JOURNAL OF APPLIED ELECTROCHEMISTRY **13** (1983) 3–22

REVIEWS OF APPLIED ELECTROCHEMISTRY 6

# *The rotating cylinder electrode: a review of development*

D. R. GABE

*Department of Materials Engineering & Design, Loughborough University of Technology, Leics LE11 3TU, UK*

F. C. WALSH

*Wolfson Centre for Electrochemical Science, The University, Southampton, Hants SO9 5NH, UK*

Received 29 March 1981

---

Recent developments in the theory and applications of rotating cylinder electrodes are reviewed. Particular attention is paid to the mass transfer behaviour and the development of turbulent flow patterns, and its exploitation in electrochemical reactors for a variety of applications including metal deposition from waste and effluent liquors.

---

**Nomenclature**

| | |
|---|---|
| $A$ | electrode area $= \pi dl$ ($cm^2$) |
| $C$ | concentration ($mol\,cm^{-3}$) |
| $C_0, C_t$ | concentration initially, and at time $t$ ($mol\,cm^{-3}$) |
| $C_R$ | reactor concentration ($mol\,cm^{-3}$) |
| $d$ | diameter of inner, rotating cylinder (cm) |
| $D$ | diffusion coefficient ($cm^2\,s^{-1}$) |
| $f_R$ | fractional conversion |
| $F$ | Faraday Constant = 96485 ($As\,mol^{-1}$) |
| $I, I_L$ | current, limiting current (mA) |
| $i, i_L$ | current density, limiting current density ($mA\,cm^{-2}$) |
| $k$ | apparent first order rate constant ($s^{-1}$) |
| $K_L$ | mass transport coefficient $= i_L/zFC$ ($cm\,s^{-1}$) |
| $K$ | a constant |
| $l$ | effective length of rotating cylinder (cm) |
| $n$ | integer, indice |
| $N$ | volumetric flow rate ($cm^3\,s^{-1}$) |
| $P$ | power requirement (W) |
| $r_I, r_0$ | radius of inner, outer cylinder (cm) |
| $U$ | peripheral velocity of cylinder ($cm\,s^{-1}$) |
| $S$ | annular gap $= r_0 - r_I$ (cm) |
| $t$ | time (s) |
| $V_{cell}$ | cell voltage (V) |
| $V_r$ | effective reactor volume ($cm^3$) |
| $W$ | number of wiper blades |
| $x$ | fractional power index |
| $z$ | number of electron change |

Greek letters

| | |
|---|---|
| $\epsilon$ | peak to valley roughness (cm) |
| $\nu$ | kinematic viscosity $= \eta/\rho$ ($cm^2\,s^{-1}$) |
| $\eta$ | dynamic viscosity ($g\,cm^{-1}\,s^{-1}$) |
| $\rho$ | fluid density ($g\,cm^{-3}$) |
| $\omega$ | angular velocity ($rad\,s^{-1}$) |
| $\rho_s^n$ | normalized space velocity ($dm^3\,dm^{-3}\,s^{-1}$) |

Dimensionless groups (definitions shown are typical)

| | |
|---|---|
| $j'_D$ | modified Chilton–Colburn factor $= St\,Sc^{0.644}$ |
| $f/2$ | friction factor |
| $Re$ | Reynolds Number $= Ud/\nu$ |
| $Sc$ | Schmidt Number $= \nu/D$ |
| $Sh$ | Sherwood Number $= K_L d/D$ |
| $St$ | Stanton Number $= K_L/U$ |
| $Ta$ | Taylor Number $= \dfrac{r_I U(r_0 - r_I)(r_0 - r_I)^{1/2}}{\nu}$ |
| $Ta'$ | Modified Taylor Number $= 2U^2(r_0 - r_I)^3/\nu^2(r_0 + r_I)$ |

0021-891X/83/010003-20$04.90/0

## 1. Introduction

Since an earlier review was published eight years ago [1] interest in the Rotating Cylinder Electrode (RCE) system has increased and considerable progress has been made towards its exploitation in industrial practice. The fundamental concepts and theory are still valid but the theory has been refined and extended, particularly in respect of the use of the RCE in electrochemical reactors.

It is inevitable that a comparison of the RCE will be made with the Rotating Disc Electrode (RDE) for which an established science and technology has been built up on the classical groundwork of Levich [2]. By contrast, the RCE has been relatively little used and it is worth considering some of the reasons for the particular success of the RDE:

(a) The RDE is normally used in an essentially laminar flow regime giving flow stability over a wide range of rotation speeds, thus making it preferable for electrode kinetics studies.

(b) An exact and rigorous solution of the mass transfer equations for the electrode exists, based on theoretical and experimental studies.

(c) Construction and operation of the RDE is somewhat easier and the rotating ring disc modification offers further unique characteristics, especially for mechanistic investigations.

(d) The relatively low rate of mass transport to a RDE restricts current requirements to a low level, allowing the use of modest power supplies.

A comparison of quantitative characteristics has been made in Table I and it may be seen that the RCE is particularly well-suited to studies of high mass transfer or turbulent flow. In addition, it lends itself to extensive physical or metallographic examination of the electrode surface especially following cathodic electrodeposition. The RCE has a substantially uniform primary and secondary current density distribution and lends itself to potentiostatic control of mass transfer in turbulent flow regimes which are developed at low critical Reynold's numbers (*Re*). With superimposed axial flow a wide variety of flow conditions are possible although the most convenient geometry for practical purposes is an inner rotating cylinder, a stationary outer concentric cylinder acting as counter electrode and a low or insignificant axial flow.

In this review much of the earlier work [1] will not be considered further and the present discussion will attempt to cover more recent theoretical and experimental developments, proprietorial developments, especially in the field of cell and reactor design, and the wide range of applications for the RCE which have appeared in the literature.

## 2. Fundamental considerations

### 2.1. *Flow regimes*

Flow in the annulus of a concentric rotating

*Table 1. A comparison of the RDE and RCE*

| *Characteristic* | | *RDE* | *RCE* |
|---|---|---|---|
| Critical Reynolds number, $Re = Ux/\nu$ | | $2 \times 10^5$ | 200 |
| Critical dimension, $x$ | | radius | diameter |
| Friction factor $f/2$, laminar flow | | $0.62Re^{-0.5}$ | $2Re^{-1.0}$ |
| Friction factor $f/2$, turbulent flow | | $0.0265Re^{-0.2}$ | $0.079Re^{-0.3}$ |
| Mass transfer correlation: | laminar flow | $Sh = 0.62Re^{0.5}Sc^{0.33}$ | $Sh = 0.97Re^{0.64}Sc^{0.33}$ |
| | turbulent flow | $Sh = 0.02Re^{0.8}Sc^{0.33}$ | $Sh = 0.079Re^{0.7}Sc^{0.356}$ |
| Mass transfer variation; $MT \propto U^n, MT \propto r^m$: | laminar flow | $n = 0.5, m = 0$ | $n = 0.33, m = 0.4$ |
| | turbulent flow | $n = 0.9, m = 0.8$ | $n = 0.7$ (smooth)<br>$n \to 1.0$ (rough) $m = 0.2$ |
| Typical electrode data: | $r$ (cm) | 10 | 10 |
| | $A$ (cm$^2$) | 314 | 3948 |
| | $\omega$ (rpm) | 95.5 | 95.5 |
| | $U$ (cm s$^{-1}$) | 100 | 100 |
| | flow regime | laminar | turbulent |
| | $Re$ | $10^5$ | $2 \times 10^5$ |
| | $f/2$ | $1.96 \times 10^{-3}$ | $2.03 \times 10^{-3}$ |

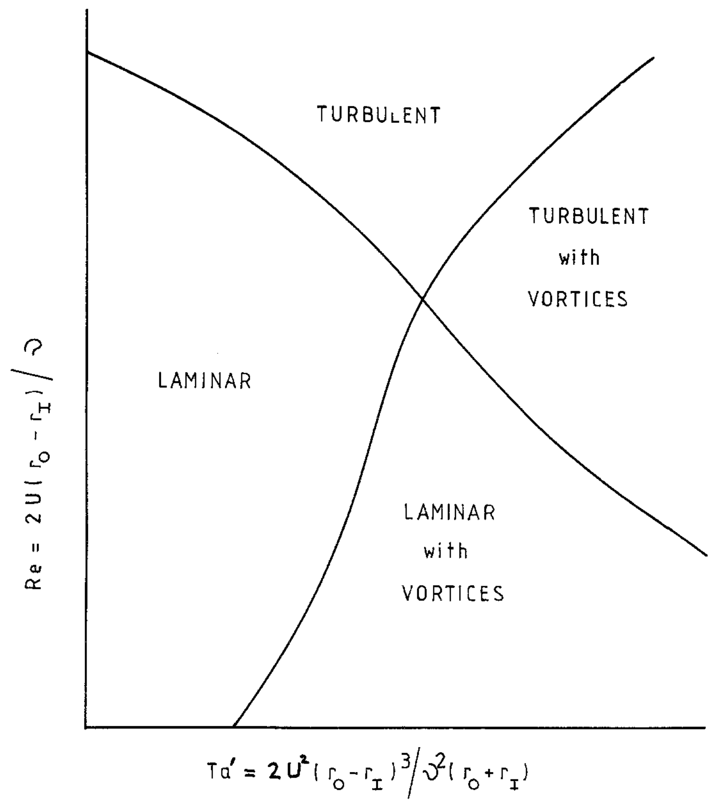

Fig. 1. Schematic representation of domains of flow regimes around a rotating cylinder. (After Kaye and Elgar [10]).

cylinder system has proved to be an interesting system to academics because the geometry appears to be relatively simple and uniform while actual fluid flow behaviour is rather complex. Furthermore, it is possible to consider a variety of special cases involving rotating inner or outer cylinders with or without superimposed axial flow together with the influence of drag modifying additives to the fluid and the effects of surface roughness on the mass transport behaviour.

As has been noted previously [1], at very low rotational speeds fluid flows in a straightforward laminar manner in concentric circles around the inner cylinder; that is, flow is tangential and laminar. On increasing the rotation speed this simple flow pattern becomes unstable and a cellular motion is imposed upon the flow producing toroidal Taylor vortices. These contain a radial component of velocity yet the bulk flow is still essentially laminar. At still higher rotational speed flow becomes fully turbulent as eddies increasingly break up the regular flow pattern. The flow transition occurs typically at $Re = 100$–$200$ (for example rotation speeds of 2–4 rpm for a 1 cm diameter RCE)* described in terms of a Taylor number ($Ta$) and recent experimental evidence now confirms this classical view that a substantial transition region may exist in practice (Fig. 1). The Taylor theory strictly applies only to small annular gaps and the case of large gaps is better treated as a separate case [3]. The critical transition conditions are often established by means of mass transfer data but by purely considering drag and friction factors the transition has been defined by [4]:

$$Re_{\text{crit}} = \left(11.8\,\frac{d}{e}\right)^{1.18} \tag{1}$$

where $d$ is the diameter of the cylinder and $e$ is its saturated roughness.

The effect of superimposed axial flow on the rotational flow pattern has recently gained considerable importance with the development of continuous RCE reactors. Two aspects need to

---

* Assuming a typical value of $\nu = 0.01\ \text{cm}^2\ \text{s}^{-1}$.

be considered. Firstly what is its effect on the rotational flow regime and its transition, and secondly what is its effect on mass transfer to the electrode surface? When rotational flow is laminar, axial flow causes the fluid to move in a helical rather than tangential manner and with rapid axial flow, the pattern approaches that of pipe flow when an axial entrance length effect is clearly apparent. In a sufficiently long annulus Couette flow may be observed when the fully developed tangential velocity distribution becomes independent of the axial coordinate. Several theoretical treatments exist [3, 5–9] and the various experimental studies broadly agree with this pattern of behaviour [10–30]. Turbulent regimes can thus be realized by large axial flow at low rotation speeds but this particular case is not very stable and not generally important compared with the case of low axial flow and large rotation rate. In this latter case the effect of axial flow becomes secondary in importance and consequently has received little theoretical attention except for air flow [31] and heat transfer under special circumstances.

From an operational point of view it must be remembered that fluid motion is attained by the supply of energy, either by a motor for cylinder rotation or by a pump for axial fluid flow. Clearly turbulence is desirable for both high mass transfer and effective stirring but is achieved at the expense of increased power consumption. Moreover the power required is markedly greater for rougher electrodes under comparable conditions. The measurement of rotational torque can thus be a means of measuring viscosity and friction factors and can be related to the mass transfer thus obtained. The tangential laminar flow requires least torque to rotate the cylinder but provides no marked enhancement of mass transfer, Taylor vortex flow requires a higher torque and contributes to mass transfer and turbulent flow requires the highest torque and contributes most effectively to an increased mass transfer while also providing vigorous stirring in the annular gap.

## 2.2. *Mass transfer*

The earlier review [1] pointed out that mass transfer correlations exist for both laminar and turbulent regimes in the RCE cell and that some theoretical justification for both had been offered. These correlations have been summarized in Table 1. Recent work has been concerned primarily with the laminar–turbulent transition region and with the effects of important additional parameters in the turbulent regime.

Macleod *et al.* [11, 25] have considered non-electrochemical mass transfer to an inner cylinder of long annulus for air and liquids and it was found to be relatively insensitive to axial flow velocity. For air the correlating expression involved $Sh \sim Ta^{0.52}$ and for liquids $Sh = 1.91 Ta^{0.7}$ which approximates to the classical Eisenberg *et al.* expression for rotational turbulent flow [32, 33]; this is somewhat surprising as the data was said to relate to laminar–vortex flow. Amongst several electrochemical studies Kataoka *et al.* [34–37] have described the interrelation between axial movement of Taylor vortices and periodically varying rates of mass transfer at the outer fixed cylinder by measurements of localized mass transfer rates. Thus axial flow resulted in movement of the Taylor vortices, with subsequent damping of vortex formation, leading to a 30–50% lowering of the average mass transfer. Ritchie *et al.* [38–40] have also studied this type of phenomenon in the same transition region and are attempting to establish a correlation with a term to account for the periodicity and local instability. They have also shown [39] that there is a substantial cylinder end-cap effect in this region which can be avoided by using insulated end-caps or a closely fitting cell. Coeuret *et al.* [41–43] have considered the relationship of axial flow and rotational flow and have separated their individual effects (see Fig. 2). In considering the general case they point out the difficulties involved and suggest an empirical relationship of the type

$$Sh = a\, Re^b\, Ta^c\, Sc^d \qquad (2)$$

For $25 < Re < 300$ and $Sc = 1382$, $a = 0.38$, $b = 0$, $c = 0.49$ and $d = 0.33$. For $Re > 300$, $a = 0.12$, $b = 0.34$, $c = 0.40$ and $d = 0.35$.

For turbulent flow generated entirely by cylinder rotation, the classical mass transfer correlation of Eisenberg *et al.* [32, 33] remains accepted.

i.e., $$j'_{\mathrm{D}} = St.\, Sc^{0.644} = 0.079\, Re^{-0.3} \qquad (3)$$

In general, departures from it may be due to variations in cell design [44, 45] or data analysis [46–50], and disregarding the implicit assumption

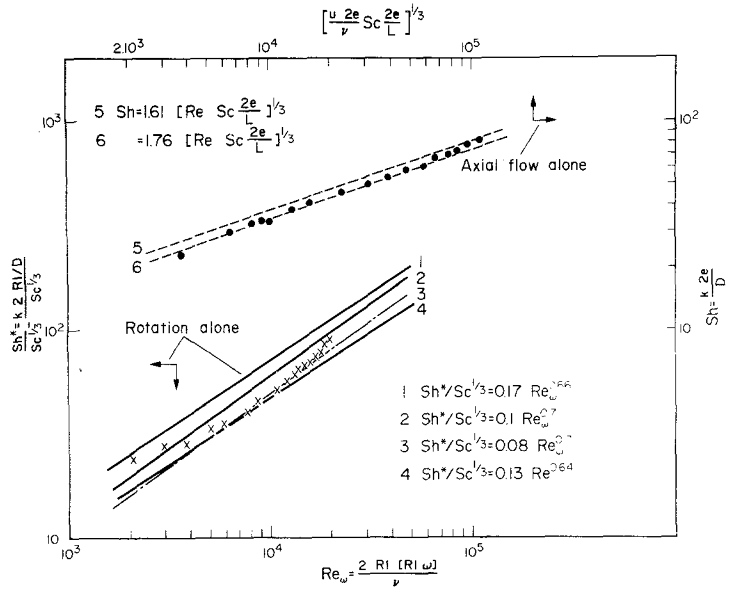

Fig. 2. Comparison of correlations for mass transfer with rotation alone and axial flow alone ($Sc = 1382$). (After Legrand, Dumargue and Coeuret [42]). Key: (1) Robinson and Gabe [46], (2) Eisenberg, Tobias and Wilke [13], (3) Newman [142], (4) Cornet and Kappesser [134], (5) Becher and Kaye [143], (6) Kataoka, Doi and Komai [34].

that the reactions must be under electrochemical mass transfer control at a smooth surface. Thus other workers have confirmed the correlation in a variety of circumstances [51–53].

The absence of a good correlation or a discrepancy with other workers is inevitably cause for some concern but there are several possible reasons for such behaviour. In order to attain a good mathematical data correlation the range of experimental variables must be wide enough for them to be real variables. In particular solution viscosity must be varied to give a good range of $Sc$ values; if it is not varied a full three-dimensional correlation is not strictly possible yet a two-dimensional correlation can lead to serious error [46, 47].

The importance of reactor geometry has only received scant attention in the past yet is particularly important in scale-up exercises and the variation in cylinder aspect ratio used only emphasises this factor [39, 54]. The problem of surface roughness is a particularly vital one which has received inadequate attention. For turbulent flow and for a surface of 'saturated' roughness the drag on a rotating cylinder is independent of $Re$ but a function of relative roughness ($e/d$) as described by the Theordorsen–Regier equation [55]:

$$\frac{1}{\left(\frac{f}{2}\right)^{1/2}} = 1.25 + 5.76 \log\left(\frac{d}{e}\right). \qquad (4)$$

This equation has been found to be true in a variety of circumstances and for roughnesses produced by sandcasting [8], corrosion [56] and machining or knurling [4]. Mass transfer may then be described by

$$St = \left[1.25 + 5.76 \log\left(\frac{d}{e}\right)\right]^{-2} Sc^{-0.644} \qquad (5)$$

and reasonable agreement has been reported [4, 56]. It has long been realized that increased roughness can appreciably enhance the mass transfer due both to an increase in active surface area and to improved hydrodynamic shear at the electrode. The above correlation implies that mass transfer is independent of $Re$ in these circumstances, and although the correlation has not fully taken into account the increased surface area this is not likely to be a limitation. The characteristic surface roughness may be readily defined for knurled surfaces although other definitions may be more convenient in practice (i.e. centre line average roughness or ratio of actual to projected surface area). A time-dependent roughness can arise in the case of electrodepositing metal powders on an originally smooth surface. Ibl [57] has considered this case generally and for a RDE [58] while Walsh and Gabe [59] have studied the RCE incorporated in a continuous reactor system designed to produce metal powder. The effect of increased roughness can be recognized in several ways including measurements of rotational torque and the in-

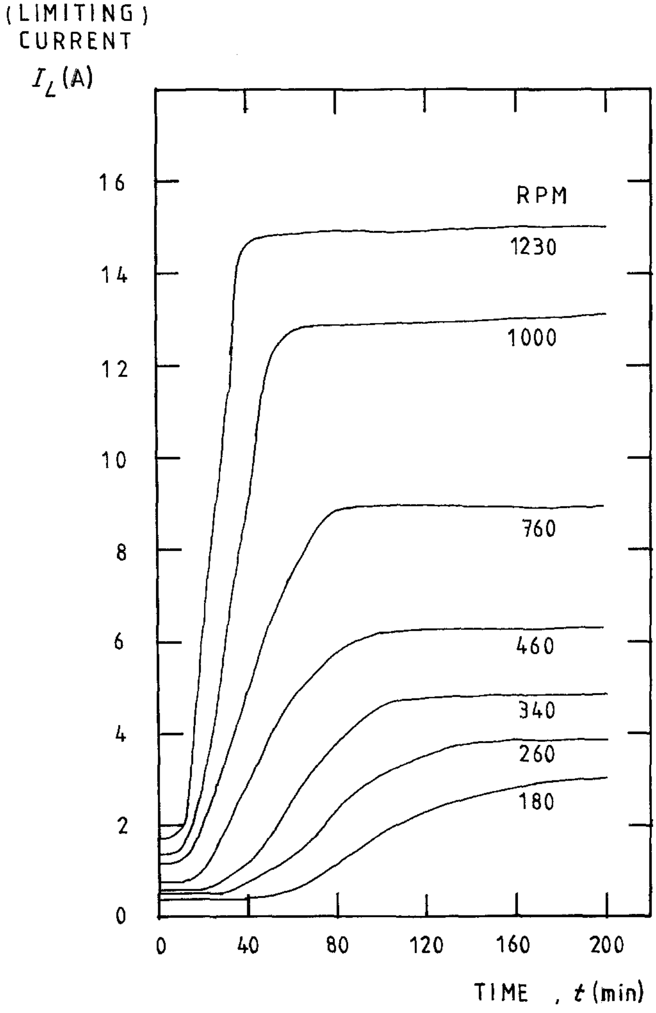

Fig. 3. Current–time history for growth of rough deposits. Potentiostatic deposition (– 1.0 V, $Hg/Hg_2SO_4$; 1 mol dm$^{-3}$ $Na_2SO_4$–scale) of copper from 0.014 mol dm$^{-3}$ $CuSO_4$ at 22° C at rotational speeds from 180–1230 rpm.

creased mass transfer achieved. Using potentiostatic control, a cathodic metal deposition reaction having a clear limiting current density plateau, gives an increasing current as the metal powder grows, roughens and eventually reaches a saturated roughness* (Fig. 3). Without knowing the true active surface area it is difficult to calculate reliably a true mass transfer coefficient although it may be reasonable to assume that the active area increase is proportional to current increase. An apparent mass transfer coefficient may of course be calculated (based on nominal electrode area) and indicates marked enhancement (Fig. 4). Using such data the enhanced mass transport leads to the power law proposed by Holland [60–62] for powder growth whose onset may be illustrated by relating limiting current to rotation speed after particular stages of powder deposit development (Fig. 5). A complete analysis of this phenomenon must take account of both the increased electrode area and the increased frictional drag and must await the establishment of data for both these parameters.

The consequence of this phenomenon is clear, however, for the application of a roughened RCE in a reactor used for the removal of metal from effluent under batch decay conditions. The concentration of metal falls much more rapidly than that predicted for a smooth electrode, once roughness is established, and the reactor performance is markedly enhanced [63] (see Fig. 6).

The case of non-saturated roughness has been

---

* A typical value of roughness is 0.02 cm.

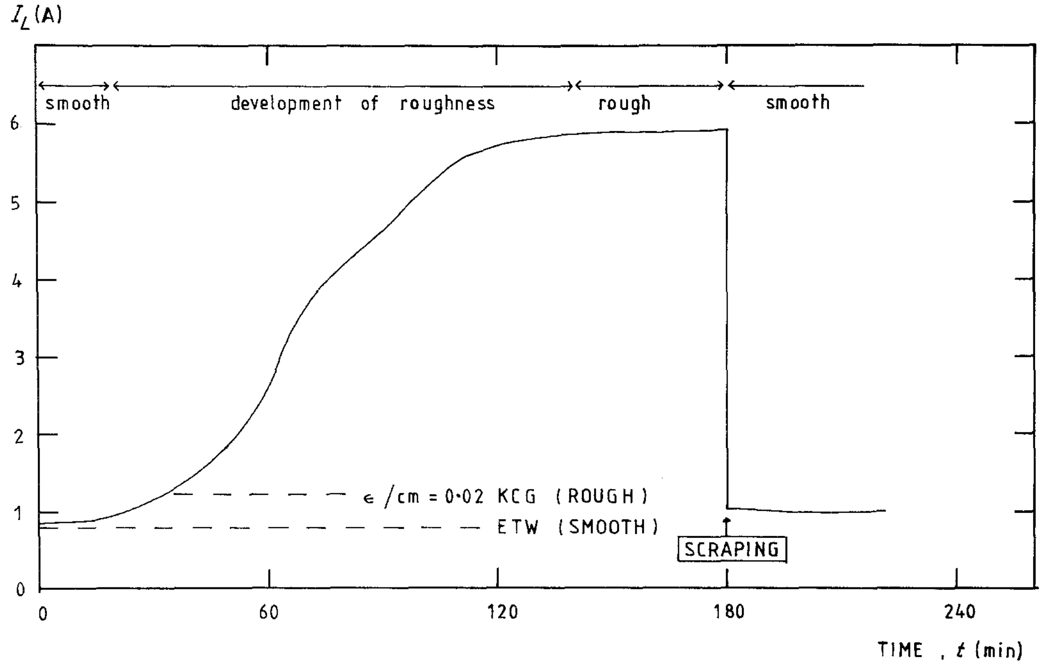

Fig. 4. Development of roughness demonstrated by expressing the limiting current as a function of time. Conditions as in Fig. 3 with $d = 6$ cm, $l = 6.3$ cm, $A = 119\,\mathrm{cm}^2$, 360 rpm and $U = 113\,\mathrm{cm\,s^{-1}}$. Values predicted by Eisenberg–Tobias–Wilke and Kappesser–Cornet–Greif correlations.

studied using a finned or slotted cylinder [64] and when compared with behaviour at a smooth cylinder a 30–140% increase in mass transfer was found with a correlation of the form:

$$j'_D = St.\,Sc^{0.644} = 0.714Re^{-0.39}\left(\frac{e}{d}\right)^{0.2} \qquad (6)$$

where $e$ is the fin height.

This is in marked contrast to Kappesser *et al.* [4] where a dependence upon $Re$ disappeared; it suggests that in non-saturated cases, the nature and pattern of roughness must be important as well as its relative value. In a separate study using planar electrodes [65] it has been shown that gas evolution on a roughened surface can be enhanced and can itself promote additional fluid motion. Sedahmed *et al.* [66, 67] have also examined the use of drag-reducing polymers in the RCE and obtained various correlations which appear to be different for different additives. An attempt to rationalize behaviour by using a viscosity factor was only partly successful because the constant in the Eisenberg equation, used as a norm, was also found to vary. Behaviour in non-Newtonian fluids has also been studied [68] and has given a correlation

$$Sh = 0.62fReSe^{0.33} \qquad (7)$$

for specific ranges of $Sc$ and $Re$ apparently in a turbulent regime.

The use of turbulence promotors has received attention for other flow configurations [69] but not specifically for the RCE presumably because it is already highly turbulent in most well-developed applications. It is interesting to note that their effect is closely similar to that of increased roughness on the RCE surface and behaviour akin to that in Fig. 5 has been found.

Fahidy *et al.* [70–72] have studied mass transfer to continuously wiped inner cylinders using spring-loaded Teflon skimmer blades. Theoretical analysis for turbulent conditions leads to

$$Sh = \frac{2}{\pi}\left(\frac{W}{1 - Wx/2\pi r_1}\cdot Re\,Sc\right)^{1/2} \qquad (8)$$

where

$$x = dK_L/D.$$

Where $W$ is the number of wiper blades. Substantial experimental data shows that the relative enhancement of mass transfer decreases at large $Re$ and with a small number of blades. For the

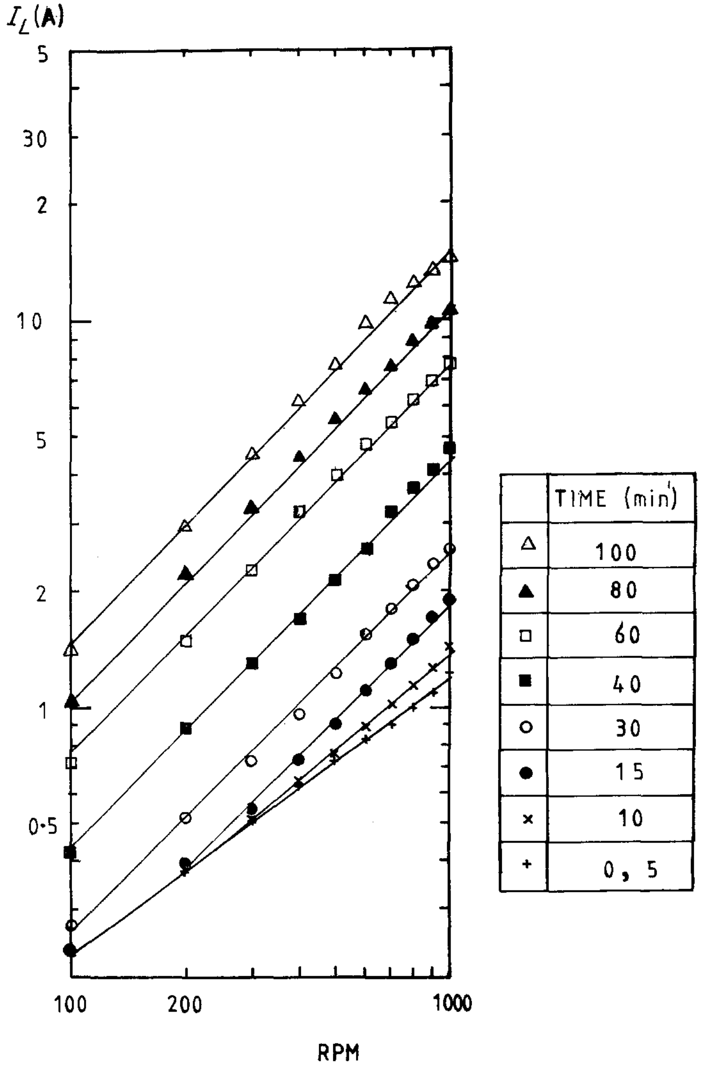

Fig. 5. Limiting current as a function of rotational speed for various times during the development of roughness (condition as in Fig. 3).

separate case of a rotating outer electrode [73, 74] the correlation took the form

$$Sh = 0.85 Re^{0.5} Sc^{0.5} \qquad (9)$$

Nadebaum and Fahidy [75, 76] have developed a bipolar RCE system using two or three axially located wiper blades which divide the cell up into two or three compartments. An outer segmented electrode in each compartment governs the potential and the rotating inner electrode may thus be bipolar or tripolar. By carefully setting the potential a transfer concentration process may be established in which deposition may take place in one segment and dissolution stripping in another.

The recovery of copper in a pilot plant scale tripolar RCE has recently been described, according to this technique. It is interesting to note that, for engineering convenience, and contrary to the bench-scale apparatus, the outer cylinder was rotated while the static inner cylinder carried the three wiper blades. This interesting development bears some features in common with the Cascade Eco-Cell and will be referred to in a later section.

Search and ingenuity continues to provide additional means of promoting mass transfer. One such means is the use of ultra-sonic agitation and experimental evidence suggests that the mass transfer can be substantially increased with an improved quality of deposit for metal electrodeposition [77, 78].

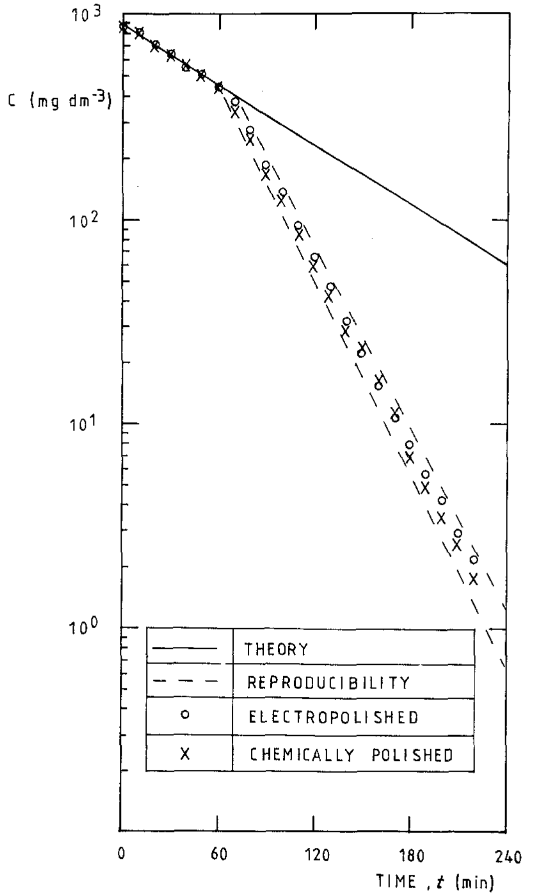

Fig. 6. Concentration decay with time for a batch rotating cylinder reactor (conditions as in Fig. 3).

## 3. Proprietary developments

In the earlier review [1] an attempt was made to trace early, and often empirical, work with the RCE, much of which made use of rod or wire electrodes rotating at relatively low *Re* values. In order to trace commercial interests it is necessary to explore the patent literature where a whole variety of RCE assemblies may be found, which have been developed for metal deposition and organic electrosynthesis. Amongst the relatively few developments in the latter category are those of Udupa *et al.* [79] for semi-continuous synthesis of salicaldehyde using a 10 cm diameter copper tube electrode (1800 rpm) and porous rubber diaphragm and capable of yielding 250 g hr$^{-1}$ of aldehyde at 18° C at 12–15 A dm$^{-2}$. Spencer *et al.* [80, 81] have synthesized dithionite by reduction of bisulphite with small bismuth, nickel or stainless steel electrodes (3 in (75 mm) high x 3 in (75 mm) diameter, 10–100 rpm) which were wiped to increase mass transfer, activate the electrode and improve current efficiency to 96%.

Of the many proposals for electrodeposition (see Table 2) it is difficult to know how many have become commercial or realistically practical. It is also difficult to see originality in many because from one of the earliest designs, Lacroix in 1912 [91], the common feature throughout is a rotating cylinder electrode and the novel features are the peripheral hardware including anodes, flow system, constructional materials, diaphragm, bearings and brush design etc. Furthermore, in many cases little or no performance data or specification has been revealed.

Some of the more important novel features may be noted. Benner [90] has used a bipolar RCE, and exploited it as a rotating assembly. The idea of a bipolar RCE has since been taken up by Nadebaum and Fahidy [70, 75, 76] who have incorporated wiper blades to improve performance on what might otherwise be an inefficient device. The earliest RCE cells were mainly proposed for the recovery of metal from leach solutions as a non-spongy deposit and so relatively low rotation rates and current densities were specified [91, 92]. Interest in silver recovery has been widespread either for its intrinsic value or as a mean of recovery from photographic solutions facilitating re-use of the fixer solutions [82, 85, 93–99]. It is noteworthy that many of these cells use polygonal anode configurations, a proposal for ease of cell manufacture rather than optimization of performance.

The use of wiper or 'doctor' blades has already been noted and these may be used to improve efficiency [71, 75, 76], to remove excess or stagnant solution [99], reactivate the electrode surface [80, 81] or scrape metal powder products from the surface [60, 61, 82, 84–89, 100]. Alternatives to wiper blades include trough systems for horizontal cathodes [86–88] and air or water jets [83].

The only proposal quantitatively based on optimized or improved performance is that of Holland for the Eco-Cell development [60, 61, 84]. When producing metal powder of large surface area he recognized markedly improved performance and expressed this as a simple power law:

*Table 2. Proprietary RCE systems and reactors*

| *Assignee* | *Date* | *Metal* | *Application* | *Anodes* | *RCE details* | | | | | | *Special features* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *Material* | *d* (cm) | *l* (cm) | *A* ($cm^2$) | *Rotation rate* (rpm) | *U* ($cm\ s^{-1}$) | |
| Cleave [82] | 1925 | Silver | Refining | Soluble | | – | – | – | – | – | Scraped RCE powder product |
| Nordblom [83] | 1968 | Nickel | Production of nickel flake | ? | Stainless steel | – | – | – | – | – | Gridded belt on RCE |
| Holland [60–62, 84] | 1977 | Various | Electrowinning, electrorefining effluent treatment | Various normally insoluble | Stainless steel<br>Titanium | | | Various | | $1–10^4$ | Scraped RCE continuous powder production |
| Arrigo Pini SpA [85] | 1963 | Silver | Refining of silver from nitrate solutions | Soluble silver | Metal | – | – | – | – | – | Scraped RCE powder product |
| Societe Industrielle des Coussinets [86] | 1961 | Copper–lead alloy | Alloy powder production | Soluble lead/copper | Steel | – | – | – | – | – | Scraped RCE powder product |
| Prunet and Guillen [87] | 1961 | Zinc | Recovery from Zincate | Insoluble | Metal | – | – | – | 5–10 | – | Scraped RCE powder product |
| Gordy [88] | 1973 | Copper | Electrowinning of ores | Ore | Copper | – | – | – | – | – | Scraped RCE possibly powder product |
| Johnson [89] | 1939 | Zinc | Electrodeposition of zinc dust | ? | Iron or nickel | – | – | – | 1 | – | Scraped RCE powder product cooled RCE |
| Benner [90] | 1969 | (Desalination) | Removal of ions from a liquid | ? | Ion XS, material may be used | – | – | – | – | – | 2 RCE's contra-rotating bipolar partially immersed flow through |
| Lacroix [91] | 1912 | Various Copper | Electrowinning | Insoluble | Metal | 31.8 | 100 | $10^4$ | 40 | 67 | Bottom bearing |
| Cowper-Coles [92] | 1915 | Iron | Electrowinning and electrorefining | Insoluble/soluble | Metal | – | – | – | – | – | Propeller |
| Schaefer [93] | 1945 | Silver | Electroplating | Silver rods | Metal (workpiece) | – | – | – | – | – | Recycling |
| Rennie et al. [94] | 1974 | Various | Electrowinning | Insoluble | Metal | – | – | – | – | – | Rotating anode + vessel (RCE) |
| Fulweiler [95] | 1971 | Silver | Recovery of silver from photographic fixer | Graphite plates (6) | Stainless steel | 30 | 14 | 1460 | 230 | 367 | Impeller at top of RCE |
| Fischer [96] | 1972 | Silver | Recovery of silver from photographic fixer | Graphite poles (4) | Stainless steel | – | – | – | 50–200 | – | Vaned RCE or polygon |
| Goold et al. [97] | 1975 | Copper and others | Electrowinning | Insoluble e.g. lead | Metal (Stainless steel) | – | – | – | – | – | Polygonal rotating electrode |
| Julien [98] | 1925 | Copper | Electroplating of foil | Soluble copper | Metal | – | – | – | – | – | Anode basket |
| Cooley [99] | 1968 | Silver | Recovery of metals | Graphite | Stainless | 13 | 25 | 323 | 150 maximum | 100 | Closely conforming counter electrode |

$$i = KCU^x. \qquad (10)$$

For a smooth initial surface $x = 0.7$ but as powder develops $x \rightarrow 1.0$, thus indicating a need to operate the cell in a powder-producing condition. This optimization will be considered later in relation to reactor design; meanwhile it may be noted that this power law is a simple and convenient formula for scale-up purposes in design and, while having some basis in theory is best considered as a semi-empirical formula.

Recent trends have been towards continuing features of different types of electrode to produce hybrid cells; for example, the rotating packed bed electrode proposed by Kreysa [101, 102]. The ingenuity of such devices is obvious but their practicality may be doubted for many mundane applications. Although the use of baffles and impellers in a fully turbulent flow system is not really necessary their use may safeguard against poor mixing and promote axial flow in continuous reactors [92, 95, 96].

## 4. The RCE reactor

### 4.1. *Principles*

The visualization of the RCE as the basis of a reactor implies certain basic assumptions; for example that an electrochemical reaction can be promoted in a special cell and optimized for high rates of reactant conversion at high efficiency. The design of the cell is clearly important and may have to be tailored to the particular reaction and its specific characteristics. The main advantageous characteristics of the RCER may therefore be:

(a) The electrode surface is substantially equipotential if set in a concentric anode configuration, and potentiostatic control becomes possible.

(b) The current density is substantially uniform giving good mass transfer control.

(c) The turbulent three-dimensional flow provides a good approximation to a continuously stirred tank reactor (CSTR).

(d) The mass transport is uniform, high and controlled primarily by rotation of the cylinder rather than axial flow through the reactor.

(e) Rough electrodes display markedly higher mass transport than their smooth counterparts while retaining dependance on rotation rate.

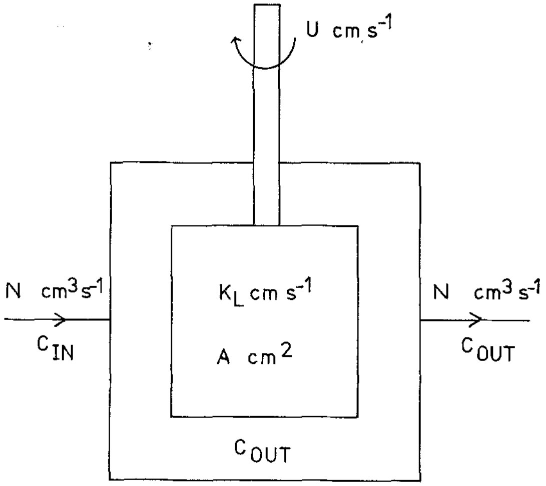

Fig. 7. Schematic diagram for a single pass rotating cylinder electrode reactor.

(f) The rotating cylindrical geometry facilitates wiping or scraping to enhance electrode activation or to remove product.

If the RCER is considered to be a continuously stirred reactor operating under mass transfer control the design equations may be arrived at simply.

The concentration–time profile is given by:

$$C_t = C_0 \exp(-kt) \qquad (11)$$

where $k$, the apparent first order rate constant, is given by $k = K_L A/V_r$ and the resulting fractional conversion $f_R$ is given by:

$$f_R = 1 - \frac{C_t}{C_0} = 1 - \exp\left(-\frac{K_L A t}{V_r}\right) \qquad (12)$$

Thus the conversion at any time may be increased by increasing the mass transport coefficient $K_L$, the electrode area $A$ or by decreasing the reactor volume $V_r$. The mass transfer coefficient may be enhanced by increasing the peripheral velocity, the relationships being

(a) for a smooth cylinder,

$$K_L = 0.079 d^{-0.3} \nu^{-0.344} D^{-0.644} U^{0.7}, \qquad (13)$$

i.e., $K_L \sim U^{0.7}$;

(b) for a rough cylinder,

$$\left(K_L = 1.25 + 5.76 \log \frac{d}{e}\right)^{-2} Sc^{-0.644} U \qquad (14)$$

i.e., $K_L \sim U$. Mass transfer is thus largely insensitive to the cylinder length but dependent upon $d$ and $U$.

The above analysis applies to a batch reactor but once continuous flow is imposed a mass balance may be calculated (see Fig. 7) for mass transfer control.

(Mass input–Mass output) = mass electrolysed

$$N(C_{IN} - C_{OUT}) = K_L A C_r \qquad (15)$$

For a continuously stirred reactor producing metal powder or deposit $C_{OUT} = C_r$ so the concentration ratio becomes

$$\frac{C_{OUT}}{C_{IN}} = \frac{1}{1 + K_L A/N} \qquad (16)$$

and the fractional conversion is given by

$$\frac{C_{IN} - C_{OUT}}{C_{IN}} = \left(1 - \frac{C_{OUT}}{C_{IN}}\right) = \frac{K_L A/N}{1 + K_L A/N} \qquad (17)$$

The factor $K_L A/N$ may be regarded as a performance factor such that for a given volumetric throughput $N$ the reactor conversion may be enhanced by increasing $K_L, A$ or both. A batch recycle mode of operation may be advantageous on small scale or laboratory processing, where a reservoir of solution can be stored, treated and dosed etc., but is not so convenient for large scale use. The effect of surface area $A$ and mass transfer coefficient $K_L$ for a given peripheral velocity is shown in Fig. 8. A fuller consideration of these design factors will be found elsewhere [54].

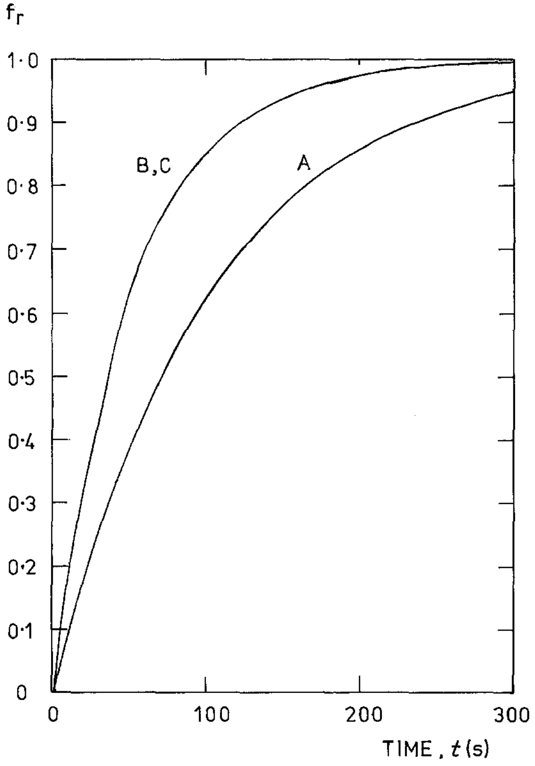

Fig. 8. Fractional conversion in a batch reactor as a function of time at 1000 cm s$^{-1}$ peripheral velocity: A, area 100 cm$^2$, $K_L$ 0.1 cm s$^{-1}$; B, area 200 cm$^2$, $K_L$ 0.1 cm s$^{-1}$; C, area 100 cm$^2$, $K_L$ 0.2 cm s$^{-1}$.

### 4.2. *Power requirements*

The power consumed by a RCER is partly Faradaic and partly rotational; in general terms, heating power is small although in specific processes it may become important. Joule heating may not be a loss, as the resultant temperature rise may enhance mass transport. The electrolytic power requirement $P_E$ is given by $P_E = V_{cell}I$ where $V_{cell}$ necessarily includes various resistive losses in busbars, contacts, membranes etc., as well as the electrode overpotentials. Typically, in the case of metal powder production, the cell voltage may be made up as shown in Table 3. A consequential temperature rise occurs given by $\Delta T(° C) = P_e 4.19 N$ where $P_e$ is the power loss in the electrolytes. Typically, $\Delta T \leqslant 10° C$ under steady state, well controlled conditions.

Donnelly and coworkers have measured torque requirements for a rotating cylinder near the critical *Re* value (ca. 200). The data, however, largely concerns small cylinders ($d \simeq 1$ cm).

Relatively little work has been reported for the power requirements for rotation in turbulent flow

*Table 3. Resistance and voltage drop components in a typical RCE reactor.*

| *Component* | *Resistance* | *Voltage drop at 1 KA or 0.2 A cm$^{-2}$* (V) |
|---|---|---|
| Anode | – | 1.5 |
| Anolyte | 2.5 Ω cm$^{-2}$ | 0.5 |
| Cathode | – | 1.2 |
| Catholyte | 7.5 Ω cm$^{-2}$ | 1.5 |
| Busbars | 0.1 mΩ | 0.1 |
| Membrane | 3.5 Ω cm$^{-2}$ | 0.7 |
| Total | | 5.2 |

and the work of Wendt [103] appears to be the only appropriate case. For higher rotation rates, or more specifically

$$\left[\frac{Ur_o - r_I}{\nu}\right] > 10^4,$$

Wendt calculated the torque transmission to the outer cylinder from a rotating inner cylinder as:

$$G = 0.073\pi r_I^4 \rho l \omega^2 \left(\frac{Sr_o}{r_I^2}\right)^{0.25} \left(\frac{\omega r_I (r_o - r_I)}{\nu}\right)^{-0.3} \tag{18}$$

The power consumed in rotation $P_{rot} = \omega G$ where $\omega = U/r_I$; whence we may see that

$$P_{rot} = \text{constant } U^{2.7} \tag{19}$$

Considerations of fluid mechanical behaviour give for a smooth cylinder:

$$P_{rot} = \frac{f}{2} \cdot \pi \rho r_I l U^3 \cdot 10^{-7} \tag{20}$$

Where $f/2 = 0.079Re^{-0.3}$ for smooth cylinders only. Thus the dependence upon rotation was similar although detailed dependence was different. Clearly there is a rapid increase in $P_{rot}$ with velocity $U$ which will be even greater for a roughened electrode surface.

In scaling-up the operations of a RCER the main purpose is often to improve reaction throughput while maintaining mass transfer performance. As a consequence larger cylinders can be rotated at lower velocities and the rotational power density may thus decrease. The geometry of the outer cell is relatively unimportant in terms of flow pattern but the size of the annular space will affect the performance of the cell as a reactor. For a perfectly concentric geometry with negligible volume at the top and bottom the cell electrolyte volume is:

$$V_r = \pi l (r_o^2 - r_I^2) \tag{21}$$

and the electroactive area is:

$$A = 2\pi l r_I \tag{22}$$

Thus the area/volume ratio is given by $2r_I/(r_o^2 - r_I^2)$. For the condition $(r_o - r_I) = 1$ cm, and also assuming a cylinder whose height and diameter are equal, for example, $2r_I = d = l$, it may be seen that $A/V \rightarrow 1$ as $r_I$ increases. Furthermore, for a given flow rate, the nominal residence time $V/N$ increases with the reactor size.

### 4.3. *The Eco-Cell reactor*

The most thoroughly developed example of a rotating cylinder electrode reactor is that originally

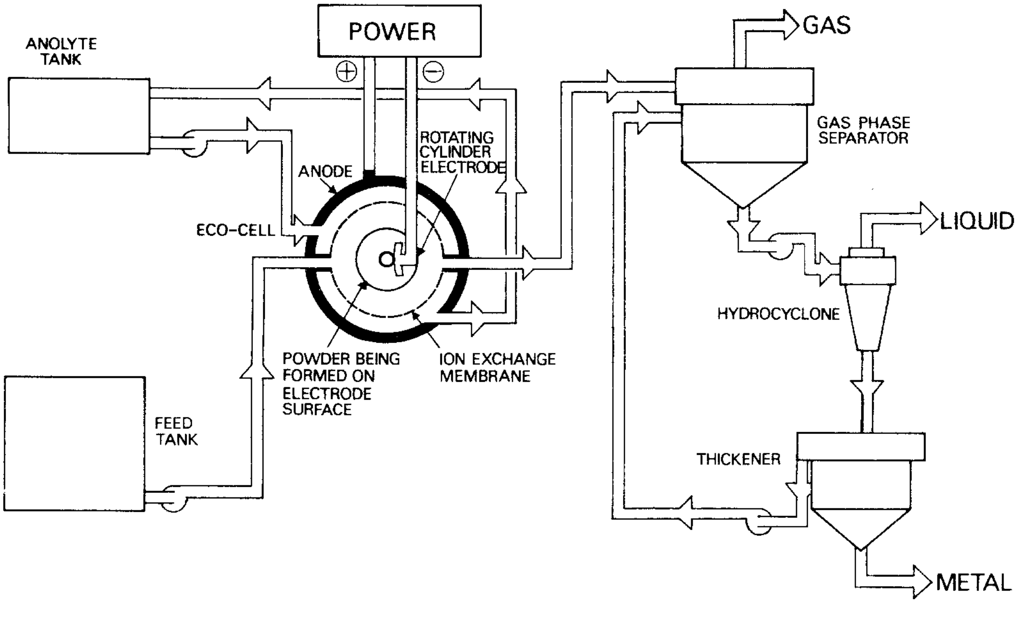

Fig. 9. Flow schematic for the Eco-Cell process.

proposed by Holland [60, 61, 62, 84, 104] and developed commercially as the Eco-Cell. This reactor is capable of continuously recovering metal from a dilute liquor or effluent as a metal powder which enables enhanced mass transfer to be exploited according to the empirical design Equation 10 where $x = 0.7$–$1.0$ according to the degree of enhancement. Continuous flow is utilized (see Fig. 9) in a divided cell, the catholyte carrying dislodged powder and some hydrogen gas to a three-phase separator system. The anode and anolyte are chosen to be compatible with the membrane and can be optimized for conductivity, minimum oxygen overpotential, and resistance to corrosion. The substantially uniform electrode potential experienced at the RCE facilitates potentiostatic control which enables a selective electroseparation of metals to be achieved [63, 105] and a reasonably reproducible deposition of metal powder to be maintained. The cell is designed to operate under fully turbulent conditions and scraping of the powder is arranged so as to allow enhanced mass transfer; thus a reciprocating point scraper is preferred to the use of a doctor blade [100]. The degree of enhancement can be measured either from throughput and mass balance considerations or from the limiting current–time history of a treatment as shown in Fig. 3.

The degree of conversion in a single stage RCER may also be enhanced by increasing the mass transport coefficient, for example by increasing rotational velocity, or by a further increase in surface area. Clearly there are practical limitations on cost, space and engineering convenience and the alternative approach is to use an array of reactors in hydraulic series. The Eco-Cascade cell uses this principle by assembling all the reactor elements on a single shaft in order to minimize engineering costs, power consumption etc., and each element of the cascade is operated under mass transport control [106]. The overall fractional conversion is given by

$$(f_R)_n = \frac{C_{IN} - C_{OUT}}{C_{IN}} = 1 - \frac{1}{(1 + K_L A/N)^n} \tag{23}$$

This concept is achieved by the use of a single cylindrical cathode inside one reactor cell which is subdivided into cascade elements by means of regularly spaced internal baffles (Fig. 10). Idealized behaviour of a cascade cell is illustrated in Table 4 where an inlet copper concentration of 100 mg dm$^{-3}$ is reduced stepwise in six compartments to an outlet of 1.6 mg dm$^{-3}$. A conversion $f_R = 0.5$ is assumed, that is concentration is halved in each compartment, a performance virtually matched in practice [106]. Assuming an electrolyte flow of 1000 cm$^3$ s$^{-1}$ individual compartment currents may then be calculated. Clearly to ensure optimum performance each compartment must be potentiostatically controlled at limiting current conditions, and although there is no necessity for fast response instrumentation this method may be expensive and impractical. A more convenient method of control is to use a constant current source with anode size and position in each compartment being tailored to yield the appropriate current profile over the reactor length.

At the present time there is considerable interest in comparing the performance of the

*Table 4. Performance of hypothetical Eco-Cascade-cell. Copper deposition under limiting current conditions, with a fractional conversion of 0.5 in each compartment. 100% cathode current efficiency*

| *Compartment number* | $C_{IN}$ (mg dm$^{-3}$) | $C_{OUT}$ (mg dm$^{-3}$) | $\Delta C$ (mg dm$^{-3}$) | $-\frac{dm}{dt}$ (g hr$^{-1}$) | $(f_R)_n$ | $I$ (A) |
|---|---|---|---|---|---|---|
| 1 | 100 | 50 | 50 | 180 | 0.500 | 151.8 |
| 2 | 50 | 25 | 25 | 90 | 0.750 | 75.9 |
| 3 | 25 | 12.5 | 12.5 | 45 | 0.875 | 37.9 |
| 4 | 12.5 | 6.25 | 6.25 | 22.5 | 0.938 | 18.9 |
| 5 | 6.25 | 3.125 | 3.125 | 11.25 | 0.969 | 9.49 |
| 6 | 3.125 | 1.5625 | 1.5625 | 5.625 | 0.984 | 4.75 |
| Overall | 100 | 1.56 | 98.44 | 354.375 | 0.984 | 300 |

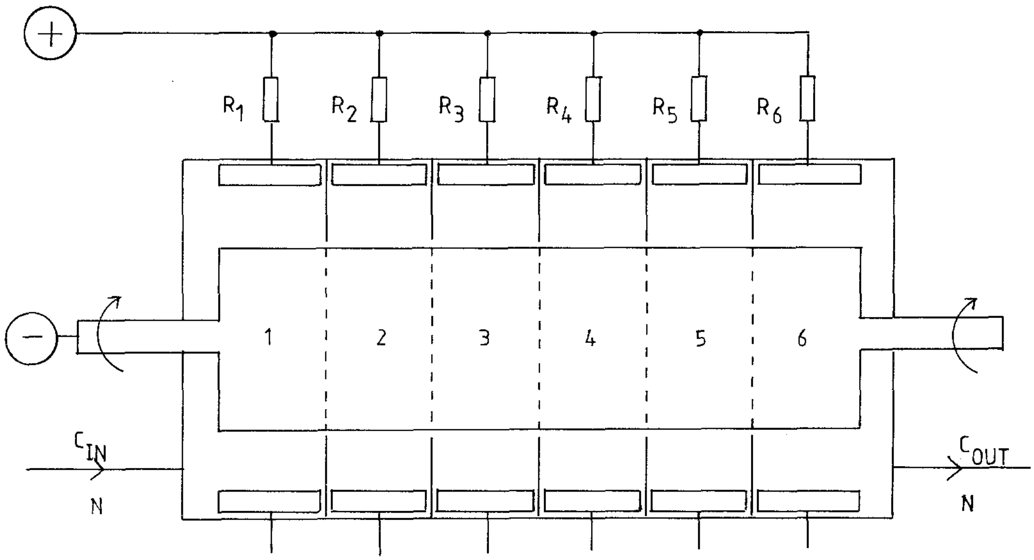

Fig. 10. Six element Cascade Eco-Cell shown without dividing membrane and with external resistive distribution of current.

many commercial reactors available on the market for metal recovery, and several approaches have been employed. Kuhn and Houghton [107] have used the limiting current density in 0.1 mol dm$^{-3}$ solutions for a two-electron reaction to make a simple scientific comparison. The mass transfer coefficient $K_L = i_L/zFC$ is a more universal concept.

In commercial operations space considerations are important and, in purely geometrical terms, the area/volume ratio $A_s$ may be useful. These two factors may be combined as a space–time yield defined by Goodridge [108, 109] as:

$$Y_{ST} = \frac{\text{amount of product}}{\text{electrolysis time} \times \text{reactor volume}} . \tag{24}$$

However, it is very difficult to quantify such behaviour adequately because so many factors are involved. Thus some reactors achieve high conversion efficiencies by virtue of high mass transfer (for example large $K_L$) while others may achieve the same level by virtue of high electroactive surface areas. Contributions have been made by Kammel and Lieber [110], Ibl [111] and Kreysa [112, 113] and are summarized in Table 5. The

*Table 5. Reactor performance compared*

| *Cell type* | *Electrode area* / *Reactor volume* (cm$^{-1}$) | *Space–time yield (Goodridge)* $Y_{ST}$(hr$^{-1}$) | *'Specific' energy consumed (Kreysa)* $E_s^e$(KWh m$^{-3}$) | *Normalized space velocity (Kreysa)* $\rho_s^n$(dm$^3$ dm$^{-3}$ hr$^{-1}$) |
|---|---|---|---|---|
| Filter press | 0.3–1.7 | 0.12–0.68 | – | – |
| Capillary gap | 1.0–5.0 | 0.4–2.0 | – | – |
| RDE | 1 | 4 | – | – |
| RCE | 0.1-1 | 0.4-4 | 1.5 | 20 |
| Packed bed | 10–50 | 4–20 | 0.12 | 28 |
| Fluidized bed | 20–100 | 8–40 | 0.27 | 30 |
| Swiss roll | 20–50 | – | 1.0–1.2 | 12–20 |
| Rolling tube | – | – | 14.2 | 0.4 |
| Rotating packed bed | – | – | 0.13 | 250 |

*Table 6. A comparison of rotating bipolar electrode and cascade Eco-Cell reactors*

| *Parameter* | *RBER* | *Cascade Eco-Cell* |
|---|---|---|
| Subdivision of reactor | radially | axially |
| Working electrodes | anode or cathode depending on compartment | normally all cathode |
| Number of elements | 2 (or 3) | 6–12 |
| Typical rotation rate (rpm) | 20 | 100–1000 |
| Flow type | nominally laminar | highly turbulent |
| Division into anolyte and catholyte | undivided | may be divided by ion exchange membranes |
| Roughness of RCE | exceptionally smooth | rough and powdery deposits |
| Wiping/scraping | PTFE blade, continuous full length wiper | metal or ceramic blade discontinuous traversing point scraper |
| Intercompartment leakage of current | very low | appreciable |
| Subdivision accomplished by | PTFE blades, touching RCE | internal baffle rings with clearance |
| Effect of wiper/scraper | increases mass transfer; divides the reactor | removes powder product from the cathode |
| Electrode potential profile | varies with compartment | normally same for each compartment |
| Mass transfer | low | very high |
| Approximation to CSTR | poor | good |

RCE reactor is primarily a high mass transport device ($0.02 \leqslant K_L \leqslant 1$ cm s$^{-1}$) of moderate surface area, but offers various advantages (Section 4.1.) including the continuous production of metal powders via scraping or the reactivation of the electrode via wiping. In this respect it is interesting to make a comparison (Table 6) between the cascade Eco-Cell and the rotating bipolar electrode reactor (RBER) discussed earlier, see Section 2.2. At the present stage of development the RBER has certain advantages but in terms of mass transfer cannot yet be said to be superior.

## 5. Applications

In this review primary concern is with the use of a rotating cylinder in electrochemical applications. Nevertheless, it should be noted that several other types of application have been exploited notably in the measurement of viscosity, heat transfer studies for rotating machinery, corrosion of rotating parts, rotating cylinder extraction columns, cyclone chamber behaviour and journal bearing simulation. The more specific electrochemical applications are in analytical chemistry, selective metal deposition, corrosion science, electrodeposition and organic synthesis and some of these studies will be cited (those involving mass transport studies have been mentioned at length earlier).

The RCE has found surprisingly little use in hydrodynamic voltammetry where the rotating disc and ring disc have become standard hardware. The reason for this is that the analytical equations for the RDE derived by Levich are of a long-standing classical nature and the laminar flow regime employed gives very reproducible conditions. High mass transfer is not normally an important consideration in this type of application and the turbulence may give fluctuation akin to electronic noise in the voltagramms [50]. The need to provide controlled potential separation of the more noble metal in an alloy is an essential part of coulometric gravimetry and a rotating platinum gauze cathode is generally employed [114–116]. It is clear that the turbulent RCE would be generally suitable for such methods [44] and the success on an industrial scale has been very encouraging [63, 105].

In corrosion studies there has been a history of use of the RCE but much of the early work is ambiguous owing to the confusion of chemical reaction and mass transfer rates as well as the stirring effects of gas evolution [117–125]. Important recent work is due to Heitz *et al.* [45, 126] who prefer the RCE to flow-through pipe rigs owing to its compactness and small electrolyte volume, accessibility of the electrode and ease of change of relative flow rate. They have also used a rotating outer cylinder to avoid Taylor vortices and centrifuged corrosion products [127]. Other studies include those of sea water erosion of copper–nickel alloys [128], effects of dissolved oxygen [129] and chloride ion [130–133]. Cathodic protection was one of the earliest fields studied [57, 134] and the study of surfactants in this [53, 135] and other systems [136] has followed. Makrides *et al.* [56, 137, 138] in particular have attempted to incorporate a roughness factor into the mass transport relationships for corroding specimens and it should now be possible to improve substantially on this particular aspect.

Many of the studies of electrodeposition have already been considered [39] but one or two further investigations may be noted. Graham and Pinkerton [139] have devised a cell using a conical anode and which therefore is akin to a spatial rotating Hull cell. They discuss its calibration and point out its possible use for studying distribution and throwing power effects in electroplating. A RCE cell has also been used to simulate electroforming in the case of iron, deposition from sulphamate solutions [140] with the usual increases in mass transport. The RCE has been used previously in studies of metal cementation (for example, chemical displacement precipitation or coating) and Strickland and Lawson [141] have continued this work for reactions which are undisputedly mass transfer controlled.

The field of organic electrosynthesis offers significant challenges but also considerable prospects because of the substantially equipotential surface of the RCE, combined with high mass transfer, thus selective oxidation or reduction of organic species may be achieved and when combined with the use of specific metal catalyst surfaces may give versatile selectivity. Udupa *et al.* [79] have synthesised salicaldehyde on a pilot plant scale using a porous rubber diaphragm cell. The larger unit operated at 300 A (12–15 A $\mathrm{dm^{-2}}$ to produce approximately 250 g $\mathrm{hr^{-1}}$ at 18° C from salicylic acid. Spencer *et al.* [80, 81] have synthesised dithionite from bisulphite by cathodic reduction on bismuth, nickel or stainless steel electrode surfaces and by wiping the electrode could increase efficiency from 26% to 96% at 20–30 A $\mathrm{dm^{-2}}$. This would appear to be a field offering considerable scope and opportunity.

## Acknowledgements

The ideas and approach embodied in this review have taken shape over a period of time and been influenced by many friends and colleagues. In particular the authors would like to express their appreciation of discussions and experimental support from Prof. I. A. Menzies, Dr. F. S. Holland and Messrs. N. A. Gardner and D. Robinson. Financial support was provided at various times by the Science Research Council and Ecological Engineering Ltd.

## References

[1] D. R. Gabe, *J. Appl. Electrochem.* 4 (1974) 91.
[2] V. G. Levich, 'Physiochemical Hydrodynamics', Prentice-Hall, New York (1962).
[3] S. Chandrasekhar, *Proc. Roy. Soc.* **A246** (1958) 301.
[4] R. Kappesser, I. Cornet and R. Greif, *J. Electrochem. Soc.* **118** (1971) 1957.
[5] S. Goldstein, *Camb. Phil. Soc.* **33** (1937) 41.
[6] B. W. Martin and A. Payne, *Proc. Roy. Soc.* **A328** (1972) 123.
[7] R. C. Di Prima, *J. Fluid Mech.* **9** (1960) 621.
[8] S. Chandrasekhar, *Proc. Roy. Soc.* **A265** (1962) 188.
[9] E. R. Krueger and R. C. Di Prima, *J. Fluid Mech.* **19** (1964) 528.
[10] J. Kaye and E. C. Elgar, *Trans. Amer. Soc. Mech. Eng.* **80** (1958) 753.
[11] J. R. Flower, N. Macleod and A. P. Shahbendrian, *Chem. Eng. Sci.* **24** (1969) 637.
[12] *Idem, ibid.* **24** (1969) 651.
[13] R. J. Donnelly, D. Fultz, D. J. Tanner and K. W. Shwarz, *Proc. Roy. Soc.* **A258** (1960) 101.
[14] *Idem, ibid.* **A246** (1958) 312.
[15] *Idem, ibid.* **A281** (1964) 130.
[16] *Idem, ibid.* **A283** (1965) 509.
[17] *Idem, ibid.* **A283** (1965) 520.
[18] *Idem, ibid.* **A283** (1965) 531.
[19] A. Fage, *ibid.* **A165** (1933) 501.
[20] F. J. Cornish, *ibid.* **A140** (1933) 227.
[21] Y. Yamada, *Bull. Jap. Soc. Mech. Eng.* **5** (1962) 302.
[22] H. A. Snyder, *Proc. Roy. Soc.* **A265** (1962) 198.
[23] K. N. Astill, *J. Heat Transfer* **86** (1964) 388.
[24] K. N. Astill, J. T. Gonley and B. W. Martin, *Proc. Roy. Soc.* **A307** (1968) 55.
[25] N. Macleod and T. Ruess, *Chem. Eng. Sci.* **30** (1975) 235.
[26] D. A. Simmers and J. E. R. Coney, *J. Mech. Eng. Sci.* **21** (1979) 59.
[27] M. M. Sorour and J. E. R. Coney, *J. Mech. Eng. Sci.* **21** (1979) 65.

[28] D. A. Simmers and J. E. R. Coney, *Int. J. Heat and Fluid Flow* **1** (1979) 77.
[29] *Idem, ibid.* **2** (1979) 85.
[30] M. M. Sorour and J. E. R. Coney, *J. Mech. Eng. Sci.* **21** (1979) 403.
[31] S. I. Kosterin, Y. A. Koshmarov and Y. P. Finatev, *Int. Chem. Eng.* **2** (1962) 460.
[32] M. Eisenberg, C. W. Tobias and C. R. Wilke, *Chem. Eng. Progr. Symp. Ser.* **51** (1955) 1.
[33] *Idem, J. Electrochem. Soc.* **101** (1954) 306.
[34] K. Kataoka, H. Doi and T. Komai, *Int. J. Heat Mass Transfer* **20** (1977) 57.
[35] K. Kataoka, H. Doi and T. Hongo, *J. Chem. Eng. Jap.* **8** (1975) 472.
[36] T. Mitzushina, R. Ito, K. Kataoka, S. Yokoyamu, Y. Nakashima and A. Fukuda, *Chem. Eng. Jap.* **32** (1968) 795.
[37] K. Kataoka, *J. Chem. Eng. Jap.* **8** (1975) 271.
[38] J. Billings and I. M. Ritchie, *Electrochim. Acta* **25** (1980) 733.
[39] J. Pang and I. M. Ritchie, *ibid.* **26** (1981) 1345.
[40] I. M. Ritchie, Private communication.
[41] F. Coeuret and J. Legrand, *J. Appl. Electrochem.* **10** (1980) 785.
[42] J. Legrand, P. Dumargue and F. Coeuret, *Electrochim. Acta* **25** (1980) 669.
[43] F. Coeuret and J. Legrand, *ibid.* **26** (1981) 865.
[44] G. Johansson, *Talanta* **12** (1965) 163.
[45] E. Heitz, *Werks. u Korr.* **15** (1964) 63.
[46] D. J. Robinson and D. R. Gabe, *Trans. Inst. Met. Fin.* **48** (1970) 35.
[47] D. R. Gabe and D. J. Robinson, *Trans. Inst. Met. Fin.* **49** (1971) 17.
[48] A. J. Arvia, J. S. W. Carrozza and S. L. Marchiano, *Electrochim. Acta* **9** (1964) 1483.
[49] A. J. Arvia and J. S. W. Carrozza, *ibid.* **7** (1962) 65.
[50] D. Matic, B. Lovreçek and D. Skansi, *J. Appl. Electrochem.* **8** (1978) 391.
[51] B. T. Ellison and W. R. Schmeal, *J. Electrochem. Soc.* **125** (1978) 524.
[52] J. Edwards and A. J. Wall, *Trans. Inst. Min. Met.* **75** (1966) C307.
[53] G. Kar, T. W. Healy and D. W. Fuerstenau, *Corr. Sci.* **13** (1973) 375.
[54] D. R. Gabe and F. C. Walsh, Proceedings A.I.Ch.E. Symposium, Cleveland, Ohio, 1982.
[55] T. Theordorsen and A. Regier, N.A.C.A. report number 793 (1944).
[56] A. C. Makrides and N. Hackerman, *J. Electrochem. Soc.* **105** (1958) 156.
[57] N. Ibl, *Adv. Electrochem. Electrochem. Eng.* **2** (1966) 49.
[58] N. Ibl and K. Schadegg, *J. Electrochem. Soc.* **114** (1967) 54.
[59] F. C. Walsh and D. R. Gabe, to be published.
[60] F. S. Holland, British Patent 1 505 736 (1978).
[61] *Idem,* U.S. Patent 4 028 199 (1977).
[62] *Idem, Chem. Ind. (London)* 1978, 453.
[63] F. C. Walsh and D. R. Gabe, *Surface Tech.* **12** (1981) 25.
[64] G. H. Sedahmed, A. Badel-Khalik, A. M. Abdallah and M. M. Farahat, *J. Appl. Electrochem.* **9** (1979) 563, 567.
[65] M. G. Fouad, G. H. Sedahmed and H. A. El-Abd, *Electrochim. Acta* **18** (1973) 279.
[66] G. H. Sedahmed, B. A. Abd El Nabey and A. Abdel-Khalik, *J. Appl. Electrochem.* **8** (1978) 473.
[67] G. H. Sedahmed and A. Abdel-Khalik, *ibid.* **10** (1980) 245.
[68] P. C. Singh and P. Mishra, *Chem. Eng. Sci.* **35** (1980) 1657.
[69] A. Storck and D. Hutin, *Electrochim. Acta* **26** (1981) 117, 127.
[70] P. R. Nadebaum and T. Z. Fahidy, *Can. J. Chem. Eng.* **53** (1975) 259.
[71] M. Farooque and T. Z. Fahidy, *ibid.* **55** (1977) 355.
[72] *Idem, Electrochim. Acta* **24** (1979) 547.
[73] T. Takahashi and T. Z. Fahidy, *ibid.* **25** (1980) 1603.
[74] T. Takahashi, M. I. Ismail and T. Z. Fahidy, *ibid.* **26** (1981) 1727.
[75] P. R. Nadebaum and T. Z. Fahidy, *Nature Phys. Sci. (London)* **241** (1973) 45.
[76] *Idem, J. Appl. Electrochem.* **5** (1975) 249.
[77] I. A. Menzies and C. Gould, Private communication.
[78] F. C. Walsh, Unpublished work.
[79] K. S. Udupa, G. S. Subramanian and H. V. K. Udupa, *Ind. Chemist* (1963) 238.
[80] M. S. Spencer, P. J. H. Carnell and W. J. Skinner, *Ind. Eng. Chem. (Proc. Des. Dev.)* **8** (1969) 191.
[81] P. J. H. Carnell, W. J. Skinner and M. S. Spencer, British Patent 1 071 923 (1967).
[82] A. H. W. Cleave, US Patent 1 535 577 (1925).
[83] G. F. Nordblom and G. W. Bodamer, US Patent 3 414 486 (1968); *Idem*, US Patent 3 419 901 (1968).
[84] F. S. Holland, British Patent 1 444 367 (1976).
[85] SPA Arrigo Pini, British Patent 1 044 776 (1966).
[86] Societe Industrielle des Coussinets, British Patent 871 698 (1961).
[87] J. Prunet and A. Guillen, French Patent 1 264 597 (1960).
[88] J. Gordy, US Patent 3 778 360 (1973).
[89] G. W. Johnson, British Patent 506 590 (1939).
[90] P. E. Benner, US Patent 3 448 026 (1969).
[91] F. Lacroix, US Patent 1 019 969 (1912).
[92] S. O. Cowper-Coles, US Patent 1 127 966 (1915).
[93] R. A. Schaefer, US Patent 2 391 039 (1945).
[94] J. Rennie, J. M. Pratt and D. J.Milner, British Patent 1 349 672 (1974).
[95] S. B. Fulweiler, US Patent 3 583 897 (1971).
[96] O. Fischer, British Patent 1 259 374 (1972); *Idem,* US Patent 3 560 366.
[97] R. Goold, C. W. Wojcik and G. D. Cooper, Austrailian Patent 59 229 (1975).
[98] M. A. Julien, British Patent 224 916 (1925).
[99] A. C. Cooley, US Patent 3 551 317 (1970).
[100] F. S. Holland and F. C. Walsh, British Patent Application 81/04624.
[101] G. Kreysa and R. Brandner, Proceedings 31st ISE Meeting, Venice, 1980.
[102] *Idem,* Proceedings 2nd World Congress Chem. Eng., Montreal, 1981.
[103] F. Wendt, *Ingen. -Arch.* **4** (1933) 577.

[104] F. S. Holland and H. Rolskov, Effluent Water Treatment Convention, Birmingham, 1978.
[105] D. R. Gabe and F. C. Walsh, Proceedings Interfinish 1980, Metal Society Japan, Kyoto, p. 486.
[106] F. C. Walsh, N. A. Gardner and D. R. Gabe, *J. Appl. Electrochem.* **12** (1982) 299.
[107] A. T. Kuhn and R. W. Houghton, 'Topics in pure and applied electrochemistry', SAEST, Karaikudi, India (1979) p. 133.
[108] F. Goodridge, Proceedings 24th International Congress Pure Applied Chemistry, Butterworths, London, **5** (1974) 19.
[109] *Idem,* Paper presented to meeting on 'Electrochemistry-Material Recovery and the Environment', Shell Research Centre, Thornton, 1979.
[110] R. Kammel and H. W. Lieber, *Galvanotechn.* **68** (1977) 413. *Idem, ibid.* **69** (1978) 687.
[111] N. Ibl, Proceedings 31st I.S.E. Meeting, Venice, 1980.
[112] G. Kreysa, *Electrochim. Acta* **26** (1981) 1693.
[113] G. Kreysa, *Metallob.* **35** (1981) 211.
[114] J. Bassett, R. C. Denney, G. H. Jeffrey and J. Mendham, 'Vogel's textbook of quantitative inorganic analysis', 4th Ed. Longmans, London, (1978).
[115] J. J. Lingane, 'Electroanalytical Chemistry', 2nd Ed. Interscience, New York (1958).
[116] G. A. Rechnitz, 'Controlled Potential Analysis', Pergamon, London (1963).
[117] C. V. King, *Trans. Electrochem. Soc.* **102** (1955) 193.
[118] *Idem, J. Amer. Chem. Soc.* **57** (1935) 828.
[119] C. V. King and M. Schack, *ibid.* **57** (1935) 1212.
[120] C. V. King and W. H. Cathkart, *ibid.* **59** (1937) 63.
[121] C. V. King and P. L. Howard, *Ind. Eng. Chem.* **29** (1937) 65.
[122] H. Salzberg and C. V. King, *J. Electrochem. Soc.* **97** (1950) 290.
[123] C. V. King and F. S. Lang, *ibid.* **99** (1952) 295.
[124] C. V. King and N. Mayer, *ibid.* **100** (1953) 473.
[125] B. Roald and W. Beck, *ibid.* **98** (1951) 277.
[126] E. Heitz, G. Kreysa and C. Loss, *J. Appl. Electrochem.* **9** (1979) 243.
[127] C. Loss and E. Heitz, *Werks. u Korr.* **24** (1973) 38.
[128] B. C. Syrett, *Corrosion* **32** (1976) 243.
[129] Z. A. Foroulis and H. H. Uhlig, *J. Electrochem. Soc.* **111** (1964) 13.
[130] G. Butler and E. G. Stroud, *Brit. Corr. J.* **1** (1965) 110.
[131] L. Giuliani, A. Tamba and C. Modena, *Corr. Sci.* **11** (1971) 485.
[132] F. Mansfeld and J. V. Kenkel, *Corrosion* **33** (1977) 236.
[133] M. A. C. de Castro and B. E. Wilde, *Corr. Sci.* **19** (1979) 923.
[134] I. Cornet and R. Kappesser, *Trans. Inst. Chem. Eng.* **47** (1969) T194.
[135] G. Kar, I. Cornet and D. W. Fuerstenau, *J. Electrochem. Soc.* **119** (1972) 33.
[136] G. H. Sedahmed, B. A. Abd El Naby and K. A. Abdel-Khali, *Corr. Sci.* **17** (1977) 865.
[137] A. C. Makrides, *Corrosion* **18** (1962) 338t.
[138] *Idem, J. Electrochem. Soc.* **107** (1960) 869.
[139] A. K. Graham and H. L. Pinkerton, *Proc. Amer. Electropl. Soc.* **50** (1963) 135.
[140] S. S. Misra and T. L. Rama Char, *J. Sci. Indust. Res. (India)* **20D** (1961) 43.
[141] P. H. Strickland and F. Lawson, in 'International Symposium on Hydrometallurgy' (edited by D. J. I. Evans and R. S. Shoemaker), AIME, Chicago (1973) p. 293.
[142] J. Newman, 'Electrochemical Systems', Prentice-Hall, Englewood Cliffs, New Jersey (1973).
[143] K. M. Becker and J. Kaye, *J. Heat Transfer* **84C** (1962) 97.