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Interrelation of current and concentration at electrodes*

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A review is presented of the laws governing the relation to current density of the changes in concentration of electroactive species at the surface of an electrode. Several diverse examples are reported. Ways in which these relationships may be used to probe fluid motion are explored.

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1. Introduction

Electrochemistry can serve as a tool in the study of fluid motion. The principle involved is to alter the concentration of a particular solute at the surface of an electrode and subsequently detect the altered concentration at the same, or another, electrode. Distinctly different results will be obtained accordingly as the fluid is quiescent or moving. In the latter case, the technique can provide information about the direction and speed of motion.

The term "monitor" will be used to describe the solute whose concentration is altered electrochemically. The monitor may be absent from the fluid initially and be generated either from the electrode itself, or from some precursor species present in the fluid. For example, Cu^{2+} monitor ions may be generated from a copper electrode.

$$\mathrm{Cu(s)} \longrightarrow \mathrm{Cu^{2+}\,(soln)} + 2e^- \qquad (1)$$

into many fluids. In saline natural waters, the hypochlorite ion can serve as the monitor, being generated by the reaction

$$\mathrm{Cl^-(aq)} + \mathrm{H_2O}(l) \longrightarrow$$

$$2\mathrm{H^+(aq)} + \mathrm{OCl^-(aq)} + 2e^- \qquad (2)$$

at an inert anode. Alternatively some preexisting solute, such as dissolved oxygen or hydroxide ion in an aqueous solution, can serve as monitor and its concentration may be either diminished

$$\mathrm{O_2(aq)} + 4\mathrm{H^+(aq)} + 4e^- \longrightarrow 2\mathrm{H_2O}(l) \qquad (3)$$

or enhanced

$$2\mathrm{H_2O}(l) + 2e^- \longrightarrow 2\mathrm{OH^-(aq)} + \mathrm{H_2(aq)} \qquad (4)$$

by a suitable electrode reaction.

Let us generalize these examples by considering the case of a monitor solute whose concentration is uniformly equal to c^b before any current is passed. Starting at time $t = 0$, a current passes through the electrode, as a result of which the concentration of the monitor at the surface of the electrode becomes different from c^b. Because the current density and/or the surface concentration may change with time, these quantities may be denoted $i(t)$ and $c^s(t)$. The purpose of this article is to investigate the relationship

$$c^s(t) - c^b \Leftrightarrow i(t) \qquad (5)$$

between the surface *concentration excursion* $c^s(t) - c^b$ and the *current density* $i(t)$. In some cases $c^s(t)$ could be zero; in others, c^b would be zero.

Let n be the number of electrons produced concurrently with one ion or molecule of the monitor

$$\text{precursor} \xrightleftharpoons[\text{consumption}]{\text{generation}} \text{monitor} + ne \qquad (6)$$

being negative when it is a reduction process that generates the monitor

$$\text{precursor} - ne \xrightleftharpoons[\text{consumption}]{\text{generation}} \text{monitor} \qquad (7)$$

Table 1 shows how the sign of n correlates with those of the current density and the concentration excursion.

2. Fundamental relationships

The connection between the monitor concentration excursion at the electrode surface and the current density is not made directly, but through the intermediacy of the flux density j^s of the monitor at the surface:

$$c^s(t) - c^b \Leftrightarrow j^s(t) \Leftrightarrow i(t) \qquad (8)$$

Faraday's law provides the simple relationship

$$j^s(t) = \frac{i(t)}{nF} \qquad (9)$$

between the surface flux density and the current density. This equation is valid whenever there is no adsorption of the monitor, or even if there is adsorption provided that its extent does not change.

The relationship between the monitor surface concentration excursion and its surface flux density is no different, in principle, from the corresponding relationship

$$c(x, t) - c^b \Leftrightarrow j(x, t) \qquad (10)$$

anywhere in the solution. Here x is used to denote the coordinate measured from, and normal to, the electrode. The form of the relationship between the local

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Table 1. Allocation of signs to electron number, concentration excursion and current density.

Monitor	*Process*	*Electrode*	n	$c^s(t) - c^b$	$i(t)$
oxidant	generation	anodic	+	+	+
oxidant	consumption	cathodic	+	−	−
reductant	generation	cathodic	−	+	−
reductant	consumption	anodic	−	−	+

concentration and the local flux is determined by which of the possible transport mechanisms – diffusion, migration and/or convection – operates. In the most general case, when all three mechanisms contribute, the flux equation is

$$-D\frac{\partial c}{\partial x} + \frac{zuc}{|z|}X_x + cv_x = j \tag{11}$$

where X_x denotes the component of the electric field along the x-coordinate and v_x denotes the component of the fluid velocity in the same direction. The diffusion coefficient, D, charge number, z, and mobility, u, of the monitor are interconnected by the Nernst-Einstein relationship [1], which permits the flux equation to be rewritten as

$$-D\left[\frac{\partial c}{\partial x} - \frac{zFc}{RT}X_x\right] + cv_x = j \tag{12}$$

Another interrelationship between concentration and flux density is provided by the conservation equation. For the purposes of the present article, this may be expressed as

$$\frac{\partial c}{\partial t} + kc = -\frac{\partial j}{\partial x} - j\frac{\partial}{\partial x}\ln A \tag{13}$$

The final term in this equation depends on the geometry of the region surrounding the electrode and reflects the rate at which the cross-sectional area, A, available for transport increases as one proceeds away from the electrode. The kc term is included in case the monitor is unstable in the fluid and decomposes by some first-order (or pseudo first-order) process with rate constant k.

The literature of electroanalytical chemistry, for example [2], and electrochemical engineering, for example [3], is replete with analytical and numerical solutions to the simultaneous equations, (12) and (13), in numerous geometric situations and subject to a variety of boundary conditions. With the help of Faraday's law, Equation 9, such solutions lead immediately to our objective: expressions relating the monitor surface concentration excursion to the current density. The next section will address examples of relationships obtained in this way.

3. Examples of interrelationships

Below follows a catalogue of six examples, presented with commentary but without proofs, of how the concentration excursion of a monitor at the surface of the electrode is related to the current density. The chosen examples are simple, but representative, ones. They are all "general" in the sense that the boundary condition at the electrode surface, which depends on the electrochemical technique, is not specified.

3.1. *Planar semi-infinite diffusion*

If the electrode is planar and the monitor is transported only by diffusion in a region that extends indefinitely from the electrode, then the interrelation between the concentration excursion and the current density is

$$c^s(t) - c^b = \frac{1}{nF\sqrt{D}}\frac{\mathrm{d}^{-1/2}}{\mathrm{d}t^{-1/2}}i(t) \tag{14}$$

[4]. Here $\mathrm{d}^{-1/2}/\mathrm{d}t^{-1/2}$ is the semiintegration operator [5]. Alternatively, the relationship may be written in terms of a convolution [6]

$$c^s(t) - c^b = \frac{i(t)}{nF} * \frac{1}{\sqrt{(\pi Dt)}} \tag{15}$$

where the asterisk signifies the operation

$$f(t)*g(t) = \int_0^t f(\tau)g(t-\tau)\,\mathrm{d}\tau = g(t)*f(t) \tag{16}$$

3.2. *Spherical diffusion*

If the electrode is a sphere (or some segment of a sphere, such as a hemisphere) of radius r, Equation 13 for a stable monitor becomes $\partial c/\partial t = -(\partial j/\partial x) - 2j/(r + x)$. The sought relationship is

$$c^s(t) - c^b = \frac{i(t)}{nF} * \left[\frac{1}{\sqrt{(\pi Dt)}} - \frac{1}{r}\exp\left(\frac{Dt}{r^2}\right)\operatorname{erfc}\left(\frac{\sqrt{(Dt)}}{r}\right)\right] \tag{17}$$

in this case [7], resembling (15) but with a more complicated convolution.

When t becomes large compared with r^2/D, the convolution reduces to the simple result

$$c^s(t) - c^b = \frac{ri(t)}{nFD} \qquad t \gg r^2/D \tag{18}$$

in which the concentration excursion is proportional to the current density. Because of their small radii this result is soon achieved at hemispherical microelectrodes, which is why steady-state voltammetry [8] may be successfully realized at such electrodes.

3.3. *Diffusion plus migration*

The inclusion of migration as a contributor to monitor transport leads to a massive increase in the complexity of the problem of deducing interrelation expressed in (5). However, the diffusion-plus-migration analogue of Equation 18 may be found (for example, see the ferricinium case in [9]) for the case in which the monitor is an ion formed by an $|n|$-electron transfer from an uncharged precursor, provided that all other ions present have charge numbers of $\pm n$. The interrelation is

$$c^s(t) - c^b = \frac{ri(t)}{2nFD}\left[1 + \frac{nFDc_i^b}{ri(t) + nFDc_i^b}\right] \qquad t \gg r^2/D \tag{19}$$

where c_i^b is the total bulk concentration of electroinactive electrolyte.

3.4. *Diffusion plus reaction*

If the monitor is electrogenerated at a planar electrode and, in addition to semiinfinite diffusion, undergoes a first-order reaction, then the relationship between the concentration excursion and the current density is again a convolution. In this case [10]

$$c^s(t) = \frac{i(t)}{nF} * \left(\frac{\exp(-kt)}{\sqrt{(\pi Dt)}}\right) \tag{20}$$

the c^b term having been omitted because there is no bulk monitor concentration.

The convolution integrals in equations such as (20) may be evaluated if the form of the current density versus time relationship is known. For instance, if the current density is a constant, equation (20) reduces to

$$c^s(t) = \frac{\operatorname{erf}\sqrt{(kt)}}{\sqrt{k}}\left(\frac{i}{nF}\right) \qquad i(t) = \text{constant} = i \tag{21}$$

Specifying the boundary condition in this way is equivalent to stipulating a particular experimental regime: in this instance, galvanostatic chronopotentiometry.

3.5. *Diffusion plus advection*

Equations 12 and 13 have been formulated in terms of a single distance coordinate and this is rarely adequate when convective transport is operative. However, in the case of porous electrodes through which the fluid can flow at a constant rate with little impediment, the hydrodynamic situation may be adequately described by these equations with v_x being a (negative) constant. The term "advection" is used to describe the simple hydrodynamic regime encountered in this instance. When diffusion and advection contribute to transport, migration being absent, the equation

$$c^s(t) - c^b = \frac{i(t)}{nF} * \left[\frac{\exp(-v^2t/4D)}{\sqrt{(\pi Dt)}} - \frac{v}{2D}\operatorname{erfc}\left(\frac{v}{2}\sqrt{\left(\frac{t}{D}\right)}\right)\right] \tag{22}$$

describes the relation between the monitor surface concentration excursion and the current density. At times long in comparison with $4D/r^2$ the function with which $i(t)/nF$ is convolved becomes a constant, so that the convolution integral reduces to a simple temporal integral

$$c^s(t) - c^b \simeq \frac{-v}{nFD}\int_0^t i(\tau)\,\mathrm{d}\tau \qquad t \gg 4D/v^2 \tag{23}$$

Thus the concentration excursion becomes proportional to the total charge passed and to the flow velocity v.

3.6. *Diffusion within a boundary layer*

The concept of a "boundary layer" – a region within which diffusion is the sole transport mode and beyond which concentrations are uniform – provides a valuable, and surprisingly accurate, model for many hydrodynamic situations [11, 12] that would otherwise be insoluble. The form of interrelation for a boundary layer of thickness L is [13]

$$c^s(t) - c^b = \frac{i(t)}{nF} * \frac{1}{L}\theta_2\left(0; \frac{Dt}{L^2}\right) \tag{24}$$

where θ_2 denotes a theta function [14]. Once again, there is a long-time simplification of this result: if the current density is effectively constant on a timescale of duration L^2/D, an effective steady state is established in which there is a proportionality

$$c^s(t) - c^b \simeq \frac{Li(t)}{nFD} \tag{25}$$

between the concentration excursion and the current density.

While Equation 24 is only an approximation in hydrodynamic situations, it applies exactly in thin-layer cells such as those described by Armitage *et al.* [15] and extended by Colyer *et al.* [16] to include migration. In these applications of Equations 24 and 25, L is the half-width of the thin layer.

4. Generalization

All the time-dependent examples considered above (and several others [13]) show a concentration excursion related by a convolution of the form

$$c^s(t) - c^b = \frac{i(t)}{nF} * g(t) \tag{26}$$

to the current density, where $g(t)$ is some function of time having the dimensions of a reciprocal length. In all cases the short-time behaviour is described by

$$\begin{aligned} c^s(t) - c^b &= \frac{i(t)}{nF} * \frac{1}{\sqrt{(\pi Dt)}} \\ &= \frac{1}{nF\sqrt{(D)}}\frac{\mathrm{d}^{-1/2}}{\mathrm{d}t^{-1/2}}i(t) \qquad t \to 0 \end{aligned} \tag{27}$$

the concentration excursion being proportional to the semiintegral of the current density.

In several cases the long-time behaviour becomes steady-state, with a direct proportionality between $c^s(t) - c^b$ and $i(t)$, if conditions remain unchanging or vary sufficiently slowly. Representing such a steady-state relationship by

$$c^s(t) - c^b = \frac{i(t)}{nFw} \qquad t \to \infty \tag{28}$$

it is evident that w has the dimensions of velocity

($\mathrm{m\,s^{-1}}$). It may be argued that steady states are possible only when it is possible to construct a velocity from the physical parameters of the system. Thus for the systems considered in sections 3.2 and 3.6, $w = D/r$ and $w = D/L$, respectively. Note that the steady state discussed in section 3.3 did not correspond to a direct proportionality between concentration excursion and current density.

5. Applications

To use relationships of the type discussed to determine transport parameters requires measurement or calculation of the current density and the concentration of monitor at the electrode surface.

Current density (more strictly the average current density) is easily determined from the measured current at an electrode of known area, but surface concentrations are not directly accessible from electrical measurements. However, two routes exist for obtaining information about surface concentrations from potential measurements.

If the electrode reaction involving the monitor is reversible, the Nernst equation permits the monitor surface concentration $c^s(t)$ to be determined from the electrode potential $E(t)$. The chain of interrelationships

$$E(t) \Leftrightarrow c^s(t) - c^b \Leftrightarrow j^s(t) \Leftrightarrow i(t) \qquad (29)$$

then exists and permits a connection to be made between two independently measurable electrical variables. For example, if a monitor is reversibly electrogenerated by a constant current density from a precursor at unit activity under conditions in which Equation 20 is obeyed then the potential evolves with time according to the equation

$$E(t) = E^0 + \frac{RT}{nF}\ln\left\{\frac{i\,\mathrm{erf}\sqrt{(kt)}}{nF\sqrt{(kD)}}\right\} \qquad (30)$$

where E^0 is the standard potential. The parameters D and k are thus experimentally accessible.

The second route by which information can be gleaned concerning $c^s(t)$ is useful when the current density is the controlled electrical variable. If a current signal is applied such that $c^s(t)$ is caused to decrease with time then, ultimately, the monitor acquires zero concentration at the electrode surface. At this instant, the so-called "transition time", the electrode potential usually displays a sudden dramatic change in value, irrespective of the degree of reversibility of the electrode reaction. For example, if the current is maintained constant in the experiment described by Equation 14, then (since the semiintegral of a constant i is $2i\sqrt{(t/\pi)}$) the transition time is $\pi n^2F^2D(c^b)^2/4i$. Thus, from measurements of the transition time, transport parameters – in this case the diffusion coefficient D – are accessible.

Similar procedures can provide data on fluid flow. The example presented in the final section of this article has a more modest objective – simply to assess whether the fluid is in motion or not.

6. Generation/recapture experiment

Consider an experiment having three phases. In the first, $t < 0$, the electrode is at rest and the monitor is absent from its vicinity. During the second phase, $0 < t < T$, the monitor is generated at the electrode by the passage of some time-dependent current density $i(t)$. The second phase ends at some arbitrary time, T. During the third phase, $t > T$, the electrode is polarized at such an extreme potential (rather negative if the monitor is an oxidant, positive if it is a reductant) that the monitor acquires a surface concentration of zero, $c^s(t > T) = 0$. Under these conditions it can be shown [17] that the third-phase current density arising from the "recapture" of the monitor generated during the second phase, is

$$i(t > T) = \frac{-1}{\pi(t - T)^{1/2}}\int_0^T \frac{i(\tau)(T - \tau)^{1/2}}{(t - \tau)}\,\mathrm{d}\tau \qquad (31)$$

provided the fluid is motionless. Any motion of the fluid leads to a smaller recapture current.

Equation 31 is valid irrespective of the way in which the generation current density depends on time. If a constant generation current is employed, the integral evaluates to

$$i(t > T) = \frac{-2i}{\pi}\left[\left(\frac{T}{t - T}\right)^{1/2} - \arctan\left(\frac{T}{t - T}\right)^{1/2}\right] \qquad (32)$$

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