

NEW ASPECTS OF SOME SMALL-SIGNAL ac FREQUENCY RESPONSE FUNCTIONS

J. Ross MACDONALD

Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27514, USA

Received 20 December 1984

Revised version received 3 January 1985

First, it is shown how an expression for the ac conductivity of an ionically conducting material derived by Almond and West and co-workers from an earlier "universal dielectric response" equation of Jonscher may be related to and subsumed under a response function proposed much earlier. Doubt is cast on the identification of a parameter in the Almond–West analysis as the ionic hopping frequency. The earlier function, first proposed by Ravaine and Souquet, is widely used to describe the depressed arcs often obtained when experimental impedance data are plotted in the complex plane. A general relation which yields either this response or that of Cole and Cole for the complex dielectric constant is discussed and shown to involve inadequate high and low frequency limits. Finally, a new distribution-of-activation-energies model which can fit both unsymmetric and symmetric arcs in either the impedance or complex dielectric constant plane is briefly discussed. This model does yield physically realistic high and low frequency limiting response as well as predictions of the temperature dependence of power-law frequency response exponents.

Some time ago Almond, West and their co-workers showed in a series of papers [1–3] how one of Jonscher's empirical "universal dielectric response" equations [4] could be transformed into a form useful for analyzing the small-signal ac response of ionic materials. Jonscher's equation was

$$\chi'' = B_1 [(\omega/\omega_p)^{n_1-1} + (\omega/\omega_p)^{n_2-1}] , \quad (1)$$

with B_1 a constant, sometimes taken as unity and the exponents restricted to the range $0 < n < 1$. Here the dielectric susceptibility $\chi \equiv (\epsilon - \epsilon_\infty)/\epsilon_0 = \chi' - i\chi''$, where the complex dielectric constant is $\epsilon \equiv \epsilon' - i\epsilon''$ and ϵ' takes on the values ϵ_0 and ϵ_∞ at sufficiently low and high frequencies. By setting $n_1 = 0$ and $n_2 = n$ in eq. (1), Almond et al. were led to the following expression for the ac conductivity:

$$\sigma(\omega) = K[\omega_p + \omega_p^{1-n}\omega^n] , \quad (2)$$

which exhibits both a non-zero dc conductivity and power-law response. The quantity K was identified as a temperature dependent constant. An improved expression for it has recently been proposed [5]. Almond et al. used eq. (2) to analyze data on single crystal Na β -alumina and other materials and identified ω_p as the thermally activated ionic hopping frequency, ν_H .

It is useful in small-signal data fitting to have available a fitting equation which includes both real and imaginary components as functions of frequency. Then nonlinear least squares fitting of both real and imaginary parts of the data can be carried out simultaneously, i.e. complex nonlinear least squares (CNLS) fitting [6]. Such fitting allows estimates of parameters based on all, rather than half, the data to be obtained. It was shown by Macdonald and Cook [5] that an admittance closely related to eq. (1) with $n_1 = 0$ and $n_2 = n$ could be written for the Na β -alumina situation as

$$Y = G_0 [1 + (i\omega\tau_0)^n] + i\omega C_\infty , \quad (3)$$

where C_∞ is the high-frequency limiting capacitance of the system, exclusive of contributions from the first term in (3). The real and imaginary parts of the first term satisfy the Kronig–Kramers relations [7] and the real part leads to the form of eq. (2) with

$$\omega_p = [\tau_0 \{\cos(n\pi/2)\}^{1/n}]^{-1} .$$

The same data on single crystal Na β -alumina that was analyzed by Almond and West by graphical methods was reanalyzed using eq. (3) with CNLS fitting in order to obtain more accurate, objective estimates of the parameter values involved [5]. This analysis showed that

the data did not lead to a well-defined value of ω_e , where $\omega_p = \omega_e \exp(-E/kT)$, and thus they did not confirm the Almond–West identification of ω_p with the ionic hopping frequency [5]. The Almond–West Na β -alumina data has recently been re-analyzed and the question of the identity of ω_p and ν_H considered in more depth [8]. The conclusion is again reached that no available evidence supports the firm identification of ω_p and ν_H , but neither does the evidence absolutely preclude the possibility.

Let us restrict attention to the first term in eq. (3). Then the impedance corresponding to this term is

$$Z = R_0/[1 + (i\omega\tau_0)^n]$$

$$= R_0/[1 + R_0 A_0 (i\omega)^n], \quad (4)$$

where $R_0 \equiv G_0^{-1}$. The first form of this result was suggested years ago by Ravaine and Souquet [9], in analogy to the Cole–Cole dielectric response function [10] and later independently proposed by others [11,12]. It has been found quite useful in fitting data which lead to a depressed semicircle when the impedance is plotted in the complex plane. It may thus be termed the ZARC function. The second form is just the combination [13] of a constant phase element (CPE) in parallel with a resistor R_0 . The CPE admittance is given [13] by $Y = A_0 (i\omega)^n$ with $0 \leq n \leq 1$. By focusing on a real rather than a complex function, Almond and West evidently did not realize that their eq. (2) was not entirely original. A sketch of a derivation of the first form of eq. (4) based on fractal dimensionality has been recently presented by Le Mehaute and Crepy [14]. Because of the generality of eq. (4), it seems unlikely that $\omega_p \equiv [R_0 A_0 \cos(n\pi/2)]^{-1/n}$ will usually fall close to the ionic hopping frequency for most ionically conducting materials. Further, rather than derive an empirical equation such as eq. (2) from another empirical equation, proposed primarily for dielectric materials, in order to obtain a result appropriate for conducting materials, it seems more reasonable to start with the well-known empirical equation (4) originally proposed for the analysis of such systems.

Eq. (4) shows two different ways to parameterize the ZARC function, one considering it as a unitary function in its own right [9] and the other taking it as a composite function [13]. Which approach is the more appropriate? Although CNLS fitting of the same data set with these two forms will yield exactly the

same fit, the actual parameter calculations and uncertainties will generally turn out differently. Of course the fit with the lowest estimated parameter correlations and parameter standard deviations is preferable. Such fitting on the 113 K Na β -alumina data mentioned above gave smaller standard deviations with the first form, and the correlation between R_0 and τ_0 was found to be -0.57 , while fitting with the second form produced a correlation between R_0 and A_0 of -0.98 ! Similar results have been found for fitting of the data at other temperatures.

It has been recently pointed out [15] that when standard dimensionless normalization is employed, any response function derived at, say, the complex dielectric constant level may be employed in exactly the same form, but possibly with different parameter values, at the impedance level and vice versa. Of course such dual response implies two different materials, one showing dielectric system response and the other conducting system response. Let us define a general normalized immittance function $I_k \equiv I'_k + iI''_k$ as

$$I_k \equiv (U_k - U_{k\infty})/(U_{k0} - U_{k\infty}), \quad (5)$$

where $k = \epsilon$ or Z , $U_\epsilon = \epsilon^* \equiv \epsilon' + i\epsilon''$, and $U_Z = Z$. Here U_{k0} and $U_{k\infty}$ are the low and high frequency limiting values of U_k . The general expression corresponding to the ZARC, eq. (4), when $k = Z$, is then

$$I_k = [1 + (i\omega\tau_{k0})^{nk}]^{-1}. \quad (6)$$

When $k = Z$, we may take $n_Z = n$. If one chooses $n_\epsilon = 1 - n$, then the admittance corresponding to $I_Z = (Z - R_\infty)/(R_0 - R_\infty)$ and that corresponding to $I_\epsilon \equiv (\epsilon^* - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty)$ both involve the same $(i\omega)^n$ power-law frequency response when $(\omega\tau_{k0})^{nk} \gg 1$. The first choice leads, of course, to the ZARC, the second to just the standard Cole–Cole dielectric response function [10]. But as eq. (6) shows, plots of I_ϵ in the complex dielectric constant plane or of I_Z in the impedance plane yield exactly the same shape when $n_Z = n_\epsilon$. It seems appropriate to term the general function, eq. (6), which subsumes both ZARC and Cole–Cole response, the ZC function. Note that the composite representation of the Cole–Cole function is that of a capacitor ($C_0 - C_\infty$) in series with a CPE.

Although the distribution of relaxation times function associated with the unitary ZC is normalizable [10], unlike that of the CPE alone [7,13], the ZC does not generally exhibit response proportional to ω

as $\omega \rightarrow 0$ and to ω^{-1} as $\omega \rightarrow \infty$, response required of all physical systems since real systems necessarily have a shortest and a longest response time [15,16]. Such response requires that the arcs in complex plane plots must approach the real axis vertically at the frequency extremes even when arc centers are displaced below the real axis [17]. A theory of small-signal frequency response applying for either a dielectric system or a conductive system, which involves a distribution of activation energies, has recently been proposed [15,18]. It can lead to either curves symmetrical in the complex plane like the ZC, to unsymmetric in the curves like those predicted by the empirical Davidson–Cole [19] and Williams–Watts [20] equations, or to curves which are well approximated over a limited frequency region as the parallel or series combination of two CPE's. For the $k = \epsilon$ dielectric situation, one of the Jonscher “universal dielectric response” empirical equations is indeed of the form of two CPE's in parallel [18]. Unlike all these empirical equations, including all the Jonscher “universal dielectric response” equations, the new physically reasonable model does indeed lead to $\omega^{\pm 1}$ response at the frequency extremes and can well represent the behavior of any of the earlier empirical equations except at the frequency extremes, regions often beyond the range of usual measurements or where the response is complicated by the presence of other processes. This model thus seems preferable to all the empirical equations, especially since it leads to specific predictions of the temperature dependence of power-law exponents, predictions in agreement with experiment for both conductive and dielectric systems [15,18], while none of the other equations does so.

Acknowledgement

I much appreciate the helpful comments of Robert A. Hurt and Stephen W. Kenkel and support of the work by the U.S. Army Research Office.

References

- [1] D.P. Almond, A.R. West and R.J. Grant, *Solid State Commun.* 44 (1982) 1277.
- [2] P.G. Bruce, A.R. West and D.P. Almond, *Solid State Ionics* 7 (1982) 57.
- [3] D.P. Almond and A.R. West, *Solid State Ionics* 9/10 (1983) 277; 11 (1983) 57.
- [4] A.K. Jonscher, *Colloid Polymer Sci.* 253 (1975) 231; *Phys. Thin Films* 11 (1980) 202.
- [5] J.R. Macdonald and G.B. Cook, *J. Electroanal. Chem.* 168 (1984) 335.
- [6] J.R. Macdonald, J. Schoonman and A.P. Lehen, *J. Electroanal. Chem.* 131 (1982) 77.
- [7] J.R. Macdonald and M.K. Brachman, *Rev. Mod. Phys.* 28 (1956) 393.
- [8] J.R. Macdonald and G.B. Cook, *J. Electroanal. Chem.*, to be published.
- [9] D. Ravaine and J.-L. Souquet, *C.R. Acad. Sci. (Paris)* 277C (1973) 489.
- [10] K.S. Cole and R.H. Cole, *J. Chem. Phys.* 9 (1941) 341.
- [11] J.R. Sandifer and R.P. Buck, *J. Electroanal. Chem.* 56 (1974) 385.
- [12] J.R. Macdonald, in: *Superionic conductors*, eds. G.D. Mahan and W.L. Roth (Plenum Press, New York, 1976) p. 88.
- [13] J.R. Macdonald, *Solid State Ionics* 13 (1984) 147.
- [14] A. Le Mehaute and G. Crepy, *Solid State Ionics* 9/10 (1983) 17.
- [15] J.R. Macdonald, *J. Appl. Phys.*, submitted.
- [16] J.R. Macdonald, *J. Appl. Phys.* 34 (1963) 538.
- [17] R. Syed, D.L. Gavin, C.T. Moynihan and A.V. Lesikar, *J. Am. Ceram. Soc.* 64 (1981) 118C.
- [18] J.R. Macdonald, *J. Appl. Phys.*, submitted
- [19] D.W. Davidson and R.H. Cole, *J. Chem. Phys.* 19 (1951) 1484.
- [20] G. Williams and D.C. Watts, *Trans. Faraday Soc.* 66 (1970) 80.