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# *Metal deposition in diaphragmless fluidized-bed electrolytic cells*

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Cell voltage is an important parameter when considering the use of fluidized-bed cells for metal deposition. The present paper shows that it is possible to run these cells in the absence of a diaphragm separating the fluidized particles from the anode and, in consequence, cell voltages are greatly reduced. Although current efficiencies are somewhat lower with the diaphragmless cell, there is nevertheless a significant saving in energy consumption. Coupled with the resulting simplified cell design, this development could be of considerable practical importance.

## 1. Introduction

Using fluidized-bed cells for metal deposition places a premium on minimizing cell voltage. In the past, industrially useful cell configurations required a diaphragm to separate bed particles from the anode. Work in the authors' laboratories has shown [1] that under certain conditions it is possible to dispense with the diaphragm altogether and yet not encounter shorting of the bed between the two electrodes. The present paper describes briefly the performance of the fluidized-bed electrode under these conditions without attempting a mechanistic explanation of the phenomenon.

## 2. Experimental

The flow-by cell construction used (see Fig. 1) had a rectangular geometry with a cross-sectional area of 100 $cm^2$ and a bed width in the direction of current flow of 2.5 cm. Bed particles were spherical, 500–700 $\mu$m in diameter, and composed of the same material as that being plated.

Metal concentrations were determined either by titration or atomic absorption spectroscopy. All experiments were performed in a batchwise manner, the electrolyte being recirculated through the cell. The latter was run vertically to give a conventional fluidized-bed at expansions ranging

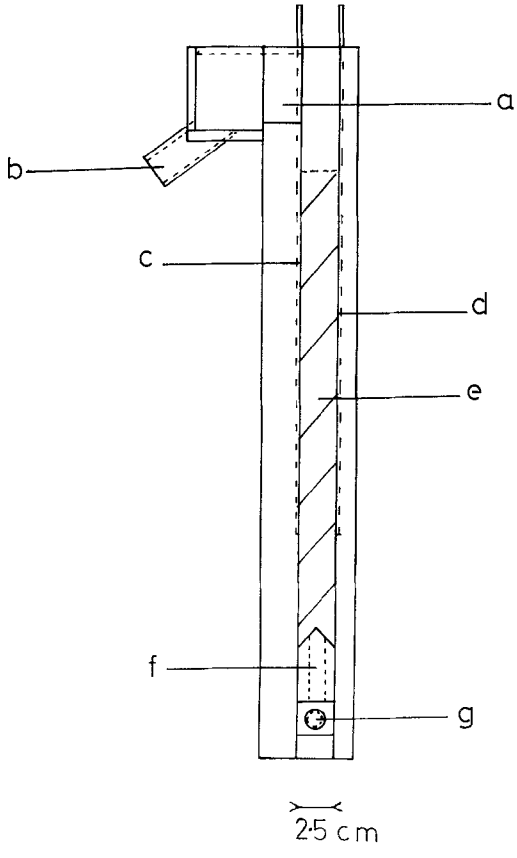


Fig. 1. The rectangular fluidized-bed cell. (a) Weir, (b) electrolyte outlet, (c) stainless steel cathode sheet, (d) anode sheet, (e) fluidized bed, (f) electrolyte distributor, (g) electrolyte inlet.

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*Table 1*

| *System* | *Metal deposited* | *Concentration range* ($g\ dm^{-3}$) | *Electrolyte* | *Anode material* |
|---|---|---|---|---|
| 1 | Cu | 4.0–0.3 | 1 M $H_2SO_4$ | $PbO_2$ on lead |
| 2 | Cu | 1.0–0.4 | pH3–1 | $PbO_2$ on mild steel |
| 3 | Ni | 63–59 | pH4–2 | $PbO_2$ on lead |
| 4 | Sn | 0.8–0.05 | 1 M $H_2SO_4$ | $PbO_2$ on lead |
| 5 | Sn | 0.3–0.05 | 1 M KOH | $RuO_2$ on titanium |
| 6 | Zn | 100–84 | 0.05 M $H_2SO_4$ | $PbO_2$ on lead |
| 7 | Zn | 2–0.2 | 2 M KOH | $RuO_2$ on titanium |

*Table 2*

| *System* | *Current density* ($kA\ m^{-2}$) | *Bed condition* | *Current efficiency* (%) | *Cell voltage* (V) |
|---|---|---|---|---|
| 1 | 3 | Fluidized† | 70 | 2.8 |
| | 6 | | 80 | 3.1 |
| | 10 | | 70 | 3.8 |
| 2 | 1.5 | | 11 | 4.2 |
| | 6 | | 8 | 6.6 |
| 3 | 6 | | 40 | 11.0 |
| 4 | 5 | | 30 | 4.0 |
| | 10 | | 30 | 4.6 |
| 5 | 6 | Spouting | 20 | 3.9 |
| 6 | 9 | | 80 | 5.1 |
| 7 | 3 | | 60 | 3.0 |
| | 6 | | 60 | 4.0 |

† Bed expansion was 30%.

from 10–50% or run at an angle of 20° from the vertical to produce a spouting fluidized bed [2].

## 3. Results and discussion

Table 1 gives a list of conditions under which the deposition of a number of metallic cations was investigated. Expansion of the bed and the nature of the anode had a critical effect on the current efficiencies obtained. Anodes tried included lead dioxide on lead or mild steel, $RuO_2$ on titanium, DSA and graphite. On the whole lead dioxide proved most effective in reducing by-pass currents due to shorting of the bed at the anode. $RuO_2$ on titanium gave reasonable current efficiencies in acid media (typically greater than 50%), although it corroded in alkaline solutions. With DSA considerable electronic shorting of the beds was experienced in acid solutions, but better results were obtained in alkaline media.

On the whole, fluidized and spouting beds (see Table 2) gave similar performances apart from the fact that for expansions above 20% the former exhibited some metal deposition on the feeder electrode. Current efficiencies for the fluidized bed decreased significantly with expansion of the bed. For example, for system 1 at 6 $kA\ m^{-2}$ current efficiency fell to below 30% at an expansion of 100%.

To appreciate the reduction in cell voltage, it must be noted that a typical value for copper deposition for a fluidized-bed cell with a diaphragm at say 3 $kA\ m^{-2}$ would be 4.8 V (current efficiency 95%) as against (Table 2) 2.8 V (current efficiency 70%) for the diaphragmless cell. In terms of energy yield these results correspond to 4.2 $kW\ h\ kg^{-1}$ and 3.4 $kW\ h\ kg^{-1}$ respectively. For zinc deposition at 6 $kA\ m^{-2}$ respective values would be 6 V (current efficiency 85%) and 5.1 V (Table 2) (current efficiency 80%) at a 50% higher current density, namely 9 $kA\ m^{-2}$ for the present cell. Respective energy yields are 5.8 $kW\ h\ kg^{-1}$ and 5.2 $kW\ h\ kg^{-1}$.

## 4. Conclusion

It is possible to obtain reasonable current efficiencies for fluidized-bed electrodes in the absence of a membrane separating the bed from the anode. This results in a considerable reduction of cell voltage and an increased simplicity of cell construction.

## References

[1] M. Fleischmann, F. Goodridge and C. J. Vance, British Patent 1513 259 (1978).
[2] F. Goodridge and C. J. Vance, *Electrochim. Acta* **23** (1977) 1073.