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Stepwise decreasing current modes. I. Electrodeposition of metals from a bath with insoluble anode and limited volume of solution

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A model of the stepwise decreasing current mode of electrodeposition of metals has been developed and checked with experiments. The electrodeposition of copper has been used for this purpose. It has been shown that the deposition time in the stepwise decreasing current mode, for sufficiently high step number, becomes close to that in potentiostatic deposition.

Nomenclature

C	concentration
C_0	initial concentration
D	diffusion coefficient
F	Faraday constant
i	integer
I	current
I_0	initial limiting diffusion current
k	integer
m	number
n	number
Q	quantity of electricity
S	electrode surface area
t	time
t_k^*	deposition time for k current steps
t^*	$\lim_{k\to\infty} t_k^*$
t_m	deposition time required to decrease concentration from $(m + 0.1)C_0$ to mC_0 by $I = mI_0$
t_n	deposition time required to decrease concentration from C_0 to nC_0 by $I = nI_0$
U	cell voltage
V	volume of solution
z	number of electrons
δ	thickness of the diffusion layer
τ	defined by Equation 3

1. Introduction

In the electrowinning of metals and in the charging of some chemical power sources the concentration of reacting species decreases with time. In these cases a maximum reaction rate occurs at overpotentials which correspond to the diffusion limiting current density plateau under potentiostatic conditions. Potentiostatic electrolysis is easily performed in laboratory size cells, but difficulties arise on a practical scale because of the need for a high power potentiostat, as well as difficulties in the measurement of potentials in closed systems. On the other hand, potentiostatic deposition of metals at limiting current produces rough and powdered deposits [1]. It was shown recently [2, 3] that electrodeposition of metals from a bath with insoluble anode and limited volume of solution can be considerably accelerated using galvanostatic stepwise decreasing current deposition without negative effects on the quality of deposit.

The purpose of this work is to present an analysis of this method of metal electrodeposition.

2. The statement of the problem

Maximum deposition rate is obtained by operating at potentials corresponding to limiting current at all concentrations of reacting species. The limiting diffusion current under diffusion control [4] varies with time according to

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) \qquad (1)$$

and concentration of metal ion according to

$$C = C_0 \exp\left(-\frac{t}{\tau}\right) \qquad (2)$$

where

$$\tau = \frac{\delta V}{SD} \qquad (3)$$

The concentration of metal ion in solution can be decreased to the desired value by choosing a corresponding deposition time.

During galvanostatic deposition the change of

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concentration is given by [2, 3]

$$C = C_0 - \frac{It}{zFD} \tag{4}$$

and the largest current which can reduce the concentration from C_0 to nC_0 with current efficiency 1, is obviously nI_0, where $n < 1$. After the concentration nC_0 is reached, the deposition current, nI_0, becomes limiting and further deposition produces dendrites after an induction time equal to the corresponding transition time [5, 6]. Taking into account, to the first approximation, that

$$I_0 = \frac{SzFDC_0}{\delta} \tag{5}$$

and substituting nC_0 and nI_0 in Equation 4 one obtains the time required for the concentration change from C_0 to nC_0 in the galvanostatic regime as

$$t_n = \frac{1-n}{n}\tau \tag{6}$$

assuming that D and δ do not change significantly with decrease of the concentration. For example, if $n = 0.1$

$$t_{0.1} = 9\tau \tag{7}$$

Obviously, the same decrease of concentration can be realized by arbitrarily chosen stepwise decrease of current if the last deposition current is $0.1I_0$. The initial current may be $0.9I_0$ and the difference between current steps $0.1I_0$. Deposition times for each current can be calculated from the equation [2]

$$mC_0 = (m + 0.1)C_0 - \frac{mSDC_0}{\delta V} t_m \tag{8}$$

as

$$t_m = \frac{0.1}{m}\tau \tag{9}$$

where $m = 0.1, 0.2, \ldots, 0.9$. The time required to decrease concentration to $0.1C_0$ by this regime is then given by

$$t = \sum_{0.1}^{0.9} \frac{0.1}{m}\tau \approx 2.8\tau \tag{10}$$

It is easy to show, using Equation 2, that the same concentration decrease in potentiostatic deposition will be obtained after

$$t = 2.3\tau \tag{11}$$

Hence, the same final concentration can be obtained by the stepwise and constant current modes, but the former gives a three times shorter deposition time, similar to potentiostatic deposition. At the same time, dendritic growth [7] in the stepwise decreasing current mode is avoided if, at the moment when the overpotential reaches the value corresponding to the transition time for the starting current $0.9I_0$, the current is reduced to the next step $0.8I_0$ and so on. The optimization of the stepwise decreasing current mode in respect of deposition time can be performed as follows.

It is obvious that for the iniital current $I_1 (I_1 < I_0)$ the deposition time according to Equation 6 is

$$t_1 = \frac{I_0 - I_1}{I_1}\tau \tag{12}$$

if

$$n = \frac{I_1}{I_0} \tag{13}$$

the corresponding quantity of electricity is given by

$$Q_1 = I_1 t_1 = (I_0 - I_1)\tau \tag{14}$$

For the second current step $I_2 < I_1$, the quantity of electricity is given by

$$Q_2 = I_2 t_2 = (I_1 - I_2)\tau \tag{15}$$

and deposition time for the two current steps is then given by

$$t_2^* = t_1 + t_2 = \frac{I_0 - I_1}{I_1}\tau + \frac{I_1 - I_2}{I_2}\tau \tag{16}$$

From the condition $\partial t_2^*/\partial I_1 = 0$ one obtains

$$I_2 = I_1 \frac{I_1}{I_0} \tag{17}$$

as the current providing minimum deposition time for the first two steps.

Substitution of I_2 from Equation 17 into Equation 16 gives

$$t_2^* = 2\left(\frac{I_0}{I_1} - 1\right)\tau \tag{18}$$

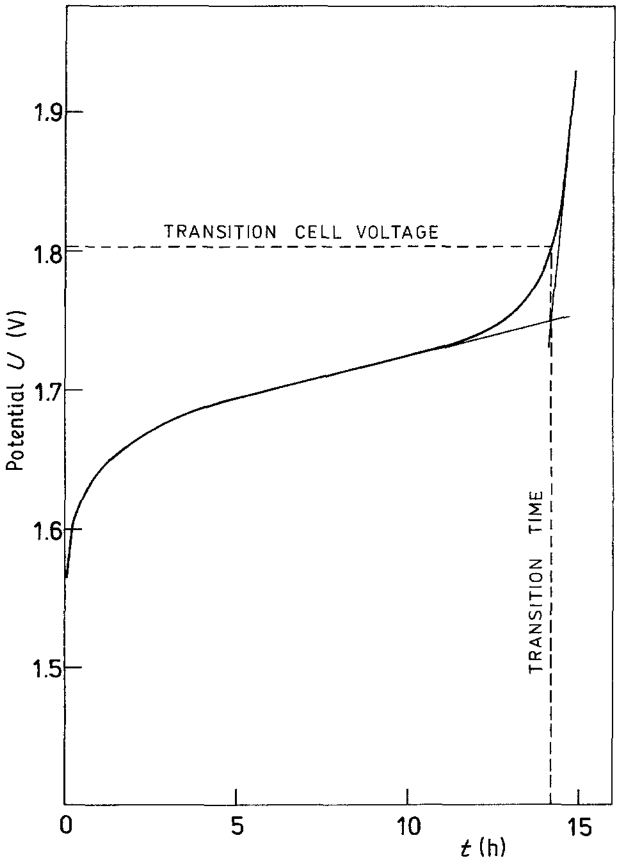


Fig. 1. Cell potential as a function of deposition time for $I = 0.1I_0$.

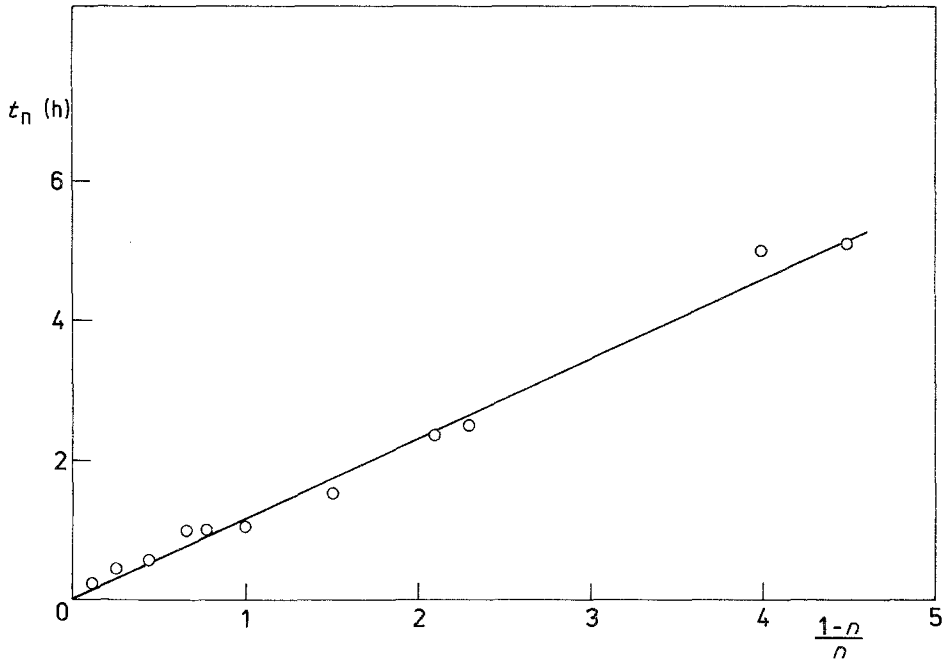


Fig. 2. t_n as a function of $(1 - n)/n$, for $\tau = 66\,\text{min}$.

meaning that

$$t_2 = \left(\frac{I_0}{I_1} - 1\right)\tau = t_1 \tag{19}$$

In the same way

$$t_3^* = t_2^* + t_3 = 2\left(\frac{I_0}{I_1} - 1\right)\tau + \frac{\frac{I_1^2}{I_0} - I_3}{I_3}\tau \tag{20}$$

and from $\partial t_3^*/\partial I_1 = 0$

$$I_3 = I_1\left(\frac{I_1}{I_0}\right)^2 \tag{21}$$

Obviously,

$$t_3^* = 3\left(\frac{I_0}{I_1} - 1\right)\tau \tag{22}$$

and

$$t_3 = t_2 = t_1 = \left(\frac{I_0}{I_1} - 1\right)\tau \tag{23}$$

It is easy to show that for the kth step

$$I_k = I_1\left(\frac{I_1}{I_0}\right)^{k-1} \tag{24}$$

and

$$t_k^* = k\left(\frac{I_0}{I_1} - 1\right)\tau \tag{25}$$

as well as

$$t_1 = t_2 = \ldots = t_k \tag{25a}$$

It follows from Equation 24 that

$$\frac{I_0}{I_1} = \left(\frac{I_0}{I_k}\right)^{1/k} \tag{26}$$

and substitution of I_0/I_1 from Equation 26 into Equation 25 gives

$$t_k^* = k\left[\left(\frac{I_0}{I_k}\right)^{1/k} - 1\right]\tau \tag{27}$$

or

$$\frac{I_0}{I_k} = \left(1 + \frac{t_k^*}{k\tau}\right)^k \tag{28}$$

and

$$\lim_{k\to\infty}\left(1 + \frac{t_k^*}{k\tau}\right)^k = \exp\,(t^*/\tau) \tag{29}$$

It follows from Equation 29 and Equation 28 that

$$I = I_0 \exp\,(-t^*/\tau) \tag{30}$$

meaning that for $k \to \infty$, Equation 30 becomes the same as Equation 1 for $t = t^*$. Hence, with sufficiently high k, the stepwise decreasing mode becomes similar to the potentiostatic mode.

The last current step determines the final concentration of the solution, and it is convenient to relate the currents of each step to the final one. It follows from Equation 24 that

$$I_1 = I_0\left(\frac{I_k}{I_0}\right)^{1/k} \tag{31}$$

I_2 is, according to Equations 17 and 31

$$I_2 = I_0\left(\frac{I_k}{I_0}\right)^{2/k} \tag{32}$$

and for the ith current step

$$I_i = I_0\left(\frac{I_k}{I_0}\right)^{i/k} \tag{33}$$

Hence, the stepwise decreasing current mode, requiring minimum deposition time (see Equation 25) for given k and given I_k/I_0 ratio can be obtained using Equation 33.

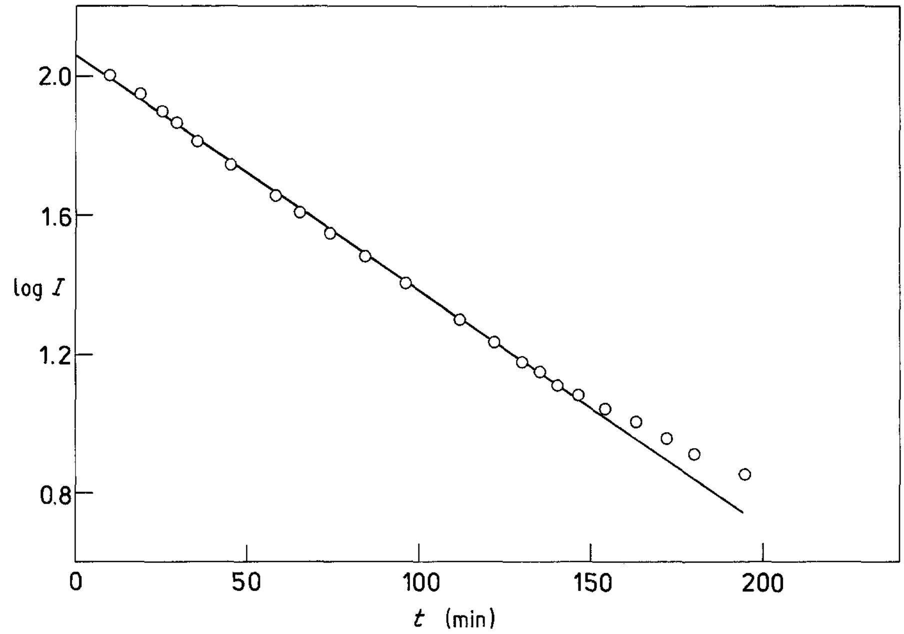


Fig. 3. log I as a function of deposition time in potentiostatic deposition, for I_0 = 120 mA and τ = 65 min.

In this case, the corresponding quantity of electricity is given by

$$Q = \sum_{i=1}^{k} I_i t_i = \tau \sum_{i=1}^{k} (I_{i-1} - I_i) = \tau(I_0 - I_k) \quad (34)$$

because of

$$t_i = \frac{I_{i-1} - I_i}{I_i} \tau \quad (35)$$

or

$$Q = Q_0 \left(1 - \frac{I_k}{I_0}\right) \quad (36)$$

where $Q_0 = I_0 \tau$. This means that the last current step determines the overall quantity of electricity used.

3. Experimental details

Copper was deposited onto a cylindrical copper electrode (surface area 20.4 cm^2) from a solution containing 0.1 mol dm^{-3} $CuSO_4$ and 0.5 mol dm^{-3} H_2SO_4 in an open cell (volume of solution 20.0 cm^3) at room temperature (22 ± 1° C). The counter electrode was made of platinum, and a reference electrode of copper was used in potentiostatic measurements. Deposition was carried out potentiostatically and galvanostatically in constant and stepwise decreasing current modes. The potential difference between the anode and the cathode was recorded. The galvanostatic experiments were carried out in two steps. Firstly, potential–time dependences for constant currents were established. This yielded the transition time and the corresponding potential. Secondly deposition was carried out using a stepwise decreasing current mode. At the moment when the potential reached the value corresponding to the transition time for the starting current the current was reduced to the next step and so on. All deposition currents were defined as fractions of limiting diffusion current.

4. Results and discussion

From polarization curves for Cu deposition, using $D = 0.67 \times 10^{-5}$ cm^2 s^{-1} it was possible to determine $\delta = 2.3 \times 10^{-2}$ cm and τ of 56 min. In Fig. 1 the potential–time relationship for $I = 0.1 I_0$ is shown. Transition times and transition cell potentials for all currents used were extracted from the plots similar to Fig. 1.

In Fig. 2 the dependence of t_n as a function of $(1 - n)/n$ is given, and τ = 66 min is determined from the slope which is in good agreement with the calculated value.

In Fig. 3 the log I–t dependence for potentiostatic deposition at 260 mV is given. The linear dependence shows that correct approximations are used up to 120 min of deposition. The value of τ, extracted from Fig. 3, is 65 min, which is in good agreement with the earlier determined value. The current densities at higher deposition times are somewhat larger than expected, probably because of reduction of dissolved oxygen and increased electrode surface roughness which leads to the increase of apparent current density in potentiostatic deposition.

On the basis of the known transition potential for each current it was possible to create stepwise decreasing current modes as shown in Fig. 4 for $k = 2$ and in Fig. 5 for $k = 4$. It is seen that the stepwise decreasing current mode, with the best current step mode calculated using Equation 33, exhibit minimum deposition time required to obtain a final concentration of $0.1 C_0$. It is also seen that the duration of the current steps in the best modes are closer to each other than in arbitrarily chosen modes, as predicted by Equation 35. The stepwise decreasing current modes with the best step differences for k = 3, 5 and 6 are

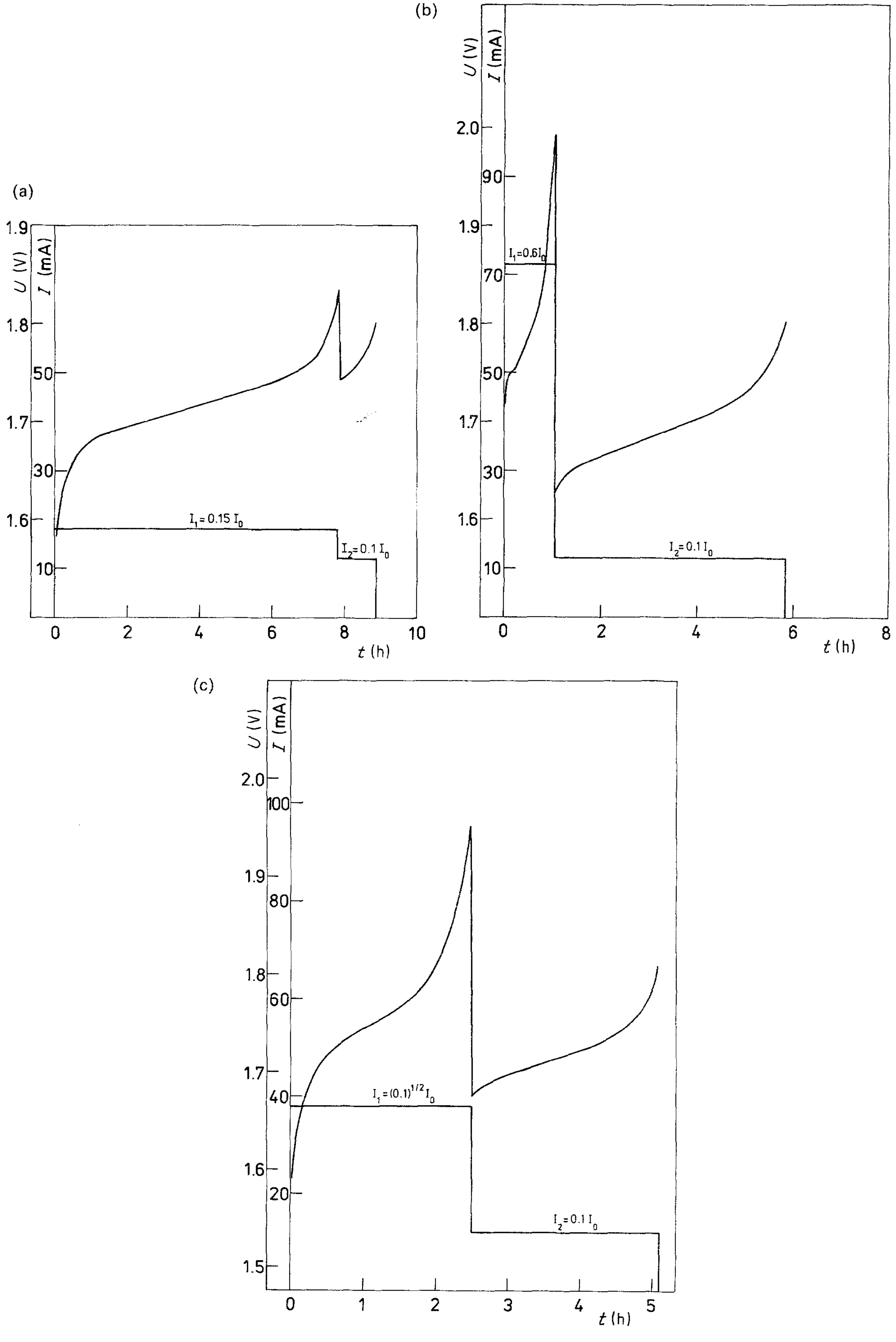
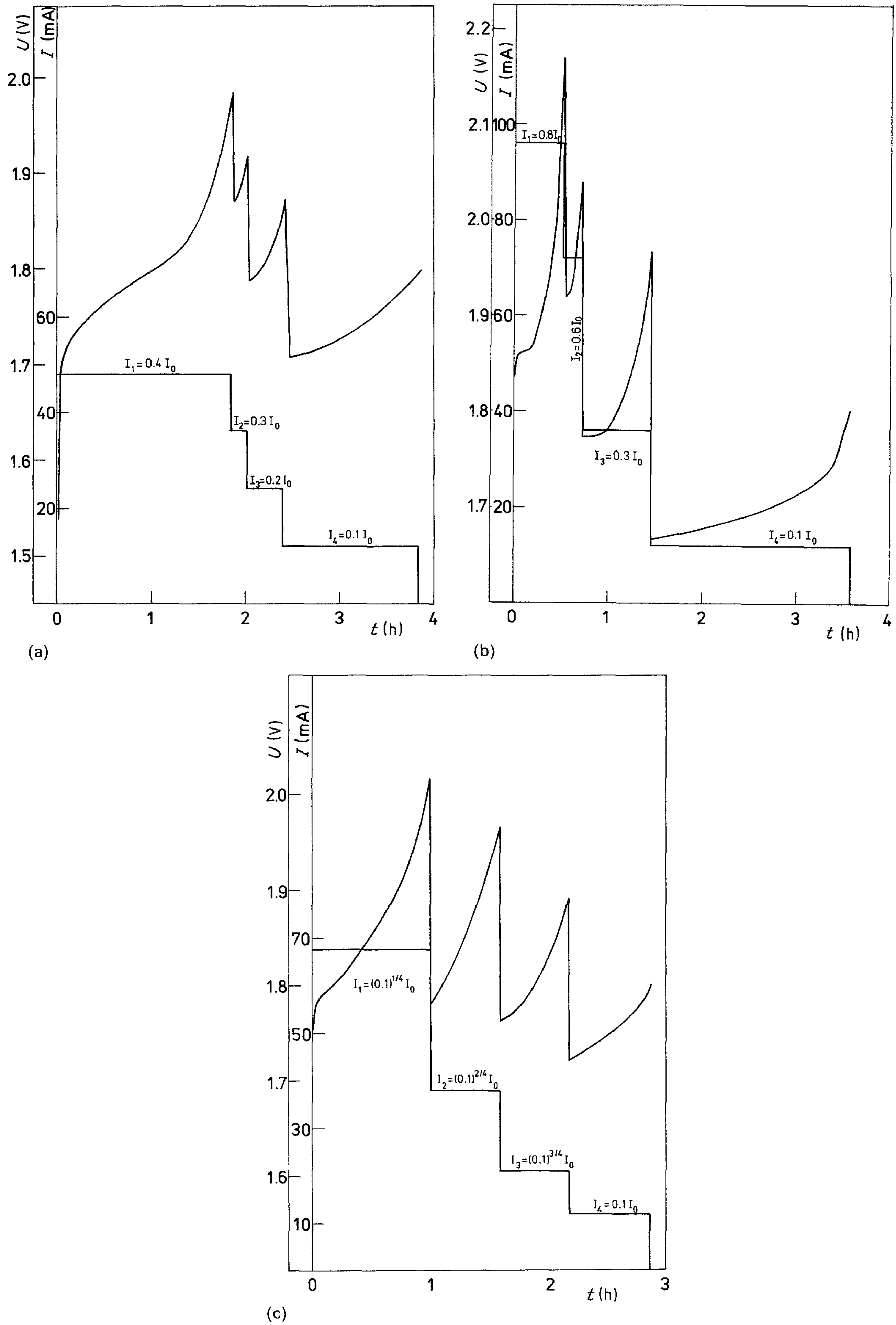


Fig. 4. Stepwise decreasing current modes for $k = 2$. (a, b) Arbitrary chosen modes; (c) the best stepwise decreasing mode.



(a) (b)

(c)

Fig. 5. The same as in Fig. 4, but for $k = 4$.

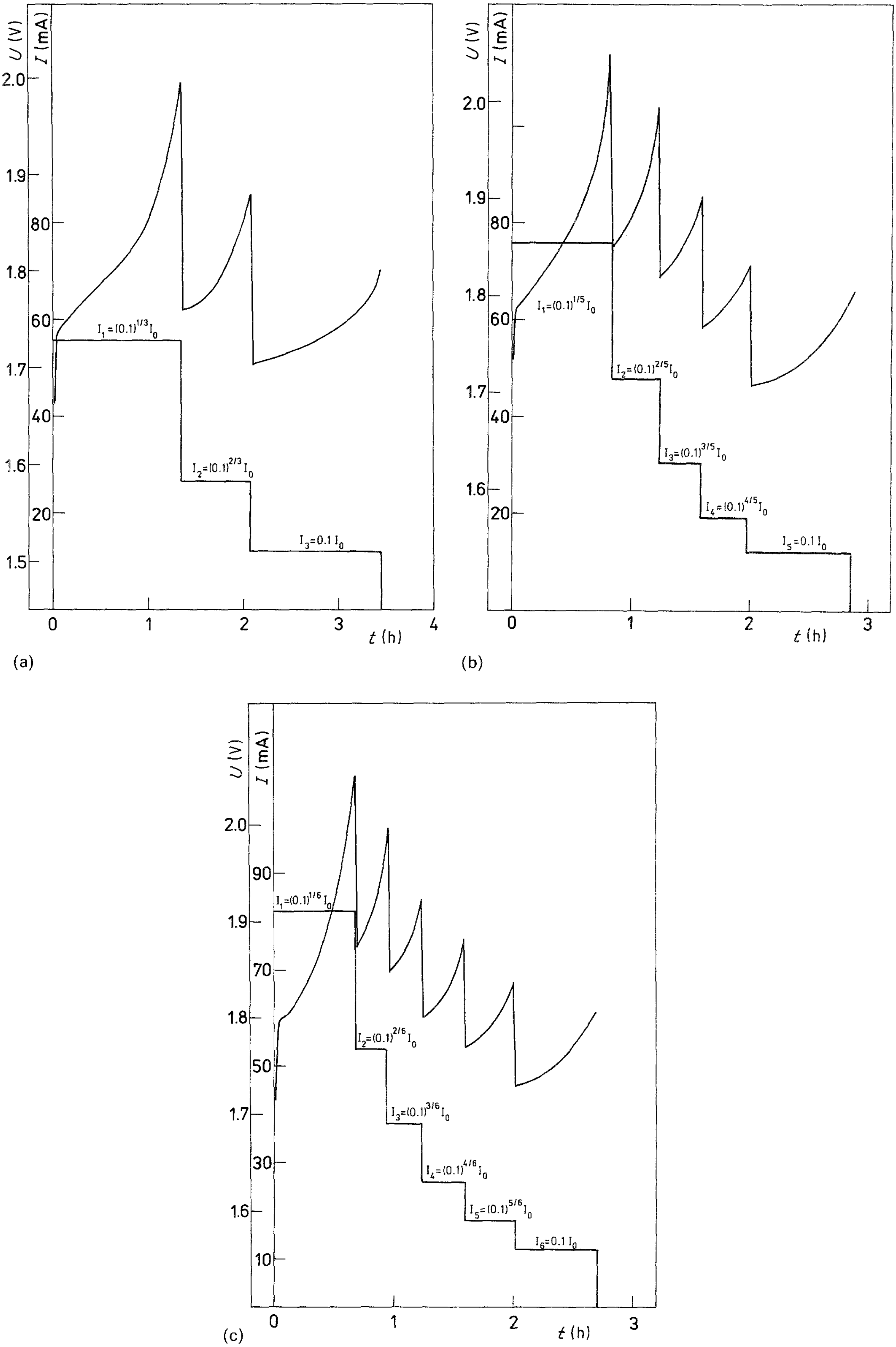


Fig. 6. The best stepwise decreasing current modes. (a) $k = 3$; (b) $k = 5$; (c) $k = 6$.

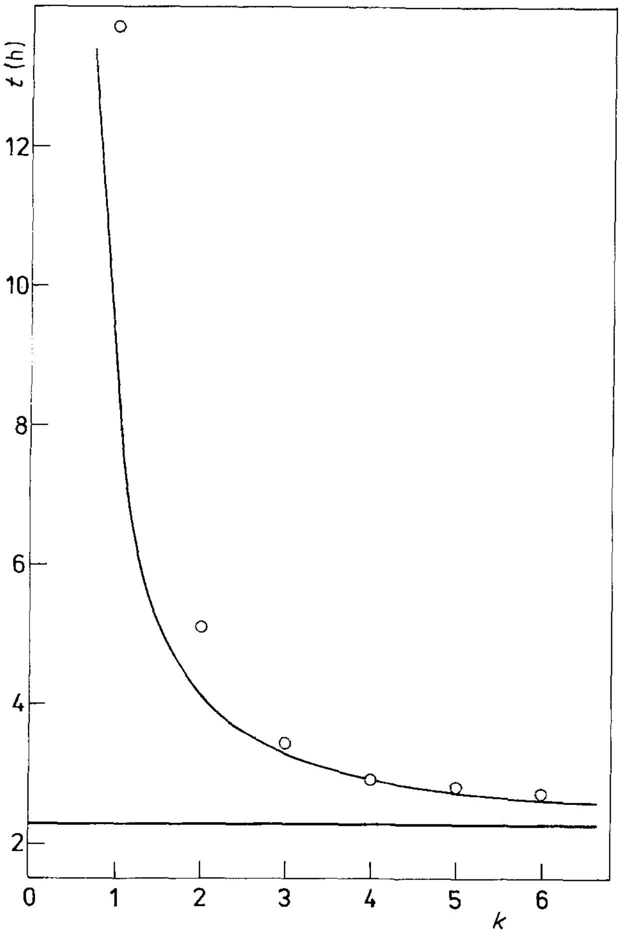


Fig. 7. The best stepwise decreasing current modes deposition time as a function of number of current steps.

shown in Fig. 6. As expected, the deposition time required to obtain a final concentration $0.1C_0$ decreases with increased number of current steps.

Deposition times extracted from Figs 4c, 5c and 6c as a function of k are shown in Fig. 7. The full line represents the dependence calculated from Equation 27 (for $t = t_k^*$) and the points are the experimental values. A stepwise decreasing current mode with six current steps is a good approximation to potentiostatic deposition with respect to deposition time. Dendritic growth in such conditions is avoided, as discussed earlier. Constant voltage electrolysis is a better approximation of potentiostatic deposition with respect to electrolysis time, but dendritic growth in such a situation is possible. The specific energy consumption at constant current efficiency depends only on cell voltage. Both potentiostatic and constant voltage electrolysis are obviously less suitable than the stepwise decreasing current modes from this point of view.

It seems, however, that the analysis of such modes is more important for application in the fast charging of storage batteries than in metal electrowinning It was shown recently [8–11] that the charging time of some storage batteries can be considerably decreased by using stepwise decreasing current modes. This paper explains the beneficial effects of such modes if diffusion in the solution is the charging rate determining step. Other aspects, such as rate control by the diffusion through the layer of reaction products, will be the object of further investigations.

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