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Author(s)	MITUYA, Atusi; IKEZAWA, Yasunari; TODA, Genjiro
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Instructions for use

ON THE MECHANISM OF ELECTRODE REACTION OF SILVER IN ACIDIC PERCHLORATE SOLUTION

By

Atusi MITUYA[*], Yasunari IKEZAWA[*]
and Genjiro TODA[*]

Abstract

The mechanism of the electrocrystallization of silver in an acidic perchlorate solution was studied by means of a galvanostatic method. Three types of the transient curves of the polarization were observed by a galvanostatic pulse according to the conditions of the pretreatment of the electrode. The $\eta-t$ curves were analysed with regard to one of the three types by means of a new mathematical treatment for the parallel reaction mechanism, in which the electrode reaction of silver proceeded through the direct electrocrystallization with an adsorption process in parallel, and for the successive reaction mechanism proposed by BOCKRIS *et al.*

The overpotential- and the current density-dependence of the concentration of adsorbed-Ag (C_{Ag}), in steady states and the impurity effect on the overpotential and C_{Ag}, were in favor of the parallel reaction mechanism. The nonlinearity and the asymmetry of the $i-\eta$ curve in the low overpotential region were discussed.

Introduction

The kinetics of electrocrystallization and dissolution process of silver in an acidic perchlorate solution have been investigated by GERISCHER and TISCHER[1], and GERISCHER[2], and MEHL and BOCKRIS[3], and DESPIC and BOCKRIS[4]. GERISCHER, and MEHL and BOCKRIS observed that the transient curve of the polarization by a galvanostatic pulse exhibited a much longer rise time than that calculated based on the charge transfer reaction which occurred in parallel with the double layer charging. They proposed a mechanism following the interpretation of crystallization from the vapor phase that the rate determining step in the low overpotential region was the surface diffusion of Ag-atom from an ordinary adsorption site to an adsorp-

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[*] Department of Chemistry, Faculty of Science, Rikkyo (St. Paul's) University, Nishi-ikebukuro, Toshima-ku, Tokyo, 171 Japan.

tion site adjacent to a lattice site. KITA, ENYO and BOCKRIS[5] proposed that the number of crystallization points (growth sites on the electrode surface) increased when the overpotential became high so that the rate determining step changed from the surface diffusion to the charge transfer.

In earlier work, ERDEY-GRUZ and VOLMER[6] proposed a discharge mechanism for the electrode reaction of silver. They suggested that the charge transfer of Ag ion in solution did not occur at the point where the ion arrived in the double layer; the diffusion of Ag ion in the double layer occurred until it arrived above a growth site of the electrode surface where the direct electro-crystallization occurred.
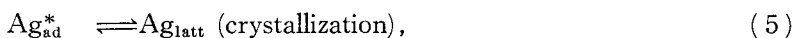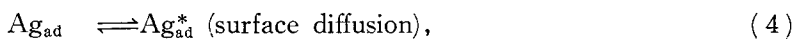
Recently the present authors proposed a mechanism for the copper electrode reaction in a sulphate solution[7] which excluded any possibility of the surface diffusion.

As shown in Fig. 1, in experimental practice, differently shaped transient curves were conditionally observed with a galvanostatic pulse. MEHL and BOCKRIS[3] analysed the B type curve and GERISCHER[2] analysed the C type curve.

In this report, the B type galvanostatic transient curves will be analyzed on the basis of a parallel reaction mechanism,

Fig. 1. Types of $\eta - t$ curves.
A : super polarization curve,
B : normal polarization curve,
C : polarization curve by activated electrode surface.

$$Ag^+ + e \rightleftharpoons Ag_{latt} , \qquad (1)$$

$$Ag^+ + e \rightleftharpoons Ag_{ad} . \qquad (2)$$

and the successive reaction mechanism (surface diffusion mechanism) proposed by BOCKRIS *et al*,

$$Ag^+ + e \rightleftharpoons Ag_{ad} , \qquad (3)$$

$$Ag_{ad} \rightleftharpoons Ag_{ad}^* \text{ (surface diffusion)}, \qquad (4)$$

$$Ag_{ad}^* \rightleftharpoons Ag_{latt} \text{ (crystallization)}, \qquad (5)$$

where reaction (1) is the direct electrocrystallization and reaction (2) is the adsorption process, in which its equilibrium depends on the electrode potential, and Ag_{ad}, Ag_{ad}^* and Ag_{latt} represent respectively the Ag atom in an ordinary adsorption site, in an adsorption site adjacent to lattice site and in a lattice site. The results of the analysis of the transient curves in the whole region from $t=0$ to $t=\infty$ will be compared between the two mechanisms.
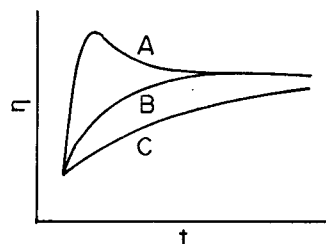
Theoretical

1. Parallel Reaction Mechanism.

The authors first treat the silver electrode reaction by the parallel mechanism. In the galvanostatic pulse method, supplied current density i_s may be composed of three components,

$$i_s = i_c + i_1 + i_2 , \qquad (6)$$

where i_c is the charging current density of the electrical double layer at the electrode-solution interface, and i_1 and i_2 are the faradaic current densities of reaction (1) and (2), respectively. Assuming that the double layer capacity is independent of the overpotential and the concentration polarization is negligible, and that the overpotential is substantially caused by charging up of the double layer, we have

$$i_c = -C \frac{d\eta}{dt} , \qquad (7)$$

$$i_1 = i_{1,0} \left[\exp\left(\frac{-\alpha F \eta}{RT} \right) - \exp\left\{ \frac{(1-\alpha) F \eta}{RT} \right\} \right] , \qquad (8)$$

where cathodic current has a positive sign, C is the double layer capacity, $i_{1,0}$ is the exchange current density of reaction (1), α is the transfer coefficient, η is the overpotential (cathodic overpotential has a negative sign), and F, R, and T have their usual significance.

The adsorption isotherm of Ag_{ad} will be given by Eq. (9) in accordance with GERISCHER[2] ;

$$\mu_{ad} = \mu_{ad}^0 + RT \ln \frac{C_{ad}}{C_{ad,max} - C_{ad}} , \qquad (9)$$

where μ_{ad} is the chemical potential of Ag_{ad}, and C_{ad} and $C_{ad,max}$ are the concentration of Ag_{ad} and its maximum value, respectively. When $C_{ad} \ll C_{ad,max}$, we have,

$$\mu_{ad} = \mu_{ad}^0 + RT \ln \frac{C_{ad}}{C_{ad,max}} . \qquad (10)$$

Further the equilibrium of reaction (2) is expressed as

$$\mu_{ad} = \mu_{Ag^+} - F\phi , \qquad (11)$$

where μ_{Ag^+} is the electrochemical potential of Ag^+ in solution, and ϕ is the electrode potential. When μ_{Ag^+} is constant, from Eqs. (10) and (11), we have,

$$\Delta\phi = -\frac{RT}{F} \ln \frac{C_{ad,I}}{C_{ad,0}} , \qquad (12)$$

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where $C_{ad,0}$ and $C_{ad,I}$ are the concentration of Ag_{ad} at the reversible state of the overall reaction and state I, respectively, and $\Delta\phi$ is the electrode potential difference between the two states. Then the rate of adsorption may be expressed as,

$$i_2 = F \frac{dC_{ad,t}}{dt}$$
$$= i_{2,0} \left[\exp\left\{ \frac{-\alpha' F}{RT} (\eta - \Delta\phi) \right\} - \exp\left\{ \frac{(1-\alpha') F}{RT} (\eta - \Delta\phi) \right\} \right], \qquad (13)$$

where $C_{ad,t}$ is the concentration of Ag_{ad} at $t=t$, and α' is the transfer coefficient of reaction (2), and $i_{2,0}$ is the exhange current density of reaction (2). When η is small as compared with RT/F, we have from Eqs. (8), (12), and (13),

$$i_1 = -i_{1,0} \frac{F}{RT} \eta, \qquad (14)$$

$$i_2 = -i_{2,0} \frac{F}{RT} (\eta - \Delta\phi), \qquad (15)$$

$$\Delta\phi = -\frac{RT\Delta C_{ad,t}}{F C_{ad,0}}, \qquad (16)$$

where

$$\Delta C_{ad,t} = C_{ad,t} - C_{ad,0} = \frac{1}{F} \int_0^t i_2 \, dt = \frac{Q}{F}, \qquad (17)$$

and Q is the quantity of electricity consumed in reaction (2). From Eqs. (7) and (14)~(17) we have

$$-\eta = \frac{RT}{i_{1,0}F} i_1 = \frac{1}{C} \int_0^t i_c \, dt = \frac{RT}{i_{2,0}F} i_2 + \frac{RT}{C_{ad,0}F^2} Q. \qquad (18)$$

It follows from Eqs. (6) and (18),

$$i_s = \frac{CRT}{i_{2,0}F} \frac{d^2Q}{dt^2} + \left(\frac{CRT}{C_{ad,0}F^2} + \frac{i_{1,0}}{i_{2,0}} + 1 \right) \frac{dQ}{dt} + \frac{i_{1,0}}{C_{ad,0}F} Q. \qquad (19)$$

The solution of Eq. (19) is given elsewhere[*] as,

$$i_2 = \frac{dQ}{dt} = \frac{i_{2,0}F i_s}{CRT(A-B)} \left\{ \exp(-Bt) - \exp(-At) \right\}, \qquad (20)$$

where

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[*] Y. IKEZAWA, Thesis, Rikkyo (St. Paul's) University, Tokyo (1976).

$$A = \frac{i_{2,0}F}{2CRT} \left[\left(\frac{CRT}{C_{ad,0}F^2} + \frac{i_{1,0}}{i_{2,0}} + 1 \right) \right.$$
$$\left. + \left\{ \left(\frac{CRT}{C_{ad,0}F^2} + \frac{i_{1,0}}{i_{2,0}} + 1 \right)^2 - \frac{4i_{1,0}CRT}{i_{2,0}C_{ad,0}F^2} \right\}^{1/2} \right], \tag{21}$$

and

$$B = \frac{i_{2,0}F}{2CRT} \left[\left(\frac{CRT}{C_{ad,0}F^2} + \frac{i_{1,0}}{i_{2,0}} + 1 \right) \right.$$
$$\left. - \left\{ \left(\frac{CRT}{C_{ad,0}F^2} + \frac{i_{1,0}}{i_{2,0}} + 1 \right)^2 - \frac{4i_{1,0}CRT}{i_{2,0}C_{ad,0}F^2} \right\}^{1/2} \right]. \tag{22}$$

The values of unknown parameters (C, $i_{1,0}$, $i_{2,0}$ and $C_{ad,0}$) in Eqs. (20)~(22) can be evaluated at the limiting cases as

$$C = - \frac{i_s}{(d\eta/dt)_{t\to 0}}, \tag{23}$$

$$i_{1,0} = - \frac{RTi_s}{F\eta_s}, \tag{24}$$

where η_s means η at a steady state. When η approaches zero,

$$(i_s - i_c)_{t\to 0} = (i_1 + i_2)_{t\to 0} = - \frac{(i_{1,0} + i_{2,0})F}{RT} \eta_{t\to 0}. \tag{25}$$

Rewriting Eq. (25), we have

$$i_{2,0} = - \frac{(i_s - i_c)_{t\to 0}RT}{F\eta_{t\to 0}} - i_{1,0}. \tag{26}$$

The value of $C_{ad,0}$ is given by Eqs. (16) and (17) and $\eta_s = \Delta\phi$, as

$$C_{ad,0} = - \frac{RT}{F^2\eta_s} \int_0^\infty (i_s - i_c - i_1)dt. \tag{27}$$

2. Successive Reaction Mechanism.

MEHL and BOCKRIS[3] presented a mathematical treatise on the surface diffusion mechanism, in which they assumed the following relations:

$$v = v_0 \frac{\Delta C_{ad,t}}{C_{ad,0}}, \tag{28}$$

$$\frac{dC_{ad,t}}{dt} = \frac{i_f}{F} - v, \tag{29}$$

$$\eta = - \frac{RTi_f}{Fi_{f,0}} - \frac{RT\Delta C_{ad,t}}{FC_{ad,0}}, \tag{30}$$

where v is the rate of the surface diffusion flux of Ag_{ad}, v_0 is the rate con-

stant, and i_f is the current density of the formation of Ag_{ad}.

Using the above relations, we have

$$i_s = i_c + i_f = i_c + Fv + F\frac{dC_{ad,t}}{dt}, \tag{31}$$

From Eqs. (7), (30) and (31), we have

$$i_s = \frac{CRT d^2 C_{ad,t}}{i_{f,0} dt^2} + \left(\frac{CRT v_0}{i_{f,0} C_{ad,0}} + \frac{CRT}{C_{ad,0} F} + F\right)\frac{dC_{ad,t}}{dt} + \frac{v_0 F}{C_{ad,0}} \Delta C_{ad,t}. \tag{32}$$

The solution of Eq. (32) is given*) as

$$\frac{dC_{ad,t}}{dt} = \frac{i_{f,0} i_s}{CRT(D-E)} \left\{\exp(-Et) - \exp(-Dt)\right\}, \tag{33}$$

where D stands for

$$\frac{i_{f,0} F}{2CRT} \left[\left(\frac{CRT v_0}{i_{f,0} C_{ad,0}} + \frac{CRT}{C_{ad,0} F} + F\right) + \left\{\left(\frac{CRT v_0}{i_{f,0} C_{ad,0}} + \frac{CRT}{C_{ad,0} F} + F\right)^2 - \frac{4CRT v_0}{i_{f,0} C_{ad,0}}\right\}^{1/2}\right], \tag{34}$$

and E stands for

$$\frac{i_{f,0} F}{2CRT} \left[\left(\frac{CRT v_0}{i_{f,0} C_{ad,0}} + \frac{CRT}{C_{ad,0} F} + F\right) - \left\{\left(\frac{CRT v_0}{i_{f,0} C_{ad,0}} + \frac{CRT}{C_{ad,0} F} + F\right)^2 - \frac{4CRT v_0}{i_{f,0} C_{ad,0}}\right\}^{1/2}\right]. \tag{35}$$

The values of unknown parameters (C, $i_{f,0}$, v_0 and $C_{ad,0}$) in Eqs. (33)~(35) can be evaluated at the limiting cases. When t approaches zero, $\Delta C_{ad,t}$ tends to 0. Then from Eqs. (30) and (31) we have,

$$(i_s - i_c)_{t\to 0} = -\frac{F i_{f,0}}{RT}\eta_{t\to 0}, \tag{36}$$

or

$$i_{f,0} = -\frac{(i_s - i_c)_{t\to 0} RT}{\eta_{t\to 0} F}. \tag{37}$$

In the steady state $i_s = Fv = i_f$, then we have from Eqs. (28)~(30),

$$\eta_s = -\frac{i_s RT}{i_{f,0} F} - \frac{i_s RT}{v_0 F^2}, \tag{38}$$

or

*) Y. IKEZAWA, Thesis, Rikkyo (St. Paul's) University, Tokyo (1976).

$$v_0 = -\frac{i_s i_{f,0} RT}{F(i_s RT + i_{f,0}\eta_s F)} \ .$$ (39)

Using the whole region of the transient from $t=0$ to $t=\infty$ and $dC_{ad,t}/dt=0$ in the steady state, $C_{ad,0}$ is given by Eqs. (28)~(31) as

$$C_{ad,0} = \frac{v_0}{i_s} \int_0^\infty (i_s - i_c - Fv)\,dt \ .$$ (40)

Experimental

1. Reagents and Solutions.

All chemicals used were of reagent grade. Perchloric acid was purified electrolytically with platinum electrodes. Silver perchlorate was prepared from purified silver carbonate (made from silver nitrate and sodium carbonate) by decomposition with perchloric acid. Water used was distilled four times in a quartz still. Before every measurement, purified nitrogen gas was introduced into the cell to purge dissolved oxygen from the solution. The concentrations of silver perchlorate and perchloric acid were given in the figures and tables. Measurements were carried out over the temperature range from 15 to $35° \pm 0.1°$C.

2. Electrodes.

The working, reference and counter electrodes were made of platinum and mounted in a cell as shown in Fig. 2. These platinum electrodes were electrolytically cleaned in a perchloric acid solution. The spherical working electrode was prepared by heating a thin platinum wire (0.5 mm in diameter) to partial melting in a flame. On the working and reference electrodes, silver was electrodeposited *in situ* just before the measurements. The surface area of the electrodeposited silver electrode was determined from the value of the double layer capacitance, assuming the standard value to be $20\ \mu\text{F/cm}^2$.
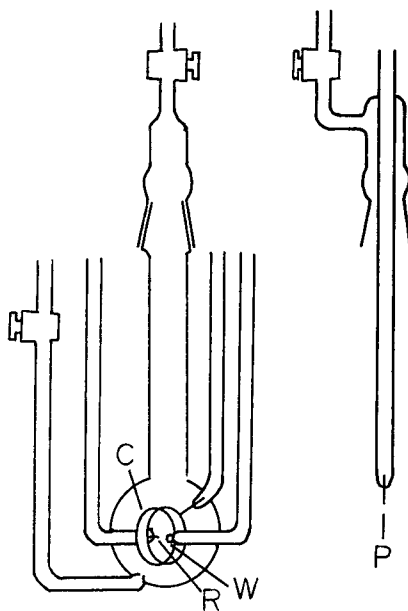

Fig. 2. Scheme of the electrolytic cell and the platinum electrode.

W: working electrode, C: counter electrode, R: reference electrode, P: pre-electrolytic electrode.

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In some cases, all-silver spherical working and reference electrodes were used.

3. Apparatus.

A galvanostatic pulse generator with rise time $< 10^{-6}$ sec was used. The electrode potential was measured with a two-channel digital wave memory (memory capacity; 7 bit, 1024 words, maximum writing rate; 100 n sec/word) through a pre-amplifier (amplification factor; 100, rise time; $< 0.1\ \mu$sec/V). The diagram of the electric circuit is shown in Fig. 3.

Fig. 3. Diagram of electric circuit.
W: working electrode,
R: reference electrode,
C: counter electrode.

Results

1. Types of $\eta-t$ Curves.

Although the shapes of $\eta-t$ curves obtained by a given magnitude of pulses differ from each other, the author classified them into three main types A, B, and C, as shown in Fig. 1. Every curve of the type A, B, or C could be intentionally obtained by an appropriate preliminary treatment of the electrode as described in the following. First, the height and the duration time of the measuring pulse were set at 0.1 mA and 5 msec, respectively. Secondly, an activation pre-pulse of 0.1 mA height and duration time of 1 sec was applied, and the working electrode was allowed to stand more than a few minutes in the solution for the de-activation of the electrode: then when a measuring pulse was applied, a curve of type A was obtained. The curves of type B and C were obtained by setting the time of the de-activation shorter, from a few seconds to one minute; the shorter the time, the more active the electrode. GERISCHER[2] obtained an active electrode of type C by a chemical etching in a cyanate solution.

In the present work the duration time of the activation pulse and the interval of the de-activation time were chosen so as to give a curve of type B in every case. It was assumed that the activity of the electrode giving a curve of type B could not be changed by a measuring pulse; *i. e.*, the surface density of the active points remained almost constant during the measuring pulse.

2. Accuracy of Analysis and Results for the Two Mechanisms.

Fig. 4 shows the results of the analysis of a galvanostatic transient curve. For this analysis, the parameters C, $i_{1,0}$, and $i_{f,0}$ were evaluated[*]
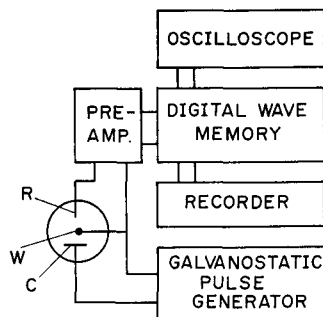
*) Y. IKEZAWA, Thesis, Rikkyo (St. Paul's) University Tokyo (1976).

respectively on the basis of Eqs. (23), (24), and (37). The accuracies of these parameters evaluated by the analysis were examined by the use of equivalent circuits[*] with known values of the parameters: the accuracy obtained by the equivalent circuit was within $\pm 5\%$ for every parameter.

Table 1 shows the four parameters obtained in the actual measurements at several current densities for both mechanisms. The constancies of these parameters, except $i_{1,0}$ and Fv_0 at high i_s, are fairly good. Since the values of measuring pulse i_s was chosen as low as 0.1 mA/cm², the assumption that the
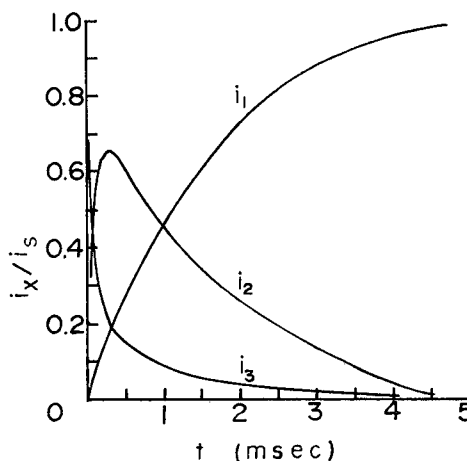

Fig. 4. Results of the analysis of a galvanostatic transient curve (for the parallel reaction mechanism). Suffix x of the ordinate represents 1, 2 or 3.

activities of crystallization points do not change by a measuring pulse, is clearly fulfilled.

TABLE 1. The four parameters of the electrode reaction of silver at several current densities.

The values of C are the same for both mechanisms, solution: 0.5 M AgClO₄+0.5 M HClO₄, temp.: 15°C

i_s mA/cm²	C μF	Parallel mechanism			Successive mechanism		
		$i_{1,0}$ mA/cm²	$i_{2,0}$ mA/cm²	$C_{ad,0} \times 10^{11}$ M/cm²	$i_{f,0}$ mA/cm²	Fv_0 mA/cm²	$C_{ad,0} \times 10^{11}$ M/cm²
0.25	16	2.4	12	5.6	14	2.4	5.6
0.50	16	2.4	13	5.0	15	2.4	3.9
0.75	16	3.0	11	5.6	14	3.0	5.1
1.00	16	3.7	13	5.5	17	3.6	4.3

The variation in the accumulation rate of Ag$_{ad}$ with time is shown in Figs. 5 and 6, respectively for the parallel and successive mechanisms. In Fig. 5., the experimental curve (full line) was obtained by Eqs. (6), (7), and (14) using observed values of $i_{1,0}$ and C, and the experimental polarization curve $\eta - t$; and the calculated curve was obtained from Eq. (20). In Fig.

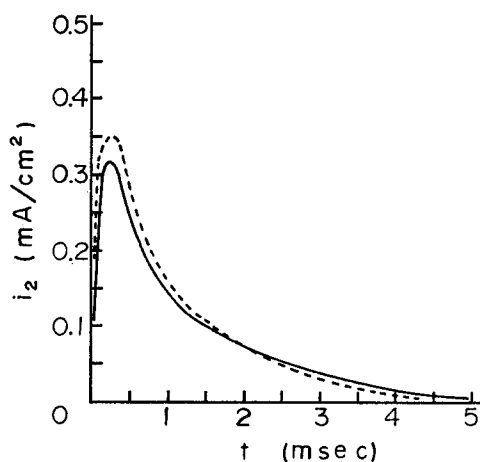[*] Y. IKEZAWA, Thesis, Rikkyo (St. Paul's) University, Tokyo (1976).

Fig. 5. Variation in the accumulation rate of $C_{ad,t}$ with time for the parallel mechanism.

———: experimental curve, - - -: calculated curve, Solution: 0.5 M AgClO$_4$+ 0.5 M HClO$_4$, Cell: Fig. 2, Temp.: 25°C.
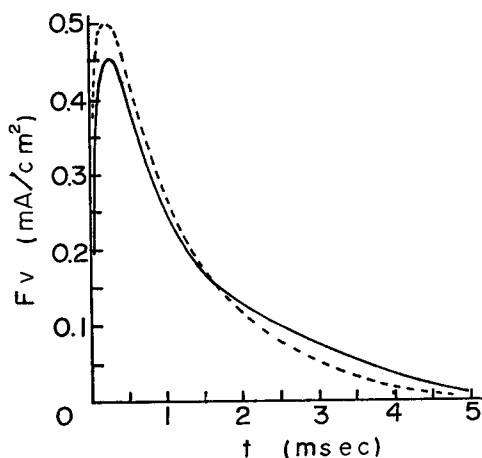
Fig. 6. Variation in the accumulation rate of $C_{ad,t}$ with time for the successive mechanism.

———: experimental curve, - - -: calculated curve, solution is the same as in Fig. 5.

6, the experimental curve was obtained from v_0, C, and the experimental polarization curve $\eta-t$ and the calculated curve was obtained from Eq. (33). The figures show good coincidence between the calculated and experimental curves for both mechanisms. Therefore it seems to be impossible to determine which mechanism is valid for the electrodeposition of silver insofar as the time dependence of $C_{ad,t}$ is concerned.

3. Criteria for Distinguishing between the Two Mechanisms.

3-a). Variation in $C_{ad,\infty}$[*] *with η_s or i_s.*

In the low overpotential region where i_s is linear against η_s, the four parameters mentioned before may be kept constant in each mechanism. From Eqs. (16) or (28), and steady state condition $\varDelta\phi=\eta_s$ or $i_s=Fv$, we have,

$$\eta_s = -\frac{RT}{F}\frac{C_{ad,\infty}}{C_{ad,0}},\tag{41}$$

or

$$i_s = \frac{Fv_0}{C_{ad,0}}C_{ad,\infty},\tag{42}$$

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[*] Hereinafter $\varDelta C_{ad,t\to\infty}$ is abbreviated simply as $C_{ad,\infty}$.

for the parallel or successive mechanism. The values of $C_{ad,\infty}$ are plotted against η_s in Fig. 7 or against i_s in Fig. 8. These figures show that the linearity between $C_{ad,\infty}$ and η_s is clearly better than that between $C_{ad,\infty}$ and i_s. Thus the theoretical treatment of the transient curve on the basis of the parallel mechanism is found to be self-consistent.
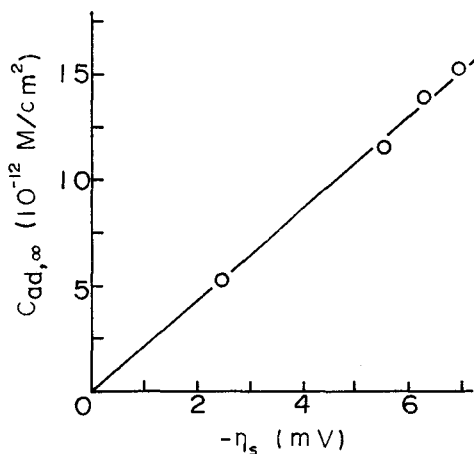

Fig. 7. Relation between η_s and $C_{ad,\infty}$ for the parallel reaction mechanism.
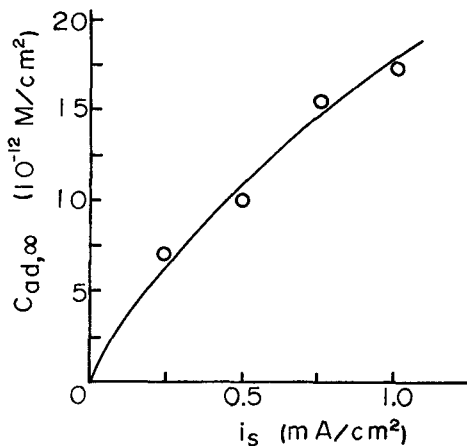Solution: 0.5 M $AgClO_4$+0.5 M $HClO_4$, Temp.: 15°C, Cell: Fig. 2.

Fig. 8. Relation between i_s and $C_{ad,\infty}$ for the successive reaction mechanism.
Solution: 0.5 M $AgClO_4$+0.5 M $HClO_4$, Temp.: 15°C, Cell: Fig. 2.

3-b). Effect of Impurities on η_s and $C_{ad,\infty}$ in the Steady State.

A small amount of Cu^{2+} ion or CS_2 was added to the solution as an impurity after the measurements had made in the pure solution, then the subsequent measurements were made. The adsorption of copper ion in an electrocrystallization process of silver has been reported[8], and the role of CS_2 added to obtain luster surface in electrocrystallization of silver has also been reported. There is no doubt that these substances are adsorbed on the electrode surface. Table 2 shows several results of the impurity effects, in which $-\eta_s$ on a contaminated sample with CS_2 is higher than that on a pure one and $C_{ad,\infty}$ on a contaminated sample with Cu^{2+} ion is much lower than that on a pure one.

According to the surface diffusion mechanism, the value of $C_{ad,\infty}$ increases with increasing value of $-\eta_s$. The experimental results are contradictory to the successive mechanism; $-\eta_s$ remained at constant on a contaminated sample with Cu^{2+} ion while $C_{ad,\infty}$ decreased to about one fouth: or $-\eta_s$ increased while $C_{ad,\infty}$ remained almost at constant. On the other hand, for the parallel

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TABLE 2. Effect of impurity on $C_{ad,\infty}$ and η_s. Current densities of Case I and II are 0.51 mA/cm² and 0.48 mA/cm², respectively. Temp.: 25°C

Case	Solution		Impurity		$-\eta_s$	Parallel mechanism $C_{ad,\infty}10^{11}$	Successive mechanism $C_{ad,\infty}10^{11}$
	AgClO₄ M	HClO₄ M	Material	Conc. M	mV	M/cm²	M/cm²
I	0.2	1.0	—	—	7.4	5.2	6.3
			Cu²⁺	10⁻⁴	7.5	1.2	1.4
II	0.25	0.5	—	—	7.5	5.6	7.0
			CS₂	10⁻⁵	9.6	5.1	6.2

mechanism, the behavior of $-\eta_s$ and $C_{ad,\infty}$ can be independent of each other, because the adsorption of impurity can occur independently on the adsorption sites of Ag_{ad} and on the crystal growth sites, the latter adsorption causes the increase of $-\eta_s$ as shown in Table 2. These results clearly show that the parallel mechanism is the more adequate one for understanding the mechanism of electrodeposition of silver.

Discussion

In this article, the authors presented new mathematical treatise on the deposition reaction of Ag⁺→Ag from acidic perchlorate solution, on the basis of the parallel and the successive mechanism under a premise that the overpotential is caused by the difference of the charging-up of the double layer with neglection of possible effect which might be caused by the change of the work function of the electrode by the adsorption of Ag. In this respect, the original treatise of BOCKRIS and others on the successive mechanism stands on the same view point. The propriety of the parallel mechanism against the successive mecanism, discussed below, is thus within a limit of the premise mentioned above. Although the occurrence of the simultaneous complicated reactions of the parallel and the successive reactions are not denied, the authors did not pay any attention to the diffusion of Ag from adsorption site to lattice site in the treatise on the parallel mechanism, and contrariwise the authors did not take any attention to the fast dissolution of Ag from adsorption site and the fast direct re-adsorption to the lattice site on the successive mechanism with the assumption of slow-surface diffusion. Thus the authors treated the both mechanism, evenly.

The nonlinearity of the $i-\eta$ curve in the low overpotential region (<10

mV) has been observed by many authors.[2,3] The asymmetry of the $i-\eta$ curve between anodic and cathodic regions has also been reported[4,9]. Similar results were obtained in the present experiments (Fig. 9). In the cathodic region where $i_s < 0.5$ mA/cm² in Fig. 9, we see that i_s is linear against $-\eta_s$. In the preceeding section, the authors showed the relation between $C_{ad,\infty}$ and $-\eta_s$ for the parallel mechanism (Fig. 7) and the relation $C_{ad,\infty}$ and i_s for the successive mechanism (Fig. 8), the latter relation may be judged as not linear, even in the low i_s region (<0.50 mA/cm²). On the otherhand the relation of $C_{ad,\infty}$ vs
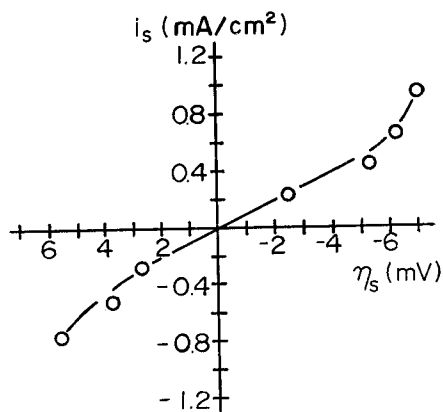

Fig. 9. $i_s - \eta_s$ curve in the steady state.

Solution: 0.5 M AgClO₄+0.5 M HClO₄, Temp.: 25°C, Cell: Fig. 2.

$-\eta_s$ for the parallel mechanism is linear and passes through the origin. It became clear that the theoretical treatments of the transient curve on the basis of the parallel mechanism and the effect of impurities on η_s and $C_{ad,\infty}$ are found not only to be self-consistent but more favoured than these obtained on the basis of the successive mechanism. DAMJANOVIC and BOCKRIS[10] had explained the non-linearity of the i_s vs η_s relation as being due to the change in the number of active points for the successive mechanism, but the same interpretation is hereby valid for the parallel mechanism. It remains not clear whether the adsorption site is one of the lattice sites which loses its activity in the early stage of the reaction or not.

The confirmation of these views by other experiments will be reported in the near future.

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