INVESTIGATION OF ELECTRODE PROCESSES OCCURRING DURING DEPOSITION AND DISSOLUTION OF SILVER IN CYANIDE SOLUTIONS

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In the literature of electrochemistry there are many papers relating to investigations on electrode processes occurring during the deposition of metals in cyanide solutions [1]. A shortcoming of these papers lies in the fact that the explanations of the mechanism of the electrode processes and the character of the polarization are based solely on the basis of the forms and slopes of the curves for the dependence of polarization on current density. However, this relationship often does not give a complete picture of the processes occurring at the electrode under investigation, for it gives no idea at all of the changes in polarization with time. It is known that in the deposition and dissolution of metals polarization is not stable and changes with time [2], so that the forms and slopes of the polarization curves depend not only on the current density (other conditions remaining constant), but also on the rate at which the determination is made [3]. In a more detailed investigation of the electrode processes, therefore, it is necessary to study not only the dependence of polarization on current density, but also the change of polarization with time*. In the present investigation a study has been made of some processes occurring at a silver electrode polarized by alternating and intermittent currents.

EXPERIMENTAL

Experimental Procedure

The deposition and dissolution of silver was effected by alternating and intermittent currents obtained with the aid of a special commutator. A diagram of the commutator and the apparatus for recording changes in polarization is given in Fig. 1. The commutator consists essentially of an electromagnetic relay 1 and a switch-over disk 5. The electromagnetic relay effects the reversal of the polarizing current in the circuit II, and the frequency of the reversal and the time for which the current passes in the forward or reverse direction is regulated with the aid of the disk 5. The disk is made of insulating material and has a number of metallic contacts on its edge which can be connected to the metal ring 6. When the disc is rotated at a definite given speed, one of the contacts (for example, ab), in passing under the brush C, periodically makes and breaks the circuit feeding the electromagnetic coil 2 for a time proportional to the length of the metallic contact. When the circuit I is broken, the movable contacts 3 of the electromagnetic relay are pressed against the lower plates, as in Fig. 1, and the current flows in one direction. When the contact ab passes under the brush C, the circuit I is closed and the current, passing through the coil of the relay, switches the movable contacts 3 over on to the upper plates 4, and so changes the current in the electrolytic cell 13 over into the other direction. The durations of the positive and negative impulses can be varied over a wide range by increasing or diminishing the length of the contact ab and by changing the rate of rotation of the disk 5 with the aid of the gear box 7, which is connected to the electric motor 8. In order to obtain an intermittent current, i.e. a current that is interrupted periodically, the switch K is switched off, so that the current will pass in one direction for a time proportional to the length of the contact ab, and no current at all will pass for a time proportional to the insulated section bca.

Thus, with the aid of this commutator electrodes can be polarized both by alternating currents and by intermittent currents over a wide range of frequencies. As the processes investigated occupied such short periods of time, the polarization was recorded automatically with the aid of a cathode voltmeter 12 and a short-period (0.01 sec) mirror galvanometer 10. The record was produced with the light beam 11, which was reflected by the mirror of the galvanometer onto highly sensitive photographic film in the camera 9.

Experimental Results

With the aid of the above-described method, a study was made of the variation of polarization with time for a given constant value of the current**. Fig. 2 shows the cathode polarization curves for a current density of 5 ma/sq.cm in the solution: $K[Ag(CN)_2]$ – 0.25N; KCN – 0.38 at 18-20°.

*This sort of investigation is particularly necessary in various cases of nonstationary electrolysis; for example, when polarization is effected by alternating current [4] or when alternating current is superimposed on direct, etc.

** Constancy of polarizing current was attained by the inclusion in the circuit of a large resistance 17, much greater than the internal resistance of the electrolytic cell.

These curves show that, after the current has been switched on, the cathodic polarization rises comparatively slowly: after 0.14 second it is 76 mv (Curve 3). When the duration of electrolysis is increased to 0.84 second, the cathodic polarization attains 110 mv (Curve 2) and after 9.15 seconds it rises to 164 mv (Curve 1). The cathodic polarization comes to a stop after 2-3 minutes, and its absolute value attains 300 mv.

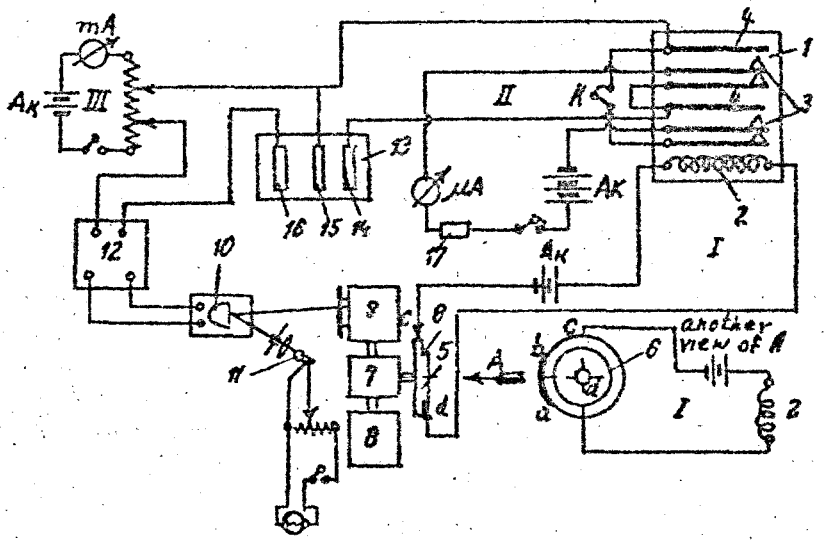

Fig. 1. Diagram of apparatus for the measurement of polarization during electrolysis with alternating and intermittent currents: 1) electromagnetic relay; 2) relay winding; 3) relay contacts; 4) upper plates; 5) Plexiglas disk; 6) metal ring; 7) gear box; 8) electric motor; 9) camera; 10) mirror galvanometer; 12) cathode voltmeter; 13) electrolytic cell; 15) investigated electrode; 16) auxiliary calomel electrode; 17) resistance

Fig. 3 shows curves for the change in anodic polarization with time, determined under the same conditions. When the current is applied to the electrode for 0.14 second, the anodic polarization attains 50 mv (Curve 3); when the duration of electrolysis is increased to 0.84 second, the polarization rises to 57 mv (Curve 2); and after 9.15 seconds it becomes 66 mv (Curve 1). Anodic polarization comes to a stop after 2-2.5 minutes, and its value attains 85 mv. When the curves in Figures 2 and 3 are compared it will be seen that the absolute values of the anodic polarization are lower than those of the cathodic polarization. This is evidence of the great difficulty of the cathode process in comparison with the anode process at the same current density (5 ma/sq.cm).

Fig. 4 shows the curve for the change in the cathodic and anodic polarizations with time determined in the same solution during electrolysis with a symmetrically alternating current. Comparison of Curves 1 in Figures 2 and 3 with the curve in Fig. 4 shows that the absolute values of the anodic and cathodic polarizations fall considerably when alternating current is used. The explanation of this lowering of the polarization is that the impoverishment of the electrode surface layer during the separation of silver is succeeded by its enrichment during the dissolution of silver. As a result, both the cathodic and the anodic polarizations are lowered.

Fig. 5 shows polarization curves determined by the rapid method [5] in the same solution at the maximum current density (50 ma/sq.cm). Curve 1 was taken at a rate of 0.416 cm/sec. One period of this curve, i.e. the sum of the time for which the electrode acted as anode and the time for which it acted as cathode, was 30 seconds. Curve 2 was taken at a rate of 4.166 cm/sec, and the durations of the cathodic and the anodic polarizations were each three seconds. Curve 3 was taken at a rate of 12.5 cm/sec, and the duration of one period was one second. As will be seen from these curves, the absolute values of the cathodic and anodic polarizations and the form of the curves depend greatly on the rate at which the determinations were made. When they were made at a low rate (0.416 cm/sec), the anode curve had quite a different appearance, and differed from the cathode curve by the presence of characteristic "steps", the physical significance of which will be examined below.

Fig. 6 shows the variation of cathodic and anodic polarizations with time in electrolysis with alternating current of density 50 ma/sq.cm. The curve shows that the limiting value of the cathodic polarization is attained after 3 seconds and has the value of 0.75 v; at the same time vigorous evolution of hydrogen occurs. When the direction of

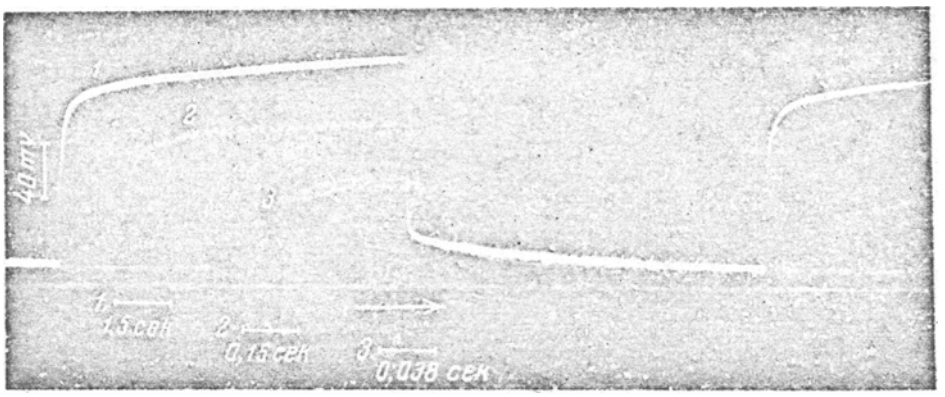

Fig. 2. Variation of cathodic polarization with time ("cek" = sec.)

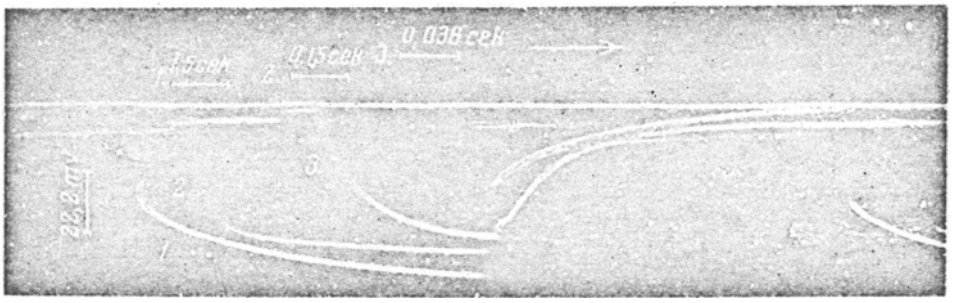

Fig. 3. Variation of anodic polarization with time ("cek" = sec.)

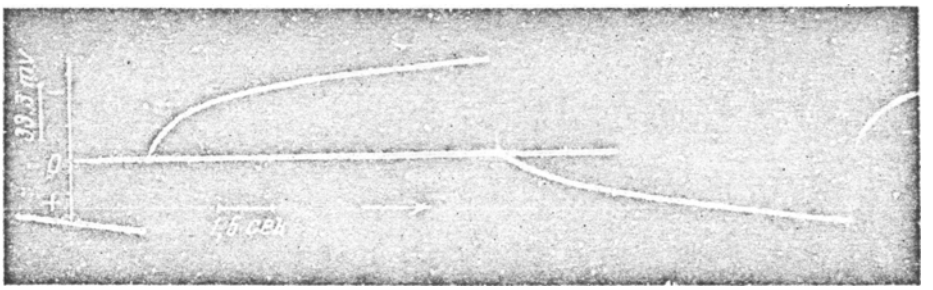

Fig. 4. Variation of polarization with time during electrolysis with alternating current. ("sec" = sec.)

Fig. 5. Polarization curves taken by the rapid method at a maximum current density of 50 ma/sq. cm.

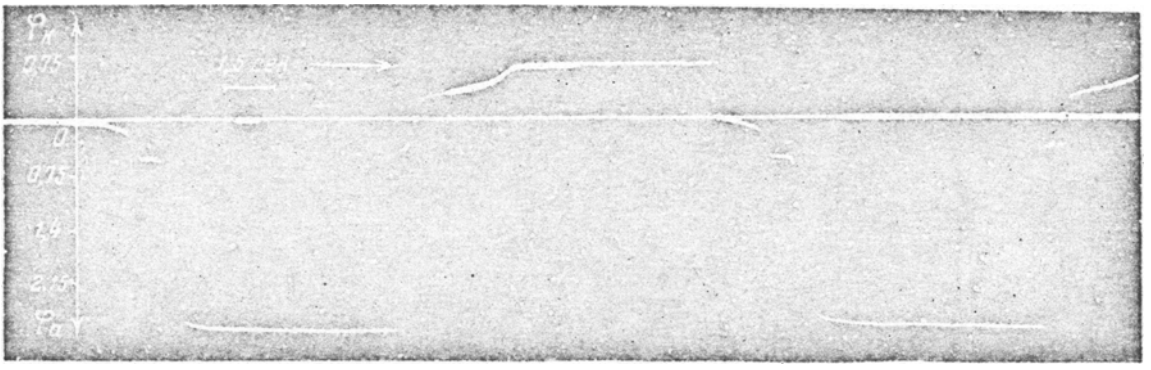

Fig. 6. Variation of polarization with time during electrolysis with alternating current.

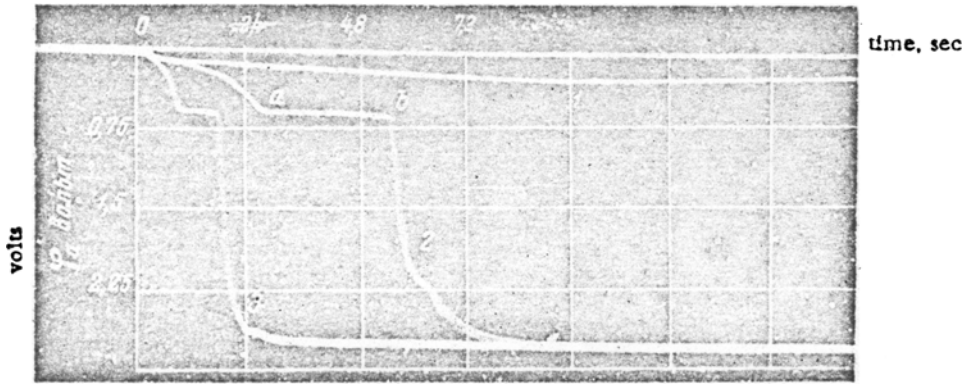

Fig. 7. Variation of anodic polarization with time.

the current is reversed, the passivation of the electrode is brought about in 2.15 seconds. The next reversal of current removes the anodic passivity, and the above-described process is repeated. When, however, the duration of deposition and dissolution of silver is diminished, conditions may be attained under which the cathodic and anodic polarizations cannot attain their limiting values.

Fig. 7 shows anodic-polarization curves taken at the same rate but at differing current densities. Curve 1 was taken at a current density of 10 ma/sq.cm, Curve 2 at 20 ma/sq.cm, and Curve 3 at 30 ma/sq.cm. On two of the curves there are characteristic plateaus. When the anodic polarization corresponds to the section Oa, the current is mainly consumed in dissolving silver with formation of complex cyanide ions. The point a corresponds to the beginning of passivation of the anode, i.e. the formation of a silver oxide film that prevents further dissolution:

$$2\,Ag + 2OH^- - 2e \rightleftharpoons Ag_2O + H_2O$$

The plateau ab is generally found at a potential of 0.6 v relative to the potential of a silver electrode in the same solution. The length of ab diminishes as the current density increases, but the quantity of electricity spent in the formation of the oxide film remains almost constant and corresponds approximately to the formation of a monomolecular layer of silver oxide. The quantity of electricity depends only on the surface relief of the anode. At the point b the whole surface of the electrode is covered by an oxide film and there is a sharp rise in the anodic polarization, corresponding to further thickening of the oxide layer and separation of bubbles of oxygen.

Fig. 8 is the curve for the variation of anodic polarization with time during the dissolution of silver by means of an intermittent current. Over the section oc the electrode is polarized by a high-density current, which renders the anode passive. At the point c the current is switched off, and section df corresponds to the variation of the potential of the electrode when there is no current. In the curve for the fall in polarization in absence of current there is a sudden check (section de) at the same potential as that at which silver oxide forms, and this corresponds to the dissolution of the oxide film in potassium cyanide with formation of a complex silver cyanide.

$$Ag_2O + 4KCH + H_2O \rightleftharpoons 2KAg(CN)_2 + 2KOH$$

The further slow fall in the potential along the section ef results from the levelling out of the concentrations of complex silver ions in the layer in immediate contact with the electrode.

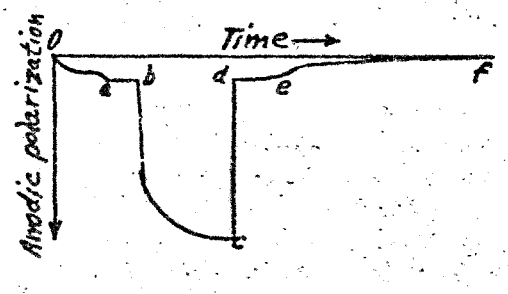

Fig. 8. Variation of anodic polarization with time during electrolysis with an intermittent current

Examination of the surface of the anode showed that at low current densities the silver dissolved with exposure of its structure. At high current density, when passivation of the anode occurred (Fig. 7, Curves 2 and 3), the surface of the silver was covered by a dark-colored oxide film; this had cracked in some places, and some of it had broken away as a result of internal strians and of mechanical disruption due to the separation of bubbles of oxygen. When the anode was polarized with an intermittent current, so that the oxide film was alternately formed and dissolved (Fig. 8), electrolytic polishing of the silver occurred.

DISCUSSION OF RESULTS

Cathodic polarization during the deposition of metals can be the result of the slowest stage of one of the following processes: 1) formation and growth of crystals on the cathode; 2) slow discharge of ions; 3) slow decomposition of complex ions; and 4) slow delivery of discharging ions to the cathode.

The curves given above, which were determined during the deposition of silver from cyanide solutions, cannot be explained by the slowness of the formation of crystals, for, as has been pointed out in a number of investigations [6], when the process is retarded by electrocrystallization, the polarization is high only at beginning of the process and falls as the crystals forming at the cathode grow. However, the polarization curves obtained (Figs. 2, 4 and 6) show exactly the opposite picture of the variation of polarization with time, indicating that cathodic polarization must be due to other causes.

Again, the observed polarization during the deposition of silver from cyanide solutions cannot be explained by the slowness with which the complex ions are dehydrated and discharged, for, if the discharge were slow, the polarization would not vary, i.e. its value would remain constant with time.

The nonvalidity of explanations of the polarization based on the slowness with which complex silver cyanide ions are decomposed has been demonstrated fairly conclusively in some previous papers [7]. We consider that the slow rise of polarization with time and the great reduction in its value in electrolysis with alternating current (Fig. 4) can be explained by a) the slowness with which the discharging ions are delivered to the electrode* (concentrational polarization); and b) the slowness with which the discharging ions [in particular $Ag(CN)_2^-$] penetrate into the electrical double layer, i.e. the slowness with which they are adsorbed and the slowness of the process of displacing other ions and particles situated at the cathode surface.

Since the rate of the electrochemical reaction is determined by the concentration of the discharging anions adsorbed on the surface of the cathode, a lowering of the polarization will be observed, both when the current is periodically switched on and off (Fig. 2), and when the direction of the current is reversed (Fig. 4). The polarization is lowered to a particularly great extent when the direction of the current is reversed, for in the cathodic impulse the electric field is directed against the adsorption forces.

The picture that we have described of the variation of polarization with time can be interpreted as a kind of concentrational polarization, although this concept would need to be extended somewhat in content and sense. This polarization differs from the usual concentrational polarization in that the migration of ions is in the reverse direction and the concentration of the discharging ions at the electrode surface depends on the rate of adsorption, i.e. on the rate at which they penetrate the electrical double layer and on the rate at which they can displace other ions and foreign species from the cathode surface.

An examination of the changes in anodic polarization with time indicates that this also is concentrational and the way in which the anodic polarization changes at low current densities is analogous to the behavior of cathodic polarization, as can be seen from the curves in Figures 2 and 3. The fact that the polarization occurring during the deposition of silver from cyanide solutions is concentrational makes it possible to deposit with an alternating current and to use high current densities, without reaching the limiting values. As a result it is possible to improve the quality of cathode deposits.

As indicated above, when the anode is polarized by high current densities, it becomes passive (Figures 5, 6 and 7). In the literature [8] the passivation of silver in cyanide solutions has often been explained by the supersaturation of the layer in contact with the anode with the silver complex salt and its precipitation on the electrode surface as a viscous, passivating film. We consider that this view is not fully substantiated in the present case, for it is impossible to explain, on its basis, the check in the fall in polarization (de, Fig. 8) when the current is switched off.

If the section ab corresponded to the crystallization of the complex silver salt on the anode, a smooth fall in potential with time should have been observed when the current was switched off. Actually, however, there was a check in the fall of the polarization when the current was switched off, and this was at the same potential as that at which the oxide was formed. The fact that the check in the rise of the polarization curve and the check in the fall of potential when the current was switched off were at the same potential level gives reason to suppose that the process occurring at the anode was the formation and dissolution of silver oxide, and not the complex cyanide.

It should be noted in conclusion that it is usual in the examination of the mechanism of electrode processes to study the dependence of the value of the polarization on the current density, without taking into account the changes of polarization with time, in spite of the fact that in some cases these changes are very important for the understanding of the kinetics of the processes.

SUMMARY

1. A simple method has been developed for the study of nonstationary electrode processes of short duration.

2. It has been shown that cathodic and anodic polarizations occurring during the deposition and dissolution of silver in cyanide solutions are essentially concentrational.

3. It has been shown that three sections can be distinguished in the curves for the variation with time of anodic polarization during electrolysis at high current densities, and that these correspond to the following processes: a) dissolution of silver with formation of complex cyanide ions; b) formation of a monomolecular layer of silver oxide on the electrode surface; and c) the further thickening of the oxide film and the evolution of free oxygen.

* The slow rise of the polarization with time cannot be explained by the charging current, since the current required for the charging of the electrical double layer is comparatively insignificant.

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Received April 3, 1954

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