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Packed bed electrodes. II. Anodic stripping and the recovery of copper from dilute solutions

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The anodic stripping of deposited copper from a packed graphite bed is shown to be a kinetically controlled process. At high anodic overpotentials the bed can be unloaded in a few seconds to form a concentrated solution of copper sulphate suitable for further processing. The fractional recovery is at least 95% on a single polarization.

1. Introduction

In the previous paper it was shown that the stripping or extraction of metal ions, in this case copper ions, from aqueous solution is speedily and effectively accomplished using three-dimensional electrodes.

In the case of a fluidized bed of say copper micro-spheres, the particle size builds up until the bed no longer functions properly whereupon it can be transferred for consolidation or other treatment. For continuous extraction it is perhaps more convenient simply to 'unload' the bed periodically by switching the bed potential to a value anodic of the reversible potential. The metal is then recovered in the form of a concentrated solution which may be disposed of, if effluent treatment is the primary object, or added to a conventional electroplating bath if metal recovery is the object. The degree of enrichment can be large and, as will be shown, depends only on the length of the initial cathodic extraction period and the flow rate during the subsequent anodic stripping process.

This procedure is entirely equivalent to conventional anodic stripping on a mercury electrode [1] and which is the basis of much of the electroanalysis of very dilute solutions. It can be studied by linear sweep [2] or potential step methods [3] and both are applied here to a packed bed electrode of graphite partially 'loaded' with copper.

2. Experimental

The experimental procedures were similar to those described in the previous paper [4]. The only significant difference arose from the fact that the anodic transients were short, and therefore required faster recording.

The general procedure for each run was to step the bed potential to a value − 0·4 V versus the S.C.E., i.e. in the region of the limiting diffusion current for the electrodeposition of copper. The potential was held constant for a specified period defined here as the concentration or extraction time, τ, after which the bed was electrically isolated for 5 s and then subjected to the anodic stripping cycle, by stepping the bed potential to + 0·4 V versus S.C.E. The anodic current was then recorded as a function of time until it fell to the value of the anodic residual current, i.e. ~ 1 mA. In a preliminary investigation, the stripping process was also studied by the linear sweep method, the potential being initiated at − 0·075 V versus S.C.E. and swept anodically to + 0·4 V.

3. Results and discussion

The anodic stripping process was first examined by cyclic voltammetry. Fig. 1 shows a cyclic voltammogram at two flow rates of 10^{-4} M $CuSO_4$ in 1 M Na_2SO_4 + 10^{-3} M H_2SO_4. The sweep rate

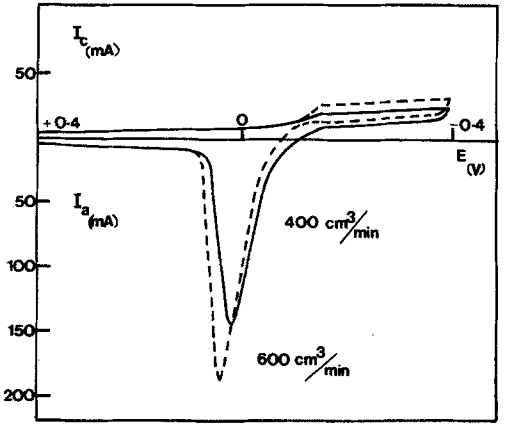

Fig. 1. Cyclic voltammograms for the cathodic deposition and anodic dissolution of copper. (Sweep rate = 0·01 V s^{-1}; bed length = 1·2 cm)

was low and was initiated from a start potential well anodic of the reversible copper potential. As is to be expected from the results of the previous paper [4], the cathodic sweep shows a limiting current plateau whereas the anodic sweep gives rise to well defined peaks. The difference in anodic peak heights is not directly the result of the different flow rates but rather the consequence of the difference in the extent of loading of the bed, since the cathodic current and hence the total cathodic coulometric yield is proportional to the flow rate.

This point is made plain in Fig. 2 which shows a series of anodic peak heights recorded at a constant flow rate and at the same sweep rate but for successively longer cathodic extraction times τ. Both the height and the area of the peak are proportional to τ. It is also evident that the anodic current falls very rapidly to the residual current and that the anodic stripping process is therefore an efficient way of recovering the metal. An advantage of the linear sweep method is that the currents are measureable throughout the transient. With the potentiostatic method the initial currents can be very large.

Fig. 3 shows a set of potentiostatic transients for four values of τ.and at a constant flow rate of 400 cm^3 min^{-1}. Once again the currents are seen to depend primarily on the degree of loading i.e. on the quantity of charge, Q_c, involved in the cathodic half cycle and given by

$$Q_c = \int_0^\tau I_c \mathrm{d}t. \qquad (1)$$

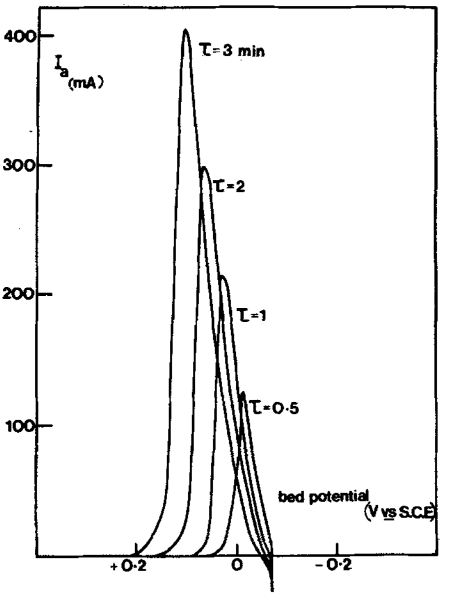

Fig. 2. Anodic stripping by linear sweep voltammetry. Anodic peak heights as a function of initial deposition time. (Sweep rate = 0·01 V s^{-1}; flow rate = 400 cm^3 min^{-1})

The independence of the anodic current on the rate of solution flow through the bed during the anodic transient is demonstrated in Fig. 4 which shows a set of anodic transients for a range of flow rates but for a single value of τ. For clarity, single values of the anodic current, I_a, are displayed about the continuous transient recorded for a single value of the flow rate (400 cm^3 min^{-1}). It follows that the anodic stripping process is not diffusion controlled and therefore from the viewpoint of recovery efficiency it might be advantageous to operate the anodic half cycle at zero flow rate and thus maximize the degree of enrichment, in this case to ~ 10^3.

Since the anodic process is not mass-transfer controlled, it follows that it is kinetically controlled and therefore dependent on the bed potential. Fig. 5 shows the effect of anodic potential on the shape of the $I_a - t$ transients for a constant Q_c value of 3·71 C and a flow rate of 400 cm^3 min^{-1}; as expected, the rate of stripping increases with anodic pverpotential. Under potentiostatic conditions, the stripping current, I_a is a function only of the corresponding electrochemical rate constant, k_a, and the fractional coverage, θ, of the graphite surface by deposited metal. Assuming that θ is

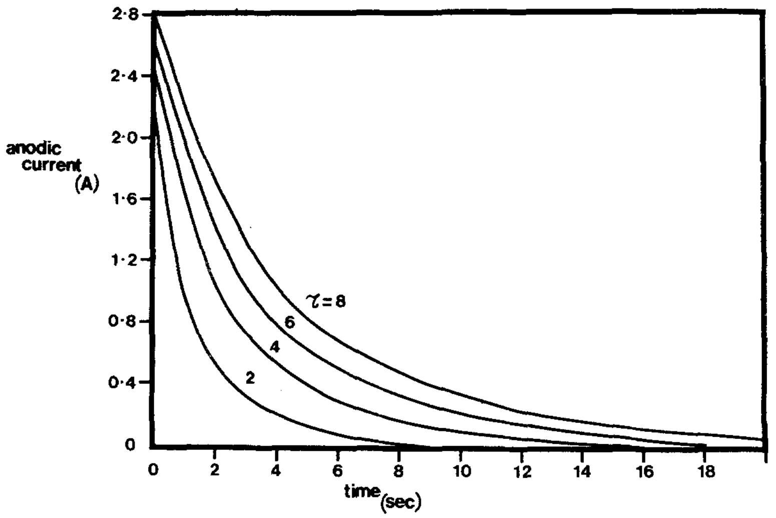

Fig. 3. Potentiostatic transients for the anodic stripping reaction of 10^{-4} M $CuSO_4$ in 1 M H_2SO_4. (Flow rate = 400 cm^3 min^{-1}; bed length = 1 cm).

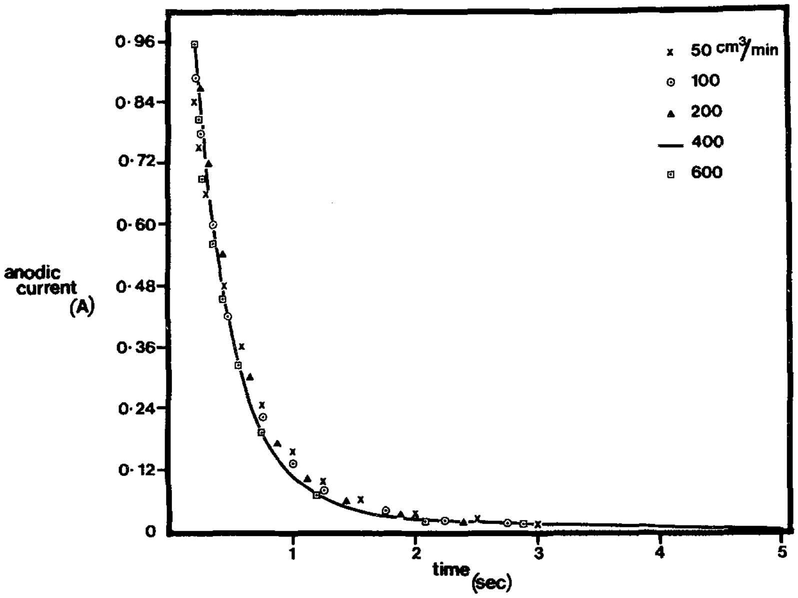

Fig. 4. Potentiostatic transients for a single value of τ but at different flow rates. (τ = 0·5 min).

uniformly distributed throughout the bed, the total anodic current can be obtained by integration over the length of the bed, L, i.e.

$$I_a = nFaALk_a\,\theta(t) \tag{2}$$

where k_a is the electrochemical rate constant and the rest of the terms have their usual significance [4].

Assuming that the potential drop in the packed bed is small, the copper metal will redissolve at approximately constant potential and the surface coverage θ will then be a function of the stripping time only. In terms of the material balance at the solid phase

$$\Omega\frac{\partial\theta}{\partial t} = \epsilon k_c Ac - k_a A\theta, \tag{3}$$

where Ω is the saturation coverage, k_c and k_a are the electrochemical rate constants for cathodic and anodic processes, respectively.

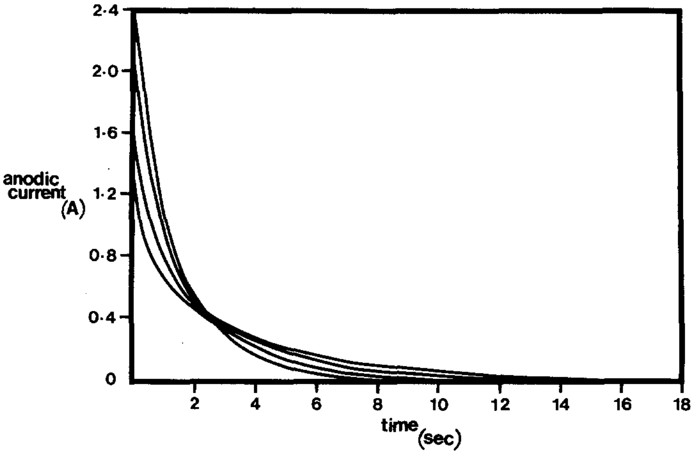

Fig. 5. Potentiostatic transients at different anodic potentials. (Flow rate = 400 cm³ min⁻¹; from top: 0·5, 0·4, 0·3 and 0·2V versus S.C.E.).

At high anodic overpotentials,

$$k_a\theta \gg k_c c \tag{4}$$

and the rate of stripping will be given simply by

$$\Omega\frac{d\theta}{dt} = -k_a A\theta. \tag{5}$$

The solution of Equation 6 is

$$\theta = \theta_0 \exp(-k_a At/\Omega) \tag{6}$$

which combined with Equation 2 leads to another expression for the anodic stripping current, i.e.

$$I_a = nFaAk_a\theta_0 L \exp(-k_a At/\Omega) \tag{7}$$

where θ_0 is the initial surface coverage (i.e. the surface coverage at $t = 0$).

Equation 7 predicts that the stripping current should decrease exponentially with time, as is observed, and it is also predicted that the current should be proportional to the initial surface coverage which is in agreement with the results shown in Fig. 3.

The linear relation between $\ln I_a$ and time is evident in Fig. 6. The slope of this plot, i.e. $k_a A/\Omega$,

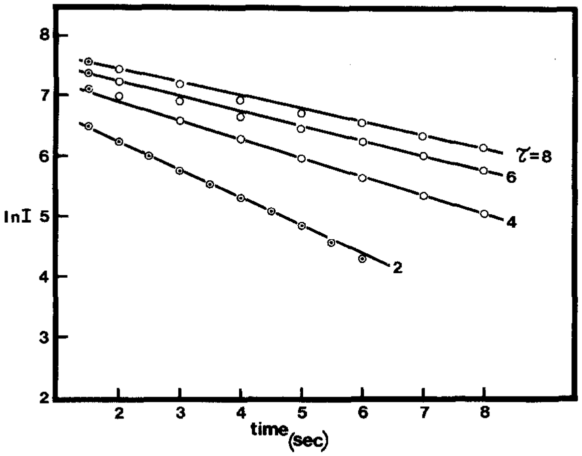

Fig. 6. Anodic stripping current as a function of time. (Data from Fig. 3).

should be a constant but in fact is seen to change slightly with τ. This may be due to the variation of k_a, which is sensitive to the characteristic of the electrode surface and in turn on the time of extraction, τ, which may determine the extent of coverage and smoothness. When t approaches zero, the instantaneous current will be

$$I_a = nFaALk_a\theta_0 \qquad (8)$$

and will have a maximum value when θ_0 reaches its saturation value.

The total charge involved during the anodic stripstripping process is given by

$$Q_a = \int_0^t I_a \mathrm{d}t \qquad (9)$$

and this was directly determined in these experiments using an electronic integrator. The upper limit, t, of the integral was taken as the time required for the stripping current to fall to the value of the residual current. The recovery of metal during the total cathodic-anodic cycle is therefore defined as

$$\text{fractional recovery} = \frac{Q_a}{Q_c} = \frac{\int_0^t I_a \mathrm{d}t}{\int_0^t I_c \mathrm{d}t} \qquad (10)$$

and values of this quantity are listed in Table 1.

Table 1. *The recovery efficiency of copper extraction as a function of deposition time and flow rate*

Flow rate (cm³ min⁻¹)		*τ (min)*	*Q_c(coulomb)*	*Q_A (coulomb)*	*Recovery (%)*
Concentrating	*Stripping*				
400	400	0·5	1·05	1·0	95
400	400	1	1·94	1·85	95
400	400	2	3·71	3·65	98
400	400	4	7·11	7·0	98
400	400	6	10·4	10·1	96
400	400	8	13·4	13·0	97
400	0	0·5	1	0·94	94
400	50	0·5	1	0·95	95
400	200	0·5	1	0·97	97
400	400	0·5	1	0·96	96
400	600	0·5	1	0·94	94

The recovery efficiency, ranging from 93 to 98%, is considered to be satisfactory. The shortfall which might be due to capacity currents and to some surface oxidation of graphite, is likely to decrease as τ is increased. A plot of recovery versus t/τ, the ratio of stripping time to concentration time, is shown in Fig. 7. The stripping of copper is initially very efficient but becomes less as t/τ becomes less than 0·04. The recovery approaches 90% for $t/\tau > 0{\cdot}04$ so that most if not all of the copper can be stripped off in a relatively short period of time. For continuous operation, it may be therefore economical to truncate the anodic stripping half cycle so that each time 90% of the loaded metal is recovered.

4. Conclusion

The electrochemical recovery of dissolved copper from dilute solution is seen to be a simple and efficient process. A packed graphite bed is a suitable electrode form for this purpose. It can tolerate high flow rates of solutions, it can be regenerated electrochemically and it has a long life. In the continuous operation of metal recovery processes the switching from the extraction step to the stripping step after an appropriate time interval will obviate any plugging of the electrode and the metal ions can be collected from the product stream during the stripping cycle.

The deposition or the extraction cycle can be made as long as is required to reduce the metal ion concentration to an acceptable level. The

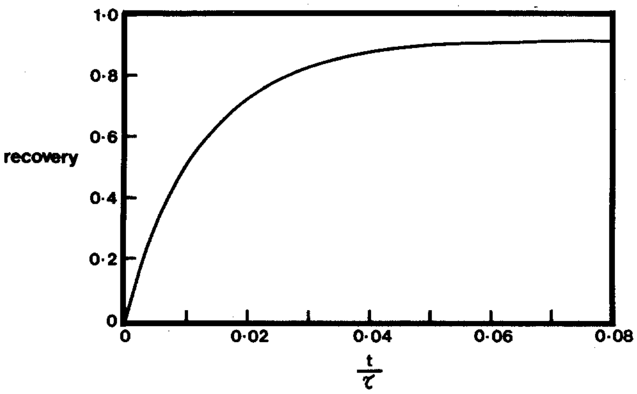

Fig. 7. Metal recovering efficiency as a function of the ratio of stripping to extraction times. (Data from Fig. 3.)

effectiveness of each pass can be increased simply by increasing the length of the bed. The anodic stripping time can be made very short and the bed can therefore be periodically unloaded without significant interruption of the electrodeposition process.

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References

[1] E. Barendrecht, 'Electroanalytical Chemistry', Vol.2, pp. 53–109. Ed. A. J. Bard, Marcel Dekker, New York, (1967).

[2] J. G. Nikelly and W. D. Cooke, paper presented at the *International Congress of Pure and Applied Chemistry, Lisbon,* September 9–16 (1956).

[3] G. Mamantov, P. Papoff and P. Delahay, *J. Am. Chem. Soc.*, 79 (1957) 211.

[4] A. K. P. Chu, M. Fleischmann and G. J. Hills, *J. Appl. Electrochem.*, 4 (1974) 323.