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A three-dimensional current feeder for fluidized bed electrodes

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A three-dimensional current feeder has been introduced for fluidized bed electrodes (FBE) to improve the current distribution in the bed and to reduce the maldistribution of potential. Experimental results using this feeder show a five-fold increase in yield and a smaller increase in current efficiency.

1. Introduction

Several applications of the fluidized bed electrode (FBE) have been proposed, for example in organic electrosynthesis [1], fuel cells [2], ore flotation [3] and metal recovery [4]. The fluidized bed presents a large specific area which, in principle, allows a high yield in the processing of dilute solutions. Furthermore, the introduction of small, and the extraction of grown particles is made possible by their mobility, thus facilitating continuity of operation.

The potential distribution within an FBE has not yet been completely defined, but it is known that its inter-granular electrical conductivity is poor [4]. To overcome this problem some innovative modifications of the fluidized bed electrode, based on the circulating mechanism of the spouted bed, have been proposed. These modified beds show an increase in current efficiency and yield [5–7].

The poor electrical conductivity of the moving granular matrix reduces the possibility of controlling local overpotential [8], thus limiting the chances of obtaining the desired reaction and of controlling its kinetics. The result is that current efficiency and yield are both low. In view of the poor conductivity of FBE, the type and arrangement of the feeder electrode is important. This problem has been studied for various combinations of anodes and cathodes [8–11]. Electrodes with poor conductivity need a feeder producing a good distribution of the current over the whole electrode and not one limited to a single point or zone.

Up to the present, the current feeder for the fluidized bed electrode has always been two-dimensional, or else made of several rods immersed in the bed itself. Thus only a small fraction of the conducting particles are in contact with the feeder.

The solution proposed here is the use of three-dimensional feeders. These have been used in the past, but only as three-dimensional electrodes, not as feeders [12–21]. They consist of stacks of metallic nets or grids possessing a high mean porosity [22], and allow the particles of the fluidized bed electrode to move freely in their voids.

The aim of this work is to compare experimentally a two-dimensional feeder with the newly proposed three-dimensional one.

2. Particle-feeder interaction

A three-dimensional feeder in a fluidized bed affects the fluidization of the particles, as well as their collision with the feeder. The form and arrangement of the feeder affect the mobility of the particles within the bed in different ways. Figure 1 shows two different modes of stacking metal grids, each of which affects the mobility of the particles in a different way. The exact superposition of the metal grids (Fig. 1a) allows a high bed expansion, but relatively few collisions between the feeder and the particles. The alternate superposition of the metal grids (Fig. 1b) reduces bed expansion and increases the number of collisions with the feeder. In the first case there is a high degree of mobility among particles distant from the feeder, while in the second there is a high degree of mobility among particles close to the feeder.

Feeder efficiency depends on the number of collisions between particles and feeder, as well as on the local density of particles close to the feeder. Thus the arrangement in Fig. 1b should be more efficient than that in Fig. 1a.

3. Experimental details

3.1. *Electrolyte flow circuit*

The electrolyte flow circuit, made of glass and PVC, is shown in Fig. 2a. The electrolyte flowed around a closed loop. The flow-rate was measured by means of a rotameter and the temperature of the fluid was measured in the tank.

3.2. *Cell*

The cell was cylindrical and made entirely of glass, with an internal diameter of 34 mm (Fig. 2b). It consisted of three distinct zones: the lowest zone, the

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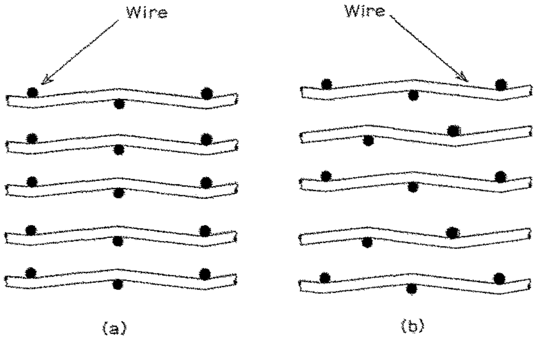

Fig. 1. Modes of stacking metal grids: (a) exact superposition, (b) alternate superposition.

calming zone, contained a fixed bed of glass beads (2 mm diam.); the middle zone contained the working fluidized bed electrode; and the upper zone, which was of a larger diameter (55 mm), contained the platinum counter-electrode. The bed electrode had three glass Luggin capillaries, placed at various heights (I = 0 mm, II = 10 mm, III = 20 mm), to measure the local solution potential. Each capillary was connected to a (Hg/Hg_2Cl_2/sat. KCl) reference electrode. The Luggins formed a bundle in the middle of the cell. When a two-dimensional feeder was used, this was placed at the bottom of the fluidized bed and two copper wires 1 cm long were horizontally inserted into the bed electrode at different heights (I = 10 mm, II = 20 mm), in order to measure its potential at these various heights.

3.3. *Working electrode and feeders*

The working electrode used was a fluidized bed electrode, measuring 34 mm in diameter and 10 mm in height. Particles were approximately spherical, 300–500 m in diameter, and made of copper (purity 99.8%). Their total weight was 52 g. The same quantity of particles was used for all experimental runs. The total surface area of the particles was approximately 875 cm^2.

Two types of feeder were used: two-dimensional and three-dimensional. The two-dimensional feeder was a circular platinum grid (wire diameter 0.1 mm, mesh 0.5 mm) placed on the bottom of the fluidized bed. The three-dimensional feeder consisted of stacks of copper spirals. Each spiral (Fig. 3) had a diameter of 33 mm, a height of 1.5 mm, and a thickness of 0.15 mm. The equation for the spiral in polar coordinates was:

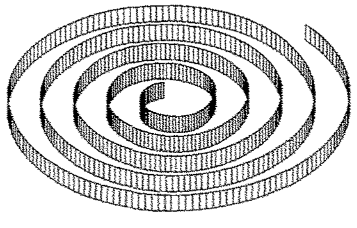

Fig. 3. Copper spiral used as feeder.

$$\rho = \frac{1.5}{\pi}\phi \qquad 4.20 < \phi < 34.50 \qquad (1)$$

where ρ is the radius in mm and ϕ is the angle in radians.

The surface of the feeder was much smaller than that of the particles, being about 2% of the total particle surface area. The whole of the three-dimensional feeder was immersed in the fluidized bed.

This form of three-dimensional feeder is probably not optimal, but is very easy to construct, and so is quite adequate for the purposes of an initial comparison between two and three-dimensional feeders.

3.4. *Conditions*

The experiments were carried out in a 1 g l^{-1} $CuSO_4$, 0.5 M H_2SO_4 solution at atmospheric pressure and at a temperature of 23° C. The electrolyte had a volume of 4 l, and its (superficial) velocity in the empty cell varied between 1 and 6 cm s^{-1}, corresponding to bed expansions of between 20 and 130%. The copper particles were cleaned with diluted HCl and H_2SO_4 before each experimental run.

The current density range was 0.15–0.80 k A m^{-2} for the two-dimensional, and 0.15–5.10 k A m^{-2} for the three-dimensional feeder. The current density was calculated on the basis of the bed cross-section. Each experiment was carried out at a fixed potential, whose value was established in relation to the reference electrode placed at the bottom of the expanded bed.

The current efficiency of the deposition process was obtained by circulating a known volume of electrolyte (4 l) from a reservoir through the cell. Samples taken at the beginning and at the end of the process were

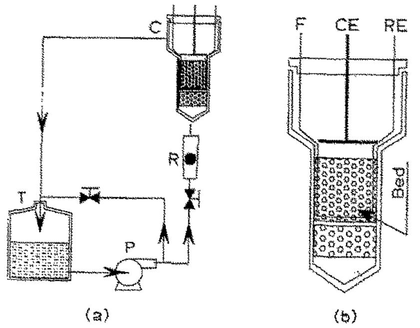

Fig. 2. Flow circuit and cell (C: cell, R: rotameter. T: tank, P: pump, F: feeder, CE: counter-electrode, RE: reference-electrode).

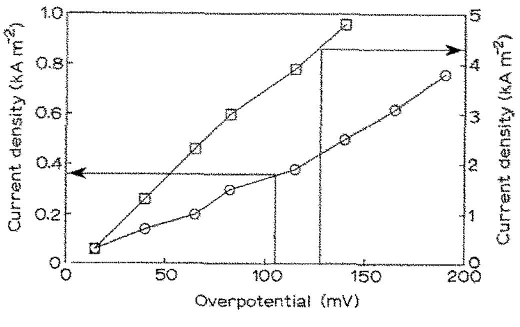

Fig. 4. Current density against overpotential for (○) two- and (□) three-dimensional feeders (Electrolyte velocity: 2.14 cm s^{-1}).

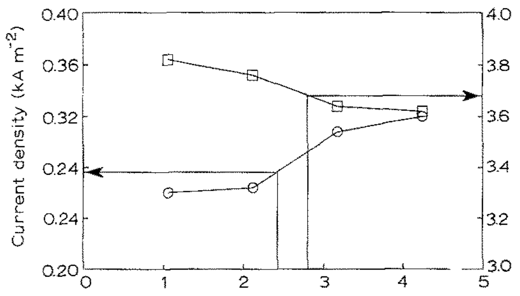

Fig. 5. Current density vs electrolyte velocity for (○) two- and (□) three-dimensional feeders (Overpotential: 90 mV).

analysed electrogravimetrically to determine their copper-ion content. Only a small quantity of copper was recovered (about 10%) in order to obtain a current efficiency for near constant concentration conditions.

4. Results

Figure 4 shows the current density against the overpotential for two- and three-dimensional feeders. The overpotential was calculated as the difference between the current and the equilibrium cathode potential. It was measured using the bottom Luggin in the bed (I = 0 mm) and the feeder.

The electrolyte velocity vs the current density for two- and three-dimensional feeders is shown in Fig. 5. It may be seen that the effect of velocity on the current density is opposite for the two cases. The fact that with the three-dimensional feeder the current density decreases as the velocity rises is probably due to the high degree of expansion in the bed, which reduces the area in contact with the feeder. The slight increase of current vs velocity with the two-dimensional feeder is probably due to the fact that the increase in mass-transfer rate is more effective than the reduction of the deposition rate.

In the case of the two-dimensional feeder and for various electrolyte velocities, the potential drop was measured in the bed electrode, by inserting the two copper wire probes at a height of 10 and 20 mm respectively from the bottom of the bed. The results are shown in Fig. 6.

Figure 7 shows the current efficiency vs the overpotential at near constant concentration conditions ($CuSO_4$ 1 g l^{-1}, H_2SO_4 0.5 M) and at constant electrolyte velocity (2.14 cm s^{-1}). The decrease in efficiency for the higher overpotential values is due to the production of hydrogen.

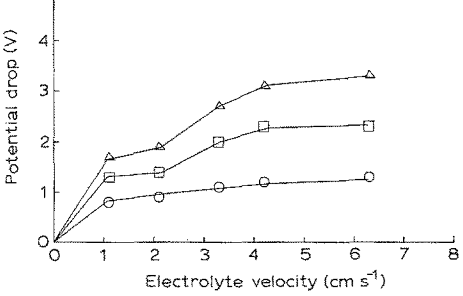

Fig. 6. Potential drop at the high respectively of 10 and 20 mm from the bottom of the bed, in fluidized bed electrode against electrolyte velocity for two-dimensional feeder. (△) 2.97, (□) 1.98, (○) 0.99 kA m^{-2}.

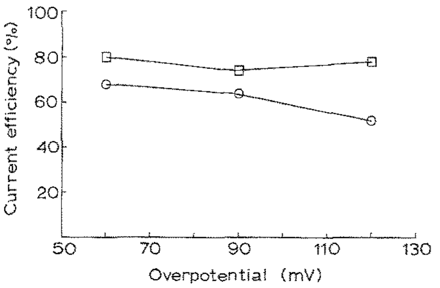

Fig. 7. Current efficiency against overpotential for (○) two- and (□) three-dimensional feeders (Electrolyte velocity: 2.14 cm s^{-1}).

5. Discussion and conclusions

The achievable current density, obtained using, respectively, a two- and a three-dimensional feeder, and under otherwise equal fluid-dynamic, overpotential and concentration conditions, was about five times higher for the latter than for the former.

Although only a limited number of experimental runs have so far been performed, these would seem to show that the three-dimensional feeder also brings about an increase in the current efficiency.

The recovery of copper-ions was kept to a minimum, in order to maintain near constant current efficiency conditions. No agglomeration phenomenon was observed for these low recovery conditions.

Further experimental work, aiming to clarify the efficiency and agglomeration phenomenon of fluidized bed electrodes and to determine the optimal type of three-dimensional feeder, is currently in progress.

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