

NON-EQUILIBRIUM THERMODYNAMICS OF TRANSPORT AND REACTION IN LITHIUM CELLS WITH LIQUID OR POLYMERIC ELECTROLYTES: APPLICATION TO IMPEDANCE ANALYSIS

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Summary

The correct flux equations from non-equilibrium thermodynamics are used to deduce appropriate differential equations for transport in thin-layer lithium cells containing liquid or polymeric electrolytes. The general theory is applied to several cases of interest in the interpretation of diffusion impedances in cells with non-blocking electrodes. The main results are: (a) the occurrence of correction terms in the usual equation for diffusion impedance for cells containing a completely- or partially-ionized electrolyte; (b) the occurrence of at least two overlapping impedance loops on Nyquist plots for cells containing an electrolyte with an ion-pair equilibrium that relaxes slowly compared with the rate of diffusion. One loop is the usual finite Warburg diffusion impedance, while the other arises from perturbation of chemical equilibrium and has the character of a somewhat depressed and contracted finite Warburg impedance.

Introduction

Equations describing electrochemical processes in thin-layer cells are of fundamental interest in providing the basis for the experimental determination of charge-transfer and transport parameters in a wide variety of electrolytes and insertion-type electrodes, and are also of practical interest in the design and prediction of operating conditions in thin-layer galvanic cells.

A number of publications have appeared, of which refs. 1 and 2 are examples, in which transport parameters for liquid and solid electrolytes have been deduced from potentiostatic or galvanostatic transients, or from analysis of impedance spectra. In general, these parameters are suspect because, at some point either an incorrect model has been assumed for the transport processes, or the inadequate Nernst-Planck equations have been used. The failure of the Nernst-Planck equations has been well documented in aqueous solutions and in ionic membranes [3]; they are correct only in the infinite dilution limit and for an uncharged phase. The former of these

conditions is never met, and the latter can attain considerable importance in a typical lithium cell using a thin-layer electrolyte and insertion electrodes.

Fortunately, the alternative to the Nernst-Planck equations is well known: correct flux equations based on non-equilibrium thermodynamics. This approach has been used by Dudley and Steele for solid electrolytes [4], but the appropriate differential equations have not been discussed adequately. In this paper, the basic flux equations from non-equilibrium thermodynamics [5, 6] are summarized and applied to three cases, all involving single-phase, two-component electrolytes: (i), single true electrolyte; (ii), (iii), single true electrolyte with an ion pair equilibrium which is established either rapidly or slowly relative to the rate of diffusion. The differential equations for transport are deduced for each case, and applied to calculation of the impedance spectra. While the differential equations are equally applicable to other electrochemical techniques, limitations of space permit only brief discussion of the results. A fuller discussion, with more applications, will be published elsewhere.

The theory excludes, for the present, processes connected with transport in double layer regions, convection, and possible anisotropic effects.

Theory

Flux equations from non-equilibrium thermodynamics

For an isothermal system in the absence of viscous forces, and containing $n + 1$ species j , with respective charge numbers z_j (which may be zero), in a single solvent (species $n + 1$), the flux equations are:

$$J_j = -\sum_k L_{jk}(\nabla \mu_k + z_k F \nabla \phi) + c_j v^a \quad j, k = 1, \dots, n \quad (1)$$

where J_j , c_j , μ_j are the flux, amount concentration, and chemical potential of species j , F is the Faraday constant, ϕ is the electric potential, and L_{jk} a phenomenological coefficient describing the linear dependence of fluxes on thermodynamic affinities (or thermodynamic forces). The linear dependence of both fluxes and affinities requires that no terms involving one component (here taken as the solvent) appear [7]. It is assumed that some particular reference velocity, v^a , is sufficiently close to zero relative to the electrodes of the cell that the product $c_j v^a$ is negligible for all concentrations. The phenomenological coefficients depend on the choice of reference velocity, but this choice has no effect on the form of the equations. The choice $v^a = v_{n+1}$, the velocity of the solvent, has been suggested [4]; a more appropriate choice may be the mean volume velocity, as in many experimental methods for measuring diffusion [6]. The Onsager relations hold: $L_{jk} = L_{kj}$, $j, k = 1, \dots, n$, and give $n(n + 1)/2$ independent coefficients. The amount-of-substance transport number of species j , or, more concisely,

the amount transport number (previously and inconsistently called the mass transport number) is defined as the fraction of the amount-of-substance of j carried by that species per unit flow of electric charge when no concentration gradients are present:

$$t_j = FJ_j/i = F^2 \sum_k z_k L_{jk} / \kappa \quad \nabla \mu_k = 0, k = 1, \dots, n \quad (2)$$

where i is the magnitude of the current density and κ the conductivity. The amount transport numbers obey the relation $\sum z_j t_j = 1$. Note that the amount transport number of a neutral species is not necessarily zero, but its charge transport number, $T_j = z_j t_j$, is zero. The equation for the current density may be used to eliminate the gradient of electrical potential, from which transformed flux equations may be found:

$$J_j = t_j i / F - \sum_k M_{jk} \nabla \mu_k \quad (3)$$

where

$$M_{jk} = L_{jk} - t_j t_k \kappa / F^2 \quad j, k = 1, \dots, n \quad (4)$$

and

$$\sum_k z_j M_{jk} = 0, \quad M_{jk} = M_{kj} \quad j, k = 1, \dots, n \quad (5)$$

For n species, relations (5) show that there are $n(n-1)/2$ independent values of M_{jk} . The coefficients M_{jk} appear to have been introduced first by Harned and Owen [8] for aqueous solutions and were subsequently generalized by Lorimer *et al.* [9] for membrane transport. Each M_{jk} coefficient consists of a diffusive part and a migration part; the latter arises from writing the flux equations in terms of the current density rather than the gradient of electric potential. Multicomponent diffusion coefficients can be defined in the usual way:

$$D_{jk} = \sum_i M_{ji} \partial \mu_i / \partial c_k \quad i, j, k = 1, \dots, n \quad (6)$$

Two-component, completely-ionized electrolyte

This example is treated in some detail to illustrate the general procedures for calculation. For the molar fluxes J_1, J_2 in a system containing a single electrolyte which ionizes completely:

$$c_{\nu_1} A_{\nu_2} \longrightarrow c_{\nu_1} z_1 + A_{\nu_2} z_2$$

$$\nabla \mu_1 / z_1 - \nabla \mu_2 / z_2 = \nu \nabla \mu / \nu_1 z_1 = -\nu \nabla \mu / \nu_2 z_2 \quad (7)$$

where $\nu = \nu_1 + \nu_2$, subscripts 1, 2 refer to cations and anions, respectively, and μ is the chemical potential of the salt. The flux eqns. (3) with (5) and (6) reduce to

$$J_j = T_j i / z_j F - D \nabla c \quad j = 1, 2 \quad (8)$$

Here, the gradient of chemical potential in terms of the thermodynamic activity factor G and the gradient of the amount concentration c has been used:

$$\nabla \mu = (\partial \mu / \partial c) \nabla c = RT(1 + \partial \ln y_{\pm} / \partial \ln c) \nabla c / c = (RTG/c) \nabla c \quad (9)$$

where R is the universal gas constant, T the thermodynamic temperature and y_{\pm} the mean ionic activity coefficient on the amount concentration scale. The salt flux is defined as $J_s = J_1 / \nu_1 = J_2 / \nu_2$ at $i = 0$, and the diffusion coefficient D is

$$D = \nu M_{12} RTG / \nu_1 \nu_2 c \quad (10)$$

Differential equations for transport

The equation of continuity for each species is

$$\partial c_j / \partial t = -\nabla \cdot J_j + r_j J \quad (11)$$

where J is the rate of a single chemical reaction involving species j , and r_j is the stoichiometric coefficient for species j in that reaction. Because $c_j = \nu_j c$, substitution of eqn. (8) in eqn. (11) gives

$$\nu_j \partial c / \partial t = -\nabla \cdot (T_j i / z_j F) + \nu_j \nabla \cdot (D \nabla c) + r_j J \quad (12)$$

For conservation of charge in the system, with ρ the charge density [5],

$$\partial \rho / \partial t = -\nabla \cdot i \quad (13)$$

For an electrically neutral system, the charge in a hydrodynamic volume element is zero, so that the right-hand side of eqn. (13) is zero. If, as well, there is no chemical reaction, and the transport numbers are independent of concentration over the range of concentrations encountered in a particular experiment, or vary more slowly with concentration than the diffusion coefficient, then eqn. (12) reduces to Fick's second law of diffusion.

We now consider a cell with a 1 - 1 electrolyte containing lithium ions between two planar lithium electrodes located at $x = 0, 2L$. As electrolysis proceeds under an applied potential, the anode dissolves, causing an increase of concentration next to the anode. Similarly, metal is deposited on the cathode, causing a decrease in concentration next to the cathode. A steep diffusion gradient is thus set up, and a diffusion potential opposes the applied potential.

The boundary conditions at the electrodes require that there is no flux of anions, or equivalently, that the cation flux from the electrode is balanced by migration and diffusion of cations. Thus,

$$T_2 i / F = -D \partial c / \partial x \quad x = 0, 2L \quad (14)$$

An electronic current flow into the anode (here the left-hand electrode, at $x = 0$) from the external circuit is taken as positive; similarly, an electronic current flow out of the cathode into the external circuit is positive. The concentration gradient in the electrolyte is negative; thus the diffusive flux from anode to cathode is positive.

The total potential, E , applied to the cell is the sum of the reaction overpotential η , the diffusion potential E_d , and the ohmic overpotential E_R . The anodic overpotential is given by the Butler-Volmer equation

$$i = i_0 \{ \exp[(1 - \beta)\eta F/RT] - (a_1/a_1^*) \exp(-\beta\eta F/RT) \} \quad (15)$$

where i_0 is the exchange current density, a_1, a_1^* the activities of the electroactive species when current flows and when no current flows (*cf.* ref. 10), and β is the transfer coefficient for a one-electron process. It is necessary to carry out calculations for only one half of the symmetric cell, *i.e.*, from $x = 0$ to $x = L$; thus the specific cathodic overpotential need not be considered. The ohmic overpotential and the diffusion potential are the respective terms in

$$E_R + E_d = i \int_{x=0}^L dx/\kappa(x) + (RT/F) \int_{x=0}^L (T_1 d \ln a_1 - T_2 d \ln a_2) \quad (16)$$

E_R is a function of both E (through i) and c , while E_d and a_1 are functions of c only. Calculation of the impedance, Z , of the cell at the equilibrium potential is carried out by the Laplace transform method [11]:

$$Z = \left\{ 1 - \sum_i (\partial i / \partial c_i) f_i(0, j\omega) \right\} / (\partial i / \partial E) \quad (17)$$

where $f_i(0, s) = \overline{\Delta c_i / \bar{i}}$, the bars indicate Laplace transforms, and s is the Laplace transform parameter. The derivatives are calculated at $x = 0$. Calculation of the derivatives $\partial i / \partial c_1$ and $\partial i / \partial E$ from eqns. (15) and (16) and use of (17) gives the total impedance as the sum of the usual charge transfer impedance RT/Fi_0 , the ohmic impedance R_c and the diffusion impedance. (Each impedance quoted is actually an impedance-area product, as given by eqn. (17).) No capacitive effects from double layers or arising from the geometry of the cell have been included; therefore the charge transfer and ohmic impedances have no imaginary components. The diffusion impedance is found to be

$$Z_d = (2GRT/Fc_0)T_2 f(0, s) \quad (18)$$

The function $f(x, s)$ is found from the solution in the Laplace plane of eqn. (12), which becomes Fick's second law:

$$\partial c / \partial t = D \partial^2 c / \partial x^2 \quad (19)$$

with boundary conditions eqn. (14) and the initial condition $c(x, 0) = c_0$. Substitution of $x = 0$ and $s = j\omega$ in the solution of eqn. (19), where ω is

the circular frequency and j is the square root of -1 , gives, finally, the well-known equation:

$$f(0, s) = \{T_2/F(sD)^{1/2}\} \tanh\{(s/D)^{1/2}L\} \quad (20)$$

The diffusion impedance is then found from eqns. (18) and (20) to be

$$Z_d = (2GRTL T_2^2/c_0 D F^2) \tanh \gamma/\gamma \quad (21)$$

where $\gamma^2 = j\omega L^2/D$. Equation (21) can be written in a more familiar form by noting that the diffusion coefficient is given by the rigorous equation

$$D = 2RTG\{L_{12}/c_0 + \lambda_1\lambda_2/F^2(\lambda_1 + \lambda_2)\} \quad (22)$$

where λ_i is the ionic conductivity of ion i at the bulk concentration of the electrolyte, and that the total cell resistance·area (also at the bulk concentration) is $2R_c = 2L/c_0(\lambda_1 + \lambda_2)$. The result is a corrected Macdonald equation [12, 13]

$$Z_d = R_c(\lambda_2/\lambda_1)(\tanh \gamma/\gamma)/(1 + Q) \quad (23)$$

where

$$Q = (F^2 L_{12}/c_0)(1/\lambda_1 + 1/\lambda_2) \quad (24)$$

Thus the Macdonald equation contains a correction term which is significant at finite concentrations of electrolyte, and which makes interpretation of the impedance at finite concentrations in terms of ratios of ionic conductivities impossible unless the full equation is used. Consistent data from which the correction term can be evaluated are unavailable for most electrolytes. For concentrated aqueous chloride solutions at 25 °C, data [14] show that Q can be as large as 0.5; for 3 mol dm⁻³ LiCl $Q = 0.4626$, and for HCl, LiCl, NaCl, and KCl, the factor $(\lambda_1/\lambda_2)/(1 + Q)$ decreases by 41, 0.5, 22 and 33%, respectively, between infinite dilution and 3 mol dm⁻³. Thus the factor $1 + Q$ cannot be ignored, and the Macdonald form, eqn. (23) of the equation for the impedance, is not the most useful. On the other hand, if D can be found from the frequency at the maximum of the diffusion impedance loop (see below), then the width of the loop gives the product GT_2^2 . Lack of knowledge of the thermodynamic factor G can result in discrepancies between transport numbers found from impedance measurements and from other techniques.

Figure 1 (dot-dash curves) shows the shape of that part of the impedance curve which arises from diffusion (*i.e.*, from the diffusion potential) and which is characterized by the ratios [15] $H/W = 0.4172$, $M/W = 0.5816$, $\omega_m = 2.5407D/L^2$ where H , W are the height and width, M is the width to the maximum, and ω_m is the frequency at the maximum. The factor $2R_c(\lambda_2/\lambda_1)/(1 + Q) = 100 \Omega$ in all plots.

Two-component electrolyte with ion pair formation

We next consider ion pair formation $C^+ + A^- \rightleftharpoons CA$, with rate constants k_1 and k_{-1} for the forward and backward reactions. If the system is initially

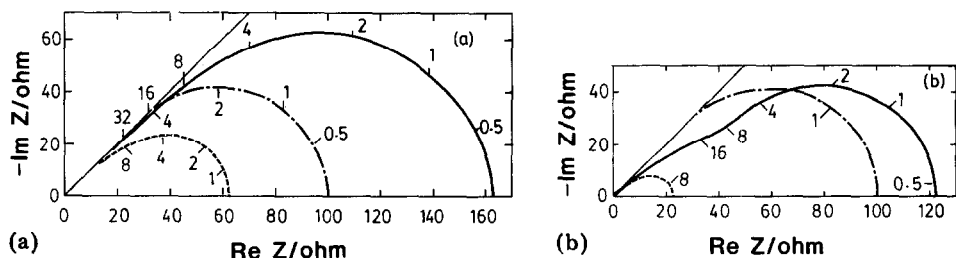


Fig. 1. Calculated impedance plots for diffusion plus chemical relaxation. Diffusion coefficient $D = 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, cell thickness $L = 2 \times 10^{-5} \text{ m}$. —, total impedance; - - -, pure diffusion; - · - ·, relaxation. (a) relaxation rate constant $k' = 10 \text{ s}^{-1}$; (b) $k' = 100 \text{ s}^{-1}$. Frequencies in Hz; pure diffusion arcs normalized to 100Ω .

at equilibrium, application of a perturbing electric field produces a change in concentration, causing, in general, a perturbation in the chemical equilibrium which relaxes at its own intrinsic rate. For a system not at chemical equilibrium, but with local conservation of charge, there are two independently-diffusing species cation (=1) and ion pair (=3), and eqns. (3), (5) and (6) give the transport equations for this ternary diffusing system as (cf. ref. 16):

$$\begin{aligned} \partial c_1 / \partial t &= D_{11} \nabla^2 c_1 + D_{13} \nabla^2 c_3 - k_1 c_1^2 + k_{-1} c_3 \\ \partial c_3 / \partial t &= D_{31} \nabla^2 c_1 + D_{33} \nabla^2 c_3 + k_1 c_1^2 - k_{-1} c_3 \end{aligned} \quad (25)$$

where the D_{jk} s are the ternary diffusion coefficients and c_i is the total perturbed concentration in the diffusion field. Linearization of the chemical rate equations, for reactions close to equilibrium, gives:

$$\begin{aligned} \partial \delta c_1 / \partial t &= D_{11} \nabla^2 \delta c_1 + D_{13} \nabla^2 \delta c_3 - 2k_1 c_{1e} \delta c_1 + k_{-1} \delta c_3 \\ \partial \delta c_3 / \partial t &= D_{31} \nabla^2 \delta c_1 + D_{33} \nabla^2 \delta c_3 + 2k_1 c_{1e} \delta c_1 - k_{-1} \delta c_3 \end{aligned} \quad (26)$$

where $\delta c_i = c_i - c_{ie}$ is a small perturbation from the equilibrium concentration (in the diffusion field) c_{1e} . The equilibrium concentrations in the diffusion field obey the pair of differential equations

$$\begin{aligned} \partial c_{1e} / \partial t &= D_{11} \nabla^2 c_{1e} + D_{13} \nabla^2 c_{3e} \\ \partial c_{3e} / \partial t &= D_{31} \nabla^2 c_{1e} + D_{33} \nabla^2 c_{3e} \end{aligned} \quad (27)$$

Subtraction of eqn. (27) from eqn. (26) gives

$$\begin{aligned} \partial \delta c_1 / \partial t &= D_{11} \nabla^2 \delta c_1 + D_{13} \nabla^2 \delta c_3 - 2k_1 c_{1e} \delta c_1 + k_{-1} \delta c_3 \\ \partial \delta c_3 / \partial t &= D_{31} \nabla^2 \delta c_1 + D_{33} \nabla^2 \delta c_3 + 2k_1 c_{1e} \delta c_1 - k_{-1} \delta c_3 \end{aligned} \quad (28)$$

We consider two cases: (a) the rate of equilibration through chemical reaction is large compared with the rate of diffusion; (b) the rate of equilibration is comparable with the rate of diffusion.

Case (a): rate of chemical reaction large relative to rate of diffusion

In this case, $\delta c_1 = -\delta c_3$, and the rate constants can then be combined into a single relaxation rate constant

$$k' = 2k_1\alpha c + k_{-1} \quad (29)$$

where $c = c_{1e}/\alpha$ is the total concentration and α is the equilibrium degree of dissociation. With the relaxation rate constant large compared with the rate of diffusion (specifically, from eqn. (28), if $(D_{11} - D_{13})/L^2 \ll k'$), δc_1 decays to zero in a few lifetimes of the chemical reaction. The single equation for the flux of salt is identical with eqn. (19), because diffusion now occurs in a two-component system: there are two constraints, electrical neutrality and chemical equilibrium, among the three species, cation, anion, and ion pair. In relation to eqn. (27), it will be shown elsewhere that, to a good approximation,

$$D = \alpha(D_{11} + D_{31}) + (1 - \alpha)(D_{13} + D_{33})$$

The solution of the diffusion equation in the Laplace plane is carried out with initial condition $c = c_0$ and boundary condition

$$(T_2 - t_3)i/F = -D(\partial c/\partial t) \text{ at } x = 0 \quad (30)$$

where t_3 is the amount transport number of ion pairs. Condition (30) states that there is no flux of salt across the electrode; individual fluxes of anions and ion pairs may be finite at the electrode, but their sum is zero. The solution of the diffusion equation in the Laplace plane is then analogous to eqn. (20):

$$f(0, s) = \{(T_2 - t_3)^2/F(sD)^{1/2}\} \tanh\{(s/D)^{1/2}L\} \quad (31)$$

In the Butler-Volmer equation, (15), the activity is now the activity of the salt; the ion pairs dissociate at an infinitely fast rate, by supposition, so that they also are involved in charge transfer. The ohmic overpotential term in eqn. (16) remains the same; an extra term $t_3 \ln a_3$ arises in the integrand of the diffusion potential term in eqn. (16) from transport of the ion pairs. Equations (15) - (17) and (31) give the diffusion impedance as

$$Z_d = \{2GRTL(T_2 - t_3)^2/c_0DF^2\} \tanh \gamma/\gamma \quad (32)$$

Substitution of

$$R_c = L/\alpha c_0(\lambda_1 + \lambda_2),$$

$$T_2 = \lambda_2/(\lambda_1 + \lambda_2)$$

and

$$D = 2GRT(M_{12} + 2M_{13} + M_{33}) = 2GRT\alpha\lambda_1\lambda_2/\{(\lambda_1 + \lambda_2)(Q_1 + Q_2)\},$$

where now

$$Q_1 = 1 - 2t_3(1 - t_3/2T_1)/T_2 \quad (33)$$

and

$$Q_2 = F^2(\lambda_1 + \lambda_2)\{(L_{12} + 2L_{13} + L_{33})/c_0\}/\alpha\lambda_1\lambda_2 \quad (34)$$

gives

$$Z_d = R_c(\lambda_2/\lambda_1)(1 - t_3/T_2)^2(\tanh \gamma/\gamma)/(Q_1 + Q_2) \quad (35)$$

Clearly, the form (32) is more useful than the form (35).

Case (b): rate of chemical reaction comparable with rate of diffusion

Equations (28), with the assumption that the equilibrium concentration c_{1e} is roughly constant in the chemical kinetic terms, may be solved rigorously by diagonalizing the matrix of diffusion coefficients via a linear transformation of the δc_j , and combining the resulting pair of equations, which are still coupled, into a single, fourth-order homogeneous differential equation with constant coefficients. The solution is algebraically very complicated, and will be discussed in detail elsewhere. For the present purposes, the general nature of the effects arising from perturbation of the equilibrium concentrations can be deduced under two approximations: (a) $D_{13} = D_{31} = 0$; (b) $\delta c_1 = -\delta c_3$, which holds strictly in the absence of the diffusion field. These two assumptions are consistent only if $D_{11} = D_{33} = D$, a common diffusion coefficient. The single differential equation for δc_1 is then

$$\partial \delta c_1 / \partial t = D \nabla^2 \delta c_1 - k' \delta c_1 \quad (36)$$

with initial condition $\delta c_1 = 0$ at $t = 0$. The boundary conditions express no separate fluxes of anion or ion pair across the electrode; in this restricted case, the condition is

$$T_2 i / F = D \partial \delta c_1 / \partial x \text{ at } x = 0, 2L \quad (37)$$

The perturbation in concentration simply adds an extra contribution to the concentration gradient at $x = 0$ and an extra contribution δi to the current density, provided that only the cation (and not the ion pair) is electroactive. The solution of eqn. (36) in the Laplace plane is then

$$\overline{\delta c_1}(0, s) = (T_2 \overline{\delta i} / F) \tanh \gamma / \gamma \quad (38)$$

where now, with $s = j\omega$,

$$\gamma^2 = (j\omega + k')L^2/D \quad (39)$$

The chemical reaction term leads to an extra impedance, essentially as a contribution to the diffusion potential: the concentrations at the anode increase, and, for a constant applied potential, less current flows.

The derivatives at zero current are as before, so that the final result for the diffusion impedance is:

$$Z_{d_1} = \{2GRTLT_2(T_2 - t_3)/c_1 DF^2\}(\tanh \gamma/\gamma) \quad (40)$$

The total diffusion impedance is the sum of eqns. (35) and (40). Using the identity

$$\{2(k' + j\omega)\}^{1/2} = \{k' + (k'^2 + \omega^2)^{1/2}\}^{1/2} + j\{-k' + (k'^2 + \omega^2)^{1/2}\}^{1/2} \quad (41)$$

in eqn. (40) shows that the imaginary and real parts of the impedance both

approach zero if $k' \gg \omega$, so that only the pure diffusion contribution Z_d remains. The impedance starts off at high frequencies with unit slope on a $-\text{Im}$ versus Re plot, just like a pure diffusion impedance. However, at lower frequencies, the effect of the finite chemical relaxation is to lower the imaginary part of the impedance to values smaller than those for pure diffusion. The arc for the total impedance is slightly flattened, and the real impedance at the maximum is slightly greater, compared with pure diffusion. These are diagnostic criteria for the possible occurrence of at least one slow chemical process. The combined diffusion and relaxation arcs may be more or less distinct, as in Fig. 1(b), or combined into one arc (Fig. 1(a)) which, superficially, looks like a single, pure diffusion arc.

Conclusions

Non-equilibrium thermodynamics is no more difficult in its application to problems of impedance in electrochemical cells with electrolytes at finite concentration or without supporting electrolyte than the inadequate and, in most cases, incorrect Nernst-Planck equations. The non-equilibrium thermodynamic equations of motion can be written in a form which leads to a systematic and rigorous description of migration, diffusion, and perturbations of chemical reactions close to equilibrium.

Application of these equations in this paper has yielded two significant conclusions: that the conventional Macdonald equation requires correction for finite concentrations, but that neglect of the correction gives an approximately correct ratio of ionic conductivities at infinite dilution; and that a simple chemical relaxation process (here represented explicitly as ion pair formation) contributes an additive term to the diffusion impedance. This chemical process can contribute significantly to the impedance behaviour at frequencies higher than those at which pure diffusion is dominant, and therefore can give rise to a marked distortion of the pure diffusion arc on a Nyquist diagram. For a range of ratios of rate constant to diffusion constant, this distorted arc has the characteristics of a depressed finite Warburg impedance.

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List of symbols

a_j	Activity of species j (mol m^{-3})
a_j^*	Activity of species j with $i = 0$ (mol m^{-3})
c	Amount concentration (mol m^{-3})

c_j	Amount concentration of species j (mol m^{-3})
c_{je}	Amount concentration of species j at chemical equilibrium in diffusion field (mol m^{-3})
c_0	Bulk concentration (mol m^{-3})
D	Binary diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
D_{ij}	Ternary diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
E	Applied potential (V)
E_R, E_D	Ohmic, diffusive contributions to cell potential (V)
$f(0, s)$	$= \Delta \bar{c}_1 / i$
F	Faraday constant (C mol^{-1})
G	$= 1 + \partial \ln y_{\pm} / \partial \ln c$
H	Height of diffusion impedance loop on Nyquist plot ($\Omega \text{ m}^2$)
i	Current density (A m^{-2})
i_0	Exchange current density (A m^{-2})
Im	Imaginary part of impedance ($\Omega \text{ m}^2$)
j	$= (-1)^{1/2}$
J	Rate of chemical reaction ($\text{mol m}^{-3} \text{s}^{-1}$)
J_j	Flux of species j ($\text{mol m}^{-2} \text{s}^{-1}$)
k'	Relaxation rate constant (s^{-1})
k_1	Rate constant for forward second-order reaction ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)
k_{-1}	Rate constant for backward first-order reaction (s^{-1})
L	Half-thickness of cell (m)
L_{jk}	Phenomenological coefficient ($\text{mol}^2 \text{kg}^{-1} \text{m}^{-3} \text{s}$)
M	Width to maximum of diffusion loop on Nyquist plot ($\Omega \text{ m}^2$)
M_{jk}	Phenomenological coefficient ($\text{mol}^2 \text{kg}^{-1} \text{m}^{-3} \text{s}$)
Q	Correction term, eqns. (24), (31)
r_j	Stoichiometric coefficient for species j in a chemical reaction
R	Universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)
R_c	(cell resistance \cdot area)/2 ($\Omega \text{ m}^2$)
Re	Real part of impedance ($\Omega \text{ m}^2$)
s	Laplace transform variable (s^{-1})
t	Time (s)
t_j	Amount transport number of species j
T_j	Charge transport number of species j
T	Thermodynamic temperature
W	Width of diffusion loop on Nyquist plot (Ω)
x	Coordinate perpendicular to electrode surface (m)
y_{\pm}	Activity coefficient on amount concentration scale
z_j	Charge number of species j
Z_D	Diffusion impedance ($\Omega \text{ m}^2$)
α	Degree of ionization
β	Transfer coefficient
γ	$= \{(j\omega + k')L^2/D\}^{1/2}$
δc	Difference between reaction-perturbed and unperturbed concentration in diffusion field (mol m^{-3})
Δc	Concentration at x less bulk concentration (mol m^{-3})

η	Charge-transfer overpotential (V)
κ	Conductivity (S m^{-1})
λ_j	Ionic conductivity of ion j ($\text{S m}^{-2} \text{mol}^{-1}$)
ν_j	Stoichiometric coefficient
ν	$= \nu_1 + \nu_2$
μ_j	Chemical potential of species j (J mol^{-1})
ρ	Charge density (C m^{-3})
ϕ	Electrical potential (V)
ω	Circular frequency (s^{-1})
∇	Gradient operator (m^{-1})
$\nabla \cdot$	Divergence operator (m^{-1})

Subscripts and superscripts

- 1, 2, 3 (subscripts) cation, anion, ion pair
 — (superscript) Laplace transform

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