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LETTER TO THE EDITOR

Some AC response results for solids with recombining space charge

J Ross Macdonald†
Texas Instruments Incorporated, Dallas, Texas, USA

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Abstract. A recent small-signal, space-charge calculation of Meaudre and Mesnard is discussed and related to other work in the field. The Meaudre–Mesnard results are shown to yield inappropriate high- and low-frequency limiting response. A recombination time constant appearing in the treatment is also a poor approximation. Finally, an approach is discussed which avoids these deficiencies.

1. Introduction

Meaudre and Mesnard (1974) (to be abbreviated as MM) have recently given a treatment of the electrical response of materials containing mobile negative charge which may recombine bimolecularly with fixed ionized centres which are uniformly distributed before ionization. They further assume that the mobile charges may discharge at the plane-parallel electrodes to a degree determined by a discharge parameter ξ. They then linearize the pertinent equations and derive approximate solutions for transient and steady state response (sinusoidal driving voltage). Since for a linearized set of equations which represents a linear system there is no difficulty in principle in passing from a given transient response to steady state AC response or from given steady state response to transient response (Macdonald and Brachman 1956), here only steady state AC response need be considered.

There are a few non-obvious defects in the MM results, arising from the various approximations they make, and insufficient comparisons with earlier work. MM emphasize that, in agreement with many experimental results, their treatment yields two time constants, one associated with recombination and the other with space-charge decay. They do not mention, however, that two such time constants were found long ago from an exact solution for the $\xi = 0$ situation (Macdonald 1953), nor that their AC results agree with earlier results of Beaumont and Jacobs (1967) for arbitrary ξ and zero recombination.

As has been pointed out earlier (Macdonald 1958, 1959, 1974a, b, c), there is a considerable amount of parallelism between the following two situations: (*a*) charge of one sign mobile and free to recombine with fixed charge of opposite sign; and (*b*) charge of both signs mobile, no recombination, but charge of one sign having a very considerably different mobility than the other. Then, in case (*b*), the high mobility charge is associated with the main space-charge time constant, τ_1, and the lower mobility charge leads to another dispersion region which may be described to some degree by the introduction of a second time constant, τ_2, with $\tau_2 \gg \tau_1$. At radial frequencies appreciably higher

†Now at Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27514, USA.

than τ_2^{-1}, the system behaves essentially as though the lower mobility charge were immobile. In the region $\tau_2^{-1} < \omega < \tau_1^{-1}$, the total parallel input capacitance of the sytem, C_P, reaches a plateau value, C_{PS}, greater than the geometrical capacitance of the sytem, C_g, but less than its zero-frequency limiting value, C_{P0}. For $0 \leqslant \omega \lesssim \tau_2{}^{-1}$, C_P increases from C_{PS} to C_{P0}. But this is just the behaviour one expects and finds for case (*a*) (Macdonald 1953). There, it is recombination which causes the final τ_2 rise at low frequencies from C_{PS} to C_{P0}, assuming, as did MM, that $\tau_2 > \tau_1$.

Because of the above parallelism we can learn a good deal about the behaviour of case (*a*) from studies of case (*b*). Now it turns out that a paper was published on the theory of case (*b*) considerably before MM submitted their own work for publication (Macdonald 1973). This treatment was quite general. Although it included no recombination, it involved arbitrary discharge parameters, r_p and r_n, for positive and negative charge having arbitrary mobilities and valence numbers. In addition, it included the possible presence of completely dissociated fixed shallow donors and acceptors. Many frequency response possibilities inherent in the solution have been discussed separately (Macdonald 1974c,d). Futher, it may readily be generalized to include bimolecular recombination of the mobile positive and negative charges. It can then cover case (*a*) exactly as well. With this background we may now consider the MM results.

2. Discussion

MM's steady state sinusoidal response readily leads to the following expression for the total input admittance per unit electrode area of their uni-univalent system:

$$Y_T \equiv G_P + i\omega C_P = G_0 + i\omega[C_g + C_1(1 + i\omega\tau_1)^{-1} + C_2(1 + i\omega\tau_2)^{-1}] \quad (1)$$

where

$$C_g \equiv \epsilon/L \quad (2)$$

$$C_1 \equiv M_1 C_g g_n{}^{-2} \quad (3)$$

$$C_2 \equiv M_1{}^2 C_g g_n{}^{-3}(2\beta n_0 \tau_{D1})\{[g_n/4\tau_{D1}M_1(k + \beta n_0)] + \tfrac{3}{4}\} \quad (4)$$

$$G_0 \equiv (r_n/2)g_n{}^{-1}G_{\infty 1} \quad (5)$$

$$G_{\infty 1} \equiv (en_0\mu/L) \equiv R_{\infty 1}{}^{-1} \quad (6)$$

$$\tau_1 \equiv C_1 G_1{}^{-1} \quad (7)$$

$$\tau_2 \equiv C_2 G_2{}^{-1} = (k + \beta n_0)^{-1} \quad (8)$$

$$G_1 \equiv g_n{}^{-1}G_{\infty 1} \quad (9)$$

and

$$G_2 \equiv C_2(k + \beta n_0) \quad (10)$$

In these expressions ϵ is the dielectric constant of the basic material; ω the radial frequency; L the separation between electrodes; $M \equiv L/2L_{D1}$,w here the one-mobile Debye length $L_{D1} \equiv (\epsilon kT/e^2 n_0)^{1/2}$; D and μ are the diffusion coefficient and mobility of the mobile negative charges; n_0 is the uniform equilibrium value of the negative charge concentration; e the protonic charge; $g_n \equiv 1 + (r_n/2)$; $r_n \equiv \xi L/D$; k and β are the generation and recombination coefficients; and $\tau_{D1} \equiv C_g R_{\infty 1}$ is the dielectric relaxation time.

Now equation (1) leads directly to the equivalent circuit of frequency-independent elements shown in figure (1*a*). We may now see some of the deficiencies of this circuit.

First, when $\omega \to \infty$, G_P should properly go to $G_{\infty 1}$, the high-frequency limiting conductance of the system. But actually $G_P \to G_{P\infty} = G_0 + G_1 + G_2 = G_{\infty 1} + G_2 \neq G_{\infty 1}$. Second, when $\omega \to 0$, C_P should go to C_{P0}, where $C_{P0} \cong \sqrt{2}M_1C_g \equiv M_2C_g = \epsilon/2L_{D2}$, just the capacitance of two double layers in series (one at each electrode) when charges of both

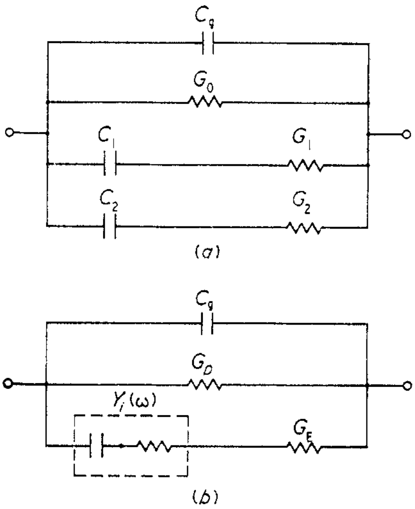

Figure 1

sign are mobile. This limiting result is necessary because nonzero recombination effectively mobilizes the fixed charge as already mentioned. Here, however, we find $C_{P0} = C_g + C_1 + C_2 = C_g\{1 + (M_1g_n^{-2})[1{\cdot}5 + (k/\beta n_0)]/[1 + (k/\beta n_0)] + 1{\cdot}5M_1^2g_n^{-3}\beta n_0\tau_{D1}\}$, quite different in form from $\sqrt{2}M_1C_g$ even when $k/\beta n_0 \ll 1$. Note that even when $k/\beta n_0 \ll 1$ and the third term is negligible, this C_{P0} is approximately $(C_g + 1{\cdot}5C_1)$, still quite different from $\sqrt{2}M_1C_g$, especially when $g_n \gg 1$. As we shall shortly see, the plateau value of C_P, $(C_g + C_1) = C_g[1 + M_1g_n^{-2}]$ is nearly correct here, however.

In the exact treatment (Macdonald 1973), a given situation is specified by values of $(r_p, r_n; \pi_m, \pi_z; \chi, M)$, where $\pi_m \equiv \mu_n/\mu_p$; $\pi_z \equiv z_n/z_p$, the ratio of charge valence numbers, here unity; χ is an extrinsic conduction parameter, zero for intrinsic conduction; $M \equiv M_2 \equiv L/2L_D \equiv L/2L_{D2}$; and $L_{D2} \equiv [\epsilon kT/e^2(z_n^2n_0 + z_p^2p_0)]^{1/2} = L_{D1}/\sqrt{2}$ in the present $z_n = z_p = 1$ case when the electroneutrality condition $z_nn_0 = z_pp_0$ is used. Here p_0 is the equilibrium bulk value of the positive charge concentration. The exact solution leads to the equivalent circuit shown in figure 1(b), where

$$Y_i^{-1} \equiv Z_i \equiv R_i + (\mathrm{i}\omega C_i)^{-1} \tag{11}$$

and R_i and C_i are the frequency-dependent series elements appearing in figure 1(b).

Let us now consider case (b), specified by $(0, r_n; \pi_m \gg 1, 1; 0, M_2)$. For this situation with $z_n = z_p = 1$ as well, one finds (Macdonald 1973) that

$$G_D = (r_n/2)g_n^{-1}G_{\infty 2} \tag{12}$$

and

$$G_E \equiv R_E^{-1} = g_n^{-1}G_{\infty 2}. \tag{13}$$

Note that here

$$G_{P0} = G_E + G_D = G_{\infty 2} \tag{14}$$

as it should, where

$$G_{\infty 2} \equiv (e/L)(\mu_n n_0 + \mu_p p_0) = (e/L)(n_0)(\mu_n + \mu_p) = G_{\infty 1}(1 + \pi_m{}^{-1}). \quad (15)$$

Comparison with equations (5) and (9) shows that $G_0 \cong G_D$ and $G_1 \cong G_E$ since $\pi_m{}^{-1} \ll 1$ here. Note that discharging negative charges have the higher mobility here, much higher than that of the completely blocked positive charges.

It further turns out in case (*b*) (Macdonald 1973, 1974c) that

$$C_{PS} \cong C_g + C_{iS} \cong C_g\,[1 + g_n{}^{-2}(M_1 - 1)] \quad (16)$$

and

$$C_{P0} \equiv C_g + C_{i0} \cong MC_g = \sqrt{2M_1}C_g. \quad (17)$$

Since M_1 is usually much greater than unity and C_{PS} is also frequently considerably greater than C_g as well, $C_{PS} \simeq M_1 C_g g_n{}^{-2}$. An exact expression for Y_T in the zero recombination case following from the exact equivalent circuit of figure 1(*b*) is

$$Y_T = G_D + \mathrm{i}\omega\left(C_g + \frac{C_i}{1 + \mathrm{i}\omega\tau_s}\right) \quad (18)$$

where

$$\tau_s \equiv C_i(R_i + R_E). \quad (19)$$

In most of the plateau region, $R_i(\omega) \ll R_E$ and $C_i(\omega) \simeq C_{iS}$. Then, we may make the identification

$$\tau_s \cong \tau_1 \equiv C_{iS}R_E. \quad (20)$$

Now

$$C_{iS} \cong g_n{}^{-2}(M_1 - 1)C_g \quad (21)$$

and for the $\pi_m \gg 1$ case, $R_E = g_n R_{\infty 2} \simeq g_n R_{\infty 1}$. Thus

$$\tau_1 \cong [(M_1 - 1)/g_n]\tau_{D1} \quad (22)$$

a result essentially inherent even in the very early work (Macdonald 1953, equation 72). This approximate time constant is close to the slightly less accurate MM value of equation (7), $(M_1/g_n)\tau_{D1}$. It arises, to good approximation, only from the motion of the charge of higher mobility. It should, therefore, be essentially the same in both cases (*a*) and (*b*).

The second time constant, τ_2, arises here primarily from the change from C_{iS} to C_{i0} as $\omega\tau_2$ becomes smaller than unity. It is really improper, however, to describe the response in this frequency region by a single Debye-dispersion type of time constant at all! Some pertinent case (*b*) results which illustrate this conclusion have already been given (Macdonald 1974c).

In the MM situation of case (*a*), we can combine previous results (Macdonald 1953, 1974c, Beaumont and Jacobs 1967) to yield a good approximation for C_i in the region where it changes from C_{iS} to C_{i0}. Let

$$g_0 \equiv [(k/\beta n_0) + \mathrm{i}\omega\tau_r]^{-1} \quad (23)$$

where

$$\tau_r = (\beta n_0)^{-1} \equiv \xi_r\tau_{D1}. \quad (24)$$

Note that this time constant is simply related to the τ_2 result found by MM. Here ξ_r, which will be much greater than unity in most cases of interest, corresponds exactly to the ξ of the very early work (Macdonald 1953). It turns out that for $\omega\tau_1 \ll 1$ and $\pi_z = 1$

$$C_i \cong (C_g/g_n^2)\left[M_2 \mathrm{Re}\left(\frac{1+2g_0}{2(1+g_0)}\right)^{1/2} - 1\right]. \tag{25}$$

This result does not include the τ_1 dispersion region, but does include that from $C_i \cong C_{i0}$, where $\omega\tau_2 \ll 1$, to $C_i \cong C_{iS}$, where $\tau_2^{-1} \ll \omega \ll \tau_1^{-1}$. In the usual case of small dissociation for solids, $k/\beta n_0 \ll 1$ and may be neglected. Then equation (25) becomes

$$C_i \cong (C_g/g_n^2)\left[M_2 \mathrm{Re}\left(\frac{1+\mathrm{i}\omega(\tau_r/2)}{1+\mathrm{i}\omega\tau_r}\right)^{1/2} - 1\right]. \tag{26}$$

This expression clearly does not yield simple Debye dispersion for the transition from C_{iS} to C_{i0}. Note that in this $\pi_z = 1$ case, $C_{i0}/C_{iS} = \sqrt{2}$, a relatively small ratio. The τ_2 dispersion is thus minor in most cases of interest, where $M_2/g_n^2 \gg 1$.

Although the basic recombination time constant τ_r enters into this expression, the series combination of $C_i(\omega)$ and $[R_i(\omega) + R_E]$ cannot be well approximated by the two simple single-time-constant dispersions of figure 1(*a*). A different approximate representation of Y_i in terms of frequency-independent elements was given, however, in the $r_n = 0$ case (Macdonald 1953). It involved C_{iS} in parallel with the series combination of $(C_{i0} - C_{iS})$ and a recombination resistance, itself well approximated by $\tau_r/M_1C_g = (\xi_r/M_1)R_{\infty 1}$. This resistance differs substantially from the $R_2 \equiv G_2^{-1}$ which follows from equation (10). In this quite approximate treatment there are indeed two simple time constants.

It is clear from the above results that the MM treatment leads to incorrect C_{P0} and $G_{P\infty}$; to approximate but usually adequate expressions for C_{PS} and τ_1; and to inaccurate frequency response in the transition region from the plateau to the low-frequency-limiting region. These deficiencies correspond to similar ones in the MM transient response. In future work, it is hoped to give exact results for the frequency response of a general system involving both recombination and arbitrary mobilities simultaneously.

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