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# Some electrode charge-transfer effects in solid ionic materials

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Recent work on electrode polarization effects in ionic conductors is discussed and extended. Contrary to a recent suggestion, analysis of the ac conduction and electrode processes occurring in such materials should involve effectively mobile charged species of both signs, not just a single mobile species. Special consideration of likely charge-transfer reactions in solid materials such as  $\beta$ -alumina with platinum electrodes leads to a new specific result for the Warburg impedance appropriate for such situations. The over-all impedance of the system involves a very high parallel capacitance showing  $\omega^{-m}$  frequency response, with  $0.5 \leq m \leq 1.5$ , of the type very frequently found experimentally.

Mitoff and Charles<sup>1</sup> have recently pointed out that their paper<sup>2</sup> was concerned with ionic solids in which conduction proceeded insofar as possible by a single mobile ionic species, and they have now identified explicitly the species they expect to be mobile in the three experimental materials they considered earlier.<sup>2</sup> They suggest that some recent discussion and criticism<sup>3</sup> of their work<sup>2</sup> are inappropriate because they were based on the results of a theory in which charges of both signs were mobile, with generally equal mobilities, and "the possibility of allowing the mobility of one of the ions to become zero is not explicitly accounted for."<sup>1</sup> In fact, the space-charge theory in question<sup>4-6</sup> allows arbitrary mobilities  $\mu_n$  and  $\mu_p$  for charge carriers of opposite sign. Thus, it can and does apply equally well to the one-mobile situation.<sup>7</sup> Furthermore, several of the suggested new explanations of the Mitoff-Charles results<sup>2</sup> were explicitly concerned with the theoretical situation where the two mobilities were very different.<sup>3</sup>

Actually, one should never expect to observe true one-mobile behavior at nonzero measurement temperatures. Not only will there always be some residual mobility for the "immobile" charge carrier but, usually more important, there will be present some recombination between immobile charged carriers and mobile carriers of opposite sign. But generation-recombination (as in the intrinsic-conduction NaCl case considered by Mitoff and Charles<sup>2</sup>) will effectively mobilize the immobile charges.<sup>4,8</sup> It is thus clear that if one goes to long enough times or to low enough frequencies of measurement, one will observe effects arising from the effective mobility of immobile charges. In this sense, it is therefore always proper to use a two-mobile (or more) theory to try to explain experimental space-charge results, and it is never appropriate, except at sufficient-

ly short times or high frequencies, to approximate matters by means of a one-mobile theory.

The Mitoff-Charles theoretical analysis incorporated a Warburg impedance associated with a single electrode,<sup>2,9</sup> although two presumably identical platinum electrodes were usually employed experimentally. The earlier comment<sup>3</sup> on their work pointed out that this impedance would be doubled for their case of two essentially identical plane-parallel electrodes. This comment was, however, based on the results of earlier theoretical work<sup>5</sup> on the binary electrolyte situation in which it was assumed that a single species of mobile ion could react directly with both electrodes, while the species of opposite sign was either completely or nearly completely blocked. The charge-transfer process at, for example, a silver cathodic electrode then transforms at Ag<sup>+</sup> ion to a Ag atom and at the silver anode transforms a silver atom to an ion. The experimental situations of Mitoff and Charles are, however, more complicated. For example, for sodium  $\beta$ -alumina the most mobile ion is Na<sup>+</sup>, but the electrodes were platinum and the material was usually in an oxygen-containing atmosphere.

For an applied ac potential without dc bias, when one platinum electrode is first made negative the mobile Na<sup>+</sup> species can discharge at this electrode. The resulting sodium atoms may diffuse somewhat into the platinum and alloy there, but, to a first approximation, one may consider them available to form Na<sup>+</sup> again when this electrode is next positive. The electrode is thus approximately reversible for sodium ions. But, when one electrode is first made cathodic the other is anodic. There are however, initially scarcely any sodium atoms at this electrode to oxidize. In sodium  $\beta$ -alumina there

will be oxygen ions available, however, and, as Mitoff and Charles pointed out,<sup>2</sup> free oxygen (or, more probably, immobile platinum oxide) must form at the anodic platinum electrode. On the next half-cycle, the reduction of this oxide will be much more thermodynamically favored than will be the reduction of Na<sup>+</sup>. Thus the charge-transfer processes occurring at the two electrodes may be quite different and may even involve different reacting species. In this situation Faradaic conduction may take place primarily with one species of mobile ion near one electrode and with another species at the other electrode.<sup>10</sup>

Now very little charge storage or ac capacitance effects would be expected to occur at the electrode where Na<sup>+</sup> may be able to discharge, as indeed was verified by Mitoff and Charles's dc and unipolar discharge measurements<sup>2</sup> on glass containing mobile Na<sup>+</sup>. The ac impedance is then dominated by the impedance of the other electrode, where oxygen ions form platinum oxide and then transform back again to mobile ions (in the absence of net loss of oxygen to the ambient) as the polarity changes. At this electrode sodium ions are essentially completely blocked but probably have a considerably higher effective mobility than do the only partially blocked oxygen ions ( $\mu_p \gg \mu_n$ ). But this is just the situation envisaged in the partially blocking space-charge theory<sup>6</sup> originally proposed<sup>3</sup> to explain the high-capacitance Mitoff-Charles results.<sup>2</sup> In the notation of the earlier work,<sup>6</sup> the general situation ( $r_p, r_n; \pi_m, \pi_e; 0, M$ ) becomes ( $0, r_n; \pi_m, 2; 0, M$ ), with  $\pi_m \equiv \mu_n/\mu_p$  probably much less than unity and  $r_n \gg 1$ . Here,  $\pi_e \equiv z_n/z_p$  is the valence-number ratio for the two mobile charged species considered and  $r_n$  defines the degree of blocking (none present for  $r_n = \infty$ ) of the negative species at the electrode. The mobility ratio  $\pi_m$  should be interpreted, as appropriate, as the ratio of effective mobilities, those arising from both true mobility and recombination.

In the frequency region where the Warburg impedance  $Z_w$  dominates, the binary-electrolyte partially blocking theory leads, for a single dominant working electrode, to the following expression for the intensive interface impedance per unit area of the electrode<sup>6,11</sup>:

$$Z_i \cong Z_w = A_0(1 - i)/\sqrt{\omega}, \quad (1)$$

where  $\omega$  is the radial frequency and, in the  $\pi_m \ll 1$  situation,  $Z_i$  is essentially equal to the total specific impedance of the system.

The single-working-electrode Warburg parameter  $A_0$  is given in general for  $r_n \gg 1$  by<sup>6,11</sup>

$$A_0 \cong \left\{ \frac{e^2}{\sqrt{2}kT} (z_n n_i + z_p p_i) \left[ (z_p D_p)^{-1} + (z_n D_n)^{-1} \right] (z_p^{-1} + z_n^{-1})^{-1/2} \right\}^{-1}. \quad (2)$$

Thus, in the present redox situation, where oxygen ions are not completely blocked,

$$A_0 \cong \left\{ \frac{4e^2 n_i}{\sqrt{3}kT} [D_p^{-1} + (2D_n)^{-1}]^{-1/2} \right\}^{-1} \cong (kT/4e^2 n_i) (3/2D_n)^{1/2}. \quad (3)$$

The diffusion coefficients appearing here are related to the mobilities by  $D_i = (kT/ez_i)\mu_i$ .  $k$ ,  $T$ , and  $e$  have their usual meanings. The reduction above used the

electroneutrality condition  $z_n n_i = z_p p_i$ , where  $n_i$  and  $p_i$  are the equilibrium bulk values of the negative and positive ionic concentrations, and  $D_p^{-1}$  was neglected compared to  $(2D_n)^{-1}$  in passing to Eq. (3). As mentioned earlier,<sup>3,6</sup> the specific series or parallel capacitance following from Eqs. (1) and (2) may be very much larger than the ordinary completely blocking double-layer specific capacitance.

It is important to note that if the sodium atoms, which are first formed at one electrode when it is cathodic, diffuse too far away into the platinum electrode to be available for oxidation back to ions when the electrode is next anodic, this electrode will also tend to become blocking for Na<sup>+</sup>, and the remaining process occurring at this electrode will be just the redox reaction of oxygen ions already mentioned as being dominant at the other electrode. This is also the situation to be expected if oxygen is freely available at both electrodes, as should be the case when the ambient atmosphere is air, since oxygen will be reduced in preference to Na<sup>+</sup>. Then the same dominating process will occur at both electrodes and the  $A_0$  given in Eqs. (2) and (3) will be doubled. This is then just the situation originally considered,<sup>3</sup> now involving oxygen ions as the reacting species. Whether or not the electrode in question is reversible or blocking for Na<sup>+</sup> will clearly depend on the availability of oxygen and on the balance between the diffusion coefficient of Na in the platinum and the period of the applied ac potential in the frequency region where the oxygen redox process occurs. The availability or lack of oxygen certainly seems to have some effect in the Mitoff-Charles experiments since the shape of their capacitance-frequency curves for  $\beta$ -alumina depends appreciably on whether the electrodes were exposed to the atmosphere or sealed from it.<sup>2</sup>

In place of the above general expression for  $A_0$ , which follows from a treatment of a binary-electrolyte system without supporting electrolyte,<sup>3</sup> Mitoff and Charles employed

$$A_0 = (kT/n^2 e^2 \rho_0) (2/D)^{1/2}, \quad (4)$$

where  $\rho_0$  is the concentration of the diffusing species and  $D$  its diffusion coefficient.<sup>2</sup>  $n$  was undefined but is commonly taken to be the number of electrons participating in the reaction per reacting ion. This result is, however, that which arises for a single working electrode in the case of a supported electrolyte when the diffusion coefficients of the oxidized and reduced species are the same and the electron transfer reaction rate constant may be approximated as infinite.<sup>9</sup> But it seems very likely that in the Mitoff-Charles experimental situations the implicit assumption of a supported electrolyte situation is inappropriate.<sup>3</sup> Furthermore, there is no reason to assume equal diffusion coefficients in these situations.

But Eq. (4) is also the result one would find if one of the species in a supported electrolyte had a much lower diffusion coefficient  $D$  than the other, and the same electrode process, involving the same ion, occurred at each of two identical electrodes. Mitoff and Charles have suggested that the Warburg diffusion mechanism they consider may entail migration of alkali metal atoms within the solid electrolyte or the electrode or

both.<sup>2</sup> Then  $n=1$ ,  $D$  pertains to Na not  $\text{Na}^+$ , and Eq. (4) seems superficially similar to Eq. (3). But we have seen that identical processes in  $\beta$ -alumina can occur at both electrodes only when  $\text{Na}^+$  is effectively blocked at the electrodes and the redox reaction involves oxygen, not sodium. Thus, this interpretation also does not seem to allow Eq. (4) to be applicable for the actual experimental situation, and the interpretation leading to the result of Eq. (3), or twice this  $A_0$ , seems more appropriate.

When  $\pi_m \ll 10^{-1}$  and the  $Z_i$  of Eq. (1) is essentially the over-all specific impedance of the material, the parallel capacitance following from this impedance will be proportional to  $\omega^{-1/2}$  in the Warburg region. Some of Mitoff and Charles's experimental curves<sup>2</sup> for  $\beta$ -alumina indeed show slopes of approximately  $-0.5$ . On the other hand, it turns out that when  $\pi_m \gtrsim 10^{-2}$ ,  $Z_i$  is still given by Eq. (1) and  $A_0$  by Eq. (3), but  $D_p^{-1}$  should not be neglected and the over-all impedance is no longer nearly equal to  $Z_i$ . The theory<sup>6</sup> then shows that the over-all parallel capacitance follows a  $\omega^{-3/2}$  law over a considerable frequency range. Again, many of the Mitoff-Charles curves, especially those for soda-lime glass, show appreciable portions with a slope of  $-1.5$ . It thus still seems likely that the general space-charge theory can explain or help explain many of the Mitoff-Charles

results, contrary to their recent conclusions.<sup>1</sup> In fact, when partial rather than complete blocking occurs, it seems rare for experimental results not to show parallel capacitance frequency response of the form  $\omega^{-m}$  with  $0.5 \leq m \leq 1.5$ .

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