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(Recivedi 3 Juni 1993 Revised form 10 August 1993)

A NOVEL APPROACH OF THE SILVER ELECTRODEPOSITION MECHANISM

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Abstract

In regard to the understanding of the silver electrodeposition process at carbom microelectrodes three different mechanisms have been proposed and its theoretical simulations are presented. A comparison between experimental and simulated voltammograms shows that several kinetic complexities occurs during the electrodeposition process.

Introduction

The electrodeposition and electrocrystallisation of silver was investigated repeatedly during the 1960s using a variety of electrochemical techniques such as A.C. impedance, galvanostatic step, potentiodynamic methods and double potential step measurements [1-8] with the purpose of understanding its mechanism. A general conclusion drawn from the investigations was that there was a relatively high concentration of silver adatoms on the substrate surface and that the exchange current for the formation of these adatoms was a fast electrochemical process characterized by having very high reaction rates. However the lattice formation process was much slower which have been interpreted as being due to the slow surface diffusion of the silver adatoms to lattice forming sites where crystal growth can take place.

As far as the crystal growth process was concerned it has been pointed out that the initial stage occurs through a one-step one-electron transfer reaction accordingly to the following mechanism [9-10]:

$$Ag^+ + 1e^- \longrightarrow Ag^0$$

(1)

The above mechanism suggest that once the silver adatoms were formed, the lattice formation process will take place forming crystal planes of silver, following the formation of repeated layers.

The use of carbon microdisk electrodes (diameter of 5-10 μ m) has been especially important in these mechanistic studies and the achieved results have been reported elsewhere [11-15]. A surprising conclusion of these studies has been that the silver electrodeposition and electrocrystallization mechanism is much more complex than the one presented in equation (1) and which has been assumed through out the years as the appropriate one. This conclusion is at variance with the results attained experimentally which suggest that the formation and growth of silver centres consist of a succession of steps (*eg* two steps of one electron transfer). Such a strategy has been important in the attempts to achieve a mechanism elucidative of the kinetics of those processes. It will be evident that the mechanisms presented hereinafter are in line with the classical mechanism of crystal growth models but presents new evidence on the role of the initial steps generated during the process. The major prediction as far as the kinetics is concerned is that there are intermediates involved in the process rather than being a single step process.

Mechanism 1:

First of all, it is postulated that an adsorbed dimmeric ion is initially formed at the substrate surface accordingly to the following mechanism:

$$2Ag^+ \rightleftharpoons (Ag_2^{2+})_{adsorbed}$$

$$(Ag_2^{2+})_{adsorbed} + 2e^- \rightleftharpoons 2Ag_{lattice}$$

(3)

(2)

where the second reaction is assumed to be the rate determining step. Therefore the surface concentration of $(Ag_2^{2+})_{adsorbed}$ is given by

$$\Theta_{dimer} = k \left(\frac{C_1^{\sigma}}{C_1^{\infty}}\right)^2 \tag{4}$$

where k is the Henry's law constant and the surface concentration (C_1^{σ}) has been normalised by the bulk concentration (C_1^{∞}) . It is also assumed that the surface concentration of the dimmer is sufficiently small that it can be described by a simple Henry's isotherm (equation (4)).

The rates for the forward and reverse reactions are:

$$\vec{k_1} k \left(\frac{C_1^{\sigma}}{C_1^{\infty}}\right)^2 \exp\left(\frac{-2\alpha_1 F \phi}{RT}\right) = \vec{k_1} k \left(\frac{C_1^{\sigma}}{C_1^{\infty}}\right)^2 \exp\left(\frac{-2\alpha_1 F \phi_r}{RT}\right) \exp\left(\frac{-2\alpha_1 F \nu t}{RT}\right)$$
(5)

$$\overline{k_1} \exp\left(\frac{2(1-\alpha_1)F\phi}{RT}\right) = \overline{k_1} \exp\left(\frac{2(1-\alpha_1)F\phi_r}{RT}\right) \exp\left(\frac{2(1-\alpha_1)F\nu t}{RT}\right)$$
(6)

The rate of crystal growth is now

$$k_{1} = -\vec{k}_{1} k \left(\frac{C_{1}^{\sigma}}{C_{1}^{\infty}}\right)^{2} \exp\left(\frac{-2\alpha_{1}F\phi_{r}}{RT}\right) \exp\left(\frac{-2\alpha_{1}F\nu t}{RT}\right)$$

$$- -\vec{k}_{1} \exp\left(\frac{2(1-\alpha_{1})F\phi_{r}}{RT}\right) \exp\left(\frac{2(1-\alpha_{1})F\nu t}{RT}\right)$$
(7)

At the reversible potential vt = 0 and $C_1^{\sigma} = C_1^{\sigma}$ which gives

$$k_1 = 0 = -\overrightarrow{k_1} k \exp\left(\frac{-2\alpha_1 F \phi_r}{RT}\right) - \overleftarrow{k_1} \exp\left(\frac{2(1-\alpha_1)F \phi_r}{RT}\right)$$
(8)

and hence for this particular mechanism

$$k_1^0 = \overrightarrow{k_1} k \exp\left(\frac{-2\alpha_1 F \phi_r}{RT}\right) = \overleftarrow{k_1} \exp\left(\frac{2(1-\alpha_1) F \phi_r}{RT}\right)$$
(9)

which gives the following rate constant

$$k_1 = k_1^0 \left[\left(\frac{C_1^{\sigma}}{C_1^{\infty}} \right)^2 \exp\left(\frac{-2\alpha_1 F \nu t}{RT} \right) - \exp\left(\frac{2(1-\alpha_1)F \nu t}{RT} \right) \right]$$
(10)

Assuming that diffusion to the surface is given by [13]:

$$k_1 = \frac{D_1(C_1^{\infty} - C_1^{\sigma})}{r}$$

(11)

Combining equation (10) with (11) gives the equation for the rate constant of the proposed mechanism which is written as

$$k_{1} = k_{1}^{0} \left\{ 2 \left(\frac{D_{1}C_{1}^{\infty}}{2k_{1}^{0}r} \right)^{2} \exp\left(\frac{2\alpha_{1}F\nu t}{RT} \right) + \frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} - \frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} \left[\left(\frac{D_{1}C_{1}^{\infty}}{2k_{1}^{0}r} \right)^{2} \exp\left(\frac{4\alpha_{1}F\nu t}{RT} \right) + \exp\left(\frac{2F\nu t}{RT} \right) + \frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} \exp\left(\frac{2\alpha_{1}F\nu t}{RT} \right) \right]^{1/2} \right\} (12)$$

The value of k_I is then used to derive the radius of the metallic centre, r(t), and this is used in turn to give the current-time transient:

$$I = 2\pi z F k_1(t) [r(t)]^2$$

= $2\pi z F \frac{k_1^0 \left[\exp\left(\frac{-\alpha_1 F \nu t}{RT}\right) - \exp\left(\frac{(1-\alpha_1) F \nu t}{RT}\right) \right] [r(t)]^2}{\left[1 + \frac{k_1^0 [r(t)]}{D_1 C_1^\infty} \exp\left(\frac{-\alpha_1 F \nu t}{RT}\right) \right]}$ (13)

The theoretical voltammogram for this mechanism is presented in Fig. 1.



Figure 1 - Calculated linear sweep voltammogram for the silver deposition using $\alpha = 0.36$, z = 2.0 and k₁^o = 1.3 . 10⁻⁷ mol cm⁻² s⁻¹, equations (12) and (13).

In Fig. 2 it is illustrated the fit between the simulated voltammogram and the experimental one obtained under the conditions listed in the figure legend. It is evident that there are discrepancies between the calculated and experimental voltammograms. However in an attempt to "force fit" the proposed mechanism to describe the experimental system, several plots using different values of a and k_1^0 have been constructed and are presented in Figs. 3 and 4 respectively. It is of interest to point out that despite all the efforts, none of the simulations fits adequately both the cathodic and anodic branches. However, the procedure followed shows that it is worthwhile to formulate a variety of mechanisms in order to get evidence consistent with the type of complexities that can be produced by essentially bimolecular reactions.



Figure 2 - Plot of the linear sweep voltammogram for the silver deposition: a) experimental using v = 100 mV/s; b) calculated (Fig. 1).



Figure 3 - Plot of the linear sweep voltammograms for the silver deposition using different values of α (ranging from 0.21 (smallest plot) to $\alpha = 0.42$ in increments of 0.03) at a fixed $k_1^{0} = 1.3 \cdot 10^{-7}$ mol cm⁻²s⁻¹; equations (12) and (13).



Figure 4 - Plot of the linear sweep voltammograms for the silver deposition calculated for different values of the parameter $k_1^{0} = 1.3 \cdot 10^{-7}$ to $1.7 \cdot 10^{-7}$ mol cm⁻²s⁻¹ in increments of 2.0 $\cdot 10^{-8}$ (equations (12) and (13)) at a fixed $\alpha = 0.36$.

Mechanism 2 :

Another mechanism that is worthwhile to investigate is the one that produces a more conventional version of the previous one, namely

$$Ag^{+} + e^{-} \rightleftharpoons Ag_{adsorbed} \tag{14}$$

$$Ag_{adsorbed} + Ag^{+} + e^{-} \rightleftharpoons 2Ag_{lattice}$$
(15)

Here it is assumed that reaction (14) is sufficiently fast so that it can be regarded as a preequilibrium to step (15). There is evidence in the literature [16-17] that this adsorption step is indeed a fast one.

Again the coverage by adatoms is assumed to be sufficiently small that it can be assumed that the adsorption follows a Henrys type isotherm

$$\theta_{ads} = k \left(\frac{C_1^{\sigma}}{C_1^{\infty}} \right) \exp\left(\frac{-\phi F}{RT} \right)$$
(16)

Then the rates of the forward and reverse reactions are given by

$$\vec{k}_{1} k \left(\frac{C_{1}^{\sigma}}{C_{1}^{\infty}}\right)^{2} \exp\left(\frac{-(1+\alpha_{1})\phi F}{RT}\right) = \vec{k}_{1} k \left(\frac{C_{1}^{\sigma}}{C_{1}^{\infty}}\right)^{2} \exp\left(\frac{-(1+\alpha_{1})\phi_{r}F}{RT}\right) \exp\left(\frac{-(1+\alpha_{1})F\nu t}{RT}\right)$$
(17)

$$\overleftarrow{k_1} \exp\left(\frac{(1-\alpha_1)F\phi}{RT}\right) = \overleftarrow{k_1} \exp\left(\frac{(1-\alpha_1)F\phi_r}{RT}\right) \exp\left(\frac{(1-\alpha_1)F\nu t}{RT}\right)$$
(18)

The rate of crystal growth is then

$$k_1 = k_1^0 \left[\left(\frac{C_1^{\sigma}}{C_1^{\infty}} \right)^2 \exp\left(\frac{-(1+\alpha_1)F\nu t}{RT} \right) - \exp\left(\frac{2(1-\alpha_1)F\nu t}{RT} \right) \right]$$
(19)

where

$$k_1^0 = \overrightarrow{k_1} k \exp\left(\frac{-(1+\alpha_1)F\phi_r}{RT}\right) = \overleftarrow{k_1} \exp\left(\frac{(1-\alpha_1)F\phi_r}{RT}\right)$$
(20)

and substituting $(C_1^{\sigma}/C_1^{\omega})^2$ into equation (19) it gives

$$k_{1} = k_{1}^{0} \left\{ 2 \left(\frac{D_{1}C_{1}^{\infty}}{2k_{1}^{0}r} \right)^{2} \exp\left(\frac{(1+\alpha_{1})F\nu t}{RT} \right) + \frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} - \frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} \left[\left(\frac{D_{1}C_{1}^{\infty}}{2k_{1}^{0}r} \right)^{2} \exp\left(\frac{2(1+\alpha_{1})F\nu t}{RT} \right) + \exp\left(\frac{2F\nu t}{RT} \right) + \frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} \exp\left(\frac{(1+\alpha_{1})F\nu t}{RT} \right)^{1/2} \right\}$$

$$(21)$$

and therefore the current transient is once again calculated based on equation (13).

The voltammogram calculated for this mechanism is presented in Fig. 5, which shows that such a mechanism is not appropriate for describing the experimental current-time transients. This can be explained on the basis that small values of α are involved, which accounts for a broadening of the current transients. Also the magnitude of k_1^0 has been decreased by a factor of 10, otherwise the current values will be of an order of magnitude higher than those observed experimentally.



Figure 5 - Plot of the linear sweep voltammograms for the silver deposition: a) experimental using v = 100 mV/s; b) calculated using $\alpha = 0.01$ and $k_1^{0} = 4.7 \cdot 10^{-8} \text{ mol cm}^{-2}\text{s}^{-1}$, equation (21).

The marked asymmetry of the calculated voltammogram is not surprising if one takes into consideration that for the initial stages when $(D_1C_1 / k_1^{0}r)$ is large, equation (21) becomes

$$k_1 = k_1^0 \exp\left(\frac{-(1+\alpha_1)F\nu t}{RT}\right)$$
(22)

which only holds for the forward sweep. The proposed mechanism would require that two adjacent Ag atoms behave essentially as an element of the lattice. It is also of interest to point out that a more detailed analysis of the mechanism will have to take account of the finite rates for both steps. Furthermore the possible applicability of Langmuir isotherm conditions to the coverage could account for the effects of changes in coverage on the rates of the two reaction

Mechanism 3 :

There is still another mechanism that should be considered. In this mechanism the adatoms act as catalysts of the lattice formation:

$$Ag_{adsorbed} + Ag^{+} + e^{-} \rightleftharpoons Ag_{lattice} + Ag_{adsorbed}$$
 (23)

where once again

$$\theta_{ads} = k \left(\frac{C_1^{\circ}}{C_{\infty}^{\circ\circ}}\right) \exp\left(\frac{-\phi F}{RT}\right)$$
(24)

and the rates of the forward and reverse reactions are

$$\vec{k}_{1} k \left(\frac{C_{1}^{\sigma}}{C_{1}^{\infty}}\right)^{2} \exp\left(\frac{-(1+\alpha_{1})F\phi}{RT}\right)$$
$$= \vec{k}_{1} k \left(\frac{C_{1}^{\sigma}}{C_{1}^{\infty}}\right)^{2} \exp\left(\frac{-(1+\alpha_{1})F\phi_{\tau}}{RT}\right) \exp\left(\frac{-(1+\alpha_{1})F\nu t}{RT}\right)$$
(25)

$$\frac{\overleftarrow{k_1}k\left(\frac{C_1^{\sigma}}{C_1^{\omega}}\right) \exp\left(\frac{-\alpha_1 F \phi}{RT}\right) = \overleftarrow{k_1}k\left(\frac{C_1^{\sigma}}{C_1^{\omega}}\right) \exp\left(\frac{-\alpha_1 F \phi_r}{RT}\right) \exp\left(\frac{-\alpha_1 F \nu t}{RT}\right)$$
(26)

The rate of crystal growth is

$$k_1 = k_1^0 \left[\left(\frac{C_1^{\sigma}}{C_1^{\infty}} \right)^2 \exp\left(\frac{-(1+\alpha_1)F\nu t}{RT} \right) - \left(\frac{C_1^{\sigma}}{C_1^{\infty}} \right) \exp\left(\frac{-\alpha_1F\nu t}{RT} \right) \right]$$
(27)

with k10 now given by

$$k_1^0 = \overrightarrow{k_1} k \exp\left(\frac{-(1+\alpha_1)F\phi_r}{RT}\right) = \overleftarrow{k_1} k \exp\left(\frac{-\alpha_1 F\nu t}{RT}\right)$$
(28)

which, following the same procedure as for the previous mechanisms, gives

$$k_{1} = k_{1}^{0} \left\{ 2 \left[\left(\frac{D_{1}C_{1}^{\infty}}{2k_{1}^{0}r} \right) \exp \left(\frac{\alpha_{1}F\nu t}{RT} \right) - \frac{1}{2} \right]^{2} \exp \left(\frac{(1-\alpha_{1})F\nu t}{RT} \right) \right. \\ \left. + \frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} - \left[\frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} - \exp \left(\frac{-\alpha_{1}F\nu t}{RT} \right) \right] \right] \\ \left. \left\{ \left[\left(\frac{D_{1}C_{1}^{\infty}}{2k_{1}^{0}r} \right) \exp \left(\frac{\alpha_{1}F\nu t}{RT} \right) - \frac{1}{2} \right]^{2} \exp \left(\frac{2F\nu t}{RT} \right) + \frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} \exp \left(\frac{(1+\alpha_{1})F\nu t}{RT} \right) \right\}^{\frac{1}{2}} \right. \\ \left. + \left[\left(\frac{D_{1}C_{1}^{\infty}}{2k_{1}^{0}r} \right) - \frac{1}{2} \exp \left(\frac{-\alpha_{1}F\nu t}{RT} \right) \right] \exp \left(\frac{F\nu t}{RT} \right)$$

$$\left. + \left\{ \left[\frac{D_{1}C_{1}^{\infty}}{2k_{1}^{0}r} - \frac{1}{2} \exp \left(\frac{-\alpha_{1}F\nu t}{RT} \right) \right]^{2} \exp \left(\frac{2F\nu t}{RT} \right) + \frac{D_{1}C_{1}^{\infty}}{k_{1}^{0}r} \exp \left(\frac{(1-\alpha_{1})F\nu t}{RT} \right) \right\}^{\frac{1}{2}} \right\}$$

and hence the current transient is derived using equation (13)

The reason why mechanism 3 does not give voltammograms anywhere near to the experimental ones is because the concentration of the catalyst adatoms will decrease with the anodic overpotential.

Although controversy can arises as to the correctness of any of the proposed mechanisms as a mean of evaluating the electrocrystallisation process, it is clear that there are several kinetic complexities which occur experimentally that cannot be accounted in the theoretical simulations.

Conclusion

As in the studies investigated before [11-15], there is indeed a good agreement between experimental and calculated voltammograms in the cathodic branch. The differences in behaviour, essentially on the forward sweep, can probably be attributed to a progressive decrease in the number of lattice forming sites with time. On the other hand, in the anodic branch there is no fit at all for any of the mechanisms herein presented.

The experimental evidence points to several kinetic complexities in the silver electrocrystallisation process. Further research in this area, it is hoped, will explain the progressive decrease in the rates of electrocrystallisation as well as the complexities of the dissolution processes. It is important to point out that this has been one of the first attempts to interpret the silver electrocrystallisation process in a more complete way.

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(Received, 29 September 1993 Accepted, 17 November 1993 ELECTROCHEMICAL STUDY OF 1 - METHYL - BENZOTRIAZOLE-, BENZIMAIDAZOLE- AND $1, NH_2$ -BENZIMIDAZOLE - PENTACYANO-FERRATE (II) COMPLEXES AT DIFFERENT pH VALUES.

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ABSTRACT

Behaviour of the 1-Methyl-benzotriazole-. Benzimidazole- and $1-NH_2$ -Benzimidazolepentacyanoferrate (II), complexes in aqueous solution of 0.5M. $NaClO_4$ at the platinum electrode has been analysed by cyclic voltammetric measurements. The electrode-rate constant, k_o , and the transfer coefficient, αn_{α} of the corresponding complexes have been estimated at different pH values.

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Portugaliæ Electrochimica Acta, 11 (1993) 279-288