Kinetic Modelling of Multicomponent Electrowinning

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1 Introduction

The problem presented at the workshop by Ning Li of Los Alamos concerned a particular process which forms part of a wider nuclear waste treatment strategy. One of the primary goals of the ADTT (Accelerator Driven Transmutation Technologies) programme at Los Alamos is to reduce the impact of nuclear waste. Accelerator-driven Transmutation of Waste (ATW) offers the possibility of sustainable nuclear future to countries that have a long history of nuclear power. The potential advantages of power generation with no accompanying problems of how to deal with spent fuel and plutonium are enormous. For countries starting nuclear energy programmes, it can also prove cheaper, safer and cleaner than conventional systems. The ATW waste treatment cycle involves reductive extraction, electrowinning and electrorefining, but in this study we shall concern ourselves solely with electrowinning. The process of electrowinning is best thought of as a generalisation of the familiar electro-plating process. In its simplest form, a potential difference is maintained across a pair of parallel conducting plates. A fluid flows between the plates and chemical reactions at the anode and the cathode deposit solids at the relevant sites. The 'fluid' may take any one of many forms; in cases analysed in the literature a popular choice for theoretical calculations has been to consider, for example, the electrowinning of copper from a sulphuric acid medium. In the particular application that interests Los Alamos, it is normally short half-life nuclear products that need to be extracted.

The main purpose of the current study is to indicate:

(1) How the existing theory fits into a coherent asymptotic and modelling framework.

(2) How existing models may be extended to multicomponent systems.

A further matter of interest concerns the order in which components are deposited. Electrowinning cells are usually controlled either by a set bias voltage or a set current. When the voltage is set, elements with oxidation potential lower than the

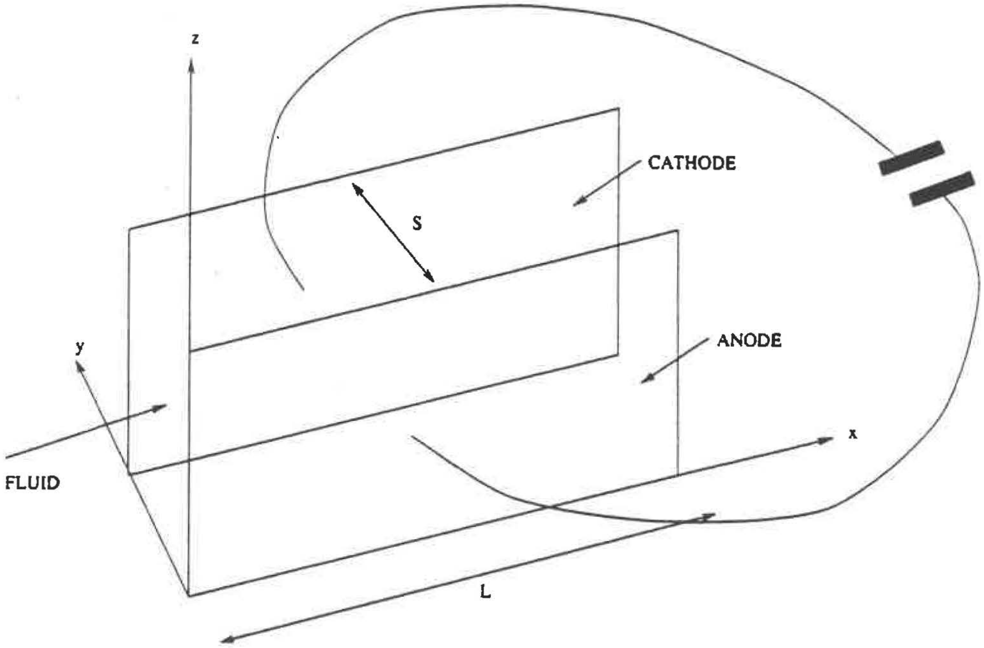

Figure 1: Schematic diagram of electrowinning cell

cell potential in the electrolyte solutions will deposit onto the cathode. When the current is set, it is less clear which elements will deposit, and the model that is developed should also be capable of addressing this problem.

2 The Basics of Electrowinning

Since some understanding of the rudiments of electrochemistry is required before a multicomponent model can be proposed, we begin by considering exactly what happens for a one-species electrowinning cell and what form of model we might expect to be appropriate for such a process. Single-species configurations have been considered previously by, for example, Lapique & Storck (1985).

Fig. 1 shows a schematic diagram of an electrowinning cell. We shall assume for the moment that the process is fully three-dimensional and that the applied voltage or current is simply 'sufficiently large' (see later discussion) to ensure that solid copper may be deposited at the cathode. For definiteness, let us assume that we wish to electrowin copper from an acid copper sulphate solution. The corresponding reactions are then

(1) $Cu^{2+} + 2e^- \rightarrow Cu$

and

(2) $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$.

Reaction (1) takes place at the cathode; as two electrons combine with the copper ions in solution, solid copper is created in a thin layer on the surface of the cathode. Reaction (2) expresses the fact that oxidation also takes place at the anode, typically manifesting itself in the form of gas bubbles.

To model this process we need to take account of the way in which the fluid moves, how mass is conserved for the solution, and how the electric field changes along and across the cell. Denoting the concentrations c_i of the species Cu^{2+}, H^+ and SO_4^{2-} in the solution respectively using subscripts 1,2 and 3 and the relevant mass fluxes by $\boldsymbol{N}_i$, conservation of mass for each species dictates that

$$c_{it} + \nabla.\boldsymbol{N}_i = 0. \tag{1}$$

Assuming further that the whole process is isothermal, gas generation effects at the anode are ignored, and the physical properties of the solution are constant, we may write for the fluid motion of the solution

$$\boldsymbol{q}_t + (\boldsymbol{q}.\nabla)\boldsymbol{q} = -\frac{1}{\rho}\nabla p + \nu\nabla^2\boldsymbol{q} \tag{2}$$

and

$$\nabla.\boldsymbol{q} = 0. \tag{3}$$

Here p denotes pressure, whilst the kinematic viscosity and density are denoted by ν and ρ respectively. It has been assumed that the fluid motion effectively decouples from the rest of the problem and is not influenced by the electric field. Electrical effects in the system are governed ultimately by Maxwell's equations. In this relatively simple configuration however, the electrostatic equations

$$\text{curl}\,\boldsymbol{E} = 0, \qquad \text{div}\boldsymbol{E} = \rho_0/\epsilon_0 \tag{4}$$

where $\boldsymbol{E}$ is the electric field and ρ_0 and ϵ_0 represent the charge density and vacuum permittivity respectively are all that are required. The first equation of (4) implies the existence of an scalar electric potential ϕ. The second, under the standard assumption that the left hand side may be neglected, gives a local equation more familiarly known as charge neutrality, which states that

$$\rho = \sum_{i=1}^{3} z_i c_i = 0 \tag{5}$$

where z_i is the charge number (number of electrons) of species i.

The equations (1), (2), (3) and (5) now constitute a closed system provided that a relationship is available to determine the mass fluxes $\boldsymbol{N}_i$ in terms of the c_i, $\boldsymbol{q}$ and ϕ. There are a number of ways in which this can be done, and the formulation of this constitutive law will be considered further below. The only features missing from the model are suitable initial and boundary conditions. In this case, these conditions are complicated by the fact that they must include details of the chemical reactions occurring at the anode and the cathode. Once again, many partly experimental and semi-empirical formulae are available to describe these reactions. For single species electrowinning cells the relations of Tafel and Butler-Volmer have gained wide acceptance. In essence they relate variables at the walls through a sequence of transcendental equations. By convention it is assumed that all reactions are occurring at each electrode: typically however the Tafel and Butler-Volmer equations give rise to reactions that are order one at one wall and exponentially small at the other.

As well as the conditions that determine the reactions, the standard boundary conditions for the Navier-Stokes equations (no-slip at a solid boundary) and for the electric potential (ϕ given at each electrode, for example) must be imposed, along with suitable initial conditions. Details of all such conditions will be given in a later section.

We have thus outlined how it is possible to propose a model for single-species electrowinning. Of course, the problem posed by (1)–(3), (5) along with all of the required boundary conditions is a formidable one. In the above formulation no simplifications arising from the geometrical properties of the electrowinning cell or the relative sizes of various terms in the equations have been exploited. It has also been assumed that the full Navier-Stokes equations have to be solved to determine the fluid motion. In its full form, the problem would therefore require numerical solution and it would probably constitute a long and difficult exercise to analyse cells for practical use in this way.

3 A Model for Multicomponent Electrowinning

Although the simple electrowinning process described above is well understood, complications arise if more than one species is to be electrowon from the solution. The purpose of the work presented below is to indicate how simple models may be generalised to cope with multiple component electrowinning, and how modelling simplifications may be made using asymptotic analysis.

First, the electrochemistry must be dealt with. In the multicomponent case a number of reactions may occur at both the anode and the cathode. It is also necessary to determine which substances will be electrowon and in what order. The electrochemical series ranks reactions according to their tendency to gain electrons as compared to hydrogen. By common consent, the reduction of hydrogen ion to hydrogen gas ($2H^+ + 2\,e^- \rightarrow H_2$) is assigned a zero reference position in the table. The electrochemical series therefore allows us to determine which substances are electrowon for a given applied voltage. Relative to hydrogen, the voltage required to electrowin copper is 1.26 V. If the solution also contains other substances appearing lower in the electrochemical series, these will also be electrowon with this voltage. For example, if a given solution contained copper, lead (-0.13V), iron (-0.44V) and zinc (-0.76V) an applied voltage of greater than 1.26V would be enough to recover all of these substances. Alternatively, the process could be started with a voltage of -0.5V, in which case only zinc would be recovered, and then continued with successive potential differences of say -0.3V, 0.5V and 2V whereupon the zinc, iron, lead and copper would be recovered in order.

For a multicomponent case, we assume that we have n species each at a concentration c_i (measured in mol/m^3). The mass conservation equation (1) becomes

$$c_{it} + \nabla . \boldsymbol{N}_i = 0 \tag{6}$$

and we are faced with the problem of how to specify $\boldsymbol{N}_i$ in terms of the other variables. There are three effects that contribute to the mass flux: diffusion down concentration gradients, drift due to the electric field effects, and convection due to the moving fluid. Allowing for each of these in turn, we thus write

$$\boldsymbol{N}_i = -\tilde{D}_i \nabla c_i - z_i u_i F c_i \nabla \phi + \boldsymbol{q} c_i \tag{7}$$

where $\tilde{D}_i$ denotes the diffusion coefficient of species i, u_i is the mobility of species i (a measure of the speed to which the molecules will accelerate in a given electric field) and F is the Faraday constant. To complete this formulation, it is necessary to state how the species mobility depends upon the other system properties. To do this we employ the classical Nernst-Einstein law which states that

$$u_i = \frac{D_i}{RT}$$

where D_i is the diffusion coefficient of species i, R is the gas law constant and T is the temperature. There is a reason for writing D_i in this relationship and $\tilde{D}_i$ in (7): for laminar flow $D_i = \tilde{D}_i$ and there is no need to distinguish between the two terms. For turbulent flow, however, we will lump the effects of turbulent diffusion into $\tilde{D}_i$. Strictly speaking, this is not correct as turbulence effects should be modelled by the convection term. However, because turbulent diffusion is typically a much stronger effect than molecular diffusion, when the flow is turbulent such effects are dominant in the first term of (7).

As well as mass conservation, the charge neutrality relationship

$$\sum_{i=1}^{n} z_i c_i = 0$$

applies and we must additionally specify how the fluid moves. As noted above, the general problem with arbitrary fluid motion is likely to prove to be suitable only for a numerical attack: we therefore simplify by assuming that the fluid motion has already been determined and takes the particularly simple form

$$\boldsymbol{q} = v(y)\boldsymbol{e}_x$$

where $v(y)$ is 'known'.

For simplicity we consider a two-dimensional version of the electrowinning cell shown in Fig. 1. The separation of the electrodes is given by S and the length of the electrowinning cell is L. We non-dimensionalise using $x = L\bar{x}$, $y = S\bar{y}$, $t = L/U\bar{t}$ (since the time scale of interest involves the time that the fluid stays in the cell), $c_i = c_{ie}\bar{c}_i$, $\phi = V\bar{\phi}$ and $\boldsymbol{q} = U\bar{\boldsymbol{q}}$ where V is a typical potential difference across the electrode, c_{ie} is the equilibrium concentration of species i (say at the start of the process) and U is a typical fluid velocity. For two dimensional operation, (dropping the bars for convenience of notation) the equations become

$$\delta^2 Re_i(c_{it} + v(y)c_{ix}) = \delta^2 c_{ixx} + c_{iyy} + \delta^2 z_i\Gamma_i(c_i\phi_x)_x + z_i\Gamma_i(c_i\phi_y)_y$$

$$\sum_{i=1}^{n} z_i c_{ie} c_i = 0$$

where the key non-dimensional parameters have been defined to be

$$\delta = \frac{S}{L}, \qquad Re_i = \frac{LU}{\tilde{D}_i}, \qquad \Gamma_i = \frac{FD_iV}{RT\tilde{D}_i}.$$

Let us now consider some typical sizes for the physical parameters. Most electrowinning cells are of small aspect ratio so that $\delta \ll 1$. Dimensions such as $L \sim 1\text{m}$, $S \sim 1\text{cm}$ are not unusual. As far as the other parameters are concerned, we have $F \sim 10^5$ Coulomb/mol and $R \sim 8$ J/mol/K and, assuming that operation is at room temperature so that $T \sim 300\text{K}$ and using a typical potential difference of $V = 1\text{Volt}$, we find that

$$\delta \sim 10^{-2}, \qquad Re_i \sim \frac{U}{\tilde{D}_i}, \qquad \Gamma_i \sim \frac{42D_i}{\tilde{D}_i}.$$

A number of asymptotic limits may now be discussed:

'No flow': $v(y) = 0$, $U \ll 1$, $D_i = \tilde{D}_i$.

now $\Gamma_i \sim 42$, $\delta^2 Re_i \sim 10^5 U$ (using a typical diffusion coefficient of 10^{-9} m^2/s, say) and the equations become

$$\delta^2 Re_i c_{it} = \delta^2 c_{ixx} + c_{iyy} + \delta^2 z_i \Gamma_i (c_i \phi_x)_x + z_i \Gamma_i (c_i \phi_y)_y, \tag{8}$$

$$\sum_{i=1}^{n} z_i c_{ie} c_i = 0. \tag{9}$$

Examining the right hand side of the first of these equations, we see that the first term may be ignored except in an 'entry region' boundary layer near to the start of the cell. These will henceforth be ignored, but it is evident from the scalings in (8) that these boundary layers will be $O(S)$ in length. The second and third terms are both order 1 or smaller, and the final term is dominant. A simple but helpful idea is to seek a steady-state solution. We assume that this represents the final state arising from some initial distribution of dissolved substances. For purposes of illustration, we consider a solution containing three species. We shall take these to be (1) Copper: Cu^{2+} (charge number 2, electrowon at 1.26V), (2) Zinc: Zn^{2+} (charge number 2, electrowon at -0.76V) and (3) Chlorine: Cl^- (charge number -1). Then with an applied voltage of 0 volts, say, the equilibrium ('outer', i.e. bulk) solution to the equations is that the concentrations are constant with $c_2 = 0$ (no zinc remains in the bulk as it has all been electrowon) $c_1 = c_{1e}$ (no copper can be electrowon at this voltage) and $c_3 = 2c_{1e}$. The potential ϕ is linear in y. If the applied voltage had been say 1.5V then both the zinc and the copper would have been electrowon. In this case, therefore, the bulk equilibrium solution would simply be $c_1 = c_2 = c_3 = 0$. The solution would thus be an insulator and the potential would not be defined.

It is worth making the point that for this case the equations (8) and (9) *cannot* possess non-constant solutions. This may easily be confirmed by using the fact that if one of the concentrations is zero, then using charge neutrality and adding the mass conservation equations it may be shown that the derivatives of the other two concentrations are constant. Symmetry may then be used to show that this constant is zero. In this case the Tafel or Butler-Volmer relationships are also irrelevant since all the reactions have already taken place.

We note in passing that if the time dependence was put back in for this case a fairly straightforward numerical problem would result.

Laminar Flow : $D_i = \tilde{D}_i$.

In this case there is still no turbulent diffusion, but the flow velocity is now important and effectively controls the performance of the device. The equations become

$$\delta^2 Re_i(c_{it} + v(y)c_{ix}) = \delta^2 c_{ixx} + c_{iyy} + \delta^2 z_i \Gamma_i (c_i \phi_x)_x + z_i \Gamma_i (c_i \phi_y)_y$$

$$\sum_{i=1}^{n} z_i c_{ie} c_i = 0,$$

indicating that the x-boundary layer is likely to be $O(S)$ in length. The 'entry region' to such devices may therefore be ignored to a large degree and we may approximate by solving the convection-diffusion system

$$\delta^2 Re_i(c_{it} + v(y)c_{ix}) = c_{iyy} + z_i \Gamma_i (c_i \phi_y)_y.$$

Some other estimates for general device properties follow from this equation: for $\delta^2 Re_i \ll \Gamma_i$ the time derivative terms are only important at the beginning of the process, whilst for $\delta^2 Re_i \gg \Gamma_i$ the flow is too quick to allow much to happen. Using the parameter values given above, this indicates that velocities of only a few mm/sec are required for the device to operate successfully.

4 The Butler-Volmer Relationships

As we shall presently see, reaction conditions are necessary to close the equations and predict how much of any given substance is electrowon at a given time. A number of different schemes have been proposed to model such reactions, which in reality may involve secondary and other reactions and be extremely complicated; in this study, for simplicity, we use the Butler & Volmer relationships, which may be thought of as a generalisation of the Tafel law. A large and sophisticated literature exists related to such laws, which have been discussed by, for example, Heyrovska (1986), Drazic & Vascic (1985) and Bortels et al. (1997).

In essence, the Butler & Volmer equations give the normal component of the current density under the assumption that reactions are one-step and proceed according to an Arrhenius-type law. The activation energy is effectively modified, however, to take into account the fact that a jump in voltage is required for the reaction to proceed. In general, we characterise the effects of the reactions occurring by writing

$$\sum_{j=1}^{m} \frac{s_{ij} i_{nj}}{n_j F} = -\boldsymbol{N}_i.\boldsymbol{n} \tag{10}$$

where $\boldsymbol{n}$ is the unit normal to the surface being considered, i_{nj} is the normal component of the current density due to reaction j, m is the total number of reactions taking place, s_{ij} is the stoichiometric coefficient of species i in reaction j and n_j is the number of electrons taking part in reaction j. The Butler–Volmer laws express how the current densities i_{nj} depend upon the species and the overpotentials. Specifically they assert that (for the anode, for example; expressions for the cathode follow similarly)

$$i_{nj} = i_{0j,ref} \left[\prod_{i=1}^{n} \left(\frac{c_{i,0}}{c_{i,ref}} \right)^{p_{ij}} \exp\left(\frac{\alpha_{aj} F E_A}{RT} \right) - \prod_{i=1}^{n} \left(\frac{c_{i,0}}{c_{i,ref}} \right)^{q_{ij}} \exp\left(\frac{-\alpha_{cj} F E_A}{RT} \right) \right] \tag{11}$$

where

$$E_A = V_A - \phi_{0A} - U_{j,ref}.$$

Here $i_{0j,ref}$ and $c_{i,ref}$ are respectively the exchange current density of reaction j and the concentration of species i at reference conditions, $c_{i,0}$ is the concentration of species i at the electrode surface, p_{ij} and q_{ij} denote respectively the anodic and cathodic reaction orders of species i in reactant j, α_{aj} and α_{cj} denote respectively the anodic and cathodic transfer coefficients for species j. V_A is the anode voltage, ϕ_{0A} is the potential on the anode surface (which, (see remarks below) is *not* the same as V_A) and $U_{j,ref}$ is the open-circuit potential of reaction j at reference conditions. We shall assume that all 'reference' variables may be regarded as data that can be 'looked up' (i.e. data that does not depend on specific details of the cell).

5 Well Mixed Bulk Flow

One case that may be considered where some helpful simplifications occur is concerns a small aspect ratio electrowinning cell where the bulk flow is 'well-mixed'. Specifically we assume that the fluid flow is two-dimensional and, although the velocity itself is non-zero, its average may be neglected. Whilst the flow continually mixes the contents of the cell, it therefore makes no contribution to net convection of the species. Under these assumptions $\boldsymbol{q}$ no longer appears in the problem and the (dimensional) equations are therefore

$$c_{it} + \nabla.\boldsymbol{N}_i = 0 \tag{12}$$

$$\boldsymbol{N}_i = -\tilde{D}_i \nabla c_i - \frac{z_i D_i F}{RT} c_i \nabla \phi \tag{13}$$

$$\sum_{i=1}^{n} z_i c_i = 0. \tag{14}$$

We seek to determine the deposition rates of the species present as functions of time, the initial conditions, and the applied voltage or current under the assumption that there is no x-dependence.

For simplicity, we will illustrate how the theory proceeds by examining the special multicomponent case considered in section 3 involving copper, zinc and chlorine; other cases may be treated similarly. Fig. 2 shows a schematic diagram of the flow. The cathode is assumed to be at a potential $V_C(t)$ and the anode at a potential $V_A(t)$. We shall consider two distinct problems, namely a cell where the total current is prescribed (and thus one of $V_A(t)$ and $V_C(t)$ is unknown - usually we take one of the two voltages to be zero without loss of generality) and a cell where the potential difference between the electrodes is prescribed so that, in effect, both voltages are known. We distinguish between three regions in the flow: the cathodic boundary layer, the bulk, and the anodic boundary layer. The width h of each of these boundary layers (in which $\tilde{D}_i = D_i$ since no turbulent mixing occurs) is assumed known, since the structure of these regions is determined by hydrodynamic considerations only and does not depend on the species concentrations. The electric potential ϕ is assumed to take the values $\phi^A(0)$ on the surface of the anode and

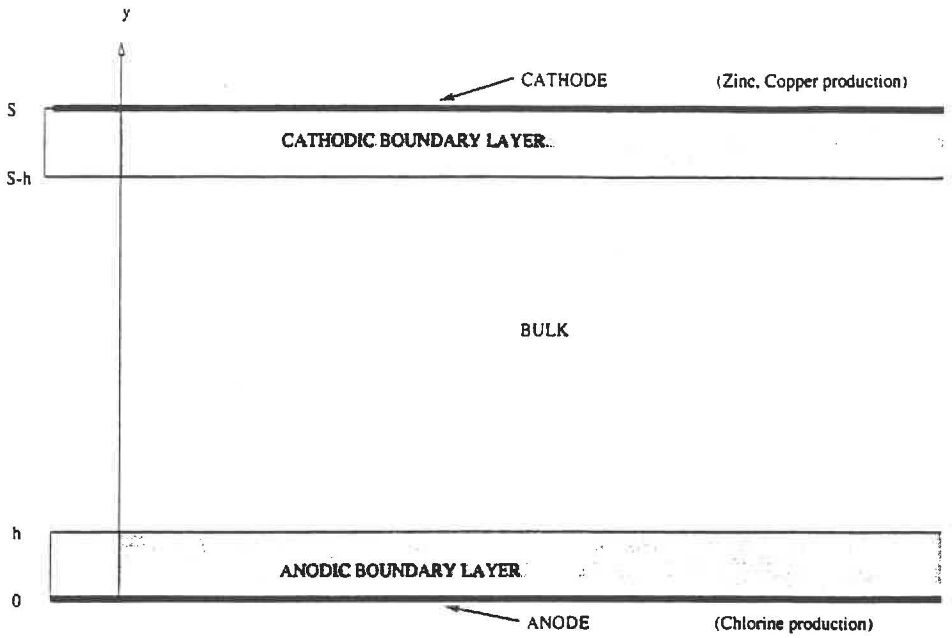

Figure 2: Multicomponent electrowinning from a well-mixed cell

$\phi^A(h)$ at the edge of the anodic boundary layer. Similar notation will be used at the cathode. It is worth pointing out that there is a jump in potential from the electrode itself to its surface. This simply reflects the fact that as a substance is electrowon at a surface, electrons must pass from the electrode to make solid metal. In reality, the voltage does not of course jump; instead it varies smoothly through the 'double layer' which is typically only a few Angstroms thick and is therefore ignored. We now propose equations in each of the three regions separately.

IN THE BULK: we scale as usual according to $t = \tau\bar{t}$, $y = S\bar{y}$, $c_i = c_{ie}\bar{c}_i$ and $\phi = V\bar{\phi}$ where τ denotes a time scale which is to be determined. We have (dropping the bars for convenience)

$$c_{it} - \left(\frac{\tilde{D}_i\tau}{S^2}\right) c_{iyy} - \left(\frac{\tau z_i D_i F V}{RTS^2}\right)(c_i\phi_y)_y = 0$$

$$\sum_{i=1}^{3} z_i c_{ie} c_i = 0.$$

In this case the mixing of the bulk means that it is appropriate to use different diffusivities as discussed earlier. The precise sizes of these quantities will depend on the particular application, but values of $D_i \sim 10^{-9}$ and $\tilde{D}_i \sim 10^{-6}$ are typical. (Normally for each species the diffusion coefficients would be different, but to simplify the subsequent computations we assume here that they are at least all the same order of magnitude.) Using the same parameters as section 3, this identifies the key non-dimensional parameters as

$$\frac{\tilde{D}_i\tau}{S^2} \sim 10^{-2}\tau, \qquad \frac{\tau D_i F V}{RTS^2} \sim \frac{\tau}{2400}.$$

This suggests that on any time scale of order greater than a few minutes, say, the time derivative terms in the mass conservation equations are negligible and the equations are simply

$$\nabla . \boldsymbol{N}_i = 0. \tag{15}$$

We therefore assume that, provided we do not wish to consider the initial stages of the process in detail, the concentrations in the bulk are functions time alone.

To completely specify the properties in the bulk we must characterise how the dissolved substances are consumed by the anode and cathode. This essentially amounts to a current balance. We have

$$(Sc_1)_t = (I_1^A(t) - I_1^C(t))/(z_1 F A_e) \tag{16}$$

$$(Sc_2)_t = (I_2^A(t) - I_2^C(t))/(z_2 F A_e) \tag{17}$$

$$(Sc_3)_t = (I_3^A(t) - I_3^C(t))/(z_3 F A_e) \tag{18}$$

where $I_i(t)$ is the current due to species i, the superscripts A and C indicate the anode and cathode respectively and A_e is the electrode area. We shall assume initially that the cell current $I(t)$ is known, so that (in the most general case where three reactions occur at each electrode)

$$I_1^A + I_2^A(t) + I_3^A(t) = I(t)$$

$$I_1^C + I_2^C(t) + I_3^C(t) = I(t).$$

The specification of the problem in the bulk region must be completed by the addition of a solvability condition so that the potential may be determined; the simplest way to derive this equation is to multiply each of the equations (12) by $z_i/\tilde{D}_i$ and add. Using charge neutrality, we then find that

$$\sum_{i=1}^{3} \frac{z_i c_{it}}{\tilde{D}_i} = \sum_{i=1}^{3} \frac{z_i^2 F D_i}{\tilde{D}_i RT}(c_i \phi_y)_y. \tag{19}$$

The need to include this equation may be easily explained if a formal asymptotic process is undertaken; essentially the limit that we are examining is the drift-dominated one, and if (16)-(18) are to be used then since (19) enters at the same order of magnitude it must be retained.

IN THE HYDRODYNAMIC BOUNDARY LAYERS: close to the electrodes, it is assumed that the hydrodynamic boundary layers prevent turbulent mixing and thus in these regions we take $\tilde{D}_i = D_i$. We also need to consider exactly which substances are being produced on each electrode: at the anode only chlorine gas is manufactured and thus

$$I^A_1 = I^A_2 = 0.$$

Conversely, both zinc and copper are being electrowon at the cathode, so that

$$I^C_3 = 0.$$

As far as the diffusion equations are concerned, although now $\tilde{D}_i = D_i$, the relevant length scale is $h \ll S$. To leading order, therefore, the concentrations are still governed by (15). Conservation of mass in the anode boundary layer therefore gives (having integrated the equations once and determined the constants by considering the currents)

$$\begin{aligned} -\tilde{D}_1 c^A_{1y} - \frac{z_1 D_1 F}{RT} c^A_1 \phi^A_y &= 0 && (20) \\ -\tilde{D}_2 c^A_{2y} - \frac{z_2 D_2 F}{RT} c^A_2 \phi^A_y &= 0 && (21) \\ -\tilde{D}_3 c^A_{3y} - \frac{z_3 D_3 F}{RT} c^A_3 \phi^A_y &= I^A_3(t)/(z_3 F A_e) && (22) \end{aligned}$$

whilst charge neutrality gives

$$z_1 c^A_1 + z_2 c^A_2 + z_3 c^A_3 = 0. \qquad (23)$$

At the cathode, similar equations apply giving

$$\begin{aligned} -\tilde{D}_1 c^C_{1y} - \frac{z_1 D_1 F}{RT} c^C_1 \phi^C_y &= -I^C_1(t)/(z_1 F A_e) && (24) \\ -\tilde{D}_2 c^C_{2y} - \frac{z_2 D_2 F}{RT} c^C_2 \phi^C_y &= -I^C_2(t)/(z_2 F A_e) && (25) \\ -\tilde{D}_3 c^C_{3y} - \frac{z_3 D_3 F}{RT} c^C_3 \phi^C_y &= 0 && (26) \end{aligned}$$

and charge neutrality

$$z_1 c_1^C + z_2 c_2^C + z_3 c_3^C = 0. \tag{27}$$

CLOSING THE PROBLEM: to close the problem the variables in the hydrodynamic boundary layers must be coupled with those in the bulk. We do this by insisting that the c_i, ϕ and ϕ_y are continuous at the boundaries between the anodic and cathodic boundary layers and the bulk. It should be emphasized that in doing this we have actually carried out a 'patching' rather than a formal matching process; it does not seem possible to carry out proper matching mainly on account of the discontinuous (order of magnitude) change that has been assumed in the diffusivities $\bar{D}_i$ from the bulk to the boundary layers. We therefore impose the conditions

$$c_1^A(h) = c_1(h), \quad c_2^A(h) = c_2(h), \quad \phi^A(h) = \phi(h), \quad \phi_y^A(h) = \phi_y(h) \tag{28}$$

$$\begin{gathered} c_1^C(S-h) = c_1(S-h), \quad c_2^C(S-h) = c_2(S-h), \quad \phi^C(S-h) = \phi(S-h), \\ \phi_y^C(S-h) = \phi_y(S-h) \end{gathered} \tag{29}$$

to patch the species concentrations and the potential. (Only two concentration conditions need to be used; the third will automatically be continuous by charge neutrality. See also later remarks concerning the last condition of (29).) To deal with the reactions we employ the Butler-Volmer laws: at the anode where species 3 is involved in a single reaction, we have

$$\frac{s_{33} i_{n3}}{F n_3} = -\boldsymbol{N}_3.\boldsymbol{e}_y.$$

Taking $n_3 = -1$, assuming that the cathodic part of (11) is exponentially small and that $p_{33} = 1$ is the only non-zero reaction order, we find that

$$\begin{aligned} \frac{s_{33} i_{03,ref}}{F}\left(\frac{c_3^A(0)}{c_{3,ref}}\right)\exp\left(\frac{\alpha_{a3}F}{RT}(V_A(t) - \phi^A(0) - U_{3,ref})\right) = \\ -\bar{D}_3 c_{3y}^A(0) + \frac{D_3 F}{RT} c_3^A(0)\phi_y^A(0) \end{aligned} \tag{30}$$

At the cathode, there are two reactions. Again, for simplicity we shall assume that s_{ij}, p_{ij} and q_{ij} are diagonal and that the terms associated with p_{ij} term are exponentially small. Assuming that the reactions are first order and taking $n_1 = n_2 = 2$, we find that

$$\frac{s_{11} i_{01,ref}}{2F}\left(\frac{c_1^C(S)}{c_{1,ref}}\right)\left(\frac{c_2^C(S)}{c_{2,ref}}\right)\exp\left(-\frac{\alpha_{c1}F}{RT}(V_C(S) - \phi^C(S) - U_{1,ref})\right) =$$

$$- \tilde{D}_1 c^C_{1y}(S) - \frac{2D_1F}{RT} c^C_1(S)\phi^C_y(S) \tag{31}$$

$$\frac{s_{22} i_{02,ref}}{2F} \left(\frac{c^C_1(S)}{c_{1,ref}}\right) \left(\frac{c^C_2(S)}{c_{2,ref}}\right) \exp\left(-\frac{\alpha_{c2}F}{RT}(V_C(S) - \phi^C(S) - U_{2,ref})\right) =$$

$$- \tilde{D}_2 c^C_{2y}(S) - \frac{2D_2F}{RT} c^C_2(S)\phi^C_y(S) \tag{32}$$

The formal specification of the problem is now complete: the equations (16)–(19), (20)–(23) and (24)–(27) must be solved subject to the boundary conditions (28), (29) and (30)–(32) with the current $I(t)$ and any two of the concentrations (the other may be calculated from charge neutrality) specified at some initial time. To check that the problem is correctly specified, it is necessary to carry out an 'equation count': the solution of (19) will require 2 arbitrary functions of time, whilst equations (16)-(18) involve only one arbitrary function (Three of the currents are zero; of the remainder, one is effectively known since the current $I(t)$ is known and the other two sum to the total current. Thus one is unknown.) Each of the systems (20)-(23) and (24)-(27) (which consist of 3 first order differential equations and one algebraic equation) will require three arbitrary functions of time. Finally, we will need to determine *one* of the electrode voltages $V_A(t)$ and $V_C(t)$ (the other may clearly be taken to be zero without loss of generality since the process can depend only on the potential difference). This totals to 10. Each of (28) and (29) provides us with four boundary conditions, and the Butler-Volmer laws (30)-(32) give another 3 to total 11. However, amongst the four anode and cathode boundary conditions there will be one redundant condition because the total current is prescribed (it seems easiest to ignore the final condition of (29)). The number of arbitrary functions required (10) is thus equal to the total number of boundary conditions (10) and we may be confident that the problem is properly specified.

A CELL WITH A PRESCRIBED POTENTIAL DIFFERENCE: Having solved the problem above where the current is prescribed, it is now simple matter to treat the case where the electrowinning process is driven instead by a prescribed potential difference. The only difference between this case and the model described above is that one of the anode and cathode voltages $V_A(t)$ and $V_C(t)$ is now known (assuming that the other is set to zero), and the total current $I(t)$ is unknown.

6 A Simple Illustrative Example

To check that the formulation described above does lead to a closed problem, it is worth briefly considering a simple example of the zinc/copper/chlorine system with some felicitously chosen constants. Specifically, we set

$$\tilde{D}_1 = \tilde{D}_2 = \tilde{D}_3 = \tilde{D}, \qquad D_1 = D_2 = D_3 = D.$$

These assumptions lead to some helpful simplifications, though it would be possible to solve the problem in closed form even without them. Physically, it does not seem out of the question that the diffusion coefficients could be similar. We also assume that the applied current $I(t) = I$ where I is a constant. On introducing the constants

$$\alpha = FSA_e, \qquad d = \frac{F}{RT}, \qquad g = \frac{1}{FA_e\tilde{D}},$$

and rearranging slightly, the equations become

BULK:

$$\begin{aligned} 2\alpha c_{1t} &= -I_1^C(t) \\ 2\alpha c_{2t} &= -I_2^C(t) = I_1^C(t) - I \\ -\alpha c_{3t} &= I_3^A(t) = I \\ 0 &= z_1^2(c_1\phi_y)_y + z_2^2(c_2\phi_y)_y + z_3^2(c_3\phi_y)_y \end{aligned}$$

which may be solved after the introduction of say $dJ_1^C(t)/dt = I_1^C(t)$ to give

$$\begin{aligned} c_1 &= -\frac{J_1^C(t)}{2\alpha} + c_{10} + \frac{J_1^C(0)}{2\alpha} \\ c_2 &= -\frac{J_1^C(0)}{2\alpha} + c_{20} + \frac{J_1^C(t)}{2\alpha} - \frac{It}{2\alpha} \\ c_3 &= -\frac{It}{\alpha} + c_{30} \end{aligned}$$

$$\phi = \frac{yB_1(t) + B_2(t)}{4(c_{10} + c_{20}) + c_{30} - \frac{3It}{\alpha}}$$

where the initial concentrations c_{10}, c_{20} and c_{30} satisfy

$$2c_{10} + 2c_{20} - c_{30} = 0$$

and $B_1(t)$, $B_2(t)$ and $J^C_1(t)$ are to be determined.

CATHODE:

$$\begin{aligned} c^C_{1y} + 2dc^C_1\phi^C_y &= gI^C_1(t)/2 \\ c^C_{2y} + 2dc^C_2\phi^C_y &= gI^C_2(t)/2 \\ c^C_{3y} - dc^C_3\phi^C_y &= 0 \\ 2c^C_1 + 2c^C_2 - c^C_3 &= 0 \end{aligned}$$

which may be solved (the process is made easier of the equations are first added and a single expression for ϕ^C is derived) to give

$$\begin{aligned} \phi^C &= \frac{1}{d}\log(ygI + 2\mathcal{C}_1(t)) + \mathcal{C}_2(t) \\ c^C_1 &= \frac{I^C_1(t)}{6I}(ygI + 2\mathcal{C}_1(t)) - \frac{\mathcal{C}_3(t)}{(ygI + 2\mathcal{C}_1(t))^2} \\ c^C_2 &= \frac{I^C_2(t)}{6I}(ygI + 2\mathcal{C}_1(t)) + \frac{\mathcal{C}_3(t)}{(ygI + 2\mathcal{C}_1(t))^2} \\ c^C_3 &= \frac{1}{3}(ygI + 2\mathcal{C}_1(t)) \end{aligned}$$

where $\mathcal{C}_1$(t), $\mathcal{C}_2$(t) and $\mathcal{C}_3$(t) must be determined.

ANODE:

$$\begin{aligned} c^A_{1y} + 2dc^A_1\phi^A_y &= 0 \\ c^A_{2y} + 2dc^A_2\phi^A_y &= 0 \\ c^A_{3y} - dc^A_3\phi^A_y &= -gI \\ 2c^A_1 + 2c^A_2 - c^A_3 &= 0 \end{aligned}$$

with solution

$$\begin{aligned} \phi^A &= -\frac{1}{2d}\log(-gIy + \mathcal{A}_1(t)) + \mathcal{A}_2(t) \\ c^A_1 &= \mathcal{A}_3(t)(-gIy + \mathcal{A}_1(t)) \\ c^A_2 &= (\frac{1}{3} - \mathcal{A}_3(t))(-gIy + \mathcal{A}_1(t)) \\ c^A_3 &= \frac{2}{3}(-gIy + \mathcal{A}_1(t)) \end{aligned}$$

where $A_1(t)$, $A_2(t)$ and $A_3(t)$ are yet to be found.

BOUNDARY CONDITIONS:

We may now impose the boundary conditions. Insisting that c_1 and c_3 are continuous at $y = h$ and $y = S - h$ (as usual, only two such conditions need to be imposed at each boundary layer edge as the third will be true automatically by charge neutrality) and also that ϕ and ϕ_y (though one of these will be redundant) are continuous at these locations gives in turn

$$\begin{aligned}
-\frac{J_1^C(t)}{2\alpha} + c_{10} + \frac{J_1^C(0)}{2\alpha} &= A_3(t)(-gIh + A_1(t)) && (33)\\
-\frac{It}{\alpha} + c_{30} &= \frac{2}{3}(-gIh + A_1(t)) && (34)\\
\frac{hB_1(t) + B_2(t)}{4(c_{10} + c_{20}) + c_{30} - \frac{3It}{\alpha}} &= -\frac{1}{2d}\log(-gIh + A_1(t)) + A_2(t) && (35)\\
\frac{B_1(t)}{4(c_{10} + c_{20}) + c_{30} - \frac{3It}{\alpha}} &= \frac{gI}{2d((-gIh + A_1(t))} && (36)\\
-\frac{J_1^C(t)}{2\alpha} + c_{10} + \frac{J_1^C(0)}{2\alpha} &= \frac{I_1^C(t)}{6I}((S-h)gI + 2C_1(t)) - \frac{C_3(t)}{((S-h)gI + 2C_1(t))^2} && (37)\\
-\frac{It}{\alpha} + c_{30} &= \frac{1}{3}((S-h)gI + 2C_1(t)) && (38)\\
\frac{(S-h)B_1(t) + B_2(t)}{4(c_{10} + c_{20}) + c_{30} - \frac{3It}{\alpha}} &= \frac{1}{d}\log((S-h)gI + 2C_1(t)) + C_2(t) && (39)\\
\frac{B_1(t)}{4(c_{10} + c_{20}) + c_{30} - \frac{3It}{\alpha}} &= \frac{gI}{d((S-h)gI + 2C_1(t))} && (40)
\end{aligned}$$

whilst the Butler-Volmer conditions at the anode and the cathode respectively give (setting $V_C(t) = 0$ without loss of generality)

$$\begin{aligned}
&\frac{2s_{33}i_{03,ref}}{3Fc_{3,ref}}A_1(t)\exp\left(\frac{\alpha_{a3}F}{RT}(V_A(t) - A_2(t) + \frac{1}{2d}\log A_1(t) - U_{3,ref})\right) = \\
&\qquad \frac{gI}{3}\left(2\tilde{D}_3 + \frac{FD_3}{RT}\right) && (41)\\
&\frac{s_{11}i_{01,ref}C_1^2(t)}{2Fc_{1,ref}c_{2,ref}}\left(\frac{I_1^C(t)}{3I} - \frac{C_3(t)}{4C_1^3(t)}\right)\left(\frac{I_2^C(t)}{3I} + \frac{C_3(t)}{4C_1^3(t)}\right) \times \\
&\qquad \exp(\left(\frac{\alpha_{c1}U_{1,ref}}{RT}\left(\frac{1}{d}\log 2C_1(t) + C_2(t)\right)\right) =
\end{aligned}$$

$$- \tilde{D}_1 \left(\frac{gI_1^C(t)}{6} - \frac{calC_3(t)}{4C_1^3(t)} \right) - \frac{FD_1gI}{RTDC_1(t)} \left(\frac{I_1^C(t)C_1(t)}{3I} - \frac{C_3(t)}{8C_1^3(t)} \right) \tag{42}$$

$$\frac{s_{22}i_{02,ref}C_1^2(t)}{2Fc_{1,ref}c_{2,ref}} \left(\frac{I_1^C(t)}{3I} - \frac{C_3(t)}{4C_1^3(t)} \right) \left(\frac{I_2^C(t)}{3I} + \frac{C_3(t)}{4C_1^3(t)} \right) \times$$

$$\exp(\left(\frac{\alpha_{c2}U_{2,ref}}{RT} \left(\frac{1}{d} \log 2C_1(t) + C_2(t) \right) \right) =$$

$$- \tilde{D}_2 \left(\frac{gI_2^C(t)}{6} + \frac{calC_3(t)}{4C_1^3(t)} \right) - \frac{FD_2gI}{RTDC_1(t)} \left(\frac{I_2^C(t)C_1(t)}{3I} + \frac{C_3(t)}{8C_1^3(t)} \right) \tag{43}$$

It is worth examining the conditions (33)-(40) to confirm that, as asserted earlier, there is a redundancy. Equating the right hand sides of (36) and (40) gives

$$2(-gIh + A_1(t)) = (S - h)gI + 2C_1(t).$$

Since subtracting (38) from (34) gives exactly this equation the expected redundancy is indeed confirmed.

Omitting the equation (40), (33)-(43) may be further manipulated until all of the unknown functions of time have been identified, thus completing the solution of this illustrative problem. The details are involved and not particularly illuminating and so have not been included here, but the main point is that predictions can be made.

7 Conclusions

Obviously much work remains if a useful predictive model is to be developed for the process of multicomponent electrowinning. A number of potentially valuable conclusions may however be drawn from this initial study:

- A consistent asymptotic approach to the theory has been developed where the status of any approximations that may be made is clear. In some studies that have appeared in the open literature the assumptions that were made were either unclear or not supported by numerical data.
- The multicomponent model may be derived as a straightforward generalisation of the single component model. There seems to be no reason why it should not predict successive electrowinning of various different substances in response to varying applied currents and voltages.

- Various special cases exist where the multicomponent model may be reduced to a manageable ordinary differential equation boundary value problem. Although the simplifying assumptions required are probably not representative of practically important circumstances, they may serve as useful test cases for the validation of numerical codes.

- The ultimate success or failure of a model for multicomponent electrowinning seems to depend upon the accuracy of the reaction model that is used. The Butler-Volmer model seems to have gained wide acceptance but is of an empirical nature. It is also necessary that accurate values are known for the many constants appearing in the Butler-Volmer laws, and this may in itself be a highly non-trivial matter.

- Other asymptotic limits that have not been examined here may also lead to interesting special cases. Their relevance to practical applications will depend on the range of parameters that may be encountered during the operation of electrowinning devices.

- The models developed are equally applicable to electrowinning cells where either the current or the potential difference is prescribed.

- Some of the literature that was examined during the week seemed to be in error. The errors were not major, but it is worth noting that some caution is required when the current literature is studied.

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Nomenclature Table

A_e	Electrode area (m^2)
c_i	Concentration of species i (mol/m^3)
c_{ie}	Equilibrium concentration of species i (mol/m^3)
$c_{i,ref}$	Reference concentration of species i (mol/m^3)
D_i	Diffusion coefficient of species i (m^2/s)
$\tilde{D}_i$	Diffusion (possibly turbulent) coefficient of species i (m^2/s)
$\boldsymbol{E}$	Electric field (V/m)
$\boldsymbol{E}_A$	Anodic activation energy overpotential term (V)
$\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z$	Unit vectors in the x, y and z directions respectively
F	Faraday's constant ($= 9.64846 \times 10^4$ Cou/mol)
L	Typical length of electrowinning cell (m)
i_{nj}	Normal component of current density from reaction j (A/m^2)
$i_{0j,ref}$	Reference exchange current density of reaction j (A/m^2)
I	Total current across electrowinning cell (A)
I_i^A	Current at anode due to species i (A)
I_i^C	Current at cathode due to species i (A)
m	Total number of reactions (-)
n	Number of species in solution (-)
n_j	Number of electrons taking part in reaction j (-)
$\boldsymbol{n}$	Unit normal to reaction surface
$\boldsymbol{N}_i$	Mass flux of species i ($mol/s/m^2$)
p	Fluid pressure (N/m^2)
p_{ij}	Anodic reaction order of species i in reactant j (-)
q_{ij}	Cathodic reaction order of species i in reactant j (-)
$\boldsymbol{q}$	Fluid velocity (m/s)
R	Gas law constant (8.31441 J/mol/K)
Re_i	Reynolds number type parameter $LU/\tilde{D}_i$ for ith species (-)
s_{ij}	Stoichiometric coefficient of species i in reaction j (-)
S	Typical width (electrode spacing) of electrowinning cell (m)
T	Temperature (K)
U	Typical flow speed in cell (m/s)
$U_{j,ref}$	Reference open-circuit potential of reaction j (V)
u_i	Mobility of species i ($m^2 mol/J/s$)
$v(y)$	Velocity profile in cell (m/s)
V	Potential difference across electrodes (V)

V_A	Anode voltage (V)
V_C	Cathode voltage (V)
z_i	Charge number of species i (-)
α_{aj}	Anodic transfer coefficient for species j (-)
α_{cj}	Cathodic transfer coefficient for species j (-)
δ	Electrowinning cell aspect ratio (-)
ϵ_0	Vacuum permittivity (farad/m)
Γ_i	Non-dimensional parameter $FD_iV/RT\tilde{D}_i$ (-)
ν	Fluid kinematic viscosity (m^2/s)
ϕ	Electric potential (V)
ρ	Fluid density (kg/m^3)
ρ_0	Charge density (cou/m^3)
τ	Time scale (s)