

## NOTE ON THE PARAMETERIZATION OF THE CONSTANT-PHASE ADMITTANCE ELEMENT

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Some background is presented on the constant-phase admittance element, frequently used as part of a circuit for fitting admittance data on solid electrolytes. Several alternate ways of writing an expression for the constant-phase element are discussed and compared, and it is suggested that one particular parameterization seems preferable to the others.

The possible importance of constant phase behavior in the dielectric response of materials was emphasized by Cole and Cole [1], who included the constant-phase impedance element in one of their equivalent circuits. Later [2], it was considered as an alternating-current system response function, the Kronig–Kramers relationship between its separate real and imaginary parts was given, and the associated (non-normalizable) distribution of relaxation time function derived. The importance of this ac response function and its possible relevance to the often found  $t^{-n}$  time domain response and to (frequency) $^{-1}$ -noise was also pointed out. Note that a phase angle independent of frequency implies [1] that the ratio of the average energy stored to the energy dissipated per cycle is also frequency independent.

In recent years the above independence for the CPE has been made the basis of the “universal dielectric response” of Jonscher [3], often expressed in the form that the imaginary part of the dielectric susceptibility,  $\chi''$ , is proportional to  $\omega^{n-1}$  ( $n < 1$ ) for many materials, where  $\omega$  is the angular frequency. Here we wish to present a comparison and critique of various forms of the CPE which have been suggested by various authors and used to fit a wide variety of ac response data, particularly those for solid electrolytes. For the sake of consistency and simplicity, we shall translate all results to admittances or non-ideal capacitances and change the  $\alpha$  of Cole and Cole to the symbol  $n$ , now more common in the present context.

If we define the constant-phase-element (CPE) admittance as  $Y_c$ , then the Cole–Cole form is  $Y_c = a_0(i\omega\tau)^n$ . Let us rewrite this for  $0 \leq n \leq 1$  as

$$Y_c = A_0(i\omega)^n, \quad (1)$$

where  $A_0$  and  $n$  may be temperature dependent. This form of the CPE has been used, for example, as part of an equivalent circuit used to fit impedance data taken at several constant temperatures for lithium nitride [4] and has also been used for fitting  $\text{TiO}_2$  data [5]. Both  $A_0$  and  $n$  were found to be temperature dependent for the results of ref. [4]. Note that the form [6,7]  $Y_c = (i\omega\tau)^n$  is unsatisfactory since it leads as  $n \rightarrow 0$  to the too specific result  $Y_c \rightarrow 1$ . On using eq. (1), we may follow Jonscher and define the “non-Debye” capacitance [8,9],

$$C_n \equiv (Y_c/i\omega) = A_0(i\omega)^{n-1}, \quad (2)$$

which has been employed by Jonscher and Réau [10] as part of an equivalent circuit used to fit impedance data on  $\beta\text{-PbF}_2$ . Of course the use of the admittance element of eq. (1) or the non-ideal capacitor of eq. (2) are equivalent ways of introducing CPE response. The CPE capacitor approach has also been recently used in the analysis of single crystal Na  $\beta$ -alumina impedance data [11].

Although there thus far appears to be no fully adequate theory of ac conduction which leads to the CPE form and establishes connections between the parameters  $A_0$  and  $n$  and more microscopic, physical mater-

ial parameters as well as temperature, it is worth mentioning that eq. (1) has been expressed by Schrama [12] in the form of an infinite continued fraction, leading to an equivalent circuit consisting of a semi-infinite, continuous, non-uniform RC transmission line. The line is uniform for the special choice  $n = 0.5$ . Later, Scheider [13] showed that the admittance of eq. (1) could also be represented by RC ladder networks with multiple branching. Both the Schrama and Scheider circuits can be interpreted in terms of non-uniform diffusion processes.

We have already pointed out the inadvisability of the CPE parameterization  $Y_c = (i\omega\tau)^n$ ; now we shall discuss other related inappropriate parameterizations. First, for future comparison, let us write (1) in expanded form as

$$Y_c = A_0\omega^n [\cos(n\pi/2) + i \sin(n\pi/2)], \quad (1')$$

a form where it is clear that the real and imaginary parts are properly related by the Kronig–Kramers relations [2]. Now Raistrick et al. [7] have employed the form

$$Y = A\omega^n + iB\omega^n, \quad (3)$$

to fit impedance data on silicates. Initially  $A$  and  $B$  were used as independent fitting parameters, but it was soon pointed out [6,7,14] that they must be related through

$$B/A = \tan(n\pi/2), \quad (4)$$

consistent with the Kronig–Kramers relations, as in (1'). It should be emphasized that the use of eq. (3) with  $A$  and  $B$  taken independent [7,15] introduces an unwarranted degree of freedom in fitting to experimental data.

Although the necessary relation (4) has been known and used by Jonscher [3] and his collaborators since 1974 and by others [11,15], I believe it can and has been used to parameterize the CPE in infelicitous ways. It has become customary to write (1') in the form

$$Y_c = P_n\omega^n [1 + i \tan(n\pi/2)], \quad (5)$$

where  $P_n$  is a constant to be determined from the fitting. But clearly  $P_n \equiv A_0 \cos(n\pi/2)$ . If  $A_0$  is temperature dependent and largely independent of  $n$ ,  $P_n$  mixes the temperature dependence of  $n$  into that of  $A_0$ . This is a matter of no great importance when

measurements are made at a single temperature, but it becomes important when data are taken for several temperatures and  $n$  is temperature dependent. (The quantity  $n$  is often found, in fact, to decrease with increasing temperature.) Then the least squares determination of  $P_n$  and  $n$  is likely to be somewhat compromised by the correlation between them. Further, (1) shows that as  $n \rightarrow 1$ ,  $Y_c \rightarrow i\omega A_0$ , involving a pure capacitance, and as  $n \rightarrow 0$ ,  $Y_c \rightarrow A_0$ , a pure conductance. Although (5) is consistent with the second of these limits, it yields ( $i\infty$ ) in the first limit when  $P_n$  is taken as a direct fitting parameter. Fitting to data for a nearly pure capacitance with this form would yield the misleading result that  $P_n \sim 0$ , or more likely, would lead to  $P_n > 0$  and an  $n$  estimate appreciably smaller than the true  $n \lesssim 1$ . This difficulty does not arise with (1) or (1').

Similarly, problems can appear with the parameterization of the  $C_n$  of eq. (2), which can be written as

$$C_n = A_0\omega^{n-1} [\sin(n\pi/2) - i \cos(n\pi/2)]. \quad (2')$$

But this (and its dielectric susceptibility equivalent) [8,9] has been reexpressed as [9,11]

$$C_n = Q_n\omega^{n-1} [1 - i \operatorname{ctn}(n\pi/2)], \quad (6)$$

where  $Q_n \equiv A_0 \sin(n\pi/2)$ , a parameter to be determined from fitting. Again  $n$  dependence is mixed with any present in  $A_0$  here, although in a different way from that above. It thus follows that as  $n \rightarrow 1$ , eq. (6) leads to the proper result  $C_n \rightarrow O_n \rightarrow A_0$ , while when  $n$  approaches zero,  $C_n \rightarrow -(i\infty)$ . But in fitting, one will usually be dealing directly with the  $Y$  associated with  $C_n$ . From (6), this  $Y \equiv Y_n$  is

$$Y_n \equiv i\omega C_n = Q_n\omega^n [\operatorname{ctn}(n\pi/2) + i]. \quad (7)$$

Again, the  $n \rightarrow 1$  limit is proper, but that for  $n \rightarrow 0$  yields  $Y_n \rightarrow \infty$  when  $Q_n$  is taken as a constant parameter determined from the fitting and its actual dependence on  $n$  suppressed or forgotten.

These problems with potential division by zero are entirely avoided when (1), (1'), (2) or (2') are used for fitting. When  $n$  varies appreciably with temperature, it may be sometimes useful to use the original Cole–Cole form of the CPE since both parameters  $a_0$  and  $\tau$  may then be determined separately from a combined least squares fitting of  $Y_c(\omega, T)$  data. Under some circumstances, this will reduce the correlations between the two parameters  $a_n$  and  $\tau$  and  $n(T)$  more than will the single-parameter form of eq. (1).

Finally, it is worth mentioning that the CPE in series with a capacitor leads directly to Cole–Cole distributed dielectric response [1], and in parallel with a resistor it leads to the depressed circular arc response often found for solid electrolytes when measured impedance is plotted in the impedance plane. The CPE is thus more general than usually realized. In actual data fitting, it will be most appropriate to use either an isolated CPE or a separate C or R combination with the CPE as above. This approach keeps the CPE parameters and the other parameters properly separated.

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