivity

ABSTRACT

The anodic current in individual and mixed thiosulfate-sulfite solutions was studied by means of voltammetry on a fresh gold RDE surface. An unexpected result was obtained: a new additional current maximum appears on the anodic voltammogram in mixed solutions; it is not observed in the individual solutions of sodium thiosulfate and sulfite. The reasons for, and mechanism associated with, this phenomenon require separate and detailed investigation. It is shown that the rate of the anodic process in sulfite solutions is limited by diffusion of discharging particles, while the rate of the anodic process in thiosulfate solutions is limited by slow (in comparison with diffusion) heterogeneous reactions. In mixed solutions, the presence of thiosulfate causes partial passivation of the electrode, while the presence of sulfite causes its partial depassivation. It is stressed that the initial stages of oxygen evolution on gold have opposite effects on anodic currents in sulfite and thiosulfate solutions.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The search for efficient and non-toxic electrolytes for the extraction of gold from ores and scrap of non-ferrous metals remains an important problem for gold hydrometallurgy. Thiosulfate electrolytes are promising from this point of view [1]. However, in spite of favorable thermodynamic possibilities, gold is poorly soluble in a pure thiosulfate solution (i.e., without other additives). The rate of gold dissolution in thiosulfate solutions can be increased if cupric amines [2] or ferric oxalate are added as oxidant to the solution [3]. The rate of gold dissolution in these solutions can also be increased with the help of such accelerating additives as Tl(I) ions [4] or thiourea [5,6]. The rate of gold dissolution in the presence of these additives is comparable with the rate of gold dissolution in cyanide solutions [7].

However, thiosulfate electrolytes with the addition of accelerators, or without them, are unstable [8]. One of the reasons for this instability may be the ability of thiosulfate ions to disproportionate at pH close to, or lower than pH = 6, according to Reaction (1):



The formation of elemental sulfur and a decrease in thiosulfate concentration with time decrease the efficiency of these electrolytes.

To enhance the stability of thiosulfate electrolytes, some amount of sodium sulfite may be added to the electrolyte [9]. The presence of sulfite in these solutions prevents thiosulfate decomposition, because the hydrolysis $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{OH}^-$ generates additional hydrosulfite ions, thus displacing the equilibrium of Reaction (1) to the left. Besides, the addition of sulfite causes a shift of pH to the alkaline region. So, even with relatively small concentrations of sodium sulfite (0.01 M) the solution is characterized by pH \approx 9.5, which also prevents decomposition of this electrolyte. These and other positive effects of sulfite explain why mixed thiosulfate-sulfite solutions are often used for practical purposes. In particular, the use of thiosulfate-sulfite electrolytes for the electrodeposition of gold is well known; it is used in the trough-mask plating technique for microelectronic and micro-system application [10]. It is obvious that the addition of sulfite may also be useful to enhance the stability of electrolytes for thiosulfate leaching or electrochemical dissolution of gold.

Meanwhile, electrode processes that take place on the gold anode in mixed thiosulfate-sulfite solutions remain poorly studied. In the present work we study the features of the kinetics of anode processes on the “fresh” surface of a gold rotating disk electrode (RDE) in solutions of sulfite, thiosulfate and in mixed thiosulfate-sulfite solutions by means of voltammetry. Identification of these features may promote understanding of the processes that take place on the gold anode in thiosulfate-sulfite electrolytes.

2. Experimental

The voltammograms in the system under investigation were recorded on the gold rotating disk electrode (RDE) with an

* Tel.: +7 3832170402; fax: +7 3833322847.

E-mail address: AZelinsky@solid.nsc.ru (A.G. Zelinsky).

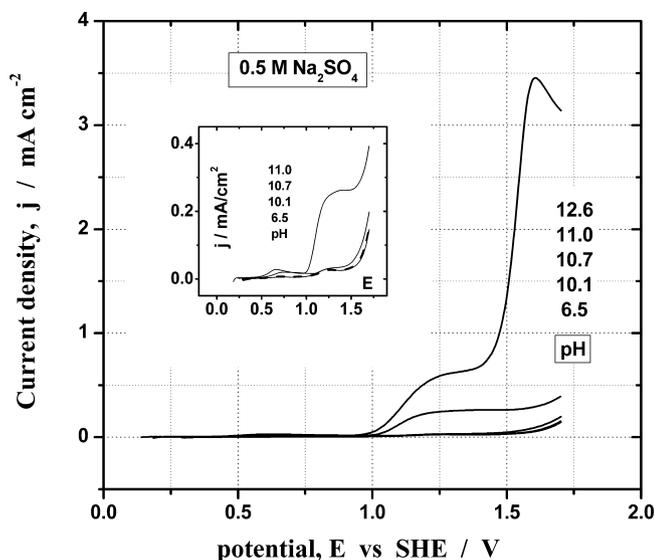


Fig. 1. Dependence of anode current density on the potential of gold electrode and pH in the solutions of 0.5 M sodium sulfate.

IPC-compact potentiostat (Inst. Phys. Chem. RAS) in a three-electrode cell with Pt counter-electrode and Ag/AgCl (saturated KCl) reference electrode. The potential of the latter is 0.197 V with respect to a standard hydrogen electrode (SHE). The values of all potentials are given in the SHE scale. The working electrode was the end of a gold wire 0.8 mm in diameter. The side surface of the wire was insulated with a teflon shell. The preparation of the working electrode for measurements involved mechanical renewal of its surface by cutting off a thin ($\approx 5 \mu\text{m}$) metal layer using a cutter made of a hard alloy. Cutting was performed directly in the solution under study. This procedure ensures rapid preparation of a “pure” and reproducible metal surface [11]. Voltammograms were measured using the following procedure. At first, the electrode was placed in the solution under study and rotated at a given speed. Then its surface was renewed by cutting off a metal layer at the open circuit potential (OCP). Then the potential of the electrode was scanned in the positive direction from the initial potential (0.0 V) to the final potential and back. Only the currents of the first direct and inverse scans were recorded. Then the procedure of voltammogram measurement was repeated at another speed of electrode rotation or in a solution of different composition. The potential scan rate was 50 mV s^{-1} . Rotating speed varied within the range from 0.0 to 1890 rpm.

Solutions were prepared using twice distilled water, $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 , Na_2SO_4 salts and KOH of analytical grade (ChimProm). A solution of 0.5 M Na_2SO_4 was used as the base electrolyte. Solution pH was provided by adding the necessary amount of KOH solution and measured with the help of the glass electrode. Oxygen was not removed from the solutions. The solutions were prepared immediately before measurements were taken to decrease the possibility of their decomposition before an experiment.

3. Results and discussion

3.1. Experimental conditions

Two factors are to be taken into account when studying the anode process on gold electrodes in solutions containing sodium sulfite. The first is that sodium sulfite is hydrolyzed in water: $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{OH}^-$. Therefore, depending on the sodium sulfite concentration, the pH of the solution will change. For

example, in agreement with the equilibrium constant ($K = 1 \times 10^{-7}$) of this reaction, within the range of sulfite concentrations from $1 \times 10^{-4} \text{ M}$ to 0.1 M, solution pH will change within the range of 8.5 to 10. The second factor is that Faraday processes of oxide formation and oxygen evolution take place on gold in the region of relatively high positive potential. The intensity of these side processes and the region in which they occur depend on the pH of the solution.

To obtain adequate information on the electrochemical process under investigation, it is necessary to choose experimental conditions for which the effect of the above-mentioned side Faraday processes on measured current is minimal. For this purpose, we measured voltammetric curves in 0.5 M Na_2SO_4 solutions with different pH (Fig. 1). These results show that at a potential more positive than 1.0 V in solutions with $\text{pH} > 10.5$ noticeable anodic current is observed on the gold electrode; this current is due to the oxidation of the electrode surface. In solutions with a pH value of 7 to 10, anodic current is insignificant until the potential of about 1.3 V. In agreement with these data, measurements of voltammograms were carried out in solutions containing sodium sulfite in concentrations not higher than 0.1 M and $\text{pH} \approx 10$. The range of potentials within which measurements were carried out was limited to the region from 0.0 V to 1.3 V (SHE).

3.2. Oxidation of sulfite

Fig. 2 shows the dependences of current density on the potential of a gold RDE (912 rpm), measured in a solution of 0.5 M Na_2SO_4 (curve 1) and in a solution of 0.5 M $\text{Na}_2\text{SO}_4 + 0.1 \text{ M Na}_2\text{SO}_3$ (curve 2). One can see that the current density in the base electrolyte is small in comparison with that in a solution containing sodium sulfite. In the solution of sodium sulfite, the current density increases with anodic potential. Then, after the voltage of about 0.9 V is achieved, a plateau is observed.

To explain the plateau on the j - e curve, we measured voltammograms at different electrode rotation speeds. The results are shown in Fig. 3. The applied potential was limited from 0.0 V to 1.3 V. One can see that current density in the region of the plateau (j^{lim}) increases with an increase in RDE rotation speed (ω). Within the rotation speed range studied, j^{lim} (A cm^{-2}) values are linearly dependent on $\omega^{0.5}$ (rad s^{-1}) (see insert to Fig. 3). This dependence of j^{lim} value is characteristic of electrode processes with diffusion

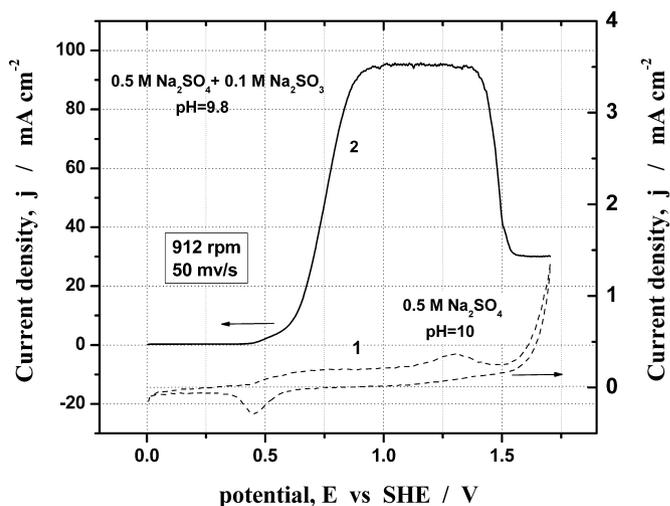


Fig. 2. Dependences of anode current density on the potential of gold electrode in the solution of 0.5 M Na_2SO_4 (1) and in the solution of 0.5 M $\text{Na}_2\text{SO}_4 + 0.1 \text{ M Na}_2\text{SO}_3$ (2).

Download English Version:

<https://daneshyari.com/en/article/184698>

Download Persian Version:

<https://daneshyari.com/article/184698>

[Daneshyari.com](https://daneshyari.com)