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SOME ASPECTS OF POLARIZATION IN IONIC CRYSTALS WITH ELECTRODE REACTIONS†

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Abstract—Space charge polarization involving an electrode reaction with surface adsorption is examined. As recently demonstrated by Lányi, the presence of such a process may be represented using a complex, frequency-dependent rate constant. Lányi's rate constant is shown to be normally a special case of a more general complex rate constant following from earlier work of Armstrong and others on electrode reactions with an adsorbed intermediate species. An exact expression, based on earlier work of one of the authors, is given for the impedance of a uni-univalent extrinsic-conduction system with mobile charges of only a single sign and for which the electrode processes involve such adsorbed intermediate species. Conditions are then found which reduce the exact results to the approximate expressions for series capacitance and resistance derived by Lányi for his special case of calcium-doped NaCl. These conditions are well satisfied for his specific choices of parameter values. Curves showing the exact frequency response of various series and parallel quantities are presented, together with complex impedance plane results. Finally, it is shown how under conditions that include the range of usual experimental interest the entire space-charge, electron reaction/adsorption system can be well represented by a simple equivalent circuit of frequency-independent elements.

INTRODUCTION

In the interesting and valuable paper by Lányi[1], "Polarization in Ionic Crystals with Incompletely Blocking Electrode", a frequency-dependent, complex electrode-reaction rate constant, $k^* \equiv k' + ik''$, is introduced in an effort to explain a.c. space charge polarization results for calcium-doped NaCl, probably measured in the range of 400–600°C. Lányi assumes that only cation vacancies are mobile (here termed a one-mobile situation) and states that his theoretical approach involving k^* leads to better agreement with experiment than is possible with earlier theories which use a real, frequency-independent rate constant[2–5].

Lányi suggests that his formalism, a generalization of earlier work[2–4] to a complex rate constant situation, particularly applies to polarization cells of the non-parent-metal electrode[6], such as Pt|NaCl|Pt, which he expects may sustain steady, stationary currents. Since his k^* approaches zero as ω, the radial frequency of the a.c. applied voltage, goes to zero, however, his treatment reduces to complete blocking in this limit and thus cannot lead to non-zero d.c. conductance, in contradistinction to the results of earlier theories. It is not clear whether Lányi includes time-invariant d.c. under "stationary" current. Note that a direct current may not actually be stationary even though it does not change perceptibly during the time of an experiment (or $\omega_{\min}^{-1}$). For such quasi-stationary situations, it is necessary that k^* be non-zero at least down to $\omega_{\min}$, the minimum frequency of measurement in the a.c. case.

Elsewhere, Lányi's work has been shown to be a special case of a more general approach involving an electrode reaction with an adsorbed intermediate species present[7]. Quasistatic calculations leading to the differential capacitance arising in an electrolyte system when specific ionic adsorption takes place at an electrode are well known[8]. In addition, there has been considerable earlier work published on small-signal a.c. response in the adsorbed intermediate situation. In particular, it is worth citing 1970 and 1974 papers by Epelboin *et al.*[9, 10] and 1972 and 1974 papers by Armstrong *et al.*[11, 12] on the a.c. impedance of complex electrochemical reactions. Other earlier related work is cited by Armstrong. These calculations, which do not involve a complex rate constant approach, apply best to a supported electrolyte situation, however, and should be appreciably less applicable to Lányi's unsupported case[7]. The complex rate constant approach, introduced by Lányi[1], can apply to either supported or unsupported conditions[7] and is thus more comprehensive. It has been shown elsewhere[7] how it may be extended to encompass more general electrode and bulk conduction conditions than those treated by Lányi.

The formal treatment of Ref. [7] demonstrates how the various specific parameters which enter the complex rate constant approach to electrode reactions with adsorption can be expressed in terms of more basic response parameters of the overall system. It also shows in principle how the a.c. response of the system may be calculated explicitly in the general intrinsic-extrinsic conduction case involving charges of both signs mobile.

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No interpretive numerical or pictorial results are given, however, and the present paper remedies this lack for Lanyi's specific case: strongly extrinsic n-type ionic Schottky-defect materials with positive charges taken immobile.

LÁNYI'S SERIES CAPACITANCE

One of Lányi's most significant results in his expression for series capacitance per unit electrode area, C_S, as a function of ω. The unit-area qualifier will be omitted for brevity in the rest of this paper. In order to make direct contact with earlier work, it will be convenient to express Lányi's result in terms of dimensionless variables. Define the dielectric relaxation time as $\tau_D \equiv \epsilon/4\pi\sigma$, where ϵ and σ are the bulk permittivity and conductivity. Introduce the normalized frequency $\Omega \equiv \omega\tau_D$. Further, let[2, 4] $r_{n\infty} \equiv (l/D_n)k_0$ and $r_{n1} \equiv \tau_D(k_r/l_0)$, where the r's are dimensionless boundary value parameters which are simply related to the real k_0 and k_r rate constants introduced by Lányi. Here l is the separation length of identical plane parallel electrodes; D_n is the diffusion coefficient for cation vacancies; k_0 and k_r are ordinary electrochemical rate constants for forward and backward reactions; and l_0 is defined by Lányi as the thickness of the layer on the surface of the electrode in which neutralized ions may be deposited. An internal relaxation time associated with the adsorption process (not necessarily that measured externally for the system as a whole) may also be defined from r_{n1} as $\tau \equiv \tau_D/r_{n1} \equiv l_0/k_r$. One then finds, on using Lányi's derived frequency dependence for k^*, the following expression for the complex, dimensionless boundary condition parameter r_n^*,

$$\begin{aligned} r_n^* \equiv r_{nL}^* = (l/D_n)k^* \equiv r'_{nL} + ir''_{nL} &\equiv \Omega r_{n\infty}/(\Omega - ir_{n1}) \\ &\equiv [\Omega r_{n\infty}/(r_{n1}^2 + \Omega^2)][\Omega + ir_{n1}]. \end{aligned} \tag{1}$$

The presence of specific adsorption has thus led to the replacement of the conventional constant boundary condition parameter by a frequency-dependent complex quantity. As $\Omega \to 0$, $r_{nL}^* \to 0$, and for $\Omega \to \infty$, $r_{nL}^* \to r_{n\infty}$. Note that when $r_{n1} = 0$, $r_{nL}^* = r_{n\infty}$, equivalent to the frequency-independent quantity previously termed r_n [5] or ρ [4]. In the one-mobile situation, the corresponding boundary condition parameter for positive charges, r_p or r_p^*, may be taken identically zero[13].

In the conventional treatment, $r_n = 0$ ensures that negative charges are completely blocked at the electrode while $r_n \to \infty$ specifies an infinitely fast (relative to other system processes) electrode reaction rate. Further interpretation of $r_{n\infty}$ will be given later in this paper. The condition $r_{n1} \to 0$ leads to $\tau \to \infty$. The resulting $r_{nL}^* = r_{n\infty}$ case may be physically interpreted as a parent metal electrode situation: that where the mobile charges in the material of interest are ions of the electrode atoms. Then the ions can discharge in the ordinary way, building up the electrode. There is therefore no effective adsorption and r_n^* will be real and frequency independent.

Now define a Debye length in the one-mobile situation as L_{D1}, and let $M_1 \equiv l/2L_{D1}$. Here

$$L_{D1} \equiv [\epsilon kT/4\pi e^2 n_0]^{\frac{1}{2}}, \tag{2}$$

where k is Boltzmann's constant, T is the absolute temperature, e is the protonic charge, and n_0 is the equilibrium bulk concentration of unassociated, mobile cationic vacancies. Lányi's approximate result for C_S (his eqn 34) may now be written in the more transparent form

$$C_S/C_0 = \frac{r_{n1}^2(1+\alpha)^2 + \Omega^2}{r_{n1}^2(1+\alpha) + \Omega^2}, \tag{3}$$

where

$$\begin{aligned} \alpha \equiv L_r/L_{D1} &\equiv [k_0/(k_r/l_0)]/L_{D1} \\ &= (\tau_D D_n/lL_{D1})(r_{n\infty}/r_{n1}) \\ &= (kT/e)(C_g/en_0L_{D1})(r_{n\infty}/r_{n1}) \\ &= (2M_1)^{-1}(r_{n\infty}/r_{n1}) = (r_{n\infty}/2M_1)(\tau/\tau_D). \end{aligned} \tag{4}$$

Here $C_g \equiv \epsilon/4\pi l$ is the geometrical capacitance of the system, and $C_0 \equiv M_1C_g \equiv \epsilon/8\pi L_{D1}$ is the capacitance of two equal diffuse double layers in series when $M_1 \gg 1$ and L_{D1} is the appropriate Debye length. Note that the high frequency limiting value of the bulk conductance is $G_\infty \equiv R_\infty^{-1} = (e/l)(\mu_n n_0)$, where the Einstein relation $D_n = (kT/e)\mu_n$ has been used in eqn (4), and μ_n is the vacancy mobility. The dielectric relaxation time, τ_D, is also equal to $R_\infty C_g$. The quantity L_r in (4) is an effective recombination or reaction length.

Equation (3) shows that $C_S \to C_0$ for $\Omega \gg r_{n1}(1+\alpha)$; i.e. $\omega \gg \tau^{-1}(1+\alpha) = (k_r/l_0) + (k_0/L_{DI})$. This limit is essentially correct[14] for a fully dissociated, one-mobile, situation as long as the resulting $\Omega \lessdot 1$, the main area of interest in space charge polarization experiments[13–15]. But note that $r_{n1}(1+\alpha)$ may possibly exceed unity. Then C_S no longer reduces exactly to C_0 and must be calculated in the $\Omega \gg 1$ region from the exact results developed later in this paper. When $r_{n1} \neq 0$ and $\Omega \to 0$, $C_S \to C_{S0} \equiv C_0(1+\alpha)$, possibly much greater than C_0. Note that the smaller r_{n1} and thus the larger α, however, the lower the frequency range at which the transition to C_{S0} takes place. Clearly, α determines the amount of low-frequency-limiting capacitance of the system, $C_0\alpha = (r_{n\infty}/2r_{n1})C_g$, arising directly from specific adsorption.

When $r_{n\infty} \neq 0$ and $r_{n1} = 0$, eqn (3) yields

$$C_S \to C_0[1 + (r_{n\infty}/2M_1)^2\Omega^{-2}], \tag{5}$$

which goes to ∞ as $\Omega \to 0$. Lányi argues that this reduction leads to the Beaumont-Jacobs (BJ) series capacitance[4], which he states also follows a ω^{-2} dependence at low ω values. This conclusion is incorrect. Beaumont and Jacobs implicitly take $r_{n1} = 0$ and actually work with the components of the polarization admittance of their system[4, 5, 16], Y_2, where $Y_2 \equiv Y_T - (G_\infty + i\omega C_g)$, and Y_T is the total admittance. They calculate no series expressions themselves. The parallel components of $Y_2 \equiv G_2 + i\omega C_2$ should not be used directly to obtain series components from $Z_2 \equiv Y_2^{-1}$ as Lányi evidently did since this procedure does not in general lead to a physically significant series capacitance.

The BJ results are actually consistent[13] with the very general equivalent circuit shown in Fig. 1[5, 13–16] for which $G_\infty \equiv R_\infty^{-1} = R_D^{-1} + R_E^{-1}$. In the one-mobile BJ

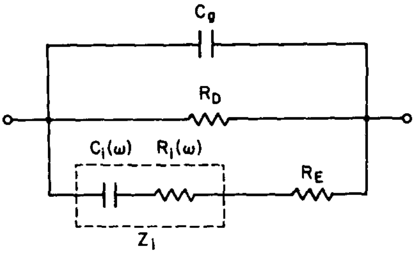

Fig. 1. General equivalent circuit for space charge situations.

situation, where $r_n^* = r_{n\infty} \equiv \rho$, the d.c. resistance, R_D, is not infinite, as it is in Lányi's treatment, unless $\rho = 0$. In fact, one finds [5, 13, 15], $R_D = (1 + 2\rho^{-1})R_\infty$ and $R_E = (1 + 0.5\rho)R_\infty$. The circuit of Fig. 1 is constructed with a maximum number of frequency-independent elements, includes the necessary C_g and R_D in their proper places, and puts all frequency dependent elements in the impedance Z_i. When the series quantities $C_i(\omega)$ and $R_i(\omega)$ are calculated[13] from the BJ result for Z_T, one finds that both C_i and R_i properly approach constant values as $\omega \to 0$. This result was, in fact, well known long before Lányi's work[5, 13–16]. The quantities C_i and R_i are the physically significant series elements here. It is not physically meaningful, however, to express the total Z_T only in terms of overall series elements (not C_i and R_i) when $R_D < \infty$ since the series capacitance thus obtained will then indeed show a ω^{-2} dependence as $\omega \to 0$. Since the high-frequency-limiting resistance R_∞ is made up from R_D, the discharge or d.c. resistance, and R_E in parallel, it is clear that when $R_D = \infty$ and the d.c. conductance is zero, R_E is just R_∞. As the following work demonstrates, this is just the case in Lanyi's $r_{n1} \neq 0$ situation of pure adsorption. It is not the case, however, where the situation is not restricted to pure adsorption and R_D is finite.

EXACT RESULTS FOR THE ONE-MOBILE CONDUCTION SITUATION

Lányi's expressions for series capacitance and resistance are derived for a uni-univalent situation in which only negative charges are mobile. An exact solution of the general space charge-electrode reaction problem has been given, however, in which valences of positive and negative charges are taken arbitrary and both positive and negative species may be mobile with arbitrary mobilities[5]. Further, this solution involves arbitrary r_p and r_n boundary condition parameters instead of the Lányi special choices $r_p = 0$ and r_n given by eqn (1). Thus, the above solution may be readily extended to include more general complex frequency-dependent expressions for r_p and r_n than those applicable in Lányi's special situation.

For example, consider the work of Armstrong and collaborators[11, 12] on reactions with adsorbed intermediates which results directly in expressions for the faradaic admittance of the surface processes. As shown above, Lányi's complex rate constant obeys the limiting conditions $r_n^* \to 0$ as $\omega \to 0$ and $r_n^* \to r_{n\infty}$ as $\omega \to \infty$. Since finite rate constants contribute to the admittance of the system and since Armstrong's analysis shows that the limiting values of the contribution to the conductance G, from electrode processes only, are (for the Armstrong–Henderson model) $G \to R_\infty^{-1}$ (*not* the R_∞ of the present paper) as $\omega \to \infty$ and $G \to R_\infty^{-1} + R_0^{-1}$ as $\omega \to 0$, the effect of an adsorbed intermediate species can cause the complex rate constant r_n^* to go not to zero as $\omega \to 0$ but to some finite value, say r_{n0}. This additional dimensionless boundary condition parameter, which will be zero (Lányi) or positive in most but not all[11] cases of interest, here determines the R_D and R_E of Fig. 1 through $R_{DN} \equiv R_D/R_\infty \equiv [1 + (2/r_{n0})]$ and $R_{EN} \equiv R_E/R_\infty \equiv [1 + (r_{n0}/2)]$ in the one-mobile situation. The expressions for the normalized quantities R_{DN} and R_{EN} are more complicated in the general case[5, 13, 15] but still involve r_{n0} and its analogue r_{p0}. The more general form of r_n^* consistent with the Armstrong–Henderson analysis is, therefore,

$$r_n^* = r_{n\infty} - \frac{(r_{n\infty} - r_{n0})}{1 + i\omega\tau}, \tag{5}$$

which correctly satisfies the above limiting conditions. In order to make contact with Lányi's complex rate constant r_{nL}^* (eqn 1) we identify the above time constant τ with τ_D/r_{n1}, giving

$$r_n^* = \frac{\Omega^2 r_{n\infty} + r_{n0} r_{n1}^2 + i\Omega r_{n1}(r_{n\infty} - r_{n0})}{r_{n1}^2 + \Omega^2}. \tag{6}$$

which reduces to Lányi's rate constant,

$$r_{nL}^* = \frac{\Omega^2 r_{n\infty} + i\Omega r_{n1} r_{n\infty}}{r_{n1}^2 + \Omega^2}, \tag{7}$$

in the limit $r_{n0} \to 0$. The above very heuristic derivation of r_n^* has been avoided in subsequent work[7]. There, an *ab initio* calculation leads to eqn (5) above for r_n^* and to explicit expressions for $r_{n\infty}$, τ, and r_{n0} as well in terms of more basic properties of the material of interest and the electrode reactions present.

Consider now an extrinsic or intrinsic conduction situation involving, for simplicity, equal valence numbers for positive and negative mobile charges but arbitrary mobilities for these species. When an adsorbed intermediate species is present, the exact impedance results for this case may be obtained merely by replacing the r_p and r_n factors appearing in the full solution[5] by r_p^* and r_n^* terms of the form of eqn (5). Such replacement is valid for eqns (A33) to (A43) of Ref. [5] but, because eqn (A43) involves the $\Omega = 0$ values of r_p^* and r_n^*, the analysis leading to an explicit expression for the $Z_i \equiv R_i + (i\omega C_i)^{-1}$ of Fig. 1 must be slightly generalized when r_p^* and r_n^* are frequency dependent.

Frequency response results and complex impedance plane plots for the above rather general situation will be published elsewhere. The general expressions for the admittance Y_2 or the impedance Z_i are quite complicated in this situation but simplify greatly in the present one-mobile case. They will, therefore, be given here for this situation only, using the general expression of eqn (5) for r_n^* rather than the eqn (1) special form following from Lányi's work. In the one-mobile situation with negative charges mobile, r_p^* may be taken identically zero since immobile carriers do not react at the electrodes.

Consider normalized quantities, denoted by a subscript "N." Normalize capacitances with C_g and resistances and impedances with R_∞. If μ_n and μ_p are the mobilities of the mobile species, the present one-mobile limit involves $\pi_m \equiv \mu_n/\mu_p \to \infty$. The parameter $\pi_z = z_n/z_p$ of the general theory is unity here in the equal valence number case. Then let $z_n = z_p \equiv z_e$. Simplification in the $\pi_m \to \infty$ limit is easiest when the $\theta_1{}^2$ eigenvalues of the theory are chosen as in eqns (A7) and (A8) of Ref. [15]. Then $\theta_1{}^2 \to i\infty$ and $\theta_2{}^2 \to \delta_n(1+i\Omega)$, where here

$$\delta_n = n_0/(n_0+p_0), \tag{8}$$

and n_0 and p_0 are equilibrium bulk values of the negative and positive charge concentrations. In the $\pi_z = 1$ intrinsic conduction situation, $n_0 = p_0$, while when the system is strongly n-type extrinsic, as in Lányi's doped NaCl case, $n_0 \gg p_0$[5].

Next, define $M \equiv l/2L_D$, where $L_D \equiv L_{D2} = [\epsilon kT/4\pi(z_e e)^2(n_0+p_0)]^{\frac{1}{2}}$. Note that $M(\delta_n)^{\frac{1}{2}} = M_1$ when $\pi_z = 1$ and L_{D1} is generalized to include z_e. Let

$$\begin{aligned} t_2 &\equiv M\theta_2 \operatorname{ctnh}(M\theta_2) - 1 \\ &= M_1(1+i\Omega)^{\frac{1}{2}} \operatorname{ctnh}[M_1(1+i\Omega)^{\frac{1}{2}}] - 1, \end{aligned} \tag{9}$$

and

$$r_{nm} \equiv (r_{n\infty} - r_{n0}). \tag{10}$$

Then, the exact expression for $Y_{iN} \equiv Z_{iN}^{-1}$ when $\pi_m \to \infty$ is

$$Y_{iN} = (i\Omega g_{n0}^{-2})[t_2(1+i\Omega)^{-1} + 0.5\xi_{na} r_{nm}(1+i\Omega\xi_{na})^{-1}], \tag{11}$$

where

$$g_{n0} \equiv 1 + 0.5 r_{n0}, \tag{12}$$

and

$$\xi_{na} \equiv r_{n1}^{-1} \equiv \tau/\tau_D. \tag{13}$$

To obtain the special Lányi situation, it is only necessary to let $r_{n0} \to 0$. Incidentally, Lányi makes the approximation $\operatorname{ctnh}[M_1(1+i\Omega)] \cong 1$, adequate when $M_1 \gg 1$, the usual experimental case.

As before, let a subscript 0 denote the $\Omega \to 0$ limit. It immediately follows from (11) that

$$C_{iN0} = g_{n0}^{-2}[s+\beta], \tag{14}$$

and

$$R_{iN0} = g_{n0}^{2}\left[\frac{(0.5r_1 - 1) + \xi_{na}\beta}{(s+\beta)^2}\right], \tag{15}$$

where

$$s \equiv M_1 \operatorname{ctnh}(M_1) - 1 \equiv r_1 - 1, \tag{16}$$

and

$$\beta \equiv 0.5\xi_{na} r_{nm}. \tag{17}$$

When $r_{n0} = 0$, $\beta = M_1\alpha$. The total parallel capacitance in the $\Omega \to 0$ limit, $C_{P0} \equiv C_{i0} + C_g$, is, in normalized form,

$$C_{PN0} = (1 - g_{n0}^{-2}) + g_{n0}^{-2}(r_1 + \beta). \tag{18}$$

Thus, C_{P0} will greatly exceed $C_0 \equiv M_1 C_g$ when $g_{n0}^{-2}(r_1+\beta) \gg M_1$. When $r_{n0} \ll 1$ and $\ll r_{n\infty}$ as well, this condition reduces to $\alpha \gg 1$ for the usual $M_1 \gg 1$ situation. Specific adsorption, where α can be much larger than unity, can thus lead to a total low frequency capacitance much greater than the ordinary double layer capacitance C_0[8, 9–12]. The specific adsorption capacitance and resistance arise from the terms involving β in eqns (11), (14) and (15).

These results agree with earlier ones[5, 13, 15] when $\beta = 0$. In particular, when $r_{n0} = 0$ the resulting value of C_{P0}, namely $r_1 C_g$, is just the exact, two-electrode diffuse double layer capacitance found for complete blocking in the limit of small applied potential difference[17, 18]. This is a required result here when r_{n0} and β are both zero since then $r_n^* = 0$ at all frequencies, a complete blocking situation.

When $r_{n0} = 0$ and $\beta \neq 0$, there should be correspondence between Lányi's results and those above. In the $r_{n0} = 0$ case, but not otherwise, one may identify Lányi's R_S and C_S with the present R_i and C_i. Lányi's approximate result for R_S may be written in the form

$$R_S/R_\infty \equiv R_{SN} = (2M_1)^{-1}\left[\frac{r_{n1}^2(1+2r_{n1}^{-1}\alpha) + \Omega^2}{r_{n1}^2(1+\alpha)^2 + \Omega^2}\right]. \tag{19}$$

Equations (3) and (19) do, in fact, agree with (14) and (15), respectively, for $\Omega \to 0$ when Lányi's assumption $M_1 \gg 1$ is made. Then $r_1 \cong M_1 \cong s$. The exact results for C_{iN} and R_{iN} which follow immediately from eqn (11) may be shown to reduce to eqns (3) and (19), respectively, under the following conditions: (a) $r_{n0} = 0$; (b) $M_1 \gg 1$; (c) $M_1 \gg r_{n\infty}$; (d) $\Omega \ll 1$; and (e) $\xi_{na} \gg 1$. All these conditions are well satisfied in Lányi's work. Equations (3) and (19) should not be used in place of (11), when some of these conditions are not satisfied.

PARAMETER VALUES

In comparing theory with Lányi's experimental results for NaCl, it is of interest to consider the magnitudes of various quantities which occur in the theory yet are not directly specified by Lányi. From Lányi's theoretically expected value of C_0, ~0.8 μF/cm^{-2} at 400°C, one obtains $L_{D1} \cong 33.2$ Å on taking $\epsilon = 6$ for NaCl. In turn, this result yields $n_0 \simeq 1.74 \times 10^{18}$ cm^{-3}, slightly smaller than the value of 2.24×10^{18} cm^{-3} expected for 100 ppm doping with $CaCl_2$ and no association. (Lányi erroneously quotes 1.25×10^{18} cm^{-3} instead of 2.24×10^{18} cm^{-3}). It is not entirely clear what value Lányi found for bulk conductance at 400°C. Using his lower quoted value of 2.5×10^{-6} (ohm-cm)$^{-1}$, one finds $D_n \simeq 4.04 \times 10^{-7}$ cm^2/sec from the present value of n_0. With $l = 0.1$ cm, one obtains $C_g \cong 5.31$ pF/cm^2 and $G_\infty = 2.5 \times 10^{-5}$ mho/cm^2, leading to $\tau_D \cong 2.13 \times 10^{-7}$ sec and $M_1 \cong 1.51 \times 10^5$. This value of τ_D corresponds, for $\Omega = 10^{-5}$, to a frequency of about 7.5 Hz. On employing Lányi's values of $k_0 = 3.9 \times 10^{-7}$ cm/sec and

$(k_r/l_0) = 0.85\ \mathrm{sec}^{-1}$, one finds $L_r \cong 4.59 \times 10^{-7}$ cm, yielding $\alpha \cong 1.38$. It follows from this result and the above value of M_1 that $(r_{n\infty}/r_{n1}) \cong 4.16 \times 10^5$. On the other hand, the relation $(r_{n\infty}/r_{n1}) = (l/\tau_D D_n)L_r$ yields 5.34×10^5, showing a small discrepancy in some of the above input figures. Agreement is adequate in view of the uncertainty in some of these figures. The relations $r_{n\infty} \equiv (l/D_n)k_0$ and $r_{n1} \equiv \tau_D(k_r/l_0)$ finally yield $r_{n\infty} \cong 0.097$ and $r_{n1} \cong 1.81 \times 10^{-7}$.

In order to account for his experimental results using a form of eqn (3), Lányi required values of C_0 and α about 25 times larger than those above. He heuristically achieved them by reducing the L_{D1} appearing in the expression for C_0 and the first form given for α in eqn (4) by the factor $\exp(-e\phi_\infty/2kT)$, where ϕ_∞ is a Frenkel-layer static potential difference between the free surface of the material and the bulk[19]. His assumed value of $\phi_\infty = -0.39$ volt yields 28.8 for the above factor at $T = 400°\mathrm{C}$. Then $M_1 \cong 4.35 \times 10^6$ and α becomes 39.9. It is likely that this method of introducing ϕ_∞ will at best be a poor first approximation[5, 19], but it will be followed here since no exact approach is yet available. The 28.8 factor leads to $\tau_D \cong 2.57 \times 10^{-10}$ sec and to $r_{n1} \cong 2.18 \times 10^{-10}$. It appears that somewhat better agreement with Lányi's experimental results for $C_S(\omega)$ of NaCl may be obtained with the slightly different choices $M_1 = 3 \times 10^6$ and $r_{n1} = 5.05 \times 10^{-10}$, leading to $\xi_{na} = 1.98 \times 10^9$. These values, together with $r_{n\infty} = 0.097$ and $\chi = 2000$ will be employed in the subsequent calculations. Here χ is a measure of the extrinsic/intrinsic concentration ratio[5]. Theoretical results are essentially independent of $|\chi|$ in the strongly extrinsic region where $|\chi| \gg 10^2$. The value of α following from the above choices is 32.01.

NUMERICAL RESULTS AND DISCUSSION

The above numerical values of the parameters have been used in a computer program to calculate Z_{TN} and related quantities using eqn (11) for the one-mobile case. Figure 2 shows some of the results as a function of normalized frequency Ω. Here the normalized parallel quantities C_{PN} and G_{PN} follow from $Y_{TN} \equiv Z_{TN}^{-1} \equiv G_{PN} + i\Omega C_{PN}$, and, in the $r_{n0} = 0$ case, $R_{DN} = \infty$, $R_{EN} = 1$, and $Z_{TN} = (Z_{iN} + 1)/[1 + i\Omega(Z_{iN} + 1)]$.

Figure 2 shows that at sufficiently large Ω, R_{iN} and C_{PN} are both proportional to Ω^{-2}. C_{PN} here reaches its high-frequency limiting value of unity by $\Omega \sim 10^{-2}$. At this same value of Ω, R_{iN} has substantially reached the limiting value of $(2M_1)^{-1} \cong 1.667 \times 10^{-7}$ which follows from eqn (19). It turns out that the approximate eqns (3) and (19) yield results for $C_{SN} = C_S/C_0 = C_{iN}$ and $R_{SN} = R_{iN}$ for the present parameter values within better than one per cent of the exact values for the range $0 \leq \Omega \lesssim 10^{-1}$. The true C_{iN} and R_{iN} values begin to drop below the Lányi high-frequency limiting values, however, for $\Omega > 10^{-1}$ and are about 10% lower by $\Omega = 1$. Such drops are usually not significant, however, since most interesting behavior occurs for $\Omega < 1$.

It is the presence of specific adsorption ($\alpha > 0$) which causes R_{iN0} to be large here and C_{iN} and C_{PN} to rise above their essentially common $\Omega \to 0$ value of $C_{0N} = M_1 = 3 \times 10^6$ when $\alpha = 0$. The approximate $\Omega^{-3/2}$ frequency dependence of C_{PN} and C_{iN}, apparent in the figure has been observed experimentally fairly frequently. Its appearance is insufficient evidence to ensure that specific adsorption is present, however, since it has been shown[13, 15] that similar behavior can occur when both positive and negative charges are mobile and r_n^* is real and constant. Detailed analysis of experimental results over a wide frequency range will, in general, be required to allow discrimination between the various situations which can lead to $\Omega^{-3/2}$ behavior. Further, the limiting C_{iN} slope found for α appreciably bigger than its present value of 32 is actually -2, not -1.5. The ≈ -1.5 slope evident in Fig. 2 thus arises here from the limited extent of the C_{iN} rise and is not an intrinsic feature of specific adsorption.

Although curves such as those in Fig. 2 are useful, an overall view of system response can be obtained by plotting the real and imaginary parts of Z_T or Z_{TN} in the complex plane as parametric functions of ω or Ω, as in Fig. 3. The small left-hand semicircle in Fig. 3 arises from C_g and R_∞ in parallel; it is a bulk effect, independent of electrode boundary conditions, and occurs for $\Omega \gtrsim 0.1$. Only when appreciable structure appears to the right of this semicircle, for $\Omega \lesssim 0.1$, will it generally be possible to explore electrode reaction, adsorption, diffusion, etc. effects[13, 15].

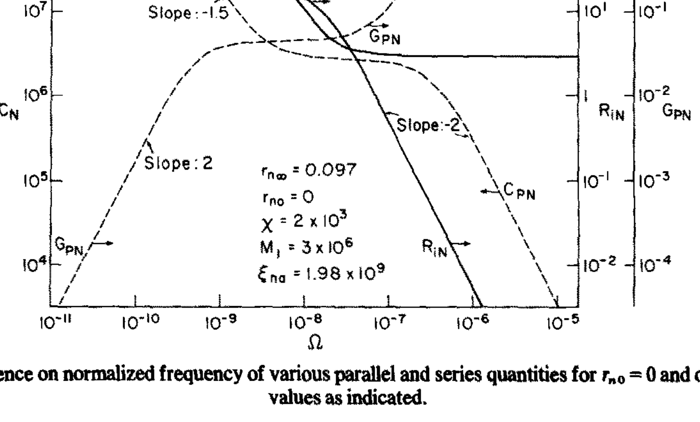

Fig. 2. Dependence on normalized frequency of various parallel and series quantities for $r_{n0} = 0$ and other parameter values as indicated.

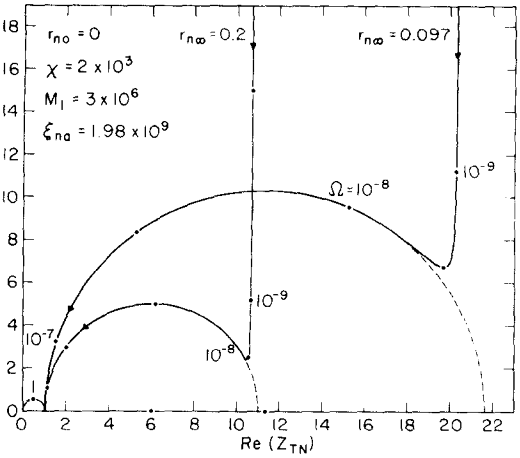

Fig. 3. Complex impedance plane plot of the complex conjugate of Z_{TN} for two values of $r_{n\infty}$.

Figure 3 includes curves for both $r_{n\infty} = 0.097$ and $r_{n\infty} = 0.2$. They show a vertical capacitive rise in $-\mathrm{Im}(Z_{TN})$ as Ω decreases, occurring at a specific real value of Z_{TN} which will be designated R_{CN}. This rise involves the normalized capacitance $C_{PN0} = 1 + C_{iN0}$ and approaches the vertical line at $Re(Z_{TN}) = R_{CN}$ asymptotically. Here $R_{CN} \equiv 1 + R_{iN0}$, where R_{iN0} is given by eqn (15) with $r_{n0} = 0$. The points marked on the $Re(Z_{TN})$ axis show the circle centers for the right-hand semicircles of Fig. 3. The unmarked points on the curves occur at Ω values $\sqrt{10}$ times the next marked smaller Ω value. It is clear from Fig. 3 that when $R_{iN0} \ll 1$, so $R_{CN} \cong 1$, there will be no significant right-hand semicircle. This semicircle can thus substantially disappear for large $r_{n\infty}$, since $R_{iN0} \to (2/r_{n\infty})$ for $\beta \gg s$ when $r_{n0} = 0$.

It has already been shown that in many specific cases of interest the general equivalent circuit of Fig. 1 may be transformed with good approximation into a Maxwell–Wagner type of circuit made up of several parallel RC circuits in series[15]. The present results are no exception. One finds for $M_1 \gg 1$ that the equivalent circuit of Fig. 4, which involves only frequency-independent elements, is a very good approximation to the exact circuit which, of course, involves the frequency dependent R_i and C_i elements. The parallel section on the left is entirely associated with bulk relaxation effects. The second parallel section arises from ordinary electrode reaction effects in the present $r_{n0} = 0$ case where $R_{iN0} \cong 2/r_{n\infty}$. Then both elements of this section are the same as those found earlier[15] for the pure electrode reaction case. Finally, the last series capacitance takes account of specific adsorption. When $r_{n1} \to 0$, this capacitance becomes infinite, R_D becomes finite, and no specific adsorption effects remain.

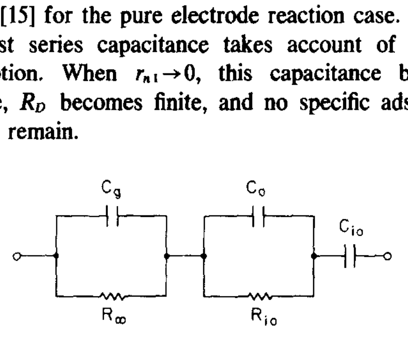

Fig. 4. Approximate form of the general equivalent circuit of Fig. 1 in the present $M_1 \gg 1$ case.

The following numerical results for the $r_{n\infty} = 0.2$ case demonstrate the quality of the present equivalent circuit approximation:

Ω	Z_{TN}
10^{-7}	$1.997 - 2.996\,i$ $2.024 - 3.031\,i$
10^{-8}	$9.924 - 3.135\,i$ $9.945 - 3.102\,i$
10^{-9}	$10.695 - 5.262\,i$ $10.695 - 5.257\,i$

The top numbers of each pair are the exact results; the bottom numbers are the appropriate ones following from the equivalent circuit of Fig. 4 together with eqns (14) and (15) for C_{iN0} and R_{iN0}, respectively. As usual, $C_0 \equiv M_1 C_g$. A generalized, slightly more accurate circuit applicable when charges of both signs may be mobile will be presented in a later paper.

Frequently in the past, the admittance Y_T has been plotted in the admittance plane or the effective complex dielectric constant, which is proportional to $(i\omega)^{-1} Y_T$, has been plotted in the complex plane as Argand diagrams. It is worth emphasizing that whenever the equivalent circuit can be well approximated by a series combination of parallel RC circuits each associated with a single, well-defined physical process as in Fig. 4, it is more natural and preferable to plot Z_T or Z_{TN} in the complex impedance plane instead of Y_T or Y_{TN}. Then, each parallel section can contribute a separate arc in the plane, provided the time constants of the sections are sufficiently well separated. Plotting Y_T or $(i\omega)^{-1} Y_T$ instead mixes together the effects of the separate parallel sections and renders analysis considerably more difficult, particularly when more than two sections are present. Even when the arcs in the impedance plane are not semicircles with centers on the real axis or when the time constants are close enough together to give some melding of arcs, impedance plane plotting is usually preferable to either of the other types of plots.

It is important to note that the general approach of Ref. [5], illustrated herein, can involve an r_n^* of any form and frequency dependence, not just the r_n^* of eqn (5). It also takes direct and integral account of any diffusion of the charged species to and from the electrode without the necessity of the somewhat *ad hoc* later introduction of such diffusion by Armstrong[12]. On the other hand, neither the present procedure nor those of Lányi and Armstrong account explicitly for any diffusion (in/on the electrode) of the intermediate species. In Armstrong's situation, it is assumed that both unadsorbed species are in the (liquid) solution and that both may diffuse. Because the present work takes proper account of the motion of the charged species in the material of interest, it automatically leads to such quantities as C_g, R_D, R_∞ and C_0 rather than requiring them to be added heuristically to the equivalent circuit, as in Armstrong's case.

The impedance and capacitance behavior of space charge systems with charge of one or both signs mobile and the r_n^* of eqn (5) will be considered in detail elsewhere for various values of r_{n0}, $r_{n\infty}$ and ξ_{na}. It will be shown that when $r_{n0} \neq 0$ Z_T may show inductive behavior over an appreciable frequency range, in agreement with experimental observations[10, 20] and the predictions of Armstrong's work[11, 12], and, when $r_{n0} < 0$, the low frequency limiting differential resistance, R_D, can even be negative as well.

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