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Short communication

COMPACT DOUBLE LAYER EFFECTS IN SMALL-SIGNAL ELECTRICAL RESPONSE *

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INTRODUCTION

In a recent paper [1] (denoted I henceforth) we presented a transformation of variables method which made it possible to relate the small-signal response of a material with two species of mobile charge carrier (not subject to generation or recombination) with overpotential-dependent reaction kinetics at two identical metal electrodes to that determined for a simple system with overpotential-independent kinetics. The electrode/material/electrode system was assumed to be flat band at equilibrium. Our method was then illustrated for a material with a single species of mobile charge carrier. Here we present two decompositions of the total system impedance into compact layer and bulk-diffuse layer parts and discuss equivalent circuit representations of these decompositions.

As in I, we assume that only negative charge carriers are mobile and that under small-signal conditions the a.c. component of the current of negative carriers, I_{n1R} at the right electrode, may be written as

$$I_{n1R} = -z_n e[k_n n_{1R} + (z_n e\eta_1/kT)\gamma_n n_e] \tag{1}$$

where k_n is a rate constant, n_{1R} is the deviation from the equilibrium concentration at a well defined plane (outer Helmholtz plane) near the electrode, γ_n is a parameter (with the dimensions of k_n) which reflects the overpotential dependence of the electrode reaction rate [1], and η_1 exp($i\omega t$) is the small-signal overpotential. (Symbols not defined in this work have the same meaning as in I.) We were able to relate the impedance of such a system to that determined for a system obeying the Chang-Jaffé condition [2,3]

$$I_{n1R} = -z_n e k_n n_{1R} \tag{2}$$

and without a compact layer (i.e. n_{1R} defined at the effective electrode surface).

We let $R_\infty \equiv l/\sigma$ denote the limiting high frequency resistance, and $C_g \equiv \epsilon/4\pi l$ denote the geometric capacitance of the bulk and diffuse layer parts of the cell, where l is the distance between electrodes less the thickness of the two compact layers, and use a subscript "N" (i.e. normalized) to indicate an impedance or resistance expressed in units of R_∞ or a capacitance expressed in units of C_g.

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Our essential result may be stated as

$$Z_N = Z_{CJN}/[1 + \Delta(\Omega)] \tag{3}$$

where Z_N is the normalized system impedance, Z_{CJN} the normalized impedance of the corresponding Chang-Jaffé system, and $\Delta(\Omega)$ a frequency-dependent correction given explicitly in I.

Minor rearrangement of eqn. (3) leads to an expression for the impedance

$$Z_N - Z_{CJN} = -Z_{CJN}\Delta/(1 + \Delta) \tag{4}$$

which may be placed in series with the normalized Chang-Jaffé impedance,

$$Z_{CJN} = \frac{2 + (1 + i\Omega)r_n + 2\,i\Omega\gamma_1}{(1 + i\Omega)[(1 + i\Omega)r_n + 2\,i\Omega\gamma_1]} \tag{5}$$

in order to reproduce the total system impedance. In the present case we find

$$Z_N - Z_{CJN} = \frac{(r_n + 2\,\gamma_1)[r_n(1 + i\Omega - \nu_n) + 2\,i\Omega\gamma_1]}{\{C_{CN}[r_n(1 + i\Omega) + 2\,i\Omega\gamma_1] + \gamma_1 r_n\nu_n\}[r_n(1 + i\Omega) + 2\,i\Omega\gamma_1]} \tag{6}$$

Here $r_n \equiv lk_n/D_n$, $\nu_n \equiv \gamma_n/k_n$, $\gamma_1 \equiv (\theta_1 M_n)\text{ctnh}(\theta_1 M_n)$, and we have defined the normalized capacitance of the cell's two compact double layers (in series) as

$$C_{CN} \equiv (\epsilon_1/8\pi d)/(\epsilon/8\pi l_h) = (\epsilon_1 l_h/\epsilon d) \tag{7}$$

where $l_h \equiv l/2$, d is the thickness of each compact layer (distance between outer Helmholtz plane and electrode surface), $\theta_1^2 \equiv 1 + i\Omega$, and $M_n \equiv l_h/L_{Dn}$, with L_{Dn} the effective Debye length for mobile negative carriers. Under completely blocking conditions ($r_n = 0$), $Z_N - Z_{CJN}$ is simply $(1/i\Omega C_{CN})$, the normalized capacitive reactance of the compact layers. This well known result suggests that we attempt to represent the total system impedance by the equivalent circuit of Fig. 1 in which the three components to the left represent the solution for Chang-Jaffé boundary conditions [1], with $C_{gN} = R_{\infty N} \equiv 1$, while the additional impedance arising from compact layer effects is represented by the compact layer capacitance in parallel with a component of impedance,

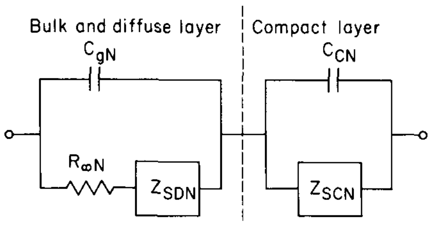
$$Z_{SCN} = \frac{(r_n + 2\,\gamma_1)[2\,i\Omega\gamma_1 + r_n(1 - i\Omega - \nu_n)]}{C_{CN}r_n[r_n(1 + i\Omega) + 2\,i\Omega\gamma_1 + i\Omega\nu_n(r_n + 2\,\gamma_1)] + r_n\nu_n\gamma_1[r_n(1 + i\Omega) + 2\,i\Omega\gamma_1]} \tag{8}$$

The d.c. limiting value of Z_{SCN} is then the resistance

$$R_{SCN_0} = (r_n + 2\,C_{DN})(1 - \nu_n)/r_n(C_{CN} + \nu_n C_{DN}) \tag{9}$$

where $C_{DN} \equiv (M_n)\text{ctnh}(M_n)$, the normalized diffuse double layer capacitance. At $\Omega = 0$ this resistance appears in series with the normalized Chang-Jaffé d.c. resistance of $1 + (2/r_n)$. As noted in I, for Butler-Volmer electrode kinetics $\nu_n = 1$ and $R_{SCN_0} = 0$.

It also seems desirable to seek a representation of the total system impedance Z_N as a diffuse double layer impedance Z'_{DN} in series with a compact double layer impedance Z'_{CN}, so that the potential drop across Z'_{CN} equals the small-signal overpotential η_1. It is useful in this context to consider the idealized half cell introduced in I, obtained by replacing half of the symmetrical cell by an



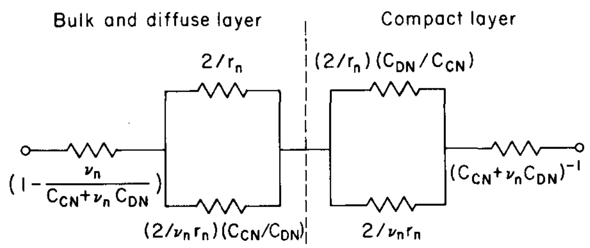


Fig. 1. Normalized equivalent circuit for cell impedance including compact layer effects.

Fig. 2. Normalized equivalent circuit for d.c. resistance of cell.

ohmic electrode. The impedance of this half cell, normalized with respect to *its* limiting high frequency resistance is the same as the normalized impedance of the symmetrical cell. We may write the small-signal normalized current as $I_{1N} \equiv V_{ah1}/Z_N$ and from eqns. (93) and (94) in I evaluate η_1/V_{ah1}. We obtain

$$Z'_{CN} \equiv \frac{\eta_1}{I_{1N}} = \frac{(r_n + 2\gamma_1)}{C_{CN}[r_n(1+i\Omega) + 2i\Omega\gamma_1] + r_n\nu_n\gamma_1} \tag{10}$$

and

$$Z'_{DN} \equiv Z_N - Z'_{CN} = \frac{2 + r_n(1+i\Omega) + 2i\Omega\gamma_1 + \nu_n r_n(\gamma_1 - 1)C_{CN}^{-1}}{(1+i\Omega)\{[r_n(1+i\Omega) + 2i\Omega\gamma_1] + \nu_n r_n \gamma_1 C_{CN}^{-1}]\}} \tag{11}$$

Adopting again the equivalent circuit of Fig. 1 with the left hand side now representing Z'_{DN} and the right hand side Z'_{CN} and retaining $C_{gN} \equiv 1$, $R_{\infty N} \equiv 1$, and C_{CN} as before, we find the remaining circuit elements to be given by

$$Z'_{SCN} = \frac{r_n + 2\gamma_1}{r_n(C_{CN} + \nu_n\gamma_1)} \tag{12}$$

and

$$Z'_{SDN} = \frac{(1+i\Omega)(2 - \nu_n r_n C_{CN}^{-1})}{r_n(1+i\Omega) + 2i\Omega(\gamma_1 - 1) + \nu_n r_n(\gamma_1 + i\Omega)C_{CN}^{-1}} \tag{13}$$

Although it might at first appear surprising that a diffuse layer property (L_{Dn} in γ_1) appears in Z'_{SCN} and a compact layer property (C_{CN}) in Z'_{SDN}, these expressions reflect the way in which the overall potential distribution is determined by processes in both parts of the cell.

It is finally instructive to examine the latter decomposition in the d.c. limit. Figure 2 shows the zero-frequency normalized resistance of the cell separated into compact layer and diffuse layer-bulk parts. At the extreme left and right are two resistors representing bulk charge transport. The charge transfer (electrode) process is represented by the series combination of two parallel pairs of resistors. One member of each pair is independent of ν_n and represents charge transfer associated with the build up of excess charge carriers at the electrode. The second member of each pair depends on ν_n and represents the overpotential effect. In the small-signal d.c. limit the charge transfer process may thus be viewed as the result of concentration and overpotential processes in parallel on each side of the outer Helmholtz plane.

REFERENCES

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