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The performance of a forced-flow parallel plate electrochemical reactor with dilute solutions

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Experimental data relating to the performance of a fast flow parallel plate electrochemical reactor are reported, using very dilute reactant solutions. The results are shown to conform to the Chilton–Colburn analogy. The significance of such reactors, in terms of both electrochemical processing and treatment of dilute aqueous effluents, is discussed.

1. Introduction

In recent years, we have seen a spate of novel designs for electrochemical reactors. There have been the fluidized bed, the restrained bed, the slurry reactor, the wiped electrode, the porous flow-through electrode, the rotating electrode and the bipolar bed, to name the main contenders. The main aims behind these designs, which are further discussed and listed in reference [1], have been, firstly to increase the surface area of the electrode per unit volume, and secondly to ameliorate the mass-transfer problems, especially with dilute solutions, or solutions of poorly soluble compounds. Such problems arise in the treatment of industrial and other effluents, and in some potentially useful electro-organic reactions leading to industrially valuable products. The idea that a very simple parallel plate reactor might offer advantages comparable to those put forward for the sophisticated cell designs cited above, provided that the mass-transfer was improved by forced flow, was advanced by one of the present authors [2] in a previous publication, while the 'capillary-gap' cell, also discussed in reference [1], is a similar approach to the problem.

In this work, a thorough study of the performance of this type of cell, using dilute reactant solutions, is reported. The test reaction was the electrochemical deposition of copper(II) ions from an aqueous sulphuric acid solution. With hindsight, while it can be seen that the results amply suffice to show that this is a system which should be further pursued, the test reaction suffers from shortcomings, which will be discussed later. Further work is in progress using other test reactions, which will obviate the problems encountered here. The cell design (described below) was not one in which hydrodynamic effects were rigorously anticipated and the diffusion layer profile will not have been fully developed by the time the electrodes were reached. On the other hand, protuberances on the electrode, either accidental or designed, create fresh turbulence and it is probable that the aim to acheive a fully-developed diffusion layer profile by the time the flow passed the electrodes is not a realistic one.

2. Experimental

2.1. *Analytical procedure*

Stock solutions of 1N sulphuric acid were made up from Analar sulphuric acid and distilled water. Cupric sulphate was added bringing the level of this to 100 ppm Cu^{2+}. Analyses of Cu^{2+} were made using a colorimetric method. For this, 5 ml samples were withdrawn, and 1 ml of diethyldithiocarbamate solution (1% in water) was added to form the coloured complex. This was triply extracted with CCl_4 solutions, which were then used in the spectrophotometer. Calibrations were carried out using previously made up solutions of known Cu^{2+} concentration. The zero was set using the procedure above but omitting to add copper salts at any stage. The method gave straight-line plots of copper concentration vs. optical density.

2.2. *Apparatus*

The stock solutions, which were always of 4000 ml total volume, were held in a polyethylene reservoir and circulated from this through the cell, using a Charles Austen pump, which had a polypropylene impeller and a polypropylene casing. All work was done at ambient temperatures. The cell was machined from three pieces of Perspex. One block held the anode, a second the cathode, while a third sheet served as a spacer to hold the two apart and so contained the electrolyte. The electrodes (Pb anode, Cu cathode) were recessed into the Perspex blocks thus providing a flush surface for the flow. They, measured 10 × 10 cm. Outside each electrode was a 2 cm track, thus minimizing turbulence from the walls of the inter-electrode spacer. Above each electrode, a similar 2 cm smooth surface existed. Above and below these, in turn, was an entrance chamber, machined from the thickness of the Perspex blocks. The chamber extended the full width of the cell, and measured 1 cm deep and 2 cm high. In the assembled form, the chambers faced one another, creating a single space 2·8 × 2 × 14 cm. These chambers were fed and exhausted with a triple pipe manifold, each pipe being 0·75 cm i.d. The cell is shown in Fig. 10.

Initial experiments were carried out with 0·7 cm interelectrode gaps. This was subsequently halved. Electric power was supplied from a Farnell 2 A stabilized d.c. source, and currents were set using the meter on this instrument, which was first calibrated against a Sangamo Weston S 82 ammeter. Voltages could be read on the Farnell meter.

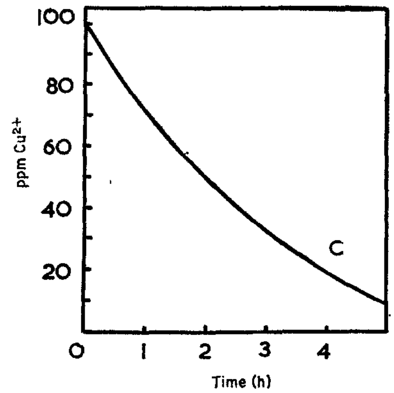
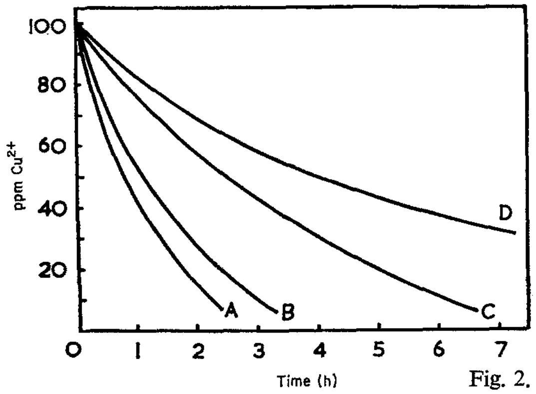


Fig. 1.



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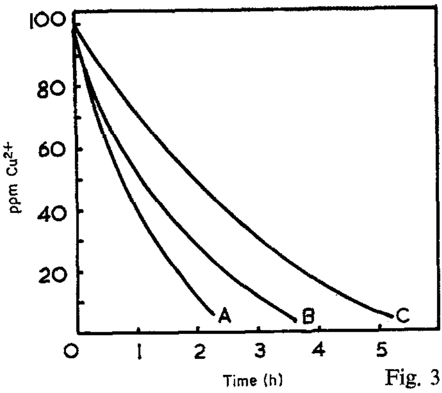

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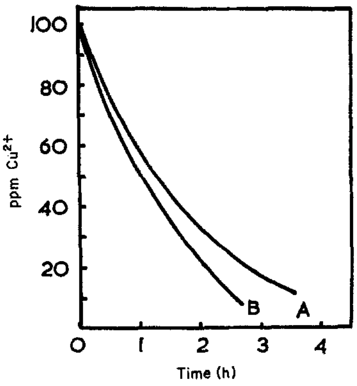
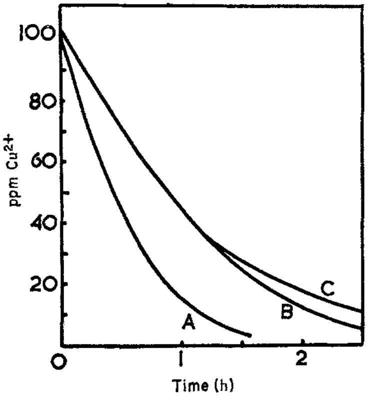


Fig. 4.

Figs. 1–4. Removal of Cu(II) ions as a function of time (hours). Electrode gap—7 mm. Flow rates: A = 24·8, B = 15·8 C = 7·8; D = 1·7 cm . s^{-1}. Fig. 1. 2 Adm^{-2}; Fig. 2. 1 Adm^{-2}; Fig. 3. 0·5 Adm^{-2}; Fig. 4. 0·25 Adm^{-2}.

3. Results

The results of the runs at various flow-rates and current-densities, with two different cell pitches are shown in Figs. 1–9. All data are based on the information in the Table, and each 'run' here is in fact the mean of two, or sometimes three, individual experiments. Efficiencies quoted are Faradaic efficiencies, that is to say the fraction of the current going to copper deposition, as opposed to hydrogen evolution. These were the competitive cathode reactions, while oxygen was evolved at the anode.



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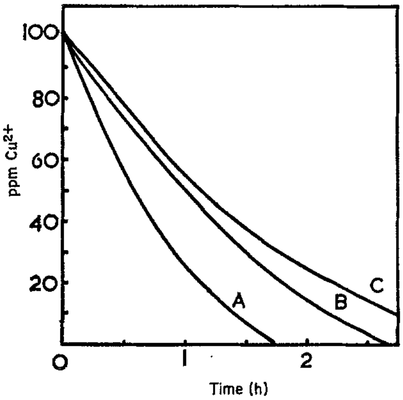

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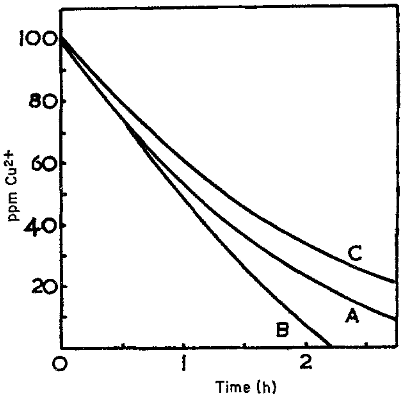

Fig. 7.

Figs. 5–7. As in Figs 1–4, with 3·5 mm electrode gap. Flow rates: A = 47·3, B = 37·7, C = 18·4 cm . sec^{-1}. Fig. 5. 1 Adm^{-2}; Fig. 6. 0·5Adm^{-2}; Fig. 7. 0·25 Adm^{-2}.

4. Discussion

4.1. *General*

The copper was deposited on the cathode, partly as a fine friable dark red powder, partly as a nodular growth. This bears discussion in a number of contexts. The effect of the nodular growths on the hydrodynamics was particularly pronounced, as might be expected, in runs with the smallest inter-electrode gap. There is no doubt that enhanced turbulence occurred as a result of these excrescences and the effect was seen in a systematic deviation of otherwise straight log k plots at low Cu^{2+} concentrations and long times. Secondly, it is known that the physical nature of copper deposits can be profoundly changed by the nature of the substrate. Recent work done by Imperial Metal Industries has shown [3] that Ti sheet substrates can promote smooth deposits of metallic copper under a variety of deposition conditions. From the quoted efficiencies, it can be seen that economically efficient copper recovery is possible using a cell of this type, at copper concentrations down to 20 ppm or so. Such results may be compared with similar data—but obtained using fluidized bed electrodes—cited in reference [4]. It will be seen that not only on the basis of current efficiency, but also on grounds of space-utilization, the forced flow cell compares well with others. One feature of the curves is the reversal of efficiencies, etc., at the lowest current densities 0·25 A, i.e. 2·5 mA cm^{-2}. This apparently anomalous situation may in fact be explained in terms of the more anodic potential which obtains at these low current densities, which do not drive the electrode so strongly in a cathodic direction. At these potentials, the process of copper deposition is challenged by one in which Cu_2O is an intermediate. The problems arising from this species were well known to early users of copper coulometers. Formation of Cu(I)

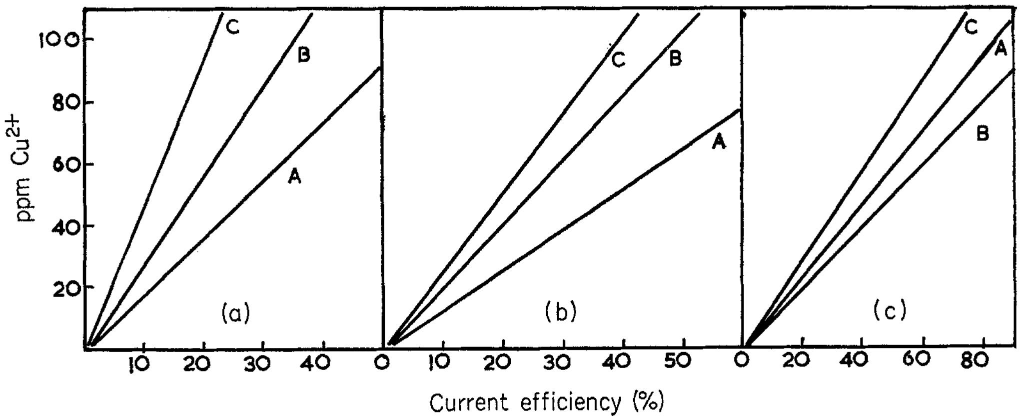

Fig. 8.

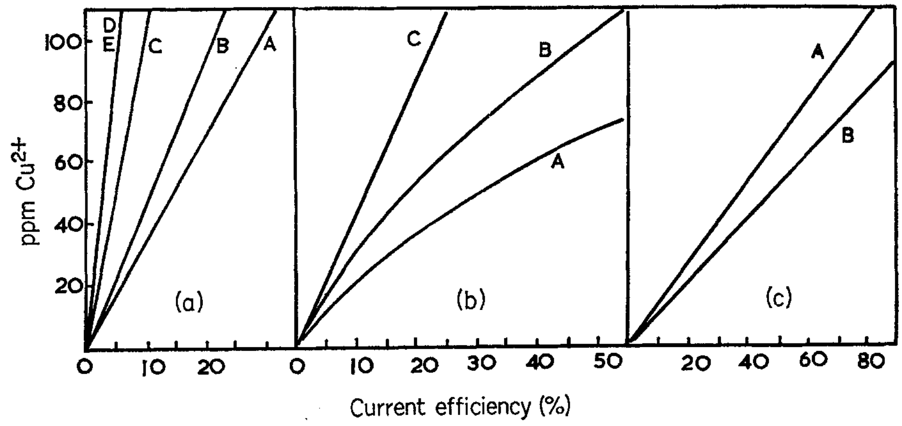

Fig. 9.

Figs. 8–9. Copper recovery expressed in terms of current efficiency (%). Fig. 8. 7 mm electrode gap, (a) at 1 Adm^{-2}(with E at 2 Adm^{-2}); (b) 0·5 Adm^{-2}; (c) 0·25 Adm^{-2}; Flow rates as in corresponding Figs. 1–4 above. Fig. 9. 3·5 mm electrode gap. Current densities as above, flow rates as in Figs. 5–7.

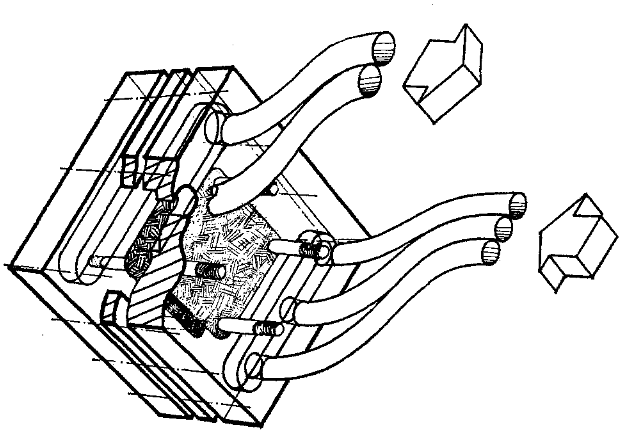

Fig. 10. Diagram of cell showing inlet and outlet manifolds, spacer, electrode and connections.

species predictably leads to loss of efficiency as shown.

4.2. *Hydrodynamic analysis*

While, as previously stated, it is not claimed that the cell design was completely rigorous from a hydrodynamic standpoint, it was nevertheless thought worthwhile to analyse the results in terms of familiar hydrodynamic concepts. It will be seen from such analyses to what extent they are justifiable.

Treating the reaction as mass-transport controlled, and thus first order, one may write:

$$\frac{-dC}{dt} = k_L\, A\, . \frac{[\mathrm{Cu}^{2+}]}{V} \qquad (1)$$

where $-dC/dt$ is the decrement of copper ion concentration with time, k_L is the mass transfer coefficient and V is the total volume of solution which, at any instant in time, will have the copper ion concentration $[\mathrm{Cu}^{2+}]$.

Plotting the data in Figs. 1–7 in logarithmic form, as indicated by the Equation (1) above (plots not shown), a series of straight lines result, the gradients of which (k) are quoted in Table 1. As previously stated, these deviate at longer times to high values of k_L, indicating that the nodular growths, which may be seen after the run on dismantling the cell, have a marked effect. Such nodules may approach 1 mm in height, and this, in the context of an overall 3·5 mm gap, will be appreciable, both as regards the added turbulence formed as well as the acceleration of linear flow velocity as a result of reduced slot cross-sectional area. The values of k tabulated in Table 1 must be corrected as shown to read directly in k_L values. This arises from calibration factors relating to the plots used. By plotting values of log k (or k_L) vs. log u, it can be shown that k = Const. $u^{0 \cdot 79}$ where u is the linear flow velocity (Fig. 11).

The plot, which is satisfactory for the 7 mm gaps, shows marked deviations for results with the narrower gap, although the linear velocities are comparable in many regions. Once again, this is attributed to enhancement as a result of modular growths.

Table 1. *Values of* k (*Equation*(1)) *vs.* u, *obtained from logarithmic plots based on Figs. 1–7 in the range* 100> (Cu^{+2})> 10 *ppm*

Run no.	*Flow* ($\mathrm{cm^3 s^{-1}}$)	*u* ($\mathrm{cm\ s^{-1}}$)	*I* ($\mathrm{A dm^{-2}}$)	*k*
1	60	6·75	0·5	−2·05
2	140	15·75	0·5	−3·55
3	220	24·75	0·5	−5·14
4	15	1·68	1·0	−0·94
5	60	6·75	1·0	−1·59
6	140	15·75	1·0	−3·57
7	220	24·75	1·0	−4·78
8	60	6·75	2·0	−1·88
9	140	15·75	0·25	−3·85
10	220	24·75	0·25	−3·12
11	65	18·41	0·25	−3·11
12	133	37·68	0·25	−3·85
13	210	47·25	0·25	−3·43
14	65	18·41	0·5	−3·12
15	133	37·68	0·5	−3·76
16	210	47·25	0·5	−7·00
17	65	18·41	1·0	−4·21
18	133	37·68	1·0	−4·56
19	210	47·25	1·0	−9·40

Each run is mean of 2 or 3 separate experiments
RUNS 1–10 = 7 mm gap
11–19 = 3·5 mm gap
(To convert k to k_L; k_L = 7·4 × k)

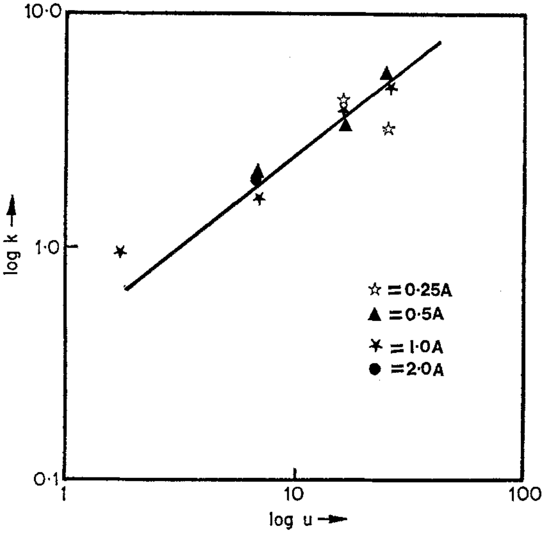

Fig. 11. Log k (Equation (1)) vs. log u (liquid flow velocity, cm . $\mathrm{s^{-1}}$). Results for 7 mm gap cell. Measured slope = 0·79. Current densities as shown.

4.3. *Flow regime obtaining during runs*

Using the formula:

$$\mathrm{Re} = \frac{d_e \,.\, u \,.\, \rho}{\mu}$$

where Re is the Reynolds number, d_e is the hydraulic mean diameter (4 × cross-sectional area, divided by wetted perimeter), u is the linear velocity and ρ is taken as 1 g . cm^{-3}, μ as 10^{-2} poise, the flow regime can be shown to be in the transitional region, ranging towards turbulent flow. Re numbers vary (with one exception) from 850 up to 3500 approximately, as calculated from above and using the data in Table 1.

4.4. *Comparison with theory*

To compare the results of the experimental work with theoretical predictions, use was made of the Chilton–Colburn analogy [5] which may be expressed as:

$$\frac{k_L}{u} \cdot \frac{P_{BM}}{\rho} \left(\frac{u}{\rho D}\right)^{0 \cdot 56} = 0 \cdot 023 \ \mathrm{Re}^{-0 \cdot 17}$$

where D is the diffusion coefficient.

Solving this for typical values of u, etc., obtained here, gave values of $1{\cdot}74 \times 10^{-3}$ cm . s^{-1} for k_L compared with achieved values of $7{\cdot}15 \times 10^{-3}$, under the same conditions. (In applying the equation, the back-pressure term (P_{BM}/ρ) was neglected.)

The enhancement factor of some 4 times may be interpreted in a number of ways.

(i) Defects of cell design including the use of right-angled flow entry, and the irregular flows consequent upon this.

(ii) The effect of the nodular 'boulders' of Cu formed at the cathode, which approached 1 mm in height. These would give rise to a straightforward increase of u values, and additionally would act as centres for breaking up the diffusion layer.

(iii) The hydrodynamic effect of gas bubbles formed from either the anodic or cathodic reactions. Little is known of the effect of such bubbles in electrochemical reactors. Ibl (6) studied enhancement of mass-transport by gassing at electrodes in an otherwise static solution. They found that:

$$k_L = \frac{D \,.\, V^{0 \cdot 5}}{1{\cdot}5 \,.\, 10^{-3}}$$

where D is the diffusion coefficient of the involved species, V is the volume of gas evolved in cm^3 . cm^{-2} . min^{-1}. The range of k_L values obtained by using values appropriate to the present work is some 10% of those actually observed. However owing to the pumped flow, the situation is hardly analogous. The authors have been informed that studies of heat transfer in boiling water nuclear reactors might produce solutions which could be transformed to cater for the present situation and this is being pursued.

5. Conclusions

It has been shown that a simple parallel plate force-flow electrochemical reactor is amenable to a quantitative treatment using the Chilton–Colburn equation. Furthermore, the results, in terms of efficiency or space-utilization, etc., bear comparison with more sophisticated cell designs which have been disclosed and studied in recent years.

Thus power densities of 15 A/dm^{-3} may be envisaged from the work quoted here. This can be compared with results quoted for the copper recovery reaction [4]. In addition, it is foreseen that this type of cell will be as valuable in handling anodic reactions which often take place in potential regions where passivation phenomena occur. Difficulties in this respect have been understood to beset 'bed' type reactors.

Studies will be pursued at the University of Salford along a number of lines. Firstly, work will be undertaken on anodic reactions, in particular the oxidation of cyanides, and aromatic species in dilute solutions. The work will be orientated both towards environmental technology and also to industrial processing. Secondly, a more detailed study will be made of mass-transfer processes, and of methods which may be used to enhance these.

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