ELECTROCHEMICAL STUDIES ON THE MECHANISM

OF GOLD DISSOLUTION IN THIOSULFATE SOLUTIONS[①]

Zhu, Guocai   Fang, Zhaoheng   Chen, Jiayong

Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing 100080, China

ABSTRACT

The dissolution of gold in aqueous thiosulfate solution and the effect of the presence of ammonia in the solution were investigated with methods of voltammetry and electrochemical impedance spectra (EIS). Results indicated that the anodic voltammetric curves of the gold electrode in thiosulfate solutions does not indicate the features of gold dissolution. The passive phenomena of gold may result from the elemental sulfur adsorbed on the gold surface due to the surface decomposition of $S_2O_3^{2-}$ or the electrochemical oxidation of s^{2-} on the electrode surface. By addition of ammonia into the system, the passivation of gold is completely eliminated, and the gold dissolution, on the other hand, seems to be catalyzed through the formation of the intermedia complex $Au(NH_3)_2^+$.

Key words: gold dissolution   thiosulfafe solution   mechanism   electrochemistry

1   INTRODUCTION

The dissolution of gold in aqueous thiosulfate was recognized in the early days of this century, and recorded as "Patera" process[1]. The study on the process became very active only in 1970s and 1980s, and much progress was achieved since then[2-5]. The process mechanism, however, has not be completely understood to now, which in turn hinders the development of the technology. Recently, Jiang Tao *et al*[6] proposed a process mechanism that the ammonia reacted with gold to form an intermediate complex as Au $(NH_3)_2^+$ at first, and then reacted with $S_2O_3^2$ to form another complex as Au $(S_2O_3)_2^3$. This proposal, however, does not reveal the dissolution mechanism of gold in the thiosulfate solution without ammonia and also does not explain whether NH_4^+ or

NH_3 is the effective piece in the process. It is therefore necessary to investigate this problem further. In this paper the dissolution of gold in the aqueous thiosulfate and the effect of ammonia on the gold dissolution were systematically investigated with methods of anodic voltammetry and EIS, and a possible mechanism will be proposed.

2   EXPERIMENTAL

Experiments were carried out in a cell with three electrodes, i. e. calomel electrode (SCE) as the reference, glass carbon electrode as the auxiliary and the pure gold wire (99. 99% Au with 0. 2 mm diameter) as the working electrode. The electric potential in the paper is thus related to SCE.

The electrochemical set up consists of Princeton EG/G model 173 potentiostat,

175 signal generator, 179 digit coulometer and 376 logarithmic current converter. The EIS was measured with Solartron Impedance Spectra System, with 1 256 alternative signal generator, computer sampling system and frequency response analysis as the main components.

3 RESULTS

3. 1 *Anodic Voltammetry in Thiosulfate Solutions*

As shown in Fig. 1, in the cyclic voltammetry there has no anodic peak recognized as the gold dissolution in aqueous thiosulfate with a low concentration, e. g. 0. 1 mol/L at a voltage sweep rate, such as 10 mV/s. Fig. 2 shows the anodic voltammetries of good electrode in different solutions. By increase of the thiosulfate concentration and addition of ammonia to the system, the anodic peak of gold dissolution appears, and the peak current increases with increase of ammonia concentration. The effects of ammonia concentration on the gold dissolution in the aqueous thiosulfate under various
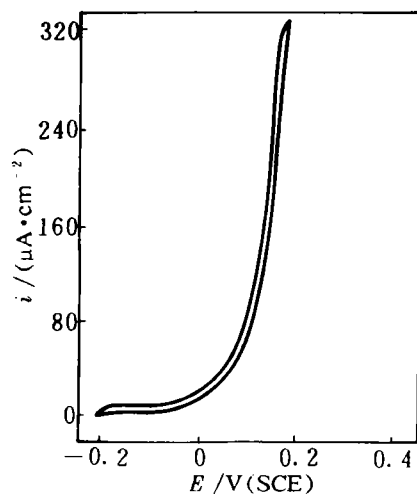
conditions are listed in Table 1. It is clear that adding ammonia is more effective for gold dissolution than adding ammonium sulphate at the same concentration level.

From the equilibrium diagram of ammonia — water system it is pointed out that the ammonium ion is the majority speices for solution pH$<$8 while ammonia is the majority species for pH$>$11, as shown in Fig. 3. Under the conditions studied the ratio of NH_3/NH_4^+ in ammonia solutions is much higher than that in ammonium sulphate solutions.

3. 2 *The EIS in Thiosulfate Solutions*

Table 1 The peak current i_p of gold electrode in 1 mol/L$(NH_4)_2S_2O_3$ solution with the addition of various concentration C of ammonia or ammonium sulphate

	C_{NH_4OH} /mol·L^{-1}			$C_{(NH_4)_2SO_4}$ /mol·L^{-1}		
	0	0. 5	1. 0	2. 0	0	0. 5	1. 0
pH	6. 4	10. 1	10. 4	10. 8	6. 4	6. 2	6. 1
i_p/ mA·cm^{-2}	0. 11	0. 64	1. 14	1. 36	0. 11	0. 44	0. 56

Fig. 1 Voltammetry of gold electrode in 0. 1 mol/L $Na_2S_2O_3$ solution
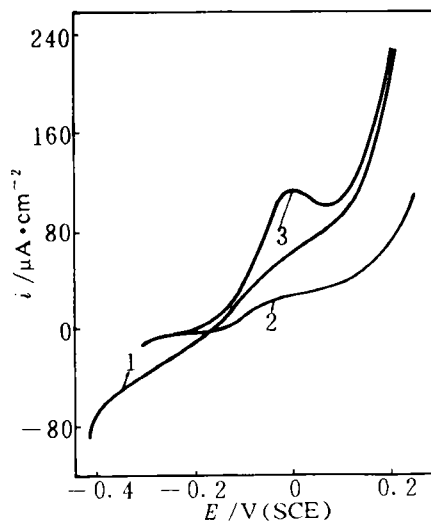
Fig. 2 Anodic voltammetrics of gold electrode in different solutions

1—1 mol/L $Na_2S_2O_3$; 2—1 mol/L$(NH_4)_2S_2O_3$;
3—1 mol/L$(NH_4)_2S_2O_3$+1 mol/L NH_3. N_2
atmosphere, 25 C, 5 mV/s sweep rate

The EIS of gold electrode in 1 mol/ LNa₂S₂O₃ and 1 mol/L Na₂S₂O₃ plus 2 mol/L NH₃ solution under different potentials are given respectively in Figs. 4 and 5. It appears that the diameter of capacitive arc of the EIS in aqueous sodium thiosulfate gradually decreases with increasing anodic potential in the range of -0.02 to 0.1 V. An inductive arc in the EIS is observed at a certain potential that demonstrates the characteristics of gold dissolution in the voltametry of the gold electrode. As seen from Fig. 4, EIS shows two capacitive areas as the anodic potential is higher than 0.1 V.
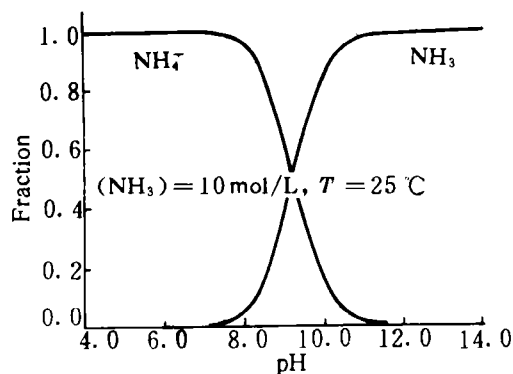
It is clear that the EIS of gold electrode

Fig. 3　Fractions of ammonia and ammonium ions in equilibrium in solutions
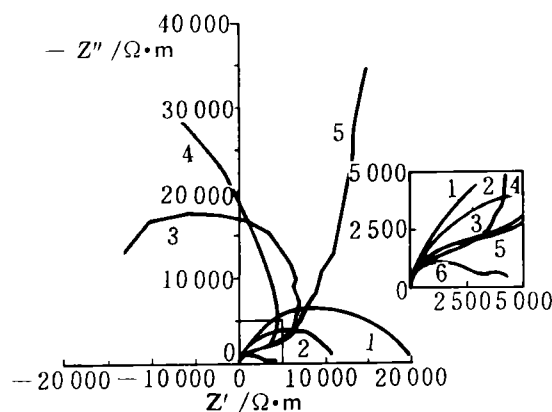
Fig. 4　The EIS of gold electrode in 1 mol/L Na₂S₂O₃ at different potentials
1— $E = 0.1$ V; 2— $E = -0.05$ V; 3— $E = -0.02$ V
4— $E = 0.05$ V; 5— $E = 0.10$ V; 6— $E = 0.20$ V

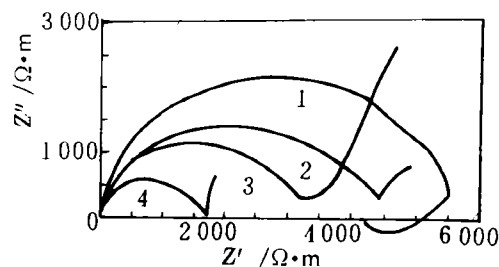Fig. 5　The EIS of gold electrode in 1 mol/L Na₂S₂O₃ plus 2 mol/L NH₃ at different potentials
1— $E = -0.10$ V; 2— $E = -0.02$ V;
3— $E = 0.05$ V; 4— $E = 0.10$ V

in 1 mol/L Na₂S₂O₃ plus 2 mol/L NH₃ solution display the capacitive arc in the range of -0.1 to 0.1 V. The diameter of the arc decreases with the increasing potential.
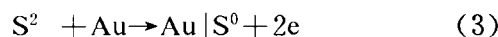
By adding sodium sulfide into thiosulfate solution, the electrochemical impedance as shown by the EIS decreases with increasing potentials in the range from -0.5 to 0.2 V. In addition, the EIS in low frequency range will show divergence, as seen in Fig. 6.

4　DISCUSSION

The decomposition reaction as shown below may occur on the surface of the gold electrode in S₂O₃²⁻ solutions as:
$$S_2O_3^{2-} \rightarrow S^0 + SO_3^{2-} \qquad (1)$$
$$3S_2O_3^{2-} + 6OH^-$$
$$\rightarrow 4SO_3^{2-} + 2S^{2-} + 3H_2O \qquad (2)$$
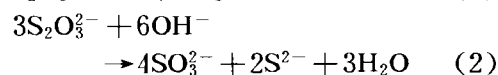
The elemental sulfur S^0 may be absorbed on the gold surface and anodic process may occur on the gold electrode surface as:
$$S^{2-} + Au \rightarrow Au|S^0 + 2e \qquad (3)$$
and the dissolution reaction of the gold may be passivated by the elemental sulfur covered on the surface.

A black film was observed when a gold disk electrode was immersed in thiosulfate solutions with the concentration from 0.09 to

0. 19 mol/L at 65 ℃ for 15-30 min[9]. The X-ray diffraction analysis show the film consisted mainly of the elemental sulfur. From the EIS shown in Fig. 4 an inductive arc was observed at the potential that demonstrates the characteristics of gold dissolution in the voltametry of the gold electrode. This is the significant feature for an active-passive electrochemical process on the metal surface[7,8]. This reaction mechanism can be represented by the reactions as

$$A^{n_1-} = A + n \, \varsigma_1^e \tag{4}$$

$$M = M^{n_2+} + n \, \varsigma_2^e \tag{5}$$
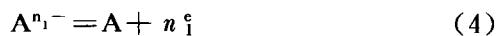
and some inductive arc in the EIS will be appeared at a certain potential, according to the theoretical model developed by Cao Cunnan[8]. In the thiosulfate system there has been a similar reaction mechanism, i. e. a passivation, which resulted from adsorption of elemental sulfur on the gold surface by decomposition of thiosulfate, and an active dissolution reaction of gold by oxidation and complex formation occurred simultaneously. The EIS of gold electrode in thiosulfate solutions therefore display an inductive arc in a certain range of potentials.
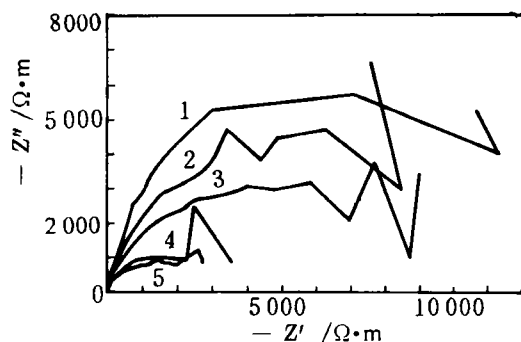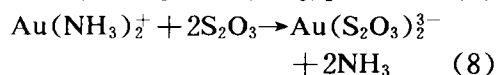

Fig. 6   The EIS of gold electrode in
1 mol/L Na₂S₂O₃ plus 0. 01 mol/L Na₂S
at different potentials.
1— $E = -0.50V$; 2— $E = -0.35V$; 3— $E = -0.30V$;
4— $E = 0.05V$; 5— $E = 0.20V$;

By adding Na₂S into the thiosulfate system at a lower concentration, the S^{2-} in the
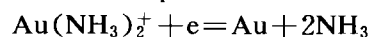
solution may accelerate the reaction of formation and then adsorption of elemental sulfur on the gold surface. This is the reason why the EIS of gold electrode in thiosulfate with 0. 01 mol/ L Na₂S is quite different from those in the pure thiosulfate solution. The diverged phenomena of the EIS in lower frequency could be caused by the external noise.

As seen from Table 1, ammonia is more effective for the gold dissolution in aqueous thiosulfate and is more possible to take place in the process. As proposed by Jiang Tao et al[6], the effect of ammonia in gold dissolution can be expressed as

$$Au \rightarrow Au^+ + e \tag{6}$$

$$Au^+ + 2NH_3 \rightarrow Au(NH_3)_2^+ \tag{7}$$

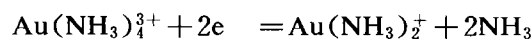$$Au(NH_3)_2^+ + 2S_2O_3 \rightarrow Au(S_2O_3)_2^{3-} + 2NH_3 \tag{8}$$

The competitive reaction of ammonia thus decreases the decomposition of thiosulfate and the adsorption of elemental sulfur on the surface of gold electrode. In the alkaline solution of ammonia the thiosulfate is more stable from the point of thermodynamics. Passivation of the gold electrode in thiosulfate is completely eliminated by adding ammonia.
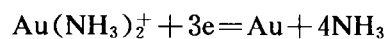
It is reported that[10]

$$Au(NH_3)_2^+ + e = Au + 2NH_3$$
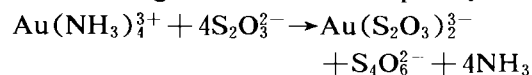
$$E^0 = 0.563V$$

$$Au(NH_3)_4^{3+} + 2e = Au(NH_3)_2^+ + 2NH_3$$

$$E^0 = 0.206 V$$

$$Au(NH_3)_2^+ + 3e = Au + 4NH_3$$

$$E^0 = 0.326 V$$

and the $Au(NH_3)_4^{3+}$ must be the major pieces in the system under study. In fact, due to the reductive nature of thiosulfate, the folowing reaction can take place:

$$Au(NH_3)_4^{3+} + 4S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + S_4O_6^{2-} + 4NH_3$$

Thus it is more   reasonable that Au

phase consisted of 30% P_{204} + sulphonating kerosene.

4 CONCLUSIONS

The SLM technique has proved to be suitable for recovering and concentrating rare earth from leaching solutions of low grade ores .

At optimum conditions the rare earth flux can achieve 5 g/m^2. h, and this technique may hold some promise of commercial recovery of rare earth from dilute solutios, for example, from the leaching solution of low grade ores.

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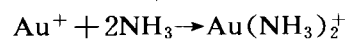$(NH_3)_2^+$ acts as the intermediate speices in the process.

5 CONCLUSIONS

The anodic process of gold electrode in thiosulfate solution consists of an active dissolution reaction as

$$Au \rightarrow Au^+ + e$$
$$Au^+ + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-}$$
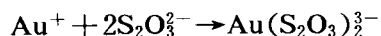
and a simultaneous passive reaction of formation and then adsorption of elemental sulfur on the surface of the electrode as

$$S_2O_3^{2-} + Au \rightarrow Au|S^0 + SO_3^{2-}$$
$$S^{2-} + Au \rightarrow Au|S^0 + 2e$$
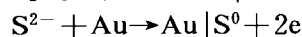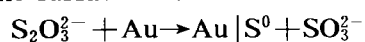
By adding ammonia into thiosulfate system, the passivation of the electrode can be eliminated, and the process may described as

$$Au \rightarrow Au^+ + e$$
$$Au^+ + 2NH_3 \rightarrow Au(NH_3)_2^+$$
$$Au(NH_3)_2^+ + 2S_2O_3 \rightarrow Au(S_2O_3)_2^3$$
$$+ 2NH_3$$

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