

phys. stat. sol. (a) 43, K169 (1977)

Subject classification: 14.3.2; 14.3.4

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Comment on the Small-Signal AC Response of Solid Electrolytes²⁾

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In a recent interesting paper /1/ Kornyshev and Vorotyntsev (henceforth referred to as KV) presented an approximate analysis of the response of a solid electrolyte to small electrical perturbations. When this paper appeared we had recently completed an analysis /2, 3/ of a somewhat more general problem than that considered by KV, without making the approximations employed by them. Here we discuss the relationship of our result to that of KV and to earlier treatments /4 to 6/ of small-signal electrical response not mentioned by KV. We hope that this comparison will help in making clear the physical implications of the approximate perturbation approach used by KV for ac and transient response and by Itskovich and KV /7/ for steady-state dc behavior.

Although Itskovich and KV /7/ remark that some treatments of electrolyte with two mobile species of charge carrier are not directly reducible to the particular solid electrolyte case in which only one species of charge carrier is considered to be mobile, the small-signal theories of Macdonald /4, 5/, Friauf /6/, and Beaumont and Jacobs /8/ are not so limited and provide a single logically consistent treatment of both the two-mobile-carrier and one-mobile-carrier cases. These treatments are somewhat restricted in their applicability, however, by their neglect of compact layer effects through their use of the Chang and Jaffé /9/ boundary condition, which, for positive charge carriers reacting with a metal electrode placed to the left of the electrolyte, may be written

$$I_{pL} = -z_p e k_p (p_L - p_e), \quad (1)$$

where I_{pL} is the current of charge carriers, z_p the valence number of the carriers, k_p a rate constant, p_L the concentration of charge carriers at the electrode surface, and p_e the equilibrium concentration of charge carriers.

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2) Work supported by U.S. National Science Foundation, Grant No. DMR 75-10739.

Our more recent analysis /2, 3/, however, made use of the boundary condition

$$I_{pL} = -z_p e \left[k_p (p_L - p_e) + (z_p e \eta / kT) \gamma_p p_e \right], \quad (2)$$

which applies in the limit of small deviations from equilibrium to a wide range of first-order electrode reactions. Here p_L is evaluated a distance d from the electrode surface, η is the potential drop across the compact layer of thickness d and dielectric constant ϵ_1 , and γ_p is a parameter (with the dimensions of k_p) which reflects the dependence of the electrode reaction rate on the overpotential η . (Our original treatment /3/ dealt with negative mobile charge carriers and defined η as the potential of the right-hand electrode minus that on the electrolyte side of the right-hand compact layer. Here, as in the treatment of KV, we consider positive charge carriers and define η as the potential of the left-hand electrode relative to that of the electrolyte side of the corresponding compact layer.) It is readily verified that for a system in which the static electric field is negligible in the absence of an applied static potential (as assumed in our treatment and that of KV) the Butler-Volmer, or Frumkin /10, 11/, expression for the rate of electrode reaction used by VR reduces to (2) with $\gamma_p = -k_p$.

Our result was derived for a slab of electrolyte between two identical metal electrodes. We let $R_\infty \equiv 1/\sigma$ denote the limiting high frequency resistance and $C_g \equiv \epsilon/4\pi l$ denote the geometric capacitance of the cell (l is the length of the electrolyte, not counting the compact layers, σ its conductivity, and ϵ its dielectric constant) 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 . Our fundamental result may be written (for mobile positive charge carriers) as

$$Z_N = Z_{CJN} + Z_N^I, \quad (3)$$

where /4 to 6/

$$Z_{CJN} = \frac{2 + (1 + i\Omega)r_p + 2i\Omega\gamma_1}{(1 + i\Omega)((1 + i\Omega)r_p + 2i\Omega\gamma_1)} \quad (4)$$

is the impedance of the cell as determined for Chang and Jaffé boundary conditions /3, 5/, and /3, 12/

$$Z'_N = \frac{(r_p + 2\gamma_1) [r_p(1 + i\Omega + \nu_p) + 2i\Omega\gamma_1]}{(C_{CN}(r_p(1 + i\Omega) + 2i\Omega\gamma_1) - \gamma_1 r_p \nu_p)(r_p(1 + i\Omega) + 2i\Omega\gamma_1)} \quad (5)$$

is a correction for compact layer effects. Here Ω is the angular frequency expressed in units of τ_D^{-1} , where $\tau_D \equiv \epsilon/4\pi\sigma$ is the dielectric relaxation time; $\nu_p \equiv \gamma_p/k_p$, which is (-1) for the electrode kinetics assumed by KV; $r_p \equiv D_p k_p/l$, where D_p is the diffusion coefficient of the charge carriers; $C_{CN} \equiv \epsilon_1 l_h/\epsilon d$ is the normalized capacitance of the compact layer; and $\gamma_1 \equiv (M_p \theta_1) \text{ctnh}(M_p \theta_1)$, where $\theta_1^2 \equiv (1 + i\Omega)$, $M_p \equiv 1/2L_{Dp}$, and L_{Dp} is the effective Debye length for mobile positive carriers. Our results, (3) to (5), constitute an exact solution to the linearized equations of charge transport /1, 3/, subject to the boundary condition (2) (and the equivalent condition at the right-hand electrode) and entail no assumptions about the relative size of l , L_{Dn} , d or r_p . The correction Z'_N is negligible in many cases but becomes potentially significant for $r_p \ll M_p$ and $M_p C_{CN}^{-1} = \epsilon d/\epsilon_1 L_{Dp} \approx 1$.

In their treatment /1/ KV consider the electrolyte to be in contact with a single polarizable electrode, obeying Frumkin ($\nu_p = -1$) delayed action kinetics, and require that at a distance L from the electrode $p = p_e$ and $\bar{\Phi} = 0$, where $\bar{\Phi}$ is the electrostatic potential. KV refer to L as the diffusion length. We feel that this terminology is unfortunate since the diffusion length concept is often associated with electrochemical cells in which there is hydrodynamic flow and frequently the presence of an indifferent or supporting electrolyte, conditions not usually encountered in the solid state. In dealing with solid electrolytes, one must in general consider all the material between two non-ohmic electrodes. It is readily shown /3/, however, that in the present case the impedance of a symmetrical cell expressed in units of R_∞ is equal to the impedance of an idealized half-cell, consisting of half the electrolyte bulk placed between a single polarizable electrode and an ohmic electrode (for which $p = p_e$ and $\bar{\Phi} = 0$) expressed in units of its high-frequency-limiting resistance, which equals $R_\infty/2$. We are thus able to interpret L , as employed by KV, as $l/2$.

KV explicitly assume $M_p \gg 1$, $C_{CN} \gg 1$, and $r_p \ll M_p$ in their treatment. Their result may be expressed as a normalized admittance $Y_N \equiv Z_N^{-1}$:

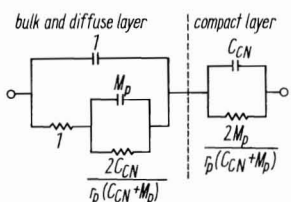


Fig. 1. Normalized equivalent circuit which reproduces Y_N (7) in the $\Omega \ll 1$ limit. Expressions for the resistive elements are given as normalized resistances, not conductances

$$Y_N = \frac{4M_p^2 \Omega^2 + r_p(r_p + 2)(1 + M_p C_{CN}^{-1})^2}{(r_p + 2)^2 (1 + M_p C_{CN}^{-1})^2 + 4M_p^2 \Omega^2} + i \frac{4M_p^2 \Omega^3 + 4M_p \Omega (1 + M_p C_{CN}^{-1})}{(r_p + 2)^2 (1 + M_p C_{CN}^{-1})^2 + 4M_p^2 \Omega^2} \quad (6)$$

(In the notation of KV, M_p , r_p , $M_p C_{CN}^{-1}$, and Ω are ϵ^{-1} , $2j^*$, γ , and Ωt_D , respectively.) Under the same assumptions concerning M_p , C_{CN} , and r_p and in the low frequency region ($\Omega \ll 1$), we obtain an expression for Y_N which in rationalized form is

$$Y_N = \frac{4M_p^2 \Omega^2 + r_p(r_p + 2)(1 + M_p C_{CN}^{-1})^2}{(r_p + 2)^2 (1 + M_p C_{CN}^{-1})^2 + 4M_p^2 \Omega^2} + i \frac{4M_p \Omega (1 + M_p C_{CN}^{-1})}{(r_p + 2)^2 (1 + M_p C_{CN}^{-1})^2 + 4M_p^2 \Omega^2} \quad (7)$$

differing from (6) only in the absence of $4M_p^2 \Omega^3$ in the numerator of the imaginary part. If higher order terms in Ω are retained until after the separation of real and imaginary parts of Y_N , (7) is obtained, but it should be noted that for $\Omega \ll 1$, $M_p^2 \Omega^3 \ll M_p^2 \Omega^2$ and should be neglected. We conclude that even under the restraints on M_p , C_{CN} , and r_p required by KV, their result is only valid for $\Omega \ll 1$, a limitation not stated by those authors, and that (7) provides an adequate expression for Y_N in that case. When $M_p C_{CN}^{-1} \ll 1$, this expression coincides in the small Ω region with the corresponding result of earlier treatments /3, 5, 6, 8/.

We present in Fig. 1 an equivalent electrical circuit which in the $\Omega \ll 1$ limit has the admittance given by (7). This admittance is readily transformed to yield an expression for the transient response to a small potential step, which should be valid for $t \gg \tau_D$. A discussion of equivalent circuit representations of the more general exact impedance of (3) to (5) has been included in a forthcoming publication /12/.

It should be noted that the above discussion applies only for a mobile species of charge which does not recombine with the oppositely charged immobile species present. An exact small-signal solution has been obtained /13/ for the intrinsic-extrinsic conduction problem with positive and negative species of arbitrary mobilities and valence numbers and arbitrary intrinsic and extrinsic generation and recombination rates, satisfying generalized Chang and Jaffé boundary conditions which incorporate the possible presence of specific ionic adsorption /14/. Work is in progress on extending this solution to include more general electrode kinetics.

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(Received July 8, 1977)