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A particulate vortex bed cell for electrowinning: operational modes and current efficiency

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The process of electrowinning of copper ions from dilute solutions has been used as a model system to assess the performance of a vortex bed cell with a three-dimensional cathode of conducting particles. Experiments were carried out under three conditions: with constant cell voltage, with constant cell current throughout the process and with exponential decrease of the operating current with time in order to underfollow the limiting current. Results from a batch recirculating system indicate that exponential decrease of operating current with time effects an improvement in current efficiency over a wide range of concentration.

Nomenclature

$a = \dfrac{6(1-\epsilon)}{d_p}$	specific surface area of particles (cm^{-1})
C, C_i	concentration of Cu^{2+} ions at the moment t, and initial concentration, respectively (M)
d_p	particle diameter (cm)
F	Faraday number (96 487 $A\,s\,mol^{-1}$)
i	current density ($A\,m^{-2}$) (calculated for the surface area of the particles)
i_{av}	average current density obtained in the constant cell voltage process ($A\,m^{-2}$)
$I_L(t), I_{L,0}$	limiting current at time t, and initial limiting current, respectively (A)
k_L	mass transfer coefficient ($cm\,s^{-1}$)
n	number of electrons transferred in the process
Q	volumetric flow rate ($dm^3\,s^{-1}$)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
t	time (s)
T	temperature (K)
U	cell voltage (V)
V	volume of electrolyte (cm^3)
V_0	volume of particles (cm^3)
η	overpotential (V)
η_e	current efficiency
ϵ, ϵ_0	bed porosity and porosity of the fixed bed, respectively
$\tau = V/Q$	residence time (s)
$\left.\begin{array}{l}\phi = \\ \alpha = \end{array}\right\}$	see Fig. 2

1. Introduction

One of the key factors in electrowinning of metallic ions from dilute solutions using a cell with a three-dimensional cathode is the current efficiency. Current efficiency depends on several parameters such as cell geometry, current density and concentration of reacting ions. For a cell of fixed geometry current efficiency for fixed concentration depends only upon operating conditions, especially the manner in which operating current or voltage are controlled.

In the case of a batch recirculating system the concentration of the reacting ionic species depletes with time [1–6], and since electrowinning processes are usually operated under constant current conditions, the current efficiency decreases with time as the metal concentration becomes increasingly small. This decrease of current efficiency is particularly significant for the concentrations less than about 0.5 g l^{-1} [2, 6, 7].

The magnitude of the current density used in an electrowinning process may have two opposing effects on current efficiency. Some investigators have concluded that current efficiency decreases with increasing current density [1, 2, 8], whereas others affirm the opposite [7]. Such contradictions may be a consequence of the applied current range used during the particular investigation. At lower current densities, i.e. lower electrode potentials, some of the deposited metal may redissolve in certain zones of the cell with a resultant lowering of current efficiency. At higher applied current densities hydrogen evolution may occur as a secondary reaction again causing a decrease in current efficiency. In recent experiments over a wide range of current densities, current efficiency was found to pass through a maximum with an increase of current density [6]. A basic requirement leading to improved current efficiency in cells with three-dimensional electrodes is the avoidance of both hydrogen evolution and metal redissolution even though metal ion concentrations may fall to low values.

The evolution of particulate and fluidized electrodes has led to recent studies of cells involving, for example, a tumbled bed [9], a moving bed [10] and a circulating bed with varying inclination [11]. The present work involves the use of a vortex bed cell.

2. Theoretical considerations

An exponential change of current with time occurs for a batch recirculating system operating throughout at limiting current as described by the following equations:

For a plug flow cell [5, 7]

$$I_{\mathrm{L}}(t) = nFQC_i\left\{1-\exp\left[-\frac{k_{\mathrm{L}}aV_0(1-\epsilon_0)}{(1-\epsilon)Q}\right]\right\} \times \exp\left(-\frac{t}{\tau}\left\{1-\exp\left[-\frac{k_{\mathrm{L}}aV_0(1-\epsilon_0)}{(1-\epsilon)Q}\right]\right\}\right) \tag{1}$$

and for a back-mixed cell [5]

$$I_{\mathrm{L}}(t) = nFQC_i\ln\left[1+\frac{k_{\mathrm{L}}aV_0(1-\epsilon_0)}{(1-\epsilon)Q}\right] \times \exp\left\{-\frac{t}{\tau}\left[1-\frac{1}{1+\dfrac{k_{\mathrm{L}}aV_0(1-\epsilon_0)}{(1-\epsilon)Q}}\right]\right\} \tag{2}$$

These equations are written in terms of V_0 rather than length of electrode due to the complex geometry of the cell. Assuming that fluid physical properties, particle size and mass transfer coefficient remain constant these equations may be reduced to the form

$$I_{\mathrm{L}}(t) = be^{-mt} \tag{3}$$

In a process with constant operating current (Fig. 1) the limiting current falls linearly with time until at point A it commences to fall exponentially following Equation 3. Up to Point A, when $I_{\mathrm{L}} > I$, the current efficiency defined for a Faradaic process by the equation

$$\eta_{\mathrm{e}} = \frac{V(C_i - C)nF}{It} \tag{4}$$

is usually satisfactory. When the limiting current falls below the operating current, i.e. $I_{\mathrm{L}} < I$, hydrogen evolution commences and current efficiency falls.

For diffusion controlled electrochemical reactions the concentration polarization can be expressed as

$$I = I_{\mathrm{L}}\left[1-\exp\left(-\frac{nF}{RT}\eta\right)\right] \tag{5}$$

For the case of constant operating current, as I_{L} decreases with time, overvoltage and hence total cell voltage increase during the process [12]. When

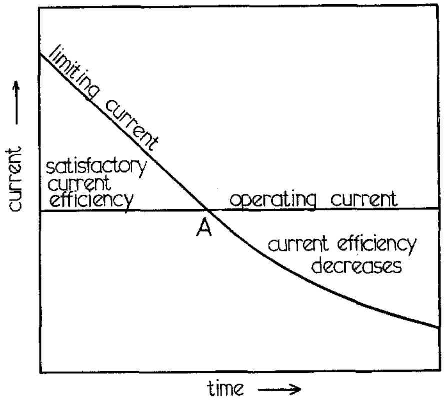

Fig. 1. Schematic representation of limiting current and constant operating current behaviour.

hydrogen evolution commences the cell voltage increases markedly to overcome the additional overpotential terms associated with this secondary process. An alternative method of operation which avoids hydrogen evolution and maintains a high current efficiency is to vary the operating current with time in a manner similar to the rate of change of the limiting current. This method could be especially useful for discontinuous electrowinning processes [13, 14].

3. Experimental details

All experiments were carried out using a cell with a vortex bed of conducting particles as a three-dimensional cathode [6, 15]. No presuppositions have been made as to the cell geometry in the theoretical considerations of this problem, so that for testing the present approach any form of three-dimensional cell could be used.

3.1. *The vortex bed cell*

The vortex bed cell, shown schematically in Fig. 2, was separated by a diaphragm into anodic and cathodic compartments of widths 1.5 and 2.5 cm, respectively. The glass cell had dimensions of 4 cm x 5 cm x 20 cm. Vortex motion of the particles was achieved by introduction of the electrolyte into the bed compartment through a slot of variable width at the cell base. This vortex motion of the particles is illustrated by the photograph of Fig. 3.

In the part of the bed where particles move downwards bed porosity is close to the porosity of the packed bed [16]. This part of the bed accounts for about 66–75% of the whole, though the entry slot dimensions have a marked influence on this value as well as the general hydrodynamics of the bed.

3.2. *Electrolyte*

Catholyte was pumped from the reservoir into the cathodic compartment of the cell and was returned from the top of the cell by gravitational recycle to the reservoir. Flow rate was measured by means of a rotameter and a similar circuit existed on the anolyte side. In all experiments a solution of copper sulphate with an initial concentration of 0.0157 M ($\approx 1\,g\,l^{-1}$) was used as catholyte. The supporting electrolyte was 0.5 M H_2SO_4, the total catholyte volume being 2 dm^3. The concentration of Cu^{2+} ions was monitored by atomic absorption spectrophotometry. 0.5 M H_2SO_4 was used as anolyte.

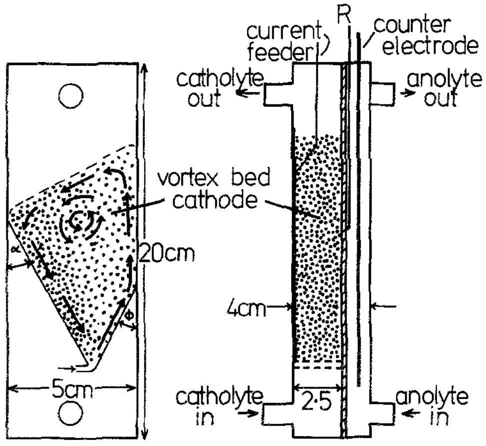

Fig. 2. Schematic view of the vortex bed cell with conducting particles. Internal dimensions in cm. $\phi = 30°$: $\alpha = 20–25°$.

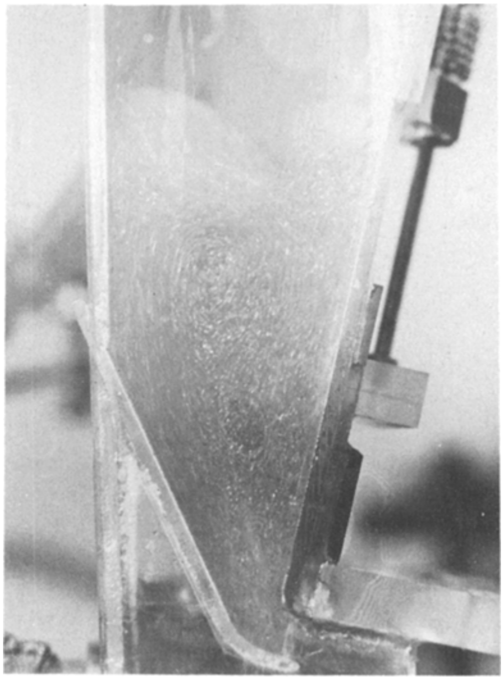

Fig. 3. Photograph of the particle flow pattern in the vortex bed.

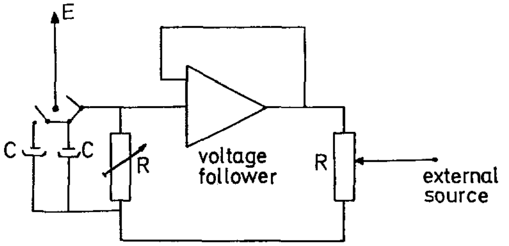

Fig. 4. Augmentation to function generator for exponentially varying current output.

3.3. *Electrodes and instruments*

The vortex bed consisted of spherical copper particles in the size range 0.5–0.63 mm (mean diameter 0.52 mm) with a specific surface area of 64 cm^{-1}. The volume of particles used (as a fixed bed) was 30 cm^3. Copper sheet served as a cathode feeder electrode and for the anode a lead plate was used. The electrode configuration was side-by-side, so that current flow was perpendicular to the electrolyte flow [17].

An Amel 10 A-20 V Model 555B potentiostat/galvanostat served as the power source. It was connected by means of an interface unit (Amel Model 560) with a recorder (Amel Model 802D). To obtain an exponential decrease of operating current with time according to Equation 3 a function generator was augmented by the circuit depicted in Fig. 4.

4. Results

Three series of experiments were carried out. The first series was under potentiostatic conditions and changes of both current and Cu^{2+} concentration were monitored with time. The second series was carried out under galvanostatic conditions at the current corresponding to the average current obtained under potentiostatic conditions. In the third series the operating current was continuously decreased with time so as to follow the limiting current as described by Equation 3 but lie somewhat below it. Integral currents were equal to those obtained under galvanostatic conditions.

4.1. *Potentiostatic and galvanostatic operations*

The change of operating current with time when the electrowinning occurred under potentiostatic conditions is shown in Fig. 5 (Curve 1). After an initial period the current is seen to fall steadily with time in the expected manner. Fig. 5 (Curve 2) also shows the change of cell voltage with time for galvanostatic operation. The voltage is seen to increase steadily after a certain time due to the limiting current being exceeded and the resultant onset of hydrogen evolution.

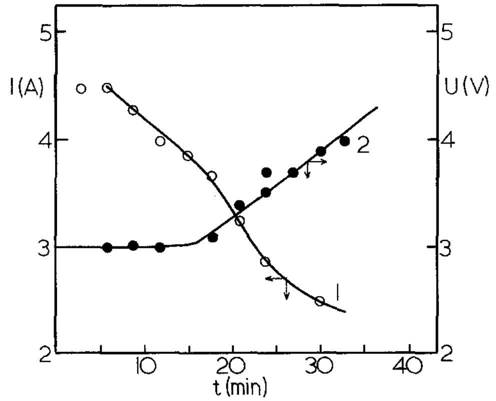

Fig. 5. Variation of current and cell voltage with time, with: 1. constant cell voltage, $U = 3.5$ V, $I_{av} = 3.55$ A; 2. constant current during process, $I = 3.55$ A.

The decrease of copper ion concentration with time for different averaged currents under potentiostatic conditions is presented in Fig. 6, and Fig. 7 presents similar results obtained under galvanostatic conditions. Comparison is made in Fig. 8 of the depletion rate achieved by the two different modes of operation for a single current

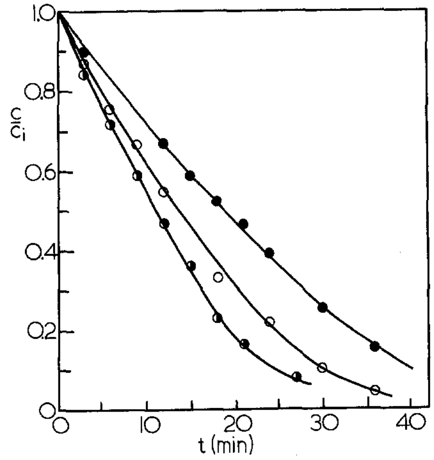

Fig. 6. Decrease of Cu^{2+} concentration with time at constant cell voltage for different average current densities: ● – 18.5 A m^{-2}; ○ – 22 A m^{-2}; ◑ – 33 A m^{-2}.

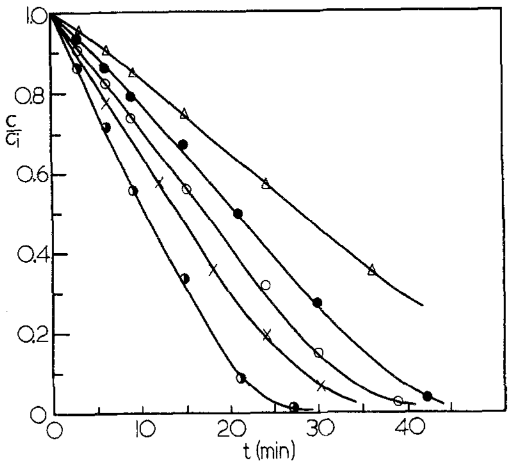

Fig. 7. Decrease of Cu^{2+} concentration for different current densities under galvanostatic conditions: △ – $15\ \mathrm{A\,m^{-2}}$; ● – $18.5\ \mathrm{A\,m^{-2}}$; ○ – $22\ \mathrm{A\,m^{-2}}$; × – $24\ \mathrm{A\,m^{-2}}$; ◐ – $26\ \mathrm{A\,m^{-2}}$.

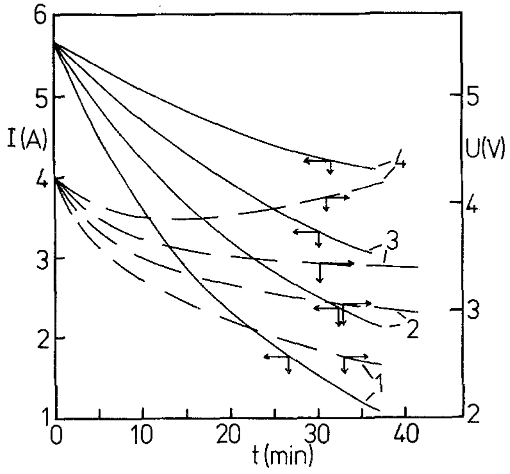

Fig. 9. Change of operating current (——) and cell voltage (– – –) with time for different values of m ($\mathrm{min^{-1}}$) (Equation 3): 1. 4.44×10^{-2}; 2. 2.6×10^{-2}; 3. 1.67×10^{-2}; 4. 0.92×10^{-2}; $i_0 = 29.5\ \mathrm{A\,m^{-2}}$.

density where it is seen that depletion is faster under potentiostatic conditions for the same averaged currents.

4.2. *Decreasing current operation*

In this series of experiments the operating current was decreased with time as suggested by Equation 3. In Fig. 9 the exponential change of operating current during the process is plotted for different values of the exponential factor m. (These curves are smoothed reproductions of recorder traces.) In the same figure corresponding curves of cell voltage are presented. For the lowest value of m (Curve 4) cell voltage passed through a minimum, prior to an increase caused by the onset of hydrogen evolution. The corresponding curves showing change of dimensionless concentration of Cu^{2+} with time for different rates of operating current decrease are given in Fig. 10. It should be noted that for higher values of m (faster decrease of operating current) the reaction approaches equilibrium after some time and redissolution of metal may lead to an increase in the concentration of metal ion. Thus the rate of decrease of operat-

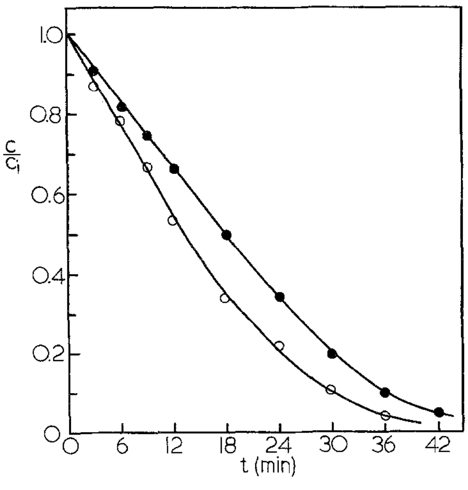

Fig. 8. Depletion of Cu^{2+} concentration with time obtained under: ● – galvanostatic conditions; ○ – potentiostatic conditions; $i = i_{av} = 22\ \mathrm{A\,m^{-2}}$.

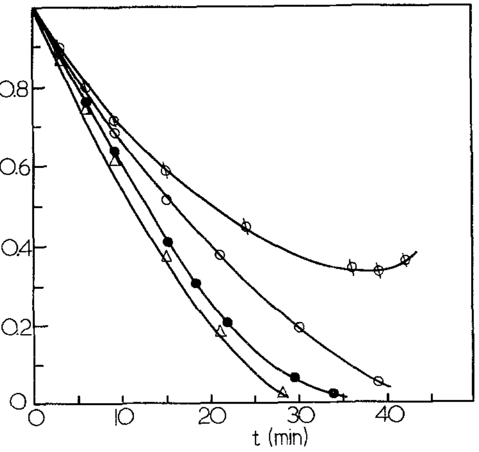

Fig. 10. Plot of copper concentration change against time, for the case of exponential decreasing current with time: $i_0 = 29.5\ \mathrm{A\,m^{-2}}$. m values ($\mathrm{min^{-1}}$) are: ϕ – 4.44×10^{-2}; ○ – 2.6×10^{-2}; ● – 1.67×10^{-2}; △ – 0.92×10^{-2}.

ing current during the process is limited by two factors:

i. too fast a decrease of operating current results in redissolution of deposited metal

ii. too slow a decrease of current leads to the simultaneous evolution of hydrogen as a secondary reaction with a resultant voltage penalty

Further, the initial current should be close to the value of the initial limiting current for the given hydrodynamic, geometric and concentration condition, and the current decrease should follow the course of the limiting current behaviour with time.

For a given bed and electrolyte and hydrodynamic conditions, it is possible to determine the values of the pre-exponential factor $I_{L,0}$ or b and the exponential factor m in Equation 3. For example, with experimental conditions:

$$Q = 35\,\text{cm}^3\,\text{s}^{-1}$$
$$\epsilon = 0.45$$
$$k_L = 1.7 \times 10^{-3}\,\text{cm}\,\text{s}^{-1}$$
$$V_0 = 30\,\text{cm}^3$$
$$V = 2 \times 10^3\,\text{cm}^3$$
$$a = 64\,\text{cm}^{-1}$$
$$C_i = 0.0157\,\text{M}$$
$$\epsilon_0 = 0.39 \text{ (measured value)}$$

the calculated values of b and m are 10.44 A and 0.09 min^{-1}, respectively.

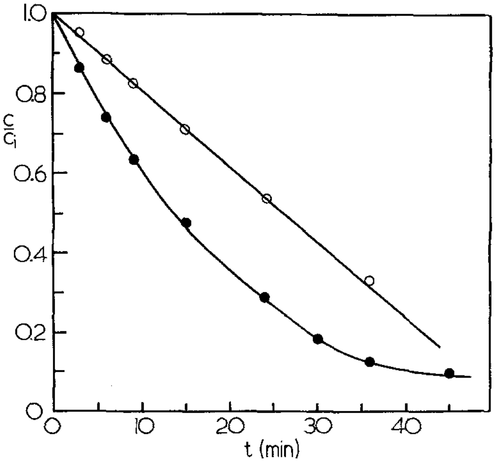

Fig. 11. Depletion of copper concentration with time obtained under: ○ – galvanostatic conditions (i = 18.5 A m^{-2}); ● – decreasing current with time (i_0 = 36.5 A m^{-2}); $m = 9.0 \times 10^{-2}\,\text{min}^{-1}$.

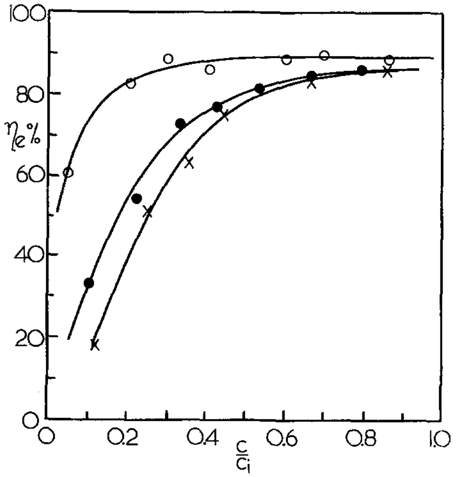

Fig. 12. Current efficiency against C/C_i for: × – constant operating current; ● – constant cell voltage; ○ – decrease of current with time in accordance with Equation 6.

Using an exponential current decay of the form

$$I(t) = 7 \exp(-0.09t) \qquad (6)$$

initial current being somewhat lower than that calculated above ($\approx 0.67 I_{L,0}$), a plot of Cu^{2+} concentration against time is presented as Fig. 11 along with a curve obtained under galvanostatic conditions for comparison.

4.3. *Current efficiency*

Current efficiency, defined by Equation 4, is plotted against dimensionless concentration of reacting ions in Fig. 12 for all three modes of operation. The upper curve was obtained with decreasing current operation according to Equation 6. It is clear that for this mode of operation current efficiency remains high (above 80%) up to extraction efficiencies of 80–90%.

5. Conclusion

The vortex bed of conducting particles may be used as a three-dimensional-cathode electrochemical reactor for metal winning from dilute solutions. Comparison of galvanostatic, potentiostatic and exponential current decrease modes of operation in a batch recirculating system confirmed that the latter mode is advantageous in conserving high current efficiency down to low metal ion concentrations.

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