JOURNAL OF APPLIED ELECTROCHEMISTRY 12 (1982) 231–234

Selective recovery of gold from spent gold sulphite solutions by electrodeposition on graphite cloth electrodes

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Received 29 June 1981

A flow-through cell, employing an array of twin graphite cloth electrodes and connected to a charge injector potentiostat was employed for the electroseparation of gold from gold sulphite, $Au(SO_3)_2^{3-}$, solution containing cadmium, copper and chloride ions. The high overvoltage for the reduction of gold ions in this medium prevents its selective deposition (copper codeposits and hydrogen gas evolves at the same time). Hydrogen peroxide, added judiciously, oxidizes sulphite to sulphate; the gold Au(I) ions complex with chloride, establishing a system similar in its electrochemical behaviour to one previously discussed. Gold chloride, $[AuCl_2]^-$, solutions disproportionate readily; to minimize this process, a double flow-through system was built, in which the sulphite and hydrogen peroxide solutions enter a small mixing chamber as separate streams, are mixed in the appropriate ratio and allowed to react only a few minutes before reaching the electrodes. Gold deposits on the first graphite screen, and cadmium and copper deposit partially on the next screen, providing an economical approach to the continuous recovery and/or separation of gold from gold sulphite effluents containing base metal admixtures.

1. Introduction

Sulphite based electroplating solutions have recently been much publicized as a new type of non-toxic bath, possessing unique levelling and throwing powers and producing relatively hard deposits which, at the same time, are also quite ductile [1, 2]. One of the obvious ways of economizing in the use of gold in the electronics industry and in decorative electroplating is alloying it with one or more base metals. The gold–copper–cadmium system has been shown to give the most satisfactory deposits; alloys containing 75–80% Au, deposited from neutral solutions, are uniform in colour, fairly ductile, not excessively stressed and retain sufficient corrosion resistance to meet the strict specifications of the electronics industry [3, 4].

The development of techniques for the selective recovery of gold from spent solutions containing base metal admixtures is justified in the light of gold prices. The recovery of gold from gold chloride solutions, in a flow cell equipped with graphite cloth screen electrodes has been reported [5]. In the present work, the selective electrodeposition of gold, copper and cadmium from their sulphite solutions was attempted, using a combination of a merging flow stream system and the flow through cell previously employed.

2. Experimental procedure

The model solution used contained 10^{-3} mol dm^{-3} $Au(SO_3)_2^{3-}$, 3×10^{-3} mol dm^{-3} $SO_{3\,(total)}^{2-}$ and 3×10^{-3} mol dm^{-3} ethylenediamine at pH 6.5–7.0. It was prepared daily from $AuCl_4^-$, by a slight adaptation of a method recommended by Smith [6]: to prepare one litre, 200 cm^3 distilled H_2O were introduced into a boiling flask equipped with three entry ports. A measured volume of $AuCl_4^-$ standard stock solution was added, to make a final concentration of 10^{-3} mol dm^{-3}. 0.2 cm^3 concentrated NH_4OH were then added, causing the solution to turn turbid, followed by 0.2 cm^3 of ethylenediamine. After thorough mixing, the flask was heated in an electric heating mantle and 0.7 g Na_2SO_3 were added. Heating was controlled to bring the contents of the flask to 50° C; Au(III) ions were reduced to Au(I) and the latter complexed as $Au(SO_3)_2^{3-}$. As soon as the solution clarified, this process was considered complete

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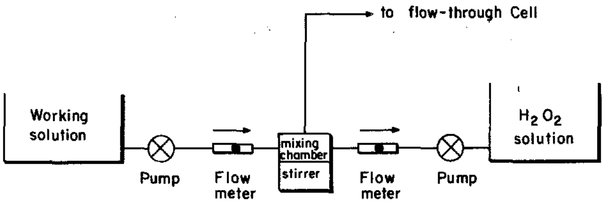

Fig. 1. Flow system for the recovery of gold from sulphite solutions.

The pH of the solution was now adjusted to 6.5–7.0 and the solution volume made up to one litre with H_2O. Total sulphite concentration, determined iodometrically, was found to be about 3×10^{-3} mol dm^{-3}.

$CuCl_2$ and $CdCl_2$ stock solutions [5] were added to bring the Cu(II) and Cd(II) ion concentrations into the desired (10^{-3} mol dm^{-3}) range and 2 g dm^{-3} analar EDTA were then added. All reagents were of AR grade. 0.1 mol dm^{-3} H_2O_2 solution was prepared by daily dilution of 30% H_2O_2.

To the experimental set-up (working cell including graphite cloth screen electrodes, etc.), described by Yarnitzky *et al.* [7], a merging chamber, 5 cm^3 in volume, set on a magnetic stirrer and equipped with two inlets at its bottom and a single outlet at the top was placed about 20 cm before the inlet of the flow-through cell (Fig. 1). This served to thoroughly mix controlled streams of the working solution (to which KCl had been added to make it 0.1 mol dm^{-3} in KCl) and acidified 1 mol dm^{-3} H_2O_2 (below pH 1), in the proper ratio (7 : 1), just before the solution entered the working cell.

The processes of recovery and separation were monitored by atomic absorption spectrometry, as described [7].

3. Results and discussion

3.1. *Gold deposition from neutral sulphite solution*

The cyclic voltammogram recorded in 10^{-3} mol dm^{-3} $Au(SO_3)_2^{3-}$, 3×10^{-3} mol dm^{-3} $SO_{3\,(total)}^{2-}$, 3×10^{-3} mol dm^{-3} ethylenediamine and 0.1 mol dm^{-3} KCl at pH 6.9, shown in Fig. 2, exhibits a single reduction peak at − 0.55 V and a single oxidation peak at 0.2 V, merging with the large sulphite oxidation current. The potential of the reduction peak is strongly affected both by the pH and the free ligand (SO_3^{2-}) concentration of the solution.

Standard potentials for the Au(III) reduction, as reported in the literature, vary; Smith [6] alone gives a negative value similar to that found in the present study which is also strongly dependent on the solution pH.

Gold recovery from the model solution, streaming through the cell at 17 cm^3 min^{-1}, was studied as a function of applied potential. In general, due to the simultaneous evolution of H_2, Au deposits were unsatisfactory, current efficiencies low and the electroactive area of the screen electrode diminished by adhering H_2 gas bubbles. At − 0.7 V, only 30% Au was recovered, although H_2 evolution was negligible. − 0.7 V is not sufficiently cathodic to bring the electrode into the limiting current region; results tended to be grossly irreproducible.

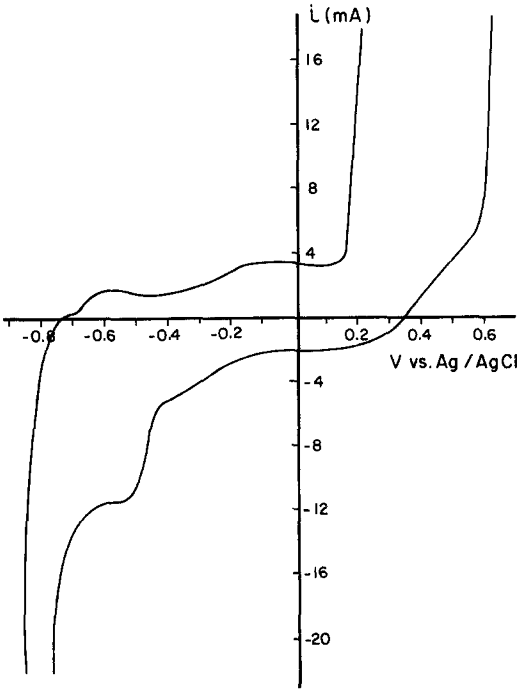

Fig. 2. Cyclic voltammogram of 10^{-3} mol dm^{-3} $Au(SO_3)_2^{3-}$, 3×10^{-3} mol dm^{-3} $SO_{3\,(total)}^{2-}$, 3×10^{-3} mol dm^{-3} $(CH_2NH_2)_2$, 2 g dm^{-3} EDTA, pH 6.9, stagnant solution; rate of potential scan 10 mV s^{-1}.

Some of the residual dissolved gold deposits on the rear face of the electrode screen and is partially swept away by the streaming solution, turning the latter turbid.

Obviously these results are unacceptable and the problem requires a different approach.

pH adjustment is ineffective, since although it increases the accessible cathodic range it also shifts the $Au(SO_3)_2^{3-}$ reduction potential towards more negative values.

The effect of reducing the concentration of sulphite (down to the limit of about double the concentration of gold ions, at which Au(I) disproportionates to Au(III) and Au), was also studied. At solution flow rates below 17 $cm^3\ min^{-1}$, gold recovery remained less than 30%. The addition of 2 $g\ dm^{-3}$ EDTA to the streaming solution, had no effect.

The cyclic voltammogram of a 10^{-3} mol dm^{-3} ethylenediamine, 2 $g\ dm^{-3}$ EDTA, pH 7, stagnant solution, shows, as may be expected on the basis of the stability constants of the complexes formed between Cu(II) and EDA and EDTA ($pK = 15.9$ and 10.72, respectively) [8], that the copper reduction peak shifts to -0.65 V, only 0.1 V on the negative side of the Au(I) reduction peak. Effective flow-through separation of the two metals under these conditions becomes impossible.

The problem was solved by introducing a ligand exchange system, in which the $Au(SO_3)_2^{3-}$ ions are converted into the weaker chloride complex $(AuCl_2)^-$ (pK $Au(SO_3)_2^{3-} = 30$, pK $(AuCl_2^-) = 9$, [8]); this reduces at less negative potentials, H_2 evolution is avoided and Au is efficiently separated from other metals (e.g. Cu and Cd).

3.2. *Selective separation of gold from copper and cadmium by electrodeposition from gold sulphite solution, in the presence of hydrogen peroxide*

The addition of a slight excess of H_2O_2 (about 20%) to a gold sulphite solution containing chloride ions, will quantitatively oxidize sulphite to sulphate, allowing the gold to complex as the monovalent $(AuCl_2)^-$ ion. The electrochemical behaviour of this system resembles that of $(AuCl_4)^-$ [5]. The system is metastable and disproportionates significantly within 30 min. To minimize disproportionation, the time interval between the removal of the sulphite ligand and the pH adjustment of the streaming solution (pH = 2), and the moment it flows past the graphite screen electrodes must be controlled and kept short. H_2O_2 and gold sulphite solutions, in the appropriate ratio (1:7), flow into the mixing chamber, are mixed and continue to the cell. Fig. 3 shows the cyclic voltammogram recorded in an Au/Cu solution after the addition of H_2O_2 at pH 2. The sharp peak at about 0.5 V is, of course, due to Au deposition (cf. Ref. [5], Fig. 1). Figure 4 shows the recovery efficiency of Au, at a flow-rate of 17 $cm^3\ min^{-1}$, as a function of applied potential. At potentials below -0.2 V,

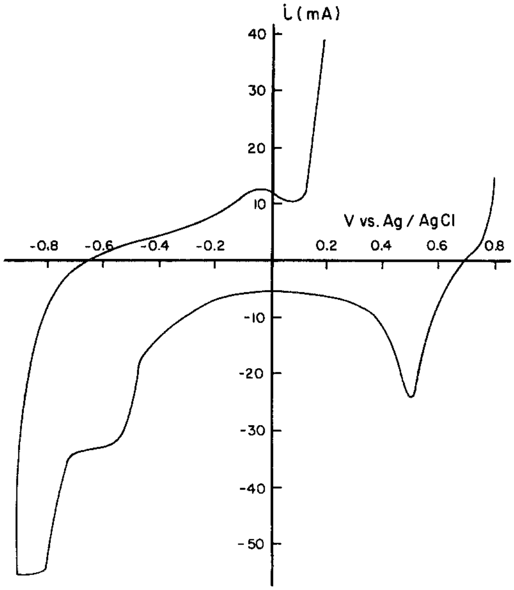

Fig. 3. Cyclic voltammogram of the same solution as in Fig. 2, after addition of 10^{-3} mol dm^{-3} $CuCl_2$ and H_2O_2; pH 2, stagnant solution; scan rate 10 $mV\ s^{-1}$.

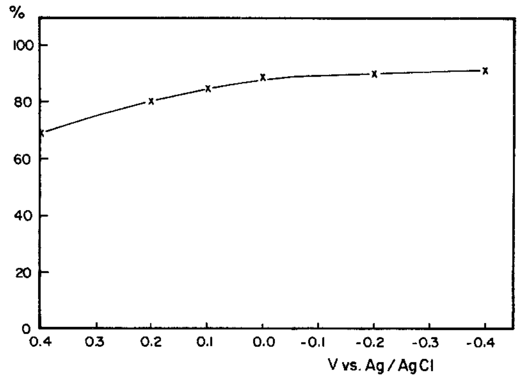

Fig. 4. Dependence of percentage recovery of gold on applied overpotential. Solution identical to that in Fig. 3; flow rate: 17 $cm^3\ min^{-1}$.

95% recovery is achieved (once the initial build-up of dendritic gold deposit has had time to form).

The oxidation of sulphite has no appreciable effect on the reduction potentials of copper and cadmium ions complexed with EDTA (except for that attributed to the pH change). This allows Au to be deposited on the first screen electrode and Cu and Cd partially on the next.

To keep EDTA from precipitating, the pH of the solution must be kept in the 2.6–4 range. Under these conditions the Au, precipitated at 0.0 V on the first screen, will contain only about 0.1% Cu and less than 0.02% Cd; the second screen, held at − 1.1 V, may be used to partially remove Cu (50%) and Cd (15%) from the effluent.

The dendritic Au deposits obtained may be stripped off mechanically from the electrodes or dissolved chemically in concentrated acids [5].

Summing up, the results described in this study may be presumed to serve as a basis for a scaled-up version for the efficient and economical recovery and/or separation of gold and other metals from streaming solutions containing base metal admixtures.

Acknowledgements

This research was supported by the Fund for the Promotion of Research at the Technion and by the Fund for Applied Industrial Research in Universities.

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