JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 737–743

The anodic dissolution of copper in a fluidized bed electrode

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Received 13 December 1978

The paper reports on the study of the anodic dissolution of copper particles forming a fluidized bed electrode in sulphuric acid solutions containing copper (II). The distribution of overpotential along the length of the fluidized bed electrode has been measured and the variation of the current efficiency for the dissolution was determined as a function of the current density and the fixed bed thickness. A comparison is made with earlier results for copper deposition in a fluidized bed electrode with the same characteristics.

1. Introduction

Several papers have reported studies of metal electrowinning, particularly copper, in fluidized bed electrodes [1–10]. Indeed this application of the fluidized bed electrode concept has often been considered the most promising although industrial developments have not yet taken place. This may be because the behaviour of these structures is not fully understood as can be seen from recent papers on the application of fluidized bed electrodes to copper electrowinning [5, 6].

The anodic dissolution of metals in fluidized form has rarely been mentioned in the literature; only Flett [2] and Wilkinson [3] have reported preliminary studies of copper electrodissolution in sulphuric acid solutions containing copper sulphate. Flett's results indicate that the current efficiencies for dissolution are generally higher than 1·00 but no explanation was proposed.

Because of the current interest in metal extraction by the electrodissolution of powdered complex minerals and metallic wastes, the anodic dissolution of purely metallic fluidized particles needs to be studied further. Indeed a pure metal may be considered as an ideal mineral for the dissolution of which no selectivity criteria are needed. Only two papers [11, 12] have discussed the dissolution of copper minerals in fluidized bed electrode form; they were overall studies oriented towards the feasibility of the dissolution.

For various sulphuric acid solutions containing copper sulphate, the distribution of overpotential within anodically polarized fluidized bed electrodes was measured and the current efficiencies were determined as a function of the fluidization parameters and the current density.

2. Experimental

2.1. *Cell and current feeders*

The cell (see Fig. 1) was similar to that described in [6] except that its internal diameter was 25 mm. The current feeder to the fluidized bed electrode was a circular grid of platinum (wire diameter 0·1 mm; mesh 0·5 mm) above a porous distributor (Vyon D) thick enough (3 mm) to ensure a uniform velocity profile at the bed entrance. The cathode was a circular perforated copper disc placed horizontally in the column downstream from the bed and at a constant distance from its top. A bigger central hole allowed a composite probe for local potential measurements to be moved axially with accurate positioning of its sensing element. The flow circuit is shown in Fig. 1; the temperature was maintained at 30° C.

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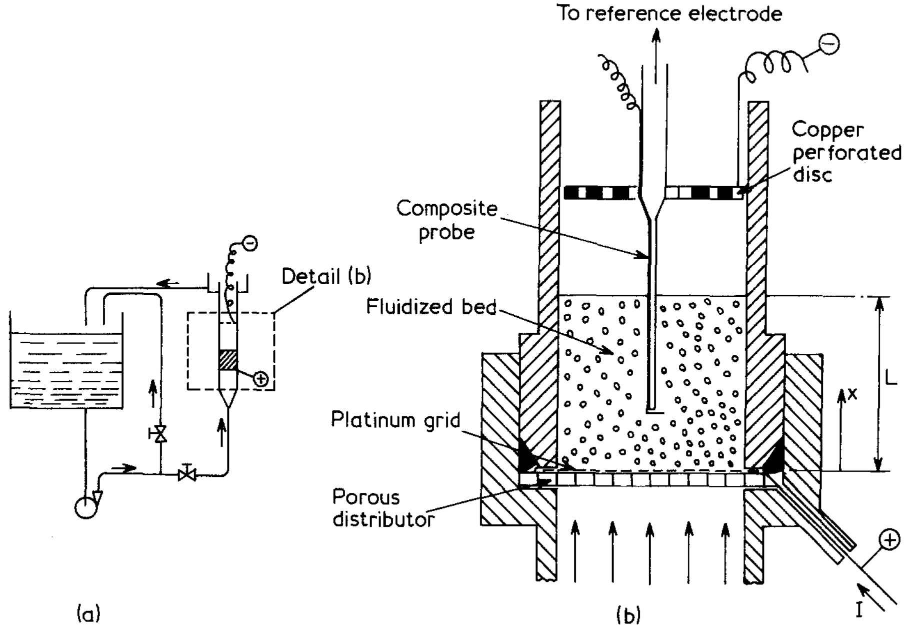

Fig. 1. (a) Schematic flow sheet of the apparatus and (b) extended view of the cell.

2.2. *Fluidized particles*

Most experiments used copper cylinders (diameter 1 mm; length 1·2 mm) obtained by automatic cutting of copper wire. Such a choice of particle geometry identical to that employed in [6] allowed a further comparison between the anodic and cathodic behaviour of the fluidized bed electrodes. Supplementary runs were performed with two classes of perfectly spherical copper particles (diameter 0·55 mm and 0·67 mm, respectively). The fixed bed heights, L_0, were chosen as 7, 14 and 21 mm. The fluidized bed porosity, ϵ, had three imposed values ($\epsilon = 0{\cdot}47$, 0·50 and 0·53) corresponding to bed expansions of 10%, 15% and 20%, respectively.

The electrolytes were:

(a) electrolyte 1: Cu 5 g l^{-1}, H_2SO_4 10 g l^{-1}
(b) electrolyte 2: Cu 25 g l^{-1}, H_2SO_4 100 g l^{-1}
(c) electrolyte 3: Cu 40 g l^{-1}, H_2SO_4 100 g l^{-1}.

They were not deoxygenated for the experiments.

2.3. *Electrochemical measurements*

The cell was controlled amperostatically with an overall current varying between 0·1 A and 1·5 A; the corresponding current density relative to the column cross-sectional area was therefore varied from 220 to 3300 A m^{-2}. At the maximum current density the electrode potentials in the more anodic parts of the beds (i.e. at the top of the bed) were lower than the potential corresponding to that for copper passivation in all three electrolytes. This was confirmed using a rotating disc electrode.

The local electrode potentials $E(x)$ when the sensing element was a distance x above the anodic current feeder was measured with a digital voltmeter. The local overpotential:

$$\eta(x) = E(x) - E_{eq}$$

was deduced from $E(x)$ and the equilibrium potential E_{eq}; for each electrolyte the latter was constant during the experiments and independent of x owing to the small residence time of the electrolyte in the bed during each pass and to copper deposition at the counter electrode.

3. Results

3.1. *Overpotential distribution along the bed axis*

The distribution of overpotential was determined for each electrolyte, the parameters of the study

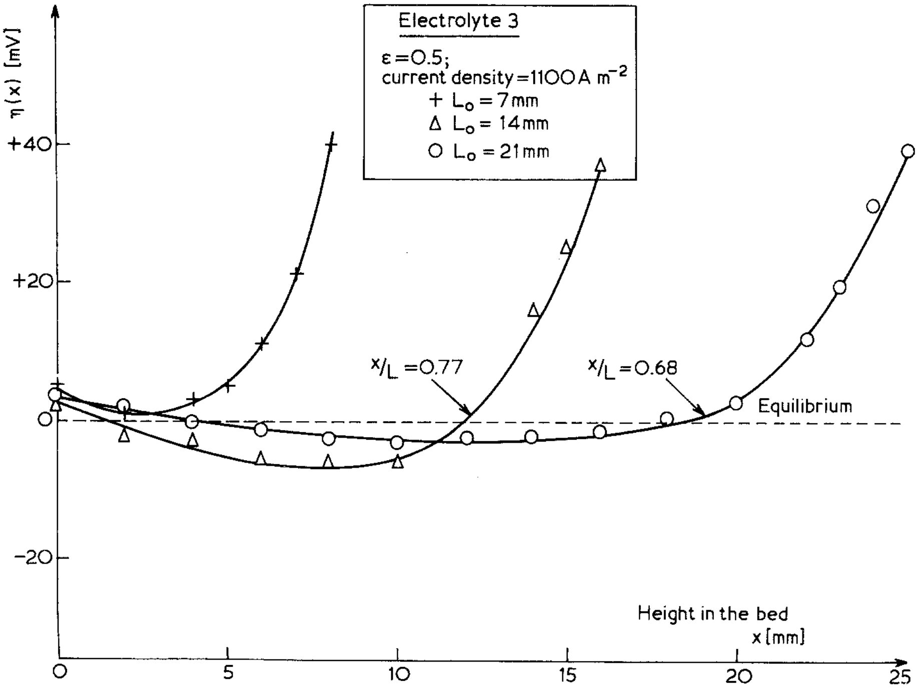

Fig. 2. Overpotential distributions along the bed axis for three fixed bed heights.

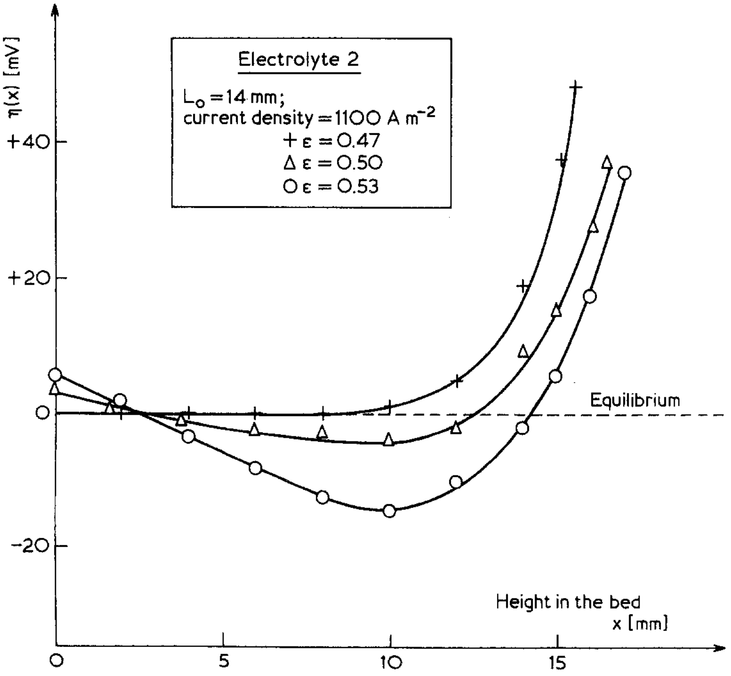

Fig. 3. Influence of the bed porosity on the overpotential distribution.

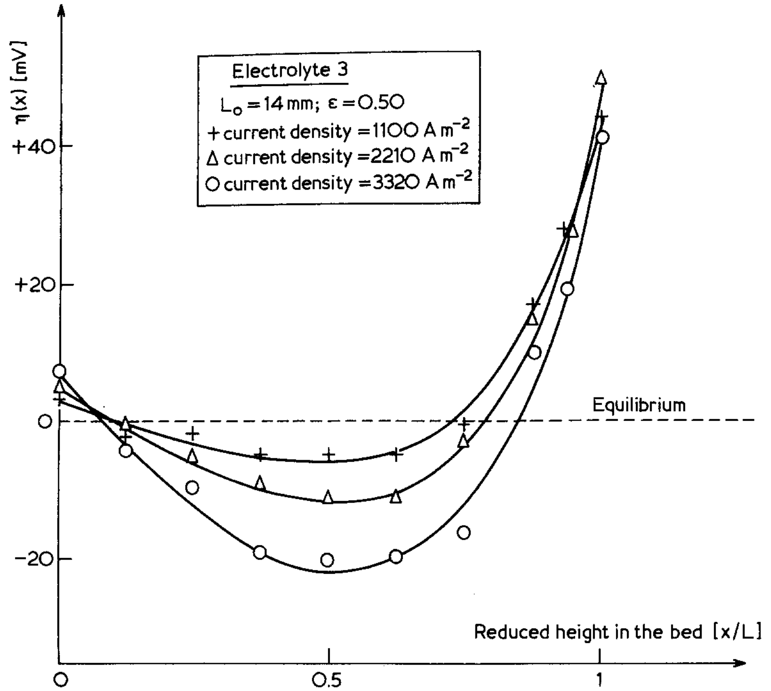

Fig. 4. Influence of current density on the overpotential distribution along the axis of a fluidized bed electrode.

being the fixed bed height, the current density and the bed porosity (or the fluidized bed height). Typical data are reported in Figs. 2–4.

Fig. 2 shows the influence of the fluidized bed height, the porosity and the current density being maintained constant. As for the cathodic case [6] the following observations may be made:

(a) A thin fluidized bed electrode is working anodically over its whole depth, the local electrochemical activity increasing rapidly with the distance from the current feeder

(b) For thicker electrodes, negative values of η appear; this is particularly the case at high bed porosities (see below the influence of ϵ). The fraction of the bed where η is negative increases with the bed height and can occupy a high percentage of this height (70%–90%).

Fig. 3 presents the influence of the bed porosity on the distribution $\eta(x)$; the fixed bed height and the current density were maintained constant. One can see that near the fixed bed state or in a just-fluidized state ($\epsilon = 0{\cdot}47$), an important fraction of the bed is at equilibrium ($\eta = 0$), the upper layers only being active. When the bed is well fluidized ($\epsilon > 0{\cdot}47$) the negative part of the overpotential distribution is accentuated by an increase of the porosity. It also has to be noted that the zone immediately neighbouring the current feeder is characterized by a positive overpotential. These results are again similar, but obviously the reverse of those observed in the same fluidized bed electrodes operated cathodically.

In Fig. 4 the influence of current density is shown. It is seen that when the current density is increased, the negative overpotential region becomes more pronounced. However the overpotentials at the two limits of the bed remain practically unchanged.

3.2. *Dissolution at different levels*

These overpotential distributions would indicate that a high percentage of the bed depth would not operate anodically. If that was true copper dissolution would occur near the top and the bottom of the bed, copper deposition occurring elsewhere. In order to test such an eventuality, the method described in [6] was used. At different levels within the bed, copper particles were simulated by stationary small horizontal sections of copper wire planted in holes regularly made along a PVC rod axially immersed in the column. The variation in weight of each piece of wire was measured after prolonged electrolysis (3 hours). It was observed that the variations were negligible except near the top of the bed where dissolution was confirmed. Such results partially contradict the overpotential distributions presented above. For the cathodic case [6] qualitative agreement was observed between the overpotential distributions and the weight variation at different levels.

3.3. *Current efficiency for anodic dissolution*

Extended electrolyses (2 or 3 hours) were carried out in order to determine the current efficiency* (CE) for the anodic dissolution as a function of current density and fixed bed height. The bed and the cathodic current feeder were weighed before and after each run, the mean copper concentration in the circuit being determined by electrogravimetric titration. All the runs show that the deposition of copper at the cathode obeys Faraday's law for a two-electron process.

Fig. 5 shows, for $\epsilon = 0{\cdot}53$ and $L_o = 14$ mm, the variations of current efficiency with current density for the three electrolytes used. Also in this figure the variations of current efficiency for copper deposition in an identical fluidized bed electrode are reported from [6]. It can be seen that the current efficiency for an anodic fluidized bed electrode is always higher than 1·00, reaching values up to 1·70 and decreasing with increasing current density. At a current density of about 3000 A m^{-2} it seems to tend to a value of around 1·20. For the cathodic deposition in the same fluidized bed electrode (see Fig. 5), current efficiency was always lower than 1·00 and increased with current density up to about 0·83 at around a current density of 3000 A m^{-2}. The variation of copper concentration during each experiment was not detectable by the titration method employed.

Finally, Fig. 6 shows the influence of the fixed bed height, L_o, on current efficiency. At any value of porosity and current density, current efficiency increases with the fixed bed height. Again it is higher than 1·00 and tends to this value only for very thin beds. The table in Fig. 6 summarizes the

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* defined as the amount of copper dissolved divided by that expected theoretically assuming a two-electron process.

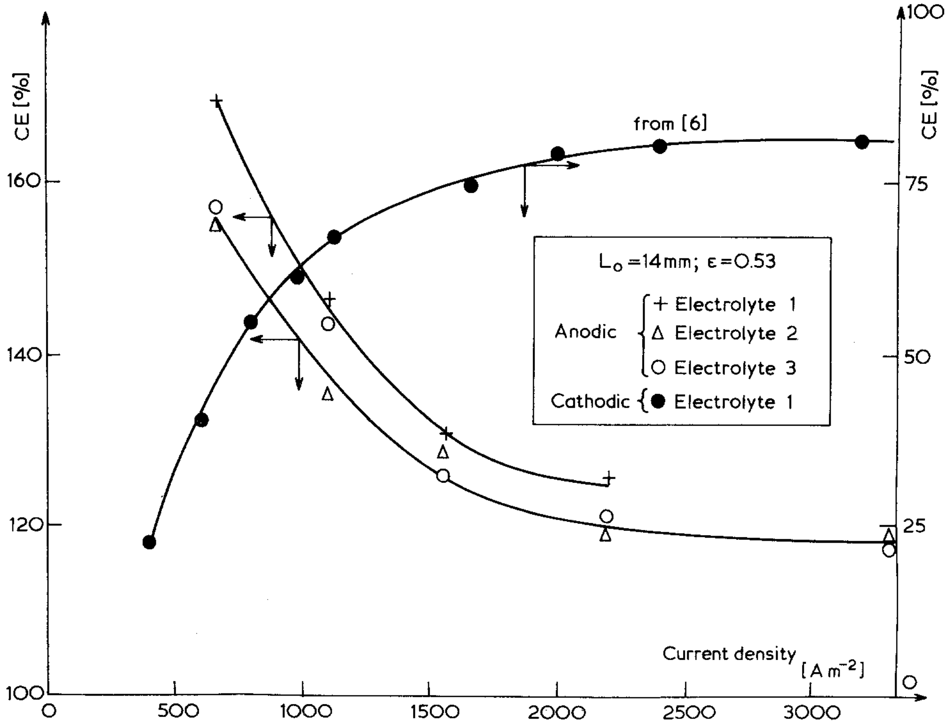

Fig. 5. Variations of current efficiency with current density and comparison between anodic and cathodic operation.

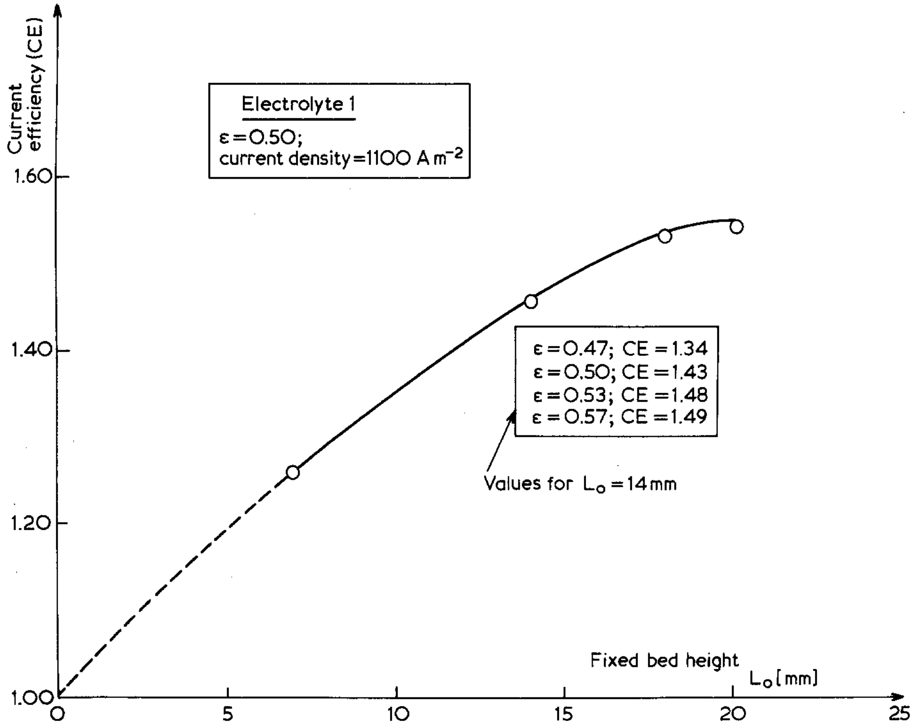

Fig. 6. Influences of the fixed bed height and of the bed porosity on the current efficiency.

influence of the bed porosity: the dissolution is improved when the porosity is increased.

The results in Table 1 indicate the variation of current efficiency with the particle diameter; as the particles become finer, current efficiency seems to increase.

4. Discussion

Three main conclusions may be drawn from the results presented above:

(a) The overpotential distribution measurements seem to reveal the existence of zones where the overpotential is negative.

(b) Copper dissolution only occurs near the top of the fluidized bed electrode whereas the particles located elsewhere seem to be unaltered.

(c) Current efficiencies are always higher than one, in accordance with Flett's results [2], and decrease with increasing current density.

At the present time, no explanation can be proposed for the apparent contradiction between observations (a) and (b); this will be the aim of further studies.

Fig. 5 merits particular attention owing to the symmetrical variations of the current efficiency for anodically and cathodically polarized fluidized bed electrodes of the same characteristics. For the cathodic case [6] the results were explained by the existence of a finite dissolution zone within the bed. Here for the anodic case a similar explanation is not possible. However, the dissolution exceeds that calculated theoretically by an amount

Table 1. Variation of current efficiency with particle diameter for electrolyte 1 ($\epsilon = 0{\cdot}5$, $L_o = 14$ mm, current density = 1100 A m^{-2})

Form of copper	*Diameter of copper* (mm)	*Current efficiency (CE)*
cylinders	1	1·46
spheres	0·67	1·48
spheres	0·55	1·52

almost equal to the parasite dissolution within a cathodically polarized fluidized bed electrode working at the same current density. By increasing the bed porosity the current efficiency increases further.

If electrolytic copper dissolution leads to the formation of cuprous ions, the calculated current efficiency would always be lower than 1·00. In sulphuric acid solutions however, copper electrodissolution generally takes place by a two-electron process, as confirmed in [6] where the dissolution of the planar copper anode satisfied Faraday's law for the transformation of copper to cupric ions. Thus it seems that an explanation has to be sought in the dispersed character of the electrodes.

Firstly it may be noted that the electronic conduction of the fluidized bed electrodes is not good and the current circulation in the metallic matrix takes place through the contact points between particles. At these contact points the current densities are unknown and obviously very high compared with the current density defined relative to the cross-sectional area of the column containing the bed. It will be difficult to support experimentally this interpretation but it is of interest for any type of anodic dissolution in dispersed systems owing to the possible passivation of the metal.

Secondly, it may be possible to observe a bipolar behaviour of the fluidized particles since the electrical conductivity of the matrix is so bad [13, 14] that the particles can be considered, at least from a hydrodynamic point of view [15], to be occupying the nodes of an expanded cubic lattice. In such a situation, a particle in some parts of the bed may behave as a bipolar electrode with different anodic and cathodic densities depending on the position of the particle with respect to the bed current feeder. Thus for a cathodic fluidized bed electrode, the partial cathodic current density on the particle itself could be so high that copper deposition could occur in the form of a powder and the particle would be dissolved. For an anodic fluidized bed electrode the anodic current density on the individual particle could be high whereas the cathodic deposition could occur normally on the other fraction of the particle surface. The weight of such a particle would be unchanged. Such a concept agrees with the behaviour of the stationary pieces of copper wire within the bed and with the current efficiency observed for fluidized bed electrodes operated cathodically, but does not explain the positive deviation of current efficiency above 1·0 as observed in the present paper. However, a bipolar behaviour is reasonable and certainly could merit further attention, especially in any process involving electrolytic treatment of powdered systems. This interpretation is supported by the work of Goodridge *et al.* [16].

5. Conclusions

The current efficiency for the anodic dissolution of copper particles in the form of a fluidized bed electrode is higher than one; it decreases with increasing current density and/or when the bed porosity is decreased. The particle diameter also influences the value of the current efficiency. A good symmetry is observed with the cathodic behaviour of fluidized bed electrodes but further research would be necessary to propose a significant interpretation.

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