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PRELIMINARY NOTE

Equivalent circuits for the binary electrolyte in the Warburg region

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The question of the most appropriate equivalent circuit to use in analyzing impedance measurements for a given electrolytic cell situation is an important one which is currently attracting renewed interest[1–5]. An incorrect choice can lead to misleading conclusions about the processes occurring in the cell. In this note, I shall consider only a cell containing a binary electrolyte; thus no supporting indifferent electrolyte is added, and only two mobile charge types of opposite sign are present. The results should apply not only to dissociated charge in liquid solvents but also to many fused salt and solid material situations.

In a recently published paper[6], a quite general exact microscopic theory of the impedance of a binary-charge system is presented which allows the charges to have arbitrary mobilities, μ_n and μ_p, and arbitrary valence numbers, z_n and z_p. The situation analyzed includes extrinsic as well as intrinsic conduction; here, however, only intrinsic will be considered. This treatment involves the usual boundary condition dimensionless parameters r_p and r_n. When one of these is zero, the electrode is blocking (ideally polarized) for the charge type involved; alternatively, when $r_n = \infty$, say, negative charges discharge and/or appear at the electrode (first-order reaction) without perturbing the steady-state concentration there, equivalent to an infinite reaction rate for the charges involved. Although r_p and r_n do not allow the possibility of rectification, they do cover the entire range of conditions from complete blocking to infinite reaction rates and are thus relatively general.

Because of the complexity of the closed-form analytical results of the above theory, only the zero-frequency limiting values of the frequency-dependent capacitance, C_i, and resistance, R_i, were examined in detail in ref. 6. A further paper is in preparation which discusses the frequency response of the overall cell impedance and admittance components in detail for all frequency regions of interest for the intrinsic conduction situation[7]. The analysis of the Warburg response region, one of the main regions of usual electrolytic interest, has yielded several unexpected results which seem likely to explain a considerable body of experimental measurements and thus warrant this preliminary discussion. It is important to mention, however, that the theoretical results follow from a linearized theory[6] and thus apply most appropriately when the equilibrium potential is coincident with that for zero net electrode charge. Thus, an alternating potential small compared to (RT/F) is applied to perturb slightly the equilibrium state of the system. Nevertheless, it is likely that the present results will apply qualitatively or possibly even semi-quantitatively for an appreciably wider static potential span around equilibrium.

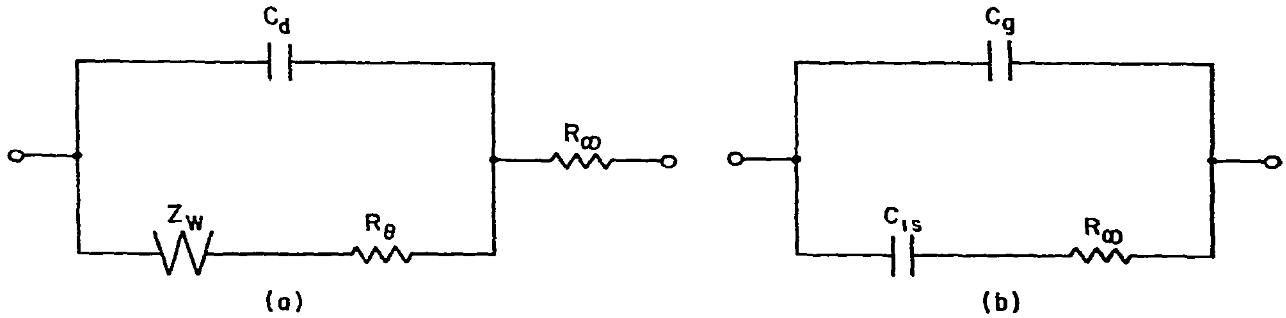

Fig. 1. (a) Conventional equivalent circuit for a Warburg frequency response region without specific adsorption. (b) Approximate binary-charge-situation equivalent circuit for the saturation frequency region which follows Warburg response when it occurs.

Figure 1a shows the usual Randles[8] equivalent circuit for a simple cell without specific ionic adsorption. As usual, a small working and a large indifferent counter electrode are considered. The circuit thus applies primarily to the working electrode. Here C_d is the double-layer capacitance (all quantities will be considered for unit electrode area), R_∞ the solution resistance, R_θ the charge transfer resistance, and Z_W a Warburg impedance,

$$Z_W \equiv A_0(1 - i)/\sqrt{\omega} \tag{1}$$

arising from a linear diffusion process. Here A_0 is the Warburg parameter, $i \equiv \sqrt{-1}$, and ω is the radial frequency. Unfortunately, while this circuit has seen yeoman service in the past, it has usually been applied indiscriminately to both supported and unsupported electrolyte situations. As we shall see, to the degree that the present results[6,7] are applicable, the circuit is inappropriate for a binary unsupported situation.

Current work on the binary case shows that the overall total cell admittance or impedance exhibits explicit approximate Warburg behavior *only* when (a) charges of one sign are completely or nearly completely blocked, and (b) charges of opposite sign are relatively free to discharge and, as well, have *much* lower mobilities than do the blocked charges. Such strongly different mobilities are unnecessary to allow the basic frequency-dependent impedance Z_i appearing in the theory[6] to exhibit Warburg response but are necessary to allow such Warburg behavior to be reflected in the externally measured impedance.

Let us adopt the nomenclature used in the earlier work[6] to represent a specific binary electrolyte situation: $(r_p, r_n; \pi_m, \pi_z; 0, M)$. Here π_m is the mobility ratio μ_n/μ_p; π_z is the valence number ratio z_n/z_p; and $M \equiv l/2L_D$. Since L_D is the ordinary Debye length, M measures the number of Debye lengths contained in half the distance l between electrodes (taken place, parallel and identical in the theory). In most cases of interest, $M \gg 10^2$, a condition assumed to hold here although the full theory applies for any M. Thus, a condition for external Warburg behavior might be written $(0, r_n; \pi_m, \pi_z; 0, M)$, where $\pi_m \ll 10^{-2}$, $r_n \gg 1$, and π_z is arbitrary but usually limited to the range $0.25 \leqslant \pi_z \leqslant 4$ by available ionic valences. An entirely equivalent situation as far as external impedance is concerned is[6] $(r_p, 0; \pi_m^{-1}, \pi_z^{-1}; 0, M)$. Note that for both cases the reacting carrier has much lower mobility than does the blocked carrier.

Now the usual expression for A_0 applying for a single working electrode when oxidizing and reducing species (diffusion coefficients D_O, D_R; concentrations c_O and c_R) are present at the electrode may be written at the equilibrium potential as[8–10]

$$A_0^{-1} = \left(\frac{\sqrt{2}n^2F^2}{RT}\right)\left\{\frac{\nu_O^2}{c_O\sqrt{D_O}} + \frac{\nu_R^2}{c_R\sqrt{D_R}}\right\}^{-1} \tag{2}$$

Here n is the number of electrons participating in the reaction, and ν_O and ν_R are the stoichiometric factors of the electrochemically active species in the overall electrode reaction[10]. Calculations leading to results of this type have, heretofore, always been carried out, either explicitly or implicitly, for a supported electrolyte situation; thus, no direct electrical interaction between active species has been assumed.

The present work[6] shows that in the unsupported case Poisson's equation leads to extremely strong coupling between positive and negative mobile charge and thus, in the Warburg situation, between blocked and reacting charges. For this reason, results such as that of eqn. (2) are inapplicable, in general, to the unsupported case. In the present charge transfer unsupported situation, we deal with faradaic conduction for the reacting species. As Grahame pointed out long ago, a faradaic process is one which allows a continuous current to flow[11]. Thus, when such a process is present one would expect that the appropriate equivalent circuit would have to contain a frequency-independent resistive path between electrodes. The circuit of Fig. 1a contains no such path nor do most previous equivalent circuits for partly blocking electrochemical situations. Such a path, represented by a resistance R_D, does arise naturally, however, as part of the present theoretical treatment[6]. A typical situation might be that represented by the cell Ag|AgF(aq.)|Ag. During one half cycle of an applied sinusoidal potential, Ag^+ is created at one electrode and the discharge process $Ag^+ + e^- \rightarrow Ag$ occurs at the other. During the next half cycle, these processes are reversed.

Let us now define $g_p \equiv 1 + (r_p/2)$ and $g_n \equiv 1 + (r_n/2)$ and take p_i and n_i as the bulk concentrations of the positive and negative mobile charges. In a neutral bulk region, electroneutrality requires $z_p p_i = z_n n_i$. Theory for the unsupported situation leads, for a single working electrode, to[6,7] where $D_i = (RT/Fz_i)\mu_i$, and we have written $(z_n n_i + z_p p_i)/2$ rather than $z_n n_i$ or $z_p p_i$ for the sake of symmetry.

$$A_0^{-1} = \left(\frac{\sqrt{2}F^2}{RT}\right)\left(\frac{g_p - g_n}{g_p g_n}\right)^2\left(\frac{z_n n_i + z_p p_i}{2}\right)\left[\left(\frac{1}{z_p D_p} + \frac{1}{z_n D_n}\right)\left(\frac{1}{z_p} + \frac{1}{z_n}\right)\right]^{-1/2} \tag{3}$$

For external Warburg behavior let us hereafter take, for example, positive charges blocked, negative charges free to react. Then $g_p = 1$ and usually $g_n \gg 1$. Thus, the term $[(g_p - g_n)/g_p g_n]^2$ will be very close to unity and may frequently be neglected. When $z_n = z_p \equiv z_e$, the above result simplifies appreciably and we obtain

$$A_0^{-1} \cong \left(\frac{z_e F^2 c_i}{RT}\right)\left[\frac{1}{D_p} + \frac{1}{D_n}\right]^{-\frac{1}{2}} \tag{4}$$

where c_i is the common value of p_i and n_i in this situation. Although this result shows some similarity to that of eqn. (2) with $|\nu_O| = |\nu_R| = 1$, appreciable differences are apparent. Let us now also take $D_O = D_R = D = D_n = D_p$, $c_O = c_R = c_i$, and $z_e = n$. Then both (2) and (4) lead to the often used expression

$$A_0^{-1} = n^2 F^2 c_i \sqrt{D/2}/RT \tag{5}$$

Note, however, that the c_i appropriate for the unsupported binary situation is defined in the bulk, *not* at the reacting electrode as required by Vetter[12] for the usual supported case.

Next, since it is necessary that $\pi_m \ll 10^{-2}$ for external Warburg response in the unsupported situation $(0, r_n; \pi_m, \pi_z; 0, M)$, $D_n \ll D_p$ and eqn. (3) reduces to

$$A_0^{-1} \cong \left(\frac{\sqrt{2} z_n^2 F^2 n_i}{RT}\right)\left(\frac{g_p - g_n}{g_p g_n}\right)^2 \left[\delta_p D_n\right]^{\frac{1}{2}} \tag{6}$$

where

$$\delta_p \equiv (1 + \pi_z)^{-1} = z_p/(z_p + z_n) \tag{7}$$

Note that no Warburg response occurs when $r_p = r_n$ and thus $(g_p - g_n) = 0$. Appreciable response thus requires $r_n \gg r_p$ or $r_p \gg r_n$.

Finally, appropriate equivalent circuits for the unsupported situation will be considered for the case of two identical, plane parallel electrodes. Define the basic normalized frequency Ω as $\Omega \equiv \omega\tau_D$, where the dielectric relaxation time τ_D is given by $C_g R_\infty$. R_∞ has already been defined and $C_g \equiv \epsilon/4\pi l$ for two identical plane parallel electrodes[1,6]. Here ϵ is the dielectric constant of the basic bulk material in the absence of mobile charge. The quantity τ_D is intensive (not a function of l) just as it should be. Obvious changes in the magnitudes of the intensive circuit elements may be made in order to transform the present results to a single working electrode situation. When plane parallel electrodes are not employed, C_g and R_∞ may either be calculated for the actual geometry used or be measured directly, if practical, at sufficiently high frequencies that these elements dominate the overall equivalent circuit of the cell, *i.e.* $\Omega > 0.1$.

For an external Warburg case such as $(0, r_n; \pi_m, \pi_z; 0, M)$ with $r_n \gg 1$, $M \gg 10^2$, and $\pi_m M < 1$, it has been found[7] that the overall cell impedance shows approximate Warburg behavior over an appreciable frequency span contained in the range $10 M^{-2} < (\Omega/\pi_m) < 1$. For $\Omega < 10\,\pi_m M^{-2}$, the overall parallel capacitance of the circuit, C_P, saturates at the very high limiting value $C_{P0} \equiv C_g + C_{i0} \gg C_g$, where a general expression for C_{i0} has recently been given[6]. For the range $10\pi_m \lesssim \Omega \leqslant 0.1$, on the other hand, the capacitative element of Z_i, C_i, maintains an essentially constant plateau value, C_{iS}, given in the plane parallel electrode case by[7]

$$C_{iS} \cong (M\sqrt{\delta_p} - 1)C_g \cong M\sqrt{\delta_p}C_g = (\epsilon/8\pi)[4\pi F^2 z_p{}^2 p_i/\epsilon RT]^{1/2} \tag{8}$$

The total parallel capacitance C_P only remains at the value $C_{PS} \cong C_g + C_{iS} \cong M\sqrt{\delta_p}C_g$ over the range $10\pi_m \lesssim \Omega \lesssim (10M\sqrt{\delta_p})^{-1}$, however.

Now it turns out[1,6] that for the complete blocking situation ($r_p = r_n = 0$) the low frequency limiting value of C_i is $C_{i0} = (M - 1)C_g$, so that $C_{P0} = MC_g$ is just the ordinary double-layer capacitance of two interface regions in series (two identical plane parallel electrodes). For $\pi_m \ll 10^{-2}$, $M \gg 10^2$, and Ω outside the low-frequency limiting region, there is a transition from C_{i0} to $C_{iS} \cong (M\sqrt{\delta_p} - 1)C_g$, the same value as found above. In addition, C_P again remains at the plateau value C_{PS} in the region $10\pi_m \lesssim \Omega \lesssim (10M\sqrt{\delta_p})^{-1}$ which may be appreciable when $\pi_m M \ll 1$, then finally falls toward C_g for $\Omega \gtrsim (M\sqrt{\delta_p})^{-1}$. In the plateau region the results are independent of the value of r_n (insufficient time for electrode reactions involving the low mobility negative charges to manifest themselves) and thus of whether charges of both signs are completely blocked or not. An approximate equivalent circuit for this region is shown in Fig. 1b. It applies for both (0, 0) and (0, r_n) cases when $\pi_m M \ll 1$. In the present $\pi_m \ll 1$ case, the plateau value C_{PS} may thus be considered the effective double layer capacitance rather than C_{P0}.

The necessary resistance R_D connecting the two electrodes in the $r_n > 0$ case[1,6,7] has been omitted here since it is always very much greater than R_∞ in the present case when $\pi_m \ll 10^{-2}$. Note that the bridging capacitance C_g appearing in Fig. 1b should also appear between the two electrodes in Fig. 1a. It has customarily been omitted from circuits of this type[4], although it is of crucial importance in the high frequency range $\Omega > 0.1$.

When the exact expression for Z_i given earlier[6] is simplified[7] for the external Warburg range and combined with the exact equivalent circuit of the situation[2,6], one may

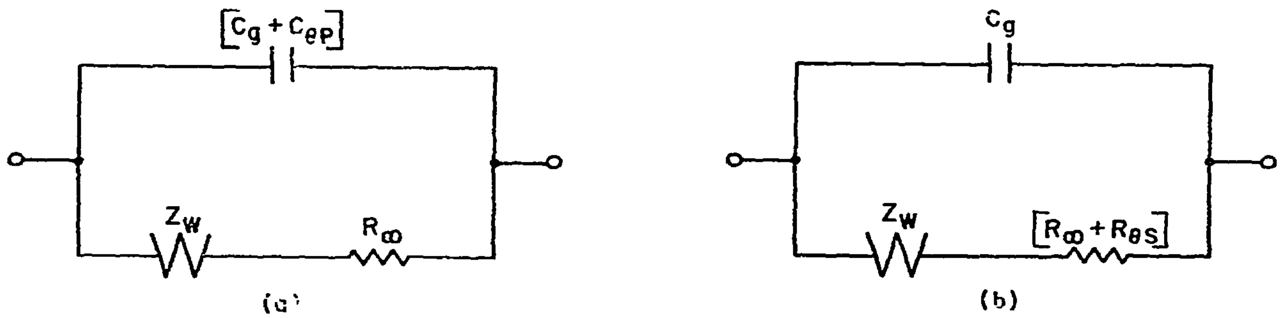

Fig. 2. Approximate equivalent circuits for the binary-charge-situation in the external Warburg frequency region.

derive two good approximate circuits for this frequency range in the unsupported case[7]. These almost equally valid circuits are shown in Fig. 2a and 2b. The Warburg impedance present in these circuits involves, for two identical plane parallel electrodes, the $A_0{}^{-1}$ given in eqn. (6) divided by two, to high approximation. Further, the elements $C_{\theta P}$ and $R_{\theta S}$ are frequency independent to good approximation over most of the external Warburg range. In the first of these circuits R_D has cancelled out almost completely in this frequency range; in the second circuit it has been neglected compared to the usually much smaller $[R_\infty + R_{\theta S}]$. A slightly more accurate version of the circuit of Fig. 2a involves $C_{\theta P}$ connected between the left electrode and the *left* terminal of R_∞ (compare Fig. 1a). When $\pi_m M \ll 1$, the usual case of interest, the magnitude of the impedance of $C_{\theta P}$ is so much larger than R_∞ in the external Warburg region, however, that the connection shown is adequate.

Comparison of Figs. 1a, 2a, and 2b yields some interesting conclusions. First, it is clear that an appreciable parallel capacitance, such as the double layer C_d of Fig. 1a and a series reaction resistance, such as the R_θ of that figure, do *not* appear together simultaneously in the same equivalent circuit for the unsupported Warburg case. It is an either/or situation.

The new quantities $C_{\theta P}$ and $R_{\theta S}$ are of particular interest. Let us consider their frequency-independent approximate constant values, C_{CP} and R_{CS}, in the Warburg region. First, these quantities are not independent but are connected by the relation

$$R_{CS} = -2 A_0{}^2 C_{CP} \tag{9}$$

where, for two identical plane parallel electrodes, A_0 here is twice that following from eqns. (3) or (6). One then has the rather shocking result that C_{CP} and R_{CS} cannot both be positive simultaneously!

It further turns out that C_{CP} and R_{CS} are made up of the difference of two frequency-independent terms. When $r_n = \infty$ (infinite reaction rate), one of these terms disappears, since it is approximately proportional to $g_n{}^{-1}$, and

$$C_{CP} = \delta_P{}^2 (M - 1) C_g \tag{10}$$

Note that $\delta_P = 0.5$ when $z_n = z_p$. It is clear that when $M \gg 10^2$, $C_{\theta P} \cong C_{CP}$ is essentially intensive, as it should be to be associated just with interface processes. It is *not*, however, equal to the $r_n = r_p = 0$ double-layer capacitance, either MC_g or C_{PS}. Now the corresponding R_{CS}, appearing in the circuit of Fig. 2b, although also intensive is negative for this situation (of course the total series resistance of the $R_{\theta S}$ branch is never negative). A good approximate expression for R_{CS} applicable for $r_n = \infty$ is

$$R_{CS} \cong -(\delta_p/\delta_n M \pi_m) R_\infty \tag{11}$$

where

$$\delta_n \equiv 1 - \delta_p \equiv (1 + \pi_z{}^{-1})^{-1} = z_n/(z_p + z_n) \tag{12}$$

Note that $|R_{CS}|$ can greatly exceed R_∞ if $\pi_m M \ll 1$.

Finally, it turns out that at $r_n \cong (2\delta_n M/\delta_p)$ the two terms of R_{CS} and C_{CP} are equal and opposite; $R_{\theta S}$ and $C_{\theta P}$ thus remain very near zero over a very appreciable frequency region; and, in this region, the overall impedance shows very nearly ideal Warburg response when the small effect of R_∞ has been removed. Usually, such ideal behavior is expected to occur for infinite reaction rate ($R_\theta = 0; r_n = \infty$). Here, it occurs instead at $R_{\theta S} \simeq 0$ but at a specific finite rate!

On the other hand, when $100 \lesssim r_n \ll 2\delta_n M/\delta_p$, the second term in R_{CS} and C_{CP} becomes dominant. Surprisingly, this term is extensive, *not* intensive. When it is strongly dominant

$$R_{CS} \cong 2R_\infty/\pi_m r_n \tag{13}$$

and

$$C_{CP} \cong -2M^2 \delta_n \delta_p C_g/r_n \tag{14}$$

Note that R_{CS} can easily be much larger than R_∞ and that $|C_{CP}|$ can be much larger than MC_g or $\sqrt{\delta_p}MC_g$. When $r_n \ll 2\delta_n M/\delta_p$, so the second term is dominant, it may be difficult to separate R_∞ and $R_\infty + R_{\theta S} \simeq R_\infty + R_{CS}$, since $R_{\theta S}$ will depend on l and concentration exactly as does R_∞ itself! Separation of R_∞ and $R_{\theta S}$ can, of course, be accomplished through measurements at $\Omega > 0.1$ where only R_∞ and C_g are important. Alternatively, since $R_{\theta S}$ decreases rapidly in the C_{1S} plateau saturation region, R_∞ can also be obtained from measurements in the range $\Omega \gg \pi_m$ as well (see Fig. 1b).

It is believed that the present theory[6,7] may explain a large body of experimental measurements on binary charge systems. While it is not pertinent to make detailed experimental–theoretical comparisons here rather than in ref. 7, it is worth mentioning, as an example, that the general extrinsic theory[6] and perhaps some of the results of the present work may explain most of the recent impedance results of Armstrong *et al.*[13] on sodium β-alumina. Their probable application to earlier β-alumina work[14], not cited by Armstrong, has already been considered[15]. Armstrong suggests that the effective surface area of his rough-disc samples was 10^2 to 10^3 times geometric and increased by about a factor of ten from 150 to 300 °C. While variation of surface area much greater than geometric with temperature may indeed have played a role in leading to Armstrong's results, it seems more likely that much of the apparent larger area and its temperature dependence may instead be associated with more nearly geometric area and a large Warburg-type pseudo-capacitance, which, in fact, can increase strongly with increasing temperature[6,15].

In summary, in the unsupported binary electrolyte situation: (a) The conventional Randles equivalent circuit is inapplicable. (b) External Warburg response only occurs if charge of one sign is blocked or is almost blocked and charge of the other sign reacts appreciably at an electrode but has much lower mobility than that of the blocked charge. (c) An apparent double-layer capacitance and an apparent reaction resistance must not appear simultaneously in the same equivalent circuit. (d) The apparent double-layer capacitance is always algebraically less than the true double-layer capacitance and may be large and negative. (e) The apparent reaction resistance may be positive or negative and may be appreciably larger in magnitude than the solution resistance R_∞. Further, since it is extensive and proportional to R_∞ when large and positive, it may easily be confused with R_∞. And, finally, (f) ideal Warburg response does not occur at an infinite reaction rate.

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