2.1
Diffusion and Migration

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Introduction

This chapter describes mass transport to electrodes by diffusion and migration. It is assumed throughout that there is no convective motion of the solution, and transport is described with respect to a reference frame fixed to the laboratory [1, 2]. Thus, many of the equations derived in this chapter cannot be directly applied to systems with bulk motion.

The chapter emphasizes migrational effects and provides analytical expressions for the electric potential drop in the solution under different experimental conditions. The fundamental concepts are discussed in detail, and a number of important restrictions are introduced for the sake of clarity. First, diluted solutions are considered throughout and the flux equations incorporate neither cross terms nor activity coefficients [2–5]. Second, one-dimensional systems are considered, except when presenting the transport equations in Sect. 2.1.1. Third, except in a couple of sections, it is assumed that there are no homogeneous reactions. Insoluble species are also absent. Fourth, since the chapter is mainly of interest to cases in which mass transport is rate controlling, reversible electrode reactions are assumed and no kinetic effects are considered. Fifth, most sections involve steady state transport because the theoretical description of transient experiments in the presence of migration is difficult and quite often requires numerical solutions that bring much more mathematical complexity than new physical insights. Nevertheless, the effect of migration is analyzed in a simple transient case. Finally, the local electroneutrality (LEN) assumption is used. This is indeed a good approximation for most experimental situations, although deviations from LEN occur under some conditions. These deviations are discussed in the last section.

2.1.1
Fundamental Concepts

This section presents the basic equations describing mass transport to electrodes: the flux equations, the continuity equation, and the LEN assumption. The flux equations are derived from the concept of electrochemical potential, which is used as a general term valid for both charged and neutral species. The connection between electric conduction and the basic transport mechanisms, diffusion and migration, is discussed in detail, and the difference between ohmic and total electric potential gradient is emphasized. The spatial region in which mass transport takes place and the coupling between mass transport and the electrode reaction are discussed next. At this point, the one-dimensional geometry to be used henceforth is introduced. The electric potential drops in the system and the sign conventions are also defined. The boundary conditions for the transport equations are written in terms of the integral transport numbers. For the sake of simplicity, parallel reactions [6] and adsorption phenomena [7] are not considered.

2.1.1.1 **Diffusion–migration Flux Equations**

The flux equations describing the behavior of electrochemical systems are intimately related to the Second Law of Thermodynamics. Consider two neighboring volume elements V' and V'' of a solution having the same temperature and pressure, but different electrochemical potentials of their constituents. The difference between the electrochemical potential of species i, $\tilde{\mu}_i'$ and $\tilde{\mu}_i''$, in these volume elements implies that there is no distribution equilibrium and this species tends to move from one volume element to the other. This motion of species i from one volume element to its neighbor is generically called transport of species i. Since the transport of the different species in solution takes place under thermal and mechanical equilibrium, the change in internal energy U of these two volume elements is [1, 8, 9]

$$\mathrm{d}U' = T\,\mathrm{d}S' + \sum_i \tilde{\mu}_i'\,\mathrm{d}n_i' \tag{1}$$

$$\mathrm{d}U'' = T\,\mathrm{d}S'' + \sum_i \tilde{\mu}_i''\,\mathrm{d}n_i'' \tag{2}$$

where T is the thermodynamic temperature, S the entropy, and n_i the number of moles of species i. Moreover, considering that the exchange of matter between V' and V'' takes place without energy exchange with their surroundings, it is satisfied that $\mathrm{d}U' + \mathrm{d}U'' = 0$ and $\mathrm{d}n_i' + \mathrm{d}n_i'' = 0$. The Second Law of Thermodynamics requires that the entropy of the isolated system formed by the two volume elements must increase

$$T(\mathrm{d}S' + \mathrm{d}S'') = \sum_i (\tilde{\mu}_i'' - \tilde{\mu}_i')\mathrm{d}n_i' \geq 0 \tag{3}$$

When the transport of species i is not coupled to that of other species, each individual term of this sum is positive. In this case, $\mathrm{d}n_i'$ is determined only by $(\tilde{\mu}_i'' - \tilde{\mu}_i')$ and species i moves towards the region in which its electrochemical potential is lower, that is, $\mathrm{d}n_i' < 0$ when $\tilde{\mu}_i'' < \tilde{\mu}_i'$ and vice versa. This happens, for instance, in the case of ionic species in diluted solutions. When the transport of different species is coupled, one or more terms in the sum can be negative, but the sum is always positive.

The transport of species i can be described in terms of either its velocity $\vec{\mathrm{v}}_i$ or its flux density $\vec{J}_i$, which are related to each other by the molar concentration, $\vec{J}_i = c_i\vec{\mathrm{v}}_i$. If the area of the surface separating the two volume elements is $\mathrm{d}A$ and its orientation is given by the unit vector $\hat{n}$(from V' to V''), the number of moles of species i crossing the surface in a time $\mathrm{d}t$ is $\mathrm{d}n_i' = -\vec{J}_i\hat{n}\,\mathrm{d}A\,\mathrm{d}t$.

When the difference between $\tilde{\mu}_i''$ and $\tilde{\mu}_i'$ is not too large, it can be assumed [10] that the rate of change of the amount of species i, $\mathrm{d}n_i'/\mathrm{d}t$, is proportional to the difference $\tilde{\mu}_i'' - \tilde{\mu}_i'$ or, more exactly, to the gradient of this potential normal to the surface, $\partial\tilde{\mu}_i/\partial n \equiv \vec{\nabla}\tilde{\mu}_i\hat{n}$. In this linear approximation, the velocity of species i is expressed as

$$\vec{\mathrm{v}}_i = -u_i\vec{\nabla}\tilde{\mu}_i \tag{4}$$

where u_i is its mobility. Similarly, the flux density takes the form

$$\vec{J}_i = c_i\vec{\mathrm{v}}_i = -u_i c_i\vec{\nabla}\tilde{\mu}_i = -\frac{D_i c_i}{RT}\vec{\nabla}\tilde{\mu}_i \tag{5}$$

where R is the universal gas constant and the Einstein relation between mobility and diffusion coefficient, $D_i = u_i RT$, has been used.

At constant temperature and pressure, the gradient $\vec{\nabla}\tilde{\mu}_i$ originates from changes in composition and electric potential ϕ so that

$$\vec{\nabla}\tilde{\mu}_i = RT\vec{\nabla}\ln c_i + z_i F\vec{\nabla}\phi \tag{6}$$

where F is the Faraday constant and z_i is the charge number of species i. Taking Eq. (6) to Eq. (5), the Nernst–Planck flux equation [11]

$$\vec{J}_i = -D_i(\vec{\nabla}c_i + z_i c_i f\vec{\nabla}\phi) \tag{7}$$

is obtained, where f denotes the ratio F/RT. The two terms in the right-hand side of this equation represent the transport mechanisms of diffusion and migration, respectively. Diffusion is a consequence of the random thermal motion of the particles, which tends to make the concentration of all species uniform. Migration accounts for the influence of the electric field, $\vec{\mathrm{E}} = -\vec{\nabla}\phi$, on the random motion of the charged particles, and Eq. (7) shows that the particles acquire a component of their velocity along the direction of the electric field as a result of this influence.

2.1.1.2 **Poisson Equation and the LEN Assumption**

Equation (5) states that the flux density of species i in a diluted solution depends on $\vec{\nabla}\tilde{\mu}_i$ but not on other gradients $\vec{\nabla}\tilde{\mu}_{j\neq i}$. In this sense, there is no correlation between the motions of two different species, i and j. The migrational term in Eq. (7), however, imposes a strong constraint on the motion of charged species by coupling their flux densities $\vec{J}_i$.

The electrical state of the system is so sensitive to small changes in composition [9] that the gradient $\vec{\nabla}\phi$ in Eq. (7) cannot be assumed, in general, to be a simple constant [12], and an additional equation is required to determine it. Given the slowness of particle motion in solution, it is justified to use the Poisson equation from electrostatics to relate the changes in electric potential to the local electric charge density ρ_e

$$\nabla^2\phi = -\frac{\rho_e}{\varepsilon} = -\frac{F}{\varepsilon}\sum_i z_i c_i \tag{8}$$

where ε is the dielectric permittivity of the solution.

Consider, for example, a 10 mM 1 : −1 electrolyte solution that contains a positive charge density of the order of 10^6 C m^{-3} counterbalanced by a negative charge of -10^6 C m^{-3}. Since the dielectric permittivity of aqueous electrolyte solutions is of the order of 10^{-9} C V^{-1} m^{-1}, the right-hand side of Eq. (8) is roughly the difference between two terms whose order of magnitude is 10^{15} V m^{-2}. The typical order of magnitude of the electric fields, however, can be estimated as 10 V m^{-1} and they are practically independent on position (except at the interfacial regions), so that $\nabla^2\phi$ is many orders of magnitude smaller than 10^{15} V m^{-2}. This means that the imbalance between cation and anion concentrations in the system that is required to set up the typical electric potential distributions is many orders of magnitude smaller than the solution concentration. Therefore, the space charge density can be neglected and use can be made of the LEN assumption [13]

$$\sum_i z_i c_i = 0 \tag{9}$$

This equation replaces Eq. (8) in the description of transport processes. Though it is customary to use the equal symbol in Eq. (9), the electric charge density is not strictly zero, and the Poisson equation cannot be reduced to the Laplace equation $\nabla^2\phi = 0$.

2.1.1.3 **Continuity Equation**

The spatial variation of the flux density of species i is determined by the principle of conservation of the amount of substance for this species, which is represented by the continuity equation. Consider an arbitrary volume V in an electrolyte solution, in which the molar concentration of species i is $c_i(\vec{r}, t)$. The amount of substance of species i within V can change as a result of either a net flow of particles through the surface S enclosing the volume V, or due to homogeneous chemical reactions occurring within V. If the surface S is divided into surface elements of area $\mathrm{d}A$ perpendicular to the unit vector $\hat{n}$ (oriented outwards from V), the number of moles of species i entering V through this surface element in a time $\mathrm{d}t$ is $\mathrm{d}n_i = -\vec{J}_i \hat{n} \mathrm{d}A \mathrm{d}t$. The homogeneous reactions generate or consume this species at a net rate $r_i(\vec{r}, t)$. Since the (net) accumulation rate of species i within V is given by the sum of the (net) generation rate due to the chemical reaction and the (net) incoming flux through S, it is concluded that

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\iiint_V c_i(\vec{r}, t)\mathrm{d}V &= \iiint_V \frac{\partial c_i}{\partial t}\mathrm{d}V \\ &= \iiint_V r_i \mathrm{d}V - \oint\!\!\!\oint_S \vec{J}_i \hat{n} \mathrm{d}A \\ &= \iiint_V (r_i - \vec{\nabla}\vec{J}_i)\mathrm{d}V \end{aligned} \tag{10}$$

where Gauss' divergence theorem has been used. Moreover, since no restrictions apply to the volume V, Eq. (10) implies that

$$\frac{\partial c_i}{\partial t} + \vec{\nabla}\vec{J}_i = r_i \tag{11}$$

which is the continuity equation for species i.

2.1.1.4 **Ohm's Law and Migrational Transport Numbers**

In a diluted electrolyte solution of uniform composition, the flux density $\vec{J}_i = c_i \vec{v}_i$ is proportional to $\vec{\nabla}\phi$, and the conduction electric current density

$$\vec{I} \equiv F \sum_i z_i \vec{J}_i \tag{12}$$

satisfies Ohm's law

$$\vec{I} = -\kappa \vec{\nabla}\phi, \quad (\vec{\nabla} c_i = 0, \ \forall i) \tag{13}$$

where

$$\kappa \equiv \frac{F^2}{RT} \sum_i z_i^2 D_i c_i \tag{14}$$

is the electrical conductivity of the solution. The minus sign in Eq. (13) means that the electric current flows in the direction of decreasing electric potential. Equation (14) evidences that the conductivity of the solution is determined by all ionic species in solution, no matter whether they are active or not. The migrational transport number

$$t_i \equiv \frac{z_i^2 D_i c_i}{\sum_j z_j^2 D_j c_j} \tag{15}$$

represents the relative contribution of species i to the conductivity of the solution.

Unfortunately, concentration gradients develop under most experimental conditions, and the motion of charge carriers takes place by both diffusion and migration as described by the Nernst–Planck equation, Eq. (7). In this case, Eqs. (14 and 15) provide the local (i.e. position-dependent) values of the conductivity and the transport number of species i, respectively. By writing the Nernst–Planck equation in terms of t_i as [1, 14]

$$\vec{J}_i = -\frac{t_i \kappa}{z_i^2 F^2}\vec{\nabla}\tilde{\mu}_i \tag{16}$$

Eq. (12) leads to the modified Ohm's law [5, 15]

$$\vec{I} = -\kappa(\vec{\nabla}\phi - \vec{\nabla}\phi_{\mathrm{dif}}) \equiv -\kappa\vec{\nabla}\phi_{\mathrm{ohm}} \tag{17}$$

in which

$$\vec{\nabla}\phi_{\mathrm{ohm}} = \frac{1}{F}\sum_i \frac{t_i}{z_i}\vec{\nabla}\tilde{\mu}_i \tag{18}$$

is the ohmic potential gradient, and

$$\begin{aligned}\vec{\nabla}\phi_{\mathrm{dif}} &= -\frac{F}{\kappa}\sum_i z_i D_i \vec{\nabla}c_i \\ &= -\frac{RT}{F}\sum_i \frac{t_i}{z_i}\vec{\nabla}\ln c_i \end{aligned} \tag{19}$$

is the diffusion potential gradient.

That is, the concentration gradients break the proportionality between the current density and the electric field; furthermore, in some cases, $\vec{I}$ and $\vec{\nabla}\phi$ are not even parallel vectors, a fact that is relevant to the tertiary current distribution [16]. This is due to the diffusion potential gradient that originates from the diffusion process, and therefore an expression similar to Ohm's law can only be recovered by subtracting the diffusion potential gradient from the total potential gradient, as shown by Eq. (17). A theoretical simplification sometimes used in the literature consists in neglecting the diffusion potential by assuming all ionic diffusivities to be equal [17, 18].

2.1.1.5 **Diffusion-conduction Flux Equation**

The introduction of the modified Ohm's law, Eq. (17), in the Nernst–Planck equation, Eq. (7), leads to the following form of the flux equation

$$\vec{J}_i = -D_i(\vec{\nabla}c_i + z_i c_i f \vec{\nabla}\phi_{\mathrm{dif}}) + \frac{t_i \vec{I}}{z_i F} \tag{20}$$

For the sake of simplicity, consider the case of a binary solution obtained by complete dissociation of a strong electrolyte $A_{\nu_1}B_{\nu_2}$ into ν_1 ions A^{z_1} of charge number z_1 and ν_2 ions B^{z_2} of charge number z_2; obviously, the relation $z_1\nu_1 + z_2\nu_2 = 0$ is satisfied. The ionic concentrations are then related to the stoichiometric electrolyte concentration c_{12} by the relations $c_1 = \nu_1 c_{12}$ and $c_2 = \nu_2 c_{12}$ which allows Eq. (20) to be rewritten as

$$\vec{J}_i = \nu_i \vec{J}_{12} + \frac{t_i \vec{I}}{z_i F} = -\nu_i D_{12}\vec{\nabla}c_{12} + \frac{t_i \vec{I}}{z_i F} \tag{21}$$

where $\vec{J}_{12}$ is the electrolyte flux density, and

$$D_{12} = \frac{(\nu_1 + \nu_2)D_1 D_2}{\nu_2 D_1 + \nu_1 D_2} \tag{22}$$

is the Nernst–Hartley expression for the diffusion coefficient of the dissociated electrolyte [3].

Equations (20 and 21) describe ionic transport as a combination of electrolyte diffusion and ionic conduction, and hence the name diffusion–conduction flux equation is suggested. Its comparison with the diffusion–migration flux equation, Eq. (7), evidences the difference between migration and conduction. Migration is due to electric fields, either external or internal, and does not require a nonzero current density. Conduction is the ionic motion associated to the part of the electric field that is controlled externally. Note that the electric current density is a measurable magnitude but not the local electric field. Conduction requires a nonzero electric current density.

Note, finally, that the dissociated electrolyte satisfies Fick's law, $\vec{J}_{12} = -D_{12} \vec{\nabla} c_{12}$, because both ions move at the same velocity in the absence of current ($I = 0$), and the dissociated electrolyte is the only independently moving substance [1]. This is not in contradiction with the fact that the ionic diffusion coefficients are different to each other, $D_1 \neq D_2$, because the diffusion potential gradient affects the ionic motion even when $I = 0$. In conclusion, although the Nernst–Planck equation establishes that the flux of species i in a diluted solution is only proportional to the gradient $\vec{\nabla}\tilde{\mu}_i$, the contribution of the electric potential gradient to $\vec{\nabla}\tilde{\mu}_i$ couples the transport of different species.

2.1.1.6 **Diffusion Boundary Layer**

In general, the electrode reaction makes the concentration of species i to vary with the distance to the electrode surface. These concentration changes occur not only for the species participating in the electrode reaction, but also to other charged species because of their electrostatic coupling. The progress of the electrode reaction is accompanied by a propagation of the concentration variations toward the interior of the solution, which affects a region that grows in thickness. It is possible, however, to confine the concentration variations to a "thin" region near the electrode by vigorous stirring, "thin" here means of the order of tenths of a millimeter. The solution can then be divided in two regions: the diffusion boundary layer (DBL) adjacent to the electrode surface, in which concentration varies with position and diffusion affects mass transport; and the bulk solution, in which concentration is made uniform by stirring and transport is due to migration and convection [5, 19, 20]. Although the transition between these two regions is actually smooth, it is practical to assume that the transition is abrupt and to assign a thickness δ to the DBL, which can be empirically determined from the stirring rate or other hydrodynamic conditions [21, 22]. The thickness δ is considered to be finite when describing steady state transport (indeed, this is a necessary condition for reaching the steady state); infinite DBL thickness, however, is assumed in Sect. 2.1.5.

In the following sections, the one-dimensional geometry described by Fig. 1 is considered. The electrode is located at $x = 0$ and the DBL in the region $0 < x < \delta$. The electric current density I is positive for anodic oxidations and negative for cathodic reductions, in agreement with the IUPAC convention. The electric potential drop in the DBL is defined as the potential in the bulk solution ($x = \delta$) relative to that at the electrode surface ($x = 0$), $\Delta\phi \equiv \phi^{\mathrm{b}} - \phi^{\mathrm{s}}$.

2.1.1.7 **Faraday's Law and Integral Transport Numbers**

The charge transfer between an electrolyte solution and an electrode (quite frequently, a metal phase) can be represented by the

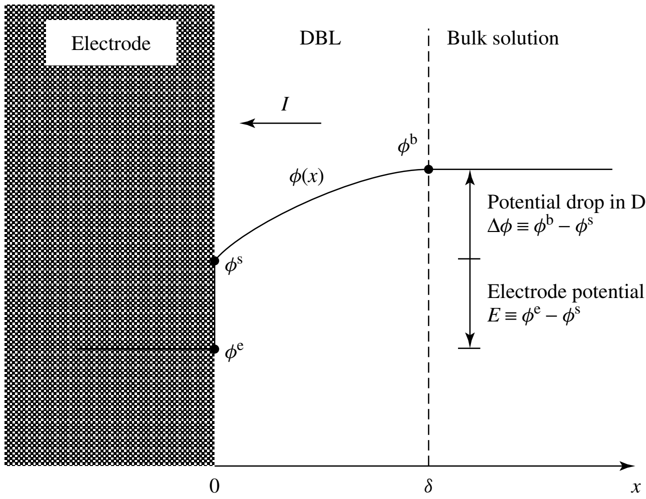

Fig. 1 Schematic drawing of the system considered. The electric potential distribution has been shown for a cathodic process ($I < 0$). Superscripts b, s, and e denote, respectively, bulk solution ($x = \delta$), solution adjacent to the electrode surface ($x = 0$), and electrode phase.

general electrode reaction equation

$$\sum_i \nu_i^{\mathrm{r}} B_i^{z_i} + ne^- = 0 \qquad (23)$$

where B_i and ν_i^{r} are the molecular formula and the stoichiometric number of species i, respectively. The value of ν_i^{r} is positive for products and negative for reactants. The stoichiometric number of the electron in the reaction, $n = \sum_i z_i \nu_i^{\mathrm{r}}$, is positive for (anodic) oxidations and negative for (cathodic) reductions. The electrons in Eq. (23) are considered to be in the metal phase, and species B_i can be either in solution or in the electrode phase; it is obviously necessary that at least one active species B_i is in solution because Eq. (23) describes charge transfer between two phases.

The evolution of the electrode reaction needs the transport of reactants from the solution to its surface and products vice versa. Faraday's law establishes that the reaction rate $\mathrm{d}\xi/\mathrm{d}t$ is proportional to the conduction electric current density and, therefore, that the flux density of species i at the electrode surface is given by

$$J_i^{\mathrm{s}} = \frac{1}{A}\frac{\mathrm{d}n_i}{\mathrm{d}t} = \frac{\nu_i^{\mathrm{r}}}{A}\frac{\mathrm{d}\xi}{\mathrm{d}t} = \nu_i^{\mathrm{r}}\frac{I}{nF} \qquad (24)$$

where A is the electrode surface area.

Equation (24) shows clearly that, at the electrode surface, the fraction of electric current density transported by species i is given by the magnitude

$$T_i^{\mathrm{s}} \equiv \frac{z_i F J_i^{\mathrm{s}}}{I} = \frac{z_i \nu_i^{\mathrm{r}}}{n} \qquad (25)$$

which is called the integral transport number of species i [23]; this magnitude is zero for the species that are not involved in the electrode reaction (i.e. the electroinactive species). It is important to observe that $\sum_i T_i^{\mathrm{s}} = 1$ but T_i^{s} is not bounded between 0 and 1. For example, in the electrode reaction

$$\mathrm{Fe(CN)_6}^{3-}(\mathrm{aq}) - \mathrm{Fe(CN)_6}^{4-}(\mathrm{aq}) + e^- = 0 \qquad (26)$$

the transport numbers at the electrode surface are $T^{s}_{\mathrm{Fe(CN)_6}^{3-}} = -3$ and $T^{s}_{\mathrm{Fe(CN)_6}^{4-}} = 4$.

Some electrode reactions, such as the anodic dissolution of copper

$$\mathrm{Cu^+(aq) - Cu(s)} + e^- = 0 \qquad (27)$$

the hydrogen evolution at a platinum electrode

$$\mathrm{H_2(g) - 2H^+(aq)} + 2e^- = 0 \qquad (28)$$

or the oxidation of silver at a Ag|AgCl electrode

$$\mathrm{AgCl(s) - Ag(s) - Cl^-(aq)} + e^- = 0 \qquad (29)$$

involve only one electroactive species ($\mathrm{Cu^+}$, $\mathrm{H^+}$, and $\mathrm{Cl^-}$, respectively), which is denoted by subscript 1 henceforth. Since the current density in these processes is due to the single electroactive species, $n = z_1\nu_1^{\mathrm{r}}$ and $T_1^{\mathrm{s}} = 1$, while $T_i^{\mathrm{s}} = 0$ for $i \neq 1$. In these simple cases, the DBL becomes depleted of this species when $J_1 < 0$ (i.e. the species is consumed at the electrode surface), and the potential drop satisfies $z_1\Delta\phi > 0$. On the contrary, when $J_1 > 0$, the DBL becomes concentrated in species 1 and $z_1\Delta\phi < 0$.

Note also that T_i^{s} is zero for neutral species but this does not imply that they are not transported towards or from the electrode. For example, in the case of nitrous acid in the electrode reaction

$$\begin{aligned}\mathrm{3H^+(aq) + NO_3{}^-(aq) - HNO_2(aq)}\\ \mathrm{- H_2O(aq)} + 2e^- = 0\end{aligned} \qquad (30)$$

$T^{\mathrm{s}}_{\mathrm{HNO_2}} = 0$ but $J^{\mathrm{s}}_{\mathrm{HNO_2}} = -I/2F$, as can be easily deduced from Eq. (24). (For the neutral species, the transference number $\tau_i \equiv T_i/z_i$ constitutes a good alternative to T_i [24].)

The integral transport number of species i can also be defined at locations different from the electrode surface as $T_i \equiv z_i F J_i/I$ [23]. Under steady state conditions and in the absence of homogeneous reactions, both the current density I and the flux density J_i do not vary with position, and T_i takes the value specified by Eq. (25) throughout the whole system even when concentration gradients are present. Otherwise, T_i is position-dependent. It is important to observe that the integral transport numbers T_i are equal to the migrational transport numbers t_i in the absence of concentration gradients only; indeed, concentration gradients originate due to the fact that $T_i \neq t_i$.

2.1.1.8 Nernst Equation and Concentration Overpotential

In order to drive an electric current density across the system depicted in Fig. 1, an electric potential difference must be applied between the electrode and the bulk solution. This potential difference can be expressed in terms of three contributions: the potential drop in the DBL, the equilibrium interfacial or Nernst potential drop, and the activation overpotential. For large enough kinetic currents, the latter contribution can be neglected [7, 25] and the potential difference required for the electrode process is $E_{\mathrm{eq}} - \Delta\phi$, where E_{eq} is the equilibrium electrode potential (i.e. the electric potential of the electrode relative to that at the adjacent electrolyte solution). The value of E_{eq} is given by the Nernst equation. For the electrode Reaction (23), the Nernst equation takes the form

$$E_{\mathrm{eq}} = E^{\circ} + \frac{RT}{nF}\sum_i \nu_i^{\mathrm{r}} \ln \frac{c_i^{\mathrm{s}}}{c^{\circ}} \qquad (31)$$

where E° is the standard (or, more exactly, the formal) electrode potential and c° is the standard concentration. The concentrations c_i^{s} of the active species in Eq. (31) are those at the electrode surface, which are evaluated by extrapolation to the electrode surface of the concentration profile within the DBL [19]. In other words, the electrode surface at position $x = 0$ should be understood as the neutral solution just outside the electrical double layer (EDL). Similarly, $\Delta\phi$ refers to the potential difference between the bulk solution and that point in the solution (that is, between the bulk solution|DBL and the EDL|DBL boundaries). Hence, no details of the EDL structure are considered when evaluating the equilibrium interfacial potential drop and the surface concentrations of the active species.

Since the interfacial concentrations of the active species vary with the electric current density, E_{eq} also does and its variation is often described in terms of the concentration overpotential [19, 26]

$$\eta_c \equiv E_{\mathrm{eq}} - E_{\mathrm{eq}}^{\mathrm{b}} \equiv \frac{RT}{nF} \sum_i \nu_i^{\mathrm{r}} \ln \frac{c_i^{\mathrm{s}}}{c_i^{\mathrm{b}}} \quad (32)$$

which represents the potential of the electrode in equilibrium with the interfacial concentrations that are established when a current density I is driven through the system, E_{eq}, relative to the (constant) potential of a similar electrode equilibrated with the bulk solution, $E_{\mathrm{eq}}^{\mathrm{b}}$. The potential difference between the electrode and the bulk solution is then $E_{\mathrm{eq}}^{\mathrm{b}} + \eta_c - \Delta\phi$.

Note, finally, that when the supporting electrolyte is used, the ionic strength of the DBL is not significantly affected by the concentration polarization of the active species, and therefore, their activity coefficients are practically independent of the current density [26]. This justifies the use of concentrations instead of activities in the above equations.

2.1.2
Steady State Current–voltage Curves of Systems with One Active Species

The finite transport rate of the electroactive species toward the electrode surface implies the existence of a limiting current density, that is the most important consequence of mass transport. This limiting current density is defined by the condition of maximum concentration gradient of the electroactive species, which is achieved when the concentration of this species tends to zero at the electrode | depleted DBL interface (or, more accurately, at the EDL | DBL boundary).

In this section, the mass transport effects on the steady state current–voltage curves are described for the (relatively common) case of systems with only one electroactive species in solution. This species is denoted by subscript 1. The integration procedure of the transport equations in multi-ionic systems is presented first and the general current–voltage curve is derived. Except in Sect. 2.1.2.5, homogeneous reactions are assumed to be absent. The interesting case of excess supporting electrolyte, in which the active species is present in very small concentration and transport takes place mostly by diffusion, is discussed. Finally, the simple cases of binary and ternary solutions are considered to illustrate the conclusions drawn from the general solution.

2.1.2.1 Integration of the Transport Equations

The fact that the flux density of the electroinactive species, $i \neq 1$, is zero simplifies significantly the solution of the transport equations. These species are in electrochemical equilibrium within the DBL, and hence their concentrations c_i are related to the electric potential ϕ by the

Boltzmann equation

$$\frac{dc_i}{dx} = -z_i c_i f \frac{d\phi}{dx} \quad (i \neq 1,\ J_i = 0) \quad (33)$$

Thus, the ionic concentrations at the electrode surface, $x = 0$, are related to those in the bulk solution, $x = \delta$, by

$$c_i^s = c_i^b e^{z_i f \Delta\phi} \quad (i \neq 1,\ J_i = 0) \quad (34)$$

where $\Delta\phi \equiv \phi^b - \phi^s$ is the electric potential drop across the DBL (see Fig. 1). Furthermore, the LEN assumption

$$\sum_i z_i c_i = z_1 c_1 + \sum_{i \neq 1} z_i c_i = 0 \quad (35)$$

implies that not only c_i $(i \neq 1)$ but also c_1 is determined by ϕ. Thus, for instance, the surface concentration of the electroactive species is

$$c_1^s = -\frac{1}{z_1} \sum_{i \neq 1} z_i c_i^s = -\frac{1}{z_1} \sum_{i \neq 1} z_i c_i^b e^{z_i f \Delta\phi} \quad (36)$$

The current–voltage relation can be obtained from the flux equation of the electroactive species

$$J_1 = \frac{I}{z_1 F} = -D_1 \left(\frac{dc_1}{dx} + z_1 c_1 f \frac{d\phi}{dx} \right) \quad (37)$$

by transforming the migration term with the help of Eq. (35) to

$$z_1 c_1 f \frac{d\phi}{dx} = -\sum_{i \neq 1} z_i c_i f \frac{d\phi}{dx} = \sum_{i \neq 1} \frac{dc_i}{dx} \quad (38)$$

Integration of Eq. (37) over the DBL then gives

$$-\frac{I\delta}{z_1 F D_1} = \Delta c_1 + \sum_{i \neq 1} \Delta c_i = \sum_{i \neq 1} \left(1 - \frac{z_i}{z_1}\right) \Delta c_i \quad (39)$$

where $\Delta c_i \equiv c_i^b - c_i^s$. Introducing the limiting diffusion current density

$$I_{Ld,1} \equiv -\frac{z_1 F D_1 c_1^b}{\delta} \quad (40)$$

and using Eqs. (34 and 36), the current–voltage relation takes the form

$$I = I_{Ld,1} \sum_{i \neq 1} \frac{c_i^b}{c_1^b} \left(1 - \frac{z_i}{z_1}\right) (1 - e^{z_i f \Delta\phi}) \quad (41)$$

Note that the definition of $I_{Ld,1}$ has not been deduced from the condition $c_1^s = 0$, but it rather corresponds to a situation in which the transport of species 1 takes place mostly by diffusion, and hence its name. Moreover, Eq. (40) corresponds to the particular case in which there is only one active species; see Eq. (78) below for the general definition.

It is interesting to observe that species 1 is the only one that moves, while the inactive species are standing still over the system. In a sense, this is similar to the conduction of electrons in a metal, in which electrons move and the ions are standing on the crystal lattice and, therefore, Ohm's law is expected to be satisfied. Indeed, Eq. (37) shows that the electric current density is proportional to the electric field, $I \equiv -\kappa_{\text{eff}}(d\phi/dx)$, in which

$$\kappa_{\text{eff}}(x) = \frac{F^2}{RT} D_1 \sum_i z_i^2 c_i(x) \quad (42)$$

is the local effective conductivity and Eqs. (33 and 35) have been used. There is, however, a difference between these two systems. The "static" distribution of the inactive species is determined by the electric potential distribution and hence, although I is only due to species 1, all species are relevant to the conduction process.

The local ohmic behavior is not in contradiction with the fact that Eq. (41) shows a nonlinear variation of I with the potential drop $\Delta\phi$. At low potentials, $f\Delta\phi \ll 1$, the DBL is practically nonpolarized (i.e. the ionic concentrations take their bulk values throughout the DBL) and the slope of the current–voltage curve is $\kappa_{\text{eff}}^{\text{b}}$. When increasing $\Delta\phi$, the slope of the current–voltage curve decreases owing to the development of concentration polarization. The effective conductivity varies then with position and this makes the overall system behavior to be nonohmic.

2.1.2.2 Solutions of Homovalent Ions, $|z_i| = z$

The theoretical analysis of ion transport requires the grouping of ions according to their valencies [27–31]. All ions of the same valency (a term used here as equivalent to charge number) are grouped together to constitute a "class" and the sum of their concentrations is termed the "class concentration" [32], denoted by C. The simplest transport problem involves only two classes corresponding to valencies z and $-z$. This is sometimes referred to as the homovalent case [33]. Some interesting conclusions are drawn from Eqs. (36 and 41) in this situation.

Denote the class of the electroactive species by subscript 1 and the other class by subscript 2. The LEN assumption requires the two class concentrations to be equal to each other

$$C_1 \equiv \sum_{z_i=z_1} c_i = \sum_{z_i=-z_1} c_i \equiv C_2 \equiv C \quad (43)$$

Equation (36) then simplifies to

$$c_1^{\text{s}} = C^{\text{b}}\text{e}^{-z_1 f\Delta\phi} + (c_1^{\text{b}} - C^{\text{b}})\text{e}^{z_1 f\Delta\phi} \quad (44)$$

and the maximum potential drop in the DBL, which is attained under limiting conditions $c_1^{\text{s}} = 0$, satisfies

$$\text{e}^{-z_1 f\Delta\phi_L} = \left(1 - \frac{c_1^{\text{b}}}{C^{\text{b}}}\right)^{1/2} \quad (45)$$

Thus, when the ionic strength of the solution is much larger than the concentration of the electroactive species ($C^{\text{b}} \gg c_1^{\text{b}}$), that is, in the presence of excess supporting electrolyte case, $z_1\Delta\phi_L$ tends to zero and the electric potential drop is then negligible [5, 26, 34]. On the contrary, in the absence of a supporting electrolyte, the electroactive species is the only species of its class, $C^{\text{b}} = c_1^{\text{b}}$, and $z_1\Delta\phi_L$ diverges. The conclusion that migration is absent when the ionic strength of the solution is much larger than the concentration of the electroactive species is not restricted to the homovalent case; note that the equation $I \equiv -\kappa_{\text{eff}}(\text{d}\phi/\text{d}x)$ implies that $\text{d}\phi/\text{d}x$ decreases as κ_{eff} increases.

In homovalent systems, the current–voltage curve, Eq. (41), takes the form

$$I = I_L \frac{1 - \text{e}^{-z_1 f\Delta\phi}}{1 - \text{e}^{-z_1 f\Delta\phi_L}} \quad (46)$$

where

$$I_L = I_{Ld,1}\frac{2C^{\text{b}}}{c_1^{\text{b}}}\left[1 - \left(1 - \frac{c_1^{\text{b}}}{C^{\text{b}}}\right)^{1/2}\right] \quad (47)$$

is the limiting current density (i.e. that corresponding to $c_1^{\text{s}} = 0$ and $\Delta\phi = \Delta\phi_L$). The value of I_L varies between $2I_{Ld,1}$ in the absence of supporting electrolyte ($C^{\text{b}} = c_1^{\text{b}}$) and $I_{Ld,1}$ in the presence of excess supporting electrolyte ($C^{\text{b}} \gg c_1^{\text{b}}$). Migrational effects in homovalent solutions can therefore account for up to a factor 2 in I_L.

2.1.2.3 Binary Electrolyte Solutions

When the solution contains only two ionic species, the concentration profiles are linear and the diffusion and migration terms in the flux equations are independent on position within the DBL. The electroinactive species can be thought to be in equilibrium as a result of the balance of diffusional and migrational terms in its flux equation. The migrational contribution to the flux of the electroactive species is equal (due to the LEN assumption) to that of the inactive species, except for a sign reversal, and hence the flux of the electroactive species can be described as the sum of two diffusional contributions, Eq. (38). This means that the slopes of the concentration profiles are proportional to the electric current, Eq. (39), and the occurrence of a limiting current is clearly associated to the maximum concentration gradient that can be established over the DBL, that is, to vanishing concentrations at the electrode surface.

The current–voltage curve of this system is a particular case of Eq. (41), which takes the simple form [34]

$$I = I_L(1 - \mathrm{e}^{z_2 f \Delta\phi}) \tag{48}$$

where

$$I_L = \left(1 - \frac{z_1}{z_2}\right) I_{Ld,1} = -\frac{(z_1 - z_2)FD_1c_2^{\mathrm{b}}}{\delta} \tag{49}$$

is the limiting current density. This curve has been plotted in Fig. 2. The figure includes the case of both cathodic and anodic processes. Consider first that the electroactive species is an anion and, consequently, that $I_L > 0$; note that the charge numbers have been defined with sign. In the depleted DBL adjacent to the anode, the current density is positive and tends to the limiting value when the (negative) potential drop increases in absolute value. In the concentrated DBL adjacent to the anode (for the same geometry described in Fig. 1, that is, electrode located at $x = 0$ and DBL extending from $x = 0$ to δ), the current is negative, and the potential drop is positive. Increasing the potential drop now leads to an increase of the electrical conductivity of the DBL, and hence of the slope of the current–voltage curve. When the electroactive species is a cation, these comments must be changed accordingly, but Fig. 2 remains valid.

Figure 3 shows the concentration, $c_i(x)$, and electric potential, $\phi(x)$, profiles given by

$$\frac{c_1}{c_1^{\mathrm{b}}} = \frac{c_2}{c_2^{\mathrm{b}}} = \mathrm{e}^{z_2 f(\phi^{\mathrm{b}} - \phi)} = 1 - \frac{I}{I_L}\left(1 - \frac{x}{\delta}\right) \tag{50}$$

which can be obtained by integration of Eq. (37) from x to δ, after use of Eq. (38). In the depleted DBL, the interfacial

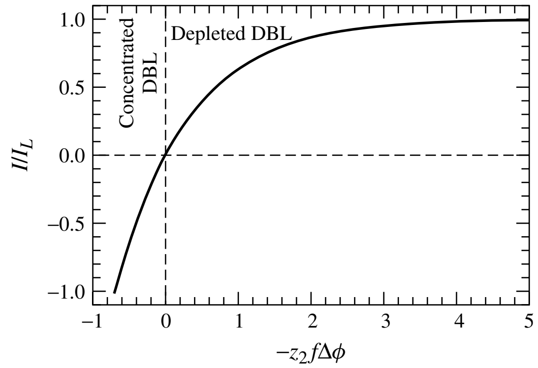

Fig. 2 Current–voltage curves of a DBL containing a strong binary electrolyte. Magnitudes z_2, $\Delta\phi$, I, and I_L are defined with sign; subscript 2 denotes the electroinactive species. Negative values of I/I_L correspond to electrode dissolution (anodic or cathodic), and positive values to single ion discharge at the electrode.

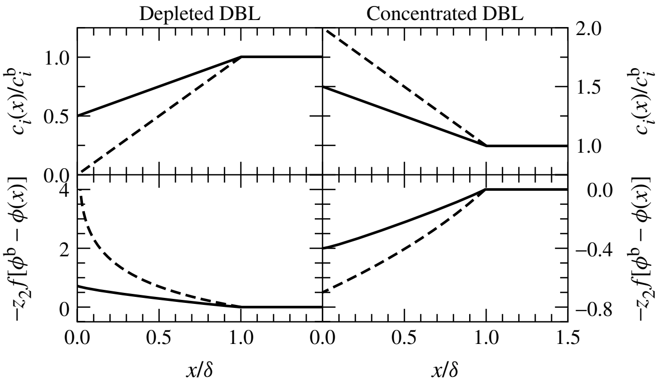

Fig. 3 Concentration and electric potential profiles for depleted ($I/I_L > 0$) and concentrated DBL ($I/I_L < 0$). The continuous lines correspond to $|I/I_L| = 0.5$ and the dashed lines to $|I/I_L| = 1.0$.

concentration c_i^s decreases with increasing $\Delta\phi$, and the limiting current I_L is reached when $z_2\Delta\phi \to -\infty$ and $c_i^s \to 0$. In the concentrated DBL, the interfacial concentration c_i^s increases with increasing $\Delta\phi$ (in absolute value).

It is important to stress that $\Delta\phi$ is the potential drop in the DBL only. There is also a potential drop at the electrode|DBL interface that changes with concentration polarization. The variation of the latter is given by the concentration overpotential that, in this case, takes the form

$$\eta_c = \frac{1}{z_1 f} \ln \frac{c_1^s}{c_1^b} = \frac{1}{z_1 f} \ln \left(1 - \frac{I}{I_L}\right) \tag{51}$$

Combining Eqs. (48 and 51), the current–voltage curve can be expressed as [34]

$$I = I_L \left\{1 - \exp\left[\frac{z_2 - z_1}{z_1 z_2} f(\eta_c - \Delta\phi)\right]\right\} \tag{52}$$

where $\eta_c - \Delta\phi$ is the change in the potential difference between the electrode and the bulk solution due to the passage of the electric current.

2.1.2.4 **Ternary Electrolyte Solutions. The Supporting Electrolyte**

Consider a ternary system in which the common ion, $i = 3$, is an inactive species. (If the electroactive species were the common ion, the system behavior would be similar to that of a binary solution.) A key feature of systems with only one electroactive species is that there is a background concentration of indifferent electrolytes that maintain a fairly uniform conductivity of the DBL. This implies that the electric potential drop is small and is quite uniformly distributed over the DBL. The concentration profile of the electroactive species is (slightly) nonlinear, and the same is true in general for the inactive ions, but the system behavior is still quite simple. In the particular case $z_1 = z_2$, the concentration profile of the common ion is linear and is given by

$$c_3(x) = c_3^b - \frac{z_1 c_1^b}{z_1 - z_3} \frac{I}{I_{Ld,1}} \left(1 - \frac{x}{\delta}\right) \tag{53}$$

which has been obtained by integration of Eq. (37) and making use of Eq. (38). The distributions of the electric potential and concentration of the other inactive ion can be obtained from Eq. (33) as

$$f[\phi^{\mathrm{b}} - \phi(x)] = \frac{1}{z_3} \ln \frac{c_3(x)}{c_3^{\mathrm{b}}} = \frac{1}{z_2} \ln \frac{c_2(x)}{c_2^{\mathrm{b}}} \tag{54}$$

Finally, the concentration profile of the electroactive species is determined from the LEN assumption, Eq. (35). Figure 4 shows these profiles for charge numbers $z_1 = z_2 = 1, z_3 = -2$, a concentration ratio $c_1^{\mathrm{b}}/c_2^{\mathrm{b}} = 0.2$, and current densities $I/I_{Ld,1} = 0.5$ and 1.0. The most significant characteristic shown by this figure is that the electric potential drop is very small, even for the case $I/I_{Ld,1} = 1.0$. As a consequence, ion transport takes place mostly by diffusion and the concentration profiles are practically linear. As could be expected from the ratio $c_1^{\mathrm{b}}/c_2^{\mathrm{b}} = 0.2$, the concentration changes associated to current transport are more important in relative terms for the electroactive species than for the inactive ones. A detail that can (hardly) be observed in Fig. 4 is that $c_1^{\mathrm{s}} \neq 0$ when $I/I_{Ld,1} = 1.0$, which is due to the fact that there is a small migrational contribution to the transport of this species. In other words, the limiting current is slightly larger than $I_{Ld,1}$ under these conditions.

For the discussion of the current–voltage relation, the homovalent case of Eq. (46) is considered. In a ternary case, this equation becomes

$$I = -\frac{2z_1 F D_1 c_3^{\mathrm{b}}}{\delta}(1 - \mathrm{e}^{-z_1 f \Delta\phi}) \tag{55}$$

while Eqs. (45 and 47) simplify to

$$\Delta\phi_L = \frac{RT}{2z_1 F} \ln(1 + c_1^{\mathrm{b}}/c_2^{\mathrm{b}}) \tag{56}$$

and

$$I_L = -\frac{2z_1 F D_1 c_3^{\mathrm{b}}}{\delta}\left[1 - \left(1 - \frac{c_1^{\mathrm{b}}}{c_3^{\mathrm{b}}}\right)^{1/2}\right] \tag{57}$$

Equations (56 and 57) have been represented in Fig. 5 as a function of the electroactive/supporting electrolyte concentration ratio. When the electroactive species

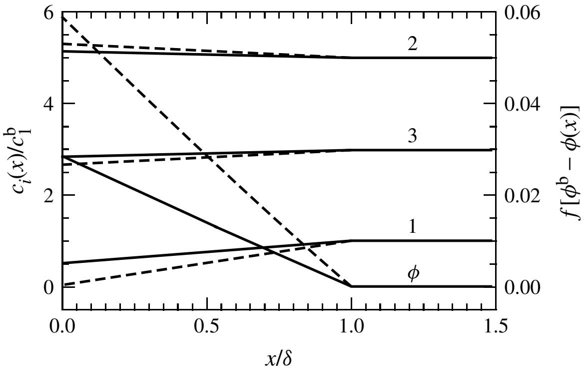

Fig. 4 Electric potential and ionic concentration profiles (marked with the respective subscripts 1, 2, 3) in a ternary system with $z_1 = z_2 = 1$, $z_3 = -2$, for a concentration ratio electroactive to inactive cation $c_1^{\mathrm{b}}/c_2^{\mathrm{b}} = 0.2$, and two values of the electric current density: $I/I_{Ld,1} = 0.5$ (continuous line) and 1.0 (dashed line).

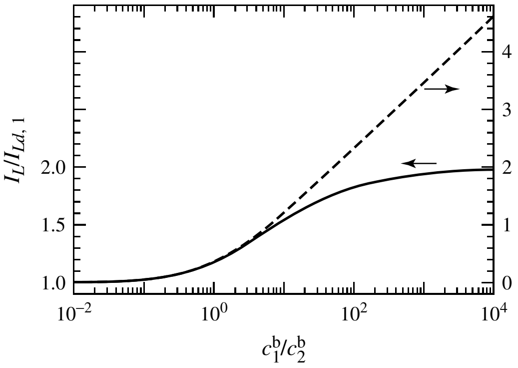

Fig. 5 Dependence of the limiting current density (continuous line) and the electric potential drop (dashed line) in the DBL under limiting conditions on the electroactive/supporting electrolyte concentration ratio.

is a tracer ion, $c_1^b/c_2^b \ll 1$, $\Delta\phi_L \approx 0$ and

$$I_L \approx -\frac{z_1 F D_1 c_1^b}{\delta}\left(1+\frac{c_1^b}{4c_2^b}\right) \approx I_{Ld,1} \tag{58}$$

On the contrary, in the absence of supporting electrolyte, $c_1^b/c_2^b \gg 1$, $I_L \approx 2I_{Ld,1}$ and $\Delta\phi_L$ diverges; the ratio $I_L/I_{Ld,1}$ tends to $(1 - z_1/z_3)$ when $c_1^b/c_2^b \gg 1$ in systems with other charge numbers, as can be deduced from Eq. (49).

The current–voltage curves given by Eq. (55) have been represented in Fig. 6. The initial slope of these curves is κ_{eff}^b, which obviously increases with decreasing ratio c_1^b/c_2^b, when the value of $I_{Ld,1}$ is fixed (i.e. c_1^b is fixed). For very low values of this ratio, $\Delta\phi$ is very small. It is then more relevant to consider also the variation of the electrode potential. Figure 7 shows the same curves as in Fig. 6 though presented in terms of $\Delta\phi - \eta_c$, where

$$\eta_c \equiv \frac{1}{z_1 f}\ln\frac{c_1^s}{c_1^b} \tag{59}$$

is the concentration overpotential. The potential drop $\Delta\phi - \eta_c$ is the change in electrode potential (relative to bulk solution) due to the concentration polarization.

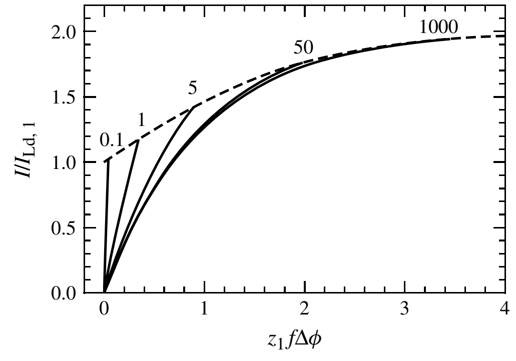

Fig. 6 Current–voltage curves of a depleted DBL for different values of the electroactive/supporting electrolyte concentration ratio, c_1^b/c_2^b, shown on the curves. $\Delta\phi$ is the electric potential drop in the DBL.

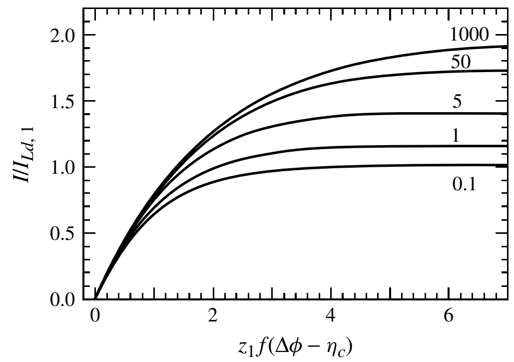

Fig. 7 Current–overall voltage drop for different values of the electroactive/supporting electrolyte concentration ratio, c_1^b/c_2^b.

A validity test for the excess supporting electrolyte assumption (in the homovalent case) can be obtained by calculating the migrational flux from Eqs. (37 and 38) as

$$J_{1,\mathrm{mig}} \equiv -z_1 D_1 c_1 f \frac{\mathrm{d}\phi}{\mathrm{d}x} = \frac{z_1^2 c_1}{\sum\limits_i z_i^2 c_i} J_1 = \frac{c_1}{2c_3} J_1 \qquad (60)$$

and comparing it to the diffusional flux

$$J_{1,\mathrm{dif}} = J_1 - J_{1,\mathrm{mig}} = J_1 \left(1 - \frac{c_1}{2c_3}\right) \qquad (61)$$

Equations (60 and 61) show clearly that the migrational contribution to J_1 is negligible compared to the diffusional one in as much as c_1 is negligible compared to c_3. Alternatively, the importance of migration can be estimated from Eq. (58), since the term $c_1^b/4c_2^b$ accounts for the migrational contribution to I_L.

When the supporting electrolyte is electroinactive (and chemically inert), its presence can be totally ignored in the description of transport processes. The absence of migration and the zero flux condition for the inactive species implies that these species have an approximately uniform concentration throughout the DBL, which is not affected by the passage of the electric current. It must be stressed, however, that this statement refers to the concentration gradients in relative terms to the bulk concentration of the respective species. In absolute terms, the concentration gradients of the inactive species are similar to that of the active species, and by no means the concentration gradient of the active species can be neglected. In fact, in the homovalent case, it can be easily shown that $\mathrm{d}c_1/\mathrm{d}x \approx 2\mathrm{d}c_3/\mathrm{d}x \approx -2\mathrm{d}c_2/\mathrm{d}x$ when migration is negligible. A straightforward implication of these comments is that the LEN assumption cannot be used in conjunction with the excess supporting electrolyte assumption.

2.1.2.5 **Weak Binary Electrolyte**

Consider an electrolyte $A_{\nu_1} B_{\nu_2}$ dissociating into ν_1 ions A^{z_1} of charge number z_1 and ν_2 ions B^{z_2} of charge number z_2

$$A_{\nu_1} B_{\nu_2} \rightleftarrows \nu_1 A^{z_1} + \nu_2 B^{z_2} \qquad (62)$$

where $z_1\nu_1 + z_2\nu_2 = 0$. Denote by $c_{12} = \alpha c_{12,T}$ and $c_{12,u} = (1-\alpha)c_{12,T}$ the concentrations of dissociated and undissociated electrolyte fractions, respectively, being α the degree of dissociation and $c_{12,T} = c_{12} + c_{12,u}$ the total electrolyte concentration. When the dissociation Reaction (62) is fast compared with the transport process, it can be assumed that the dissociated and undissociated electrolyte fractions are in equilibrium and the mass action law

$$K = \frac{c_1^{\nu_1} c_2^{\nu_2}}{c_{12,u}} = c_{12,T}^{\nu_{12}-1} \frac{\nu_1^{\nu_1} \nu_2^{\nu_2} \alpha^{\nu_{12}}}{1-\alpha} \qquad (63)$$

allows then to determine α as a function of $c_{12,T}$. In deriving Eq. (63), the following relations have been used, $c_1 = \nu_1 c_{12}$, $c_2 = \nu_2 c_{12}$, and $\nu_{12} \equiv \nu_1 + \nu_2$.

Because of the electrolyte dissociation, the flux densities J_i of the ions and that of the undissociated electrolyte

$$J_{12,u} = -D_{12,u} \frac{\mathrm{d}c_{12,u}}{\mathrm{d}x} \qquad (64)$$

vary with position. The same applies to the flux density of the dissociated electrolyte, J_{12} [35]. The total electrolyte flux

$$J_{12,T} = J_{12,u} + J_{12} = -D_{12,u} \frac{\mathrm{d}c_{12,u}}{\mathrm{d}x} - D_{12} \frac{\mathrm{d}c_{12}}{\mathrm{d}x} = -D_{12,T} \frac{\mathrm{d}c_{12,T}}{\mathrm{d}x} \qquad (65)$$

however, is constant throughout the system as required by the continuity equation, Eq. (11). In spite of this fact, the total electrolyte concentration $c_{12,T}$ does not vary linearly with position because the effective diffusion coefficient of the electrolyte

$$D_{12,T} \equiv \frac{\nu_{12}(1-\alpha) D_{12,u} + \alpha D_{12}}{\nu_{12}(1-\alpha) + \alpha} \qquad (66)$$

is a function of α, and α is a function of $c_{12,T}$. Exception is made for the special cases of very weak electrolyte ($\alpha \to 0$, $K \to 0$, $D_{12,T} \to D_{12,u}$), very strong electrolyte ($\alpha \to 1$, $K \to \infty$, $D_{12,T} \to D_{12}$), and $D_{12,u} = D_{12}$, when $D_{12,T}$ is a constant and $c_{12,T}$ varies linearly.

If only species 1 is electroactive, the boundary conditions at the electrode surface are $J_{12,u}^{\mathrm{s}} = 0$, $J_2^{\mathrm{s}} = 0$, and $J_1^{\mathrm{s}} = I/z_1 F$, and therefore the flux density $J_{12,T}$ can be evaluated, from Eq. (21) and $J_2^{\mathrm{s}} = 0$, as

$$J_{12,T} = -\frac{t_2}{z_2 \nu_2} \frac{I}{F} \qquad (67)$$

The concentration profile of the electrolyte $c_{12,T}$ could then be determined from Eqs. (63, 65, and 67), and the boundary value $c_{12,T}^{\mathrm{b}}$. Note that the transport numbers are constant in a binary system.

For the determination of the current–voltage characteristics of this system, the integration of Eq. (65) over the DBL

$$-J_{12,T}\delta = \frac{t_2}{z_2 \nu_2} \frac{I\delta}{F} = D_{12,u} \Delta c_{12,u} + D_{12} \Delta c_{12} \qquad (68)$$

can be conveniently rewritten in the form

$$I = I_{L,T} \left[1 - \frac{D_{12,u} c_{12,u}^{\mathrm{s}} + D_{12} c_{12}^{\mathrm{s}}}{D_{12,u} c_{12,u}^{\mathrm{b}} + D_{12} c_{12}^{\mathrm{b}}} \right] \qquad (69)$$

where

$$I_{L,T} = \frac{z_2 \nu_2 F}{t_2 \delta} (D_{12,u} c_{12,u}^{\mathrm{b}} + D_{12} c_{12}^{\mathrm{b}}) \qquad (70)$$

is the limiting current density defined from the condition that the electrolyte concentration (both dissociated and undissociated) becomes zero at the electrode surface when $I \to I_{L,T}$. This limiting current density reduces to

$$I_{L,u} \equiv \frac{z_2 \nu_2 F D_{12,u} c_{12,T}^{\mathrm{b}}}{t_2 \delta} \qquad (71)$$

and

$$I_L \equiv \frac{z_2 \nu_2 F D_{12} c_{12,T}^{\mathrm{b}}}{t_2 \delta} = -\frac{z_1 \nu_{12} F D_1 c_{12,T}^{\mathrm{b}}}{\delta} \qquad (72)$$

in the limits of very weak ($\alpha \to 0$) and very strong electrolyte ($\alpha \to 1$), respectively. Indeed, Eq. (70) can be easily transformed to

$$I_{L,T} = I_L \left[\frac{D_{12,u}}{D_{12}}(1 - \alpha^b) + \alpha^b \right] \quad (73)$$

where α^b is the degree of dissociation at $x = \delta$.

Figure 8 shows the dependence of the limiting current on the dissociation degree for the cases of 1 : −1 and 2 : −1 electrolytes and different values of the ratio $D_{12,u}/D_{12}$. At very low electrolyte concentration or very high dissociation constant, the electrolyte is completely dissociated and $I_{L,T} = I_L$. At very high electrolyte concentration or very low dissociation rate constant, the electrolyte is practically undissociated and $I_{L,T} = I_{L,u}$. The ratio $I_{L,T}/I_L$ is then equal to $D_{12,u}/D_{12}$. Surprisingly, in this limit of negligible dissociation when there are no ions in solution, the system conducts electric current and, moreover, the limiting current can be greater than for a fully dissociated electrolyte if $D_{12,u} > D_{12}$. Note also from Fig. 8 that the limiting current density becomes independent of the dissociation constant K when $D_{12,u} = D_{12}$, for in this case, $I_{L,T} = I_{L,u} = I_L$.

The paradoxical results mentioned above can be explained in terms of the electric potential drop across the DBL (see Appendix A for its derivation)

$$\Delta\phi = -\frac{RT}{z_2 F} \ln \frac{c_{12}^b}{c_{12}^s} - \frac{RT}{F} \frac{\nu_{12} D_{12,u}}{z_2(\nu_{12} - 1) D_2} \times \left[\frac{c_{12,u}^b}{c_{12}^b} - \frac{c_{12,u}^s}{c_{12}^s} \right] \quad (74)$$

This potential drop increases when K decreases and there are less ions to conduct the electric current. In particular, $\Delta\phi_{\mathrm{dif}}$ vanishes and $\Delta\phi_{\mathrm{ohm}}$ diverges when $K \to 0$, so that the sentence in the previous paragraph should have been written as follows: the system is able to conduct an electric current in the limiting case $\alpha \to 0$, provided that an infinite potential difference is applied across the depleted DBL.

The current–voltage curves of this system can be obtained by combining Eqs. (69 and 74). Figure 9 shows these curves for a 1 : −1 electrolyte, with an electroactive cation, and different values of

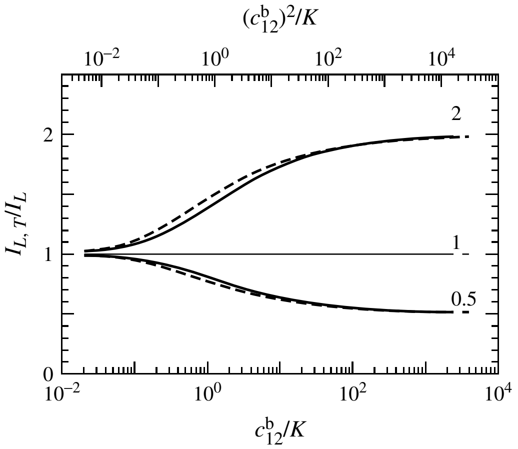

Fig. 8 Limiting current density in a depleted DBL containing a weak electrolyte solution relative to the value corresponding to complete dissociation. The lower abcisa scale and the continuous lines correspond to a 1 : −1 electrolyte. The upper abcisa and the dashed lines correspond to a 2 : −1 electrolyte. The ratio $D_{12,u}/D_{12}$ has been given the values 0.5, 1, and 2, as shown on the curves.

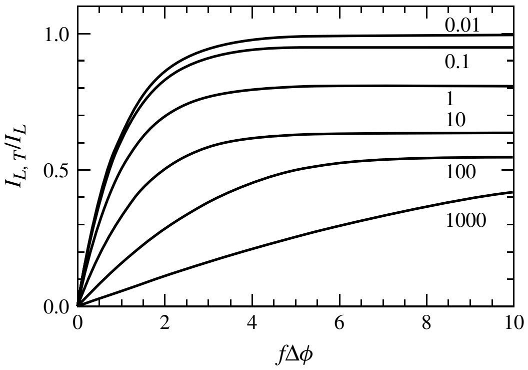

Fig. 9 Current–voltage curves of a depleted DBL containing a weak 1 : −1 electrolyte for the values of the ratio $c^{\mathrm{b}}_{12,T}/K$, which are shown on the curves. Both the ratio $D_{12,u}/D_{12}$ and the transport number t_1 have been set equal to 0.5.

the bulk electrolyte concentration relative to the dissociation constant, $c^{\mathrm{b}}_{12,T}/K$. When the dissociation degree is close to one, that is at low values of the ratio $c^{\mathrm{b}}_{12,T}/K$, the curves are practically identical to that in Fig. 2. However, when the ratio $c^{\mathrm{b}}_{12,T}/K$ is high and the electrolyte is mostly undissociated, the electric conduction becomes difficult. Thus, for instance, in the case $c^{\mathrm{b}}_{12,T}/K = 100$ where $\alpha^{\mathrm{b}} = 0.031$ and $I_{L,T}/I_L = 0.516$, the electric potential drop in the DBL, $\Delta\phi$, must be of the order of 15 times RT/F for the current density to be close to this limiting value. No need to mention that large values of the ratio $c^{\mathrm{b}}_{12,T}/K$ also imply lower concentration of the electroactive species close to the electrode and, therefore, larger electrode|solution potential drops (i.e. Nernstian potential drops in the case of reversible electrode reactions). However, the current–voltage curves do not change qualitatively when the electrode potential is taken into account in the voltage drop.

Note, finally, that the boundary condition $J^{\mathrm{s}}_{12,u} = 0$ requires (except in the trivial case $I = 0$, which lacks interest) that the dissociation degree α is unity in the vicinity of the electrode, independent of the values of I and K. This is equivalent to stating that the value of α^{s} is independent of $c^{\mathrm{s}}_{12,T}$, which is inconsistent with Eq. (63). It is then concluded that Eq. (63) is not valid in the vicinity of the electrode. The study of the limiting current without the assumption that the dissociation reaction is fast compared with the electrodiffusion process has been carried out by Kharkats and Sokirko [36, 37]. The validity of the dissociation equilibrium assumption and the drastic changes in concentrations that occur when $I \to I_L$ have been considered by Vorotyntsev [38].

2.1.3
Steady State Current–overpotential Curves in the Presence of Supporting Electrolyte

The use of an excess amount of inactive electrolyte makes negligible the migrational contribution to mass transport and therefore simplifies the theoretical modeling of experimental observations. In particular, the absence of potential drop in the DBL eliminates the coupling of ionic fluxes. The current–voltage curves are then presented in terms of the concentration overpotential. Mass transport in the presence of homogeneous reactions can be described with relative simplicity in these systems, as shown in the last section.

2.1.3.1 Systems with One Electroactive Species

In the absence of migration, the flux density of the electroactive species is

$$J_1 = \frac{I}{z_1 F} \approx -D_1 \frac{\mathrm{d}c_1}{\mathrm{d}x} = -D_1 \frac{c_1^{\mathrm{b}} - c_1^{\mathrm{s}}}{\delta} \tag{75}$$

and the interfacial concentration can be expressed as

$$c_1^{\mathrm{s}} = c_1^{\mathrm{b}} \left(1 - \frac{I}{I_{Ld,1}}\right) \tag{76}$$

where $I_{Ld,1}$ is the limiting diffusion current density defined by Eq (40). Equation (76) can be rewritten in terms of the concentration overpotential, Eq. (32), as

$$I = I_{Ld,1}(1 - \mathrm{e}^{z_1 f \eta_c}) \tag{77}$$

This equation is valid both for a depleted DBL, in which $I/I_{Ld,1} > 0$ and $z_1 \eta_c < 0$, and for a concentrated DBL, in which $I/I_{Ld,1} < 0$ and $z_1 \eta_c > 0$.

2.1.3.2 Systems with Several Electroactive Species

When several species are involved in the electrode reaction described by Eq. (23), the reaction rate is determined by the reactant ($\nu_i^{\mathrm{r}} < 0$) with slower diffusion rate. Thus, the limiting current exhibited by the system is the smallest of the limiting diffusion current densities [26]

$$I_{Ld,i} \equiv -\frac{nFD_i c_i^{\mathrm{b}}}{\nu_i^{\mathrm{r}} \delta} \tag{78}$$

of the reactants. Note that I can be either positive or negative, but it is always of the same sign as $I_{Ld,i}$ for the reactants.

From Eqs. (25 and 78), the interfacial concentration of species i is given by

$$c_i^{\mathrm{s}} = c_i^{\mathrm{b}} + \frac{J_i \delta}{D_i} = c_i^{\mathrm{b}} \left(1 - \frac{I}{I_{Ld,i}}\right) \tag{79}$$

The concentration overpotential in Eq. (32) then takes the form

$$\eta_c = \frac{1}{nf} \sum_i \nu_i^{\mathrm{r}} \ln \left(1 - \frac{I}{I_{Ld,i}}\right) \tag{80}$$

Consider, for example, the anodic oxidation of iron(II)

$$\mathrm{Fe}^{3+}(\mathrm{aq}) - \mathrm{Fe}^{2+}(\mathrm{aq}) + e^- = 0 \tag{81}$$

in a situation in which the bulk (aqueous) solution is equimolar in ferrous and ferric ions. Since the ferrous ion is consumed at the electrode, the limiting current exhibited by the system is the diffusion limiting current of this ion and the current–overpotential curve is

$$\begin{aligned} \eta_c &= \frac{1}{f} \ln \frac{1 - I/I_{Ld,\mathrm{Fe}^{3+}}}{1 - I/I_{Ld,\mathrm{Fe}^{2+}}} \\ &= \frac{1}{f} \ln \frac{1 + (D_{\mathrm{Fe}^{2+}}/D_{\mathrm{Fe}^{3+}}) I/I_{Ld,\mathrm{Fe}^{2+}}}{1 - I/I_{Ld,\mathrm{Fe}^{2+}}} \end{aligned} \tag{82}$$

which has been represented in Fig. 10.

2.1.3.3 Diffusion-reaction Processes

The general strategy for solving transport problems in which the electrode reaction, Eq. (23), is coupled to a homogeneous reaction in the DBL

$$\sum_i \nu_i C_i^{z_i} = 0 \tag{83}$$

is outlined in this section. The stoichiometric numbers are defined to be positive for products and negative for reactants. Chemical equilibrium is assumed for both reactions, which is justified from the fact that chemical kinetics is usually much faster than diffusion processes.

The homogeneous reaction is considered to be reversible. The chemical equilibrium assumption, $\sum_i \nu_i \tilde{\mu}_i \approx 0$ or $K \approx \prod_i c_i^{\nu_i}$, applied to transport problems

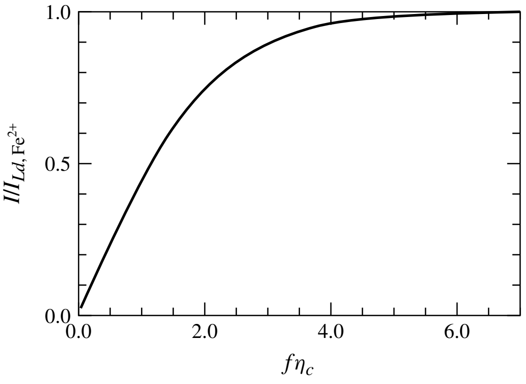

Fig. 10 Current density versus concentration overpotential for the anodic oxidation of iron(II) from an equimolar solution of ferrous and ferric ions. The diffusion coefficients $D_{\mathrm{Fe}^{3+}} = 0.604 \times 10^{-5}$ cm^2 s^{-1} and $D_{\mathrm{Fe}^{2+}} = 0.719 \times 10^{-5}$ cm^2 s^{-1} [39] have been used.

means that the forward and backward reaction rates are much larger than the mass transport by diffusion, and hence their difference can be neglected in a first approximation. Actually, there is a small difference between the forward and backward reaction rates, the net reaction rate

$$r \equiv \frac{r_i}{\nu_i} = \frac{1}{\nu_i}\frac{\mathrm{d}J_i}{\mathrm{d}x} \qquad (84)$$

which is responsible for the spatial changes of the flux densities of the reactive species. In the description of transport processes, this equation can be used to set up relations among the flux density gradients of the reactive species and to evaluate the reaction rate. If the reaction rate constants are known, the validity of the fast chemical equilibrium assumption should also be checked a posteriori.

The continuity equation under steady state conditions, Eq. (84), states that the flux densities of the reactive species change with position because they are either consumed or generated in the homogeneous reaction. The reaction involves the transformation of chemical species by the exchange of atoms or groups of atoms among them, but the total amount of a given chemical element is not modified. It is then correct to state that the sum of the flux densities, multiplied by a convenient stoichiometric coefficient, of all species that contain a given chemical element involved in Reaction (83) is independent of position. By consideration of all the chemical elements, a large number of equations are obtained. The elimination of those that are simply linear combinations of the others leads to a much smaller number of independent equations. Alternatively, those groups of atoms that are not modified by the reaction can be considered as a unique entity. This is the so-called formalism of constituents, which leads faster to the same number of independent equations. Consider, for instance, that the chemical reaction involves several species with a cyanide group. The reaction cannot make the cyanide group disappear but it can simply bind it to one or another chemical species. Thus, the flux of cyanide constituent (defined as the group of chemical species that contain cyanide) is not affected by the chemical reaction and is constant throughout the DBL (under steady state conditions).

These conservation equations (one for each constituent) are generically written in the form

$$\frac{\mathrm{d}J_j}{\mathrm{d}x} = \sum_i \nu_{j,i} \frac{\mathrm{d}J_i}{\mathrm{d}x} = 0 \qquad (85)$$

where the sum extends over all species i that contains the constituent (or chemical element) j, and $\nu_{j,i}$ is the stoichiometric number of constituent j in species i. Taking into account that the flux densities of the different species at the electrode surface are given by Eq. (24), and neglecting migration owing to the presence of excess supporting electrolyte, Eq. (85) can be written as

$$\sum_i \nu_{j,i} J_i = -\sum_i \nu_{j,i} D_i \frac{\mathrm{d}c_i}{\mathrm{d}x} = \frac{I}{nF} \sum_i \nu_{j,i} \nu_i^{\mathrm{r}} \qquad (86)$$

Note that the equation for the conduction current density, Eq. (12), is implicit in the system of Eqs. (86).

As an example, consider the dissolution of a cadmium metal electrode

$$\mathrm{Cd}^{2+}(\mathrm{aq}) - \mathrm{Cd}(\mathrm{metal}) + 2e^- = 0 \qquad (87)$$

in a solution containing iodide ion, which can complex to cadmium to form tetraiodocadmiate

$$[\mathrm{CdI_4}]^{2-}(\mathrm{aq}) - \mathrm{Cd}^{2+}(\mathrm{aq}) - 4\mathrm{I}^-(\mathrm{aq}) = 0 \qquad (88)$$

Denoting the species Cd^{2+}, I^-, and $[\mathrm{CdI_4}]^{2-}$ by subscripts 1 to 3, respectively, and considering cadmium Cd and iodine I as two constituents, Eq. (86) takes the form

$$D_1 \frac{\mathrm{d}c_1}{\mathrm{d}x} + D_3 \frac{\mathrm{d}c_3}{\mathrm{d}x} = -\frac{I}{2F} \qquad (89)$$

$$D_2 \frac{\mathrm{d}c_2}{\mathrm{d}x} + 4D_3 \frac{\mathrm{d}c_3}{\mathrm{d}x} = 0 \qquad (90)$$

where $\nu_2^{\mathrm{r}} = \nu_3^{\mathrm{r}} = \nu_{\mathrm{I},1} = \nu_{\mathrm{Cd},2} = 0$, $\nu_1^{\mathrm{r}} = \nu_{\mathrm{Cd},1} = \nu_{\mathrm{Cd},3} = \nu_{\mathrm{I},2} = 1, n = 2$, and $\nu_{\mathrm{I},3} = 4$. These two equations are to be solved together with the chemical equilibrium condition

$$K \approx \frac{c_3}{c_1 c_2^4} \qquad (91)$$

using the bulk concentration values as boundary conditions. The diffusion coefficients and complexation equilibrium constants are $D_1 = 0.7 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$, $D_2 = 2.0 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$, $D_3 = 0.5 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$, and $K = 2 \times 10^6\ \mathrm{M^{-4}}$ [39, 40].

A simple way to solve this equation system is to consider c_3 as the independent variable and evaluate c_2 and c_1 from Eqs. (90 and 91), respectively. Finally, integration of Eq. (89) yields the position variable. Figure 11 shows the concentration profiles thus obtained for the cases of anodic dissolution ($I > 0$) and cathodic discharge of cadmium ($I < 0$). In the first case, the cadmium and complex ion concentration gradients are negative (i.e. surface concentration larger than bulk value) and the iodide concentration gradient is positive. The DBL is then concentrated in the cadmium constituent. In the second case, the cadmium ion is consumed by the electrode reaction and the DBL is depleted in the cadmium constituent. The reaction rate evaluated from Eq. (84) has also been represented. It is thus evidenced that the rate of the complexation reaction is large in the case of the anodic dissolution and that the reaction front shifts towards the bulk solution with increasing current. On the contrary, the reaction rate is negligible in the case of the cathodic discharge, in which the concentration profiles are practically linear. The electric current values have been presented relative to the limiting diffusion current density of cadmium ion, $I_{Ld,1} = -2FD_1c_1^{\mathrm{b}}/\delta$. It can be

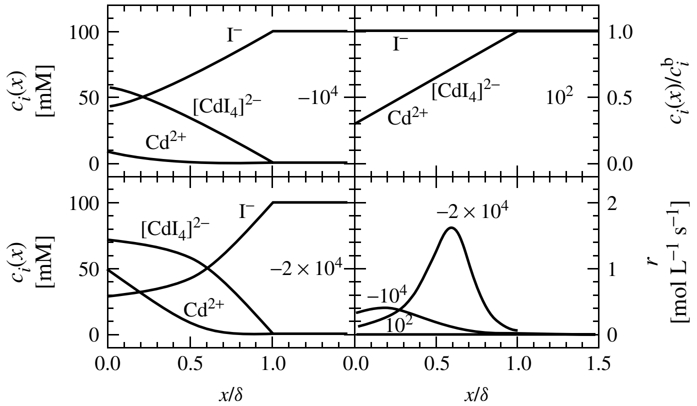

Fig. 11 Concentration profiles in a cadmium iodide solution adjacent to a cadmium metal electrode and the rate of formation of tetraiodocadmiate ion. The bulk concentrations are $c_1^b = 5\ \mu$M, $c_2^b = 100$ mM, $c_3^b = 1$ mM, and the three values of the electric current density have been considered: $I/I_{Ld,1} = 10^2$ (cathodic cadmium discharge), -10^4 and -2×10^4 (anodic cadmium dissolution).

deduced from Eq. (89) that the limiting current density (corresponding to $c_1^s = c_3^s = 0$) is $I_L = -2F[D_1 c_1^b + D_3 c_3^b]/\delta$. For the bulk concentrations considered in Fig. 11, $c_1^b = 5\ \mu\text{M}$, $c_2^b = 100\ \text{mM}$, $c_3^b = 1\ \text{mM}$, and a DBL thickness $\delta = 10^{-3}$ cm, these currents are $I_{Ld,1} = -0.67$ and $I_L = -97.2\ \text{mA cm}^{-2}$.

2.1.4
Steady State Current–voltage Curves of Systems with Several Active Species

There are electrochemical processes in which little or no supporting electrolyte is used. This is the case, for instance, of the study of overlimiting currents [34, 41, 42], and of microelectrode [43–45], and different voltammetric techniques [17, 18, 46–48], in which the absence of supporting electrolyte increases the sensitivity of the detection of the redox species. In this section, a general procedure for solving the electrodiffusion equations is presented. The procedure is based on determining first the electric potential distribution and then the current–voltage curves or the ionic concentration distributions in the DBL. The generality of the method, and the inherent complexity of the nonlinear migration term in the flux equations could make it not very attractive for the nonexpert, and therefore simpler solutions based on the Goldman constant field (GCF) assumption are also presented. For the sake of simplicity, no homogeneous reactions are considered.

2.1.4.1 Kramer's Integration Method

The mathematical difficulty of the electrodiffusion equations, Eq. (7), arises from the nonlinear migration term, which couples the Nernst–Planck equations of the different ionic species. By assuming that the electric field is constant (GCF assumption), this difficulty is removed and analytical solutions are easy to find. Unfortunately, the validity conditions for this approximation are not always satisfied in electrochemical systems [12, 49], and it is then needed either to derive approximate expressions for the electric potential distribution in some other way [50] or to calculate the exact distribution as described below. In any case, if the electric field distribution $\mathsf{E}(x)$ or, equivalently, the electric potential distribution

$$\phi(x) = \phi^{\mathrm{b}} + \int_x^\delta \mathsf{E}\mathrm{d}x \qquad (92)$$

is considered to be known, the transport equations can be formally integrated by Kramer's transformation [51]. This consists of multiplying both terms of Eq. (7) by $\mathrm{e}^{z_i f \phi}$ and integrating from x to δ to obtain [8, 52, 53]

$$c_i(x) = \left\{ c_i^{\mathrm{b}} + \frac{J_i}{D_i} \int_x^\delta \mathrm{e}^{z_i f[\phi(x') - \phi^{\mathrm{b}}]} \mathrm{d}x' \right\} \times \mathrm{e}^{z_i f[\phi^{\mathrm{b}} - \phi(x)]} \qquad (93)$$

The surface concentration c_i^{s} is obtained by setting $x = 0$ in this equation.

When the GCF approximation $\phi(x) = \phi^{\mathrm{b}} + (\delta - x)\mathsf{E}$ is valid, the integral in Eq. (93) can be evaluated and this equation becomes

$$c_i(x) = \left(c_i^{\mathrm{b}} - \frac{J_i}{z_i D_i f \mathsf{E}} \right) \mathrm{e}^{z_i f \mathsf{E}(x - \delta)} + \frac{J_i}{z_i D_i f \mathsf{E}} \qquad (94)$$

2.1.4.2 **The Equation for the Electric Field under the LEN Assumption**

Nikonenko and Urtenov [54, 55] have presented an algorithm for the solution of the steady state transport equations in multicomponent systems, which is based on calculating first the electric field E and then using Eqs. (92 and 93). Their method is outlined here for the particular case when the LEN assumption is used. Unlike Schlögl's method, that uses the concept of valency classes [32], these authors proposed to rewrite the Nernst–Planck equation system for N species in terms of the magnitudes

$$S_k \equiv \sum_{i=1}^N z_i^k c_i, \quad k = 0, 2, 3, \ldots, N \qquad (95)$$

$$G_k \equiv \sum_{i=1}^N z_i^k J_i / D_i, \quad k = 0, 1, 2, \ldots, N-1 \qquad (96)$$

instead of the N concentrations c_i and flux densities J_i. The LEN assumption in this notation takes the form $S_1 \equiv \sum_i z_i c_i = 0$, and this justifies the absence of index $k = 1$ in Eq. (95). The aim of the method is obtaining an equation for the electric field in which the unknown concentrations are eliminated by using their relation to the flux densities, which are known from Eq. (24).

Multiplying the Nernst–Planck equation, Eq. (7), by $-1/D_i$ and summing over species i, the electric field is eliminated and the concentration sum $S_0 \equiv \sum_i c_i$ is shown to follow the linear profile

$$S_0(x) = S_0^{\mathrm{b}} + (\delta - x) G_0 \qquad (97)$$

Similarly, multiplying the Nernst–Planck equation by z_i/D_i and summing over species i, it is obtained that

$$G_1 = f \mathsf{E} S_2 \qquad (98)$$

which could be used to evaluate the electric field if the relation between S_2 and S_0 were known. Note that S_2 is equal to double the ionic strength of the solution, and the advantages of using it as a variable in the formulation of transport problems have also been emphasized by other authors [17, 18]. Some simple cases are considered next and the general approach is presented later.

In the case of a binary solution, $S_2 = -z_1 z_2 S_0$ the electric potential can be obtained from Eq. (98) as

$$\phi(x) = \phi^{\mathrm{b}} + \frac{\Gamma}{f} \ln \frac{S_0(x)}{S_0^{\mathrm{b}}} \tag{99}$$

where

$$\Gamma \equiv -\frac{1}{z_1 z_2} \frac{G_1}{G_0} \tag{100}$$

Moreover, introducing the limiting current density

$$I_L \equiv -\frac{S_0^{\mathrm{b}}}{\delta} \frac{I}{G_0} \tag{101}$$

the steady state current–voltage curve can be deduced from Eq. (99) as

$$\begin{aligned} \Delta\phi &= -\frac{\Gamma}{f} \ln \frac{c_i^{\mathrm{s}}}{c_i^{\mathrm{b}}} \\ &= -\frac{\Gamma}{f} \ln \left(1 - \frac{I}{I_L}\right) \end{aligned} \tag{102}$$

In a multi-ionic, homovalent solution, $|z_i| = z$, $S_2 = z^2 S_0$ and Eq. (99) is again obtained [56–58], though Γ is now defined as $\Gamma \equiv G_1/z^2 G_0$. Since the integral in Eq. (93) can be evaluated by using Eqs. (97 and 99) as

$$\begin{aligned} \int_0^\delta \mathrm{e}^{z_i f(\phi-\phi^{\mathrm{b}})} \mathrm{d}x &= -\frac{\int_0^\delta S_0^{z_i\Gamma} \mathrm{d}S_0}{G_0 (S_0^{\mathrm{b}})^{z_i\Gamma}} \\ &= \frac{S_0^{\mathrm{b}}}{G_0(1+z_i\Gamma)} \left[\left(1 + \frac{\delta G_0}{S_0^{\mathrm{b}}}\right)^{1+z_i\Gamma} - 1\right] \end{aligned} \tag{103}$$

the interfacial concentration is finally given by

$$\begin{aligned} c_i^{\mathrm{s}} = c_i^{\mathrm{b}} \Bigg\{ 1 &+ \frac{I_L}{(1+z_i\Gamma) I_{Ld,i}} \\ &\times \left[\left(1 - \frac{I}{I_L}\right)^{1+z_i\Gamma} - 1\right] \Bigg\} \left(1 - \frac{I}{I_L}\right)^{-z_i\Gamma} \end{aligned} \tag{104}$$

which reduces to $c_i^{\mathrm{s}} = c_i^{\mathrm{b}}(1 - I/I_L)$ in the binary case. In deriving Eq. (104), note that $-J_i\delta/D_i c_i^{\mathrm{b}} = I/I_{Ld,i}$.

In the case of nonhomovalent multi-ionic systems, the solution procedure is necessarily more complicated because there is no simple relation such as $S_2 = z^2 S_0$, a problem that was first encountered and solved in different ways by Schlögl [59] and Brady and Turner [60]. If the system contains N different ionic species, the N Nernst–Planck equations for the N flux densities J_i are replaced by

$$G_k = -\frac{\mathrm{d}S_k}{\mathrm{d}x} + f\mathsf{E}S_{k+1}, \quad k = 0, 1, 2, \ldots, N-1 \tag{105}$$

In order to solve the system of Eqs. (105), a closure relation between S_N and other sums is needed. Such a relation is

$$\begin{aligned} S_N &= q_1 S_{N-1} - q_2 S_{N-2} + q_3 S_{N-3} \\ &\quad - \cdots + (-1)^{N-1} q_N S_0 \end{aligned} \tag{106}$$

where

$$q_1 = z_1 + z_2 + \cdots + z_N \tag{107}$$

$$\begin{aligned} q_2 &= z_1 z_2 + z_1 z_3 + \cdots + z_1 z_N + z_2 z_3 + \cdots \\ &\quad + z_2 z_N + z_3 z_4 + \cdots + z_{N-1} z_N \end{aligned} \tag{108}$$

$$\begin{aligned} q_3 &= z_1 z_2 z_3 + \cdots + z_1 z_2 z_N + z_1 z_3 z_4 + \cdots \\ &\quad + z_1 z_3 z_N + \cdots + z_{N-2} z_{N-1} z_N \end{aligned} \tag{109}$$

$$\vdots$$

$$q_k = \sum_{i_1=1}^{N+1-k} \sum_{i_2=i_1+1}^{N+2-k} \cdots \sum_{i_k=i_{k-1}+1}^{N} z_{i_1} z_{i_2} \cdots z_{i_k} \tag{110}$$

Some particular cases are considered in the next sections.

2.1.4.3 **Ternary Electrolyte Solutions**

In a ternary system ($N = 3$), Eqs. (97 and 98) must be solved together with

$$G_2 = -\frac{\mathrm{d}S_2}{\mathrm{d}x} + f\mathsf{E}S_3 \tag{111}$$

$$S_3 = q_1 S_2 + q_3 S_0 \tag{112}$$

After some algebra, Eq. (111) can be transformed into the following equation for the electric field

$$\frac{G_1}{\mathsf{E}}\frac{\mathrm{d}\mathsf{E}}{\mathrm{d}x} = (G_2 - q_1 G_1)f\mathsf{E} - q_3(f\mathsf{E})^2 S_0(x) \tag{113}$$

which has to be integrated numerically from $x = \delta$ to x using the boundary condition $\mathsf{E}^{\mathrm{b}} = G_1/fS_2^{\mathrm{b}}$.

As an example, consider the case of a redox system such as $FeCl_2 + FeCl_3$ in the absence of supporting electrolyte in a potential range in which the only possible electrode process is the anodic oxidation of ferrous ion

$$Fe^{3+}(aq) - Fe^{2+}(aq) + e^- = 0 \tag{114}$$

Denoting the ions Fe^{2+}, Fe^{3+}, and Cl^- by subscripts 1, 2, and 3, respectively, the ion fluxes are $J_1 = -J_2 = -I/F$, and the parameters G_k take the values

$$G_0 = \left(\frac{1}{D_2} - \frac{1}{D_1}\right)\frac{I}{F} = 0.1904\frac{I}{FD_1} \tag{115}$$

$$G_1 = \left(\frac{z_2}{D_2} - \frac{z_1}{D_1}\right)\frac{I}{F} = 1.5712\frac{I}{FD_1} \tag{116}$$

$$G_2 = \left(\frac{z_2^2}{D_2} - \frac{z_1^2}{D_1}\right)\frac{I}{F} = 6.7136\frac{I}{FD_1} \tag{117}$$

where $D_1 = 0.719 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$ and $D_2 = 0.604 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$ [39]. Equation (113) can be rewritten in terms of the dimensionless electric field $e \equiv f\mathsf{E}\delta$ as

$$\frac{de}{d(x/\delta)} = e^2\left\{0.2729 + e\left[0.7271\left(1 - \frac{x}{\delta}\right) + 11.456\left(1 + \frac{4c_2^{\mathrm{b}}}{3c_1^{\mathrm{b}}}\right)\frac{I_{Ld,1}}{I}\right]\right\} \tag{118}$$

where $I_{Ld,1} = FD_1c_1^{\mathrm{b}}/\delta$ is the limiting diffusion current density of ferrous ion.

Equation (118) can be integrated by standard numerical methods, such as fourth-order Runge–Kutta method [61], starting from position $x = \delta$, in which the boundary condition $e^{\mathrm{b}} = G_1\delta/S_2^{\mathrm{b}}$ is applied as

$$e\left(\frac{x}{\delta} = 1\right) = \frac{I}{I_{Ld,1}}\frac{0.2619}{1 + 2c_2^{\mathrm{b}}/c_1^{\mathrm{b}}} \tag{119}$$

The potential drop $\Delta\phi$ (and its distribution, if needed) can then be calculated by numerical integration of the electric field using, for example, a fourth-order Newton–Cotes method [61]. This procedure yields the current–voltage curves shown in Fig. 12 in the case of a DBL depleted of ferrous ions, that is, for $I/I_{Ld,1} > 0$ and $\Delta\phi < 0$. These curves end when they meet the dashed line that corresponds to the limiting current density, that is, to vanishing surface concentration of ferrous ion. The limiting current density is a bit smaller than the limiting diffusion current density $I_{Ld,1}$ because the ferrous cation is driven towards the anode by its concentration gradient against an electric field that pushes it away from the electrode. The strength of this electric field is reduced when the solution conductivity increases, that is, when the bulk concentration ratio $c_2^{\mathrm{b}}/c_1^{\mathrm{b}}$ increases for a fixed value of c_1^{b}, and the limiting current density tends to $I_{Ld,1}$ when this occurs.

The ionic concentration distributions in the DBL are represented in Fig. 13.

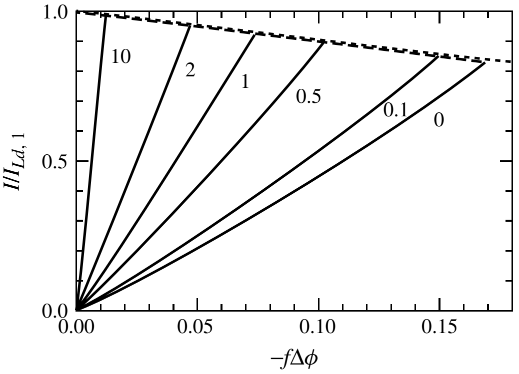

Fig. 12 Current–voltage curves of a ternary system $FeCl_2 + FeCl_3$ in the absence of supporting electrolyte for different values of the bulk concentration ratio c_2^b/c_1^b shown near the curves. The dashed line represents $I_L/I_{Ld,1}$ obtained from the (exact) numerical solution, and the dotted line represents $I_L/I_{Ld,1}$ obtained from the GCF assumption.

The ferrous ion concentration is obtained from Eq. (93) and using the relation $-J_1\delta/D_1c_1^b = I/I_{Ld,1}$. The chloride ion follows Boltzmann's equation $c_3 = c_3^b e^{f(\phi-\phi^b)}$, and the ferric ion concentration is obtained from the LEN assumption $c_2 = (c_3 - 2c_1)/3$.

Figures 12 and 13 evidence that the potential drop in the DBL is small and is distributed quite uniformly. It is then expected that the GCF assumption, $\mathsf{E} = -\Delta\phi/\delta$, provides reasonable estimates. Indeed, by setting $c_1^s = 0$ in Eq. (94), the limiting current density can be estimated as

$$\frac{I_L}{I_{Ld,1}} = \frac{2f\Delta\phi}{1 - e^{-2f\Delta\phi}} \tag{120}$$

which has been represented in Fig. 12 and agrees very well with the exact numerical solution.

2.1.4.4 Quaternary Electrolyte Solutions

Equations (97, 98 and 111), and

$$G_3 = -\frac{dS_3}{dx} + f\mathsf{E}S_4 \tag{121}$$

$$S_4 = q_1S_3 - q_2S_2 - q_4S_0 \tag{122}$$

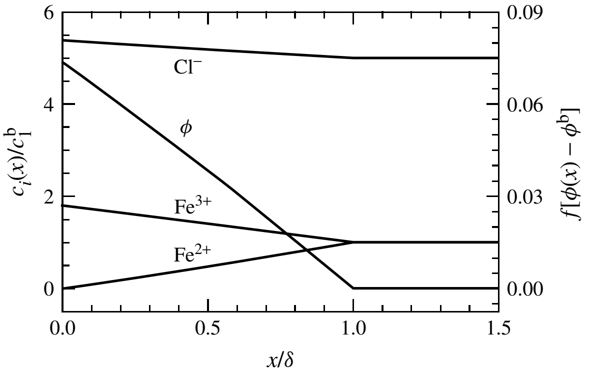

Fig. 13 Electric potential and concentration profiles of Fe^{2+} ion ($i = 1$), Fe^{3+} ion ($i = 2$), and Cl^- ion ($i = 3$) for a bulk concentration ratio $c_2^b/c_1^b = 1.0$ and the limiting current density $I = I_L = 0.9261 I_{Ld,1}$.

lead in this case to the following equation for the electric field

$$\frac{G_1}{\mathsf{E}}\frac{\mathrm{d}^2\mathsf{E}}{\mathrm{d}x^2} - \frac{3G_1}{\mathsf{E}^2}\left(\frac{\mathrm{d}\mathsf{E}}{\mathrm{d}x}\right)^2 + (G_2 - q_1G_1) \times f\frac{\mathrm{d}\mathsf{E}}{\mathrm{d}x} - (G_3 - q_1G_2 + q_2G_1 + q_4S_0 f\mathsf{E})(f\mathsf{E})^2 = 0 \tag{123}$$

which has to be integrated numerically from $x = \delta$ to x using the boundary conditions $\mathsf{E}^\mathrm{b} = G_1/fS_2^\mathrm{b}$ and

$$\left.\frac{\mathrm{d}\mathsf{E}}{\mathrm{d}x}\right|_{x=\delta} = \frac{G_1}{f(S_2^\mathrm{b})^2}\left(G_2 - G_1\frac{S_3^\mathrm{b}}{S_2^\mathrm{b}}\right) \tag{124}$$

Although the mathematical difficulty of this equation system is not very high, the GCF assumption, with the electric field estimated, for example, as $\mathsf{E} \approx \mathsf{E}^\mathrm{b} = G_1/fS_2^\mathrm{b}$, is a much simpler alternative to be considered when the ionic strength is roughly uniform over the DBL.

2.1.5
Ion Transport under Transient Conditions

Needless to say, transient transport conditions involve a higher level of mathematical complexity to the description of ion transport in electrochemical systems. The only case that can be worked out with ease is that of binary solutions. Ternary and multi-ionic solutions necessarily involve systems of partial differential equations coupled through the migration term that require advanced numerical methods. Given this situation, it is by no means surprising that most theoretical studies of transient problems neglect migration and use the diffusion equation (or Fick's second law) to describe the transport of ionic species. (The analysis of the role of supporting electrolytes in Sects. 2.1.2.2 and 2.1.2.4 was restricted to steady state conditions, but it is expected that a large excess of supporting electrolyte makes migration negligible under transient conditions too.)

This section describes diffusion and migration under transient conditions in some simple illustrative cases. For the sake of simplicity, an infinite DBL thickness $\delta \to \infty$ is considered, which is justified in the absence of stirring. Current and voltage steps in semi-infinite planar geometry (and in the absence of homogeneous reactions) are described. Both Laplace transforms and Boltzmann's change of variables are used. The influence of migration is discussed analytically (whenever possible) by using the latter technique, which is introduced in Appendix B. Other solution techniques of the diffusion equation [62–64], and the electrodiffusion equations are available in the literature [13, 65–72]. Further information on electrochemical techniques can be found in Ref. [73].

2.1.5.1 Fick's Second Law for a Strong Binary Electrolyte

The diffusion–conduction equation, Eq. (21), expresses the flux density of an ionic species from a strong binary electrolyte in terms of the electrolyte flux J_{12} and the current density I. Under transient conditions, both J_i and J_{12} are position-dependent, but I is not. Thus, taking into account Eq. (21) and the relation $c_i = \nu_i c_{12}$, the continuity equation, Eq. (11), leads to Fick's second law

$$\frac{\partial c_{12}}{\partial t} = D_{12}\frac{\partial^2 c_{12}}{\partial x^2} \tag{125}$$

The transient ionic electrodiffusion can then be described as electrolyte diffusion and solved by standard techniques [62–64].

2.1.5.2 Systems with One Active Species and Supporting Electrolyte

The transport of the active species in the presence of excess supporting electrolyte under transient conditions is described by the equation

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} \tag{126}$$

which is obtained from the continuity equation, Eq. (11), by neglecting the migrational contribution to the flux density J_1. Although Eq. (126) resembles Fick's second law, it should be observed that Fick's laws are valid for (neutral) electrolytes. Ion transport takes place by electrodiffusion and satisfies pseudo-Fick's laws only when migration is negligible.

For a simple electrode process, like cathodic deposition or anodic dissolution (without contribution of nucleation), the initial value is $c_1(x, t = 0) = c_1^{\mathrm{b}}$ and the boundary value at the bulk solution is $c_1^{\mathrm{b}}(t) = c_1^{\mathrm{b}}$. The boundary condition at the electrode surface can be either Eq. (24), in the form

$$\left.\frac{\partial c_1}{\partial x}\right|_{x=0} = -\frac{I(t)}{z_1 F D_1} \tag{127}$$

or the Nernst equation, Eq. (31), for the case of a single active species

$$E_{\mathrm{eq}}(t) = E^\circ + \frac{RT}{z_1 F} \ln \frac{c_1^{\mathrm{s}}(t)}{c^\circ} \tag{128}$$

When the system is perturbed by applying a known function, $I(t)$, Eq. (127) is used to evaluate the chronopotentiometric response of the system. Analogously, when the system is perturbed by applying a known function $E_{\mathrm{eq}}(t)$, Eq. (128) describes the chronoamperometric response of the system.

2.1.5.3 Voltage Step in the Presence of Supporting Electrolyte

The boundary condition, Eq. (128), for a voltage step perturbation reads

$$c_1^{\mathrm{s}}(t) = c_1^{\mathrm{b}} \exp[z_1 f \Delta E H(t)] \tag{129}$$

where $H(t)$ is the step function [$H(t) = 0$ if $t < 0$, $H(t) = 1$ if $t > 0$], and ΔE is the width of the voltage step.

Using Laplace transformation with respect to time, the general solution of Eq. (126) in the Laplace domain is [62]

$$\tilde{c}_1(x, s) = \frac{c_1^{\mathrm{b}}}{s} + A\mathrm{e}^{x(s/D_1)^{1/2}} + B\mathrm{e}^{-x(s/D_1)^{1/2}} \tag{130}$$

where $\tilde{c}_1(x, s)$ is the Laplace transformed concentration and s is the Laplace variable. Since the concentration must be bounded, the integration constant A vanishes. The boundary condition, Eq. (129), gives the value for B, resulting in

$$\tilde{c}_1(x, s) = \frac{c_1^{\mathrm{b}}}{s} \left[1 + (\mathrm{e}^{z_1 f \Delta E} - 1) \times \mathrm{e}^{-x(s/D_1)^{1/2}}\right] \tag{131}$$

By inverse Laplace transformation, the concentration profile is obtained as

$$c_1(x, t) = c_1^{\mathrm{b}}[1 + (\mathrm{e}^{z_1 f \Delta E} - 1)\mathrm{erfc}(\zeta)] \quad (t > 0) \tag{132}$$

where $\zeta \equiv x/(2D_1^{1/2} t^{1/2})$ is the Boltzmann variable (see Appendix B) and erfc stands for the complementary error function.

The electric current response is obtained from Eqs. (127 and 132) as

$$I(t) = -z_1 F D_1 \left.\frac{\partial c_1}{\partial x}\right|_{x=0} = z_1 F c_1^{\mathrm{b}} (\mathrm{e}^{z_1 f \Delta E} - 1) \left(\frac{D_1}{\pi t}\right)^{1/2} \tag{133}$$

If the potential step width is large enough, $-z_1 f \Delta E \gg 1$, the surface concentration of the electroactive species is negligible and Eq. (133) reduces to the Cottrell equation [73]

$$I(t) = -z_1 F c_1^{\mathrm{b}} \left(\frac{D_1}{\pi t} \right)^{1/2} \qquad (134)$$

2.1.5.4 **Current Step in the Presence of Supporting Electrolyte**

Consider that the function $I(t)$ in Eq. (127) is a current step $I(t) = I_0 H(t)$, where I_0 is the constant current applied from $t = 0$. Equation (130) reduces now to

$$\tilde{c}_1(x, s) = \frac{c_1^{\mathrm{b}}}{s} + \frac{I_0}{z_1 F D_1^{1/2}} s^{-3/2} \mathrm{e}^{-x(s/D_1)^{1/2}} \qquad (135)$$

whose inverse transform provides the concentration distribution

$$c_1(x, t) = c_1^{\mathrm{b}} + \frac{2 I_0 t^{1/2}}{z_1 F D_1^{1/2}} \times [\pi^{-1/2} \mathrm{e}^{-\zeta^2} - \zeta \,\mathrm{erfc}(\zeta)] \qquad (136)$$

The potential response is given by Eq. (128) with the surface concentration determined from Eq. (136) at $\zeta = 0$, that is,

$$E_{\mathrm{eq}}(t > 0) = E^{\circ} + \frac{RT}{z_1 F} \times \ln \left[\frac{c_1^{\mathrm{b}}}{c^{\circ}} + \frac{2 I_0}{z_1 F c^{\circ}} \left(\frac{t}{\pi D_1} \right)^{1/2} \right] \qquad (137)$$

In cathodic processes ($I_0 < 0$), the surface concentration becomes zero at the transition time

$$\tau = \pi D_1 \left(\frac{z_1 F c_1^{\mathrm{b}}}{2 I_0} \right)^2 \qquad (138)$$

This relationship is called the Sand equation [73].

2.1.5.5 **Voltage Step in the Absence of Supporting Electrolyte**

Although it is important for practical purposes to attempt the treatment of systems which are not stripped of so many features that they no longer bear resemblance to reality, the simultaneous treatment of a reasonable fraction of these features makes the mathematical problem so complex that there is a danger of obscuring the real problem [74]. It is then suggested to simplify the present analysis of a large voltage step in a ternary solution (where the common ion is inactive) by making equal all diffusion coefficients, $D_i = D$, for $i = 1,2,3$, and hence eliminating the diffusion potential. This allows for a better understanding of the effect of migration on the transient response of the system.

The treatment in Sect 2.1.4.3 is followed and magnitudes S_k and G_k are used instead of ionic concentrations and flux densities, respectively. However, the relations between c_1, c_2, c_3, and S_0, S_2, are still needed because the Nernst equation, Eq. (31), involves ionic species.

The basic equations describing this problem are the continuity equations, Eq. (11), which owing to the simplifying assumption $D_i = D$ reads as

$$\frac{\partial S_k}{\partial t} = -D \frac{\partial G_k}{\partial x} \qquad (139)$$

and Eq. (105) for $k = 0$, 1, and 2,

$$G_0 = -\frac{\partial S_0(x, t)}{\partial x} \qquad (140)$$

$$G_1 = -f \frac{\partial \phi(x, t)}{\partial x} S_2(x, t) \qquad (141)$$

$$G_2 = -\frac{\partial S_2(x, t)}{\partial x} + q_1 G_1 + q_3 G_1 \frac{S_0(x, t)}{S_2(x, t)} \qquad (142)$$

where the closure relation, Eq. (112), and Eq. (141) have been used to obtain Eq. (142). Equation (141) is Ohm's law, Eq. (13), for this system.

At the electrode surface, Eq. (24) requires that

$$G_0^{\mathrm{s}}(t) = \frac{I(t)}{nFD}\sum_i \nu_i^{\mathrm{r}} \tag{143}$$

$$G_2^{\mathrm{s}}(t) = \frac{I(t)}{nFD}\sum_i z_i^2 \nu_i^{\mathrm{r}} = \frac{I(t)}{FD}(z_1 + z_2) \tag{144}$$

which are used as boundary conditions in chronopotentiometric techniques or to evaluate the system response in chronoamperometric techniques. In the second equality of Eq. (144), the common ion is considered to be inactive, $\nu_3^{\mathrm{r}} = 0$. The parameter $G_1 = I(t)/FD$ is only a function of t.

Combining Eq. (139) for $k = 0$ and Eq. (140), the partial differential equation for G_0 is

$$\frac{\partial S_0}{\partial t} = -D\frac{\partial G_0}{\partial x} = D\frac{\partial^2 S_0}{\partial x^2} \tag{145}$$

which is subject to the initial and boundary conditions $S_0(x, t = 0) = S_0^{\mathrm{b}}$ and $S_0(x \to \infty, t) = S_0^{\mathrm{b}}$, in addition to Eq. (143). The DBL thickness is considered to be infinite due to the absence of stirring. The solution of Eq. (145) can be obtained by following the method explained in Sect. 2.1.5.3 as

$$S_0(x, t) = S_0(\zeta) = S_0^{\mathrm{b}} + (S_0^{\mathrm{s}} - S_0^{\mathrm{b}})\,\mathrm{erfc}(\zeta) \tag{146}$$

Combining Eq. (139) for $k = 2$ and Eq. (142), the partial differential equation for S_2 is

$$\frac{\partial S_2}{\partial t} = D\frac{\partial^2 S_2(x,t)}{\partial x^2} - q_3 D G_1 \frac{\partial}{\partial x}\left(\frac{S_0(x,t)}{S_2(x,t)}\right) \tag{147}$$

The difficulty introduced by the second term in the right-hand side of Eq. (147) makes it very convenient to introduce a further simplifying assumption.

When the number of electroactive species is conserved by the electrode reaction, $\sum_i \nu_i^{\mathrm{r}} = 0$, it is satisfied that $G_0^{\mathrm{s}} = 0$, and the only solution to Eq. (145) is the trivial result $S_0 = S_0^{\mathrm{b}}$. This is the principle of unchanging total concentration established by Oldham and Feldberg [17]. Equation (147) then reduces to

$$\frac{\partial S_2}{\partial t} = D\frac{\partial^2 S_2}{\partial x^2} + \frac{q_3 I S_0^{\mathrm{b}}}{F}\frac{1}{S_2^2}\frac{\partial S_2}{\partial x} \tag{148}$$

The initial and boundary conditions for this equation are Eq. (31), $S_2(x, t = 0) = S_2^{\mathrm{b}}$ and $S_2(x \to \infty) = S_2^{\mathrm{b}}$.

In the case of a large voltage step, $f|\Delta E| \gg 1$, Eq. (31) is approximated by the condition of zero surface concentration of the reactant, $c_1^{\mathrm{s}}(t) = 0$ (or $S_2^{\mathrm{s}} = -z_2 z_3 S_0^{\mathrm{b}}$), and both boundary conditions for S_2 turn out to be independent of time. This implies that S_2 is a function of x and t through variable $\zeta \equiv x/(2D_1^{1/2}t^{1/2})$. Moreover, since the electric current density is obtained from Eqs. (142) and (144) as

$$\left.\frac{\partial S_2}{\partial x}\right|_{x=0} = \frac{I(t)}{FD}(z_3 - z_1) \tag{149}$$

it is concluded that $I(t)$ is proportional to $t^{-1/2}$.

Equation (148) can then be transformed into the ordinary differential equation for $S_2(\zeta)$ (see Appendix B)

$$0 = \frac{\mathrm{d}^2 S_2}{\mathrm{d}\zeta^2} + 2\zeta\frac{\mathrm{d}S_2}{\mathrm{d}\zeta} + \gamma\frac{(S_2^{\mathrm{b}})^2}{S_2^2}\frac{\mathrm{d}S_2}{\mathrm{d}\zeta} \tag{150}$$

Parameter γ in Eq. (150) is related to the current density by

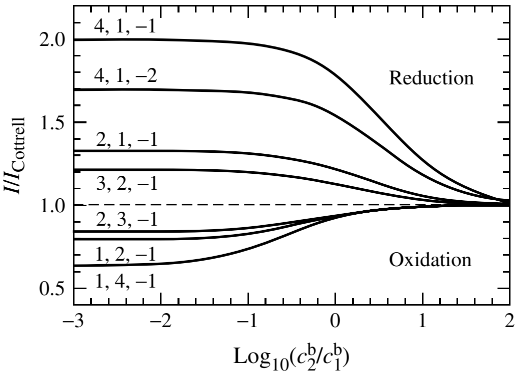

Fig. 14 Current density in a voltage step of large width relative to that in absence of migration, given by Cottrell Eq. (152), as a function of the bulk concentration ratio product/reactant. The charge numbers z_1, z_2, z_3 are shown close to the curves.

$$I = \gamma \frac{F(S_2^{\mathrm{b}})^2}{2q_3 S_0^{\mathrm{b}}} \left(\frac{D}{t}\right)^{1/2}$$

$$= \gamma \frac{(z_3 - z_1)(S_2^{\mathrm{b}})^2 \pi^{1/2}}{2q_3 S_0^{\mathrm{b}}(S_2^{\mathrm{b}} + z_2 z_3 S_0^{\mathrm{b}})} I_{\mathrm{Cottrell}} \quad (151)$$

where

$$I_{\mathrm{Cottrell}} = (z_2 - z_1) F c_1^{\mathrm{b}} \left(\frac{D}{\pi t}\right)^{1/2} \quad (152)$$

is the classical result obtained by Cottrell in the absence of migration. The value of γ must be obtained from the numerical solution of Eq. (150) by the shooting method starting from $S_2(0) = S_2^{\mathrm{s}} = -z_2 z_3 S_0^{\mathrm{b}}$ and

$$\left.\frac{\mathrm{d}S_2}{\mathrm{d}\zeta}\right|_{\zeta=0} = \gamma \frac{(z_1 - z_3)(S_2^{\mathrm{b}})^2}{q_3 S_0^{\mathrm{b}}} \quad (153)$$

and modifying it by iteration until $S_2(\infty) = S_2^{\mathrm{b}}$ is satisfied.

Myland and Oldham [18] have compiled the results for the case in which the product of the electrode reaction is absent in bulk solution, $c_2^{\mathrm{b}} = 0$. Figure 14 shows the current density as a function of the bulk product/reactant concentration ratio for several values of the charge numbers in the case of cationic redox couples. The current is then larger than in the absence of migration in the case of reductions and smaller in the case of oxidations. It is observed that, for a given stoichiometric number of the electron $n = z_2 - z_1$ in the electrode reaction, increasing the charge numbers of either the inactive anion or the active cations reduces the effect of migration. Moreover, the effect of migration is larger when $|n|$ increases.

The results of these numerical simulations can be understood by the following intuitive arguments. Consider, for example, the oxidation of a cationic species [$I > 0,\ n > 0,\ z_1 > 0,\ z_2 = (n + z_1) > 0,\ z_3 < 0$]. According to Ohm's law, the electric potential gradient in solution pushes the cations away from the anode, so that their gradients are smaller (in absolute value) than in absence of migration. Since the voltage step makes the surface concentration of the reduced species zero, $c_1^{\mathrm{s}} = 0$, the flux density of this species at the electrode surface is only due to diffusion,

$$\left.\frac{\mathrm{d}c_1}{\mathrm{d}x}\right|_{x=0} = -\frac{I}{(z_1 - z_2)FD} \quad (154)$$

and a smaller concentration gradient implies then smaller current density. Contrarily, in the case of reduction of cations, migration pushes the cations towards the cathode, so that the concentration gradients are steeper. Since Eq. (154) still applies, this implies larger current densities than in absence of migration.

Consider, finally, the oxidation of an anion [$I > 0, n > 0, z_1 < 0, z_2 = (n + z_1) < 0, z_3 > 0$]. The electric potential gradient in solution pushes the anions towards the anode, so that the concentration gradients are steeper and the current density is larger than in the absence of migration. The opposite effect is observed in the reductions of anions.

2.1.6
Deviations from Local Electroneutrality

This last section is devoted to the space charge density and its variation with time and position. The dielectric permittivity of the solution is assumed to be constant, which is a good approximation for moderate concentrations and electric fields [75–77]. It is further assumed that the relaxation of the dielectric (i.e. the reorientation of water molecules) is much faster than the redistribution of the space charge density [78].

2.1.6.1 Space Charge Density

The Poisson equation, Eq. (8), identifies the space charge density in an electrolyte solution, $\rho_e = F \sum_i z_i c_i$, as the source of the electric field. Thus, whenever the electric field changes with position, there is a space charge distribution over the system.

In general, ρ_e is a function of both position and time. Its time derivative is

$$\begin{aligned}\frac{\partial \rho_e}{\partial t} &= -\varepsilon \frac{\partial^3 \phi}{\partial t \partial x^2} \\ &= \frac{\partial}{\partial x}\left[\frac{\partial}{\partial t}\left(-\varepsilon \frac{\partial \phi}{\partial x}\right)\right] = \frac{\partial I_d}{\partial x} \qquad (155)\end{aligned}$$

where I_d is the displacement current, that is, the time derivative of the electric displacement $\mathsf{D} = \varepsilon \mathsf{E}$. Alternatively, $\partial \rho_e / \partial t$ can be evaluated from the continuity equation, Eq. (11) with $r_i = 0$, as

$$\begin{aligned}\frac{\partial \rho_e}{\partial t} &= F \sum_i z_i \frac{\partial c_i}{\partial t} \\ &= -F \sum_i z_i \frac{\partial J_i}{\partial x} = -\frac{\partial I}{\partial x} \qquad (156)\end{aligned}$$

where I is the conduction electric current density. Equation (156) represents the conservation of electric charge and its combination with Eq. (155) leads to

$$\frac{\partial I_T}{\partial x} = \frac{\partial I}{\partial x} + \frac{\partial I_d}{\partial x} = 0 \qquad (157)$$

which states that the total electric current density I_T that flows through an electrochemical cell is independent of position, and is made up of two contributions, the conduction and the displacement current densities [66–69, 79]

$$I_T = I + I_d = F \sum_i z_i J_i - \varepsilon \frac{\partial^2 \phi}{\partial t \partial x} \qquad (158)$$

The current density I_T is equal to that due to the electrons flowing through the external circuit connected to the electrodes.

In the absence of concentration gradients, no space charge density can exist in the solution under steady state conditions. Moreover, if by any means some electrical charge density is generated at any position within the system, the time required for this charge to disappear (in fact, to migrate to the system boundaries) is of the order of nanoseconds. This time is the so-called electrical relaxation time of the system, τ_e, and can be obtained from Eqs. (8, 13, and 156) as

$$\begin{aligned}\frac{\partial \rho_e}{\partial t} &= -\frac{\partial I}{\partial x} = \kappa \frac{\partial^2 \phi}{\partial x^2} \\ &= -\kappa \frac{\rho_e}{\varepsilon} \equiv -\frac{\rho_e}{\tau_e} \qquad (159)\end{aligned}$$

so that $\tau_e \equiv \varepsilon/\kappa \sim 10^{-9}$ s for a 100 mM aqueous solution.

Concentration gradients, however, are present in most situations of electrochemical interest, and the time evolution of ρ_e is then determined by the time variation of the conditions imposed on the system, which always involve times much larger than τ_e.

Usually, space charge regions exist close to the system boundaries, such as the EDL at a planar electrode. In the presence of concentration gradients, Eq. (159) becomes

$$\frac{\partial \rho_e}{\partial t} = \frac{\partial}{\partial x}\left(\kappa \frac{\partial \phi_{\text{ohm}}}{\partial x}\right) = \frac{\partial}{\partial x}\left(\kappa \frac{\partial \phi}{\partial x}\right) - \frac{\partial}{\partial x}\left(\kappa \frac{\partial \phi_{\text{dif}}}{\partial x}\right) \quad (160)$$

which is much smaller, in magnitude, than ρ_e/τ_e. Under equilibrium conditions, $I = 0$, the two terms on the right-hand side cancel out. In the presence of conduction current, these terms are very similar to each other and much larger in magnitude than $\partial\rho_e/\partial t$. An order of magnitude analysis of these two terms allows us to estimate the characteristic length for the space charge distribution, L_{D}. Because of the large electric fields existing in space charge regions, the ions have a strong tendency to migrate. If the ions were indeed migrating, the space charge distribution would disappear, so that the necessary condition for an equilibrium space charge distribution is that this tendency to migrate has to be compensated by a strong tendency to diffuse in the opposite direction [68]. The diffusional flux associated to concentration changes is of the order of Dc/L_{D}, where c is a typical ion concentration. The magnitude of the charge density can be estimated as $\rho_e \approx Fc$, and the Poisson equation, Eq. (8) tells that the field associated to this charge density over a region of thickness L_{D} is of the order of $\rho_e L_{\text{D}}/\varepsilon$. The migrational flux density associated to this field is of the order of $FDc\rho_e L_{\text{D}}/\varepsilon RT$. The condition for the existence of an equilibrium space charge density is $Dc/L_{\text{D}} \approx FDc\rho_e L_{\text{D}}/\varepsilon RT$, which yields the expression of the Debye length

$$L_{\text{D}} \approx \left(\frac{\varepsilon RT}{F\rho_e}\right)^{1/2} \approx \left(\frac{\varepsilon RT}{F^2 c}\right)^{1/2} \quad (161)$$

Space charge distributions are then expected to exist over regions of thickness L_{D}, which is of the order of 10^{-7} cm for a 100 mM aqueous solution. A practical consequence of this comment is that the behavior of electrochemical systems comprising microgeometries is affected by space charge layers [80–82].

Note, finally, that ionic motions associated to space charge redistribution involve distances of the order of L_{D}, which suggests that τ_e can be interpreted as the time $\tau_e \approx L_{\text{D}}^2/D$ required for the ions to diffuse over L_{D} [79, 83–85].

2.1.6.2 Deviations from Local Electroneutrality

Planck suggested that the electric potential calculated from the LEN assumption, $\phi^{(0)}$, could be used to check the validity of this assumption [27, 31]. When this approximate electric potential is introduced in the Poisson equation, the space charge density obtained

$$\rho_r \equiv \varepsilon \frac{\partial \mathsf{E}^{(0)}}{\partial x} = -\varepsilon \frac{\partial^2 \phi^{(0)}}{\partial x^2} \quad (162)$$

provides an idea of the deviations from LEN, which would be required to create the distribution $\phi^{(0)}(x, t)$. To make clear the difference between the true ρ_e in the Poisson equation, Eq. (8), and ρ_r defined by Eq. (162), the latter is often named residual space charge density [13, 86].

Consider, for instance, the steady state electric field in a binary solution under current flow conditions with species 2 being inactive. From Sect. 2.1.4.2, $\mathsf{E}^{(0)} = S_2/fG_1 = -z_2S_0/fG_0$ and the residual space charge density required to establish this approximate electric field is

$$\rho_r = -\frac{\varepsilon RT}{z_2F}\left(\frac{I}{I_L\delta}\right)^2\left(\frac{c_2^{\mathrm{b}}}{c_2(x)}\right)^2 = -\frac{\varepsilon RT}{z_2F\delta^2}\left(\frac{I_L}{I}+\frac{x}{\delta}-1\right)^{-2} \quad (163)$$

where Eqs. (97 and 101) have been used; note also that $G_1 = z_1G_0 = I/FD_1$. This shows that significant deviations from the LEN only occur at the limiting current and close to the electrode surface $x = 0$, in which the ionic concentrations tend to zero and ρ_r diverges [34, 42, 87].

The actual space charge density in this binary solution can be obtained from the (exact) electric field E by using the same formalism and the Poisson equation

$$\frac{\mathrm{d}\mathsf{E}}{\mathrm{d}x} = \frac{\rho_e}{\varepsilon} = \frac{FS_1}{\varepsilon} \quad (164)$$

First, integrating Eq. (105) for $k = 0$

$$-G_0 = \frac{\mathrm{d}S_0}{\mathrm{d}x} - f\mathsf{E}S_1 \quad (165)$$

from x to δ, and using Eq. (164), Eq. (97) is modified to

$$S_0(x) = S_0^{\mathrm{b}} + (\delta - x)G_0 + \frac{\varepsilon\mathsf{E}^2}{2RT} \quad (166)$$

where the electric field in bulk solution has been neglected. Then, substituting Eqs. (164 and 166) into Eq. (105) for $k = 1$

$$-G_1 = \frac{\mathrm{d}S_1}{\mathrm{d}x} - f\mathsf{E}S_2 = \frac{\mathrm{d}S_1}{\mathrm{d}x} + z_1z_2f\mathsf{E}S_0 \quad (167)$$

and introducing the limiting current density $I_L \equiv -S_0^{\mathrm{b}}I/(\delta G_0)$ defined in Eq. (101), the equation for E becomes

$$\frac{L_{\mathrm{D}}^2}{\mathsf{E}}\frac{\mathrm{d}^2\mathsf{E}}{\mathrm{d}x^2} = z_1\frac{I}{I_L}\left\{\frac{1}{f\mathsf{E}\delta} - z_2\left[\frac{I_L}{I}+\frac{x}{\delta}-1 + (f\mathsf{E}L_{\mathrm{D}})^2\frac{I_L}{2I}\right]\right\} \quad (168)$$

where $L_{\mathrm{D}} \equiv (\varepsilon RT/F^2S_0^{\mathrm{b}})^{1/2}$ is the Debye length.

Analytical studies of Eq. (168) have used different changes of variables to write the electric field in terms of either Painlevé transcendents [68] or Jacobian elliptic functions [88]. Alternatively, asymptotic expansions have also been used [68, 87, 89, 90]. The approximate solution methods have neglected different terms of Eq. (168). Thus, while Urtenov and Nikonenko [55, 91, 92] have considered that the space charge density is quasi-uniform, $\mathrm{d}S_1/\mathrm{d}x \approx 0$, Bass [93] assumed that $\varepsilon\mathsf{E}^2 \ll RTS_0^{\mathrm{b}}$ and $I/I_L \ll \delta/L_D$ to express the electric field as the sum of the electroneutral electric field, which can be derived from Eq. (99), and a modified Gouy distribution corrected for the presence of current. In any case, both analytical and numerical [94, 95] solutions have shown that in the range of underlimiting currents, the deviations from LEN are confined to the EDL and that the latter is not significantly perturbed by the electric current.

In conclusion, ρ_r in Eq. (163) is a physically meaningful magnitude that is very similar to the actual ρ_e when LEN is a good approximation. Contrarily, when deviations from LEN occur, the actual electric potential surely differs from that obtained by using the LEN, and then the actual ρ_e is likely to show no resemblance to ρ_r.

Although the equations presented in this chapter cannot account for this fact, overlimiting currents can be observed in practice [41]. The study of these currents requires not only to abandon the LEN assumption but also to take into account the electroconvective motions that originate due to the electrical force $\rho_e \mathbf{E}$ acting on the electrolyte solution in space charge regions [68, 90, 91, 95–97].

2.1.6.3 **Validity of the LEN Assumption**

MacGillivray [98] was the first to provide a mathematical justification for the LEN assumption on the basis of the perturbation theory. The idea behind such a justification is that an order of magnitude analysis of the Poisson equation, Eq. (8), shows that

$$\frac{\rho_e}{Fc} = -\frac{\varepsilon}{Fc}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\right) \approx \frac{\varepsilon}{Fc}\frac{RT/F}{L^2} = \left(\frac{L_\mathrm{D}}{L}\right)^2 \equiv \lambda \ll 1 \qquad (169)$$

where L is a typical length for variation of the electric potential, which is considered to be of the order of the size of the electrochemical cell and hence much larger than the Debye length L_D. This suggests that the solution of the Nernst–Planck and Poisson equations can be found by writing the concentrations and the electric potential as an asymptotic expansion in terms of the "small parameter" $\lambda \equiv (L_\mathrm{D}/L)^2$,

$$c_i = c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots \qquad (170)$$

$$\phi = \phi^{(0)} + \lambda\phi^{(1)} + \lambda^2\phi^{(2)} + \cdots \qquad (171)$$

Thus, the zeroth-order approximation (in λ) of the Poisson equation is $\rho_e^{(0)} = 0$. In other words, the LEN assumption is a consequence of the Poisson equation when $\lambda \ll 1$. Moreover, the first-order term of the Poisson equation is

$$\lambda\rho_e^{(1)} = -\varepsilon\frac{\mathrm{d}^2\phi^{(0)}}{\mathrm{d}x^2} \qquad (172)$$

Since $\phi^{(0)}$ is the electric potential calculated from the transport equations at zero order in λ (that is, making use of the LEN assumption), the residual space charge density defined in Eq. (162) is identified as $\rho_e^{(1)}$. The use of higher-order terms in the Expansions (170 and 171) is only needed when $\rho_e^{(1)}$ is of the order of Fc [13, 27, 31, 67]. A different validity test for the LEN assumption, namely $\lambda\rho_e^{(2)} \ll \rho_e^{(1)}$, has been recently proposed by Feldberg (with a different notation) [99].

Note that it is possible to use either the full Poisson equation or the terms of its asymptotic expansion, such as the LEN assumption or Eq. (172), but $\rho_e^{(0)}$ can never be interpreted as the full ρ_e in the Poisson equation. This would lead to the wrong conclusion that the LEN assumption implies a constant electric field.

Appendix A

The total potential drop across the DBL in Eq. (74) can be obtained as the sum of the diffusion and ohmic potential drops. The former is given by Eq. (19) as

$$\Delta\phi_\mathrm{dif} = -\frac{RT}{F}\left(\frac{t_1}{z_1} + \frac{t_2}{z_2}\right)\Delta\ln c_{12} \qquad (173)$$

To integrate the ohmic potential gradient, it is convenient to introduce first the molar conductivity of the electrolyte as

$$\Lambda_{12} \equiv \frac{\kappa}{c_{12}} = -z_1 z_2 \frac{F^2}{RT}(\nu_2 D_1 + \nu_1 D_2) \qquad (174)$$

where the last equality is known as the Nernst–Eintein relation [3]. Equation (17) then implies

$$\mathrm{d}\phi_\mathrm{ohm} = -\frac{I}{\kappa}\mathrm{d}x = -\frac{I}{\Lambda_{12}}\frac{\mathrm{d}x}{c_{12}} \qquad (175)$$

Eliminating the position variable from Eqs. (65) and (67) as

$$-\mathrm{d}x = \frac{z_1\nu_1 F}{t_2 I}(D_{12,u}\mathrm{d}c_{12,u} + D_{12}\mathrm{d}c_{12}) \tag{176}$$

and using Eq. (63) to deduce that $\mathrm{d}\ln c_{12,u} = \nu_{12}\mathrm{d}\ln c_{12}$, Eq. (175) is transformed to

$$\begin{aligned}\mathrm{d}\phi_{\mathrm{ohm}} &= \frac{z_1\nu_1 F}{t_2\Lambda_{12}}\frac{1}{c_{12}}(D_{12,u}\mathrm{d}c_{12,u} \\ &+ D_{12}\mathrm{d}c_{12}) = \frac{RT}{F}\left(\frac{\nu_{12}t_1}{z_1\nu_1}\frac{\mathrm{d}c_{12}}{c_{12}}\right. \\ &\left. - \frac{D_{12,u}}{z_2 D_2}\frac{\mathrm{d}c_{12,u}}{c_{12}}\right) = \frac{RT}{F}\left[\frac{\nu_{12}t_1}{z_1\nu_1}\mathrm{d}\ln c_{12}\right. \\ &\left. - \frac{\nu_{12}D_{12,u}}{z_2(\nu_{12}-1)D_2}\mathrm{d}\left(\frac{c_{12,u}}{c_{12}}\right)\right]\end{aligned} \tag{177}$$

Straightforward integration over the DBL and addition of $\Delta\phi_{\mathrm{dif}}$ yields Eq. (74).

Appendix B

The perturbation of the concentration field introduced by the electrode propagates at a finite rate determined by the diffusion coefficients and only affects a region close to the electrode whose thickness is of the order of the diffusion length $2D_1^{1/2}t^{1/2}$. Boltzmann showed that the diffusion equation, Eq. (126), can be reduced to an ordinary differential equation under certain conditions if expressed in terms of the variable $\zeta \equiv x/(2D_1^{1/2}t^{1/2})$ [62, 100].

To obtain the diffusion equation in terms of the variables (ζ, t), the elementary concentration variation is first expressed as

$$\mathrm{d}c_1 = \left(\frac{\partial c_1}{\partial \zeta}\right)_t \mathrm{d}\zeta + \left(\frac{\partial c_1}{\partial t}\right)_\zeta \mathrm{d}t \tag{178}$$

The partial derivatives of c_1 with respect to x and t (at constant x) are then given by

$$\begin{aligned}\left(\frac{\partial^2 c_1}{\partial x^2}\right)_t &= \left(\frac{\partial \zeta}{\partial x}\right)_t \left(\frac{\partial}{\partial \zeta}\left[\left(\frac{\partial \zeta}{\partial x}\right)_t \left(\frac{\partial c_1}{\partial \zeta}\right)_t\right]\right)_t \\ &= \frac{1}{4D_1 t}\left(\frac{\partial^2 c_1}{\partial \zeta^2}\right)_t\end{aligned} \tag{179}$$

$$\begin{aligned}\left(\frac{\partial c_1}{\partial t}\right)_x &= \left(\frac{\partial c_1}{\partial \zeta}\right)_t \left(\frac{\partial \zeta}{\partial t}\right)_x + \left(\frac{\partial c_1}{\partial t}\right)_\zeta \\ &= -\frac{\zeta}{2t}\left(\frac{\partial c_1}{\partial \zeta}\right)_t + \left(\frac{\partial c_1}{\partial t}\right)_\zeta\end{aligned} \tag{180}$$

and the diffusion equation becomes

$$\frac{\partial^2 c_1}{\partial \zeta^2} + 2\zeta\frac{\partial c_1}{\partial \zeta} = 4t\frac{\partial c_1}{\partial t} \tag{181}$$

When the boundary conditions imposed by the experiment allow for the separation of variables ζ and t (linear sweep voltammetry, for instance, does not), a solution of the form $c_1(\zeta, t) = c_1^{\mathrm{b}} + \mathrm{Z}(\zeta)T(t)$ transforms Eq. (181) into

$$\frac{1}{\mathrm{Z}}\left(\frac{\mathrm{d}^2\mathrm{Z}}{\mathrm{d}\zeta^2} + 2\zeta\frac{\mathrm{d}\mathrm{Z}}{\mathrm{d}\zeta}\right) = \frac{4t}{T}\frac{\mathrm{d}T}{\mathrm{d}t} = \lambda \tag{182}$$

where λ is a constant.

In the chronoamperometric case, the boundary condition, Eq. (129), does not introduce any dependence on t, and $\lambda = 0$ in Eq. (182). Then, the solution of this equation is

$$\mathrm{Z}(\zeta) = c_1(\zeta, t) - c_1^{\mathrm{b}} = A\mathrm{erf}c(\zeta) + B \tag{183}$$

where erf$c(\zeta)$ is the complementary error function. The boundary condition $c_1(x \to \infty, t) = c_1^{\mathrm{b}}$ imposes $B = 0$, and Eq. (132) is obtained.

In the chronopotentiometric case, the boundary condition, Eq. (127), becomes

$$\left.\frac{\partial c_1}{\partial \zeta}\right|_{\zeta=0} = T(t)\left.\frac{\mathrm{d}\mathrm{Z}}{\mathrm{d}\zeta}\right|_{\zeta=0} = -\frac{2I_0}{z_1 F D_1^{1/2}}t^{1/2} \tag{184}$$

which makes $\lambda = 2$ in Eq. (182). The solution of the ordinary differential equation for the function $\mathrm{Z}(\zeta)$ are the first integrals of the complementary error function [61]

$$Z(\zeta) = A[\pi^{-1/2}\mathrm{e}^{-\zeta^2} - \zeta\mathrm{erf}c(\zeta)] \tag{185}$$

where the boundary condition $c_1(x \to \infty, t) = c_1^{\mathrm{b}}$ has been taken into account.

Finally, the use of Eq. (184) to determine A yields Eq. (136).

List of important symbols

Latin symbols

C	class concentration (mol m^{-3}), Eq. (43)
c_i	molar concentration (mol m^{-3})
D	diffusion coefficient (m^2 s^{-1})
E_{eq}	equilibrium electrode potential (V), Eq. (31)
$\vec{\mathsf{E}}$,E	electric field (V m^{-1})
e	$\equiv f\,\mathsf{E}\delta$ dimensionless electric field, Eq. (118)
F	Faraday constant (C mol^{-1})
f	$\equiv F/RT$ (V^{-1})
G_k	$\equiv \sum_i z_i^k J_i/D_i$ (mol m^{-4}), Eq. (96)
I	electric current density (A m^{-2}), Eqs. (12, 158)
J_i	ionic flux density (mol m^{-2} s^{-1}), Eq. (5)
K	equilibrium constant [(mol m^{-3})$^{\sum \nu_i}$], Eq. (63)
L_{D}	Debye length (m), Eq. (161)
N	number of ionic species, Eq. (95)
n	$= \sum_i z_i \nu_i^{\mathrm{r}}$ stoichiometric number of the electron, Eq. (23)
n_i	number of moles of species i (mol)
q_k	auxiliary variable, Eq. (110)
R	gas constant (J mol^{-1} K^{-1})
r	chemical reaction rate (mol m^{-3} s^{-1}), Eqs. (11, 84)
S_k	$\equiv \sum_i z_i^k c_i$ (mol m^{-3}), Eq. (95)
s	Laplace variable (s^{-1}), Eq. (130)
T	temperature (K)
T_i	integral transport number, Eq. (25)
t	time (s)
t_i	migrational transport number, Eq. (15)
u_i	ionic mobility (m^2 V^{-1} s^{-1}), Eq. (4)
$\vec{\mathrm{v}}_i$	ionic velocity (m s^{-1}), Eq. (4)
x	position (m)
z_i	charge number, defined with sign

Greek symbols

α	degree of dissociation, Eq. (63)
δ	DBL thickness (m)
Δ	difference defined as bulk minus surface value
ε	dielectric permittivity (C V^{-1} m^{-1}), Eq. (8)
ϕ	electric potential (V)
Γ	$\equiv -G_1/z_1 z_2 G_0$ auxiliary variable, Eq. (100)
η_c	concentration overpotential (V), Eq. (32)
κ	conductivity (Ω^{-1} m^{-1}), Eq. (14)
κ_{eff}	$\equiv -I/(\mathrm{d}\phi/\mathrm{d}x)$ effective conductivity (Ω^{-1} m^{-1}), Eq. (42)
Λ_{12}	molar conductivity (m^2 Ω^{-1} mol^{-1}), Eq. (174)
$\tilde{\mu}_i$	electrochemical potential (J mol^{-1})
ν_{12}	$\equiv \nu_1 + \nu_2$, Eq. (63)
ν_i	stoichiometric number, Eqs. (62, 83)
ν_i^{r}	stoichiometric number in electrode reaction, Eq. (23)
ρ	charge density (C m^{-3}), Eq. (8)
τ_e	electrical relaxation time (s), Eq. (159)
ξ	reaction coordinate (mol), Eq. (24)
ζ	$\equiv x/(2D^{1/2}t^{1/2})$ Boltzmann variable, Eq. (132)

Subscripts and superscripts

d	displacement, Eq. (155)
dif	diffusion, Eqs. (19, 61)
e	electrical, Eq. (8)
i	ionic species
ij	dissociated electrolyte, Eq. (63)
ij, T	total electrolyte, Eq. (63)
ij, u	undissociated electrolyte, Eq. (63)
j	constituent, Eq. (85)
k	power of charge number, Eq. (95)
L	limiting, Eq. (47)

Ld, i	limiting diffusion (current density), Eq. (78)
mig	migration, Eq. (60)
ohm	ohmic, Eq. (18)
T	total, Eq. (158)
(i)	perturbation order, Eq. (170)
b	bulk solution ($x = \delta$)
○	standard state, Eq. (31)
r	electrode reaction, Eq. (23)
s	electrode surface ($x = 0$)

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