

Electrochemistry and Mechanism of Leaching Gold with Ammoniacal Thiosulphate

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ABSTRACT

The electrochemistry of leaching gold with thiosulphate has been studied systematically by using electrochemical techniques. Results show that the current peak of anodic dissolution of gold occurs at about 50 mV(SCE) and there is passivation in the polarisation curve in the thiosulphate solution in the absence of ammonia. Ammonia markedly improves the anodic dissolution rate of gold and reduces the passivation as well as making the current peak shift negatively. Results also show that there is no current peak for a cathodic process in the range of 0 ~ -900 mV(SCE) in the thiosulphate solution in the presence of oxygen but absence of cupric ions and ammonia. In the solution containing 0.1 mol/L cupric-ammonia ions, the peak occurs at about -400 mV (SCE) and the cathodic process is characteristic of a catalytic reaction. Oxygen presents a predominate effect on the cathodic process.

Based on the electrochemical investigation, the following mechanism of leaching gold with ammoniacal thiosulphate has been proposed. Ammonia reacts primarily with gold ions on the anodic surface of gold and the formed $Au(NH_3)_2^+$ reacts then with $S_2O_3^{2-}$ in solution to form the stabler $Au(S_2O_3)_2^-$. $Cu(NH_3)_4^{2+}$ gains electrons on the cathodic surface and is reduced to $Cu(NH_3)_2^+$, which is then oxidised by oxygen and regenerated into $Cu(NH_3)_4^{2+}$ after entering the solution.

INTRODUCTION

Although many papers (Umetsu and Tozawa, 1972; Berezowsky and Sefton, 1979; Kerley, 1981 and 1983; Flett, Derry and Wilson, 1983; Zipperian, Raghavan and Wilson, 1988) have been published on the thiosulphate extraction of gold in the last decade, few fundamental investigations have been made. Particularly, a study on the leaching electrochemistry which is significant to the leaching mechanism of gold has not been reported so far. There has been a lack of knowledge about the leaching mechanism, which obstructs the development and application of the technology. The purpose of the research work reported in this paper was to find out the anodic and cathodic behaviours of gold in thiosulphate solution and reveal the leaching mechanism of gold with ammoniacal thiosulphate through electrochemical investigations.

RESEARCH METHODS

The investigations were carried out with a Model 173 Potentiostat/Galvanostat from Princeton Applied Research Company, USA. The working electrode was prepared with 99.999 per cent gold powder by melting. Platinum sheet was made as the counter electrode. Saturated calomel electrode (SCE) was used as the reference electrode. Solutions used in testing were prepared with analytically pure reagents dissolved in double-distilled water. Oxygen was removed from testing solutions by nitrogen gas. All tests were conducted in the atmosphere of nitrogen at the temperature of 20°C apart from special explanation.

RESULTS AND DISCUSSIONS

The behaviours and mechanism of anodic dissolution of gold

Figure 1 is the steady state anodic polarisation curve of gold in thiosulphate solution. There are current peaks at about 50 mV(SCE) and 620 mV(SCE) in the range of 0 ~ 800mV (SCE). According to thermodynamical potential, it is deduced that the anodic dissolution of gold occurs at peak I at 50 mV and at peak II of 620 mV, the anodic oxidation of thiosulphate ions occurs. When a platinum electrode is used to replace the gold as working electrode, the peak I disappears but peak II still is present, which further shows that the peak I responds to the anodic dissolution of gold and peak II to anodic oxidation of thiosulphate ions.

Figure 2 is the potentiodynamic voltammogram of anodic dissolution of gold in the thiosulphate solution in the presence of neither cupric ions nor ammonia. Effects of ammonia on the anodic process are shown in Figures 3 and 4. It is found that the anodic behaviour of gold is greatly changed in the presence of ammonia. Ammonia markedly improves the anodic dissolution rate of gold and reduces the passivation as well as making the current peak shift negatively.

Effects of cupric ions and cupric ammonium complex ions on the anodic process were tested. Results show that the effects of them are not evident.

Cyclic voltammograms of anodic dissolution of gold in the solution of 1.0 mol/L $S_2O_3^{2-}$ and 1.0 mol/L NH_3 are showed in Figure 5. The parameters in the curves are labelled in Table 1.

TABLE 1
Parameters in the cyclic voltammogram in Figure 5.

v(mV/s)	i_p^a ($\mu A/cm^2$)	i_p^c ($\mu A/cm^2$)	$ i_p^c/i_p^a $	$i_p^a/v^{1/2}$
10	1367	500	0.37	432.3
40	2700	1033	0.38	426.9
80	3067	1533	0.50	342.9
130	3900	1966	0.50	342.1

The results show that the anodic dissolution of gold in thiosulphate solution is characteristic of electrochemical-chemical (EC) reaction.

Two possible action mechanisms of ammonia are that ammonia is adsorbed on the electrode surface to improve its reactivity and ammonia takes part in anodic electrode reactions. A current step technique was used to find out the action mechanism of ammonia. Step current (i), transition time (τ) and consumed quantity (Q) of electric charge are shown in Table 2.

It is known that the total quantity of electric charge consumed (Q) should be

$$Q = Q_0 + Q_c$$

where Q_0 is the electric charge consumed in the adsorption layer and Q_c is the charge consumed for diffusion. Based on Sand equation (Liu, 1987):

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$$Q_c = \frac{n^2 F^2 \pi D (C^0)^2}{4i}$$

hence

$$Q = Q_o + \frac{n^2 F^2 \pi D (c^0)^2}{4i}$$

Q is shown in Figure 6 as a function of i^{-1} . When i^{-1} tends to 0, Q is equal to Q_o . That is, Q_o is zero. No adsorption on the surface of gold is proved and the adsorption mechanism of ammonia is hence excluded.

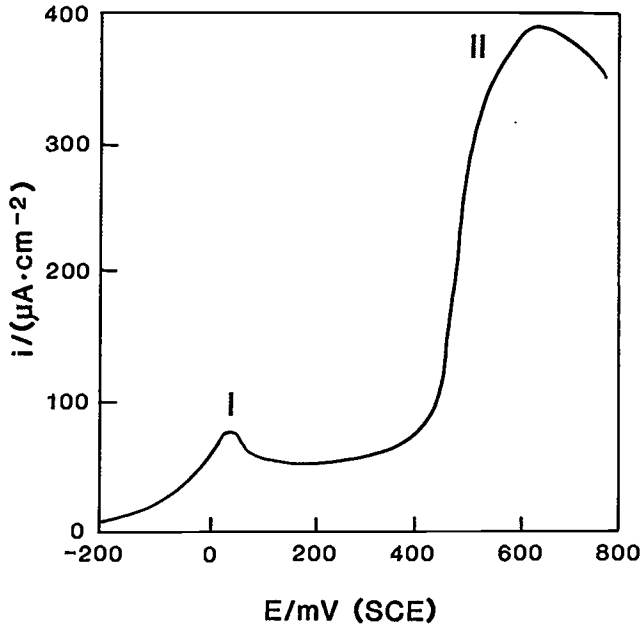


FIG 1 - The steady state anodic polarisation curve (2.0 mol/L $S_2O_3^{2-}$, no cupric ions and ammonia, pH = 10).

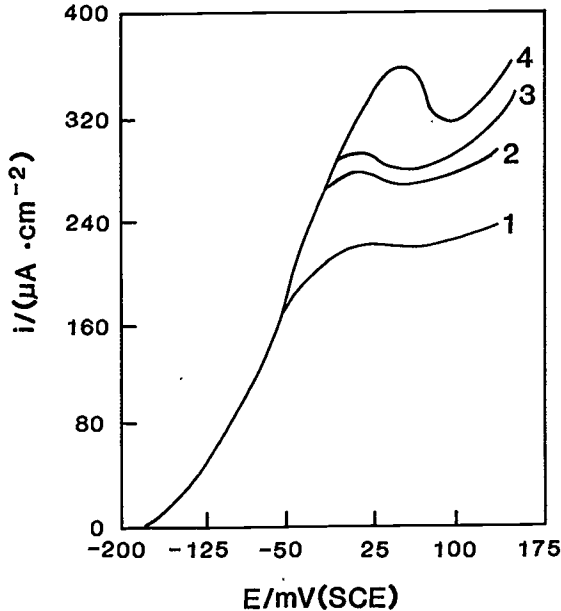


FIG 2 - Voltammogram of anodic dissolution of gold (1.0 mol/L $S_2O_3^{2-}$, pH = 10, no cupric ions and ammonia. 1 $v = 1$ mv/s; 2 $v = 3$ mv/s; 3 $v = 5$ mv/s; 4 $v = 10$ mv/s.

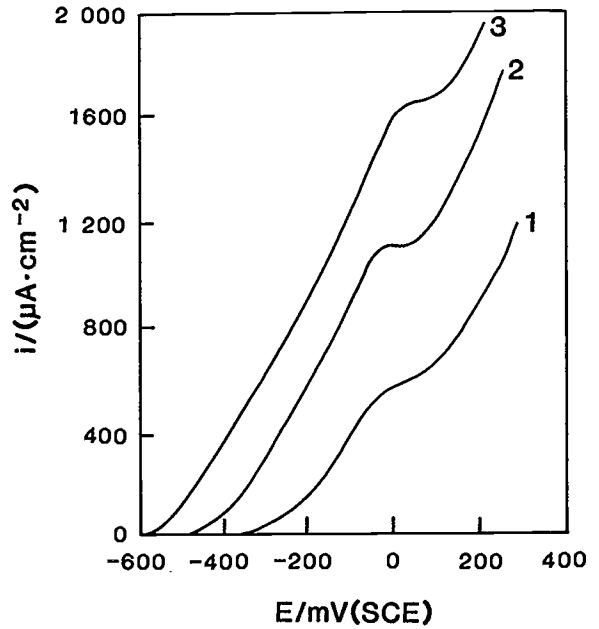


FIG 3 - Voltammogram of anodic dissolution of gold (1.0 mol/L $S_2O_3^{2-}$, pH = 10, 1.0 mol/L NH_3 , no cupric ions). 1 $v = 2$ mv/s; 2 $v = 5$ mv/s; 3 $v = 10$ mv/s.

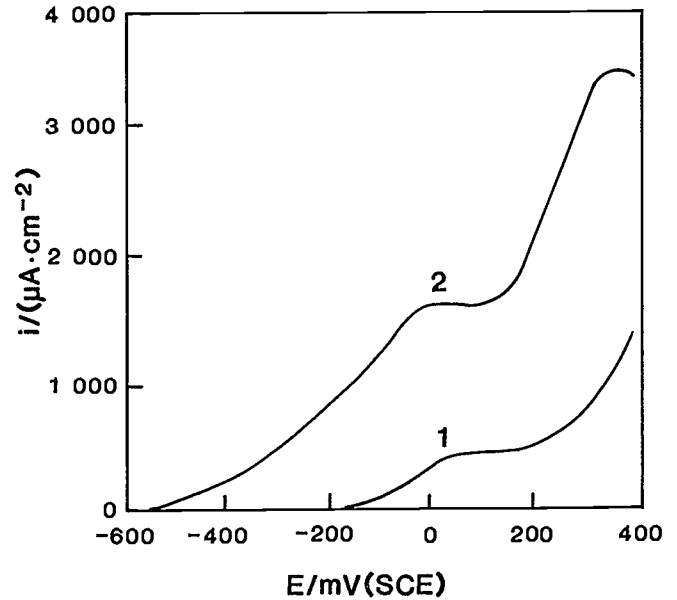
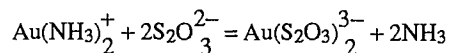
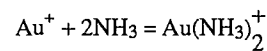
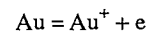


FIG 4 - Effect of ammonia on anodic dissolution of gold (1.0 mol/L $S_2O_3^{2-}$, $v = 10$ mv/s; pH = 10, no cupric ions. 1 $[NH_3] = 0$; 2 $[NH_3] = 1, 0$ mol/L.

Based on above results, anodic dissolution mechanism of gold in ammoniacal thiosulphate solution was proposed as follows:



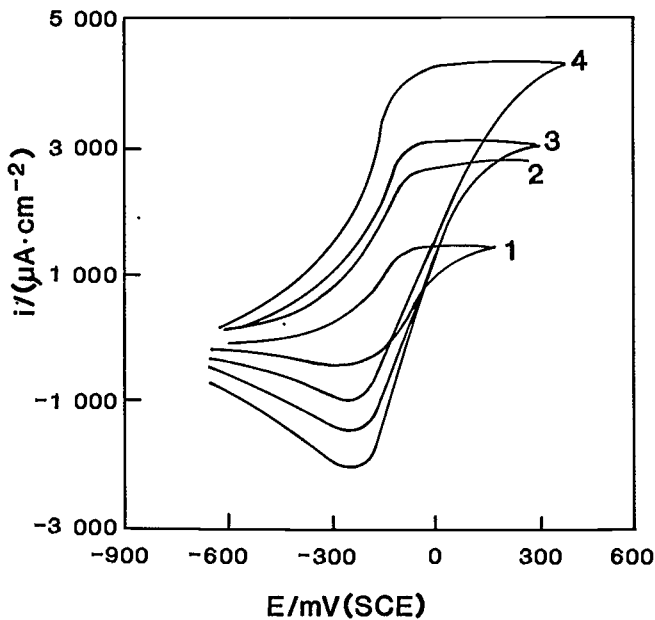


FIG 5 - Cyclic voltammograms of anodic dissolution of gold (1.0 mol/L $S_2O_3^{2-}$, 1.0 mol/L NH_3 pH = 10).

TABLE 2
Results of current step.

step current i (mA/cm ²)	2.0	2.5	3.0	4.0	5.0
transition time τ (s)	11.0	7.0	5.0	2.8	1.8
electric charge consum $Q (=i\tau)$	22.0	17.5	15.0	11.2	9.0

There are other four facts to support the mechanism in addition to the last investigation:

1. Passivation in polarisation curves disappears in the presence of ammonia;
2. Negative charge of electrode surface becomes greater with the increase of ammonia concentration, which is unfavourable for transport of thiosulphate ions into the surface but has no influence on the transport of ammonia;
3. The stability constant of gold-thiosulphate ions is greater than that of gold - ammonia ions;
4. Leaching tests have shown that in the absence of thiosulphate very little gold is extracted.

The behaviour and mechanism of cathodic process

Polarisation curves of cathodic process of gold-thiosulphate system are shown in Figure 7. The addition of cupric ammonium ions entirely changes the behaviour of the cathodic process. There is no current peak of cathodic process in the range of 0 ~ -900 mV/SCE in the absence of cupric ammonium ions. A bright peak appears at -400 mV/SCE in the solution containing 0.1 mol/L cupric ammonium ions. Figure 8 shows that oxygen evidently promotes the cathodic process. Investigations show that ammonia and cupric ions have no direct effect on the cathodic process. Based on above results, the mechanism of cathodic process of gold leaching of ammoniacal thiosulphate was put forward as follows:

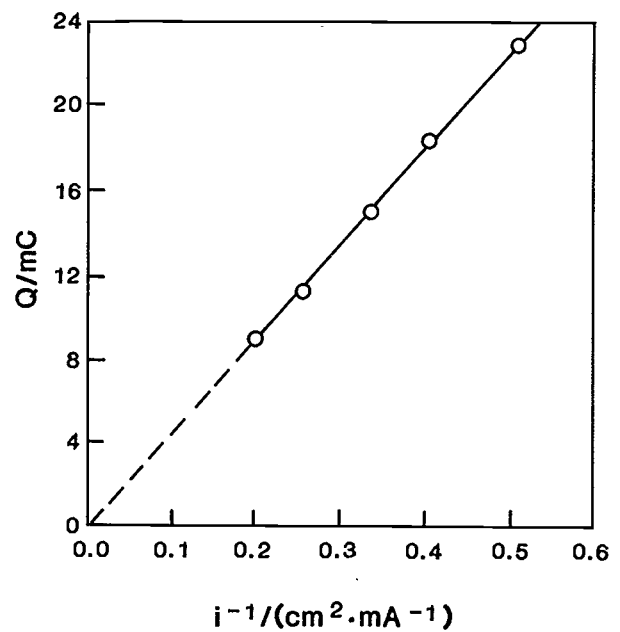
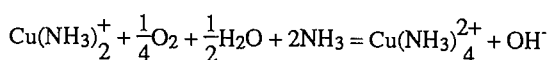
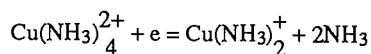


FIG 6 - Q as a function of i^{-1} .

Cyclic voltammetry investigations were carried out to further confirm the mechanism. The results are shown in Figure 9. The parameters of current peaks are given in Tables 3 and 4. The parameters obtained in a nitrogen atmosphere (Table 3) are characteristic of a quasi-reversible process and the parameters in oxygen (Table 4) are characteristic of catalytic reactions (Kemp, 1985). These results are consistent with the mechanism proposed above.

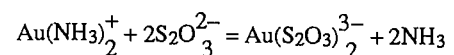
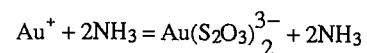
There are still another four facts to support the mechanism:

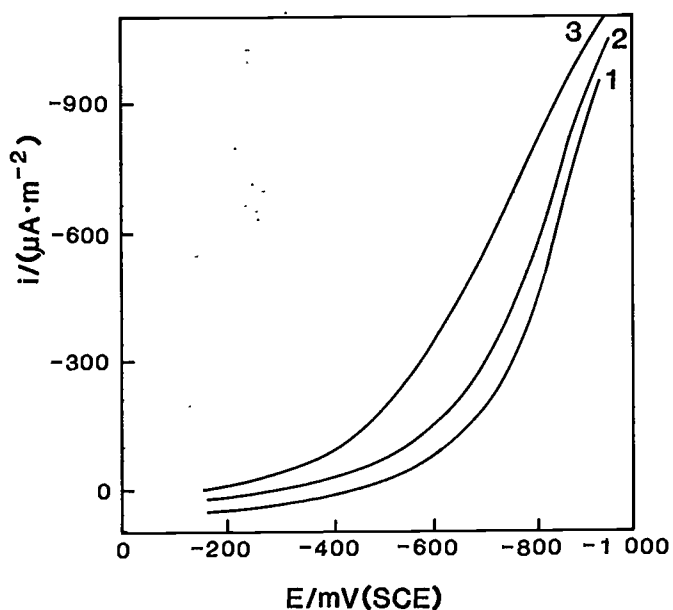
1. The solubility and concentration of cupric ammonium ions are greater than that of oxygen in water solution;
2. copper (II) - ammonia ions can reach gold surface with the help of electric migration;
3. Reversibility of oxidation - reduction of $Cu(NH_3)_4^{2+}/Cu(NH_3)_2^+$ is better than that of oxygen;
4. The rate of regeneration of $Cu(NH_3)_2^+$ to $Cu(NH_3)_4^{2+}$ is quite fast in the presence of oxygen.

The mechanism and model of leaching gold with ammoniacal thiosulphate

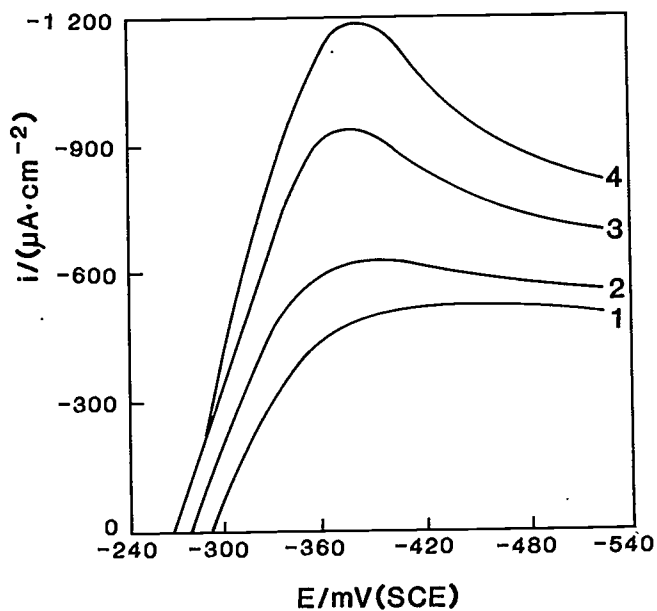
Summarising the above results, we proposed the mechanism of leaching gold with ammoniacal thiosulphate is as follows. Ammonia reacts preferentially with gold ions on the anodic surface of gold, and the $Au(NH_3)_2^+$ which is formed reacts then with $S_2O_3^{2-}$ after entering the solution to form the stabler $Au(S_2O_3)_3^{3-}$. $Cu(NH_3)_4^{2+}$ gains electrons on the cathodic surface and is reduced to $Cu(NH_3)_2^+$, which is then oxidised by oxygen and regenerated into $Cu(NH_3)_4^{2+}$ after entering the solution. This mechanism also can be displayed by the following electrochemical reactions or model in Figure 10.

Anodic process:

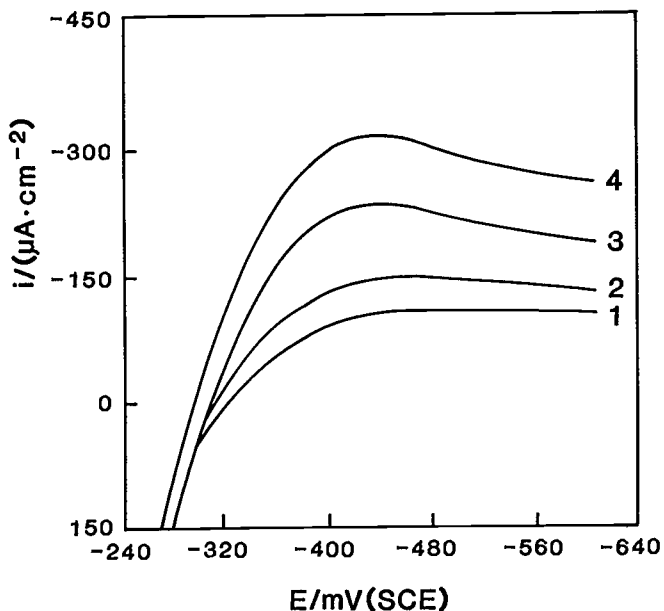




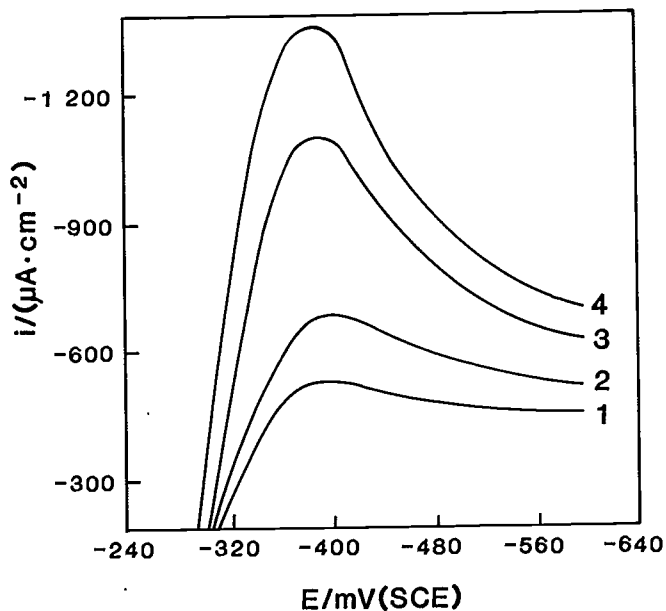
(a)



(a)



(b)



(b)

FIG 7 - Voltammogram of cathodic process of gold in thiosulphate solution

(1.0 mol/L $S_2O_3^{2-}$; pH = 10, in air).

(a) No $Cu(NH_3)_2^{2+}$; 2v = 5mv/s; 3 v = 10 mv/s.

(b) 0.1 mol/L $Cu(NH_3)_4^{2+}$; 1 v = 1 mv/s; 2 v = 2mv/s; 3 v = 5 mv/s; 4v = 10 mv/s.

Cathodic process:

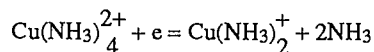


FIG 8 - Voltammogram of cathodic process of gold in thiosulphate solution

(1.0 mol/L $S_2O_3^{2-}$, pH = 10).

1 v = 1.0 mv/s; 2 v = 2.0 mv/s; 3 v = 5 mv/s; 4 v = 10 mv/s.

(a) In nitrogen; (b) In oxygen.

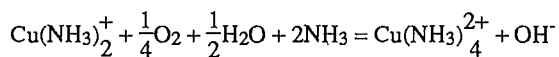


TABLE 3

The parameters of current peaks of voltammogram in atmosphere of nitrogen.

v(mV/s)	i_p^c ($\mu\text{A}/\text{cm}^2$)	$i_p^c/v^{1/2}$	E_p^c (mv)	E_p^a (mv)	$E_p^a - E_p^c$
1	507	507	-308.3	-222.9	85.4
2	720	509	-318.7	-216.7	102.0
5	1130	505	-325.0	-212.5	112.5

TABLE 4

The parameters of current peaks of voltammogram in atmosphere of oxygen.

v(mV/s)	i_p^c ($\mu\text{A}/\text{cm}^2$)	i_p^a ($\mu\text{A}/\text{cm}^2$)	i_p^a/i_p^c	$i_p^c/v^{1/2}$
1	608	167	0.27	608
2	792	350	0.44	560
5	1208	541	0.45	540

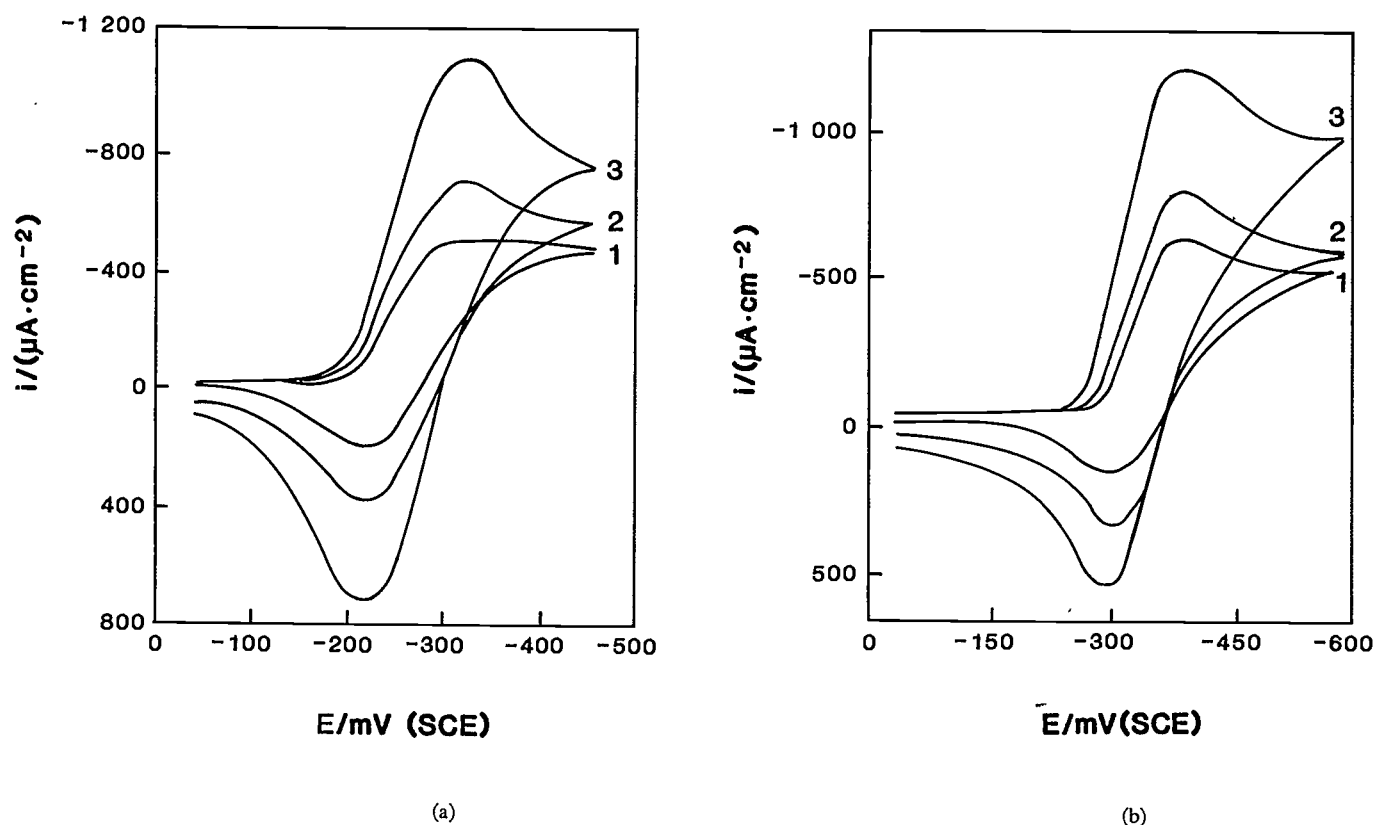


Fig 9 - Cyclic voltammogram of cathodic process of gold in thiosulphate solution

$$(1.0 \text{ mol/L } \text{S}_2\text{O}_3^{2-}, 0.1 \text{ mol/L } \text{Cu}(\text{NH}_3)_4^{2+}, \text{pH} = 10).$$

$$1 v = 1 \text{ mV/s}; 2 v = 2 \text{ mV/s}; 3 v = 5 \text{ mV/s}.$$

(a) In nitrogen, (b) In oxygen

CONCLUSION

The current peak of anodic dissolution of gold occurs at about 50 mV(SCE) and there is passivation in the polarisation curves in the thiosulphate solution in the absence of ammonia. Ammonia reduces the passivation and improves the anodic dissolution rate of gold. Cupric ions and cupric - ammonia ions have no evident effects on the anodic process.

There is no current peak of cathodic process in the range of 0 ~ -900 mV(SCE) in the presence of oxygen but absence of cupric ions and ammonia. In the presence of cupric ions and ammonia, the peak occurs at about -400 mV(SCE). Oxygen presents a predominate effect on the cathodic process. Effects of neither cupric ions nor ammonia on the cathodic process have been found.

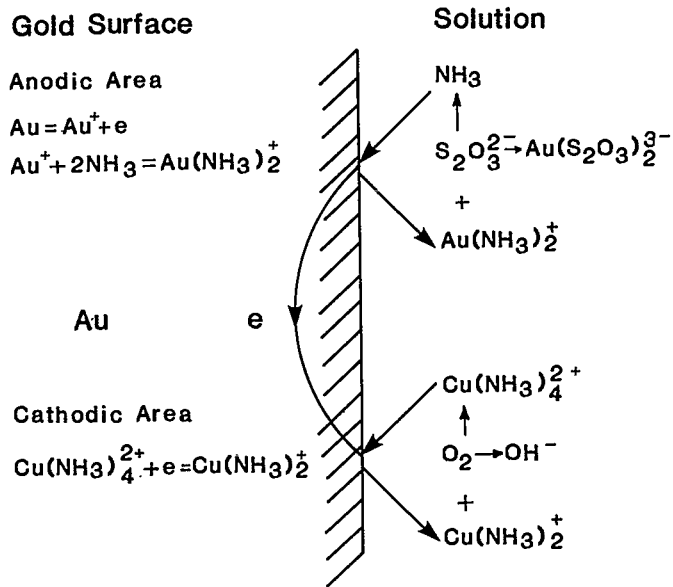


FIG 10 - The model of electrochemical - catalytical mechanism of ammoniacal thiosulphate leaching of gold.

Based on the investigation, the mechanism of leaching gold with ammoniacal thiosulphate was proposed as follows. Ammonia preferentially complexes gold ions on anodic surface of gold and the formed $\text{Au}(\text{NH}_3)_2^+$ reacts then with $\text{S}_2\text{O}_3^{2-}$ after entering solution to the form stabler $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$. $\text{Cu}(\text{NH}_3)_4^{2+}$ gains electrons on the cathodic surface and is reduced to $\text{Cu}(\text{NH}_3)_2^+$ which is then oxidised by oxygen and regenerated into $\text{Cu}(\text{NH}_3)_4^{2+}$ after entering the solution. That is, ammonia catalyses the anodic process and $\text{Cu}(\text{NH}_3)_4^{2+}$ catalyses the cathodic process of thiosulphate leaching of gold.

ACKNOWLEDGEMENT

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New Gold Technology

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