THE IMPEDANCE OF A GALVANIC CELL WITH TWO PLANE–PARALLEL ELECTRODES AT A SHORT DISTANCE

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LIST OF SYMBOLS

C_g	$\varepsilon/4\pi l$; geometric capacitance/unit area (μF cm^{-2})
C_0	Total low-frequency limiting capacitance/unit area (μF cm^{-2})
D	Diffusion coefficient when $D_p = D_n \equiv D$ (cm^2 s^{-1})
D_n	Diffusion coefficient for negative charge carriers (cm^2 s^{-1})
D_p	Diffusion coefficient for positive charge carriers (cm^2 s^{-1})
F	The faraday (C mol^{-1})
L_D	$[\varepsilon kT/4\pi e^2(z_n^2 n_0 + z_p^2 p_0)]^{\frac{1}{2}}$; binary electrolyte Debye length (cm)
M	$l/2L_D$; number of Debye lengths in a half cell length
R	Gas constant (V C K^{-1} mol^{-1})
R_D	$M^{-1}R_\infty$ (Ω cm^2)
R_∞	$l/e(z_n n_0 \mu_n + z_p p_0 \mu_p)$; bulk resistance-unit area (Ω cm^2)
T	Absolute temperature (K)
Z_D	$(i)^{-\frac{1}{2}} \tanh(Ms)$; normalized impedance
Z_F	$(\Omega)^{\frac{1}{2}} Z_{iM}/4$; normalized impedance
Z_i	"Interface" impedance-unit area (Ω cm^2)
Z_T	Total system impedance-unit area (Ω cm^2)
c_0	Equilibrium homogeneous bulk concentration of positive and negative charge carriers when $z_p = z_n$ (cm^{-3})
e	Protonic charge (C)
i	$(-1)^{\frac{1}{2}}$
k	Boltzmann's constant (V C K^{-1})
l	Distance of separation of two plane, parallel electrodes (cm)
l_d	Diffusion length; for $z_p = z_n \equiv 1$ and $D_p = D_n \equiv D$ equal to $(D/\omega)^{\frac{1}{2}}$ (cm)
n_0	Equilibrium homogeneous bulk concentration of negative charge carriers (cm^{-3})
p	$(1+s^2)^{\frac{1}{2}}$
p_0	Equilibrium homogeneous bulk concentration of positive charge carriers (cm^{-3})
s	$(i\Omega)^{\frac{1}{2}}$
z_n	Valence number for negative charge carriers ($z_n > 0$)
z_p	Valence number for positive charge carriers ($z_p > 0$)
Λ	$l/2l_d$; number of diffusion lengths in a half cell length; for $z_p = z_n \equiv 1$ and $D_p = D_n \equiv D$ equal to $M|s| = [M^2\Omega]^{\frac{1}{2}} = (l/2)(\omega/D)^{\frac{1}{2}}$

Ω $\omega\tau_D$; basic normalized frequency variable

ε Dielectric constant of solvent plus solute

μ Mobility when $\mu_p = \mu_n \equiv \mu$ $(cm^2\ V^{-1}\ s^{-1})$

μ_n Mobility of the negative charge carrier $(cm^2\ V^{-1}\ s^{-1})$

μ_p Mobility of the positive charge carrier $(cm^2\ V^{-1}\ s^{-1})$

τ_D $C_g R_\infty$; dielectric relaxation time (s)

ψ Phase angle of an impedance

ψ_D Phase angle of Z_D

ψ_F Phase angle of Z_F

ω Radial frequency (s^{-1})

Subscript M   Designates normalization with R_D

Subscript N   Designates normalization with R_∞

Subscript 0   Designation of (0,0) binary electrolyte case

Subscript 1   Designation of $(0,\infty)$ binary electrolyte case

Subscript 2   Designation of Sluyters' supported electrolyte case

INTRODUCTION

Some time ago, Sluyters[1] treated the subject of the title theoretically and experimentally. In his analysis he implicitly assumed the presence of an excess of unstirred indifferent electrolyte and thus separately solved Fick's second law of diffusion for each component of a redox couple, present in low concentration. This approach, while adequate for the experimental situation he investigated, does not result in the exact satisfaction of Poisson's equation in the cell, and ignores electromigration[2], the geometrical capacitance of the cell, C_g, and the high-frequency-limiting bulk resistance, R_∞ (arising from the redox components). Soon after Sluyters' work, Drossbach and Schulz[3] independently treated much the same problem with the same approximations.

Sluyters was particularly concerned with the dependence of the total (small-signal) cell impedance, Z_T, arising from the redox process, upon electrode separation distance, l (denoted a by Sluyters), of his parallel electrodes. He thus considered only fixed-frequency conditions. For sufficiently close spacing, the magnitude of the impedance and the magnitude of its phase angle, ψ, both increased linearly with increasing spacing, as might be expected. This extensive behavior disappeared as l further increased, with both $|Z_T|$ and $|\psi|$ reaching maximum values, then decreasing slightly to final, constant, intensive (independent of l) values in the Warburg impedance region. Here, of course, the limiting phase angle was the usual Warburg $\psi = -45°$.

Since Warburg behavior has recently been identified in two-electrode situations where *no* supporting electrolyte is present even for ideally polarized electrodes[4], it seems of interest to compare total impedance results for this case with those of Sluyters and Drossbach. Two situations have been investigated for equal bulk-region equilibrium concentrations of univalent positive and negative ions having equal diffusion coefficients[4] (these restrictions are partly removed later in the paper). In the first situation, designated by (0, 0), both electrodes were taken as ideally polarizable in the region of operation. In the second, the $(0, \infty)$ case, positive charges were assumed, as before, to remain completely blocked at both electrodes while negative charges were taken as free to pass into and out of both electrodes without impediment (infinitely fast, first-order electrode reaction).

These two treatments involved solving the full transport equations and Poisson's equations exactly, and thus did not neglect electromigration, geometrical capacitance, and cell resistance. Further, for simplicity the charge distributions were taken uniform in the absence of the small applied sinusoidal potential, and inner-layer complications were ignored. The results thus apply most closely at the equilibrium potential when it is coincident with the potential of zero charge; approximate applicability when these restrictions are relaxed has also been discussed[4]. No applied static potential was thus included in the theoretical analysis—the situation also investigated theoretically and experimentally by Sluyters[1].

On the other hand, Levart and Schuhmann[5] have recently treated nearly the $(0,\infty)$ case (for a single electrode) in an approximate manner which allows consideration of appreciable overpotentials. Their system includes only electroactive ions of one species and associated counter-ions. Unfortunately, among their approximations is the neglect of mutual interaction of the ions (neglect of Poisson's equation), an important factor when no supporting electrolyte is present. Levart and Schuhmann point out that there has been a renaissance of interest in investigations of electrolysis in the absence of a supporting electrolyte, and they give many relevant references. An example of a situation where the present $(0,\infty)$ boundary condition might be quite applicable in an electrolytic situation with no supporting electrolyte is electrorefining, as in the cell $Cu\,|\,Cu(NO_3)_2(aq)|\,Cu$, where the anionic species is blocked.

Finally, it is worth mentioning that a theoretical treatment of the impedance in the absence of a supporting electrolyte (for a two-electrode, blocking situation), calculated from appropriate transport equations and involving exact satisfaction of Poisson's equation, dates back to 1953 at least[6]. This treatment, like almost all that have followed it, does, however, make the approximation of ignoring any change of transport properties, such as diffusion coefficients, with position and concentrations in the electrolyte.

ANALYSIS RESULTS

The total impedance results for the various cases can be expressed and compared most economically and generally in normalized form. First, define the normalized frequency $\Omega \equiv \omega\tau_D$, where ω is the radial frequency of the applied sinusoidal signal, and τ_D, the dielectric relaxation time, is $C_g R_\infty$. We shall express all impedances and their components for unit electrode area. In the present uni-univalent, equal-diffusion-coefficient case $(D_n = D_p \equiv D)$, then $R_\infty = l/(2e\mu c_0)$, where c_0 is the common equilibrium bulk concentration of positive and negative ions (redox components), and $\mu = (e/kT)D \equiv (F/RT)D$. Here e is the protonic charge.

Next define the important ratio $M = (l/2)/L_D$, the number of Debye lengths contained in a half cell length. In the present case, $L_D \equiv (\varepsilon kT/8\pi e^2 c_0)^{\frac{1}{2}}$, where ε is the dielectric constant of the bulk material (solvent plus solute, but usually dominated by solvent). Note that the geometrical capacitance per unit area is just $\varepsilon/4\pi l$, where the unit-area designation will be ignored from now on for simplicity. Another most important ratio is $\Lambda \equiv (l/2)/l_d$, the number of diffusion lengths contained in $(l/2)$. Since l_d is defined[4] as $(D/\omega)^{\frac{1}{2}}$, it follows that $\Lambda \equiv (l/2)(\omega/D)^{\frac{1}{2}} \equiv [M^2\Omega]^{\frac{1}{2}}$, a frequency and separation-length dependent quantity.

We shall begin by normalizing all impedances with R_∞ [$2R_\infty$ was used for the

$(0, \infty)$ case in earlier work[4]]. Let the subscript "N" indicate such normalization. Also let $s^2 \equiv i\Omega$ and $p^2 \equiv 1 + s^2$, and note that $Ms = i^{\frac{1}{2}} \Lambda = (\Lambda/2^{\frac{1}{2}})(1 + i)$. Then, for the completely-blocking $(0, 0)$ case, earlier results[4,6,7] lead to

$$Z_{TN} \equiv Z_T/R_\infty = Z_{TN0} \equiv [\tanh(Mp) + Mps^2]/(Mp^3 s^2)$$
$$= [Ms^2 p^3 \coth(Mp)]^{-1} + [p^2]^{-1} \tag{1}$$

The corresponding result for the $(0, \infty)$ case, following from previous work[4], may be put in the similar instructive form

$$Z_{TN} = Z_{TN1} \equiv \{Msp^3[p \coth(Ms) + s \coth(Mp)]\}^{-1} + [p^2]^{-1} \tag{2}$$

Finally, it turns out that Sluyters' impedance can be expressed in a considerably simpler form than he gave. For the present equal-diffusion-coefficient, uni-univalent case with equal bulk concentrations of redox couple components, we find

$$Z_{TN} = Z_{TN2} \equiv [4 \tanh(Ms)]/(Ms) \tag{3}$$

Drossback and Schulz[3] obtained almost the same result (when normalization is carried out) but with the factor of four replaced by unity. They considered, however, only a region from $x = 0$ to $x = l/2$ (termed d by these authors) and only a single active ionic component. A *tanh* term of somewhat similar complex argument (but involving a Nernst diffusion layer instead of electrode separation) appears in the results of Levart and Schuhmann[5].

COMPARISON OF FREQUENCY-DEPENDENCE RESULTS

(0, 0) and (0, ∞) Impedances

Elsewhere[4], the normalized impedances Z_{TN0} and Z_{TN1} (or their equivalents) have been analyzed into individual circuit elements having minimum frequency response, and the equivalent circuits applying in various normalized frequency regions have been examined in detail. Here these circuits may be subsumed as in Fig. 1. The

(a)   (b)

Fig. 1. Equivalent circuits for: (a) $(0, 0)$ blocking case, (b) $(0, \infty)$ discharge case; no indifferent electrolyte present in either case.

two different $(0, 0)$ and $(0, \infty)$ Z_i impedances[4] generally consist, in their simplest form, of a frequency-dependent capacitance and a frequency-dependent resistance in series. $|Z_i|$ approaches infinity as $\Omega \rightarrow 0$ and zero as $\Omega \rightarrow \infty$. In intermediate ranges for the $(0, \infty)$ case, Z_i involves both usual and unusual Warburg response[4].

Fig. 2. Complex impedance plane representation of the $(0, 0)$ and $(0, \infty)$ total normalized impedances for $M = 10^3$, with the parametric frequency variables Ω and Λ.

In Fig. 2, the $(0, 0)$ and $(0, \infty)$ quantities Z_{TN0} and Z_{TN1} are plotted in the complex impedance plane [with $-Im(Z_{TN})$ taken in the conventional way for the positive ordinate scale] with the parametric variables Λ and Ω. The Ω values are shown outside, and the Λ values inside, the bonding lines. The results of Fig. 2 have been calculated for $M = 10^3$, and the rest of the discussion will apply primarily to the $M \gtrsim 100$ situation, for which there is no separate dependence of Z_{TN1} and Z_{TN2} on M, only dependence on the $\Lambda \equiv |Ms| \equiv M \Omega^{\frac{1}{2}}$ and Ω variables. For most electrolytic cells and solute concentrations of interest, $M \gg 100$.

Figure 2 shows that the p^{-2} term in (1) and (2) leads to simple Debye dispersion involving the normalized frequency variable Ω, for both the $(0, 0)$ and $(0, \infty)$ cases in the region $0.1 \lesssim \Omega < \infty$. For the large-$M$ case considered here, the results in this region are completely independent of M and arise solely from the parallel combination of C_g and R_∞. In the more usual case of a supporting electrolyte of high concentration, the cell resistance is so low that the frequency corresponding to $\Omega \sim 1$ (*i.e.* $\omega \sim \tau_D^{-1}$) is far above the practical measurement region, and this p^{-2} dispersion is never seen. In the present case of no indifferent electrolyte, however, R_∞ may be so large that $\Omega \sim 1$ occurs in a readily measurable frequency region. When $\Omega = 1$, the diffusion and Debye lengths are equal and also the magnitude of the capacitative reactance of C_g is equal to R_∞.

Note that as Ω decreases much below 0.1, the total normalized impedance in the ideal polarized electrodes case, Z_{TN0}, approaches $1 + (iM\Omega)^{-1}$. It thus depends on the variable $M\Omega \equiv \Lambda \Omega^{\frac{1}{2}}$ in this range, rather than on Λ or Ω separately. For $\Omega < 1$, we earlier found[4,6,7] that, to good approximation, $Z_{iN} \to [(2M)^{-1} + \{i\Omega(C_0 - C_g)/C_g\}^{-1}]$, with $(C_0 - C_g)/C_g = \{M \coth(M) - 1\}$. For large M, Z_i thus approaches just the intensive low-frequency limiting capacitance $MC_g \equiv \varepsilon/8\pi L_D$ for $0 \le \Omega < 1$. Note that the usual diffuse-double-layer capacitance associated with a *single* blocking electrode is just $\varepsilon/4\pi L_D$. Here C_0 is, of course, the full low-frequency limiting capacitance of the

complete two-electrode system. The circuit of Fig. 1a, with Z_i replaced by the series double-layer capacitance MC_g, is thus useable over a wide frequency range. Buck[8] has given a similar but less general and less applicable equivalent circuit for this same blocking-electrodes situation.

For the $(0, \infty)$ case when $\Omega \ll 1$, Z_{TN1} depends essentially only on Λ, being approximately $1 + (Ms)^{-1} \tanh (Ms)$ for $M \gtrsim 100$. For $\Lambda \gtrsim 3$, $Z_{TN1} - 1 \cong (Ms)^{-1} = (i^{\frac{1}{2}} \Lambda)^{-1} = (iM^2\Omega)^{-\frac{1}{2}}$, approximating Davidson–Cole dispersion[9] (with the Davidson–Cole parameter $\beta = 0.5$), which is of the form $[1 + iM^2 \Omega]^{-\frac{1}{2}}$ for the frequency variable $M^2\Omega = \Lambda^2$. By plotting $Z_{TN2}/4 = (Ms)^{-1} \tanh (Ms)$ in the complex plane, Drossbach and Schulz found that the imaginary part of this impedance reaches a negative maximum at $\Lambda \cong 1.59$, in close agreement with the present results for Z_{TN1}.

Independently, in a study of high resistance systems Buck[10] found the maximum to be at $\omega\tau = 5.069$, in agreement with $\Lambda \cong 1.59$ when Buck's incorrect τ is corrected to $l^2/2D$. Note that $\Lambda^2 \equiv M^2\Omega \equiv \omega(l^2/4D)$. Buck assumed electroneutrality everywhere in his glass-electrode surface films, even though he treated a binary electrolyte situation. Thus, his results correspond more to the Sluyters' situation[1,3] than they do to the present analysis where no indifferent electrolyte is present.

$(0, \infty)$ and Sluyters' results

As Fig. 2 indicates, in the frequency region determined by the conditions $\Lambda \gtrsim 10$ and $\Omega \lesssim 0.1$, the $(0, \infty)$ total impedance, Z_{T1}, is essentially R_∞. This region may extend over a wide range of Ω, allowing a good high-frequency-extrapolation determination of R_∞. For example, if $M = 10^5$, then $Z_{T1} \cong R_\infty$ for $10^{-6} \lesssim \Omega \lesssim 0.1$.

The Sluyters' case leads to quite a different behavior in the above frequency range. Z_{T2} depends only on Λ and, for large Λ, goes as $4R_\infty/i^{\frac{1}{2}}\Lambda$. There is thus no limiting high frequency R_∞ (since the equations solved involve no conduction terms), and $Z_{T2} \rightarrow 0$ as Ω and Λ increase. Of course, $Z_{T1} \rightarrow 0$ also as $\Omega \rightarrow \infty$, but for a quite different reason: the dispersion produced by C_g and R_∞ in parallel.

Since there is no C_g included in the Sluyters' treatment, the comparison of its results with those of the $(0, \infty)$ analysis can be expected to yield comparable results only in the $\Omega \ll 1$ region, where the only significant frequency variable is Λ. The contribution of C_g to Z_{T1} is then negligible and the equivalent circuit of Fig. 1b becomes that at the left of Fig. 3a. Under these conditions, $p^2 \cong 1$, and the resulting $Z_{TN1} = [1 + (Z_{iN}/2)]/[1 + (Z_{iN}/4)] \cong 1 + (Ms)^{-1} \tanh (Ms)$. Further, the complicated expression for Z_i given in ref. 4 simplifies in this case to

$$Z_{iN} \equiv Z_i/R_\infty \cong 4/\{(Ms) \coth (Ms) - 1\} \tag{4}$$

It may be readily established that the two equivalent circuits of Fig. 3a have exactly the same Z_{TN1} when Z_i is the same quantity in both. There are thus two distinct ways that Z_i may be obtained from measurements of Z_{T1}. The conventional method in electrolyte work is first to subtract the R_∞ found from high frequency extrapolation. The right-hand side of Fig. 3a shows, however, that in the present case of no supporting electrolyte, one must then peel off the R_∞ in parallel with $Z_i/4$ to finally obtain the latter. Alternatively[4], one must remove a parallel $2R_\infty$ from Z_{T1}, then a series $2R_\infty$ from the result to get Z_i.

When the diffusion coefficients and valences of the positive and negative charge carriers are unequal, the structure of the circuits of Fig. 3a remains unchanged but the
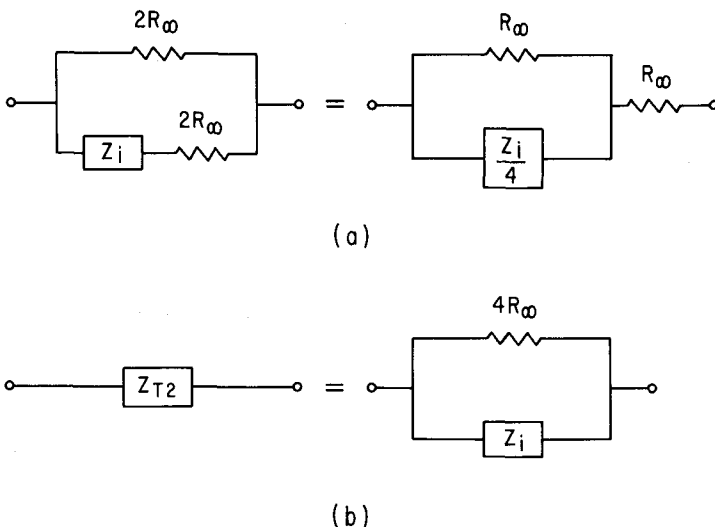
(a)

(b)

Fig. 3. Equivalent circuits for: (a) $(0, \infty)$ discharge situation when $\Omega \ll 1$, (b) situation of a redox couple in a high concn. indifferent electrolyte.

element values are altered. Let μ_p and μ_n and z_p and z_n $(z_p, z_n > 0)$ be the mobilities and valence numbers of positive and negative carriers, respectively. Then, in the general case of arbitrary $\mu_p, \mu_n, z_p,$ and z_n, first Z_i itself is no longer given by (4) even for $\Omega \ll 1$. The parallel $2R_\infty$ and the series $2R_\infty$ of the left-hand circuit of Fig. 3a become, for the present $(0, \infty)$ case, $1/z_n e n_0 \mu_n$ and $1/z_p e p_0 \mu_p$, respectively. Here p_0 and n_0 are the equilibrium bulk concentrations of the positive and negative charge carriers. Further, in the present situation of electroneutrality at equilibrium[7], $z_p p_0 = z_n n_0$. When $z_p = z_n$, $p_0 = n_0 \equiv c_0$. For the equivalent right-hand circuit, the series R_∞ remains but is given by the general form $1/e(z_n n_0 \mu_n + z_p p_0 \mu_p)$. The parallel R_∞ becomes $(\mu_p/\mu_n)R_\infty$, and $Z_i/4$ changes to $[\mu_p/(\mu_n + \mu_p)]^2 Z_i$, where Z_i is the same Z_i which occurs in the left-hand circuit. Its exact calculation in this general case is quite complicated but has been carried out recently and will be presented in a later paper. From an experimental determination of Z_T over a frequency range for which C_g may be neglected, it is straightforward to obtain the corresponding Z_i. Normalizing with the general R_∞, the circuits of Fig. 3a and the above generalizations lead to

$$Z_{iN} = \left[\frac{\mu_p + \mu_n}{\mu_p}\right]^2 \left[\frac{Z_{TN} - 1}{1 - (\mu_n/\mu_p)(Z_{TN} - 1)}\right] \tag{5}$$

for the $(0, \infty)$ case. Thus, the transformation from Z_{TN} to Z_{iN} does not involve the valences directly at all.

Although the two circuits of Fig. 3a are equivalent as far as total impedance is concerned, they do not seem to me to yield equivalent insight into the processes occurring, especially when $\mu_n \neq \mu_p$. In the $(0, \infty)$ case, negative charge carriers are not blocked and lead, for the left-hand circuit, to the parallel resistance $1/z_n e n_0 \mu_n$. This frequency-independent element depends only on the free, or electroactive, negative carriers. Correspondingly, we see that the "interface" impedance Z_i is only charged

through the $l/z_p ep_0 \mu_p$ resistance, which, in turn, depends only on the blocked carriers. Here we put "interface" in quotes since Z_i is not intensive for all frequencies and is thus not associated only with the region near the electrodes at low frequencies[4].

The situation is somewhat more mixed up for the right-hand circuit, even though this circuit is more directly in keeping with the usual process of direct subtraction of the high-frequency cell resistance, R_∞. The parallel resistance $(\mu_p/\mu_n)R_\infty$ clearly depends on carriers of both sign, and only in the limit of zero frequency $(Z_i \rightarrow \infty)$ does a simple current path involving only the electroactive species appear [since $(\mu_p/\mu_n)R_\infty + R_\infty \equiv l/z_n en_0 \mu_n$]. Yet it seems plausible to expect that the physical process present involves such a path at all frequencies (within the approximation of assuming infinitely rapid electrode reactions).

Note that when the boundary conditions for positive and negative carriers are interchanged, so that negative carriers are blocked and positive ones are free to pass in and out of the electrodes [the $(\infty, 0)$ case], the above μ_p and μ_n mobilities and z_p and z_n valence numbers need only be interchanged appropriately. Finally, it is clear that adding back C_g in parallel to the circuits of Fig. 3a allows them to apply for any Ω, although Z_i is then, of course, more complicated than it is when $\Omega \ll 1$. For the remainder of the paper, I again assume $\mu_p = \mu_n$ and $z_p = z_n = 1$.

For Sluyters' situation with equal mobilities $Z_{TN2} = 4(Ms)^{-1} \tanh (Ms)$, equal to $Z_{iN}/[1 + (Z_{iN}/4)]$ when the $(0, \infty)$ expression of eqn. (4) is used. We see that although Sluyters' Z_{T2} plays somewhat the role of the $(0, \infty)$ "interface" impedance Z_i, the two quantities are only essentially equal when $|Z_{iN}| \ll 4$, i.e. $\Lambda \gg 1$. Figure 3b shows directly how Z_{T2} involves the Z_i of eqn. (4). Note that since $|Z_i| \rightarrow \infty$ as $\Lambda \rightarrow 0$, the zero-frequency limiting values of Z_{T1} and Z_{T2} are $2R_\infty$ and $4R_\infty$, respectively. Further, since the Z_i of (4) approaches zero as $\Lambda \rightarrow \infty$, in this limit (taken consistent, however, with $\Omega \ll 1$) $Z_{T1} \rightarrow R_\infty$ and $Z_{T2} \rightarrow 0$.

For $0 \leq \Lambda \lesssim 3$, we found[4] that $Z_{iN} \rightarrow \{(4/5) + [i\Omega(C_0 - C_g)/C_g]^{-1}\}$, with $(C_0 - C_g)/C_g \cong M^2/12$ for $M \gtrsim 100$. A somewhat more complicated expression for $(C_0 - C_g)/C_g$, holding for any M, is also available[4]. Note that $(C_0 - C_g)$ is here an extensive, not an intensive quantity. In this low frequency range, the Z_i of the Fig. 3 circuits may be directly replaced by the capacitance $M^2 C_g/12$ and the resistance $4R_\infty/5$ in series. Of course, $Z_i/4$ involves a quarter of the resistance and a four-times larger capacitance. Note that the reactive and resistive components of Z_i are equal in magnitude at $\Lambda \cong (15)^{\frac{1}{2}}$. Below this Λ, the capacitive reactance dominates.

The present $(0, \infty)$ $(C_0 - C_g)$ is $M/12$ times larger than that appearing in the $(0, 0)$ blocking case. It is proportional to l and may thus be extremely large when M is large. For example, if $M = 10^5$, $l = 0.1$ cm, and $\varepsilon = 81$, then $C_g \cong 71.7 \times 10^{-6}$ μF cm^{-2}, and $C_0 \cong 6 \times 10^4$ μF cm^{-2}.

The present results show that one must be careful in deriving an appropriate Warburg impedance from measured results. Consider the usual Warburg region $(\Lambda \gg 1, \Omega \ll 1)$. Then $Z_{T2} \cong 4R_\infty/Ms$, and Z_i also approaches this value. Incidentally, it may be written in more conventional notation as $2^{\frac{3}{2}} RT(1-i)/F^2 c_0(\omega D)^{\frac{1}{2}}$. On the other hand, in the $(0, \infty)$ situation, $(Z_{T1} - R_\infty) \cong R_\infty/Ms$, in agreement with the $Z_i/4$ of the right-hand circuit of Fig. 3a. Thus, if one obtains a Warburg impedance in the conventional way, by subtracting R_∞ from the total impedance, one finds a different value (four times smaller in the case of equal diffusion coefficients) than that obtained from the interface Z_i impedance which, in this range, is truly intensive. Finally, note

that the impedance associated with a single electrode in this intensive range is just half of the values above.

It is of interest to point out that the Warburg region in Fig. 2, the straight-line part of the right-hand curve, would extend upward at a 45-degree slope indefinitely as the frequency was decreased were not a finite electrode separation l assumed. Most treatments implicitly or explicitly take l infinite and obtain such behavior. Levart and Schuhmann[5] give a complex impedance plot of much this form, for example. Here, it is the spreading of a diffusion length through the entire region between electrodes which causes the departure from a 45-degree line shown in Fig. 2 and eventually results in finite values of capacitance and resistance in the low-frequency limit.

To summarize the present frequency response comparisons, one can say that the results of the calculation for a high-concentration supporting electrolyte show both important similarities and differences from those of the $(0, \infty)$ case, where no indifferent electrolyte is assumed. The differences are important at low relative frequencies $(\Omega \ll 1, \Lambda \lesssim 1)$ and at high relative frequencies[4] $(\Omega \gtrsim 0.1)$, and the results for the "interface" impedance (Z_{T2} and Z_i) are essentially the same in the intermediate Warburg range $(\Omega \ll 1, \Lambda \gg 1)$.

TABLE 1

DEPENDENCES OF IMPORTANT CAPACITANCES/UNIT AREA AND TIME CONSTANTS ON VARIOUS QUANTITIES

The Table shows the powers of the quantities entering the appropriate expressions for C_g, MC_g, etc.

	$[l]$	$[c_0]$	$[\varepsilon]$	$[T]$	$[\mu]$
C_g	-1	0	1	0	0
MC_g	0	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	0
$M^2 C_g$	1	1	0	-1	0
τ_D	0	-1	1	0	-1
$M\tau_D$	1	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	-1
$M^2\tau_D$	2	0	0	-1	-1

Three capacitances: C_g, MC_g, and $M^2 C_g/12$, have entered naturally in the $(0, 0)$ and $(0, \infty)$ analyses. In addition, associated with these capacitances are the time constants[4] τ_D, $M\tau_D$ and $M^2\tau_D$. It is finally of interest to show how these quantities depend directly on such parameters of the material and situation as l, c_0, ε, T, and μ. Such dependence is summarized in Table 1, where only the powers of quantities are indicated. Thus, for example, C_g is proportional to $l^{-1}c_0^0\varepsilon^1 T^0 \mu^0$. Of course, implicit dependences, such as those of ε and μ on T, are not indicated.

COMPARISON OF LENGTH-DEPENDENCE RESULTS

(0, ∞) and Sluyters' results

For frequency dependence comparisons, it was convenient to normalize impedances with R_∞, a frequency-independent quantity. On the other hand, R_∞ depends directly on l and is thus inappropriate when length dependence is investigated. A suitable quantity to use, however, is the intensive "Debye" resistance, $R_D \equiv M^{-1} R_\infty = L_D/\mu e c_0$. Let us denote normalization with R_D by the subscript "M". Thus, $Z_{TM} \equiv$

$Z_T/R_D = MZ_{TN}$. Further, let us consider here only a fixed frequency in the region $\Omega \ll 1$.

With the above definitions, one has

$$Z_{TM1} \equiv s^{-1}[Ms + \tanh(Ms)] \tag{6}$$

$$Z_{TM2} \equiv 4s^{-1}\tanh(Ms) \tag{7}$$

It is clear that because of the presence of the series R_∞ term in Z_{T1}, it and Z_{TM1} will contain a term linear in l which will eventually dominate Z_{TM1} for large $\Lambda \equiv |Ms|$. Thus, in the $(0, \infty)$ discharge case, Z_{T1} always contains an extensive term and is never intensive in behavior.

In order to compare $(0, \infty)$ and Sluyters length dependence (using Λ now as an electrode separation variable), it is therefore reasonable to compare $(\Omega)^{\frac{1}{2}}(Z_{T1} - R_\infty)/R_D = \Lambda(Z_{TN1} - 1)$ and $(\Omega)^{\frac{1}{2}}Z_{TM2}/4$, two quantities equal to $(i)^{-\frac{1}{2}}\tanh(Ms)$. There is thus no difference between the two results, and we need investigate only the Λ dependence of $Z_D \equiv (i)^{-\frac{1}{2}}\tanh(Ms) = (i)^{-\frac{1}{2}}\tanh(i^{\frac{1}{2}}\Lambda)$. Sluyters has already plotted $|Z_D|$ and its phase angle $\psi \equiv \psi_D$ against $2^{\frac{1}{2}}\Lambda$. Therefore, it is here only worthwhile to show computer calculated results for these quantities in the neighborhood of their maxima.

Figure 4 shows calculated results for $|Z_D|$ and the negative of its phase angle, $-\psi_D$. $|Z_D|$ reaches a maximum of about 1.143 at $\Lambda \cong 1.67$ and shows a small under-shoot below its final limiting value of unity. Likewise, $-\psi_D$ shows both an overshoot and undershoot about its final value of 45°. For $\Lambda \cong 5$, $|Z_D|$ and ψ_D have both be-come very close to their final intensive values. Sluyters' experimental results (with a relatively high concentration of indifferent electrolyte) are in good qualitative agree-ment with his results for $|Z_D|$, although the small undershoot of Fig. 4 is not evident in either his theoretical or experimental results.

For simplicity, we have thus far compared the length dependence of total impedance quantities, but Fig. 3b shows that Sluyters' Z_{T2} is actually somewhat
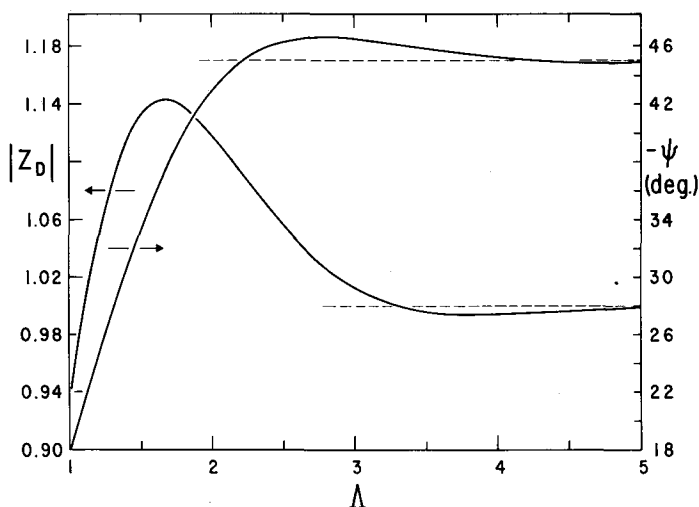

Fig. 4. Dependence of $|Z_D|$ and $-\psi$ on Λ, showing how the magnitude of normalized cell impedance and its phase angle depend on electrode separation at fixed frequency with $\Omega \ll 1$.

TABLE 2

COMPARISON OF THE Λ-DEPENDENCE OF THE NORMALIZED QUANTITIES $|Z_D|$ AND $|Z_F|$ AND THEIR PHASE ANGLES

Λ	$|Z_D|$	$|Z_F|$	$-\psi_D$ (degrees)	$-\psi_F$ (degrees)
0.1	0.010	30.000	0.19	89.96
0.5	0.498	6.002	4.76	89.05
1.0	0.931	3.012	17.96	86.20
2.0	1.119	1.593	42.91	75.75
3.0	1.013	1.258	46.47	64.16
4.0	0.994	1.179	45.23	57.31
6.0	1.000	1.124	44.98	52.59
10.0	1.000	1.073	45.00	49.35

more comparable to Z_i than to Z_{T1}. If we calculate a Z_i from the Z_T of either Fig. 3a or 3b, then it is of some interest to investigate how this quantity depends on electrode separation. On normalizing as above, one obtains $(\Omega)^{\frac{1}{2}}Z_{iM}/4 \equiv Z_F \equiv \Lambda/[(Ms)\coth(Ms) -1]$, a quantity which approaches Z_D for large Λ. Rather than plot the dependence of Z_F on Λ, we show for comparison in Table 2 a few values of $|Z_D|$, $|Z_F|$, and their phase angles, ψ_D and ψ_F. Table 2 indicates the great difference between Z_D and Z_F for small Λ. One of these quantities is resistive in the $\Lambda \to 0$ limit, the other capacitative. Although corresponding quantities approach equal values as Λ increases, even at $\Lambda = 25$, ψ_F is still about $-46.7°$.

SUMMARY

A comparison is made, for frequency and electrode-separation dependence of total cell impedance and "interface" impedance, between electrolyte situations with and without a supporting indifferent electrolyte. When no indifferent electrolyte is present, a binary electrolyte situation, two boundary conditions are considered: that of ideally polarized electrodes (complete blocking), and that where charges of one sign are blocked at the electrodes and those of opposite sign are able to pass freely in and out of the electrodes. Further, electroneutrality is not assumed. The usual solution when an indifferent electrolyte is present assumes the presence of reactions of charges of both signs at the electrodes and electroneutrality everywhere. All electrode reactions are taken to be infinitely fast and no specific adsorption is present. Further, no applied static overpotential is assumed, so the results apply most closely at the equilibrium potential. Comparison of the results for the various cases indicates both important similarities and differences. It is shown that when there is no indifferent electrolyte, particular care must be taken in analyzing the total impedance to obtain an appropriate "interface" impedance. Finally, equivalent circuits pertinent for the various situations are considered in detail, and an important equality between structurally different circuits is pointed out.

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