

Influence of charge and discharge of electric double layer in pulse plating

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In pulse plating the useful values of the on and off times are limited by the rate of charging and discharging, respectively, of the electrical double layer at the electrode-solution interface. The charging and discharging times are calculated as a function of the relevant parameters (pulse current density, exchange current density i_0 , capacitance C of the double layer and others). Simple, approximate relationships are also presented for the case in which no experimental values for i_0 and C are available. In order to quantify the damping of the Faradaic current the concept of 'degree of flattening' is introduced to describe the extent of the capacitive effects. The influence of a high degree of flattening on some deposit properties is illustrated by examples.

Nomenclature

a	$\alpha zF/RT$
A	proportionality factor between current and potential
C	capacitance of the electric double layer
E	potential
i	current density
i_0	exchange current density
i_C	capacitive current density
i_F	Faradaic current density
i_m	average current density in pulsed current
i_p	pulsed current density
i_t	total current density ($i_C + i_F$)
Q	charge
T	used in $RT =$ temperature in K
T	pulse length
T'	interval between two pulses (off time)
t_c	charging time of the double layer (up to 99% of i_p)
t_c^*	charging time of the double layer (with $j_F = 0$ during the charge)
t_c^{**}	charging time of the double layer (up to 98.2% of $\eta_{a,\infty}$ and constant resistance for electron transfer)
t_d	discharging time of the double layer (from $i_F = 0.999i_p$ to $0.01i_p$)
t_n	time interval corresponding to the n th increment of potential

z	number of charges per ion
α	transfer coefficient
η	overpotential of the electrode
η_a	activation overpotential
$\eta_{a,\infty}$	activation overpotential by $i_F = i_p$

1. Introduction

Pulse plating has received much attention in recent years [1-4]. The range of useful conditions (in particular with respect to the duration of the pulse) is limited by the charge and discharge of the electric double layer at the cathode/solution interface. The purpose of the present paper is to discuss quantitatively this effect and its role in pulse plating.

We will deal with the case of galvanostatic pulses with a period of zero current (Fig. 1). We start with a few qualitative considerations.

Any current density for metal deposition, i_F , corresponds to a certain overpotential. Therefore, at the beginning of each pulse the cathode potential must be raised to the value corresponding to this overpotential. This takes time because the electric double layer at the interface represents a capacitor of molecular dimensions and has a high capacity. Therefore, at the beginning of a pulse the total current i_p supplied by the generator consists of two parts: a capacitive current, i_C (which charges

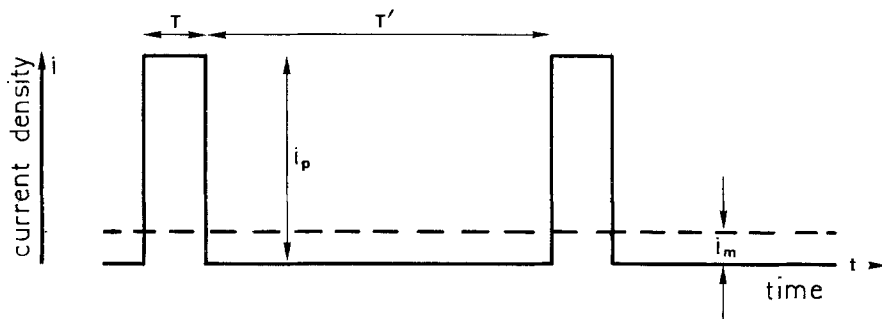


Fig. 1. Time dependence of applied current in pulse electrolysis $i_m = i_p T / (T + T')$.

the double layer), and a Faradaic current, i_F (which corresponds to the rate of metal deposition):

$$i_p = i_C + i_F = i_t \quad (1)$$

The charging time is the time before the cathode potential reaches the value corresponding to the pulse current, i.e. until i_F becomes equal to the total current supplied by the generator (Fig. 2b). If the charging time is longer than the duration of the pulse, this potential is never reached and i_F

remains smaller than i_p during the whole pulse (Fig. 2c, d).

A similar phenomenon occurs after the end of the pulse. The double layer must be discharged and it takes some time before the potential drops to the value corresponding to zero current. Therefore, it takes some time before i_F drops to zero (Fig. 2b). If this time is longer than the off time the double layer is not completely discharged and i_F never decreases to zero.

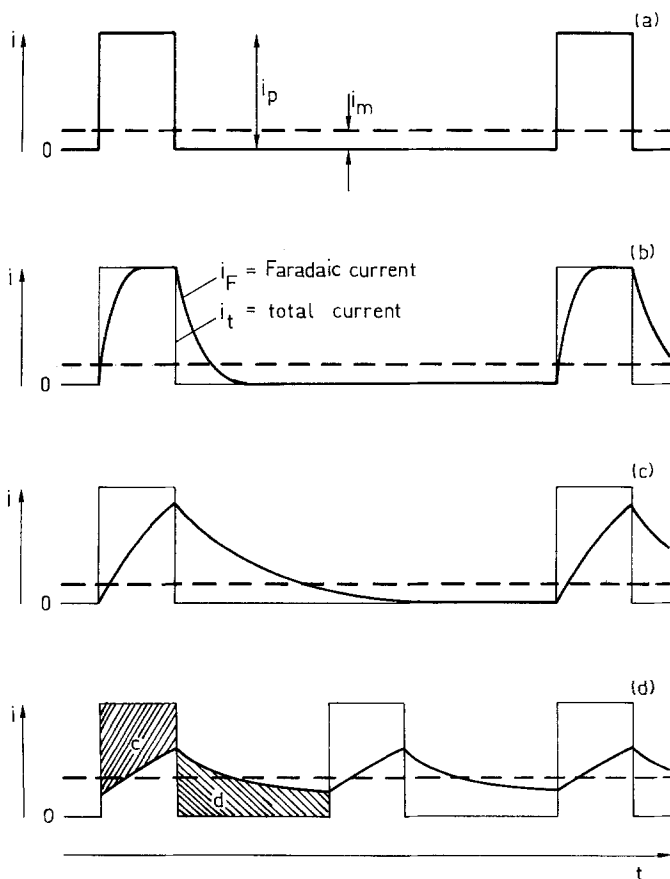


Fig. 2. Damping of Faradaic current. (a) $t_c \ll T$ no damping. (b) $t_c < T$ small damping. (c) $t_c > T$. (d) $t_c \gg T$ and $t_d \gg T'$. (c) and (d) strong damping.

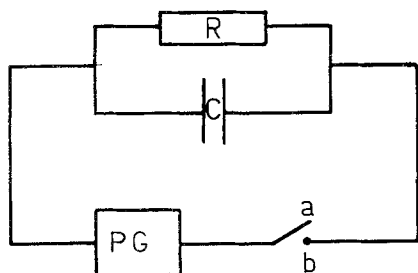


Fig. 3. Equivalent circuit of an electrode. Position a: off time, external circuit open. Position b: on time, external circuit closed. PG, pulse generator; C, condenser, R, resistance.

Qualitatively, we may thus sum up the situation as follows. If the charge and discharge time are negligibly small as compared to the duration of the pulse and the off time respectively, i_F is virtually equal to the total current supplied by the generator (Fig. 2a). Otherwise we have the cases of Fig. 2b and c: although the total current fed to the cell is a rectangular pulse, the current depositing the metal is not and is more or less damped. If the capacitive effect is strong i_F only oscillates around an average value and never drops to zero (Fig. 2d). In the following we will describe quantitatively the damping by introducing the concept of the degree of flattening and we will show under which conditions the effect can be expected to become significant in plating.

2. Calculation of charge and discharge time

2.1. Principle of computation

We will assume that the overpotential associated with the metal deposition is due to charge transfer alone and is linked with the Faradaic current through the equation

$$i_F = i_0 [\exp(\alpha z F \eta_a / RT) - \exp(-(1 - \alpha) z F \eta_a / RT)]. \quad (2)$$

This implies that there is no concentration overpotential, i.e. that the concentration of the metallic cations at the interface remains virtually the same as in the bulk of the solution during the pulse. The conditions under which this assumption is fulfilled can be calculated along the lines given in a preceding paper [5].

To visualize the system, we may represent the electrode solution interface with its double layer

by an equivalent circuit consisting of a capacitor C and a resistor R (Fig. 3). C is the capacity of the electric double layer and R is the resistance for the charge transfer at the interface; it is given by $d\eta_a/di_F$. According to this model the current supplied by the generator divides into a current flowing through the capacitor and one flowing through the resistor. It is to be noted, however, that as can be deduced from Equation 2 $d\eta_a/di_F$ and therefore R depends on i_F .

The capacitive current is given by the following equation:

$$i_C = dQ/dt = C d\eta/dt. \quad (3)$$

The total current is the sum of the Faradaic and capacitive currents

$$i_t = i_F + i_C = i_p \quad (1a)$$

as we consider a galvanostatic pulse

$$di_t = 0 \quad (4)$$

$$di_F = -di_C.$$

If we consider increments of potential sufficiently small the variation of the Faradaic current can be taken as linear in the interval considered. In the n th interval

$$i_F = \frac{1}{A_n} \eta + B \quad (5)$$

where A_n is a proportionality factor between the current and the potential in the n th interval and B is a constant,

$$A_n = \frac{\eta_n - \eta_{(n-1)}}{i_{Fn} - i_{F(n-1)}} \quad (6)$$

$$d\eta = A_n di_F. \quad (7)$$

Equations 3, 4 and 7 give:

$$i_C = -CA_n(di_C/dt) \quad (8)$$

$$t_n = C \frac{\eta_n - \eta_{(n-1)}}{i_{Fn} - i_{F(n-1)}} \ln \frac{i_{C(n-1)}}{i_{Cn}}. \quad (9)$$

Equation 9 gives the time, t_n , needed to change the potential for the n th interval.

2.1.1. Charging of the double layer.

$$i_t = i_p \quad (10)$$

$$i_F = i_p - i_C. \quad (11)$$

The charging time t_c is defined as the time elapsing before the Faradaic current i_F is 99% of i_p .[†] t_c has been calculated with a computer. It equals the sum of the times t_n (Equation 9) until the Faradaic current is 99% of i_p . For the computation the increment of potential was 1 mV. For each increment $d\eta/di$ was calculated from Equation 2. At the end of the charge, the increment of potential was decreased until the end value of i_F lies between 0.99 and 0.991 i_p .

The charging time can also be calculated in more simple ways:

(a) by assuming that the total current is capacitive as long as the double layer is not charged. This charging time is denoted by t_c^* .

$$t_c^* = \frac{C\eta_{a,\infty}}{i_p}; \quad (12)$$

(b) the charging time t_c^{**} is the time needed to increase the potential η_a up to 98.2% of $\eta_{a,\infty}$. For a resistance R and a capacity C in parallel [6]

$$t_c^{**} = 4RC, \quad (13)$$

R is given by

$$R = d\eta_a/di_F \quad (14)$$

in the Tafel region of the polarization curve:

$$i_F = i_0 e^{(\alpha z F/RT)\eta_a} \quad (15)$$

$$\frac{di_F}{d\eta_a} = \frac{\alpha z F}{RT} i_0 e^{(\alpha z F/RT)\eta_a} \quad (16)$$

$$\frac{d\eta_a}{di_F} = \frac{RT}{\alpha z F i_p} = R \quad (17)$$

where we put $\eta_a = \eta_{a,\infty}$ corresponding to $i_F = i_p$.

This calculation does not take into account the change in resistance R during the charge. With increasing i_F the activation resistance decreases down to a minimum at $i_F = i_p$ and the calculated t_c^{**} is therefore too small.

[†] In reality the Faradaic current, i_F , tends asymptotically to i_t and the charging and discharging times up to 100% are theoretically infinite. It is, therefore, necessary to define arbitrary charging and discharging times for the double layer.

2.1.2. Discharge of the double layer during the off time.

$$\begin{aligned} i_t &= 0 \\ i_F &= -i_C \end{aligned} \quad (18)$$

At the end of a pulse, when the circuit of Fig. 3 is in position a, the accumulated charge in the condenser flows through the resistance R . The discharging time, t_d , is defined as the time elapsing from $i_F = 0.999i_p$ to $i_F = 0.01i_p$. The computation for the discharge is similar to that of the charge. The increment of potential was also 1 mV. At the end of the discharge the increment of potential was decreased in order that the final i_F lay between 0.01 i_p and 0.010 i_p .

Equation 1a is to be replaced by Equation 18 and the increments of potential are subtracted instead of added.

2.2. Results

The variation of t_c , t_c^* and t_c^{**} as a function of i_p is shown in Fig. 4 for $\alpha = 0.5$, $z = 2$, $C = 50 \mu\text{F cm}^{-2}$, $i_0 = 5 \times 10^{-3} \text{ A cm}^{-2}$, which are typical values. These values correspond to those we have in a concentrated copper sulphate in sulphuric acid solution [7]. The charging time t_c^* is always smaller than t_c . This is due to the approximation in the computation of t_c^* . The total current is assumed to charge the double layer but in reality only a part of the current is capacitive during the charge. Nevertheless, for the conditions considered in the computation of Fig. 4, the simple calculation gives relatively good results, t_c^* and t_c differ only by a factor 2. This factor increases strongly for small i_p , i.e. $i_p/i_0 < 100$. The approximation for t_c^* is much better for high i_p than for small ones. For t_c^{**} it is the contrary because the hypothesis of a constant resistance R is more incorrect at the higher i_p . It is interesting to see that on the whole the simple calculations (t_c^* and t_c^{**}) give a good approximation for practical applications where we often wish only to verify the order of magnitude.

Fig. 4 is only useful for a given system. In Fig. 5 t_c and t_d are included in a dimensionless number and can be read for large ranges of i_p , α , z , i_0 and C . For $i_p/i_0 > 100$ the log-log representation of Fig. 5 shows straight lines of slope -1 . That means that the *charging time and the discharging*

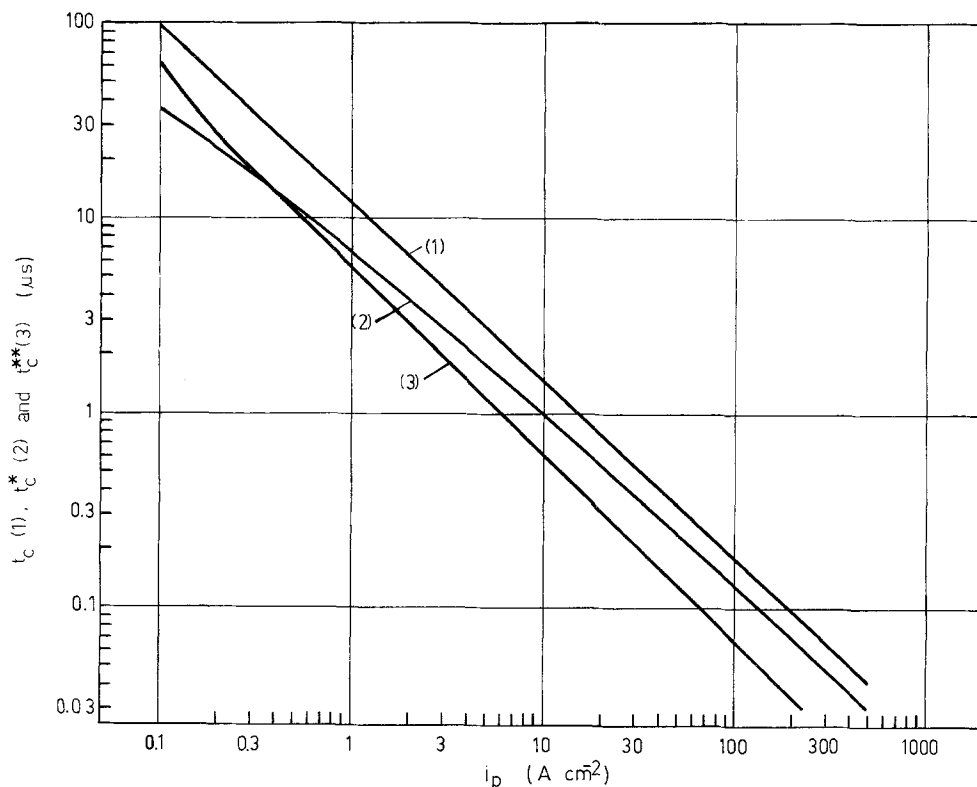


Fig. 4. Charging time of the double layer as a function of pulse current density. (1) t_c (charging until $i_F = 0.99i_p$) (Equation 9). (2) t_c^* ($i_c = i_t$ and $i_F = 0$ during the charge) (Equation 12). (3) t_c^{**} (charging until $\eta = 98.2\% \eta_\infty$ and constant R) (Equation 13). $i_o = 5 \times 10^{-3} \text{ A cm}^{-2}$, $C = 50 \mu\text{F cm}^{-2}$, $\alpha z = 1$, temp. = 298 K.

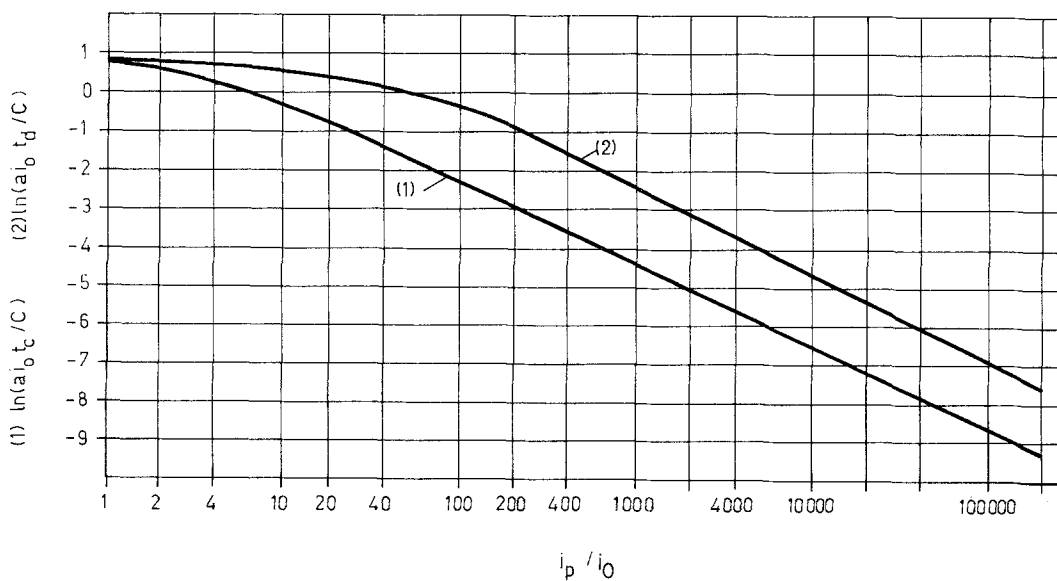


Fig. 5. Dimensionless representation of t_c and t_d as a function of the ratio i_p/i_o . $a = \alpha z F / RT$.

time are then independent of i_0 . This fact is very important because the exchange current density is often not known with any accuracy.[†] In pulse plating one tends to use instantaneous current densities much higher than in d.c. plating; therefore the linear domain of the curves of Fig. 5 is often reached. t_c and t_d can then be read without knowing i_0 precisely.

When the pulse current density is close to the exchange current density ($i_p/i_0 < 100$), the dimensionless terms on the ordinate of Fig. 5 are no longer simply inversely proportional to i_p/i_0 . t_c and t_d thus depend on i_0 which is then to be known with a reasonable accuracy. When i_p tends to i_0 , t_c and t_d tend to a common constant value. For $i_p/i_0 > 100$, the discharging time is always about seven times longer than the charging time of the double layer;

t_c and t_d are always proportional to C and temperature but inversely proportional to α and z .[‡] The values of z and temperatures are generally known and for α , 0.5 is usually a reasonable value. C has often been measured on mercury drops but only a few publications consider solid electrodes. C is related to a number of factors which are discussed in [11]. The potential of the electrode is important. On either side of the potential of zero charge (pzc), C shows different values. For the system Pt/ Na_2SO_4 1 N, at potentials more negative than the pzc, C is about $22 \mu\text{F cm}^{-2}$ whereas, positive to the pzc, C is about $7 \mu\text{F cm}^{-2}$. The surface state is also important, aluminium is easily covered by oxide layers the capacity of which is very low. On aluminium, C can vary by a factor of 10 depending on whether the electrode has been cathodically pretreated. C is sensitive to the covering of the surface by organic additives and can, therefore, be influenced by the ageing of an industrial bath because the nature and the concentration of organic additives are not constant. For the system Cu/ Na_2SO_4 1 N, the curve $C = f(E)$ goes through a sharp minimum at the pzc ($21 \mu\text{F cm}^{-2}$) and rapidly reaches

[†] For metal deposition on polycrystalline substrates, the range of possible exchange current densities is very large (a few nA cm^{-2} up to a few tens or a few hundreds of mA cm^{-2}) [8–10]. With additives, i_0 of the system Cu/ $\text{CuSO}_4/\text{H}_2\text{SO}_4$ can reach several A cm^{-2} .

[‡] The proportionality of t_c and t_d with C is rigorous. With α , z and temperature it is not, but can be accepted with good approximation.

$50 \mu\text{F cm}^{-2}$ on both sides of the minimum. These values are measured and are related to the apparent (projected) surface. In reality the surface can be 2 or 3 times larger if the roughness is taken into account [12]. C measured on a rough nickel (Ni/ H_2SO_4 1 N) is $80 \mu\text{F cm}^{-2}$ (referred to the projected area) [13]. On silver (Ag/ Na_2SO_4 1 N) we can find values which range from $45 \mu\text{F cm}^{-2}$ [11] to $100 \mu\text{F cm}^{-2}$ [14].

The range of variation of C (10 to $100 \mu\text{F cm}^{-2}$) is relatively large and is the weakest point[†] in the estimation of t_c and t_d on Fig. 5. If the C of the system used is not known and if we do not want to measure it (several methods are given in [11]), a typical value of $40\text{--}50 \mu\text{F cm}^{-2}$ can be accepted. In the linear domain of the curves of Fig. 5, t_c and t_d can then be estimated as follows

$$t_c = 17/i_p \quad (19)$$

$$t_d = 120/i_p \quad (20)$$

where t_c and t_d are measured in μs , and i_p in A cm^{-2}

$$\frac{\alpha z F}{RT} = 39.59 \text{ V}^{-1}$$

$$C = 50 \mu\text{F cm}^{-2}.$$

Equations 19 and 20 allow us to estimate the value of t_c and t_d even if we do not know anything about the system. They give the user of pulse current a rapid method of verifying if T and T' are reasonably chosen for the applied i_p . C and i_0 have to be known precisely when accurate values of t_c and t_d are required but in most technical applications the order of magnitude is sufficient. Often we only need to verify if the order of magnitude of t_c and t_d is such that the pulse is not appreciably disturbed.

It is to be noted that in the foregoing calculation of t_c , t_c^* , t_c^{**} and t_d the actual length of the pulse and of the off time were ignored, i.e. it was assumed that T and T' are large enough for i_F to reach the value of i_t (situation of Fig. 2b). As we have already seen qualitatively, this is not always the case (Fig. 2c and d). In case d the overpotentials corresponding to $i_F = i_t$ and $i_F = 0$ are never reached and the upper and lower limits in

[†] Although the range of possible values of i_0 is much larger than that of C , the imprecision in the calculation of t_c and t_d is more affected by C than by i_0 because when $i_p \gg i_0$, t_c and t_d are no longer dependent on i_0 .

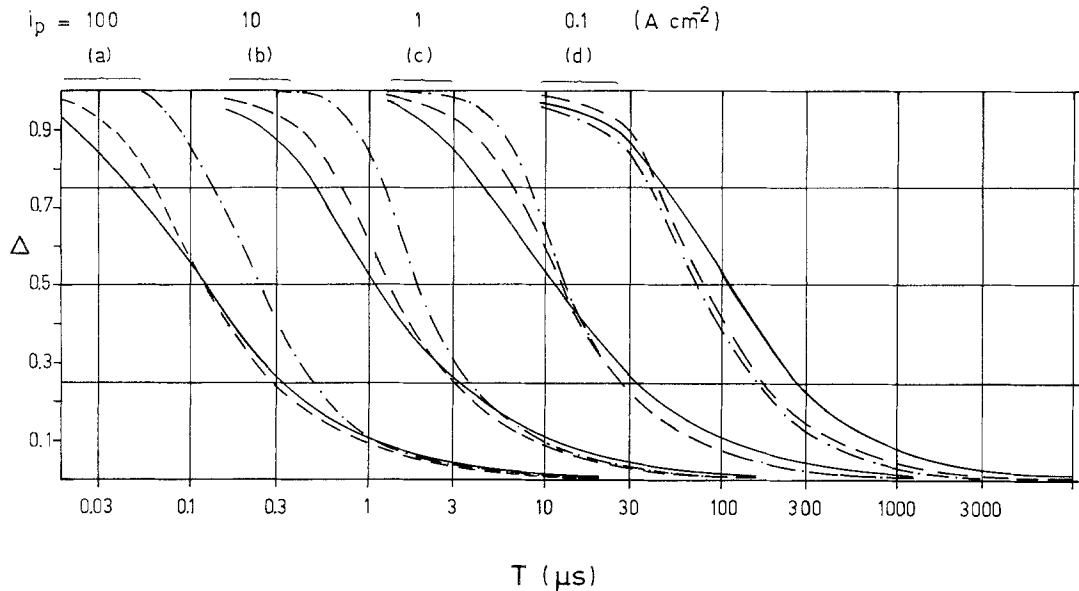


Fig. 6. Degree of flattening Δ of the Faradaic current as a function of i_p , T'/T and T . — $T'/T = 1$. --- $T'/T = 10$. - · - · - $T'/T = 1000$. $i_o = 5 \times 10^{-3} \text{ A cm}^{-2}$, $C = 50 \mu\text{F cm}^{-2}$, $\alpha z = 1$, temp. = 298 K.

the integration of Equation 9 are no longer given by i_p alone but depend on T and T' . This complicates the problem mathematically. This is discussed in the next section.

3. Degree of flattening of the Faradaic current

In the case of Fig. 2c and d the current for depositing metal is strongly damped and, in particular, in the case of Fig. 2d, one approaches d.c. conditions. One cannot then expect the usual advantage of employing a pulsed current since one has, in fact, a metal deposition process which is more or less d.c. To describe quantitatively the degree of approach to d.c. (or of departure from the original rectangular pulse) we introduce the concept of the degree of flattening defined as

$$\Delta = \frac{\int_T^{T'} i_F dt}{i_m T'} = \frac{i_p T - \int_0^T i_F dt}{i_m T'} \quad (21)$$

The degree of flattening varies between 0 and 1. The numerator represents the amount of metal deposited during the off time which is zero when the pulse is not disturbed. The denominator represents the amount of metal which would be deposited if a current equal to the average value

i_m were flowing during the interval between two pulses.

The degree of flattening Δ has been computed as follows: with Equations 9 and 1a, by incrementing the potential, we compute the sum of $i_F dt$ until the sum of dt equals T but is smaller than $1.001 T$ or until i_F equals i_p . An analogous computation is made during the off time. We start with the i_F reached at T and sum the $i_F dt$, in-

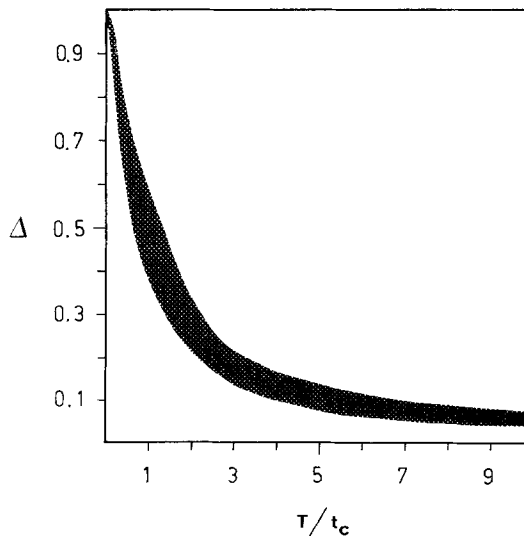


Fig. 7. Degree of flattening Δ of the Faradaic current as a function of T/t_c (approximation).

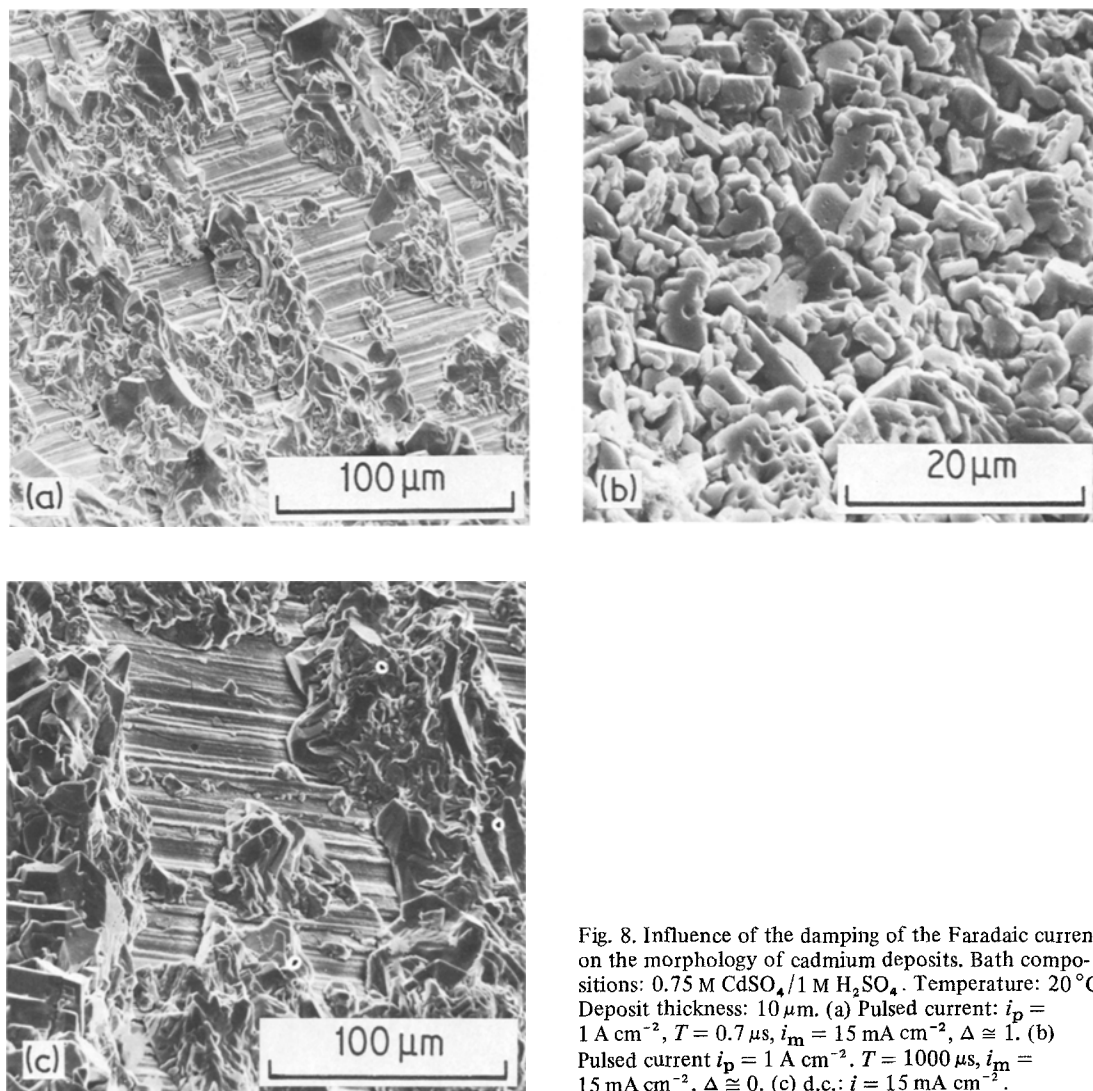


Fig. 8. Influence of the damping of the Faradaic current on the morphology of cadmium deposits. Bath compositions: 0.75 M CdSO_4 /1 M H_2SO_4 . Temperature: 20 °C. Deposit thickness: 10 μm . (a) Pulsed current: $i_p = 1 \text{ A cm}^{-2}$, $T = 0.7 \mu\text{s}$, $i_m = 15 \text{ mA cm}^{-2}$, $\Delta \cong 1$. (b) Pulsed current $i_p = 1 \text{ A cm}^{-2}$. $T = 1000 \mu\text{s}$, $i_m = 15 \text{ mA cm}^{-2}$, $\Delta \cong 0$. (c) d.c.: $i = 15 \text{ mA cm}^{-2}$.

crement by increment, until the sum of dt equals T' but is smaller than $1.01T'$ or until i_F equals 0. The increments of potential were 1 mV but they have been adjusted towards the end of T and T' in order to satisfy the above-mentioned limiting conditions. The potential at the beginning of the pulse has been adjusted in order that the surface c representing the capacitive part of the pulse equals the surface d (cf. Fig. 2d) representing the Faradaic current during the discharge of the double layer.

In Fig. 6 we show the degree of flattening, Δ , as function of the pulse length, There are four groups of curves, each group corresponds to a given i_p

and each curve in a group corresponds to a given ratio T'/T . This computation has been made for a given system where $i_o = 5 \times 10^{-3} \text{ A cm}^{-2}$, $RT/(\alpha z F) = 0.026 \text{ V}$ and $C = 50 \mu\text{F cm}^{-2}$. When T decreases from $10t_c$ to t_c , Δ increases more and more rapidly up to a value between 0.4 and 0.6 at $T = t_c$. At $T = 0.1t_c$ Δ lies between 0.9 and 1 depending on T'/T' .

In a group of curves (i_p constant) the values of Δ do not depend much on the ratio T'/T when $T > t_c$ which is precisely the interesting range when the damping of the Faradaic current is to be avoided. For higher Δ the influence of the ratio T'/T is stronger.

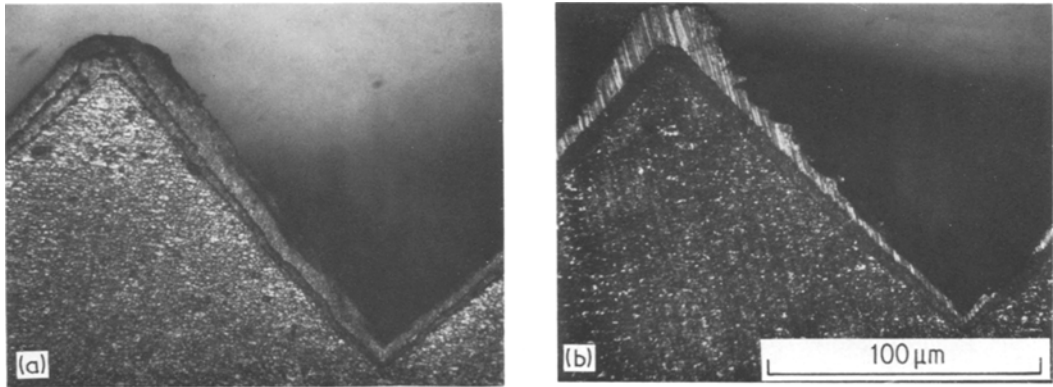
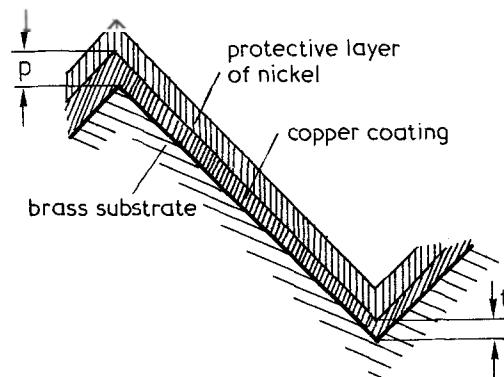


Fig. 9. Current distribution on a sawtooth surface. Bath: 0.5 M CuSO₄, 25° C. (a) d.c.: $i = 33 \text{ mA cm}^{-2}$; $p/t = 4.2$. (b) Pulsed current: $i_p = 100 \text{ mA cm}^{-2}$, $T = 0.2 \mu\text{s}$, $i_m = 33 \text{ mA cm}^{-2}$, $\Delta \cong 1$, $p/t = 2.5$.



For the groups a, b and c ($i_p = 100, 10$ and 1 A cm^{-2}) i_o has no influence on Δ which can then be read for different systems under the condition that $RT/(\alpha zF) = 0.026 \text{ V}$ and $C = 50 \mu\text{F cm}^{-2}$.

The representation of Fig. 7 ($\Delta = f(T/t_c)$) is dimensionless. It has the advantage of being valid not only for different i_o but also for different C and $a \cdot t_c$ is, however, to be known. It can be either computed by the method presented in Section 2 or estimated by Equation 19.

4. Influence of the damping of the Faradaic current

As shown in a previous paper [5] the damping of the Faradaic current does not decrease the current efficiency for the metal deposition because the charges accumulated during the pulse are recuperated during the off time. This constitutes the fundamental hypothesis for our computation of Δ and was checked experimentally (Table 2 of [5]). It has also been pointed out by Baraboshkin and Isaev [15].

The nucleation and the relative speed of two simultaneous reactions are strongly influenced by the damping of the Faradaic current. These two phenomena are related to the instantaneous overpotential of the electrode and, therefore, to the shape of the Faradaic response. For $\Delta \cong 0$, $\eta_a(t)$ always equals $\eta_{a,\infty}$ whereas for $\Delta \cong 1$, $\eta_a(t) = \eta_a$ corresponding to $i_F = i_m$. The influence of Δ on the nucleation is illustrated by Fig. 8. Three scanning electron micrographs of cadmium deposits are shown obtained (a) by pulsed current with a Δ near 1, (b) by a pulsed current with a Δ near 0, and (c) by d.c. (c) shows the same morphology as (a), whereas when $\Delta \cong 0$ the grain is much smaller and the substrate is well covered, which corresponds to what is expected in pulsed current deposition [16].

The damping of the Faradaic current can have an influence on the current distribution for the following reason. When the Faradaic current is flowing between the anode and the cathode, the excrescences have a larger current density than the recesses because of the additional ohmic drop in

the solution for the latter. However, when the external current is switched off there is no ohmic drop in the solution although there is still a Faradaic current due to the discharge of the double layer. For a homogeneous distribution of charges it is then expected that the Faradaic current from the discharge of the double layer is uniform over the surface and therefore the current distribution will be improved by pulsed current when Δ tends toward 1. In reality the charges are not uniformly distributed along the profile of the electrode at the end of the pulse but an improvement of the current distribution may still result because the above non-uniformity of charge distribution will tend to equalize during the off time and the process may be faster than the charge transfer through the electrode. Each system will behave differently and the characteristic length of excrescences will also be determinant. For example, for copper deposition from a copper sulphate bath (Fig. 9), with a Δ near 1, the current distribution in pulsed current is better than in d.c. [17] whereas for small Δ , which is the most common situation in pulsed current, the secondary current distribution is expected to be less uniform than in d.c. (see [17]).

5. Discussion

The computations presented in this paper allow a decision as to whether T and T' have been chosen reasonably according to the limitations caused by the charge and discharge of the double layer. For a precise computation, the parameters i_0 , C , α , z and temperature have to be known. Even if these

parameters are not known, simpler relationships allow an estimate of the order of magnitude of t_c , t_d and Δ . The simple relationships 19 and 20 allow a rapid estimation of t_c and t_d . One need not measure the above parameters but can nevertheless set the pulse parameters without serious disturbances by capacitive effects.

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