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Industrially Successful Cell Designs and Meaningful Optimization Procedures [and Discussion]

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ELECTROCHEMICAL ENGINEERING

Industrially successful cell designs and meaningful optimization procedures

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A number of designs, including filterpress-type cells, de Nora's Seachlor cell, Capenhurst's Chemelec cell, Nalco's packed bed cell and Akzo's fluidized-bed cell, are described briefly. An attempt is made to determine the reasons why these particular designs are finding application in industry. It is shown that each performs a necessary function with the minimum of complexity. Thus filterpress-type cells are relatively compact, and provided current densities are not too low will be the first choice where the electrodes do not change dimensions during the reaction. The Seachlor cell, by virtue of its particular bipolar electrode arrangement, controls pH and therefore minimizes any deposition of magnesium hydroxide during the production of hypochlorite from seawater. The Chemelec cell increases limiting currents for metal deposition in a relatively simple manner while the Nalco cell solves the problem of the participation of its lead anodes in the manufacture of lead tetraalkyls. The fluidized-bed electrode, with its high space time yield and the production of very pure metals, makes up for its more complex character. The paper shows why some of the alternatives to the above designs are less attractive to industry.

Having decided upon a particular design, the paper then discusses some erroneous ideas on optimization encountered occasionally in the literature. An example is given where the 'optimization' of the cell in isolation of its associated plant can result in a very misleading 'optimum'. It is demonstrated that failure to consider the process as a whole, right from its earliest stages of development in the research laboratory, can lead to severe problems when engineering of the process is eventually required.

INTRODUCTION

The last two decades have seen significant developments in electrolytic cells, partly by the application of chemical engineering principles to their design and partly by the development and use of new materials of construction. This has resulted in a trend away from the concept of an electrolytic cell as represented by a number of plate electrodes dipping into a rectangular tank and has led to the use of the so-called three-dimensional electrodes in the form of fixed (Goodridge & Hamilton 1980) and fluidized (Goodridge & Vance 1979) beds of electronically conducting particles in contact with a usually metallic plate, rod or gauze, termed the current feeder. As a result of these developments, electrolytic cells are now competitive with catalytic reactors in terms of space time yield, i.e. the amount of product produced per unit reactor volume in unit time.

It is my intention in this paper to review a number of cell designs that have found application in industrial practice and try to identify the reasons for their success. One of these designs will then be used to illustrate the dangers of 'optimizing' cell performance in isolation from the rest of the plant since interactions are almost invariably present in organic electrosynthesis.

Review of cell designs

Plate and frame cell

The cell most frequently employed in industrial organic electrochemical synthesis is the plate and frame or filterpress-type design. The reductive dimerization of acrylonitrile (Baizer 1973, pp. 936–939) to adiponitrile and the reduction of *o*-phthalic acid to $\Delta^{3,5}$-dihydrophthalic acid (Suter *et al.* 1972) are just two examples of large-scale industrial processes that use this type of cell. As shown in figure 1, anolyte and catholyte streams flow in parallel and are separated from each other by a diaphragm, often semipermeable in nature. Electrodes are normally linked in a bipolar manner. Over recent years, there has been a trend towards undivided cells, resulting in a simpler design, less maintenance and lower capital costs, at the possible expense of some loss of product at the counterelectrode.

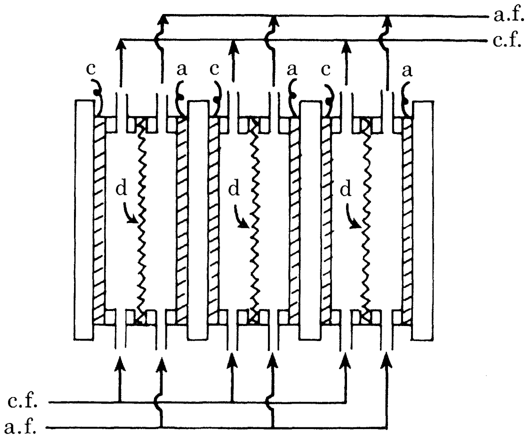

FIGURE 1. Schematic drawing of a plate and frame cell. c, cathode; a, anode; d, diaphragm; a.f., anolyte flow; c.f. catholyte flow.

There are two possible approaches towards the aim of achieving high mass transfer rates. One is to employ very high flow rates of electrolyte with a correspondingly large pressure drop. Alternatively, as shown in figure 2, one can use a system of baffles that produce flow reversal and hence high mass transfer rates at relatively lower flow rates. The disadvantage of the latter approach is the increased complexity of construction.

Seachlor cell

The Seachlor cell, shown schematically in figure 3, was designed by De Nora for the production of hypochlorite from seawater. It is an undivided cell with bipolar electrodes, and its most important feature is the flow of electrolyte through successive anodic and cathodic regions. In this way the design avoids the deposition of hydroxides on the cathode when the pH becomes too high.

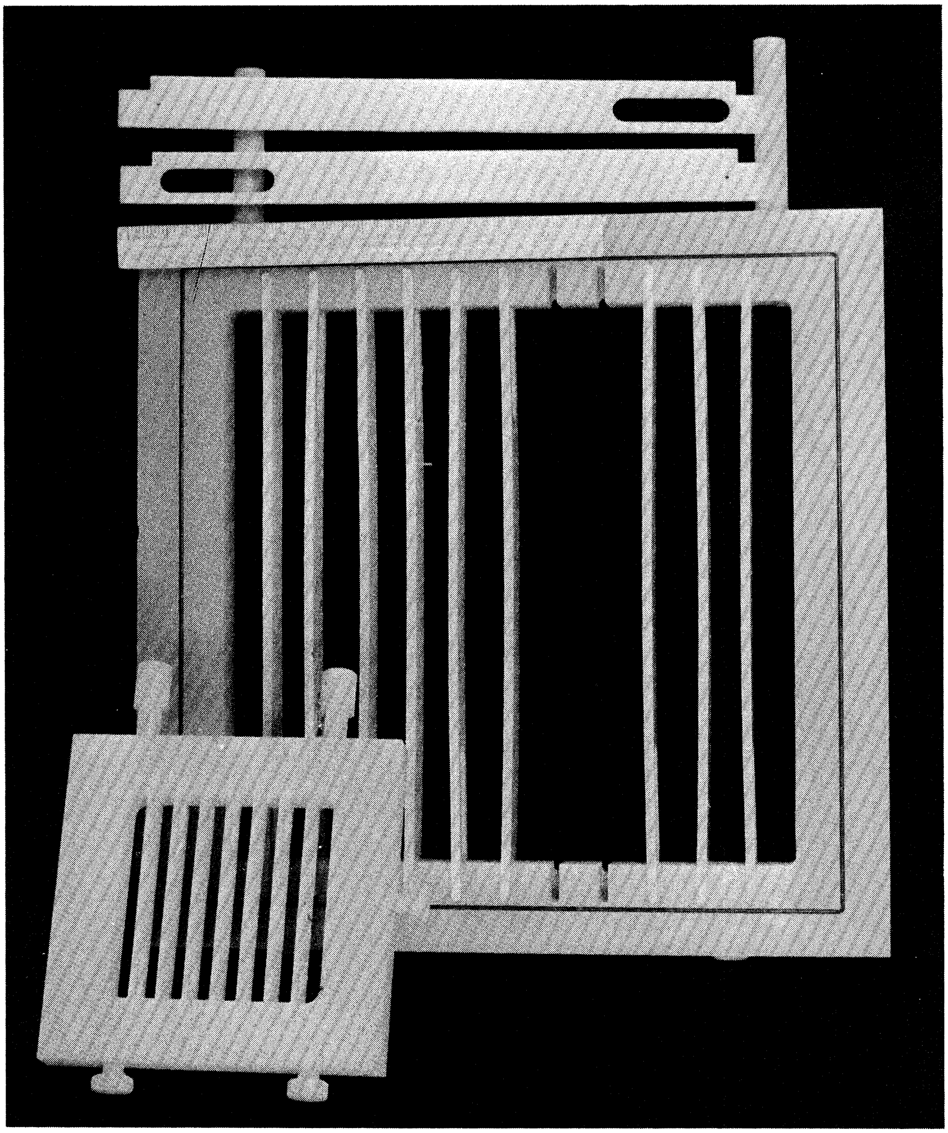

FIGURE 2. Photograph of baffled frames.

Chemelec cell

This design was developed by the Electricity Research Council at Capenhurst for the removal of metal from dilute solutions; its basic construction is similar to the plate and frame cell shown in figure 1. The metal is deposited on a gauze cathode in contact with a bed of non-conducting glass beads, 500–1000 μm in diameter, which are fluidized by the flow of electrolyte. In this way, mass transfer rates to the gauze and hence limiting currents are significantly increased and the quality of deposit is improved.

Fluidized-bed cell

If one replaces the non-conducting beads in the Chemelec cell with conducting metal beads, one moves away from the plate or gauze electrode used in a plate and frame cell and arrives at the first example employing a three-dimensional electrode. Figure 4 shows a cross

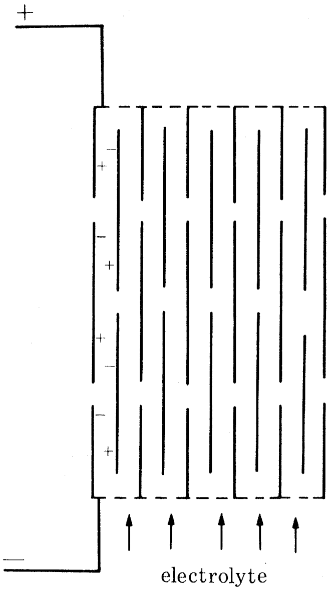

Figure 3. Schematic diagram of a Seachlor cell.

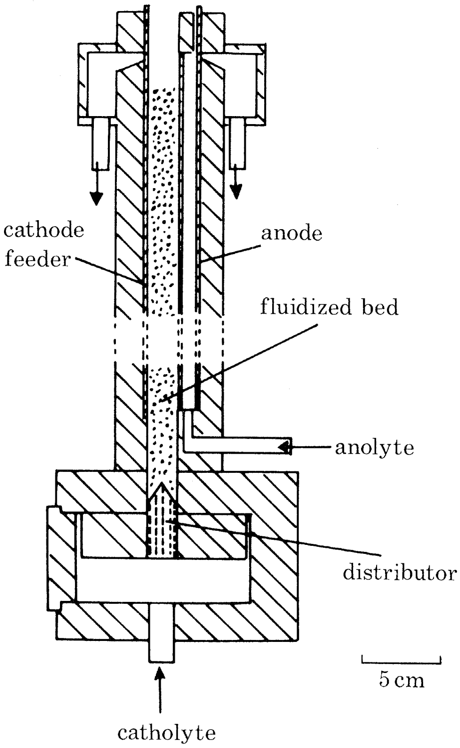

Figure 4. Pilot plant size fluidized-bed cell with rectangular geometry.

section through a rectangular fluidized-bed cell (Goodridge & Vance 1979). Fluidized-bed electrodes were first developed in my laboratories; as the term three-dimensional implies, when modelling the behaviour of the electrode one has to make allowance for possible variations in potential not only along the two dimensions of the current feeder, but also in the direction of current flow, which in this instance is at right angles to the flow of electrolyte. This is a more complex system than the Chemelec cell, but has a number of advantages. First, one can run the process of metal deposition in a continuous mode by elutritating particles from the cell once they have reached a given size; secondly, one can cope with lower metal concentrations; and thirdly, in some instances such as copper deposition one can obtain refined metal purity from very impure solutions.

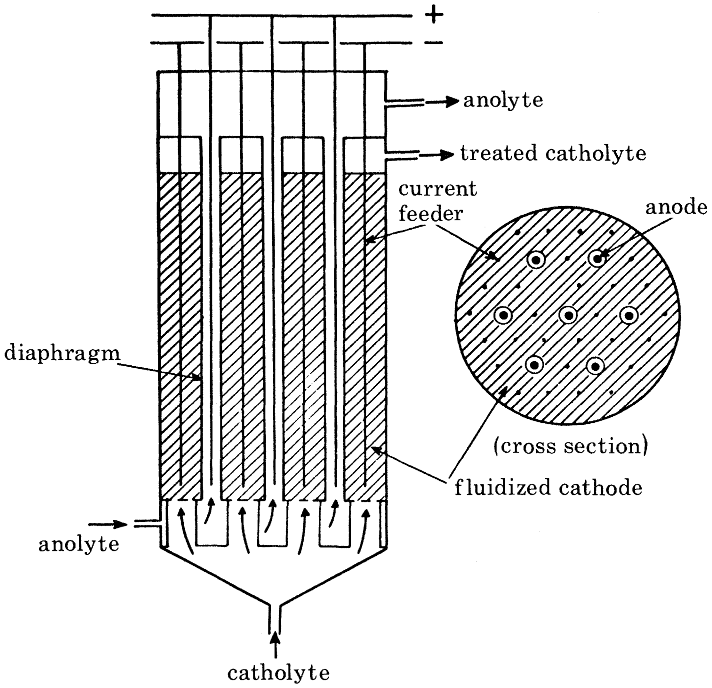

Figure 5. Commercial size fluidized-bed cell with cylindrical geometry.

Figure 5 shows an example of a commercial development by Akzo Zout Chemie (van der Heiden *et al.* 1978) for the removal of metals from dilute solutions. The cell here has a cylindrical geometry and can, for example, reduce copper concentration from 800 to less than 1 μg/g and cadmium from 800 to 1 μg/g from a zinc electrolyte flowing at 200 $m^3 h^{-1}$.

Fixed bed cell

The final design to be mentioned is the fixed bed cell. Figure 6 shows an example (Blackmar 1971) developed by the Nalco Chemical Company for the production of alkyl lead compounds. This at its inception nearly two decades ago was a novel and courageous solution to the problem of one electrode's being gradually used up in the electrochemical reaction. As with the fluidized-bed cell, potential distribution in three dimensions must be considered, but modelling is easier (Goodridge & Hamilton 1980) since the metal particles are in close contact with each other and hence charge transfer by electron flow as through a continuous conductor can be assumed.

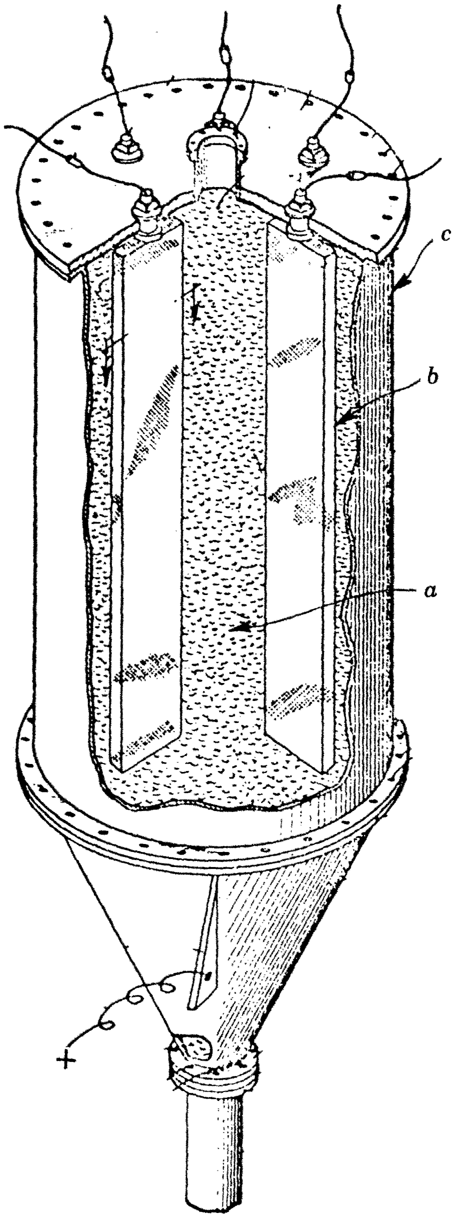

FIGURE 6. Fixed-bed cell. (*a*) Particulate anode; (*b*) steel cathode insulated by a membrane; (*c*) cylindrical shell.

CELL DESIGN AND INDUSTRIAL SUITABILITY

It is of interest to speculate why the particular designs mentioned above have found application in industry. The thesis considered here is that for a particular design to be adopted, it must either perform a required function that alternative options are not able to, or, if this is not so, it must perform this function in the simplest possible manner and hence at lower cost. It is therefore, no accident that the cells, as we have considered them, gradually increase in complexity.

Thus the plate and frame cell is a relatively simple and compact design. Provided that current densities are not too low and there are no complications such as passivation or a dimensional change of electrodes, it will be the first choice for a number of reactions. The Seachlor cell avoids passivation by preventing the deposition of hydroxides on the cathode. Alternative designs cannot perform this function and they operate by ejecting any hydroxide formed through high flow rates of electrolyte, but one must add that the situation is not clear-cut because other hypochlorite cells have undergone industrial development.

The Chemelec cell removes metal from effluent streams in a relatively simple manner, provided continuity of operation is not a requisite and the desired outlet concentration from the cell is not too low. The actual value of this limit will depend on the nature of the system to be treated, e.g. the conductivity of the electrolyte and the nature of the metal to be removed, and only a comparative costing between alternative cell designs will determine the viable concentration range. Therefore, if either continuous operation or a non-viable outlet concentration is a necessity, then recourse to the more complex fluidized-bed cell must be made. The fixed bed, although simpler than the fluidized bed in operation, is not very satisfactory if a large amount of metal has to be deposited, because periodic redissolution is necessary. It is, however, particularly suitable when, as in the Nalco process, an electrode material is used up in the reaction.

OPTIMIZATION INVOLVING A PLATE AND FRAME CELL

If one aims to optimizing the performance of a metal-refining plant (Ibl & Robertson 1973), it is justified to include cell parameters only because they will determine first-order costs. If, however, one considers a process involving organic electrochemical synthesis, this is no longer true and very misleading results can be obtained, as can be illustrated by an example of a plant consisting of a plate and frame cell linked to a distillation column (Plimley 1980).

If a plant is made up of N items of equipment to which individual capital and production costs, C and P, can be assigned, then one can write a series of equations as

$$C_1 = f_1(a_1, a_2, \ldots, a_j), \tag{1.1}$$

$$C_2 = f_2(a_1, a_2, \ldots, a_j), \tag{1.2}$$

$$\vdots$$

$$C_N = f_N(a_1, a_2, \ldots, a_j); \tag{1.N}$$

and

$$P_1 = g_1(a_1, a_2, \ldots, a_j), \tag{2.1}$$

$$P_2 = g_2(a_1, a_2, \ldots, a_j), \tag{2.2}$$

$$\vdots$$

$$P_N = g_N(a_1, a_2, \ldots, a_j); \tag{2.N}$$

where $a_1, a_2, \ldots, a_j$ represent the process variables.

The total capital and production cost associated with the plant would be

$$C = \sum_{n=1}^{N} C_n \quad \text{and} \quad P = \sum_{n=1}^{N} P_n. \tag{3}$$

The optimum value of the process variable a_j would be given by

$$\frac{\partial C}{\partial a_j} = -t\frac{\partial P}{\partial a_j}, \tag{4}$$

where t is the allowable 'payback' time. When only two items of equipment have to be considered, (4) can be written in the form

$$\frac{\partial C_1}{\partial a_j} + \frac{\partial C_2}{\partial a_j} = -t\left(\frac{\partial P_1}{\partial a_j} + \frac{\partial P_2}{\partial a_j}\right). \tag{5}$$

In the present example a first-order cost model is used and the optimization involves only one process variable; conversion. The electrochemical reaction is the reduction of a hypothetical material A to product B, in aqueous solution, according to the equation

$$A + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{B}. \tag{6}$$

The only reaction competing with (6) is hydrogen evolution

$$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2. \tag{7}$$

At the anode the only product is oxygen

$$4\mathrm{OH}^- \rightarrow \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e}^-. \tag{8}$$

A plate and frame cell is suitable for (6), and since current density does not interact with the design of the distillation column, a preliminary optimization of the cell with current density as the process variable results in a value of 2000 A m^{-2}, which is used throughout. This value is arrived at by considering the installed capital costs of the cell and associated power source, together with running costs which include, for example, electrode replacement.

Details of the following optimization can be found in Plimley (1980), and only the conclusions will be discussed here. At some stage specific data in conjunction with a computer have to be used, and these are listed in table 1.

TABLE 1. DATA EMPLOYED IN THE OPTIMIZATION

rate of production of B	1.00 kmol h^{-1}
cost of feedstock, A	£200 kmol^{-1}
cost of cooling water	£0.02 m^{-3}
latent heat of all components	4×10^4 kJ mol^{-1}
allowable rise in temperature of cooling water	10 K
cost of steam	£0.004 kg^{-1}
cost of installed cell	£10000 $S^{0.9}$ (S, electrode area in square metres)
cost of installed power supply	£190 $C^{0.8}$ (C, power rating in kilowatts)
superficial vapour velocity in the distillation column	1.0 m s^{-1}
specific volume of vapour in the distillation column	0.04 m^3 kmol^{-1}
relative volatility with respect to water:	
of A	1.5
of B	2.25
cost of installed distillation column (including reboiler and condenser)	£1850 Nd (N, number of plates; d, column diameter in metres)

Figure 7 shows the result when the cell is considered in isolation. Although the minima are fairly flat, indications are that the optimum conversion is in the range 0.1–0.3. A very different situation is demonstrated by figure 8, which now presents a plot of the capital and production cost of the cell taken in conjunction with the distillation column. The optimum conversion.

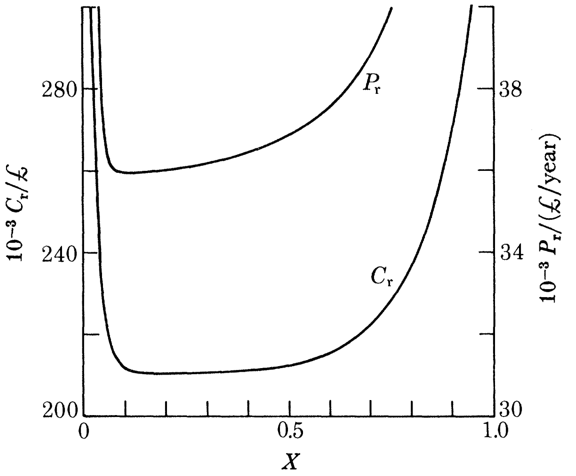

FIGURE 7. Effect of conversion, X, on (*a*) the capital cost, C_r, and (*b*) the production cost, P_r, of the electrochemical cell. Current density, 2000 A m^{-2}.

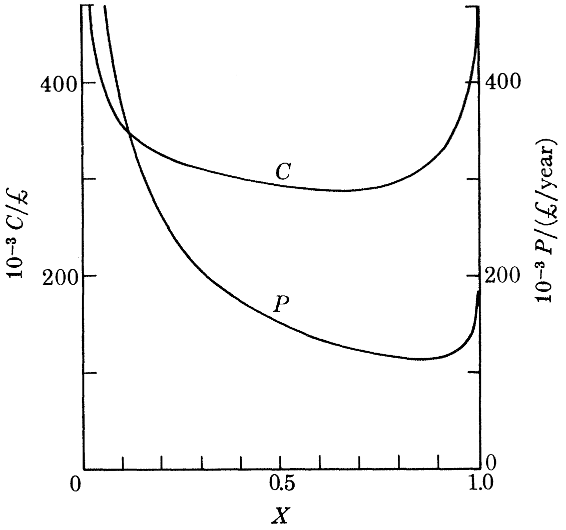

FIGURE 8. Effect of conversion, X, on (*a*) process capital cost, C, and (*b*) on production cost, P. The process costs are those of the cell and column taken in conjunction. Current density, 2000 A m^{-2}.

has now moved from 0.3 to 0.85. In physical terms this means that the distillation costs for a dilute mixture overshadow the added reactor costs for higher conversions.

This example clearly demonstrates the value of process modelling. First, it will identify the most probable process conditions and guide research effort into those areas where process data will be needed. Thus in the present case it is important to obtain data for conversions round 0.8 rather than 0.3. Secondly, a process model will quantify the sensitivity of process economics to uncertainties in the physical data and will therefore help in deciding on priorities for supporting research. For instance, in the present case the model shows that costing is particularly sensitive to the values assigned to the relative volatilities of A and B, and therefore determination of particularly accurate values of these quantities should be given high priority in any programme of experimental determination of physical properties.

CONCLUDING REMARKS

Since this is part of a Discussion Meeting entitled 'Prospects for industrial electrochemistry', it seems proper to finish with some comments in this context. It is my impression, based on personal experience during the last 6 months, that in spite of the country's industrial plight, considerable interest is being shown by industry in electrochemical techniques. I am therefore truly hopeful that the discussion is concerned with an expanding technology.

REFERENCES (Goodridge)

Baizer, M. M. 1973 *Organic electrochemistry*. New York: Marcel Dekker.

Blackmar, G. E. 1971 U.S. Patent no. 3,573,178.

Goodridge, F. & Hamilton, M. A. 1980 *Electrochim. Acta* **25**, 481–486.

Goodridge, F. & Vance, C. J. 1979 *Electrochim. Acta* **24**, 1237–1242.

Ibl, N. & Robertson, P. 1973 *Electrochim. Acta* **18**, 897–906.

Plimley, R. E. 1980 *J. Chem. Technol. Biotechnol.* **30**, 233–243.

Heiden, G. van der, Raats, C. M. S. & Boon, H. F. 1978 *Chemy Ind.*, no. 13, pp. 465–468.

Suter, H., Wirth, F. & Nohe, H. 1972 In *Phthalsäureanhydrid und seine Verwendung*, pp. 134–148. Darmstadt: Dietrich Steinkopff Verlag.

Discussion

A. T. KUHN (*Department of Bio-materials Science, Institute of Dental Surgery, London, U.K.*). Might I ask Professor Goodridge why, in his opinion, it took nearly 15 years for the fluidized-bed reactor first conceived by himself and Professor Fleischmann to enter commercial use, and why, in his opinion, it was in the end not a U.K. firm that achieved this success?

F. GOODRIDGE. May I first of all correct Dr Kuhn by emphasizing that there were two additional inventors, namely Dr J. R. Backhurst and Dr R. E. Plimley. Unfortunately, there is no simple clearcut answer. Part of the reason lies in the fact that the single British company that was involved in the initial development pulled out owing to a number of circumstances. The foreign company that eventually produced the first industrial units had the advantage of an initial in-house application, which enabled it to develop the device without outside interference. The timescale is long but one is involved with a relatively radical change in technology.

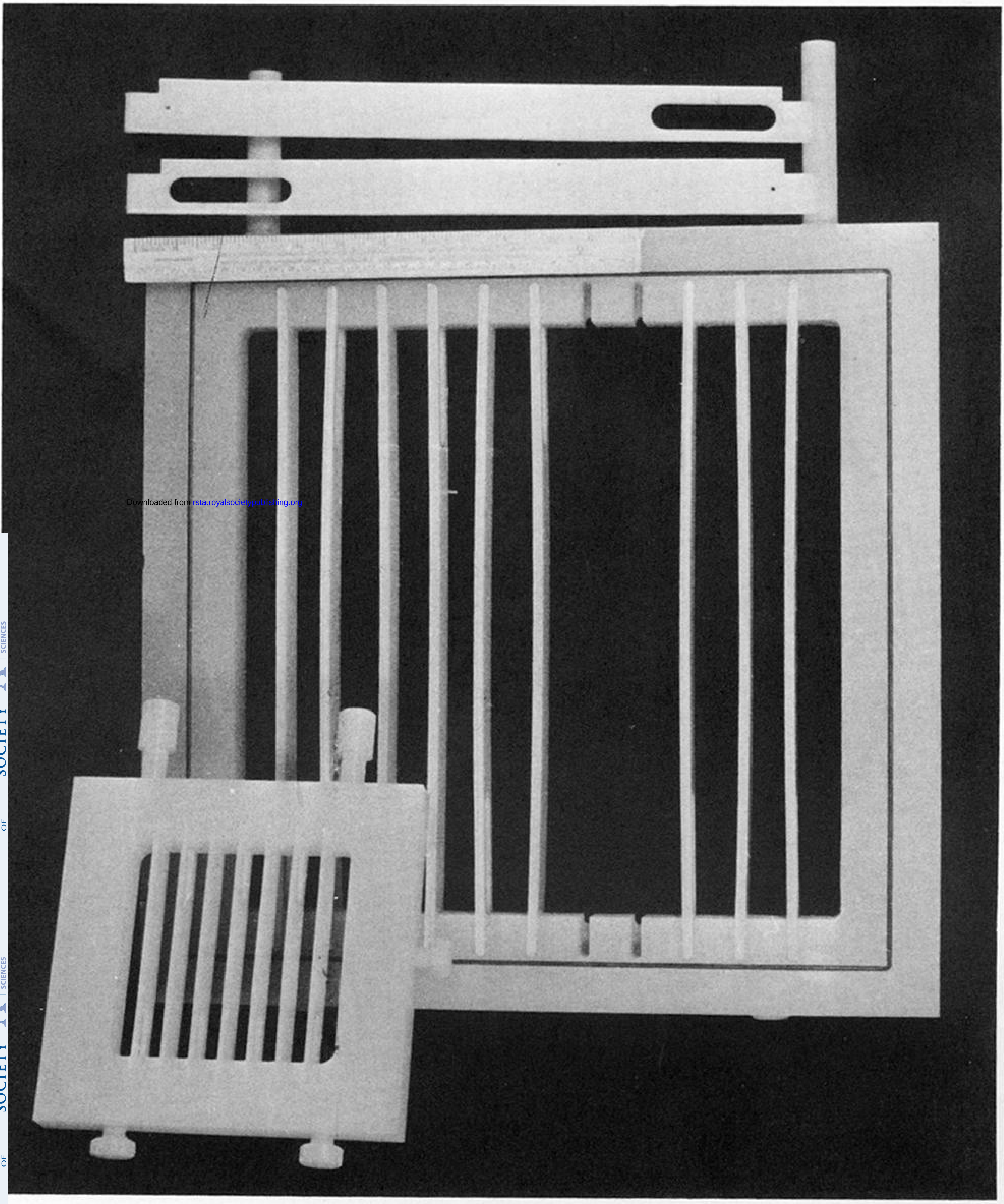

FIGURE 2. Photograph of baffled frames.