

Table 2.1 Comparative data for limiting current densities and electrode surface areas in conventional and alternative cell designs

Cell type	Mass transport	Approximate i_{lim} (mA/cm ²)	Electrode area (cm ² /cm ³)
Parallel plate (vertical)	Natural convection	0,8 - 1,3	0,13
Parallel plate (horizontal)	Natural convection	2,8	0,13
Parallel plate (pumped flow, capillary gap)	Forced convection	2,6 - 8,0 (depending on velocity)	1,0 - 5,0
Filter press	Forced convection	0,5 - 1,0	0,3 - 1,7
Rotating disk / cylinder	Mechanically promoted convection	3 - 38 (depending on speed)	0,1
Packed bed	Forced convection	115 (6)*	10 - 50
Fluidised bed	Forced convection	115 (6)*	20 - 100
'Swiss roll'	Forced convection	2 - 4	20 - 50

* See text for distinction

It is apparant from the data presented in Table 2.1 that the packed and fluidised bed designs achieve limiting current densities comparable with the best values obtained in other designs. In the case of packed and fluidised bed electrodes however, the electrode surface area to volume ratio is much greater than for alternative designs and hence, for a given duty, cells of this type are smaller and less expensive. Packed and fluidised bed electrodes have the additional advantage of being able to treat very weakly conducting

solutions without suffering the penalty of an excessively large potential drop, although a degree of non-uniformity in the potential distribution within the bed may lead to undesirable side reactions.

Packed bed electrodes may be considered as a particular case of the fluidised bed electrode and similar mathematical modelling techniques apply to both types. Some authors claim improved mass transfer enhancement in the fluidised electrode (24, 25) whereas others have obtained better results with a restrained packed bed (41, 44). The fluidised electrode has the other advantages of allowing greater selectivity in the electrode reaction (by virtue of its more uniform potential profile) and of being immune to plugging by the reaction products or entrained solids. These advantages must be weighed against the greater pumping power required, the increased mechanical complexity of the cell, increased difficulty of operation and the poor electrical conductivity of the matrix phase when fluidised.

It is felt that any advantages attached to the fluidised configuration are outweighed by the disadvantages. No further theoretical or experimental consideration is therefore given to fluidised bed electrodes in the present work, which is confined to a study of the packed bed electrode. The majority of the theoretical results may, however, be extended to the fluidised electrode case with very little modification.

2.2.2 One-dimensional Porous Electrodes (Flow-through electrodes)

The one-dimensional electrode, in which electrolyte flow is parallel to current flow, lends itself to relatively straightforward theoretical treatment and facilitates experimental measurement. It is hardly surprising then, that this geometry formed the basis of virtually all the early theoretical and experimental investigations of packed bed electrodes, and that most packed bed electrode theory has been developed for the one-dimensional situation. Schematic representations of one- and two - dimensional electrode systems are given in Figure 2.6.

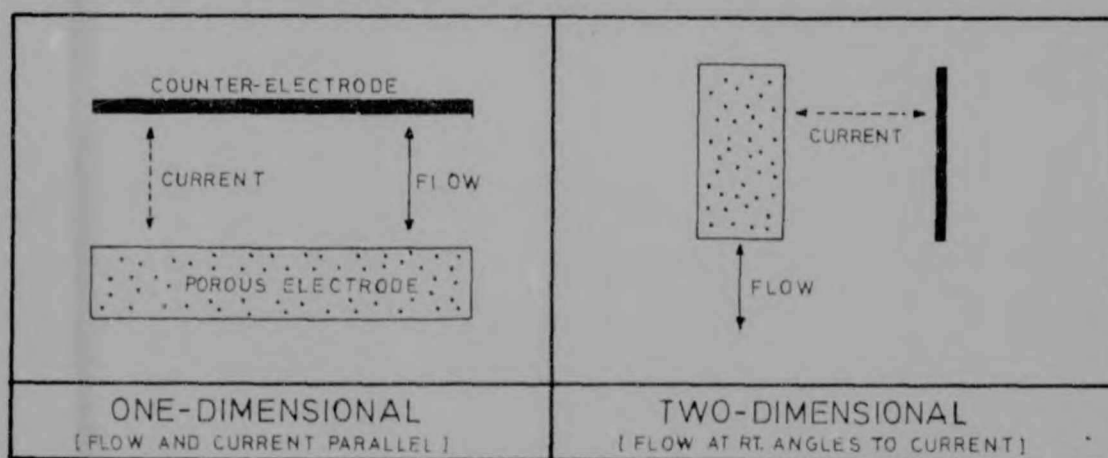


FIGURE 2.6. SCHEMATIC REPRESENTATION OF ONE- AND TWO-DIMENSIONAL POROUS ELECTRODES.

Early work in the field is summarised by Grens and Tobias (39) who comprehensively review the work published before 1963. The historical development of the macroscopic model for the porous electrode (in which the actual geometric details of the pore structure are not considered) is outlined and the basic kinetic and transport equations for the modelling of a single electrode reaction are given. They apply the model to the analysis of the steady state and dynamic behaviour of a flooded porous electrode in the case of a reaction with Butler-Volmer type kinetics. The effects of changes in the kinetic parameters for the electrode reaction, once again for the flooded electrode configuration in which bulk flow is absent, are discussed by other investigators (34, 40). Some work has indeed been done on electrodes in which the detailed geometry is taken into account (73) but the macroscopic model remains the basis of most current investigations.

Work done in more recent years is the subject of detailed reviews by Newman & Tiedemann (35, 109) who further outline the derivation of the basic equations for the one-dimensional macroscopic model. Consideration is given to flow-through reactors and to problems not treated in the studies of flooded electrodes. These additional considerations include the effect of mass transfer limitations, the effect of channelling and the best placing of the counter-electrode. Some quantitative and qualitative design procedures are outlined and the results of a number of other experimental investigations are briefly summarised. There have been a number of experimental investigations at limiting current density in which good correspondence between the experimental results and the theoretical predictions of the macroscopic one-dimensional model have been obtained. One of the earliest was that of Bennion and Newman (20) who studied the removal of copper from acidified solutions of copper sulphate (~ 650 ppm Cu) with 0.8 molar sodium sulphate as the supporting electrolyte. Two beds of graphite particles formed the anode and cathode. Copper was deposited on the cathode from the dilute solution and stripped from the anode as a concentrated solution for recovery by conventional means. The cell was operated continuously, with each bed serving alternately as anode and cathode. The anodic stripping process has been further investigated by Chu and Hills (19). Other investigations of copper removal at limiting current density have been performed by Chu et al (18) and by Alkire and Gracon (14). In the latter investigation the current distribution within the electrode was measured but was found to be in poor agreement with the theoretically predicted distribution; theoretical and experimental limiting current values were, however, in excellent agreement.

A number of other investigations have been undertaken, also at limiting current, in which the electrochemical reduction of potassium ferricyanide to ferrocyanide was used to further explore the performance of one-dimensional packed bed electrochemical systems(14, 44, 45, 116, 119). Good agreement between theory and experiment was generally observed.

An investigation of packed bed electrode performance at very low overpotentials (linear electrochemical kinetics) has been reported by Coeuret et al (17). The results were generalised to extend the treatment to high overpotential operating conditions by means of a semi-empirical kinetic expression (16).

The performance of packed bed electrochemical reactors under circumstances for which the conventional Butler-Volmer kinetic expression is not valid has been described in a series of papers by Ateya in co-operation with other investigators. Situations which have been investigated include reversible one-electron transfer reactions (52) and consecutive two-electron transfer reactions (Sn^{4+} reduction and O_2 reduction) (51, 53, 54). Considerable attention was paid to hydrodynamic effects in these and other(15,121)papers. A criterion was developed for use in deciding whether axial diffusion effects are likely to be of significance under given conditions: the experimental results of Sioda (49) satisfy this criterion and serve as further confirmation of its validity.

It has long been known that as the thickness of a packed bed is increased in the direction of current flow the benefits become increasingly less worthwhile (74). The electrode reactions are confined to an active area of definite thickness and any increase in bed thickness beyond this value merely represents wasted material. A number of expressions

have been proposed for estimating the effective bed thickness (17,24,25,35,113) and the effects on the useful thickness of modifying the bed conductivity and altering the position of the counter-electrode have been the subject of theoretical and experimental investigations (37, 50, 118, 123).

Design procedures for electrochemical systems incorporating packed bed electrochemical reactors have not been widely reported. Pickett (12) provides simplified one-dimensional design relationships for packed bed and fluidised bed reactors operating at limiting current density, which may then be applied to the calculation of overall system performances for a packed bed reactor with continuous circulation of electrolyte. Some experimental results are available for such systems (116, 130). However, no results describing two-dimensional flow-by reactor systems with multiple reactions conducted both at and below the limiting current density, as was the case in this investigation of nickel reduction, are known.

Other workers have derived design equations of varying complexity to describe one-dimensional porous electrodes (17, 35, 47, 48). In particular, the work of Kreysa and Heitz (47, 48) gives a good qualitative description of packed bed electrode design philosophy and provides a set of equations, some of which are approximate, for quantitative cell design. A good review of applications is given and added insight into the performance of packed bed electrodes is afforded by means of three-dimensional drawings showing the current-voltage-flowrate and current-voltage-bed thickness characteristics of typical packed bed electrodes.

2.2.3 Two-dimensional Porous Electrodes (Flow-by electrodes)

Analysis of two-dimensional porous electrodes is considerably more difficult than is the analysis of the one-dimensional situation. Consequently very little work has been done in this direction and the only detailed analysis known is that of Alkire and Ng(13,31).

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The analysis makes use of the conventional macroscopic model equations for porous electrodes. These equations are written for cylindrical co-ordinates and include both radial and axial components. The equations, written in dimensionless form to reduce the number of independent parameters which influence the system, may be solved numerically to determine the concentration and potential distributions throughout the reactor. Integration of the local reaction rate distribution yields the volumetric reaction rate and total cell current. Experimental results for copper removal from acidified solution agreed to within fifteen per cent with the theory over the entire range of cases studied.

Alkine and Ng have highlighted the deficiencies of the one-dimensional reactor configuration. Principal among these is the fact that, on account of limited electrolyte conductivity, the electrical current may not penetrate very deep into the bed. Much of the bed may therefore be inactive if it is too thick when viewed from the direction of the counter-electrode and, depending on the potential distribution, reaction selectivity may be poor.

In most applications it is necessary to provide an adequate residence time by matching the electrolyte flowrate to the bed length in the direction of flow. Any locally non-uniform flow or channelling is detrimental to the attainment of the desired residence time and can adversely affect the overall mass transfer rate. Such channelling effects are usually minimised by using beds of uniform porosity which are thick when viewed along the direction of fluid flow.

When the directions of fluid flow and electrical current flow are parallel a dilemma can arise in choosing an electrode thickness which simultaneously provides an acceptable potential distribution and yet allows for the desired residence time and the

absence of channelling. In the case of dilute systems having poor electrical conductivity there may, in fact, be no acceptable compromise possible with the parallel configuration. With a perpendicular configuration, however, in which the electrode is thin as seen by the counter-electrode and long as seen by the flowing fluid, these conflicting requirements may be satisfied. The electrode can be designed to simultaneously provide an acceptable potential profile and an adequate residence time.

The two-dimensional electrode is therefore particularly advantageous for treating dilute solutions of low conductivity.

Alkine and Ng have also calculated an expression for the effective penetration depth of the reaction into the electrode. By comparing the volume current density for the reactive region in the two-dimensional electrode with the corresponding expression for a one-dimensional electrode (35) a further criterion could be developed for deciding when the perpendicular configuration is preferred over the parallel configuration. The criterion for preference of the two-dimensional configuration is

$$\frac{v_y}{ak_m L_y} > 1 \quad [2.31]$$

Where v_y (cm/sec) is the electrolyte velocity, a (cm^2/cm^3) the specific surface area, k_m (cm/sec) the mass transfer coefficient and L_y (cm) the electrode length in the direction of electrolyte flow. The arrangement with current and electrolyte flows at right angles to each other is therefore the preferred choice when design considerations call for high velocities and coarse packing (with the latter factor resulting in both low a values and low k_m values).

Pickett and Stanmore have reported an experimental

study of a single layer packed bed electrode which was operated with current flow perpendicular to the direction of electrolyte flow (22). An experimental mass transfer correlation for this geometry was developed.

The effect of upward co-current gas flow on the rate of ferricyanide ion reduction in a two-dimensional packed bed reactor has recently been investigated (111). Considerably larger mass transfer coefficients were measured at low liquid flowrates but the advantages of gas addition became negligible once turbulent liquid-phase flow became established.

Two-dimensional flow-by reactors have also been applied to the electroreduction of nitrobenzene to p-aminophenol (126), the electroreduction of oxygen to hydrogen peroxide (125) and the electro-oxidation of benzene to quinone (117).

2.2.4 Simultaneous Reactions

In many electrochemical systems of practical interest there exists the possibility that a number of electrode reactions may take place simultaneously. This situation has not been the subject of much theoretical or experimental study however, and none of the references in this chapter thus far have dealt with more than a single reaction.

Existing experimental work, which has principally dealt with analytical applications, has been reviewed by Alkire and Gould (32), who have developed a one-dimension porous electrode model for multiple reaction sequences. Theoretical results are presented, over a wide range of parameter space, for the simultaneous deposition of several metals, the deposition of a metal in the presence of a redox system and for an electrochemical-chemical-electrochemical (ECE) reaction sequence.

Their model predictions were tested against experimental results for metal deposition from solutions of iron and copper and of copper and cobalt (115). No consideration was given in the model to the process of hydrogen evolution in the overall cell reaction. Since the hydrogen evolution reaction in some cases constituted 15% of the overall cell reaction it is understandable that fairly significant differences between some experimental and predicted values were observed.

A similar mathematical treatment was used by Trainham and Newman (36) in their development of a model for metal ion removal from dilute streams in the presence of competing reactions. The validity of the model was demonstrated using the results of earlier experimental investigations (14, 20). This and other related papers (38, 76) provide the basis of the mathematical treatment used in the present work which will be given in detail at a later stage.

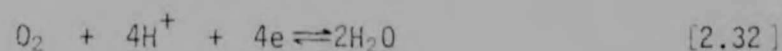
The effects of diffusion and dispersion on conversion, selectivity and yield for multiple competing reactions in channel flow electrochemical reactors have been investigated (136, 137). These effects are of no significance under the experimental conditions of this investigation (refer section 5.4).

The work of Young (11), on copper removal from acidified solution with simultaneous hydrogen evolution, contains the results of an early theoretical and experimental investigation of multiple reactions in porous electrodes. Semi-empirical kinetic expressions were used in the fitting of a mathematical model to the experimental results and an ambiguous fit resulted. These experimental data are re-examined in the present work.

2.2.5 Experimental Techniques

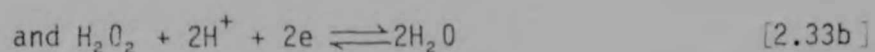
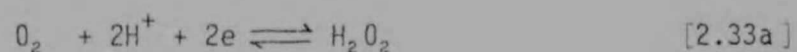
General surveys have been published (35, 41) which outline the experimental techniques used by a number of workers in investigating the theory and application of porous electrodes. These and other observations which have a bearing on the experimental work undertaken during this investigation are briefly summarised here.

Many different materials have been used to form the packed bed electrode itself. These include granular carbon (16-21, 27, 28, 50-53, 112-114, 125) and lead (11, 16, 26, 28) or copper (15, 16, 22, 50, 54) spheres and cylinders. Tin has been proposed as a suitable material when chemical recovery of the deposited metal is to be practised (29). In their studies of ferri-cyanide reduction Coeuret and co-workers (17, 43-45) have used bronze spheres plated first with nickel and then with gold. Sectioned cathodes made of copper (13), monel (126) or platinum (14, 115, 127) mesh have been used in experiments to determine the current distribution within the electrode by direct measurement of the mass of material deposited at various positions. De-aeration of electrolyte solutions in order to remove dissolved oxygen which otherwise takes part in a competing cathodic reaction has been widely practised (17, 18, 21, 22, 44, 52, 53, 115, 119, 122, 127). This is usually achieved by bubbling nitrogen gas through the solution. An alternative approach is to subject all solutions to pre-electrolysis before the electrochemically active reagents are added (18, 77). The overall competing reaction in acid solution is usually considered to be (11, 66)



The cathodic reaction proceeds via H_2O_2

as an intermediate product (66, 148), according to the reactions



Extensive use was made of supporting electrolytes in all the experimental investigations reported in this literature survey. The choice of supporting electrolyte was governed by the electrochemical reaction being investigated and included 0,5 - 1,5 molar sulphuric acid (11, 13-16, 18, 19, 22, 54, 115) 0,1 - 1,0 molar sodium sulphate (18 - 20, 112) 1,0 - 4,0 molar hydrochloric acid (51 -53), 1,0 molar sodium hydroxide (17, 43, 44) and 0,1-1,0 molar potassium chloride (14, 115).

In a number of experimental studies the polarisation curves of the packed bed electrodes were measured by means of fixed probes connected to reference electrodes (13, 14, 19, 20, 24). Potential profiles within the electrode itself have been measured by means of fixed (22, 50, 126) or movable (16, 17, 43-45, 118) probes.

2.2.6 Application of Packed Bed Electrodes to Metal/Metal Ion Systems

In this section the literature on the performance of packed bed electrodes in industrial-type applications is briefly reviewed. Only metal/metal ion systems and the related topic of cyanide oxidation are considered and no mention is made of electro-organic synthesis applications.

A number of early theoretical investigations concentrated on copper removal and, as a result, a number of applications in this direction have already

received detailed consideration. Possibly the first investigation which considered the practical aspects of cell operation and the cost of effluent treatment was that of Bennion and Newman (20). Incoming flow to their apparatus was split: 99 per cent was directed to the cathode compartment for metal removal and one per cent to the anode compartment from which a concentrated (0,74M CuSO_4) solution was obtained by anodic dissolution. Two beds, each constructed of graphite chips, served alternately as anode and cathode. In the packed bed cathode the copper concentration of the incoming solution was reduced from about 600 parts per million to as little as 0,55 parts per million. Operation was at pH 2,5 - 2,6 and the electrolyte conductivity was maintained in the range 0,16 - 0,19 mhos per centimetre by means of 0,8 molar sodium sulphate supporting electrolyte. The flow velocity through the cell was very low, the Reynolds number for the catholyte flow being of the order of 3×10^{-3} .

Extremely low copper concentrations have been obtained in the treatment of distillation plant brines (21) containing up to fifty grams per litre of sodium chloride. In a cell containing a bed of copper turnings, one square foot in cross section and six inches deep, copper concentrations were reduced from 1,5 parts per million to less than 0,2 parts per million in flowing streams of up to 10 000 gallons per day. When even more dilute feeds were treated copper concentrations of as low as 0,012 parts per million were achieved.

The development of an industrial cell for wastewater treatment, in which the cathode surface is formed from a fluffy stainless steel mesh, has also recently been announced (23, 78). Over eighty per cent removal at fifty per cent current efficiency is claimed for inlet streams containing 10 - 100

parts per million of copper. A 100 gallons per minute prototype (12V/2000A) has been operated, with onstream periods of 4-24 hours alternating with thirty minute off-line periods during which metal deposits are leached from the cathode by a mixed sulphuric acid/hydrogen peroxide solution.

Electrolytic recovery of silver from photographic fixing solutions in flat plate cells has long been practised. Where these conventional cells have been used the practise is to dump solutions containing upwards of 100 parts per million. Such levels are now far in excess of existing effluent control standards. Van Zee and Newman (27) have obtained treated effluents containing less than one part per million of silver from solutions initially containing 1000 parts per million. The apparatus used was similar to that of Bennion and Newman and operated at approximately forty five per cent current efficiency. In another reported investigation up to 99,5 per cent removal was achieved from fixing solution wastes containing thirty parts per million of silver (26).

The practicality of using a porous carbon cathode in removing mercury from simulated chlor-alkali plant brines and lead from organolead manufacturing plant effluents has been demonstrated (26). A mercury removal efficiency of over 99,9 per cent was achieved for inlet concentrations in the range 10 - 600 parts per million. Lead concentrations of less than fifty parts per billion were obtained when treating a solution containing 0,6 parts per million in a porous carbon cathode. Poorer performance was obtained with a bed made of lead shot.

Lead shot cathodes with particle diameters of 1,1 and 2,60 millimetres have successfully been used for the reduction of Sb^{3+} ions (28). A limiting concentration of five parts per million was achieved

and no further reduction below this level was possible. Current efficiencies of up to fifty per cent were measured. It is interesting to note that Trainham and Newman (123) have subsequently presented a thermodynamic analysis which determines the equilibrium antimony concentration for the multiple reaction sequence as a function of electrode potential. The analysis predicts a minimum total antimony concentration at around -0,38 volts versus the saturated calomel electrode.

Cyanides are frequently encountered in heavy metal effluents and attention has therefore been devoted to the simultaneous oxidation of cyanides and reduction of metals (10, 29, 30). A number of patents have been issued for the use of packed bed electrodes in this particular application. Typical cell performances which have been reported for the treatment of mixed metal/cyanide effluents are given in Table 2.2 (10).

Table 2.2 Results for treatment of mixed metal/cyanide effluents in a packed bed cell

Component	Feed concentration (ppm)	Effluent concentration (ppm)
CN ⁻	10	1
Cu ²⁺	5	0,1
Zn ²⁺	5	1
Cd ²⁺	2	0,05

The theoretical and experimental results of this investigation have been applied to the design of a pilot plant for the treatment of various electroplating wash-water effluents (108, Appendix I).

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2.3. Mathematical Model of the Packed Bed Electrode

2.3.1 Introduction

In this section the derivation of the equations for the mathematical model of the packed bed electrode is outlined. Provision is made for multiple electrode reactions which may be subject to mass transfer limitations. The treatment is similar to that of Trainham and Newman (36) and of Alkire and Gould (32).

Two sets of solutions to the equations for the model are given. In the first, it is shown how electrochemical parameters for simultaneous reactions may be calculated analytically provided experimental potential data for the packed bed are available. A numerical solution is given for cases where potential data are not available and must be calculated.

The fact that the model is derived for a one-dimensional configuration is not particularly restrictive. The application may easily be extended to include two-dimensional situations provided the two-dimensional electrode is considered to be composed of a number of thin, one-dimensional slices, over which concentration changes are sufficiently small. Such an approach has been followed elsewhere (11, 16) and is again used in the present work.

2.3.2 Assumptions Used in the Derivation

The thin two-dimensional porous electrode for which a one-dimensional model is developed is shown schematically in Figure 2.7.

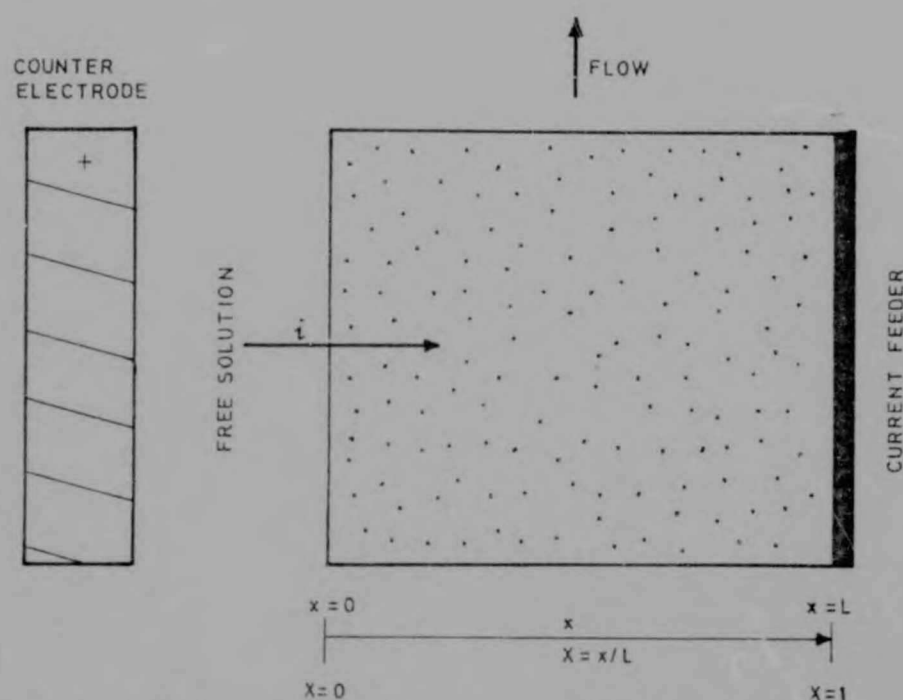


FIGURE 2.7. POROUS ELECTRODE REPRESENTATION USED IN THE MATHEMATICAL MODEL.

The following restrictions and assumptions apply:

- (a) The porous matrix can be described, without reference to exact geometric details, by its porosity (ϵ), surface area per unit volume (a) and volume average conductivity (σ) which remain constant in time.
- (b) The electrode is isothermal, isotropic and no appreciable structural changes occur during operation.
- (c) The hydrodynamics are characterised by the superficial flow velocity and an average mass transfer coefficient. Deviations from plug flow by axial diffusion and dispersion are negligible.
- (d) The electrolyte is sufficiently dilute that the transport properties are constant and activities may be replaced by concentrations.

- (e) Density variations in the electrolyte due to concentration changes are negligible.
- (f) Operation is at steady state.
- (g) The flowrate of electrolyte through the electrode is sufficiently high for turbulence to destroy any concentration gradients in the direction of current flow. Furthermore, the length of electrode in the direction of solution flow is sufficiently small for concentration differences in this direction to be averaged and the entire electrode to be taken as operating at this average concentration.
- (h) The conductivity of both the matrix and pore-solution phases is uniform. The conductivity of the solid matrix is very much greater than that of the electrolyte.
- (i) A principal electrode reaction occurs with current efficiency ϵ . The rate of this reaction may be subject to mass transfer limitations.
- (j) An unspecified number of simultaneous side reactions may take place. The rates of these reactions may be described by conventional electrochemical kinetics and may be subject to mass transfer limitations.
- (k) If gas evolution occurs in the side reaction the gas either remains in solution or, if bubbles are evolved, the velocity distribution, interfacial area and void volume are not significantly affected.
- (l) The assumption of electroneutrality (equation [2.29]) holds for the electrolyte throughout the electrode.

2.3.3 Equations for the One-dimensional Packed Bed Electrode Model for the Flow-by Electrode

The derivation of the equations describing the packed bed electrode is somewhat complex and is therefore given in detail in Appendix B.

The complete solution of the general equations is only shown for a specific case, namely that of a single side reaction which may be described by Butler-Volmer kinetics and which is not subject to significant mass transfer limitation. As will be demonstrated in Chapter 5, this simplification adequately describes the systems considered in this investigation with an accuracy consistent with application to electrochemical reactor design, even though in the nickel case a number of processes competing with the main reaction are lumped into a single effective side reaction.

Under these conditions a fairly simple equation is obtained to describe the one-dimensional potential distribution within the electrode. This potential is given by

$$\frac{d^2 \eta}{dx^2} = b \left[k_2 e^{\beta_2 \eta} + \frac{k_1 k_L C_R e^{\beta_1 \eta}}{k_L C_{R,ref} - k_1 e^{\beta_1 \eta}} \right] \quad [2.34]$$

Obviously every system must be the subject of individual analysis which will then lead to expressions of the same general form as equation [2.34], with the number and form of the terms within the square brackets depending on the number and degree of mass transfer limitation of the simultaneous reactions.

The various terms have the following values:
full explanations of the symbols may be found
in Appendix B.

$$b = a \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right) \quad [2.35]$$

$$k_1 = -i_{oR, \text{ref}} \quad [2.36]$$

$$k_2 = -i_{oS, \text{ref}} e^{-\beta_2 \Delta U} \quad [2.37]$$

$$k_L = nFk_m \quad [2.38]$$

$$\beta_1 = \frac{-\alpha_{cR} F}{RT} \quad [2.39]$$

$$\beta_2 = \frac{-\alpha_{cS} F}{RT} \quad [2.40]$$

It may be seen that the model equation incorporates a concentration dependence, C_R , for the principal reactant which is related to a reference concentration $C_{R, \text{ref}}$. The terms k_1 and k_2 are related to the exchange current densities for the main and side reactions respectively at chosen reference concentrations. The expression for the side reaction contains an additional term which takes into account the difference between the open circuit potential of the main and side reactions.

The terms β_1 and β_2 contain the transfer coefficients for the cathodic electrochemical reactions and are related to the Tafel slopes for the two reactions (equation [2.17]) Mass transfer limitations on the main reaction are governed by

k_L which is directly proportional to the mass transfer coefficient. Solution and bed conductivities, as well as the specific interfacial area of the bed are lumped into the constant b .

The two expressions within brackets correspond to the partial current densities for the main and side reactions. The sum yields the local current density within the packed bed electrode. The second of the two expressions, which applies to the main reaction, can take on limiting values which describe both the exponential and limiting current sections of the typical polarisation curve given in Figure 2.3. In the case where mass transfer resistance in the main reaction becomes negligible ($k_L \rightarrow \infty$) the limiting value is given by

$$\lim_{k_L \rightarrow \infty} \frac{k_1 k_L C_R e^{\beta_1 \eta}}{k_L C_{R,ref} - k_1 e^{\beta_1 \eta}} = i_{oR,ref} \frac{C_R}{C_{R,ref}} e^{\beta_1 \eta} \quad [2.41]$$

and normal Tafel kinetics apply. When mass transfer limitations become controlling the limiting value at high cathodic overpotentials ($\eta \rightarrow -\infty$) is given by

$$\lim_{\eta \rightarrow -\infty} \frac{k_1 k_L C_R e^{\beta_1 \eta}}{k_L C_{R,ref} - k_1 e^{\beta_1 \eta}} = -nF k_m C_R \quad [2.42]$$

which is simply the magnitude of the limiting cathodic current density.

As may be seen from Figure 2.7 the entire electrode current is carried by the solution phase at the face of the electrode which forms the free solution interface. Within the electrode the current is partitioned between the matrix and solution phases and at the face immediately adjacent to the current feeder the entire electrode current is carried by the matrix phase. The boundary conditions on equation [2.34] are thus

$$\text{At } x = 0 : \frac{dn}{dx} = \frac{-i}{\kappa} \quad [2.43]$$

$$\text{At } x = L : \frac{dn}{dx} = \frac{i}{\sigma} \approx 0 \quad [2.44]$$

where i (A/cm^2) is the superficial current density for the current feeder, given by dividing the total electrode current by the current feeder area. The zero approximation at $x = L$ comes about as the result of the large matrix conductivities which are generally applicable and which result in a negligible potential gradient within the matrix phase.

The model equations and the boundary conditions may also be expressed in terms of the dimensionless length $X = x/L$ as follows:

$$\frac{d^2 n}{dX^2} = B \left[\frac{k_2 e^{\beta_2 n} + k_1 k_L c_R e^{\beta_1 n}}{k_L c_{R,ref} - k_1 e^{\beta_1 n}} \right] \quad [2.45]$$

$$\text{where } B = \frac{L^2}{b} \quad [2.46]$$

The boundary conditions are

$$\text{At } X = 0: \frac{d\eta}{dX} = -\frac{iL}{\kappa} \quad [2.47]$$

$$\text{At } X = 1: \frac{d\eta}{dX} = 0 \quad [2.48]$$

2.3.4 Solutions of the Model Equation

The detailed calculations for the solution of equation [2.45] are given in Appendix B.

The analytical solution is

$$\frac{-i^2}{2b\kappa^2} = \frac{k_L C_R}{\beta_1} \ln \left[\frac{k_1 e^{\beta_1 \eta_0} - k_L C_{R,ref}}{k_1 e^{\beta_1 \eta_1} - k_L C_{R,ref}} \right] - \frac{k_2}{\beta_2} \left[e^{\beta_2 \eta_0} - e^{\beta_2 \eta_1} \right] \quad [2.49]$$

where η_0 and η_1 are the bed overpotentials measured at the free solution interface and current feeder respectively.

It is possible to measure η_0 and η_1 by means of probes suitably positioned within the electrode (16, 17, 22, 43 - 45, 50). If a number of experiments are conducted under varying conditions of flowrate, concentration and current density a set of equations may be written in terms of the measured potentials which may be solved simultaneously for the electrochemical kinetic parameters. Because the potential terms appear as exponents, the results obtained by this method are extremely sensitive to slight fluctuations in potential. The method may therefore only yield meaningful results when very accurate potential measurements are available.

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