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Interpretation of Finite-Length-Warburg-Type Impedances in Supported and Unsupported Electrochemical Cells with Kinetically Reversible Electrodes

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ABSTRACT

The origin of finite-length-Warburg-type impedances in supported and unsupported systems is examined within a common framework and with reference to previous exact and approximate results. While close agreement is found between an approximate treatment based on bulk electroneutrality and an exact solution of the Nernst-Planck-Poisson equation system for unsupported systems of many Debye length thicknesses with rapid electrode reaction kinetics, the approximate treatment is unjustified when the electrode reaction is slow or the electrode separation is less than or comparable to the Debye length.

In the years since Warburg (1) published his classic study of diffusion under ac conditions in a supported electrolyte placed between kinetically reversible electrodes, response functions of the Warburg type have been obtained by numerous authors for a wide range of systems involving both supported and unsupported electrolytes. Among recent theoretical treatments, especially those dealing with finite-length effects, differences in notation, approximations, and terminology have tended to obscure both similarities and differences between the situations considered and the results obtained. In particular, published discussions of thin layer effects often assume that while electrode separation is small compared to the effective diffusion length for the electrolyte, it is still large compared to the Debye length. While the latter condition is almost always met in systems with aqueous electrolytes, it need not apply in solid materials and membrane situations. Further, quite similar results have been obtained in treatments which both include and explicitly neglect Poisson's equation. In the present brief communication we compare three different approaches leading to a finite-length Warburg impedance of the form

$$Z_W(\omega) = Z_W(0) \{ \tanh(i\Lambda)^{0.5} / [i\Lambda]^{0.5} \} \quad [1]$$

where Λ is proportional to the angular frequency ω . Specifically examined are cases of (i) a supported electro-

lyte placed between kinetically reversible parent ion electrodes, (ii) an unsupported electrolyte with similar electrodes with electroneutrality assumed, and (iii) a treatment of the latter case based on an exact solution of the Nernst-Planck-Poisson equation system. We use a consistent notation throughout and comment upon related treatments to be found in the literature.

Supported Systems

Consider a supported electrochemical system of the form



where the planar electrodes are parallel and a distance d apart. The supporting electrolyte allows us to neglect the migration term in the Nernst-Planck equation

$$J_p = -D_p(\partial c_p / \partial x) + \mu_p c_p E \quad [3]$$

since the electric field E is very small within the electrolyte. Here J_p is the flux of the M^{z+} ion, D_p the diffusion coefficient, for the ion, c_p its concentration, and μ_p its electrical mobility. On setting $E = 0$ in Eq. [3], we obtain Fick's first law of diffusion. Under small-signal ac conditions, the system variables may be separated into steady-state and time-dependent parts, i.e.

$$c_p = c_{p0} + c_{p1} \exp(i\omega t) \quad [4a]$$

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and

$$J_p = J_{p0} + J_{p1} \exp(i\omega t) \quad [4b]$$

On substituting these forms in Eq. [3] and equating the time-dependent terms, one obtains

$$J_{p1} = -D_p(dc_{p1}/dx) \quad [5]$$

If M^{z+} does not participate in any bulk chemical reaction, Fick's second law then can be written in the small-signal form (2)

$$i\omega c_{p1} = D_p(d^2c_{p1}/dx^2) \quad [6]$$

It may be noted that it follows from the linearity of the first term in Eq. [3] that Eq. [5] and [6] hold even when c_{p0} varies with position. The general solution of Eq. [6] may be written

$$c_{p1}(x) = A \sinh [(i\omega/D_p)^{0.5}x] + B \cosh [(i\omega/D_p)^{0.5}x] \quad [7]$$

where A and B are constants which must be selected to satisfy the boundary conditions. For the system under consideration here one constant may be eliminated by a symmetry argument. Place the center of the system at $x = 0$, so that the electrolyte extends between $x = -d/2$ and $x = d/2$. Note that the physical situation at any time t will be the mirror image of that at time $t - \pi/\omega$, i.e., the electrodes will have reversed polarity and the current will be equal in magnitude but opposite in direction. With the coordinate system chosen, this behavior requires from Eq. [4a] that $c_{p1}(-x) = -c_{p1}(x)$ and thus that $B = 0$. The constant A can be related to the magnitude of the time-dependent part of the applied potential difference, $V_{\text{appl},1} \exp(i\omega t)$. We assume that this potential difference is evenly divided between the two interfaces and can be described by Nernst's equation which, after linearization of the logarithmic term, yields (3)

$$V_{\text{appl},1} = (RT/zFc_{p0})[c_{p1}(-d/2) - c_{p1}(d/2)] \quad [8]$$

where R is the gas constant, T the absolute temperature, and F the Faraday. This quantity is the limiting potential difference for exchange rates of potential-determining species that are rapid in comparison with mass transport. It is consistent with the electrode kinetic models of Butler-Volmer and Chang-Jaffé, for example. When we calculate the electrical current (per unit area), $I_1 = zFJ_{p1}$, and divide into $V_{\text{appl},1}$, we find the impedance (also per unit area)

$$Z(\omega) = [2RT/z^2F^2c_{p0}(i\omega D_p)^{0.5}] \tanh [(i\omega/D_p)^{0.5}(d/2)] \quad [9]$$

On comparing Eq. [9] with Eq. [1] we find that $\Lambda = \omega(d/2)^2/D_p$, which may also be written as $\Lambda = (d/2)^2/L_{\text{diff}}^2$, where $L_{\text{diff}} = (D_p/\omega)^{0.5}$ is the effective diffusion length, at the frequency of measurement, for the electroactive ion. The reason that the system length appears as divided by two is the symmetry of the system, which requires c_{p1} to be zero at the center. The divisor of two was unfortunately omitted by two of the present authors in a recent review (4). An expression in the form of Eq. [1] appears first to have been derived in a biological context by Labes and Lullies (5). An expression of the same form, but with a factor d (rather than $d/2$) appearing in the argument of the tanh function was obtained by Llopis and Colom (6), who considered the diffusion of a single electroactive species through a Nernst layer of thickness d established at a stationary electrode in a stirred electrolyte. There is no symmetry of c_{p1} in this case because c_{p1} is zero at the solution side of the Nernst layer. A similar result was obtained by Drossbach and Schultz (7). Sluyters (8) examined the ac behavior of a thin layer of supported electrolyte with identical, kinetically reversible, electrodes and both reduced and oxidized species diffusing within the electrolyte, and obtained a result equivalent (2) to placing two impedances of the form of Eq. [9], in series, one with a diffusion coefficient equal to that of the reduced species, the other with the diffusion coefficient of the oxidized species. An impedance of the form of Eq. [1] can also arise when a neutral product species must diffuse through, or along the internal pores of, an electrode to exchange with the ambient atmosphere (9, 10). In this case we have $\Lambda = \omega d^2/D_p$, where d is the thickness of a sin-

gle electrode and D the diffusion coefficient of the discharged species in the electrode.

One of the present authors has extended the treatment of the ac response of the parent-metal-type cell to the case where the electrode reaction occurs with arbitrary and different potential-dependent rates at the two electrodes (2). In this treatment, Butler-Volmer reaction kinetics were assumed and the displacement current through the compact double layer was explicitly included. The exact impedance result is consistent with Eq. [9] for identical electrodes and with the Llopis and Colom result (6) when one electrode is kinetically reversible and the other not. Results for non-planar electrode geometries are given by Sluyters-Rebach and Sluyters (11).

Unsupported Systems, Electroneutrality Assumed

The treatment in this section is based on the approach of Buck (12). Consider now an unsupported system



where the salt MX is fully dissociated into M^{z+} and X^{z-} ions, with concentrations denoted by $c_p(x)$ and $c_n(x)$, respectively. The transport of cations is described by Eq. [3] as before, while the transport of anions is described by a second Nernst-Planck equation

$$J_n = -D_n(\partial c_n/\partial x) - \mu_n c_n E \quad [11]$$

The mobilities μ_p and μ_n are generally taken to be related to the corresponding diffusion coefficients through the Einstein relation $\mu_i = D_i z F / RT$.

If electroneutrality is assumed to hold, it follows that $c_p = c_n$ and that J_p and J_n are equal except for a spatially invariant term related to the faradaic current I_f

$$J_p - J_n = I_f / zF \quad [12]$$

On setting $c_n = c_p$ in Eq. [3] and [11] and eliminating the concentration gradient terms, one obtains the electric field in the electroneutral region as

$$E = \frac{RT}{F} \frac{J_p/D_p - J_n/D_n}{2zc_p} \quad [13]$$

Alternatively, on using Eq. [12] to eliminate J_n from Eq. [11] and then combining Eq. [11] and [3] to eliminate E , one finds

$$J_p = D_s(\partial c_p/\partial x) + t_p I_f / zF \quad [14]$$

or, using Eq. [12] again and noting that $c_n = c_p$

$$J_n = D_s(\partial c_n/\partial x) - t_n I_f / zF \quad [15]$$

Here

$$D_s = 2D_n D_p / (D_n + D_p) \quad [16]$$

is the coupled diffusion coefficient, and $t_p = D_p/(D_n + D_p)$ and $t_n = 1 - t_p$ are the transport numbers of the positive and negative species, respectively.

As in the supported case, the concentration and other system variables can be separated into equilibrium and sinusoidally varying parts. Specifically, Eq. [4] can still be assumed to hold and, since I_{f1} does not vary with position, Eq. [6] and [7] become

$$i\omega c_{p1} = D_s(d^2c_{p1}/dx^2) \quad [6]$$

and

$$c_{p1} = A \sinh [(i\omega/D_s)^{0.5}x] \quad [7]$$

where again a symmetry argument has been used to eliminate one constant of integration.

The potential drop $V_{\text{appl},1}$ across the system is taken, in a segmented potential model (12), as the sum of the Nernstian potential difference, $V_{1,\text{int}}$, created by the concentration perturbations at the electrodes and given by Eq. [8], and the potential drop, $V_{1,\text{en}}$, across the electroneutral region, which can be obtained from Eq. [13]. When one then substitutes Eq. [14] and [15] into Eq. [13], linearizes, and

then integrates across the thickness d of the electrolyte, one finds

$$V_{1, \text{en}} = \frac{RT}{2zF c_{p0}} \left(\frac{D_s}{D_p} - \frac{D_s}{D_n} \right) [c_{p1}(-d/2) - c_{p1}(d/2)] + \frac{RT}{2z^2 F^2 c_{p0}} \left(\frac{t_p}{D_p} + \frac{t_n}{D_n} \right) I_{f1} d \quad [17]$$

so that

$$V_1 = \frac{-4RTt_n}{zF} A \sinh [(i\omega/D_s)^{0.5}(d/2)] + \frac{RT}{2z^2 F^2 c_{p0}} \left(\frac{t_p}{D_p} + \frac{t_n}{D_n} \right) I_{f1} d \quad [18]$$

To evaluate A in the present case, one may set $J_{p1} = I_{f1}/zF$ at $x = \pm d/2$, since the flow of negative charge is zero at the electrodes, and thus from Eq. [14]

$$D_s(d c_{p1}/dx) = t_n I_{f1}/zF \quad [19]$$

so that $A = -t_n I_{f1}/zF (i\omega D_s)^{0.5}$. Then, on taking the ratio $Z = V_1/I_{f1}$, one obtains the impedance

$$Z(\omega) = \frac{4RTt_n^2}{z^2 F^2 c_{p0} (i\omega D_s)^{0.5}} \tanh [(i\omega/D_s)^{0.5}(d/2)] + \frac{RTd}{z^2 F^2 c_{p0} (D_n + D_p)} \quad [20]$$

where the first term is a finite-length Warburg impedance and the second term may be recast, using the Einstein relations, as

$$R_\infty = d/[zF(c_{p0}\mu_p + c_{n0}\mu_n)] \quad [21]$$

the bulk resistance of the electrolyte. In the low-frequency limit, Eq. [20] reduces to $R_p = d/zF c_{p0}\mu_p$, the dc resistance of this system. In the high-frequency limit, the first term vanishes and Eq. [20] reduces to R_∞ .

In earlier work Buck (12) obtained the approximate result

$$Z(\omega) = [4RTt_n/z^2 F^2 c_{p0} (i\omega D_s)^{0.5}] \tanh [(i\omega/D_s)^{0.5}(d/2)] \quad [22]$$

in a treatment which parallels the present one but ignores (sets to zero) the last terms in Eq. [12], [14], [15], [17], and [18]. This result is identical to the first term in Eq. [20], with the single exception of the factor t_n which appears here to the first power rather than the second. While Eq. [22] reduces to R_p in the dc limit, it fails to yield R_∞ in the limit of high frequencies. Since Eq. [22] yields the proper behavior in the dc limit, we will refer to the approximations employed as the "quasi-static" electroneutral approach.

Unsupported Systems, Exact Treatment

In 1973, J. R. Macdonald obtained an exact solution (14) to a well-defined mathematical model of the small-signal ac response of a slab of unsupported electrolyte placed between two identical plane parallel electrodes. The model included Nernst-Planck and continuity equations for both negative and positive mobile charge, and involved full satisfaction of Poisson's equation and full consideration of the Maxwell displacement current throughout the electrolyte. The system was assumed to be free of intrinsic space charge layers in the absence of an applied potential difference, and allowance was made for a possible uniform background of immobile charge. In later work Macdonald and Franceschetti extended the model to allow the time-dependent generation and recombination of stationary and mobile charge (15). The electrode kinetics were incorporated through the assumption of boundary conditions of the Chang-Jaffé type

$$J_p = \pm k_p(c_p - c_{p0}) \quad [23]$$

with a similar condition for negative charges.

Although the Chang-Jaffé boundary conditions do not possess the same degree of physical realism as the equations of Butler-Volmer electrode kinetics, they lead to precisely the same form in the small-signal dc limit, and in the limit considered in this paper where the rate constant k_p becomes infinite (15). By making the rate constant complex and frequency-dependent, it is possible to take into account the occurrence of one or more adsorbed intermediate states for the discharging ion and to allow for the diffusion of a neutral product into the electrode or into the electrolyte (8, 16).

The full solution obtained by Macdonald is quite complicated, and Macdonald devoted several subsequent papers to exploring equivalent circuit representations of various limiting cases (16, 18). An important result (14, 18) in the present context was the first expression for Λ which involved arbitrary valence numbers, z_n and z_p , as well as arbitrary diffusion coefficients, D_n and D_p . In the condensed notation of the earlier work, the expression is $\Lambda = M^2 b \omega R_\infty C_g$. It can be readily expanded and becomes (19), on using the Einstein relation and the bulk electroneutrality condition, $z_n c_{n0} = z_p c_{p0}$

$$\Lambda = (\omega d^2/4) \left[\frac{D_n z_n + D_p z_p}{(D_n D_p)(z_n + z_p)} \right] = (\omega d^2 F/4RT) \left[\frac{\mu_n^{-1} + \mu_p^{-1}}{z_n^{-1} + z_p^{-1}} \right] \quad [24]$$

a result in full agreement with the Λ term implicit in Eq. [22] when $z_n = z_p = z$.

Franceschetti and Macdonald (15) obtained an approximate hierarchical ladder network circuit which was broadly applicable in the case in which only one of the mobile species reacts at the electrodes and the electrolyte thickness includes many Debye lengths. For the present case of equal charges and very fast electrode kinetics, this circuit reduces to three elements, the bulk resistance, Eq. [21], in series with the finite-length Warburg element, expressed in that work as

$$Z_w(\omega) = (R_\infty/\pi_m) \tanh (i\omega\tau_D H_N)^{0.5}/(i\omega\tau_D H_N)^{0.5} \quad [25]$$

the combination being in parallel with the geometric capacitance of the electrolyte

$$C_g = \epsilon/4\pi d \quad [26]$$

Here ϵ is the dielectric constant of the electrolyte, $\pi_m = \mu_n/\mu_p = D_n/D_p$ is the mobility ratio, $\tau_D = R_\infty C_g$ is the dielectric relaxation time, and

$$H_N = (d/4L_D)(\pi_m^{-1} + 2 + \pi_m)^{0.5} \quad [27]$$

where L_D is the Debye length

$$L_D = [\epsilon RT/8\pi F^2 z^2 c_{p0}]^{0.5} \quad [28]$$

for the present fully dissociated equivalent case.

Although Eq. [25], taken together with Eq. [27] and [28] bears no striking resemblance to the finite-length Warburg impedance derived in the previous section, we shall now show that the result is identical. Using the Einstein relations for μ_n and μ_p and the definition of D_s , Eq. [16], we can easily show that

$$H_N^2 = d^2(D_p + D_n)/(8L_D^2 D_s) \quad [29]$$

and then using Eq. [21], [25], and the Debye relation to relate τ_D to L_D , we find that

$$\tau_D H_N^2 = d^2/4D_s \quad [30]$$

With this substitution in Eq. [24], expressing R_∞ and π_m in terms of D_n and D_p and a little further manipulation, one finds that $Z_w(\omega)$ is now identical to the first term in Eq. [20]. Thus, with the exception of the geometric capacitance, which is frequently negligible in practice, the approximate circuit developed by Macdonald and co-workers from the full solution of the Nernst-Planck-Poisson equation system is, for a system of the type discussed here, with many Debye lengths between the electrodes and kinetically reversible electrodes, identical to that obtained in the previous section.

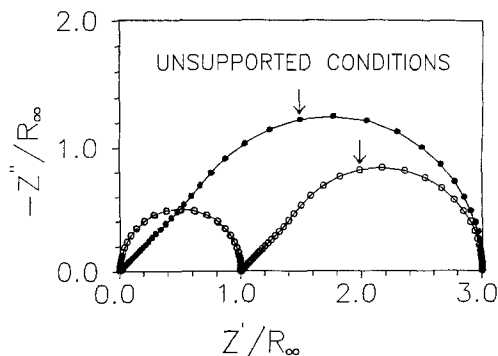


Fig. 1. Complex plane plots for system impedance calculated from "quasi-state" electroneutral approach (solid circles) and exact solution to Nernst-Plank-Poisson System (open circles). Here $D_n = 2D_p$ and impedance is plotted in units of R_∞ , Eq. [21]. The arrows indicate the frequency at which $\Lambda = \sqrt{10}$. Frequency increases by $10^{0.1}$ between neighboring plotted points.

Discussion

Although the approximate equivalent circuit developed from the exact solution of the unsupported case discussed above coincides with the result developed assuming bulk electroneutrality, it should be noted that the exact solution applies also in cases in which the electrode separation is less than or comparable to the Debye length. Bulk electroneutrality cannot then be assumed. Further, when the electrode reaction is not very fast, the use of the Nernst equation, as in Eq. [8], (which describes potential drops at thermal equilibrium) is not allowed. In addition, the quasi-static electroneutral treatment leads to incorrect behavior at high frequencies, as is shown in Fig. 1, where the impedance functions derived from the exact and quasi-static electroneutral treatments are compared for $D_n = 2D_p$.

In some very recent publications, Lorimer (20) and Pollard and Compte (21) discuss corrections to the electroneutral treatment arising from interactions between ions. Lorimer considers the coupling of ion fluxes and the diffusion of ion pairs. Pollard and Compte consider in addition the possible presence of an inert phase. While the corrections discussed by these authors may be important in specific situations, since both treatments assume electroneutrality their results cannot be considered valid for systems with electrode separations comparable or less than the Debye length. Further, the implication of Pollard and Compte that all earlier analyses of diffusion effects which use concentrations rather than activities, such as the present and nearly all earlier work, are only useful "in the limit of an infinitely dilute, single-phase electrolyte," should be put to the test of experiment. In actuality, the dilute approximation, which uses concentrations, is excellent for a great many real situations up to quite high concentrations, and it is rare in practice to find that a treatment using activities is indispensable.

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LIST OF SYMBOLS

c_i concentration of species i , mol/cm³
 C_g geometric capacitance of electrolyte per unit area, F/cm²

d thickness of cell, cm
 D_i diffusion coefficient of species i , cm²/s
 E electric field, V/cm
 F Faraday constant 96,487 C/equiv
 H_N dimensionless quantity related to mobility ratio, Eq. [27]
 I electric current density, A/cm²
 J_i flux density of species i , mol/cm² s
 k_i electrode reaction rate constant, mol/cm/s
 L_{diff} diffusion length, cm
 L_D Debye length, cm
 M electrode metal
 R universal gas constant, 8.3144 J/mol K
 R_∞ electrolyte resistance per unit area, Ω cm²
 t time, s
 t_i transference number of species i
 T absolute temperature, K
 V electrical potential difference, V
 x position within cell, cm
 Z impedance per unit area, Ω cm²

Greek letters

Λ dimensionless multiple of angular frequency, Eq. [1]
 μ_i electrical mobility of species i , cm²/V s
 π_m mobility ratio μ_n/μ_p
 τ_D dielectric relaxation time, s
 ω angular frequency, rad/s

Subscripts

f faradaic
n negative species, anion
p positive species, cation
s coupled, positive and negative
W Warburg
0 steady-state component
1 sinusoidally varying component
appl applied
en electroneutral
int interfacial

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