# THE MECHANISM OF METAL ELECTRODEPOSITION FROM SOLUTIONS OF SIMPLE AND COMPLEX SALTS

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At the present time there is sufficient literature and experimental data to show that in an electrode process the ions taking part are not free simple ions, but are always complex or hydrated ions, irrespective of the sign of their charge [1]. Experimental proofs of the accuracy of this hypothesis were earlier obtained in work by O. A. Essin [2] and A. I. Levin [3], in which several branches were detected on the polarization curves in the case of the precipitation of metals from their simple and complex electrolytes. In this work the existence of two, three and more breaks in the curve was explained by the discharge of the different ions present in the solution being studied.

In the analysis, in each case, of the problem of which ions are taking part in the cathode reaction, it has to be borne in mind that, in the absence of any current flowing in the solution, and with a given cation (for example, copper) present together with an excess of a complex-forming substance (for example, potassium cyanide) a whole series of complex forms may exist, for example, $Cu(H_2O)_p^{\cdot}$, CuCN, $Cu(CN)_2^{\prime}$, $Cu(CN)_3^{\prime\prime}$, $Cu(CN)_4^{\prime\prime\prime}$ etc., whose concentration is determined by their instability constants and by solvation equilibria.

In contrast to ionic and acid-base equilibria, which are established practically instantaneously, solvation equilibria of the type $[M(Q)_x] + nH_2O \rightarrow M(H_2O)_p^{\cdot} + xQ(H_2O)_q^{\prime}$ proceed over a time interval. The rates of the reactions of complex formation may differ by multiples of the order of $10^{10}$, which corresponds to a difference in activation energies of 14 kcal [4]. At the same time, polyvalent ions, in reactions with other ions in the solution and with molecules of solvent, may split up to give simpler compounds [5]. Consequently, although the concentration of one of the ions may exceed that of the others, the existence of its homologs in the electrolyte is by no means excluded [6].

It is difficult to tell beforehand, in a particular case, which of the ions present in a solution are taking part directly in the electrode reaction. Gerischer [7], on the basis of direct measurements of the exchange current density $i_0$ of zinc and cadmium electrodes in equilibrium, came to the conclusion that in the majority of cases the ions taking part in the discharge were complexes of the type $Zn(OH)_2$, $Zn(C_2H_4)$, $Zn(CN)_2$ etc., i.e., the compounds with low coordination number and smallest negative charge. The same conclusion was reached by A.G. Stromberg [8], who determined the composition of the zinc ions being discharged, from the difference in the anode and cathode half-wave potentials in the irreversible electrode process at a dropping amalgam electrode.

It has been shown earlier in our work [9] that in those cases where two complex-forming species are present in solution, the less stable complex takes part in the discharge process. Thus, for example, when sodium citrate is added to a copper pyrophosphate electrolyte, $Cu(C_6H_5O_7)'$ ions are reduced at the cathode, while the concentration of $Cu(P_2O_7)_2^{-6}$ or $Cu(P_2O_7)^{-2}$ remains high.

It should be noted that since the overwhelming majority of solutions of complex compounds belong to the class of strong electrolytes and obey the same laws as simple strong electrolytes, the equilibrium state of such systems cannot indicate the composition of the ions predominating in the solution layers next to the electrodes or the rate of their reaction in electrolysis. The exceptionally large changes in the nature and the shifts of the ionic equilibrium which are observed during electrolysis provide evidence for the fact that the thermodynamic stability of the complex does not predetermine the kinetics of the actual electrode process at a given current density. In actual fact the ions taking part in an electrode reaction may be not only the ions predominating in the electrolyte before the current is passed, but other ionic species which are formed and concentrated in the layers

close to the electrodes during the electrolysis process. The bath used for galvanic chromium plating may be taken as an example of this.

It is known that when no current is passing we have the equilibrium

$$2CrO_4'' + 2H^+ \rightleftarrows 2HCrO_4' \rightleftarrows Cr_2O_7'' + H_2O,$$

which is moved to the left as the pH is increased and the solution is diluted. The studies which we have made of the concentration changes in the layers close to the electrodes in chrome baths, together with measurements of electrode polarization [10] show that extensive shifts in the ionic equilibrium in the catholyte take place as the current density is increased. On the first part of the $i - \varphi$ curve (Fig. 1), i.e., at relatively low current densities (pH 0.08–0.2), reduction of $Cr_2O_7''$ anions to trivalent chromium takes place, according to the reaction

$$Me\,(Cr_2O_7'')_{ads} + 6e + 14H^+ \longrightarrow Cr^{\cdots} + 7H_2O$$

(which agrees with the data given by A. T. Bagramyan and N. D. Usachev [11]). Increase of pH in the cathode zone to 2.6 with increase in current density leads to a shift of the ionic equilibrium in the direction of $CrO_4''$ formation, so that on the second part of the curve, together with the reduction of $Cr_2O_7''$ to $Cr^{\cdots}$, we have the process

$$Me\,(CrO_4'')_{ads} + 3e + 8H^+ \longrightarrow Cr^{\cdots} + 4H_2O.$$

Finally, on the third part of the $i - \varphi$ curve (at pH 3-4) the $CrO_4''$ completely displaces the previously absorbed $Cr_2O_7''$ ions from the cathode. These shifts in the ionic equilibrium with change in pH evidently take place instantaneously, as is confirmed, for example, by the study of the adsorption spectra [12]. As a result, the process of reduction of $CrO_4''$ ions to metallic chromium becomes possible

$$Me\,(CrO_4'')_{ads} + 6e + 4H_2O \longrightarrow Cr + 8OH^-$$

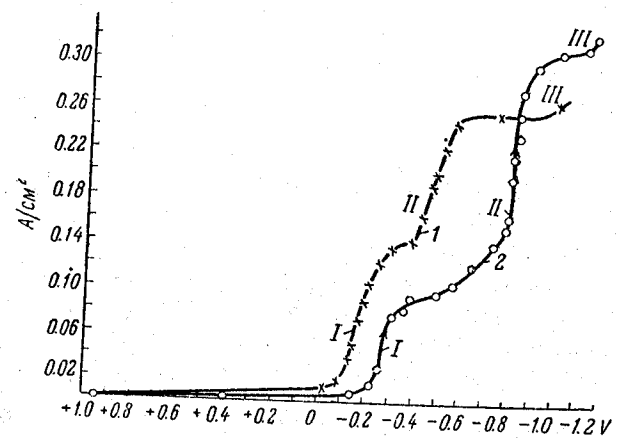


Fig. 1. Polarization of Pt cathode in solutions of chromic anhydride.
1) 1 M $CrO_3$ + 0.01 M $H_2SO_4$, 2) 2 M $CrO_3$ + 0.02 M $H_2SO_4$.

Discharge of $H^+$ ions and partial reduction of $CrO_4''$ to $Cr^{\cdots}$ take place simultaneously. It is not difficult to see that at high current densities, as a result of chemical and concentration polarization and the accompanying discharge of hydrogen, the pH of the catholyte may move so far towards the alkaline region that the point of hydrate formation is reached (pH 5.3-6). The hydroxide and basic salts of chromium in the freshly-precipitated state have the properties of a gel, whose particles carry a positive charge. They are adsorbed by the surface of the cathode and in this way reduce its negative charge (the potential of zero charge for chromium lies at a approximately –0.45 v [13]). This last effect facilitates the discharge of chromate anions on the cathode.

Analogous phenomena are observed in a copper pyrophosphate bath. It may be taken as established that in this case the cathode process at relatively low $Na_4P_2O_7$ concentration and low current densities is the discharge of $Cu(P_2O_7)^{2-}$ anions (instability constant $K_1 = 1.2 \cdot 10^{-6}$). With increase in $Na_4P_2O_7$ content and current density, the equilibrium $Cu(P_2O_7)^{2-} \rightleftharpoons Cu(P_2O_7)_2^{6-}$ is moved in the direction of the hexavalent complex pyrophosphate anion, as a result of which the previously adsorbed $Cu(P_2O_7)^{2-}$ anions are displaced from the cathode surface by $Cu(P_2O_7)_2^{6-}$ ions (instability constant $K_2 = 1.3 \cdot 10^{-11}$ [14]). Outwardly these changes are shown in the constant value of the current over a fairly wide potential range (Fig. 2). After the limiting conditions for the discharge of the anions with the lowest negative charge have been reached, we have the second part of the $i - \varphi$ curve corresponding to the discharge of $Cu(P_2O_7)_2^{6-}$.

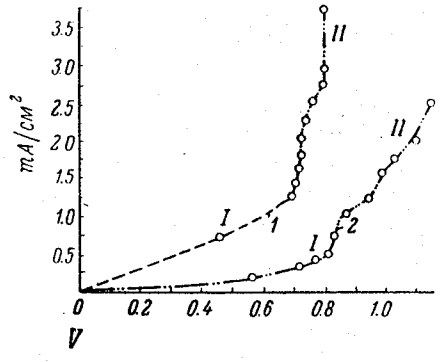


Fig. 2. Polarization of Cu cathode in pyrophosphate electrolytes.
1) 0.05 M $CuSO_4$ + 0.1 M $Na_4P_2O_7$
2) 0.06 M $CuSO_4$ + 0.153 M $Na_4P_2O_7$

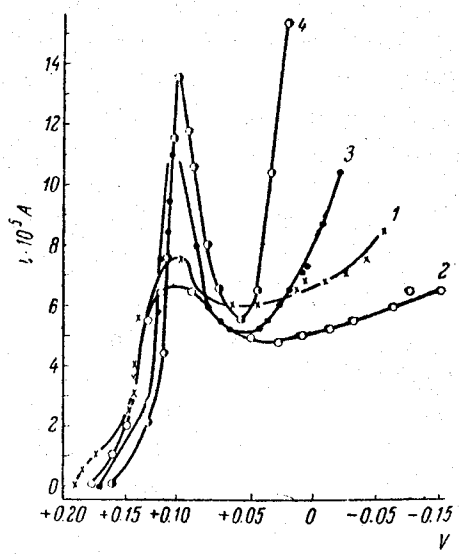


Fig. 3. Polarization of Cu cathode in pyrophosphate electrolytes near the zero charge point.
1) 0.0115 M $CuSO_4$ + 0.016 M $Na_4P_2O_7$
2) 0.0098 M $CuSO_4$ + 0.008 M $Na_4P_2O_7$
3) 0.02 M $CuSO_4$ + 0.03 M $Na_4P_2O_7$
4) 0.03 M $CuSO_4$ + 0.05 M $Na_4P_2O_7$

Experiment shows that no matter which of the anions indicated is reduced: $M[Cu(P_2O_7)^{2-}]_{ads.} + 2e \rightarrow Cu + P_2O_7^{4-}$, or $M[Cu(P_2O_7)_2^{6-}]_{ads.} + 2e \rightarrow Cu + 2P_2O_7^{4-}$, the result of the electrode reaction is the formation of a copper deposit on the cathode, accompanied simultaneously by an increase in the $P_2O_7^{4-}$ concentration in the catholyte [15]. This last effect results in the formation of very thin (apparently monomolecular) adsorbed layers consisting of compounds of the type $Cu^{\cdot\cdot} - P_2O_7^{\cdot\cdot\cdot\cdot} - Cu^{\cdot\cdot}$. When concentrated solutions of the pyrophosphate complex are used, the formation of salt films of crystalline structure as a separte phase is observed [16].

The formation of films of varying structure and composition, passivating the surface of the cathode, is also possible in a particular case as a result of changes in pH and shifts in the ionic equilibrium taking place in the region close to the electrode.

Further studies have shown that in a pyrophosphate complex electrolyte [17] and in a chrome bath [18], besides the formation of stable, compact adsorbed layers, we have the specific phenomenon of retardation of the cathode process of reduction of the complex anions. This effect is observed as the potential passes through the point of zero charge (Fig. 3). This is shown outwardly by the onset of sudden fall of current on the $i - \varphi$ curves. This drop in the current, in agreement with A. N. Frumkin's retarded discharge theory, may be explained by recharging of the surface and the development of repulsive forces between the cathode and the negatively charged complex ions [19].

As follows from Fig. 3, the zero charge point for copper in a pyrophosphate bath is close to + 0.05 v. Thus over a fairly wide working range of current density (Fig. 2) the cathode surface has a positive charge (the left-

hand ascending portion of the electrocapillary curve). In this case the adsorption of anions of the type $Cu(P_2O_7)^{2-}$, $Cu(P_2O_7)_2^{6-}$ etc. is facilitated.

When considering the ability of the complex anions to be discharged not only on the positively charged surface of the electrode, but also after the drop in current, when the cathode surface acquires a large negative charge (the right-hand branch of the electrocapillary curve), it should be noted that different authors explain this experimental fact in different ways. Billiter [20] suggests that in the cathode field the complex anions behave as dipoles, with their positive poles, i.e. the metal cation, turned toward the electrode. As a result of the "stretching" of the complex ion, from the electrostatic forces, the removal of the metal is facilitated. T. A. Kryukova [21] explains the ability of anions to be discharged on the cathode as due to the screening effect of stray positive ions present in the solution, while these positive ions, for some reason or other, , cannot be discharged themselves. Indeed, studies of the effect of small additions of tetrabutylammonium sulfate (0.03-0.3 mg/ liter) have shown [17, 18] that these additions lower the cathode polarization in the discharge of anions of the type $Cu(P_2O_7)_2^{6-}$. The $\varphi - f(c)$ curve is asymptotic; this fact provides evidence that the effect of the cationically active additions is due to their adsorption characteristics.

The adsorption of tetrabutylammonium cations makes the adsorption potential $\psi_1$ more positive; from this it follows that the polarization ($\Delta\varphi$) should decrease. In fact, it follows from A. N. Frumkin's equation for the retarded discharge

$$\Delta\varphi = a \pm \frac{n_a \pm \alpha}{\alpha}\psi_1 - \frac{RT}{\alpha n_k F}\ln i$$

that the surface concentration of the anions being reduced at the cathode depends on all the factors which influence the $\psi_1$ potential.

The value of the $\psi_1$ potential may be given approximately by the expression

$$\psi_1 = \text{const} \pm \frac{2RT}{n_a F}\ln(\pm\varphi_a) - \frac{RT}{n_a F}\ln c$$

Here: c is the electrolyte concentration, $n_a$ is the valency of the complex anion, and $\varphi_a$ is the potential at the electrode surface, relative to the potential in the bulk of the solution, taken arbitrarily as zero [22]. A plus sign is put before $\varphi_a$ if $\psi_1 > 0$, a minus sign if $\psi_1 < 0$.

The value of $\psi_1$ thus depends on the total electrode potential, the electrolyte concentration, the valence of the ions, the presence of extraneous added reagents, etc. When the surface-active tetrabutylammonium cations are adsorbed, they reduce the negative charge on the cathode and thus facilitate the reduction of the complex pyrophosphate anions on the cathode. We have seen that in the case of a chrome electrolyte a similar part is played by the hydroxide and basic salts of chromium.

Thus when chrome and certain other complex electrolytes are used, the part of the extraneous capillary-active added reagents, which influence the kinetics of the electrode reactions, is played by substances formed directly in the layers near the electrode during the electrolysis process. The determining factor is here the screening of the negatively charged cathode surface, as a result of which the activation energy required for the reduction of the chromate anions to the metal is lowered.

Finally, A. N. Frumkin suggests [23] that the reaction involving the reduction of the anions on the negatively charged surfaces may take place via a tunnel mechanism, without direct contact between the ions being discharged and the metal of the electrode.

In this connection we would point to a number of works by foreign authors, who have shown with the help of labeled atoms that a rapid exchange reaction can take place between polyvalent anions such as $Mo(CN)_8^{3-}$ and $Mo(CN)_8^{4-}$ or $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$. The analogy between these charge exchange reactions and the reduction of anions at the strongly negatively charged metal surface speaks for itself.

There are thus many facts in support of the hypothesis that complex anions take part directly in the cathode process.

The point of view put forward concerning the mechanism of electrocrystallization has proved extremely fruitful in connection with the improvement and control of electrode reactions in a copper pyrophosphate bath and in the galvanic chromium plating process.

## SUMMARY


1. Studies carried out have provided evidence that there is no special mechanism for the discharge of ions from complex electrolytes in comparison with solutions of simple salts, since in all cases the ions taking part in the cathode process are not simple ions but complex or solvated ions.

2. The discharge potentials of ions are directly dependent on the stability of the appropriate complexes and on their charge: a) if the complex is not very stable and the excess of complex-forming species sufficiently small, the discharge of "simple", i.e., hydrated, metal cations becomes possible; b) if the stability of the complex is sufficiently high, and the concentration of the complex-forming species negligible, then it is more probable that the lower complex form will take part in the discharge; for example, when $Cu(P_2O_7)^{2-}$ and $Cu(P_2O_7)_2^{6-}$ are present the process $Cu(P_2O_7)^{2-} + 2\bar{e} \rightarrow Cu + P_2O_7^{4-}$; c) if the concentration of complex-forming species is high, then at sufficiently high current densities more complex anions may be reduced on the cathode, for example: $Cu(P_2O_7)^{6-} + 2\bar{e} \rightarrow Cu + P_2O_7^{4-}$ etc.

3. The concentration changes in the layers close to the electrodes, which take place during electrolysis, may lead to sudden shifts in the ionic equilibria and to the formation of new complex species.

4. In the mechanism of electrochemical electrode reactions, a special role is played by the position of the zero charge point characteristic of a given metal. A knowledge of the value of the zero charge potentials is necessary for the determination of the charge of the electrode surface, and hence for the determination of the conditions under which the electrode reaction should take place.

5. Adsorption processes at the metal–solution boundary have a very real influence on the course of the electrode reaction. In a number of cases they facilitate the reduction of the complex anions on the negatively charged cathode surface.


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Received July 16, 1956

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