

Short communication

COMMENTS ON SOME PAPERS OF R.D. ARMSTRONG ET AL.

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In the valuable paper, *The Metal–Solid Electrolyte Interphase* [1], Armstrong mentions that the geometric capacitance,  $C_g$ , is not placed across the total cell because the displacement current would then be counted twice over. Instead, he uses the conventional blocking-electrode equivalent circuit of Fig. 1a, where  $R_\infty$  is the bulk resistance and  $C_{dl}$  is a frequency-independent double-layer capacitance. This connection of  $C_g$  is certainly well justified in Armstrong's case from a practical viewpoint since  $C_{dl} \gg C_g$ , and it will thus generally be difficult or impossible to distinguish experimentally between the two situations. It is also well justified theoretically for any value of  $s \equiv C_{dl}/C_g$  provided one assumes that the ions in the first atomic layer abutting the electrode are unpolarizable. It is from these ions alone that Armstrong assumes that  $C_{dl}$  arises. In this approximation,  $C_{dl}$  is a Stern inner-layer capacitance.

While the difference in connection of  $C_g$  is not significant in the Armstrong case, it is worth pointing out that the circuit of Fig. 1a is exactly equivalent at all frequencies (assuming frequency-independent elements) to the circuit shown in Fig. 1b, where  $\mu \equiv s/(s+1)$ . Clearly when  $s \gg 1$ ,  $\mu \cong 1$  and the two different connections of  $C_g$  are essentially indistinguishable. There are, however, some experimental situations where non-equivalence is not hidden by inescapable experimental error. One should then pick the equivalent circuit best justified by theoretical considerations.

An exact treatment of the charge transport equations, together with Poisson's equation, has been given for the case of no supporting electrolyte (as in many solid systems, fused salts and silicates, unsupported liquid electrolytes, etc.) and two identical completely blocking plane-parallel electrodes [2–4]. It involves the usual idealizing assumptions of point charges (a single negative species of arbitrary mobility and valence and a single positive species of arbitrary mobility and valence), no inertial effects, and a continuous dielectric. This treatment leads to a closely related but somewhat different equivalent circuit from that of Fig. 1a. When it is transformed [5] to apply to the single-working-electrode situation considered by Armstrong, it takes the form of Fig. 2a. Note that here  $C_g$  indeed spans the entire circuit. The theory leads to  $s \equiv C_{dl}/C_g = 2r \equiv 2Mctnh(M)$ , where  $M \equiv l/2L_D$ . Here  $l$  is the separation between the working electrode and the indifferent electrode and  $L_D$  is the appro-

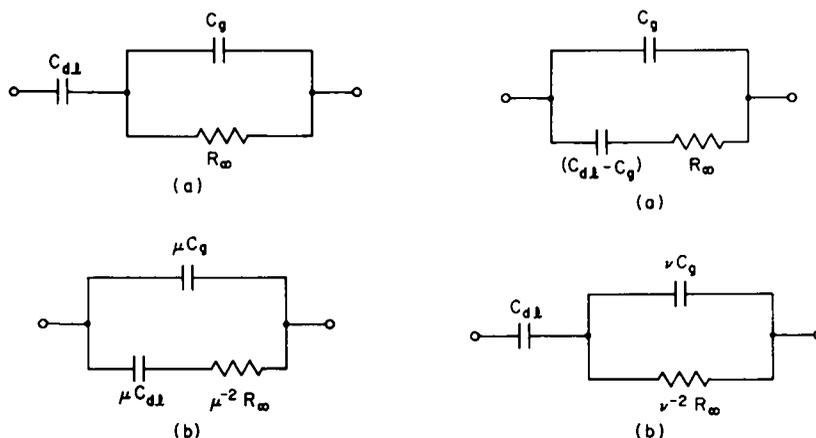


Fig. 1. (a) Conventional equivalent circuit for an electrode-interphase region. (b) Circuit equivalent to (a) at all frequencies. Here  $\mu \equiv s/(s + 1)$  and  $s \equiv C_{dl}/C_g$ .

Fig. 2. (a) Accurate equivalent circuit for completely blocking, unsupported-electrolyte, electrode-interphase region. (b) Circuit equivalent to (a) at all frequencies. Here  $\nu \equiv s/(s - 1)$  with  $s \equiv C_{dl}/C_g$  as before.

priate Debye length. The above derived result for  $s$  holds accurately only when the indifferent electrode is plane, parallel to the working electrode, and of the same shape and area,  $A$ . Then  $C_g = \epsilon A/4\pi l$ , and  $C_{dl} = (\epsilon A/4\pi L_D) \text{ctnh}(M)$ . For the usual situation of  $M \gg 3$ ,  $\text{ctnh}(M) \cong 1$  and  $C_{dl}$  reduces to the usual result for a diffuse double-layer capacitance without any charge-free inner layer contribution. The neglect of the finite size of mobile ions in a completely blocking solid electrolyte situation is valid when any inner layer capacitance present is much greater than the diffuse layer capacitance; it may also be an adequate approximation in some situations where adatoms and/or specific adsorption is present, although these effects should, most properly, be treated separately [1,6].

The equivalent circuit of Fig. 2a following from the above treatment only involves a frequency-independent  $C_{dl}$  element up to  $\omega \lesssim \tau_D^{-1}$ , where  $\tau_D \equiv R_\infty C_g$  is the dielectric relaxation time. Nevertheless, this covers the principal frequency region of interest, and  $\tau_D^{-1}$  often is a higher radial frequency than is experimentally accessible. When the circuit of Fig. 2a is transformed to one of the form of Fig. 1a, one obtains the circuit of Fig. 2b, where  $\nu \equiv s/(s - 1)$ . Comparison of Figs. 1a and 2b shows that if 1a is used to analyze data more appropriate for 2a and 2b,  $C_{dl}$  will be obtained correctly but  $\nu C_g$  will be improperly identified with  $C_g$  and  $\nu^{-2} R_\infty$  with  $R_\infty$ . When  $M \gg 1$  and thus  $\nu \cong 1$ , no significant error will be made, but when this condition is not well met, it is inappropriate to use 1a rather than 2b. In the  $M \rightarrow 0$  limit, for example,  $\nu \rightarrow 2$ . In most of Armstrong's specific experimental situations involving solid electrolytes it appears likely that the condition  $M \gg 1$  will be very well met. Nevertheless, it

is worthwhile pointing out that the conventional circuit of Fig. 1a may sometimes be less appropriate for analyzing impedance measurements than are those of 2a and 2b.

Next, Armstrong [1] considers an incomplete blocking situation where cation exchange can occur between the metal electrode and the cations in a solid electrolyte. He states that under conditions where the concentration of metal cations in the first layer of the solid electrolyte does not change, no Warburg impedance can appear. This is indeed true to the degree that charges of only a single sign are mobile [3,4,7], the situation he envisages. He primarily considers a model in which the first-layer concentration does not change, although he mentions that it may actually vary slowly with applied potential. Even in a completely blocking situation, it seems more likely that this cation concentration will be appreciably potential dependent unless it remains at its sterically-limited maximum value over a finite applied potential range. With very strong specific adsorption, this is probably possible. One wonders, however, whether such adsorption is indeed potential independent in the range around zero applied static potential for the situations considered by Armstrong. In the partial blocking situation, the assumption of concentration independence of first-layer cations may be even more tenuous since these cations are not completely blocked at the electrode.

An exact, no-indifferent-electrolyte treatment of completely and partially blocking conditions [3,4,7] shows (a) that finite-length Warburg response may occur even for completely blocking conditions at both electrodes (when the diffuse layer is potential dependent) in the frequency range  $\omega > \tau_D^{-1}$ , outside the main range of interest, and (b) that such response may also occur with experimentally measurable magnitude [7] in the lower frequency region  $0 \leq \omega < \tau_D^{-1}$  when charge of one sign is blocked at the electrode to a different degree from charge of opposite sign. A certain minimum reaction rate for partially blocked charge is necessary for such response to be significant, however, compared to other contributions to the overall impedance of the system [7]. When finite-length Warburg response is important, one can obtain very much larger values of low-frequency capacitance than those predicted by ordinary double layer theory ( $\sim 50 \mu\text{F cm}^{-2}$  for Armstrong's model [1]) without the necessity of assuming any static specific adsorption at all.

Finally, Armstrong considers [1] a partially blocking situation where he believes Warburg response can in fact occur. He modifies the circuit of Fig. 1a by connecting the series combination of an ordinary (infinite length) Warburg impedance and a reaction resistance in parallel with  $C_{dl}$ . There seem to be several possible problems here. First, Armstrong's resulting circuit (his Fig. 6) has no d.c. path between electrodes, but such a path is a necessity when blocking is incomplete. Second, since the circuit of Fig. 1a is possibly approximate to begin with for Armstrong's situation, it will also be when thus modified, although the  $C_g$ -connection approximation here is probably very good, as already discussed. The exact treatment of the unsupported-electrolyte partially blocking situation already mentioned [3,4,7] leads to an equivalent circuit

related to that of Fig. 2a which does not suffer from these defects although it again neglects the finite size of charge carriers. It has been further shown [4,7] that when  $M \gg 1$ , the exact circuit can often be well approximated by three parallel RC circuits in series, somewhat similar to Armstrong's Fig. 6, which involves two such circuits. But while Armstrong combines  $C_{dl}$ , reaction resistance, and infinite-length Warburg impedance in a single sub-circuit, the above treatment shows [7] that to good approximation when  $M \gg 1$  one parallel circuit is made up of  $C_g$  and  $R_\infty$  in parallel, as in Armstrong's case, another involves frequency-dependent *finite*-length Warburg elements, and the third involves just  $C_{dl}$  and the reaction resistance in parallel. In this treatment,  $C_{dl}$  is essentially just the ordinary diffuse-layer capacitance.

It should be especially noted that  $C_{dl}$  only appears explicitly in the approximate equivalent circuit when  $M \gg 1$  and thus when separation of the exact circuit into three series RC's in parallel is well justified. The double-layer capacitance  $C_{dl}$  itself actually never occurs explicitly in the exact circuit. In place of it one finds a more complicated interface admittance which accounts for both approximate  $C_{dl}$  and finite-length Warburg effects simultaneously [4,7]. Thus, Armstrong's equivalent circuit, which includes an infinite-length Warburg impedance and no d.c. path, is likely to be somewhat inappropriate for an unsupported electrolyte situation, and analysis of data using it may lead to inaccurate estimates of the values of the true circuit elements involved in the conduction-reaction process.

In a later paper [8], Armstrong, Dickinson and Willis have considered the impedance of powdered and sintered solid ionic conductors both theoretically and experimentally. They first discuss the effect of electrode surface roughness (either rough metallic electrodes or rough surfaces abutting originally smooth electrodes) in a completely blocking situation and show that when the complex conjugate total impedance,  $Z^*$ , is plotted parametrically in the complex plane in the usual way the low-frequency line, which is drawn vertical for a completely smooth surface (pure frequency-independent  $C_{dl}$  effect), bends to the right and shows deviation from the vertical when the frequency is not too low. But it has been shown theoretically [7] that just such deviations from vertical can also occur for completely smooth electrode surfaces as well, for both completely and partially blocking situations.

In the completely blocking situation, deviation occurs when the ratio of mobilities of positive and negative mobile charges is either very large or very small. In a partially blocking situation where charge of one sign is completely blocked and the other partially blocked, it will often be experimentally impossible to distinguish the situation from a completely blocking one when the reacting charge has a very much smaller mobility than that which is completely blocked [7]. These results show that deviations from the vertical line in an impedance plane plot do not necessarily imply surface roughness, nor does a close approximation to vertical over a wide frequency range necessarily even imply complete blocking of all charges. In actual experimental situations, surface roughness, large mobility ratios, and some degree of incomplete

blocking may all be present simultaneously, requiring quite accurate experimental results and detailed analysis for full or partial separation of the various effects. Thus, in the experimental results found by Armstrong et al. [8], surface roughness may not be the dominant factor leading to deviations from verticality in all cases although it is clear that it plays an important role in these experiments.

Finally, Armstrong et al. [8] have presented some interesting and useful computer simulations of the overall impedance of  $m$  powder or sinter particles in series between smooth blocking electrodes. The circuit from which the impedance was calculated is like that of Fig. 1a except that  $m$  parallel  $RC$  circuits with possibly different element values appear in series in place of the  $m = 1$  situation of Fig. 1a. It is worth mentioning that the resulting circuit, composed of an arbitrary number,  $n$ , of parallel  $RC$  circuits in series, is well-known and well analyzed. In the theory of viscoelasticity, its mechanical analogue is known as the Maxwell model [9,10]. It has been used in the theory of dielectric relaxation [11] and particularly appears as the general circuit for  $n$ -layer Maxwell–Wagner interfacial polarization [12,13]. In the Armstrong et al. work,  $n = m + 1$  since the first element in the Armstrong circuit,  $C_{dl}$ , may also be considered a parallel Maxwell–Wagner  $RC$  subcircuit with infinite parallel resistance. Equations for the general arbitrary- $n$  case are given and discussed by Volger [13]. Although Armstrong et al. find only one approximate semicircle in the impedance plane arising from their  $m = 5$  and  $m = 11$  simulation cases, it is worth emphasizing that  $n$  parallel  $RC$  circuits in series can lead in general to  $n$  such separate semicircles when the  $RC$ 's involved are all well separated [4,7].

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