Constant-current unsupported electrolysis in a thin cell: a comparative study of analytical and simulative modelling

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Abstract

The features of digital simulation, analytical modelling and semianalytical modelling are contrasted. Two of these approaches are applied to an electrolysis experiment in which a neutral substrate, in solution in a thin-layer cell, is oxidized to an ionic product. The resistance of the cell, initially high, diminishes with time in the constant-current experiment. The cell voltage reflects both the decreasing ohmic polarization and the increasing concentration polarizations. Ultimately, exhaustion of substrate at the anode leads to a catastrophe at a transition time. The experiment is modelled simulative and analytically and the results are compared. A bookkeeping procedure is employed to assess the reliability of the numerical model.

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1. Introduction

In most electrochemical, and all voltammetric, experiments, some signal (usually a perturbation in the cell voltage or the imposition of a current) is applied to a resting cell and one of the system’s properties (usually that complementary to the applied signal) is measured as a function of time. Such experimental results, however, are of little worth without a model of the electrochemical processes involved. The motive for the modelling is to predict what the experimental output would be under assumptions made about the chemistry. Beyond this immediate goal, the modeller may also seek to determine other properties of the system, such as the way in which solute concentrations vary during the experiment. Modelling may even be carried out prior to experimentation, as a guide to suggest which of alternative experiments might be preferable [1].

The modelling of electrochemical processes has become an important and well-developed field. Though the classification is not rigorous, we may distinguish three broad modelling strategies.

In simulative modelling the space occupied by the ionically conducting medium, usually a solution, is dissected into many small regions and approximated physical laws are used to predict the interaction of each region with its immediate neighbours and thereby ultimately with the electrodes. The electrochemical processes are followed numerically, using digital computation. The modeller follows how the properties of the regions, and especially those that embrace the electrodes, evolve in time during the simulated experiment. A feature of simulative modelling is that it is progressive. By this it is meant that knowledge of the system’s properties at one instant in time relies on data for these properties at earlier times. Skilful simulation can produce results of high accuracy, but the precision of simulative (or “numerical”) modelling is necessarily limited by the inherent discretization in space and time.

In analytical modelling, mathematical tools are used to solve the problem in its entirety and produce a formula by which the sought property of the system is related to the known parameters. There is no necessity that the final formula

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be simple. Nor need it involve only well-established mathematical functions; indeed it is by similar analytical (or “mathematical”) modelling that most of the “established” functions of applied mathematics were originally discovered. Thus “unsummable” infinite series or “unintegrable” integrands may validly appear in the formula. Calculations leading to the analytical formula are performed algebraically, not arithmetically, though computer assistance is generally called upon to convert the final formula into a tabular or graphical representation. A satisfactory analytical model should be capable of producing numerical values of the sought quantity to any chosen precision. Analytical modelling is not progressive: the properties of the system at a chosen time instant are accessible without knowledge of its prior behaviour.

As its name suggests, *semianalytical modelling* occupies ground between the other two techniques. A high degree of mathematical sophistication is often involved, but numerical procedures are also incorporated. The technique, of which there are many variants, may be successful in the large number of cases for which a truly analytical solution is elusive. This approach has a distinguished history; Nicholson and Shain’s seminal work on cyclic voltammetry [2] was semianalytical. A common semianalytical strategy is to solve the spatial aspects of the problem analytically, without discretization, but to rely on a progressive, numerical, approach to address the time evolution. Integral equation methods and convolutive modelling are cases in point. In convolutive modelling [3–9], the mathematical operation of convolution is employed to couple the temporal and spatial aspects of the problem, the former being treated numerically, the latter analytically. The outcome in semianalytical modelling is generally an algorithm, rather than a formula. As befits the hybrid character of semianalytical modelling, its precision is intermediate between those of the other two techniques.

In this paper, we model electrolysis in a thin-layer cell. One uncharged and two ionic solutes are involved in transport and in the chemistry. The electrochemical system and cell geometry closely resemble those in experiments that have been studied recently [10–21], but this paper will emphasize the comparison of modelling options, rather than the exploration of chemical features. In the present paper, electrolysis is carried out by constant current and modelling will be simulative and analytic. An upcoming paper will address electrolysis at constant cell voltage, and incorporate a comparison of simulative and semianalytical modelling of that case. Except in Sections 5, 8 and 9 the following discussion applies indiscriminately to any electrolysis regime and the developments in the other sections will serve both publications.

2. Theoretical development

The cell consists of a layer of solution, of thickness \( Z \) and area \( A \), with parallel, planar electrodes forming the floor and ceiling of the cell. Initially the solution (in acetonitrile, for example) filling the space between the electrodes contains a dissolved neutral oxidizable substrate \( S \) (for example ferrocene) at a concentration \( c_{0}^{S} \). As well, the solution initially contains a smaller concentration \( c_{0}^{X} \) of the salt \( S^{+}X^- \) (for example ferricinium chloride) of the oxidation product. The reaction, proceeding reversibly, at the lower electrode is the one-electron oxidation of the substrate

\[
S^{\text{soln}} - e^- \rightarrow S^+^{\text{soln}} \tag{2.1}
\]

To maintain electroneutrality, the creation of each \( S^+ \) cation at the lower (working) electrode is accompanied by the injection of an \( X^- \) anion into the solution by the reaction

\[
MX(s) + e^- \rightarrow M(s) + X^-^{\text{soln}} \tag{2.2}
\]

at the upper electrode (for example an \( \text{Ag/AgCl} \) reference). This latter reaction also occurs reversibly, without activation polarization. Because only two ions are present, the electroneutrality principle requires that their concentrations be common at all points in the cell and at all times \( t \). We shall represent this joint concentration by \( c_{\pm}(z,t) \), where \( z \) represents the distance coordinate measured through the cell with \( z = 0 \) at the lower electrode and \( z = Z \) at the upper electrode. Similarly, the local concentration of the substrate will be denoted \( c_{0}(z,t) \).

Prior to the experiment the cell is open-circuit and at equilibrium. This initial condition is described by the equation set

\[
c_{0}(0 < z < Z,0) = c_{0}^{S}, \quad c_{\pm}(0 < z < Z,0) = c_{\pm}^{X}, \quad I(0) = 0, \tag{2.3}
\]

where \( I(t) \) denotes the faradaic current. We ignore any non-faradaic currents. Because the incipient cell reaction is

\[
S^{\text{soln}} + MX(s) \rightarrow S^+^{\text{soln}} + X^-^{\text{soln}} + M(s) \tag{2.4}
\]

the Nernst equation shows the initial cell voltage to have its null value, namely
\[
\Delta E(0) = E_{S/S^+}^0 - E_{MX/MX^+}^0 + \frac{RT}{F} \ln \left\{ \frac{a(M)a(S^+)}{a(MX)a(S)} \right\} = \Delta E^0 + \frac{RT}{F} \ln \left\{ \left( \frac{c_0^0}{c_0} \right)^2 \right\},
\]

(2.5)

where the \(E^0\) terms are standard electrode potentials, \(a\)'s are activities, \(\Delta E^0\) is the conditional or formal cell voltage, and \(c_0^0\) is the standard concentration.

Both electrodes behave reversibly and, accordingly, the concentration dependence of the cell voltage remains Nernstian after electrolysis has commenced. However, the bulk concentration terms in (2.5) become replaced by diffusion and, because there is no excess supporting electrolyte, migration is a component of transport for the \(S^+\) and \(X^-\) species.

Notice that, although the anion and cation share a common concentration, their flux densities are distinct. The diffusion potential, \(\phi\), is a function of time but not of location:

\[
\phi(z,t) = \frac{\partial}{\partial z} \phi(z,t)
\]

(2.8)

between the electric field \(\xi\) and the electrical potential \(\phi\). The logarithmic term in (2.7) represents the concentration overvoltage, \(\eta_{\text{conc}}(t)\), generated at the two electrodes. The final term is the cell’s ohmic overvoltage, \(\eta_{\text{ohm}}(t)\), plus a small contribution from the diffusion potential, \(\eta_{\text{assym}}(t)\). There is no term representing activation overvoltage because of our assumption that each of the two electrodes functions reversibly.

Current flows through the lower electrode by the anodic oxidation of \(S\) to \(S^+\). Therefore, by Faraday’s law, the flux density of each of these species at \(z = 0\) is proportional to the current density \(I(t)/A\). The \(X^-\) anion cannot cross the \(z = 0\) plane. With \(j\) denoting the flux density of the subscripted species, these facts imply

\[
-j_0(0,t) = j_+(0,t) = \frac{I(t)}{FA} \quad \text{and} \quad j_-(0,t) = 0.
\]

(2.9)

On the other hand, the conditions at the \(z = Z\) plane dictate that

\[
-j_-(Z,t) = \frac{I(t)}{FA} \quad \text{and} \quad j_0(Z,t) = j_+(Z,t) = 0.
\]

(2.10)

Notice that, although the anion and cation share a common concentration, their flux densities are distinct. The difference between these two flux densities is proportional to the current density flowing through the cell, which may be a function of time but not of location:

\[
j_+(z,t) - j_-(z,t) = \frac{I(t)}{FA}.
\]

(2.11)

Though the cell behaviour depends greatly on whether the current or the voltage is the controlled variable during the experiment, all the equations in this section hold, irrespective of this regime choice.

3. Transport

The solution is considered quiescent, so that no convective transport occurs. All three solute species are subject to diffusion and, because there is no excess supporting electrolyte, migration is a component of transport for the \(S^+\) and \(X^-\) species.

The symbols \(D_0\), \(D_+\) and \(D_-\) will be used to represent the diffusivities of \(S\), \(S^+\) and \(X^-\). \(D_\pm\) will represent the harmonic mean of the two ionic diffusivities:

\[
D_\pm = \frac{2D_0 D_\pm}{D_- + D_+}.
\]

(3.1)
We shall denote the mobilities of the two ions by \( u_+ \) and \( u_- \). However, it is convenient to replace them by diffusivities via the Nernst–Einstein relationships

\[
u_+ = \frac{FD_+}{RT} \quad \text{and} \quad \nu_- = \frac{FD_-}{RT}
\]

(3.2)

these relations being employed in Eqs. (3.5) and (3.6).

Being uncharged, the substrate is transported solely by diffusion and therefore its flux density obeys Fick’s first and second laws:

\[
\frac{j_0(z,t)}{D_o} = -\frac{\partial}{\partial z} c_0(z,t)
\]

(3.3)

and

\[
\frac{1}{D_o} \frac{\partial}{\partial t} c_0(z,t) = \frac{\partial^2}{\partial z^2} c_0(z,t).
\]

(3.4)

Compared with Eq. (3.3), the expression for the flux density of each ion has an additional term representing migratory transport:

\[
j_+(z,t) = -D_+ \frac{\partial}{\partial z} c_+(z,t) - u_+ c_+(z,t) \frac{\partial}{\partial z} \phi(z,t) = D_+ \left[ -\frac{\partial}{\partial z} c_+(z,t) + \frac{F c_+(z,t) \xi(z,t)}{RT} \right]
\]

(3.5)

and

\[
j_-(z,t) = -D_- \frac{\partial}{\partial z} c_-(z,t) + u_- c_-(z,t) \frac{\partial}{\partial z} \phi(z,t) = D_- \left[ -\frac{\partial}{\partial z} c_-(z,t) - \frac{F c_-(z,t) \xi(z,t)}{RT} \right].
\]

(3.6)

Making a weighted sum of Eqs. (3.5) and (3.6) to

\[
\frac{j_+(z,t)}{D_+} + \frac{j_-(z,t)}{D_-} = -2 \frac{\partial c_\pm(z,t)}{\partial z}
\]

(3.7)

followed by \( z \)-differentiation, we find

\[
\frac{1}{D_+} \frac{\partial j_+}{\partial z}(z,t) + \frac{1}{D_-} \frac{\partial j_-}{\partial z}(z,t) = -2 \frac{\partial^2 c_\pm(z,t)}{\partial z^2}.
\]

(3.8)

Away from the electrodes, each ion must independently obey the conservation law

\[
\frac{\partial c_+}{\partial t} + \frac{\partial j_+}{\partial z} = 0
\]

(3.9)

and therefore

\[
\frac{\partial j_+}{\partial z}(z,t) = -\frac{\partial c_+}{\partial t} (z,t) = \frac{\partial j_-}{\partial z}(z,t).
\]

(3.10)

This relationship, combined with (3.8) leads to

\[
\frac{1}{D_\pm} \frac{\partial}{\partial t} c_\pm(z,t) = \frac{\partial^2}{\partial z^2} c_\pm(z,t)
\]

(3.11)

after definition (3.1) is invoked. This shows, as is well known for a binary electrolyte, that the ions jointly obey Fick’s second law, even though his first law is not obeyed. The effective diffusivity, for the singly charged ions that alone we are addressing, is the harmonic mean of the individual diffusivities as given by Eq. (3.1).

If we substitute Eqs. (3.6) and (3.5) into relationship (2.11), we find that

\[
\frac{I(t)}{FA} = (D_- - D_+) \frac{\partial c_\pm(z,t)}{\partial z} + \frac{F(D_- + D_+)}{RT} \xi(z,t) c_\pm(z,t).
\]

(3.12)

The first right-hand term in this equation arises from asymmetry in the rates of diffusion of the two ions and will generally be much smaller than the final term, which represents ohmic polarization (or “IR drop”) in the solution. It is useful to rearrange Eq. (3.12) to

\[
\xi(z,t) = \frac{RTI(t)}{F^2 A(D_- - D_+) c_\pm(z,t)} + \frac{RT}{F} \left( \frac{D_- - D_+}{D_- + D_+} \right) \frac{\partial}{\partial z} \ln c_\pm(z,t)
\]

(3.13)

because this may be integrated to
\[
\int_0^Z \xi(z,t) \, dz = \frac{RTI(t)}{F^2A(D_+ + D_-)} \int_0^Z \frac{dz}{c_s(z,t)} + \frac{RT}{F} \left( \frac{D_+ - D_-}{D_+ + D_-} \right) \ln \left\{ \frac{c_s(Z,t)}{c_s(0,t)} \right\}
\]  
(3.14)
in which the first and second right-hand terms represent the ohmic and diffusion overvoltages. Combination with Eq. (2.7) into
\[
\eta(t) = \frac{RT}{F} \ln \left\{ \frac{c^b_0}{c^0(0,t)} \right\} + \frac{RTD_+}{FD_+} \ln \left\{ \frac{c_s(0,t)}{c_s^b} \right\} + \frac{RTD_-}{FD_-} \ln \left\{ \frac{c_s(Z,t)}{c_s^b} \right\} + \frac{RTD_- I(t)}{2F^2AD_+D_>} \int_0^Z \frac{dz}{c_s(z,t)}
\]  
(3.15)
definition (3.1) having also been employed, yields an expression linking the overvoltage to concentrations.

In this section thus far, equations have been derived that apply throughout \(0 < z < Z\). However, simpler relations apply at the electrodes. By combining Eq. (3.3) with the appropriate member first of (2.10) and then of (2.9), one discovers the following expressions for the gradient of the substrate’s concentration at the electrodes
\[
\frac{\partial c_0}{\partial z}(Z,t) = 0 \quad \text{and} \quad \frac{\partial c_0}{\partial z}(0,t) = \frac{I(t)}{FAD_0}.
\]  
(3.16)

Similar expressions hold for the concentration gradient of \(S^+X^-\) at the electrodes, but in this case there is an alternative expression involving the local electric field. Thus from (3.5), (3.6) and (2.10) one may derive
\[
\frac{I(t)}{2FAD_-} = \frac{\partial c_+}{\partial z}(Z,t) = \frac{F}{RT} c_s(Z,t) \xi(Z,t).
\]  
(3.17)
Likewise, Eqs. (3.5), (3.6) and (2.9) together lead to
\[
\frac{I(t)}{2FAD_+} = -\frac{\partial c_+}{\partial z}(0,t) = \frac{F}{RT} c_s(0,t) \xi(0,t).
\]  
(3.18)

All the transport relationships in this section apply, irrespective of whether the experiment is being conducted at constant current or with constant applied cell voltage, or indeed in some third way.

4. Numerical simulation generalities

We shall adopt the aboriginal simulative method of fully-explicit finite-difference digital simulation pioneered by Randles [22], popularized by Feldberg and coworkers [23], and described in detail in the excellent monograph by Britz [24], and précised in a popular textbook [25]. There exist superior methods, but they are less transparent and their advantages are diminishing as the convenience, speed and capacity of computers become ever greater.

Divide the \(0 \leq z \leq Z\) dimension into a large number \(N\) of regions (boxes), such that Box \(n\) corresponds to the space \((n - 1/2)\Delta \leq z \leq (n + 1/2)\Delta\), where \(n = 1, 2, 3, \ldots, N - 1\) and \(\Delta = Z/N\). The indices \(n = 0\) and \(n = N\) denote special “half-boxes”, adjacent to the electrodes, as illustrated in Fig. 1. Scalar properties (concentration, potential) are regarded as uniform within a box, varying discontinuously across the interbox boundaries. Vector properties (concentration gradient, electric field) are assumed uniform between the nodal planes, which are shown as dots in the figure.

Likewise time is discretized by replacing events that, according to Fick’s laws, occur continuously, by a jerky process in which changes occurs only at evenly spaced instants \(t = m\delta\). \(\delta\) is a time interval small enough that all pertinent diffusivities well exceed \(\Delta^2/\delta\). We chose \(D_{\pm}\), as the basis for defining the so-called “model diffusion coefficient”
\[
\beta = \frac{D_{\pm}\delta}{\Delta^2}.
\]  
(4.1)

To avoid computational instabilities, \(\beta\) must be small. The criterion \(\beta < \frac{1}{2}\) is often applied, but a more stringent restriction is needed here because of our use of half-boxes at the electrodes and because other diffusivities may exceed \(D_{\pm}\). We employed \(\beta = 0.2\).

The essence of numerical simulation is to replace each continuous variable (in space and/or time) by a corresponding discrete variable. Since they will be represented in a computer by pure numbers, it is convenient to fashion the discrete variables as dimensionless quantities. Table 1 lists the six variables treated in this way. Notice that we avoid the need to discretize either flux density or electric field.

Our choice of normalizing factors has ensured that, immediately after the start of the (constant current or constant voltage) experiment, before any concentration polarization has time to develop, the discrete current and voltage variables are equal, \(I(0) = \eta(0)\).
If there is an inequality in the flux densities of a species $i$ between the $z = \frac{n-1}{2}A$ and $z = \frac{n+1}{2}A$ boundary planes of Box $n$, then the concentration in the box must change at a rate proportional to the difference in the flux densities. In continuous variables, this means

$$\frac{\partial}{\partial t} \int_{(n-1/2)A}^{(n+1/2)A} c_i(z,t) \, dz = - \left[ j_i \left( nA + \frac{A}{2} \right) - j_i \left( nA - \frac{A}{2} \right) \right].$$

(4.8)

This is an integrated form of the conservation law, Eq. (3.9).

For the uncharged species $S$, the flux densities in (4.8) may be replaced via Fick’s first law, Eq. (3.3). By also incorporating the approximations of the box model, Eq. (4.8) thereby becomes
\[ c_0(nA, t + \delta) - c_0(nA, t) = D_\theta c_0(nA + \Delta, t) - \frac{c_0(nA, t) - c_0(nA - \Delta, t)}{\Delta}, \]

which rearranges to

\[ \frac{\partial}{\partial t} \int_0^{A/2} c_i(z, t) \, dz = -\left[ j_i \left( \frac{A}{2}, t \right) - j_i(0, t) \right]. \]

Because digital simulation is approximate, there are several routes that could be followed, starting from Eq. (4.14). The one described below has some merit. The integral in (4.14) may be represented by the average concentration at \( z = A/4 \) which in turn can be replaced by the concentrations at the adjacent nodes in a 3:1 ratio. Thus

\[ \frac{3}{4} c_i(0, t + \delta) + \frac{1}{4} c_i(A, t + \delta) - \frac{1}{4} c_i(0, t) - \frac{1}{4} c_i(A, t) = -j_i \left( \frac{A}{2}, t \right) + j_i(0, t). \]

We shall apply this approximation first to the substrate and then to the ions. There is an analogous relationship applicable to the region adjacent to the anode.

For the uncharged substrate \( S \), the flux density at \( z = A/2 \) in Eq. (4.15) is replaceable from a discretized version of Fick’s first law, while that at \( z = 0 \) follows from Eq. (2.9):

\[ \frac{3}{4} c_0(0, t + \delta) + \frac{1}{4} c_0(A, t + \delta) - \frac{1}{4} c_0(0, t) - \frac{1}{4} c_0(A, t) = \frac{D_\theta c_0(A, t) - c_0(0, t)}{\Delta} - \frac{I(t)}{FA}. \]

Moreover, because it relates to Box 1, a standard box, the \( c_0(A, t + \delta) - c_0(A, t) \) term may be replaced by recourse to the \( n = 1 \) version of Eq. (4.9). When this replacement is made, and the discrete variables are introduced from definitions (4.1)–(4.6), one finds after tedious rearrangements that, for Box 0

\[ \hat{c}_0(0, m + 1) = \left( 1 - \frac{3\beta D_\theta}{D_\pm} \right) c_0(0, m) + \frac{10\beta D_\theta}{3D_\pm} c_0(1, m) - \frac{\beta D_\theta}{3D_\pm} \hat{c}_0(2, m) + \frac{16\beta D_\theta D_\pm c_0^b}{3ND_\pm^2} \hat{j}(m). \]
For Box $N$, the first member of the equation pair (4.9) may be replaced, after discretization, by
\[ \hat{c}_0(N, m + 1) = \hat{c}_0(N - 1, m + 1) - \frac{\beta D_b}{D_\pm} \hat{c}_0(N - 2, m) + \left( 1 - \frac{\beta D_b}{D_\pm} \right) [2\hat{c}_0(N - 1, m) - \hat{c}_0(N, m)]. \] (4.18)

The two most recent equations supplement equation (4.10), being applicable to the half-boxes adjacent to the electrodes, where (4.10) does not hold. Other developments might lead to equations similar to these, but differing in their coefficients [24].

For the cation $S^+$, the flux density at $z = A/2$ in Eq. (4.14) is replaceable from Eq. (3.5) and that at $z = 0$ from Eq. (2.7):
\[ \frac{1}{2} \frac{\delta}{D_+} \frac{c_+}{0, t + \delta} + \frac{1}{4} \frac{c_+}{A, t + \delta} - \frac{1}{4} c_+(0, t) / \frac{A}{2} = D_+ \left[ \frac{c_+(A, t) - c_+(0, t)}{A} - \frac{F \xi_+}{RT} \left( \frac{4}{3}, t \right) + \frac{I(t)}{FA} \right]. \] (4.19)

The corresponding expression for the anion $X^-$ lacks a current term and is
\[ \frac{1}{2} \frac{\delta}{D_-} \frac{c_-}{0, t + \delta} + \frac{1}{4} \frac{c_-}{A, t + \delta} - \frac{1}{4} c_-(0, t) / \frac{A}{2} = D_- \left[ \frac{c_-(A, t) - c_-(0, t)}{A} + \frac{F \xi_-}{RT} \left( \frac{4}{3}, t \right) \right]. \] (4.20)

Similarly to a procedure used earlier, we can multiply Eqs. (4.19) and (4.20) by $D_-$ and $D_+$, respectively, then add the two to obtain
\[ (D_+ + D_-) \left[ \frac{\delta}{2} c_+(0, t + \delta) - \frac{1}{2} c_+(0, t) + \frac{1}{4} \left[ c_+(A, t + \delta) - c_+(A, t) \right] / A \right] = \frac{D_- I(t)}{FA}. \] (4.21)

Conversion to discrete variables, use of the $n = 1$ version of Eq. (4.13), and algebraic tidying produces
\[ \hat{c}_+(0, m + 1) = (1 - 3\beta) \hat{c}_+(0, m) + 10\beta \frac{3}{3} \hat{c}_+(1, m) - \frac{\beta}{3} \hat{c}_+(2, m) + \frac{8\beta D_b}{3N D_+} \hat{I}(m). \] (4.22)

The similar derivation of the corresponding formula, namely
\[ \hat{c}_+(N, m + 1) = (1 - 3\beta) \hat{c}_+(N, m) + 10\beta \frac{3}{3} \hat{c}_+(N - 1, m) - \frac{\beta}{3} \hat{c}_+(N - 2, m) + \frac{8\beta D_b}{3N D_+} \hat{I}(m) \] (4.23)

for the box adjacent to the anode, will be omitted. The two most recent equations are replacements, applicable to Boxes 0 and $N$, for the inapplicable equation (4.18). Unlike the latter equation, they include a current-dependent term.

At this stage, we have developed dimensionless equations, namely (4.17), (4.10) and (4.18), to describe the evolution of the concentration of the substrate, and a similar set of equations, numbered (4.22), (4.13) and (4.23) to describe the evolution of the joint ionic concentration. Three of these six equations contain a term proportional to the current. It remains only to develop a dimensionless equation to link the cell overvoltage to the evolving concentrations. This development from Eq. (3.15) is straightforward and leads to
\[ \hat{\eta}(m) = -\ln \left( 1 - \hat{c}_0(0, m) \right) + \frac{D_+}{D_+} \ln \left( 1 + \hat{c}_+(0, m) \right) + \frac{D_-}{D_-} \ln \left( 1 + \hat{c}_-(N, m) \right) \]
\[ + \frac{\hat{I}(m)}{N} \left[ \frac{1}{2[1 + \hat{c}_+(0, m)]} + \frac{1}{2[1 + \hat{c}_+(N, m)]} + \sum_{n=1}^{N-1} \frac{1}{1 + \hat{c}_+(n, m)} \right]. \] (4.24)

The final, tripartite, term in this equation represents ohmic polarization ($IR$ drop). The first three right-hand terms correspond mainly to concentration polarization, but also include a small contribution from diffusion potential. This contribution disappears if $D_- = D_+$.  

5. Numerical modelling with constant current

The low initial concentration of ions means that the cell resistance is high initially. Hence, for constant-current electrolysis, there will be a very large cell voltage during the early stages. As electrolyte steadily accumulates, first around the electrodes then more generally, the resistance, and thence the cell voltage, falls. Eventually, however, the solution will become denuded of substrate and $\eta$ will rise, ultimately to infinity at a transition time $t_{\text{trans}}$.
At the outset, choices must be made of the constant \( I \) and of the ratios \( D_0 = D_0/C_0 \), \( D_+ = D_+/C_0 \) and \( c_b/C_6 \). The model parameters \( N \) and \( \beta \) must be selected. Otherwise, no other numerical values are needed to run the simulation though, of course, correlation with a real experiment requires that all salient parameters be specified.

Temporary records need to be kept of \( \hat{c}_0(n, m) \) and \( \hat{c}_+/C_6(n, m) \) for \( n = 0, 1, 2, \ldots, N \) and \( m = 0, 1, 2, \ldots \); all these quantities are initially zero. The only permanent records needed are of \( \hat{y}(m) \), but it could be of interest to record the ohmic component on the right-hand side of (4.24) separately from the three nernstian terms.

The simulation, which is summarized in Fig. 2, consists of the sequential calculation of \( \hat{c}_0(0, 1), \hat{c}_0(1, 1), \hat{c}_0(2, 1), \ldots, \hat{c}_0(N - 1, 1), \hat{c}_0(N, 1), \hat{c}_+(0, 1), \hat{c}_+(1, 1), \hat{c}_+(2, 1), \ldots, \hat{c}_+(N - 1, 1), \hat{c}_+(N, 1), \hat{y}(1), \hat{c}_0(0, 2), \hat{c}_0(1, 2), \hat{c}_0(2, 2), \ldots \) by implementation of Eqs. (4.17), (4.10), (4.10), (4.10), (4.18), (4.22), (4.13), (4.13), (4.13), (4.23), (4.24), (4.17), (4.10), (4.10), \ldots. There are \( 2N + 3 \) calculations for each time-step. The points in Fig. 3 were determined by this method.

6. Audit

With simulative modelling, one can never be 100% sure that results are reliable, even if the results are virtually insensitive to the choices of \( N \) and \( \beta \). The standard approach to providing assurance is to apply the modelling...
procedure to some simpler problem for which an analytical solution exists. An alternative strategy, rarely employed by modellers, is to assess (although not guarantee) the reliability of simulated data by using internal checks of the modelling. In the present case, two methods of such internal auditing the results suggest themselves.

The stoichiometry of the reaction dictates that the total amount of the substrate S plus its ion S⁺ remains constant and equal to their initial amount. In continuous variables, this means

$$\int_0^Z [c_0(z, t) + c_\pm(z, t)] \, dz = \left( c_0^b + c_\pm^b \right) Z,$$

which translates to

$$\frac{c_0^b}{c_\pm^b} \left[ \frac{\dot{c}_0(0, m) + \tilde{c}_0(N, m)}{2} + \sum_{n=1}^{N-1} \tilde{c}_0(n, m) \right] = \frac{\dot{c}_\pm(0, m) + \tilde{c}_\pm(N, m)}{2} + \sum_{n=1}^{N-1} \tilde{c}_\pm(n, m)$$

in discrete variables.

Faraday’s law dictates that the increase in ionic content matches the total electric charge passed, which implies

$$FA \int_0^Z \left[ c_\pm(z, t) - c_\pm^b \right] \, dz = \int_0^t I(t) \, dt$$

in continuous, or

$$\dot{c}_\pm(0, m) + \tilde{c}_\pm(N, m) + \sum_{n=1}^{N-1} \tilde{c}_\pm(n, m) = \frac{2 \beta D_z \cdot D_z}{D_z^2 N} \sum_{\mu=1}^{m} \tilde{I} (\mu)$$

in discrete, variables. The left-hand side of this latter equation is the right-hand side of Eq. (6.2) and therefore there are three expressions that should be continually equal.

During our numerical simulation, we monitored the three supposedly equal quantities to assess discrepancies. We found that these three quantities agree to better than 1%, except during the initial stages and close to the transition time.

7. Analytical modelling generalities

Transport of the substrate S is purely diffusive. Changes in the substrate’s concentration, \( c_0(z, t) \), are governed by Fick’s second law, Eq. (3.4), and the initial and boundary conditions found in Eqs. (2.3), (2.9) and (2.10). The Laplace transform of Eq. (3.4), which also incorporates the initial condition, is

$$\frac{s}{D_0} \tilde{c}_0(z, s) - \frac{c_0^b}{D_0} = \frac{d^2}{dz^2} \tilde{c}_0(z, s)$$

of which the general solution is

$$\tilde{c}_0(z, s) = \frac{c_0^b}{s} + w_0 \exp \left\{ -Z \sqrt{\frac{s}{D_0}} \right\} + w_0' \exp \left\{ Z \sqrt{\frac{s}{D_0}} \right\},$$

where \( w_0 \) and \( w_0' \) are weighting functions, independent of \( z \), which must be chosen to satisfy the boundary conditions. By combining the Laplace transforms of Eqs. (2.10) and (3.3) with the \( z \)- derivative of Eq. (7.2), we find

$$0 = \tilde{j}_0(Z, s) = -D_0 \frac{d \tilde{c}_0}{dz}(Z, s) = -\sqrt{D_0 s} \left\{ -w_0 \exp \left\{ -Z \sqrt{\frac{s}{D_0}} \right\} + w_0' \exp \left\{ Z \sqrt{\frac{s}{D_0}} \right\} \right\}$$

from which it follows that

$$w_0' = w_0 \exp \left\{ -2Z \sqrt{\frac{s}{D_0}} \right\}.$$
Similarly, by combining the Laplace transforms of Eqs. (2.9) and (3.3) with the z-derivative of Eq. (7.2), we find
\[
\frac{-I(s)}{FA} = J_0(0, s) = -D_0 \frac{dc_0}{dz}(0, s) = -\sqrt{D_0 s} \left[ -w_0 + w' \right] = w_0 \sqrt{D_0 s} \left[ 1 - \exp \left\{ -2Z \sqrt{\frac{s}{D_0}} \right\} \right].
\]  
Eq. (7.4) was used in the last step of this latest development. The most recent two equations provide a means of relating each weighting function to the current transform. Putting these relationships into Eq. (7.2) leads to
\[
\bar{c}_0(z, s) = \frac{c_0}{s} - \frac{I(s)}{FA \sqrt{D_0 s}} \left[ 1 - \exp \left\{ -2Z \sqrt{\frac{s}{D_0}} \right\} \right] = \frac{c_0}{s} - \frac{I(s)}{FA \sqrt{D_0 s}} \exp \left\{ (Z - z) \sqrt{\frac{s}{D_0}} \right\} \cosh \left\{ (Z - z) \sqrt{\frac{s}{D_0}} \right\}.
\]  
Albeit in Laplace space, this equation links the concentration of the substrate, at any location in the cell, and at any instant in time, to the current flowing at that time, whether that current is constant or not.

Let us turn now to ion transport. By analogy with Eq. (7.2), the general solution, in Laplace space, to the partial differential Eq. (3.11) is
\[
\bar{c}_\pm(z, s) = \frac{c_0}{s} + w_\pm \exp \left\{ -z \sqrt{\frac{s}{D_\pm}} \right\} + w'_\pm \exp \left\{ z \sqrt{\frac{s}{D_\pm}} \right\}
\]  
and therefore, on differentiation
\[
\frac{dc_\pm(z, s)}{dz} = \frac{s}{\sqrt{D_\pm}} \left[ -w_\pm \exp \left\{ -z \sqrt{\frac{s}{D_\pm}} \right\} + w'_\pm \exp \left\{ z \sqrt{\frac{s}{D_\pm}} \right\} \right].
\]  
By setting \( z = 0 \) and comparing the result with the Laplace transform of the first equality in (3.18), one finds
\[
w_\pm - w'_\pm = \frac{I(s)}{2FAD_\pm} \sqrt{\frac{D_\pm}{s}}.
\]  
Similarly, the result of combining the transform of the first equality in (3.17) with the \( z = Z \) version of Eq. (7.8) is
\[
-w_\pm \exp \left\{ -Z \sqrt{\frac{s}{D_\pm}} \right\} + w'_\pm \exp \left\{ Z \sqrt{\frac{s}{D_\pm}} \right\} = \frac{I(s)}{2FAD_\pm} \sqrt{\frac{D_\pm}{s}}.
\]  
Eqs. (7.9) and (7.10) are a pair of simultaneous equations in \( w_\pm \) and \( w'_\pm \). They can be solved to provide expressions for these two weighting functions. The result, when substituted back into Eq. (7.7), leads to
\[
\bar{c}_\pm(z, s) = \frac{c_0}{s} + \frac{I(s)}{2AF} \sqrt{\frac{D_\pm}{s}} \left[ \cosh \left\{ (Z - z) \sqrt{\frac{s}{D_\pm}} \right\} + \cosh \left\{ z \sqrt{\frac{s}{D_\pm}} \right\} \right].
\]  
In Laplace space, this equation links the common concentration of the ions, at any location in the cell, and at any instant in time, to the current flowing at that time.

8. Analytical model of constant-current electrolysis

If the current has a constant value \( I \) at all times \( t > 0 \), then \( I(s) = I/s \) so that from Eq. (7.6)
\[
\bar{c}_0(z, s) = \frac{c_0}{s} - \frac{I(s)}{FA \sqrt{D_0 s}} \exp \left\{ (Z - z) \sqrt{\frac{s}{D_0}} \right\} \cosh \left\{ (Z - z) \sqrt{\frac{s}{D_0}} \right\}.
\]  
Inversion of this expression, using (8.11), gives the concentration of the substrate at all points in the cell
\[
c_0(z, s) = \frac{c_0}{s} - \frac{IZD_0}{FAD_0} i94 \left\{ Z - z \sqrt{\frac{D_0 t}{Z^2}} \right\}.
\]  
Our prime interest, however, is in the substrate’s concentration at the cathode, to find which we need only find the invert of the \( z = 0 \) instance, namely
\[
\bar{c}_0(0, s) = \frac{c_0}{s} - \frac{I}{FA \sqrt{D_0 s}} \cosh \left\{ Z \sqrt{\frac{s}{D_0}} \right\}
\]  
of Eq. (8.1). From standard tables [26] it is known that the Laplace invert of
\[
\frac{1}{\sqrt{s}} \coth \left\{ a\sqrt{s} \right\} = \frac{1}{a} \theta_3 \left\{ 0; \frac{t}{a^2} \right\} \quad (8.4)
\]

and therefore inversion of (8.3) gives
\[
c_0(0,t) = c^b_0 - \frac{1}{\text{FAZ}} \int_0^t \theta_3 \left\{ 0; \frac{D_0 t}{Z^2} \right\} dt = c^b_0 - \frac{ZI}{\text{FAZ}b} \pi \theta_3 \left\{ 0; \frac{D_0 t}{Z^2} \right\}, \quad (8.5)
\]

where \( \theta_3 \) is the theta-three function and \( \pi \theta_3 \) is an integral of this function with respect to its second argument. See Appendix A for a brief description of these functions.

Eq. (8.5) is all that is needed to predict the transition time. This is found by solving the implicit equation
\[
i \theta_3 \left\{ 0; \frac{D_0 t_{\text{trans}}}{Z^2} \right\} = \frac{\text{FAZ}b}{ZI} \pi \theta_3 \left\{ 0; \frac{D_0 t}{Z^2} \right\},
\]

because \( t_{\text{trans}} \) is the instant at which \( c_0(0,t) \) becomes zero.

Eq. (8.5) is an exact analytical expression giving the concentration at the surface of the anode at all times \( t \) during the constant-current experiment. It is equally straightforward to find \( c_\pm(0,t) \) and \( c_\pm(Z,t) \), though the outcome is more complicated. From the \( z = 0 \) version of Eq. (7.11), we know that to find the ionic concentration at the cathode requires inversion of
\[
\tilde{c}_\pm(0,s) = \frac{c^b_0}{s} + \sqrt{D_\pm} s^{3/2} \left[ \coth \left\{ \frac{Z\sqrt{s/D_\pm}}{D_\pm} \right\} + \csch \left\{ \frac{Z\sqrt{s/D_\pm}}{D_\pm} \right\} \right],
\]

which gives a result [26] analogous to (8.5), namely
\[
c_\pm(0,t) = c^b_\pm - \frac{ZI}{\text{FAZ}} \left[ \frac{1}{D_\pm} \i \theta_3 \left\{ 0; \frac{D_\pm t}{Z^2} \right\} + \frac{1}{D_-} \i \theta_3 \left\{ 0; \frac{D_\pm t}{Z^2} \right\} \right], \quad (8.8)
\]

Similarly
\[
c_\pm(Z,t) = c^b_\pm - \frac{ZI}{\text{FAZ}} \left[ \frac{1}{D_\pm} \i \theta_3 \left\{ 0; \frac{D_\pm t}{Z^2} \right\} + \frac{1}{D_-} \i \theta_3 \left\{ 0; \frac{D_\pm t}{Z^2} \right\} \right], \quad (8.9)
\]

With Eqs. (8.6), (8.8) and (8.9), we now have the information needed to formulate the first three right-hand terms in Eq. (3.15).

It remains to find the final term in Eq. (3.15). En route to that goal, values of \( c_\pm(z,t) \) are required for all points in \( 0 \leq z \leq Z \). Now [26], the inverse Laplace transform of
\[
c = \frac{1}{\sqrt{s} \sinh \left\{ a\sqrt{s} \right\}}\ 
\]

and therefore the inverse transform of
\[
c = \frac{1}{\sqrt{s} \sinh \left\{ a\sqrt{s} \right\}} \int_0^t \theta_3 \left\{ 0; \frac{b}{2a} ; \frac{t}{a^2} \right\} dt \quad \text{or} \quad a \i \theta_4 \left\{ 0; \frac{b}{2a} ; \frac{t}{a^2} \right\}, \quad (8.11)
\]

With the aid of the third equation in Appendix A, result (8.11) allows the inversion of Eq. (7.11) to
\[
c_\pm(z,t) = c^b_\pm - \frac{ZI}{\text{FAZ}} \left[ \frac{1}{D_\pm} \i \theta_3 \left\{ \frac{z}{2Z} ; \frac{D_\pm t}{Z^2} \right\} + \frac{1}{D_-} \i \theta_3 \left\{ \frac{Z}{2Z} ; \frac{D_\pm t}{Z^2} \right\} \right], \quad (8.12)
\]

Notice that Eqs. (8.8) and (8.9) are subsumed in (8.12). Data calculated from Eqs. (8.2) and (8.11) were used to create the full lines in Fig. 3. Evidently, there is excellent agreement between the analytical and simulative results.

After Eqs. (8.5), (8.8) and (8.9) and (8.12) are inserted into Eq. (3.15), we arrive at the final result
\[
\eta(t) = \left( \frac{RT}{F} \right) \left[ -1 - 2A c^b_0 \i \theta_3 \left\{ 0; \frac{D_0 t}{Z^2} \right\} \right] + \frac{D_+}{D_-} \ln \left[ 1 + \frac{A}{D_-} \i \theta_3 \left\{ 0; \frac{D_+ t}{Z^2} \right\} + \frac{A}{D_-} \i \theta_3 \left\{ 0; \frac{D_+ t}{Z^2} \right\} \right] + \frac{D_+}{D_-} \ln \left[ 1 + \frac{A}{D_-} \i \theta_3 \left\{ 0; \frac{D_+ t}{Z^2} \right\} + \frac{A}{D_-} \i \theta_3 \left\{ 0; \frac{D_+ t}{Z^2} \right\} \right] + \frac{AD_+}{D_-} \i \theta_3 \left\{ \frac{Z}{Z} ; \frac{D_+ t}{Z^2} \right\},
\]

(8.13)
where, to economize on space, the abbreviation

\[
A = \frac{ZI}{2FAc_0^2}
\]  

(8.14)

has been used. Eq. (8.13) is an analytical formula expressing the evolution of the cell voltage during constant-current electrolysis.

9. Summary and discussion

Fig. 4 is a polarization inventory diagram [27] showing how the predicted overvoltage changes during a typical experiment. The asymmetry overvoltage, \( \eta_{\text{asym}} \), arising from the diffusion potential, never amounted to more than 0.6% of the total and has been included with \( \eta_{\text{ohm}} \). There is no significant difference between data generated analytically or simulatively, though of course early simulated data is inevitably in error. The transition time found by either method agrees with that from Eq. (8.6).

When, unlike the present situation, there is no analytical result with which to compare a simulation, there is always doubt as to the validity of the prediction. Errors can arise either from numerical causes or from programming blunders. The use of “auditing” procedures, as developed here, can sometimes guard against such problems, though without providing a guarantee of accuracy. In the present study we found the auditing discrepancy approximately matched the difference between the simulative and analytical results, being negligible at intermediate times, but amounting to several percent close to the beginning and end of the experiment.

Most published derivations of voltammetric behaviour apply to semi-infinite systems with excess supporting electrolyte. We have demonstrated that the finitude of the transport field and the absence of excess electrolyte need be no barrier to the prediction of voltammetric behaviour by analytical or simulative methods.

Of course, not all voltammetric experiments are amenable to analytic solution and in such circumstances semianalytic modelling can be a valuable substitute. The present electrochemical system, under conditions of applied constant voltage, is a case in point. A manuscript presently in preparation will compare simulative and semianalytic treatments of the constant-voltage experiment.

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Appendix A

With arguments pertinent to this paper, the theta-three and theta-four functions [28] are defined by
\begin{align}
\hat{g}_3 \left\{ \frac{Z}{2Z^2} \frac{dt}{Z^2} \right\} &= \frac{Z}{\sqrt{\pi dt}} \sum_{n=-\infty}^{\infty} \exp \left\{ \frac{-(2nZ + z)^2}{4dt} \right\} \quad (A.1) \end{align}

and

\begin{align}
\hat{g}_4 \left\{ \frac{Z}{2Z^2} \frac{dt}{Z^2} \right\} &= \frac{Z}{\sqrt{\pi dt}} \sum_{n=-\infty}^{\infty} \exp \left\{ \frac{-(2nZ + Z + z)^2}{4dt} \right\} \quad (A.2) \end{align}

in which the summation index runs over all integer values, negative, zero, and positive. The two functions are interrelated by

\begin{align}
\hat{g}_3 \left\{ \frac{Z - z - dt}{2Z^2} \frac{dt}{Z^2} \right\} = \hat{g}_4 \left\{ \frac{Z - z}{2Z^2} \frac{dt}{Z^2} \right\} \quad \text{and} \quad \hat{g}_4 \left\{ \frac{Z - z - dt}{2Z^2} \frac{dt}{Z^2} \right\} = \hat{g}_3 \left\{ \frac{Z - z}{2Z^2} \frac{dt}{Z^2} \right\}. \quad (A.3) \end{align}

Definitions (A.1) and (A.2) show the \( i \) functions to be expressible as

\begin{align}
\hat{i}_3 \left\{ \frac{Z}{2Z^2} \frac{dt}{Z^2} \right\} &= \frac{2\sqrt{\pi}}{Z} \sum_{n=0,2} \text{ierfc} \left\{ \frac{nZ + z}{\sqrt{4dt}} \right\} + \sum_{n=2,4} \text{ierfc} \left\{ \frac{nZ - z}{\sqrt{4dt}} \right\} \quad (A.4)\end{align}

and

\begin{align}
\hat{i}_4 \left\{ \frac{Z}{2Z^2} \frac{dt}{Z^2} \right\} &= \frac{2\sqrt{\pi}}{Z} \sum_{n=1,3} \left[ \text{ierfc} \left\{ \frac{nZ + z}{\sqrt{4dt}} \right\} + \text{ierfc} \left\{ \frac{nZ - z}{\sqrt{4dt}} \right\} \right]. \quad (A.5)\end{align}

where \( \text{ierfc} \{ \} \) is the error function complement integral.

References