

SHORT COMMUNICATION**Equivalent circuits for electrochemical cells containing an indifferent electrolyte—
response to comments by R. D. Armstrong**

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The paper¹ to which Armstrong² refers was an exact theoretical treatment of a space-charge situation involving two mobile, non-combining, positive and negative, species of charge. Thus, its theoretical results do not apply to an electrolyte situation where an indifferent electrolyte is present. They do apply, however, to a two-electrode situation where Poisson's equation is satisfied exactly everywhere, electroneutrality is not assumed, and electromigration is not ignored. They include consideration of both complete blocking (0, 0) and discharge (0, ∞) at the electrodes, but apply most closely at the equilibrium potential when this potential is coincident with the potential of zero charge. Further consideration of this two-ion problem has been recently published³. My Fig. 19 equivalent circuit¹ (Armstrong's Fig. 2, to be designated A-2 hereafter) for the indifferent electrolyte case was thus *not* a theoretical consequence of the analysis¹ as Armstrong seems to assume, but, instead a plausible guess based on the explicit neglect of coupling between a simple Faradaic process (ion concentrations c_0) and isolated indifferent electrolyte behavior (ion concentrations c_1 , with $c_1 \gg c_0$). It was stated that the circuit might be useful under some conditions, and its range of validity was implied to be limited. The circuit was presented to stimulate either an exact treatment of the four-ion problem and/or a careful comparison with experiment. Thus, detailed qualitative attention of the type Armstrong brings to bear on the circuit seems scarcely warranted by its loose derivation and approximate character. Nevertheless, I am grateful for the present opportunity to respond to Armstrong's comments and to discuss further the important matter of equivalent circuits for electrolyte situations.

First, Armstrong states that it is obvious that his Fig. 1 (to be designated A-1 hereafter) is inappropriate because (a) it does not include the effect of the geometric capacitance between electrodes; (b) it does not take the finite separation of the electrodes into account properly; and (c) it does not include the finite rate of double layer charging. Points (a) and (c) were apparently not so obvious to the electrochemistry fraternity before the first exact treatment of the blocking situation appeared in 1953⁴. I believe that point (b), which is particularly concerned with diffusion length growth at low frequencies in a cell of finite electrode separation, has only become obvious with recent work¹. For example, Sluyters⁵ considered the dependence of the impedance

of a finite-length, supported-electrolyte cell on electrode separation. By not considering as well the low-frequency limiting behavior of an "interface" impedance derived from his total impedance^{1,3}, he did not discover the constant values of "interface" capacitance and resistance which arise at frequencies sufficiently low that the electrode separation and diffusion length become comparable¹.

Armstrong points out some deficiencies in the conventional equivalent circuit, Fig. A-1, but does not discuss how the necessary "slight modifications" might be carried out. It is pertinent to mention that the first one may indeed be readily remedied^{1,3,4}. The constant geometrical capacitance $C_g (= \epsilon A / 4 \pi l$ for plane, parallel electrodes, where ϵ is the dielectric constant of the solution, A the effective electrode area, and l the electrode separation) must appear connected directly between the two electrodes, as in Fig. A-2. The second difficulty of the conventional circuit is also remedied in the suggested circuit. For any finite value of l , the Warburg impedance of Fig. A-1 (also included in Fig. A-2) must be replaced at sufficiently low frequencies by frequency-independent capacitance and resistance elements in series. Figure A-2 incorporates this necessity since $R_{si}(\omega)$ and $C_s(\omega)$ show just such behavior^{1,3}. Finally, Fig. A-2 seems to avoid deficiency (c) since the d.l. capacitance C_1 is charged directly through R_B , the solution resistance arising from the indifferent electrolyte. To a casual observer it may thus appear strange that Armstrong objects to an equivalent circuit which remedies the deficiencies that he himself points out occur in the conventional circuit!

An exact theoretical treatment of the four-ion problem with $c_0 \ll c_1$ would be quite complicated and does not seem justified until appropriate boundary conditions at both electrodes of a finite cell can be found. Such boundary conditions, which might have to be slowly time varying, should be required to lead to good agreement between theory and experiment when a constant total overpotential is applied and the resulting cell current measured. Such agreement should, of course, extend over a considerable overpotential range. No such boundary conditions are currently available to my knowledge. When they become available, the small-signal impedance of the cell could be calculated (assuming differential linearity) by applying a very small step function increment to the applied total overpotential, then Laplace transforming the resulting transient response into the frequency domain. The resulting impedance would, however, only be applicable above a certain frequency f_0 if the boundary conditions and bulk ionic concentrations were slowly time varying. Such time variation would determine f_0 , which, of course, would be zero when the cell and electrode properties were time invariant.

Unfortunately, no well-established, fully adequate boundary conditions seem available even in the two-ion case (no indifferent electrolyte). Several authors have thus used the time-invariant discharge parameters (r_p, r_n) of Chang and Jaffé⁶ in theoretical studies of the two-ion situation. The infinitely rapid Faradaic electrode reaction considered in refs. 1 and 3 and Fig. A-2 corresponds to the discharge parameter choices $(\infty, 0)$ or $(0, \infty)$.

It has been conventional thus far to apply the same (r_p, r_n) parameter values to both electrodes of a cell, and it is worthwhile to mention that this general case, with arbitrary ion mobilities and valencies, has recently been worked out to give the complete small-signal impedance in the two-ion situation⁷. Nevertheless, in most practical electrolyte situations, whether two or n -ion cases, it seems plausible to require that

the boundary conditions differ appreciably at the two electrodes when the total overpotential is considerably different from zero. This possibility, in a different context, was recently brought to my attention by private discussion with Dr. P. W. M. Jacobs. Thus, to the degree that the Chang-Jaffé parameters are adequate boundary conditions, it may be necessary to take the values (r_{p_1}, r_{n_1}) at one electrode and (r_{p_2}, r_{n_2}) at the other, with these quantities all possibly slowly time varying and potential dependent. For AgNO_3 in aqueous solution, for example, one would use $(r_p, 0)$ at the negative electrode and $(0, r_n)$ at the positive one for sufficiently large total overpotential. Here the zero denotes complete blocking of the designated ion. Finally, if the finite rates of reaction at the electrodes were always much faster than all other processes in the cell, the parameter choices $(\infty, 0)_-$ and $(0, \infty)_+$ would be appropriate under these conditions and would not need to be time varying.

Meanwhile, Armstrong believes that the reason for my "theoretical" behavior arises because the $(0, \infty)$ boundary condition requires that the discharging ion (his species A) maintain time-invariant concentration at the electrode where it discharges. This conclusion, applied to Fig. A-2, seems somewhat dubious. If the electrode reaction were very fast but not infinitely fast, r_n would be very large but not infinite. Then the concentration of species A would indeed change with time and, in fact, it would include a sinusoidal component. But the main result of a large but finite r_n would be only the introduction of a small electrode reaction resistance in series with R_F of Fig. A-2 and a small increase in R_c . Thus, the form of the circuit would remain unaltered to at least first order. Therefore, Armstrong's demonstration that the concentration of the species A ion cannot remain constant at the electrode does not seem particularly germane to his purpose of showing that Fig. A-1 is superior to Fig. A-2.

There is nothing in the two-ion treatment^{1,3,4} or in Fig. A-2 which would preclude Armstrong's suggestion of electron tunneling across the inner layer of the double layer at the two electrodes. This may likely be energetically favored over the situation of ions displacing solvent molecules from the inner layer before the electrode reaction occurs. The important point remains that charge carriers of one kind or another must pass *through* the inner layer. Such passage, together with the in-phase motion of species-A ions in the bulk of the solution, must necessarily lead to a non-infinite, frequency-independent resistance, connected directly between the two electrodes, such as R_F of Fig. A-2. This resistance, arising from the Faradaic process and the bulk resistance of the discharging ion, will be far greater than R_B when $c_1 \ll c_0$, and it cannot have a capacitance in series with it. In the general case, R_F may indeed show secular variation, but it must nevertheless represent a direct (conduction) current path from electrode to electrode (even if the actual species of current carrier changes one or more times from one electrode to the other).

It seems quite significant to me that the conventional circuit of Fig. A-1 shows *no* such direct current path (the Warburg impedance approaches infinity as $\omega \rightarrow 0$). It seems that, theoretically, such a path is absolutely necessary in the Faradaic discharge situation¹. In practice, the usual very large value of the ratio R_F/R_B and possible slow time variation of R_F probably make it extremely difficult to isolate the effects of R_F in conventional electrolyte measurements and analysis. Thus, while Armstrong is probably correct in stating that Fig. A-1 can successfully interpret many experimental results, he seems to me to be incorrect in principle in maintaining that Fig. A-1 with slight modifications is *the* appropriate circuit.

All equivalent circuits are idealizations of nature and are thus approximate. Neither Fig. A-1 nor Fig. A-2 is based on a full theoretical treatment. Ideally, the equivalent circuit most appropriate for a given frequency range should be obtained by simplification pertinent in this range of the results of such theoretical analysis. Failing this approach for the time being, it seems to me useful for Armstrong to carry out such slight modifications as he believes appropriate in Fig. A-1, then compare the result with Fig. A-2 in terms of experimental explicative power. Which circuit can best fit the largest amount of data, maintaining frequency-independent values of all circuit elements not explicitly shown frequency variable? I believe that one should not automatically accept the *status quo*. Clearly an improvement of Fig. A-1 is needed. Although Fig. A-2 may well not prove to be such an improvement, the matter does not seem to me to be closed by Armstrong's remarks, and I shall be happy if our discussion stimulates further thinking about this important area.

- 1 J. R. Macdonald, *J. Chem. Phys.*, 54 (1971) 2026.
- 2 R. D. Armstrong, *J. Electroanal. Chem.*, 40 (1972) 437.
- 3 J. R. Macdonald, *J. Electroanal. Chem.*, 32 (1971) 317. A few printing errors in ref. 1 above are corrected in this paper.
- 4 J. R. Macdonald, *Phys. Rev.*, 92 (1953) 4; see also *Phys. Rev.*, 91 (1953) 412.
- 5 J. H. Sluyters, *Recl. Trav. Chim.*, 82 (1963) 100.
- 6 H. Chang and G. Jaffé, *J. Chem. Phys.*, 20 (1952) 1071.
- 7 J. R. Macdonald, to be submitted to *J. Chem. Phys.*

J. Electroanal. Chem., 40 (1972)