Silver Reduction from Low-Cyanide-Concentration Solutions: Special Features from an EQCM

By H. Sanchez & Y. Meas

A silver reduction process was studied in a low-cyanide-concentration solution in which the predominant species is the ion $Ag(CN)_2^-$. The electrochemical behavior showed the presence of adsorbed electroactive species on the electrode surface and this was corroborated with the aid of an electrochemical quartz crystal microbalance (EQCM). The adsorption process is slow at open circuit and under this condition a simultaneous electroless deposition of silver was detected with the EQCM.

Silver deposits are widely used for decorative purposes and to improve electrical conductivity in electronic devices. In the classical baths for silver electrodeposition, the electrolytic solutions contain high concentrations of cyanide ions and this implies the existence of highly complexed silver species, as can be shown from thermodynamic considerations.[1] Because of their high toxicity and for ecological reasons, the current tendency is to diminish the cyanide content in this type of electrolytic solution. It is necessary, however, to avoid alteration of bath stability and the quality of the electrodeposits.

In this study, we used an electrolytic solution prepared from potassium pyrophosphate and potassium cyanide in such a way that the predominant silver species was $Ag(CN)_2^-$. In an earlier paper,[1] the kinetic and mechanistic aspects of silver electroreduction were discussed for such solutions. The process is quasi-reversible at 20 °C and kinetics are enhanced with temperature increase. Moreover, at low overpotentials, the silver reduction is preceded by the adsorption process of the complexed electroactive silver species.

The aim of this paper is to report additional evidence about the existence of adsorbed silver species on the electrode surface. The application of electrochemical techniques under unsteady diffusion conditions, simultaneously with the use of an EQCM, proves this. In addition, the quantity of adsorbed species is a function of time at open circuit and, in this situation, an electroless phenomenon was detected.

Experimental Procedure

The electrochemical cell, working, counter and reference electrodes were described in an earlier paper.[1] The electrolytic solution was prepared from 0.3027 M $K_4P_2O_7$, 0.1228 M KCN and 0.0185 M AgCN at pH 10.8. As in the previous paper, the working electrodes of copper were covered by a nickel deposit, using a hard-Watts bath[2] and a predeposit of silver was realized *in situ* prior to each silver reduction experiment. The electrode potentials appearing in this study are given with respect to a saturated calomel reference electrode (SCE).

For the experiments using the EQCM, the sensor was a thin quartz crystal covered with a gold film and used as the working electrode. To avoid interdiffusion of the silver and gold, a nickel deposit (3 µm thick) was electrochemically deposited from a classical Watts bath[2] at 50 °C under a -850 mV applied potential. Because rotation is not possible for the microbalance sensor, the first step of nickel plating was then followed by a potentiostatic predeposition of silver under -900 mV, so leading to a 0.2 µm thickness of silver. To avoid frequency changes of the sensor resulting from ther-

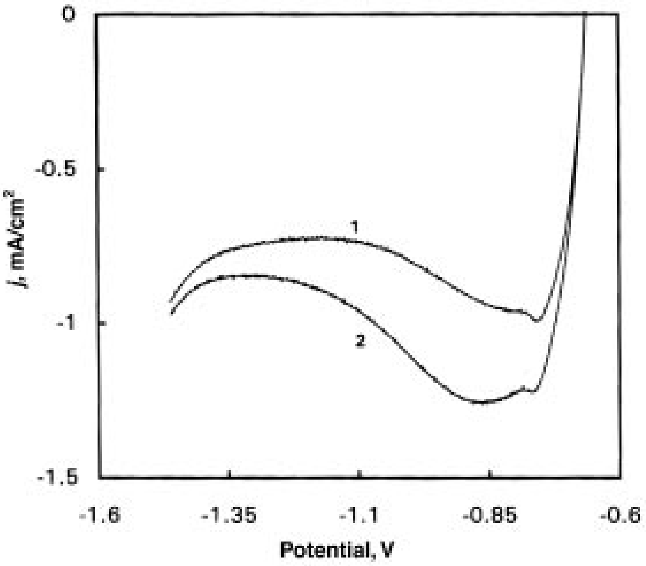

Fig. 1—Single scan voltammetry of silver reduction at 10 mV/sec (curve 1) and 20 mV/sec (curve 2).

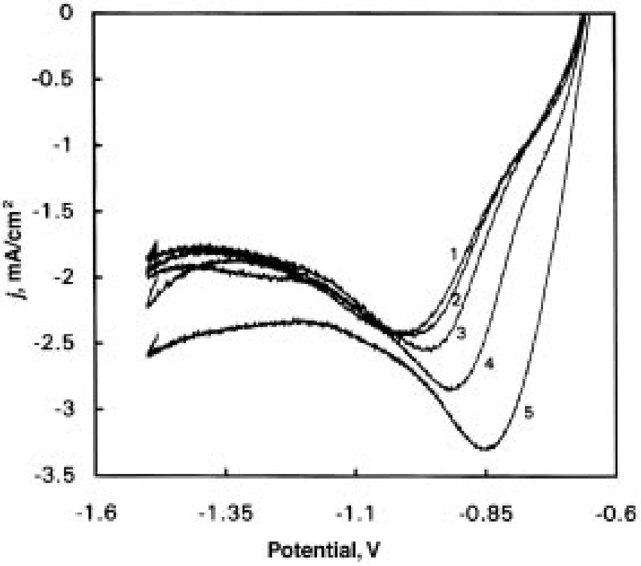

Fig. 2—Linear sweep voltammograms (50 mV/sec) for silver reduction as a function of the stabilization time of the electrode at open circuit, 1: 0 min, 2: 10 min, 3: 20 min, 4: 30 min and 5: 60 min.

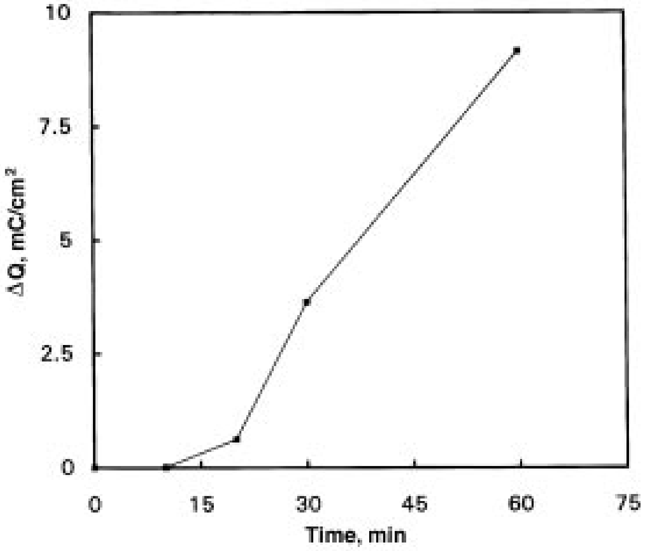

Fig. 3--Excess of charge resulting from silver reduction as a function of the stabilization time of the working electrode.

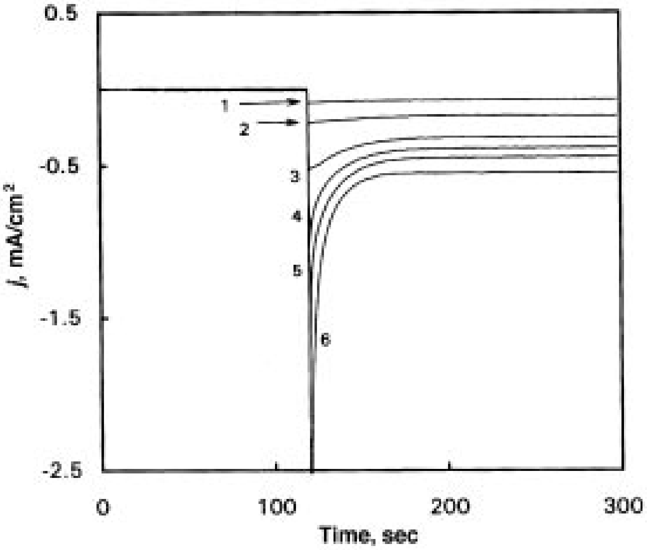

Fig. 4—Current-time response for different overpotential steps applied to the microbalance sensor; 1: -25 mV, 2: -50 mV, 3: -100 mV, 4: -150 mV, 5: -250 mV, 6: -450 mV.

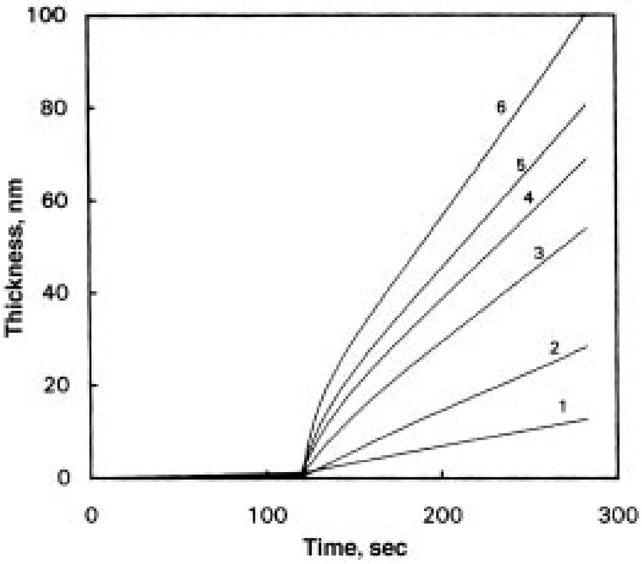

Fig. 5—Deposit thickness as a function of time for different reduction overpotential steps applied to the microbalance sensor; 1: -25 mV, 2: -50 mV, 3: -100 mV, 4: -150 mV, 5: -250 mV, 6: -450 mV.

mal drift, the sensor was stabilized in the bath at least 30 min before each set of silver deposition experiments (20 ±0.01 °C).

The EQCM used 5-mHz crystals. The electrochemical experiments were performed with a computer-controlled potentiostat.

Results & Discussion

According to the distribution diagram for soluble silver species in a cyanide medium and pH 10.8 (Fig. 1 in Ref. 1), in our electrolytic solution (pCN = 1) silver is mainly complexed as $Ag(CN)_2^-$ (70%). Then, the silver electrochemical reduction is globally expressed as:

$$Ag(CN)_2^- + e^- \longleftrightarrow Ag + CN^- \qquad (1)$$

This silver electrochemical reduction was first studied by means of linear sweep voltammetry in an unsteady-state diffusion regime. The voltammograms for 10 and 20 mV/sec scan rates are shown in Fig. 1. The voltammograms of silver reduction show two peaks, one of them becoming more observable for a scan rate of 20 mV/sec. Their appearance can be explained by two successive steps:[3-5] The first peak at less negative potentials is related to the consumption of a strongly adsorbed electroactive species and the second corresponds classically to diffusion control.

By using the microbalance sensor as working electrode and simultaneously measuring the increment of deposit thickness as a function of time, permitted the conclusion that the electrochemical process involves reduction of silver adsorbed species at low overpotentials, as discussed in Ref. 1. The application of low potential scan rates and short stabilization times of the working electrode at open circuit, allowed in this case observation of the peak preceding the one indicative of diffusion control.

When the potential scan rate was increased (20 mV/sec), however, the peak resulting from reduction of the adsorbed species became lower than the diffusional peak (curve 2 in Fig. 1). This behavior continued until a partial overlapping of both peaks was observed when the potential scan rate was 50 mV/sec, as shown by curve 1 in Fig. 2. The same figure shows the appearance of the voltammograms (at the same potential scan rate) as a function of the stabilization time of the working electrode at open circuit. Clearly, the quantity of adsorbed species rises with time and, for 60 min at open circuit, the voltammogram is similar to the ones shown in Fig. 1 at low overpotentials, but the peak caused by reduction of the adsorbed species is now completely overlapped by the diffusional process.

Integration of the areas under the peaks (from the initial potential up to -1.2 V) gave the quantity of charge consumed by silver reduction. The excess of charge with respect to the first voltammogram (curve 1 in Fig. 2) is plotted as a function of the stabilization time at open circuit in Fig. 3. From this figure, clearly, the application of stabilization times higher than 10 min produces a very important accumulation of electroactive species in the vicinity of the electrode, which should explain the complexity of the silver reduction process, as has been previously pointed out.[6] To avoid repro-

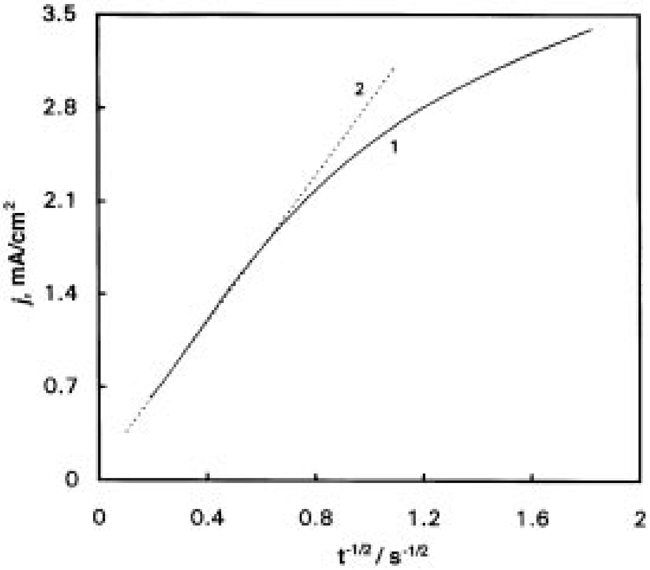

Fig. 6--Plot of j vs. $t^{1/2}$ for silver reduction after application of a reduction overpotential step (-450 mV) without agitation; 1: experimental result; 2: Cottrell relation.

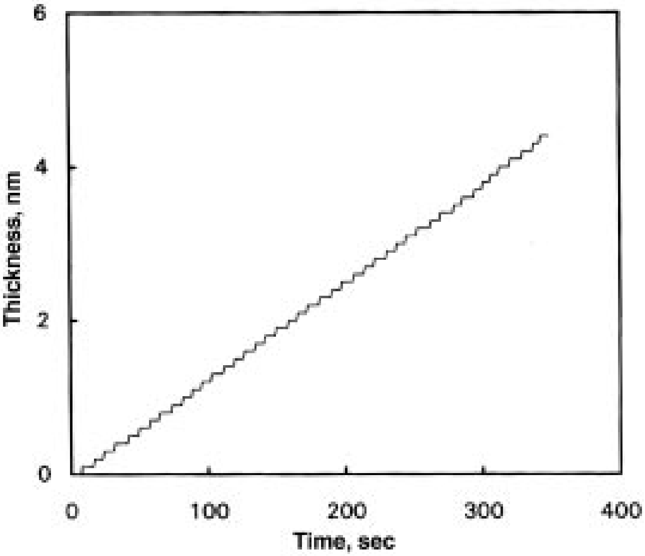

Fig. 7--Thickness of silver deposit vs. time under open circuit conditions.

ducibility problems, therefore, when non-stationary electrochemical techniques are used, the electric stabilization time between consecutive experiments with a silver electrode in a cyanide bath should not be greater than 10 min. In Fig. 2, it is important to note a slight displacement of the initial (rest) potential to less negative values when the stabilization time was increased; this is a normal result from a thermodynamic point of view and it is a consequence of the great accumulation of electroactive silver species at the interfacial level.

When different potential steps were applied to the microbalance sensor, the corresponding current-time response was simultaneously obtained with the thickness variation. From Fig. 4, for overpotentials lower than -50 mV, the measured current did not show an exponential decrease as normally expected for a diffusional process.[7] This is caused by the high quantity of silver species existing in the vicinity of the electrode surface. Subsequently, an almost constant value of current was observed, depending only on the overpotential value. Consequently, the deposit thickness shows a linear variation with time, even from the start of the experiment, as shown in Fig. 5 (curves 1 and 2). In Figs. 4 and 5, the potential step began at 120 sec; however, data acquisition began two min before to show the electric stabilization of the electrode in the cyanide bath when the open circuit potential is imposed.

On the other hand, when the applied overpotentials are higher than -50 mV, the current-time responses show the normal decay observed in chronoamperometric experiments[7] (curves 3-6 in Fig. 4). The deposition rate is high at the start of the potential step and this corresponds to a high slope at the start of the experiment on the thickness-time curves (3-6) shown in Fig. 5.

Finally, for reduction overpotentials as high as -450 mV, the current-time curve is quite independent of the overpotential value and the silver reduction process is limited by diffusion (curve 6 in Fig. 4). The thickness-time curve then shows a rapid increase (maximum deposition rate) at the start of the experiment and after a constant minor increase of thickness is observed (curve 6 in Fig. 5). It is important to note in Fig. 5 that the slope of the curve at the start of the experiment rises from a low value to a relatively high value when the overpotential is increased and this pronounced change is observable because of the great tendency of silver ions to be adsorbed on the electrode surface.[1,8] In an electrochemical process with little or no adsorption phenomena of the electroactive species, the observation of a similar electrochemical behavior should not be as clear as that described above, in the same time scale.

The presence of significant quantities of adsorbed silver species on the electrode surface caused the Cottrell relation[7]

$$j = \frac{nFD^{1/2} C^*}{\pi^{1/2} t^{1/2}} \qquad (2)$$

where j is current density, D is the diffusion coefficient, C^* is bulk concentration of silver ions, t is time, not to be obtained, as shown in Fig. 6. In this figure, the beginning of the potential step (120 sec in Figs. 4 and 5) was adjusted to zero sec. As the Cottrell relation predicts for a diffusional process, however, the j-$t^{-1/2}$ curve shows linear behavior, but only for relatively high values of t (dashed line in Fig. 6). This is possible only after consumption of the adsorbed silver species during the first stages of electrolysis. The curve then shows the transition from a mechanism through adsorbed species to a direct reduction process limited only by diffusion. Moreover, the first mechanism implies a total current lower than expected for the same process under conditions of direct reduction, as shown in Fig. 6, which confirms that previously discussed in Ref. 1.

Other experiments were performed in addition with the EQCM and they showed that, at open circuit (E = -665 mV), a slow and continuous deposition phenomenon occurs at the sensor surface. Figure 7 reveals that the thickening increases vs. time despite open circuit conditions and, from the slope, a deposition rate of 0.78 $\mu g/cm^2/min$ was obtained.

In alkaline solution, the cyanide ion can act as a reducing agent[9,10] and this makes thermodynamically possible electroless deposition of silver through the following reaction sequence:

$$CN^- + 2OH^- \longleftrightarrow CNO^- + H_2O + 2e^- \qquad (3)$$

$$2Ag(CN)_2^- + 2e^- \longleftrightarrow 2Ag + 4CN^- \qquad (4)$$

or after adding:

$$2Ag(CN)_2^- + 2OH^- \longleftrightarrow 2Ag + CNO^- + H_2O + 3CN^- \qquad (5)$$

The Nernst equation is written for reactions (3) and (4) respectively as:

$$E_{CNO^-/CN^-} = E^\circ_{CNO^-/CN^-} - \frac{RT}{2F}\ln([CN^-][OH^-]^2) + \frac{RT}{2F}\ln([CNO^-]) \qquad (6)$$

and

$$E_{Ag(CN)^-_2/Ag} = E_{Ag(CN)^-_2/Ag} - \frac{2RT}{F}\ln([CN^-]) + \frac{RT}{F}\ln([Ag(CN)^-_2]) \qquad (7)$$

with

$$E^\circ_{CNO^-/CN^-} = -1.211 \text{ V vs. SCE} \qquad (8)$$

$$E^\circ_{Ag(CN)^-_2/Ag} = -0.636 \text{ V vs. SCE} \qquad (9)$$

Considering that the free cyanide concentration is about 0.1 M, an effective concentration of $Ag(CN)_2^-$ of 0.013 M and pH 10.8, the corresponding cyanate concentration necessary for reaching the equilibrium

$$(E_{CNO^-/CN^-} = E_{Ag(CN)^-_2/Ag})$$

of reaction (5) is close to 3.6 x 10^{12} M. Evidently, this concentration of cyanate is not possible, even in the vicinity of the electrode; in addition, the continuous removal of cyanate from the electrode surface by diffusion and convective effects provides favorable conditions for the continuous electroless deposition of silver on the electrode, according to reaction (5).

Conclusions

The electrochemical reduction of silver from cyanide solutions is complex and it involves the existence of adsorbed electroactive and nonelectroactive species on the electrode surface. The quantity of adsorbed electroactive species rises with time even at open circuit conditions; then, care must be taken to avoid reproducibility problems when silver reduction is studied by means of electrochemical techniques. The use of an EQCM is an additional way to investigate the existence of adsorbed species and, as in this work, electroless phenomena taking place on the electrode surface can be detected.

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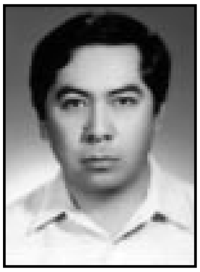

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