

Electrode polarization of ionic conductors

J. Ross Macdonald

Texas Instruments Incorporated, Dallas, Texas 75222
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A theoretical analysis by Mitoff and Charles of electrode processes for an ionic material is criticized and corrected. These authors introduce three separate capacitances into their equivalent circuit where only one need appear. This frequency-dependent diffusion-discharge capacitance is calculated incorrectly by Mitoff and Charles, and earlier relevant work is ignored. Partial blocking small-signal theory is used to show that Mitoff and Charles's experimental results on three different ionic materials can quite possibly be understood using such an approach, contrary to these authors' expectations.

INTRODUCTION

The recent paper by Mitoff and Charles¹ (hereafter abbreviated MC) seems to involve some misconceptions which may mislead the reader, contains some errors, and fails to make use of pertinent earlier work. MC found very large parallel capacitances and concomitant dc discharge currents for β -alumina, soda-lime glass, and single-crystal NaCl. They do not clearly identify the mobile species responsible for electrical conduction in two of these three materials but evidently assume conduction by vacancies or ions, with charges of one sign possibly much more mobile than those of the other sign.

Although MC suggest that space-charge effects arising from the presence of completely blocking electrodes cannot yield sufficiently high capacitances to explain any of their results, they do not refer to previous published treatments^{2,3} of partial blocking situations, where some discharge occurs and space-charge effects are still present.^{3,4} Although they do cite Friauf's basic work, they only mention his completely-blocking-electrodes theory.^{2,5} But Friauf also considered the (Faradaic process⁶) situation where an electrochemical reaction occurs at an electrode and involves mobile charge carriers.² Such a reaction leads to partial or zero blocking for the discharging species and to exceptionally high capacitances, termed pseudocapacitances in the electrochemistry area. On the other hand, MC state¹ that "space-charge theory, as developed for blocking or even partially blocking electrodes, is not applicable as a description of the anomalous capacitance observed during the electrolytic conduction of common ionic solids". This broad statement is incorrect and may perhaps be associated with MC's failure to cite and use any relevant published work later than 1960. MC thus do not recognize that their own analysis can be considered to be an example of a partially-blocked-electrodes space-charge theory. An excellent treatment of blocking, partly blocking, and reversible electrodes on solids has been given by Kröger.⁷

Since MC did not associate partial blocking with a Faradaic process,^{3,6} they developed their own theory of such an effect, unnecessarily distinguishing it from a partially blocking space-charge situation. Their treatment is, however, *ad hoc* and probably less applicable than the results of earlier published work²⁻⁵ which solves the basic charge transport equations directly and exactly. MC concluded from their work that "the storage of electrical charge, however, is accomplished at the elec-

trode by adsorbed metal atoms rather than electrons". This statement may be misleading. First, electrical charge is not directly stored in the form of neutral atoms (except, of course, for ordinary dielectric polarization, which does not involve free charge). Even adatoms have a fractional effective charge. Second, the high effective capacitance arising from an electrode reaction is not primarily associated with stored charge at all, either distributed charge, as in a space-charge region, or localized adsorbed charge, as in specific ionic adsorption.³ Instead, what is stored is the potential energy of an electrochemical reaction, as in a storage battery. This stored energy, associated with the instantaneous nonequilibrium difference in electrochemical potential between two electrodes, is converted to kinetic energy when a current of charged particles flows. Although such flow usually involves a very high pseudocapacitance not associated with stored space charge, this capacitance is frequently obscured in ac measurements by the in-phase component of current flow. Now though metal ions may discharge at the electrode while it is cathodic and the resulting adsorbed metal atoms may ionize when it is anodic, the large pseudocapacitance produced is associated with the discharge-ionization process itself,^{3,6} not specifically with any metal atoms stored at the electrode which do not participate in the reaction.

Finally, MC's use of the concept of an effective dielectric constant is inappropriate for a situation where large capacitances arise from space-charge or electrode reactions. The dielectric constant is an intensive quantity, whereas the effects of space-charge or electrode reactions are not. Thus, the large capacitances arising from such processes should not properly be described by means of a dielectric constant, effective or not.

THE MITOFF-CHARLES ANALYSIS

MC begin by considering a simple electrode reaction which leads to adsorbed (desorbed) atoms. They introduce a frequency-independent adsorption capacitance in their equivalent circuit to account for this process. Since neither a complete physical explanation nor a theoretical derivation of this adsorption capacitance is provided, it should be emphasized for the reader that it is not that associated with the common electrochemical process of specific ionic adsorption.

Next, MC separately consider the diffusion of "electrically altered" species toward and away from the elec-

trode. These considerations lead to the introduction of a Warburg diffusion impedance^{3,8,9} into the equivalent circuit. This separation of discharge (adsorption capacitance) and Warburg diffusion impedance into two separate processes seems to be incorrect. It is the diffusion toward and away from an electrode of species which participate in an electrode reaction and their discharge (or generation) at the electrode which leads to the usual Warburg impedance. There is only one capacitance arising from this process, not two.³

There are also some difficulties in MC's treatment of the Warburg impedance Z itself. They begin by writing essentially

$$Z = \beta / (\omega D)^{1/2}. \quad (1)$$

Here ω is the radial frequency, D the diffusion constant of the reacting species, $\beta \equiv RT/n^2 F^2 \rho_0$, R is the gas constant, F the Faraday, n the number of electrons participating in the reaction, and ρ_0 the concentration of the diffusing species. This equation and its application to the MC situation of two equal-area electrodes are wrong on several counts. First, Eq. (1) defines a resistance, not a complex impedance and applies for unit-area electrodes. Let $(-1)^{1/2} \equiv i$. Then the right-hand side of (1) must be multiplied by $2/\sqrt{i}$ to lead to MC's next equation,

$$Z = (1 - i)\beta(2/\omega D)^{1/2}. \quad (2)$$

Second, Eq. (2), which is the usual expression for the unit-area Warburg impedance for a single (forward-reverse) reaction at a single working electrode,^{3,8,9} was originally derived for the usual electrochemical case of quasineutrality, that where a supporting indifferent electrolyte is present.^{3,4} But for the MC situation of mobile positive and negative charge carriers in a solid, there is no supporting electrolyte and quasineutrality is therefore a poor approximation. There thus seems to be no *a priori* reason to expect that (2) should apply to the MC case. Only recently, in fact, has Warburg behavior actually been identified, from a detailed microscopic treatment, as being present in an unsupported situation, such as that usually found in solids and fused salts.^{3,4}

The one-electrode Warburg expression is pertinent to the usual liquid-electrolyte situation because there a large-area counterelectrode is generally used together with a working electrode of much smaller effective area. Thus, only processes occurring at the working electrode contribute appreciably to the over-all impedance. When two similar plane-parallel electrodes of equal or nearly equal area are present instead, the usual MC case, the situation is different.^{3,4} Consider a single reacting species which, at a given instant, might be undergoing the oxidizing phase of the reaction at one electrode and the reducing phase at the other. If we take ρ_0 as the unperturbed bulk concentration of this species, then the result equivalent to (2) for two equal-area electrodes is

$$Z = 2(1 - i)\beta(2/\omega D)^{1/2}, \quad (3)$$

in agreement with the earlier detailed analysis of a partial blocking situation where charges of one sign discharge freely, those of the other sign are completely

blocked at the electrodes, and charges of both signs have the same mobility.³

But even Eq. (3) is not entirely applicable to the MC situation. It has been shown^{3,4} that (3) no longer holds when the diffusion length, here $(D/\omega)^{1/2}$, becomes comparable to the electrode separation l . For lower frequencies, the theoretical capacitance no longer follows (3) in indefinitely increasing but begins to saturate towards a final low-frequency limiting value. Thus, MC's *ad hoc* procedure of adding in a conventional Warburg impedance should be replaced by the results of a coordinated detailed treatment of the situation. Incidentally, such a treatment shows^{3,4} that it is inappropriate to break out a separate diffuse-layer frequency-independent capacitance as MC have done or to have no frequency-independent conducting path from electrode to electrode. MC have no such path in their equivalent circuit, Fig. 6, since their $R_D \rightarrow \infty$ as $\omega \rightarrow 0$. Finally, in place of MC's three separate capacitances (adsorption, diffusion, and diffuse double layer), the microscopic analysis leads to a single frequency-dependent capacitance, dominated by the diffusion-discharge process. Note that although the above analysis omits consideration of the inner solvent layer found next to the electrodes in liquid electrolytes, there should be no such layer in solids. Although the geometrical capacitance of the system in the absence of mobile charge has not been mentioned, it is included in earlier treatments²⁻⁵ and by MC.

BLOCKING AND DISCHARGE THEORIES

Although the presently published^{3,4} detailed treatments of the two-electrode, discharge, Faradaic process, electrochemical reaction, partly blocking situations involve unit valences and equal mobilities of the oppositely charged mobile species, these restrictions have been lifted in subsequent work.¹⁰ It turns out for partial blocking that the zero-frequency limiting capacitance, which is properly independent of the mobility ratio, can be as much as $\frac{1}{2}M$ times larger than that applying for completely blocking electrodes.^{2-4,10} Here $M \equiv l/2L_D$, l is the electrode separation, and L_D is the bulk Debye length. Since the quantity M may readily be 10^4 – 10^7 or so, the partial blocking discharge theory can yield tremendous capacitances per unit area, as large as anyone has measured thus far. Thus, it can easily explain the magnitude of the MC results without the introduction of the physically implausible small Debye lengths mentioned by MC.

The previously published main space-charge completely and partially blocking theories²⁻⁵ are all concerned with an intrinsic conduction situation.⁵ The new ac space-charge discharge theory¹⁰ includes all conditions from completely intrinsic to strongly extrinsic, a useful generalization since many authors have used the available intrinsic theories to analyze experimental results obtained at temperatures where extrinsic conduction was dominant. The consequent neglect of minority carriers, especially when they are the discharge species, is a probable reason for some of the disagreement found between theory and experiment.

FURTHER ANALYSIS OF MC RESULTS

NaCl

MC studied high-purity single-crystal NaCl fitted with platinum electrodes. Their ac and dc measurements were made at 720 °C; they attributed their results principally to the atom adsorption process; and they expected conduction to involve primarily sodium ion vacancies. Here it is of interest to discuss briefly to what degree the MC results¹ can be explained by the coordinated blocking-discharge theory.^{3-5,10} The MC ac results exhibit ω^{-2} response of the parallel capacitance, C_p , beginning to show some approach toward saturation at the lowest frequency employed, 10 Hz. The saturated value appears to lie between 2 and 4 μF . Now complete blocking theory^{3,5} leads to both ω^{-2} response and to $C_{p0} \approx MC_g \equiv \epsilon A / 8\pi L_D$. Here ϵ is the bulk dielectric constant, A the electrode area, C_g the geometric capacitance, and C_{p0} the low-frequency limiting parallel capacitance. Using MC's values of ϵ , L_D , and A , we find $C_{p0} \approx 2.8 \mu\text{F}$, in excellent agreement with the above estimate. Further, the situation should indeed be intrinsic in a high-purity NaCl crystal at 720 °C. Since the C_{p0} estimate and C_p frequency response are both in good agreement with apparently applicable completely-blocking-electrode space-charge theory, it would be easy to conclude that such a theory can explain the results. Further confidence could have been gained had parallel conductance as a function of frequency been reported as well, and its dependence also found consistent.

MC reject the completely blocking space-charge explanation because dc time-voltage discharge results require a value of $C_{p0} > 100 \mu\text{F}$ and a concomitant Debye length much smaller than plausible. But recent results for the intrinsic partially blocking case¹⁰ show that when the mobilities of positive and negative carriers are very different and that of the discharging carrier is lowest, one obtains the following sort of frequency response for C_p : At high relative frequencies, $C_p \propto \omega^{-2}$. At lower frequencies, it saturates at a value of $MC_g/\sqrt{2}$ (these results also follow from complete blocking theory⁵) over a frequency region whose length depends on the mobility ratio, then at even lower frequencies, $C_p \propto \omega^{-1/2}$ until it reaches the final partial blocking low-frequency limiting value, $\frac{1}{12}M^2C_g$. Thus, it is clear that a given material may behave essentially as if the electrodes were completely blocking for an upper frequency range and as partially blocking at lower frequencies down to zero.

Unfortunately, MC give no value of l . If it is 10^{-2} cm, for example, $M \approx 2 \times 10^4$, and the ratio of the two constant- C_p regions ($\frac{1}{12}M^2C_g$ and $MC_g/\sqrt{2}$) is about 2350. This would lead to an actual value of the partial-blocking C_{p0} of over 4000 μF . Although such a value is appreciably larger than is indicated by MC's dc result, it may still be consistent with their result. Their dc measurements showed appreciable nonzero discharge current for about 20 sec, thus involving a time response region quite different from the 10-Hz minimum ac response region. Discharge occurred through an external $10^4\text{-}\Omega$ resistor and no correction was made for internal discharge. As we have seen, however, partial blocking treatments^{3,10} indicate that there will evidently be a

frequency-independent parallel conductance of discharge path between electrodes when blocking is only partial and some discharge of internal charge carriers occurs at the electrodes. Thus, the external charge recovered in a partially blocking dc discharge experiment will³ always be less than the charge which would be stored at the applied charging voltage in a true capacitance equal to C_{p0} .

The above discussion suggests that the partial blocking space-charge explanation is possible and plausible. Certainty for NaCl one would indeed expect a considerable difference in the mobilities of positive and negative ion vacancies, and there is no reason to believe that one or both of these species might not discharge (with different discharge rate constants) at the electrodes.

Soda-lime glass and β -alumina

Neither of these materials was single crystalline, and MC carried out no experiments to determine the concentrations and mobilities of the mobile charge. Let us assume that only a single positive mobile species and a single negative mobile species contributed appreciably to the conductivity. If equilibrium concentrations and mobilities were known, the MC results for these solids could be analyzed with the new intrinsic-extrinsic partial blocking theory.¹⁰ In the absence of such information, only the intrinsic partial blocking theory will be qualitatively applied to the MC results.

From an external dc discharge experiment, MC found an equivalent capacitance of about 2000 μF for β -alumina. If a Faradaic process were involved, again we would expect that the actual C_{p0} would be appreciably greater than this value. The ac results, which again only extend down to around 10 Hz, are consistent with such a large value. It cannot be adequately explained by a completely blocking space-charge theory, but, as before, partial blocking and concomitant discharge afford a likely explanation.

For both soda-lime glass and β -alumina, relatively large values of $C_p(\omega)$ were observed together with ω^{-m} frequency dependence.¹ The exponent m varied from less than $\frac{1}{2}$ to somewhat more than $\frac{3}{2}$, depending on material, temperature, and frequency range. Several well-defined regions with $m = \frac{1}{2}$ and $\frac{3}{2}$ are apparent in the results. Further, the curves generally move to higher C_p values (at constant ω) as the temperature is increased. All these results are quite consistent with the partial-blocking hypothesis. We have already seen that intrinsic-case partial blocking can lead to $\omega^{-1/2}$ and ω^{-2} response when the discharging species has very much less mobility than the completely blocked one. On the other hand, as the mobility ratio increases from very small values, appreciable regions of $\frac{1}{2} \leq m \leq \frac{3}{2}$ appear until finally, for ratios near unity and greater, only $\omega^{-3/2}$ behavior remains, except near low-frequency saturation. Finally, when neither mobile carrier is completely blocked, frequency response regions with $0 < m < \frac{3}{2}$ appear, depending on the degree of blocking and discharge present.¹⁰

Although MC give insufficient data to allow a detailed comparison of the partial-blocking hypothesis with their

experimental measurements, both qualitatively and even semiquantitatively partial blocking appears to yield a possible explanation of the MC results. Note that when $C_{p0} = \frac{1}{12} M^2 C_g$, C_{p0} is proportional to the mobile charge concentration divided by absolute temperature when any temperature dependence of ϵ is ignored. If the equilibrium charge concentration increases faster with temperature than linearly, as is the case for both an intrinsic and an incompletely dissociated extrinsic situation, then C_{p0} will increase with increasing temperature. Although MC did not obtain C_{p0} itself, the increases they observed in C_p with temperature seem consistent with such behavior.

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found in "Comments on 'Electrode Polarization of Ionic Conductors'" by S. P. Mitoff and R. J. Charles on page 3786 of this issue.)

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