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The comparison of galvanostatic and potentiostatic copper powder deposition on platinum and aluminium electrodes

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Experiments have been carried out on copper powder electrodeposition by constant overpotential and constant current on aluminium, graphite, platinum and copper electrodes. It is shown that for one and the same quantity of electricity, electrode material, electrode surface area, electrolyte, temperature and time of deposition, different particle size distribution curves, current efficiency and specific energy consumption are obtained in galvanostatic and potentiostatic deposition.

1. Introduction

It is well known that copper powder is the most important electrolytically deposited metal powder. A detailed survey of copper powder deposition, properties of electrolytic powders and the relationships between powder formation and mass transfer processes was given by Ibl for galvanostatic copper powder deposition [1].

In recent times, the qualitative discussion of the effect of conditions of electrolysis on the morphology and particle size distribution of copper powders deposited potentiostatically [2, 3] was performed on the basis of theories of dendritic growth initiation and dendritic growth [4–7].

The purpose of this work was to discuss the properties of galvanostatically deposited copper powders in a similar way and to compare galvanostatic and potentiostatic copper powder electrodeposition.

2. Experimental

The deposition was carried out from 0·1 M$CuSO_4$ in 0·5 M H_2SO_4 using a constant overpotential and constant current on platinum, aluminium, graphite and copper wire electrodes. In all cases the electrode surface area was 0·63 cm^2. Copper was deposited at overpotentials of 600, 700 and 800 mV. The constant currents in galvanostatic deposition were the average values of current during potentiostatic deposition.

The experimental set-up was the same as the one previously reported [8]. A Wenking potentiostat was used as a galvanostat in the galvanostatic experiments. In some experiments the quantity of hydrogen evolved was measured in order to determine the current efficiency of the process. In these experiments the working electrode was placed in a glass tube. The temperature of the electrolyte was 25 ± 0·1° C and room temperature was 25 ± 1·0° C.

The powder was removed by tapping the electrodes, then washed with distilled water and alcohol and dried in air. The microphotographs of powder particles were made under magnifications of × 110, × 100 and × 50, depending of the size of the particles. The particle size distribution curves were plotted on the basis of effective diameters calculated for 1000 different particles in each case. All copper powders obtained corresponded to a quantity of electricity of 100 mA h.

3. Results and discussion

The current–time relationships for copper powder deposition on platinum and aluminium electrodes at different overpotentials are presented in Figs. 1 and 2. The overpotential–time relationships for galvanostatic deposition on the same electrodes are presented in Figs. 3 and 4. Similar plots were obtained for deposition on graphite and copper electrodes. The current increases with time in potentiostatic deposition because the real current

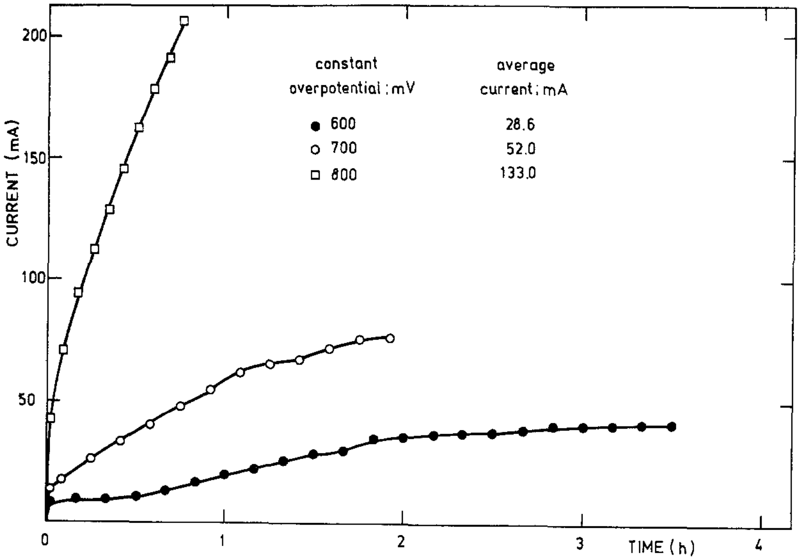

Fig. 1. Current–time relationships for copper powder deposition at different constant overpotentials on platinum electrodes.

density remains constant, while the electrode surface area increases with time [6, 9]. The overpotential during galvanostatic deposition decreases, because the surface of electrode increases with time [10] and real current density decreases. The particle size distribution curves for potentiostatic and galvanostatic copper powder deposition on platinum are presented in Figs. 5 and 6.

The same distribution curve for aluminium is shown in Figs. 7 and 8. It is seen from Figs. 5 and 7 that an increase of overpotential leads to the formation of smaller particles and to narrower particle size distribution curves. This is in accordance with results reported earlier [2, 3]. Particle size distribution curves for deposition at 800 mV on platinum and on aluminium are practically the same. This is probably due to the remarkable hydrogen evolution in these experiments, because the current density at 800 mV is larger than the

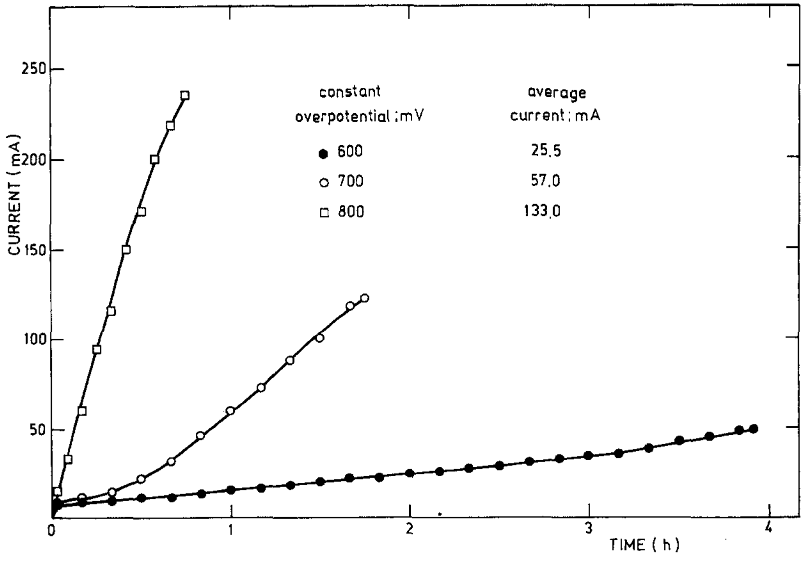

Fig. 2. The same as in Fig. 1 for aluminium electrodes.

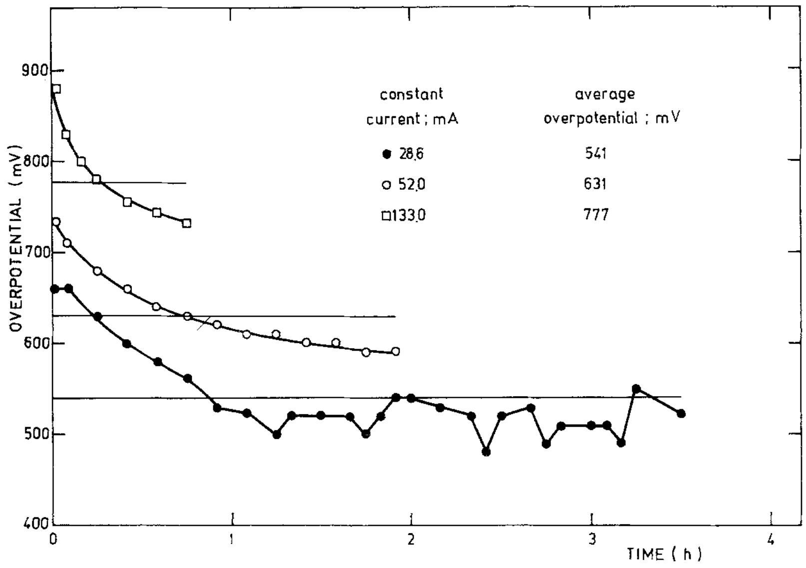

Fig. 3. Overpotential–time relationships for copper powder deposition at different constant currents on platinum electrodes.

limiting diffusion current density of copper ion in this system. This is seen from Fig. 9. At lower overpotentials, smaller particles and narrower distribution curves are obtained for the deposition on a platinum electrode than on an aluminium one. It is known that aluminium is covered with a relatively thick oxide film. Because of this, the electrode–solution interface differs from that on platinum, having an enlarged ohmic resistance. Deposits obtained on aluminium electrodes correspond to deposits obtained on platinum electrodes at lower overpotentials. The particle size distribution curves presented in Figs. 6 and 8 can be discussed in a similar way. Larger particles and less narrow distribution curves are obtained with galvanostatic deposition on platinum, com-

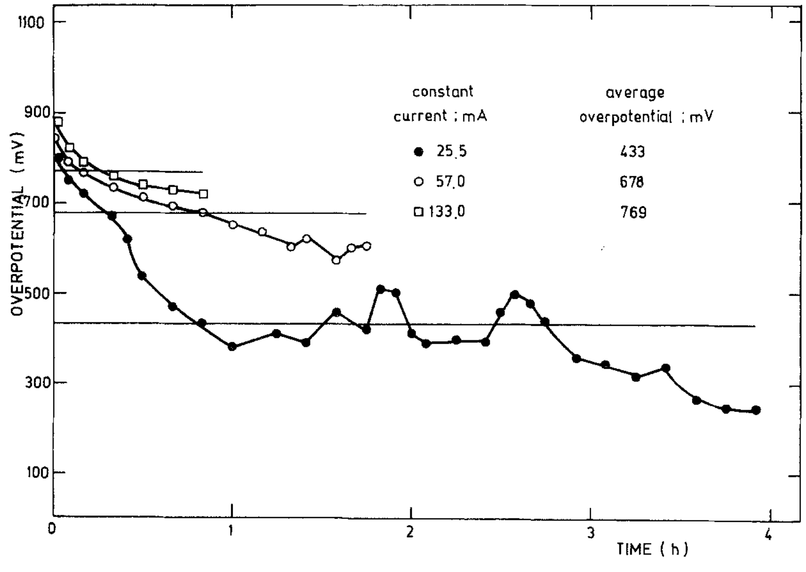

Fig. 4. The same as in Fig. 3 for aluminium electrodes.

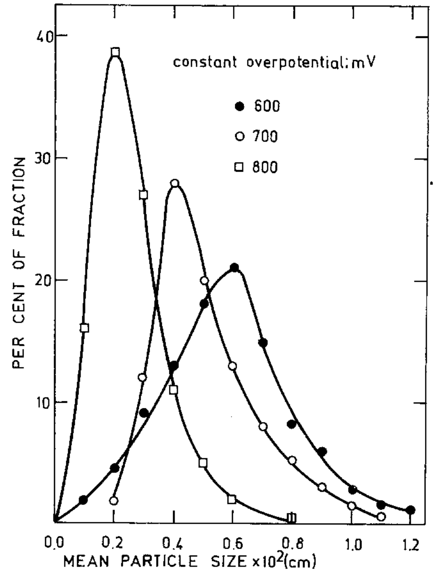

Fig. 5. Particle size distribution curves for copper powders deposited by different constant overpotentials on platinum electrodes.

pared to those obtained by potentiostatic deposition. It is seen from Fig. 3 that the overpotential decreases from some maximal value, which is larger than the corresponding overpotential in potentiostatic deposition, with increasing time of electrolysis. The difference between the initial overpotential and that in potentiostatic deposition is small for 28·6 mA and 52 mA (average currents for potentiostatic deposition at 600 mV and 700 mV, respectively). After a short time the overpotential becomes less than that in potentiostatic deposition. At 133 mA (average current for potentiostatic deposition at 800 mV) hydrogen evolution controls the process and the situation becomes quite different.

It is known that the dendrite growth velocity is maximal for some optimal tip radius [4]. The optimal tip radius increases with the decrease of overpotential. The difference between the maximal velocity and the actual velocities for dendrite growth with tip radii different from the optimal one, becomes smaller with decreasing overpotential. Hence, because of the decrease of overpotential during galvanostatic deposition the formation of larger and less dentritic particles can be expected as well as less narrow particle size distribution curves. This is shown in Figs. 5, 6 and 10 (a and b). It can be seen from Figs. 7 and 8 that smaller particles and narrower particle size distribution curves are obtained by galvanostatic deposition on an aluminium electrode, compared to those obtained in the potentiostatic case. Corresponding overpotential–time relationships are presented in Fig. 4. The difference between initial overpotentials and the corresponding values in potentiostatic deposition are large, and overpotentials in galvanostatic deposition remain larger than

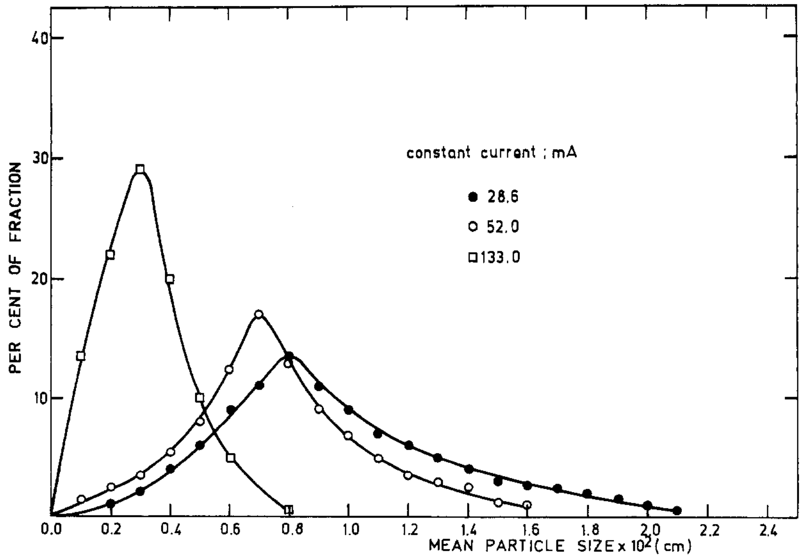

Fig. 6. Particle size distribution curves for copper powder deposited by different constant currents on platinum electrodes.

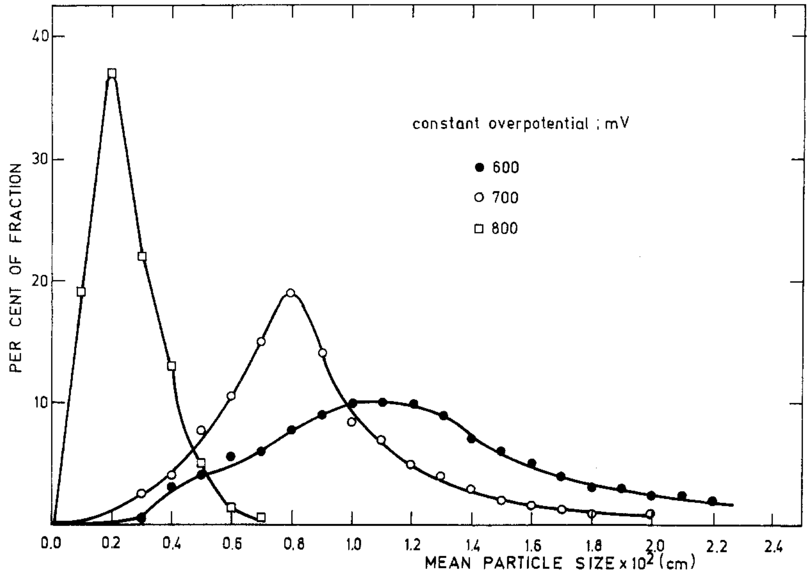

Fig. 7. The same as in Fig. 5 for aluminium electrodes.

the corresponding values in the potentiostatic case over relatively long periods. This is due to the presence of oxide layers on the aluminium electrodes and to the enlarged ohmic resistance of the interface. Hence, because nucleation takes place at more negative overpotentials, smaller particles are formed and narrower particle size distribution curves are obtained. The particles obtained by galvanostatic deposition on aluminium are less dendritic than those deposited in the potentiostatic case, as can be seen from Figs. 10c and d. This is because the overpotential at the end of the deposition is less negative than that in the corresponding potentiostatic deposition.

The particle size distributions for copper powder deposition by constant overpotential and constant current on copper and graphite electrodes are presented in Figs. 11 and 12. It is obvious that similar effects are obtained on copper and platinum as well as on aluminum and graphite electrodes.

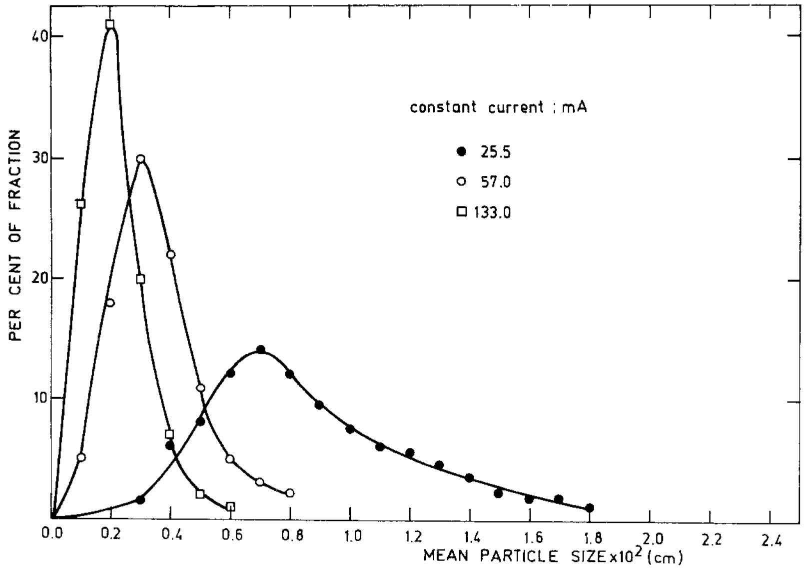

Fig. 8. The same as in Fig. 6 for aluminium electrodes.

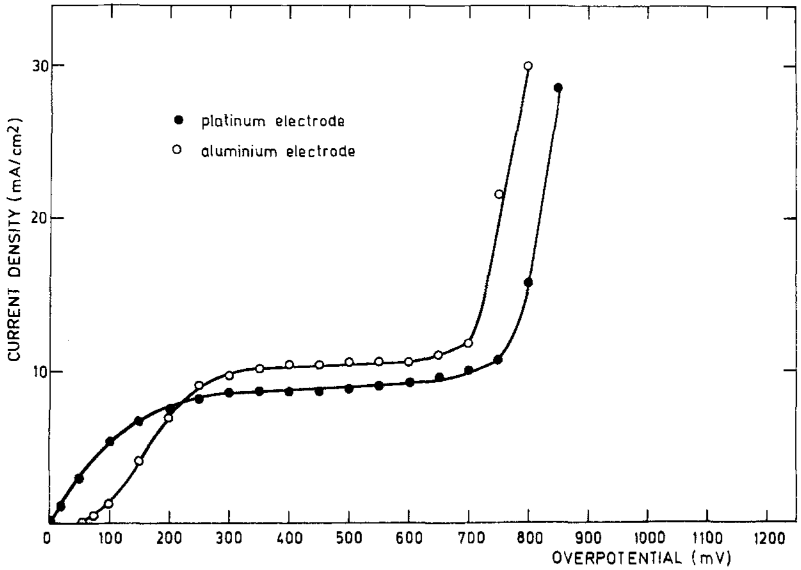

Fig. 9. Polarization curves for constant potential deposition of copper on platinum and aluminium electrodes.

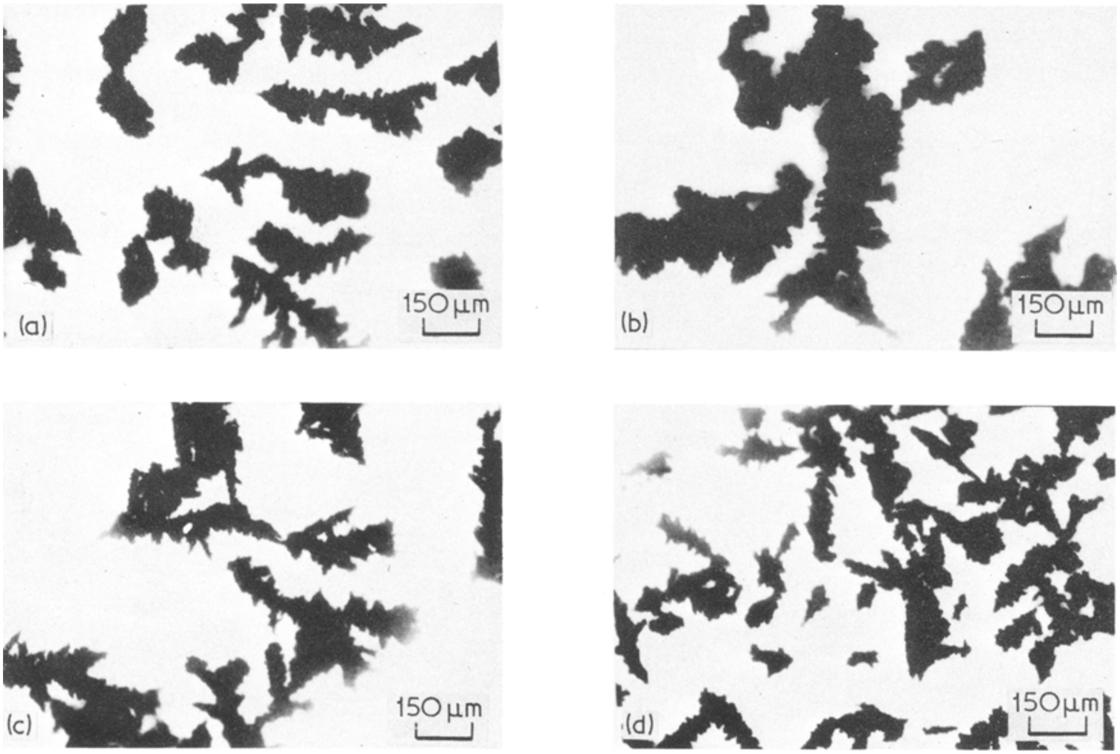

Fig. 10. Copper powders deposited by constant overpotentials and constant currents on platinum and aluminium electrodes. (a) Platinum electrode, overpotential 700 mV; (b) platinum electrode, current 52 mA; (c) aluminium electrode, overpotential 700 mV; (d) aluminium electrode, current 57 mA.

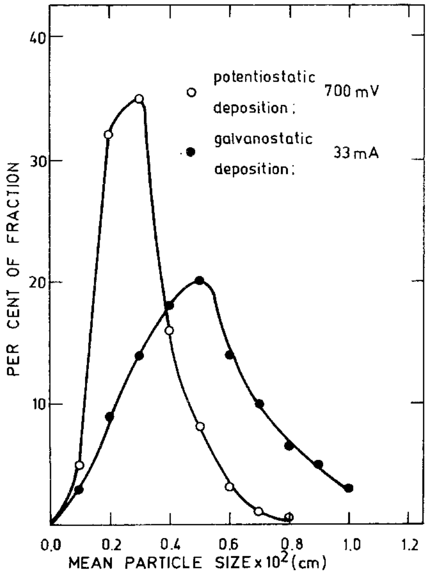

Fig. 11. Particle size distribution curves for copper powders deposited by constant overpotential and constant current (average current in potentiostatic deposition) on copper electrodes.

Hence, depending on the substrate (metal or oxide and metal–semiconductor) the conditions of the electrolysis have different effects on the powder particles obtained.

The hydrogen evolved was measured during deposition on platinum and aluminum electrodes and volume–time relationships were plotted. These results are presented in Figs. 13–16. It is seen from Figs. 13 and 15, that the volume of hydrogen evolved increases with time in a similar way to the deposition current (Figs. 1 and 2). This is because the real current density is constant during deposition but the electrode surface area increases. In galvanostatic deposition (Figs. 14 and 16) the rate of hydrogen evolution decreases with time, because of the decrease of the overpotential of deposition (Figs. 3 and 4).

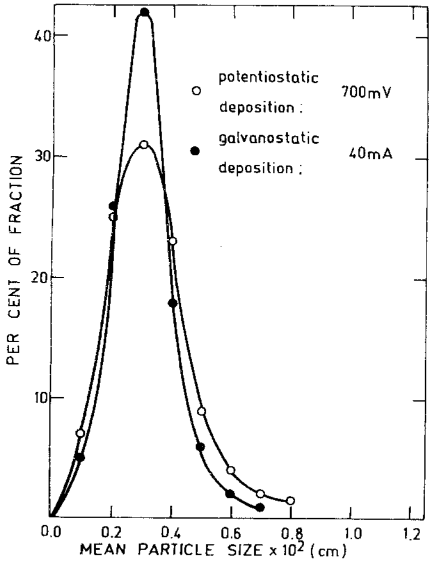

Fig. 12. The same as in Fig. 11 for graphite electrodes.

From volume–time plots the slopes were measured and the current efficiency for hydrogen evolution, η_{H_2} calculated according to Equation 1.

$$\eta_{H_2} = \frac{(dV/dt)\,(1/\mu_{H_2})}{I} \times 100\,(\%) \qquad (1)$$

and current efficiency for copper powder deposition,

$$\eta_{Cu} = 100 - \eta_{H_2}\,(\%) \qquad (2)$$

where μ_{H_2} electrochemical equivalent of hydrogen
V volume of hydrogen evolved
t time
I current (in potentiostatic experiments extracted from Figs. 1 and 2)

In Figs. 17–20 the current efficiency for copper deposition as a function of time of deposition for the potentiostatic and the galvanostatic deposition on platinum and aluminium electrodes is presented. In general, there is no difference between deposition on platinum and deposition on aluminium electrodes. In potentiostatic deposition (Figs. 17 and 19) current efficiency tends to a constant value in each case. In galvanostatic cases current efficiency increases with time in each case. This is in accordance with earlier discussed effects of time of deposition on real current densities and overpotentials.

On the basis of the average values of current efficiency extracted from Figs. 17–20, the overpotential of deposition in potentiostatic cases and the average overpotentials extracted from Figs. 3 and 4 for galvanostatic deposition, the specific energy consumption, W_{sp}, for each case was calculated using Equation 3

$$W_{sp} = \frac{\eta}{\mu_{Cu}\eta_{Cu}} \qquad (3)$$

where η is the overpotential (or average overpotential).

In Fig. 21 the specific energy consumption in

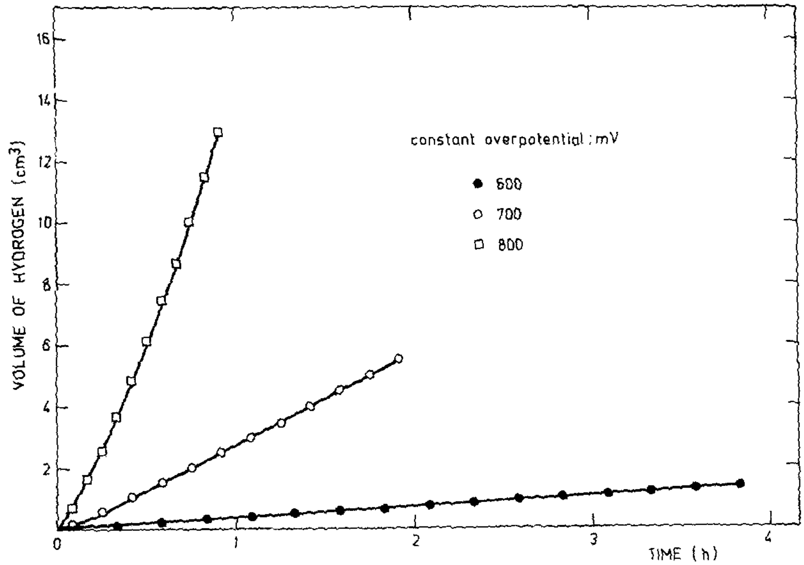

Fig. 13. The volume of hydrogen evolved as a function of time with constant overpotential copper powder deposition on platinum electrodes.

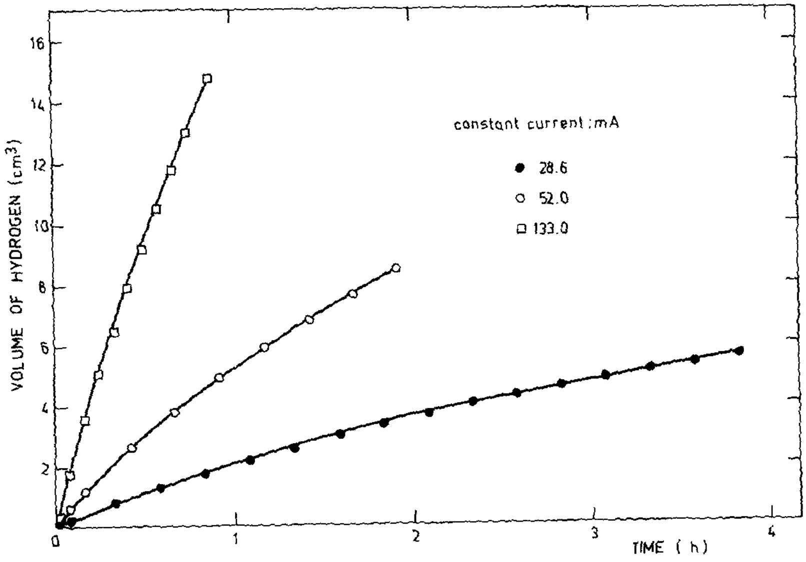

Fig. 14. The volume of hydrogen evolved as a function of time with constant current copper powder deposition on platinum electrodes.

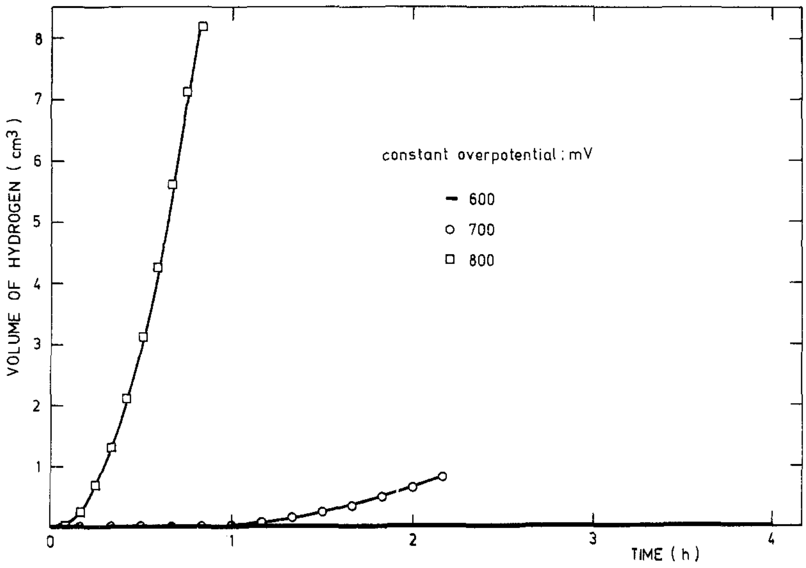

Fig. 15. The same as in Fig. 13 for aluminium electrodes.

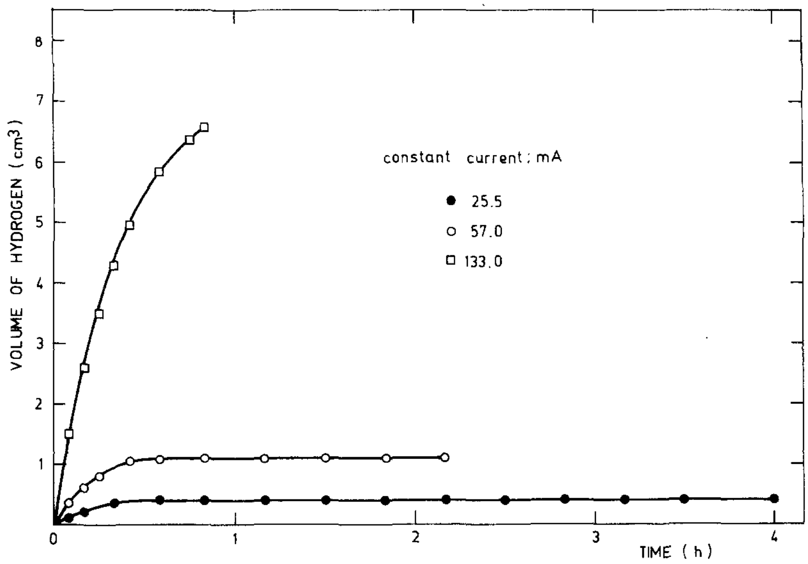

Fig. 16. The same as in Fig. 14 for aluminium electrodes.

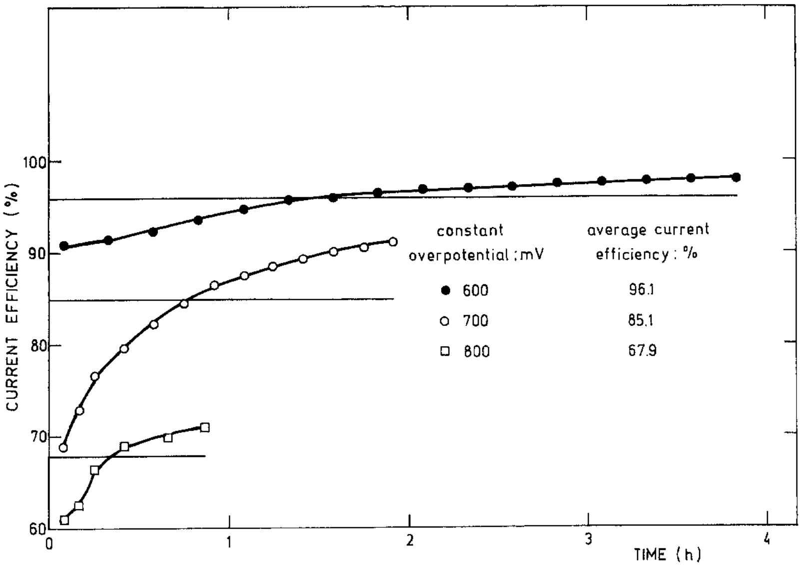

Fig. 17. Current efficiency for copper powder deposition by different constant overpotentials on platinum electrodes as a function of time.

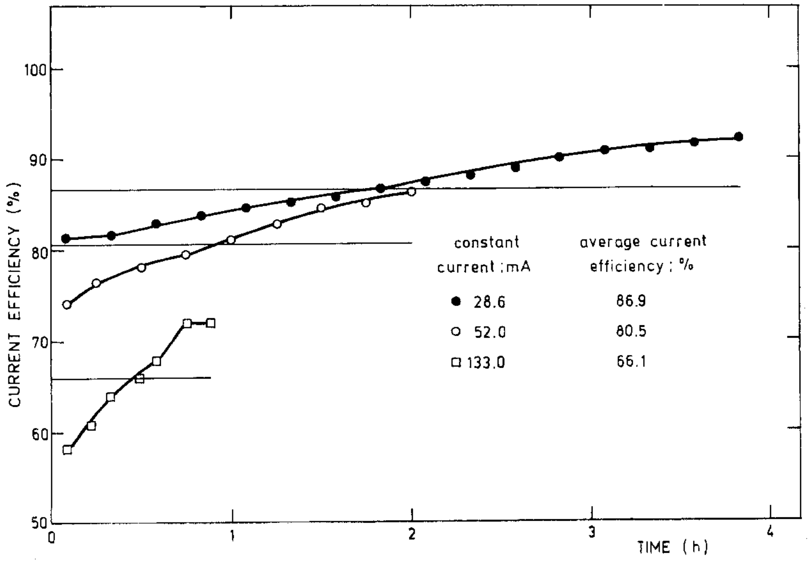

Fig. 18. Current efficiency for copper powder deposition by different constant currents on platinum electrodes as a function of time.

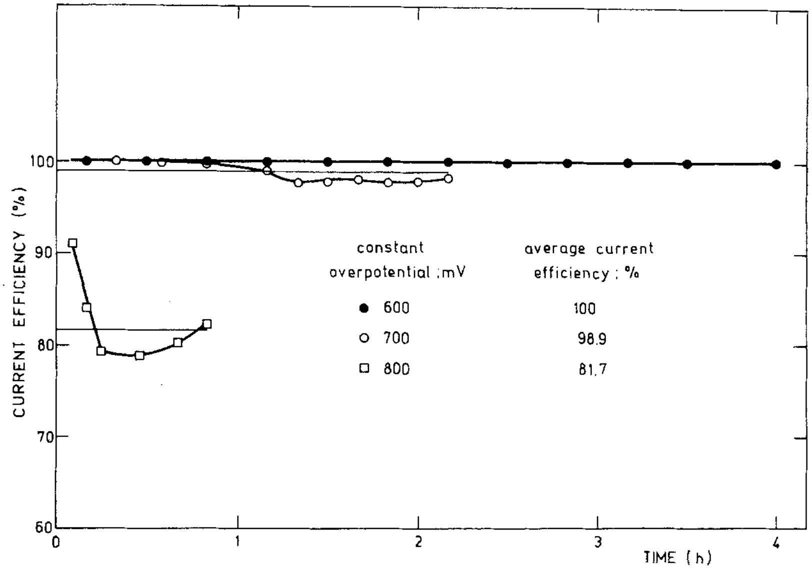

Fig. 19. The same as in Fig. 17 for aluminium electrodes.

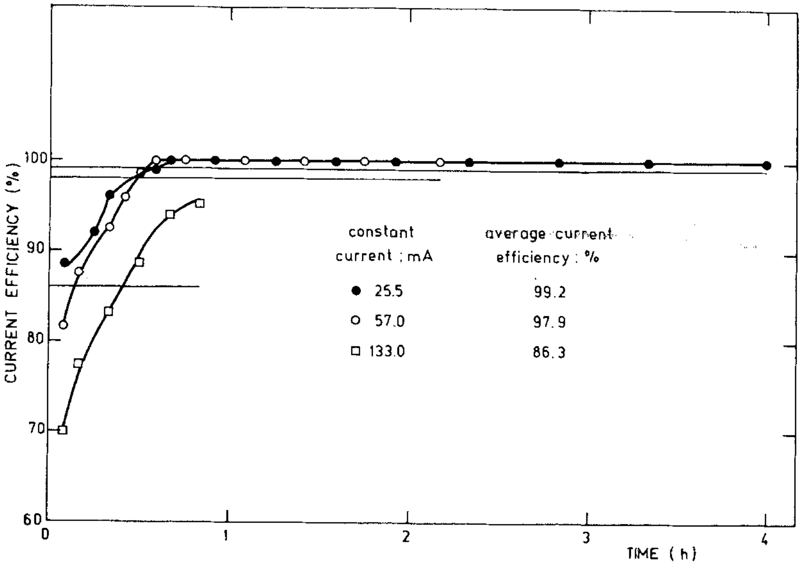

Fig. 20. The same as in Fig. 18 for aluminium electrodes.

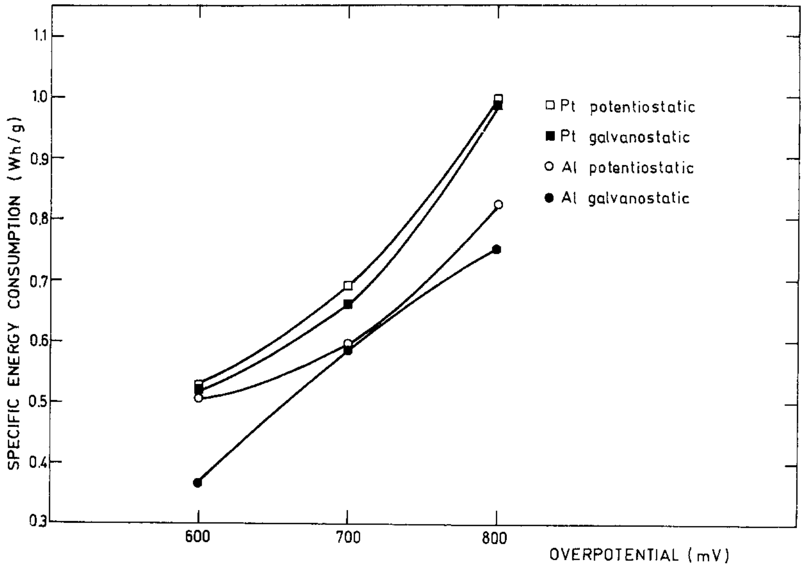

Fig. 21. Specific energy consumption in potentiostatic and galvanostatic copper powder deposition by constant overpotentials and constant currents on platinum and aluminium electrodes. Results for galvanostatic deposition (at the average current of potentiostatic deposition) are related to corresponding overpotentials.

the potentiostatic and the corresponding galvanostatic experiments is shown as a function of overpotential in potentiostatic deposition. It is seen that the specific energy consumption is smaller for deposition on aluminium electrodes than for deposition on platinum electrodes. At the same time, galvanostatic deposition requires a smaller energy consumption than does potentiostatic deposition.

It should be noted that the above discussion is valid for a quantity of electricty of 100 mA h. For other quantities of electricity and different experimental conditions different results can be expected, according to Drumiler *et al.* [11] and Maksimović *et al.* [12].

Regardless of this, it can be concluded that morphology and particle grain size, as well as current efficiency and specific energy consumption can be varied in the way described by using different cathode materials and potentiostatic or galvanostatic methods of electrodeposition.

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References

[1] N. Ibl in 'Electrochemistry and Electrochemical Engineering' (eds. P. Delahay and C. W. Tobias), Vol. 2, Interscience, New York (1962) p. 50.
[2] K. I. Popov, D. N. Keča and M. D. Maksomović, *J. Appl. Electrochem.* 7 (1977) 77.
[3] K. I. Popov, M. D. Maksimović and G. R. Ostojić, *ibid* 7 (1977) 331.
[4] J. L. Barton and J. O'M. Bockris, *Proc. Roy. Soc.* **A268** (1962) 485.
[5] A. R. Despić, J. Diggle and J. O'M. Bockris, *J. Electrochem. Soc.* **115** (1968) 507.
[6] J. W. Diggle, A. R. Despić and J. O'M. Bockris, *ibid* **116** (1969) 1503.
[7] A. R. Despić and M. M. Purenović, *ibid* **121** (1974) 329.
[8] K. I. Popov, D. N. Keča, S. I. Vidojković, B. J. Lazarević and V. B. Milojković, *J. Appl. Electrochem.* **6** (1976) 365.
[9] N. Ibl and K. Schadegg, *J. Electrochem. Soc.* **114** (1967) 54.
[10] I. B. Murashova and A. V. Pomosov, *Electrokhim.* 3 (1967) 1117.
[11] D. W. Drumiler, R. W. Moulton and G. L. Putnam, *Ind. Eng. Chem.* **42** (1950) 2099.
[12] M. D. Maksimović, M. G. Pavlović and K. I. Popov, *Hem. Indust.* in press.