J. Electroanal. Chem., 193 (1985) 57–74
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REPLY TO COMMENTS BY ALMOND AND WEST ON Na β-ALUMINA IMMITTANCE DATA ANALYSIS

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(Received 30th January 1985; in final form 25th April 1985)

ABSTRACT

We begin by summarizing the background of the present controversy. Because the Almond/West data on Na β-alumina are the only published small-signal ac results for the low temperature range from 83 K to 151 K, they are particularly important and deserve careful and full analysis. We first discuss the data themselves, pointing out certain deficiences in them, and then compare the somewhat subjective analysis methods employed by Almond and West with the more objective ones we have used. Next, we discuss appropriate fitting models and show that the model used by Almond and West is equivalent to one long used in the ionic conductor field. We then examine the analysis and interpretation of fitting results in some detail. The main original contribution of Almond and West in this area is their complete identification of a parameter ω_p appearing in their fitting model with the average thermally activated hopping frequency, ν_H. Our detailed examination of this assumption indicates that there is, so far, no strong theoretical basis for it and no fully trustworthy experimental evidence for it either. We have re-analyzed the data for all nine temperatures between 83 K and 151 K by complex nonlinear least squares fitting and find that better fits than we earlier obtained for the three highest temperatures are possible, giving results in this range much closer to the earlier ones of Almond and West. Nevertheless, thermal activation plots still exhibit strong, well defined breaks and discontinuities between 102 K and 110 K, possible evidence for a glass-like transition in this material. Finally, for comparison with future measurements and results for Na β-alumina in the low temperature regime, we have tabulated all our fitting estimates.

INTRODUCTION

In this note we respond to the comments of Almond and West [1] (hereafter A/W) on some of the results of our recent paper on Na β-alumina [2]. In their comments A/W call into question some of the Macdonald/Cook (hereafter M/C) analysis methods and results. Although these matters will be addressed in detail herein, we believe that a short initial discussion of some of the background of the matter will provide a useful perspective on it.

First, we wish to thank Dr. Anthony West once more [2] for very kindly supplying the 1977 A/W 83K-151K Na β-alumina data to us. When we noted that these data had been used by Ngai and Strom [3], and that the various earlier analyses of the data by Almond, West, and co-workers seemed, in our opinion, to leave something

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to be desired, one of us (J.R.M.) requested the data from West in March 1983 [4], After some preliminary analysis of the received data was carried out, Dr. West was invited [4] in June 1984 to be a co-author of a paper we hoped to write on the analysis of these data. In a letter from West received in November 1984 after the paper had been essentially completed [5], he elected not to be a co-author.

Second, we wish to thank Almond and West for their recent comments [1], which have stimulated us to re-examine our analysis and have led to the useful results discussed below. We believe that a reply to the A/W comments intelligible and valuable to the general reader requires some discussion of the data in question, more comparison of the analysis methods used by A/W and M/C, and further discussion and extension of past fitting results. Such discussion is presented in the following work.

THE Na β-ALUMINA DATA

The data comprise nine sets of small-signal ac impedance/admittance results generally extending from 10^2 to 7×10^6 Hz and spanning the temperature range from 83 K to 151 K. The material was single crystal Na β-alumina melt-grown by Union Carbide; its non-stoichiometry fraction was unknown but it probably fell in the range of 0.2 to 0.3. West and his co-workers have earlier published data plots and discussion of some of these data sets in at least the eleven papers mentioned in refs. 6–16. With this many papers devoted at least in part to the same data, there is, in our opinion, considerable overlap among many of them. Almond and West have mentioned [13] a $\approx$ 2 K error in their nominally 113 K data set. This suggests that there may be this much temperature error in all nine sets.

But in addition to possible problems with temperature control there appear to be other accuracy problems with the A/W data [2]. These problems are illustrated in the 3-D perspective plots of Fig. 1 for the 83 K A/W data. Figure 1a shows that the lowest frequency point (largest $|Z''|$ value) is apparently inconsistent with the others. It is important to note that this anomaly does not show up at all in the conventional plots of $-Z''$ vs. $\log(\nu)$ and Z' vs. $\log(\nu)$, shown as projections in Fig. 1(a)! Here $Z = Z' + iZ''$ and ν is the measurement frequency. When the modulus function $M = M' + iM'' \equiv (i\omega C_c)Z$ is plotted for these same data, two other problems appear which were not apparent in the Z plots. Here C_c is the capacitance of the empty measuring cell and $\omega \equiv 2\pi\nu$.

First, we see that M' reaches a maximum and even begins to decrease at the highest frequencies, quite contrary to the behavior expected from any reasonable model. Second, an appreciable glitch appears at intermediate frequencies where the experimentors shifted from one type of measuring bridge to another. Evidently, the calibration of the two bridges was inconsistent near their cross-over frequencies. Again notice that this glitch, and even the anomalous M' behavior at high frequencies, does not show up in all the projection plots. These and other similar results suggest that all the data should not be trusted at the lowest and highest frequencies and that, in addition, somewhat anomalous results may possibly be expected from fitting of data through the glitch region.

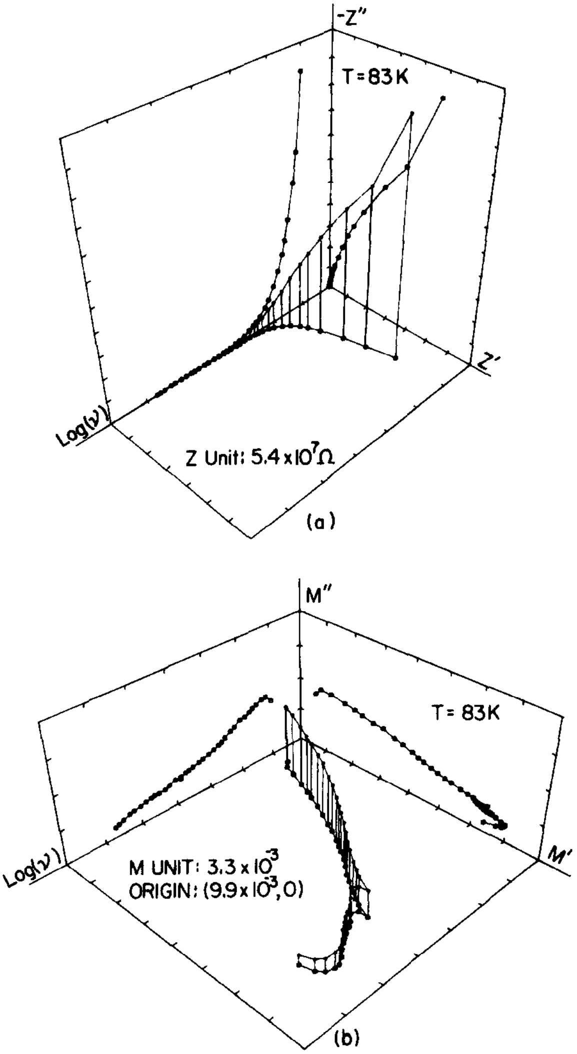

Fig. 1. Three-dimensional perspective plots of the 83 K A/W Na β-alumina data. (a) The conjugate impedance Z^*; (b) the modulus function, M.

COMPARISON OF ANALYSIS METHODS

There are three distinct aspects to this topic. The first deals with what model to use; the second involves how best to obtain model parameter estimates by confronting model and data; and the third involves the most appropriate way to further analyze and interpret the parameter estimates obtained from data fitting. We shall discuss these matters in turn.

Model selection

Figure 2 shows the equivalent circuit model we proposed and used in our original fitting [2]. Here a constant phase element (CPE) admittance is given by $Y = A_0(i\omega)^n$, where A_0 and n are temperature-dependent constants. As mentioned earlier [2], C_g and R_b are bulk elements; in contrast, CPE_2 is likely to be associated with interface effects. Constant phase response was first discussed by Fricke [17] and later by Cole and Cole [18]. A recent paper considers appropriate parameterization of the CPE [19]. It also points out that the combination of a CPE and an ideal resistor in parallel leads to a depressed semicircle arc (the ZARC response) when the impedance of the combination is plotted in the complex plane. Such response was first proposed by Cole and Cole [18] in 1941 for complex dielectric constant plots and by Ravaine and Souquet [20] for conducting systems in 1973. Its impedance may be written, for example, as

$$Z_{\text{ZARC}} = R_B/\left[1 + (i\omega\tau)^n\right], \tag{1}$$

where $\tau = (R_B A_0)^{1/n}$. The unitary R_B, τ, n parameterization is often found superior to the composite R_B, A_0, n parameterization of Fig. 2, see discussion below.

Now A/W have essentially used Fig. 2 without CPE_2 in their fitting and/or discussions; thus they take no account of low-frequency interface effects, particularly important for their higher-temperature data sets. More precisely, A/W have used only the real part of the admittance of the ZARC model (which includes the discrete resistor-CPE combination) in refs. 9, 11, and 12. They have given the full ZARC admittance, plus that of the geometrical capacitance, C_g, in refs. 10, 13, 15, and 16. Although they now mention in their comments [1] that their earlier analysis employed a single CPE, none of their equations was so identified [9–16]. In ref. 10 they wrote their distributed element admittance as $Y = \omega^n[A + iB]$, then curve-fitted to obtain A and B parameter estimates separately, and did not note that A and B are not independent but must be connected by the Kronig–Kramers relations [21] in

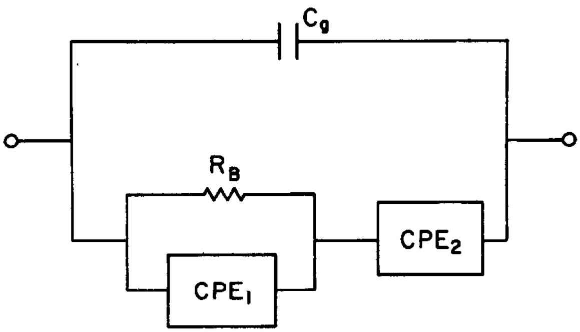

Fig. 2. Fitting circuit used herein. The parallel elements R_B and Z_{CPE1} may be replaced with the ZARC impedance (eqn. 1), with no change in overall circuit impedance or fit.

consonance with the CPE model, i.e., $B = A\ \tan(n\pi/2)$. In later work [13], the K–K connection is indeed cited, but n, A, and B are still tabulated as separate quantities.

Model-data fitting

As mentioned in their comments [1], A/W have principally used their "inspection method" to obtain parameter estimates from their data. Although no detailed description of this method has been provided by A/W, it seems to involve fitting the real part only of the admittance to the data in order to obtain estimates of R_B and the two distributed-element (CPE) parameters. Such fitting, which clearly does not yield C_g estimates, is probably graphical (on log-log plots) rather than by means of nonlinear least squares. It therefore involves subjective elements.

By contrast, we have used complex nonlinear least squares [22] (CNLS) to fit the real and imaginary parts of the impedance or admittance of the entire circuit of Fig. 1 simultaneously [2]. Whenever practical we have allowed all independent parameters of the circuit to be free, yielding estimates of them all which reflect all the data, not just a part of it. (Note that A, B, and n of the A/W form of the CPE are not all independent, as discussed above). Further, CNLS fitting is an objective procedure, when all parameters are free and convergence to an actual least squares solution is obtained. On this basis alone it is superior to any approximate subjective procedure; more importantly its resolution is such that processes whose effective time constants are close together can usually be well separated [22]. Finally, it yields an objective measure of the overall goodness of fit, the fitting standard deviation σ_f, and, in addition, leads to useful estimates of the relative standard deviations of the parameter estimates, showing immediately which are important and which, if any, are poorly determined by the data.

Analysis and interpretation of data fitting results

In this section we will restrict attention, in order to parallel the A/W approach, to just the R_B and CPE$_1$ (or ZARC) parameters of Fig. 1. At the admittance level, one can then write from the circuit,

$$Y_1 = G_B + G_B(i\omega\tau_1)^{n_1} \equiv G_B + A_1(i\omega)^{n_1} \tag{2}$$

where $G_B \equiv R_B^{-1}$ and $A_1 \equiv G_B(\tau_1)^{n_1}$. The complex conductivity, $\sigma(\omega)$, is just gY_1, where $g \equiv l_c/A_c$, the cell constant. Here l_c is the electrode separation in the measuring cell and A_c is the electrode area.

To obtain an equation for the real part of $\sigma'(\omega)$, i.e. $\sigma(\omega)$, A/W did not start from consideration of ZARC or CPE circuits but made some interesting alternative assumptions [9]. They started with an empirical equation for the imaginary part of the dielectric suspectibility, χ'', given by Jonscher [23,24]

$$\chi'' \propto \left[(\omega/\omega_p)^{n_a-1} + (\omega/\omega_p)^{n_b-1}\right] \tag{3}$$

where ω_p was identified by Jonscher only as a characteristic thermally activated frequency. It can readily be shown [25] that this sort of behavior involves at the full complex dielectric constant level just two CPE's in parallel. The real part of $\sigma(\omega)$ corresponding to eqn. (3) may be written [9]

$$\sigma_1'(\omega) = K\left[\omega_p^{1-n_a}\omega^{n_a} + \omega_p^{1-n_b}\omega^{n_b}\right] \tag{4}$$

where K is a parameter which will be discussed later.

Next, A/W made a leap of the imagination. Although Jonscher restricted his fractional exponent values to the range $0 < n < 1$, A/W set $n_a = 0$ and $n_B = n_1$ (our notation). Equation (4) thus reduces to

$$\sigma_1'(\omega) = K\left[\omega_p + \omega_p^{1-n_1}\omega^{n_1}\right] \equiv \sigma_{10}\left[1 + (\omega/\omega_p)^{n_1}\right] \tag{5}$$

We see that this result is of exactly the general form of the long-known ZARC model or resistor-CPE combination; for example, compare the real part of eqn. (2) with $\tau_1[\cos(n_1\pi/2)]^{1/n_1} \equiv \omega_p^{-1}$. It was thus unnecessary for A/W to invoke the empirical Jonscher equation at all. The ZARC, proposed earlier than Jonscher's equation above, has long been used for analysis of conducting materials, just as its dielectric analog, the Cole–Cole model [18], has been used in the dipolar material area.

When one compares the real part of eqn. (2) with Eqn. (5), one obtains the equations

$$\omega_p = gK^{-1}G_B \tag{6}$$

and

$$\omega_p = \tau_1^{-1}\left[\sec(n_1\pi/2)\right]^{1/n_1} = \left[G_B/\{A_1\cos(n_1\pi/2)\}\right]^{1/n} \tag{7}$$

As pointed out by A/W, these results establish a relation between the dc component of $\sigma'(\omega)$ and the $\omega > 0$ ac component. But until ω_p (or τ_1) is interpreted, the relationship is only a reparameterization and is of no more value than that inherent in eqn. (2).

The most crucial step in the A/W approach is their many-times-repeated assertion that ω_p is the thermally activated hopping rate. This assumption is connected with their use of a random-walk diffusion expression cited by Huggins [26] to yield a formula for the dc part of $\sigma_1'(\omega)$, σ_{10}. The result may be written

$$\sigma_{10} = K_0T^{-1}\nu_H \tag{8}$$

where ν_H is defined as the average jump frequency and K_0 involves the carrier concentration and other parameters of the motion [2,26]. When the σ_{10} of eqn. (8) is set equal to $K\omega_p$ from eqn. (5) one obtains

$$K = (K_0/T)(\nu_H/\omega_p) \tag{9}$$

Almond and West made the ad hoc assumption that $\omega_p \equiv \nu_H$ and gave no theoretical justification for this conclusion. Then K_0 and ω_p estimates may be calculated from the parameter estimates obtained from the data fitting itself and then compared with expectations. Finally, note that even if one makes the less stringent assumption $\omega_p = a_1 \nu_H$, where a_1 is a proportionality factor which might be thermally activated itself, K cannot be calculated without independent knowledge of a_1.

Although equations essentially the same as eqn. (8) have been used in the past for Na β-alumina [26] the appropriateness of the equality $\omega_p = \nu_H$ seems not to have been considered thus far in the literature. Since this assumption appears to be the principal original element in the many A/W papers on the analysis of their Na β-alumina data, and since it was also used uncritically by us with only some modification in ref. 2 (an improved expression for K_0 was given in ref. 2, an expression which seems to be somewhat more appropriate specifically for Na β-alumina than the original general diffusion expression of Huggins [26]), it deserves some further scrutiny.

In a fairly recent paper on dc and ac conduction in hopping systems [27] Hill and Jonscher state: "The position with regard to the interpretation of dc hopping data is, therefore, that at present we are essentially unable to account quantitatively for most observations in terms of parameters that are known separately from other sources...". Previous work on the dc conduction problem suggests that anharmonic-mode phonon effects may contribute to σ_0, but such effects are not included in the Huggins expression of eqn. (8). Hill and Jonscher write $\sigma(\omega)$ in the form

$$\sigma'(\omega) = \sigma_0(T) + \sigma_a'(\omega) \tag{10}$$

and Jonscher has often proposed that $\sigma_a'(\omega) \propto \omega^n$, as in eqns. (2) and (5). Finally, Hill and Jonscher believe that $\sigma_a'(\omega)$ should always include some contribution from the lattice itself [24,27]. No such contribution appears in the $\sigma_a'(\omega)$ term of eqn. (5) when eqns. (8) and (9) are used with $\omega_p = \nu_H$. The above considerations suggest that there is, so far, no strong theoretical justification for the $\omega_p = \nu_H$ A/W assumption and perhaps even some uncertainty in the appropriateness for β-alumina of the Huggins form of eqn. (8).

In spite of the apparent lack of a strong physical basis for the assumption $\omega_p = \nu_H$, it is of interest to compare the results found by A/W and M/C using this assumption. On assuming that ω_p is thermally activated, A/W write [9,11-13,15]

$$\omega_p = \omega_e \exp[-E_a/kT] \tag{11}$$

where ω_e is taken to be an effective attempt frequency for hopping and E_a is identified as the activation energy for ionic conduction. Clearly, E_a is actually an enthalpy for the ω_p process. Now A/W found [13] a value of $\omega_e = 1.2 \times 10^{12} s^{-1}$ from the analysis, as above, of their 113 K data, a value which compares quite well with that of about $2 \times 10^{12} s^{-1}$ obtained by direct measurement in the far infra red.

Although the above agreement seems to bolster the case for $\omega_p = \nu_H$, it should be remembered that in order to obtain an estimate of ω_e accurate estimates of ω_p are needed. But as eqn. (7) shows, ω_p must be calculated from uncertain estimates of G_B, A_1, and n_1. In particular, the A/W A values (closely related to A_1) are stated to have only ±20% accuracy [9]. Alternatively, ω_p can only be obtained, again approximately, from the second form of eqn. (5) when the Y_1 of eqn. (2) can be isolated from the total Y of the system and when its real part can be shown to be closely proportional in its frequency dependence to the $\sigma_1'(\omega)$ of eqn. (5). With only $\pm 20\%$ accuracy of the A parameter, A/W can scarcely be said to have done this. Now ω_e itself is a prefactor in eqn. (11), and it is notoriously difficult to obtain a meaningful value of an exponential prefactor unless the data are exceptionally accurate. Macdonald and Cook [2] obtained ω_p estimates from those of G_B, A_1, and n_1 and then derived ω_e and E_a estimates from nonlinear least squares fitting to eqn. (11) directly (not by using an ordinary least squares fit to $\log(\omega_p)$, a procedure which introduces bias of its own). The results obtained were $\omega_e \cong (6.82 \pm 3.57) \times 10^{10} \mathrm{s}^{-1}$ for $T \leqslant 102$ K and $\omega_e \cong (7.1 \pm 8.3) \times 10^{15} \mathrm{s}^{-1}$ for $110 \leqslant T \leqslant 151$ K. As one can see, neither of these results is near 2×10^{12} s^{-1} but, more importantly, their uncertainties are so great that they cannot be interpreted as valid predictions in any case. Yet these results were obtained from the best fits of the data available at the time. It thus appears that until appreciably more accurate data than that of A/W are available for Na β-alumina, it will not be possible to show unequivocably that any ω_e derived objectively from the data is indeed close to 2×10^{12} s^{-1}. It is likely that comparably great uncertainty in ω_e values and the uncertainty in the $\omega_p = \nu_H$ assumption apply as well to the other [12,14–16] hopping conduction materials analyzed by A/W.

Although it seems clear that the case for a numerical estimate of ω_e derived from the electrical data which is close to the independent far infra red value remains unproven, it is not in fact necessary to obtain ω_e to prove $\omega_p = \nu_H$. One only needs to obtain ν_H independently and then show that at different temperatures $\omega_p \cong \nu_H$. Now Fig. 6 of the A/W comments [1] indeed shows that ω_p derived from admittance measurements appears to agree excellently with "ν_H" values derived from ultrasonic mechanical relaxation measurements. Case made? Not necessarily! First, A/W have stated [12]:"...the apparent hopping frequency indicated by the electrical modulus loss peak is not generally a measure of the true hopping frequency and the good agreement with mechanical relaxation results in Na β-alumina (see ref. 8) is somewhat fortuitous." In later work [13], A/W have pointed out that the frequencies of the peaks of $-Z''$ and M'' curves usually differ appreciably, depending on n. Further, neither of these peak positions corresponds simply to ω_p. The ω_p values of Fig. 6 coming from electrical measurements were derived from graphically fitted Y' data, not from peak positions at all. These various statements seem to lead to a curious inconsistency, one which may be summarized as follows:

(a) ultrasonic ω_p's and modulus-peak ω_p's are in good agreement (ref. 8);
(b) ultrasonic ω_p's and Y' ω_p's are in good agreement (Fig. 6 of Ref. 1);
(c) but, modulus-peak ω_p's and Y' ω_p's are different and do not measure the same quantity.

An alternative way to obtain an estimate of ω_p from small-signal ac measurements, one which takes all the data into account, is to use eqn. (7) with fitting estimates of G_B and

$$A_{c1} \equiv A_1 \cos(n_1 \pi/2) \qquad (12)$$

Here A_{c1} is the quantity termed A in the A/W work. This was the approach used in our earlier paper [2]; it is not clear that it is the one used by A/W at all the nine different measurement temperatures. It is important to emphasize that the ω_p derived from this approach, or even from eqn. (5), is not the same as the one obtained from the peak $-Z''$ value. From eqn. (1), one finds that the peak value of $-Z''_{\text{ZARC}}$ occurs at

$$\omega_{\text{pm}} \equiv \tau_1^{-1} = \left[\cos(n_1\pi/2)\right]^{1/n_1}\omega_p \tag{13}$$

Thus, only as $n_1 \to 0$ do the two ω_p's approach equality. Here we have used a subscript of one to refer to the ZARC or CPE-R_B elements of Fig. 1.

From a logical point of view, if the empirical eqn. (1) applies it seems much more plausible to take ω_{pm} equal to ν_H than to set $\omega_p = \nu_H$ as A/W have done. But there still remains much uncertainty in setting either ω_{pm} or ω_p equal to ν_H. Since the electrical and mechanical relaxations are associated with different physical processes in a hopping conductor such as Na β-alumina, there is no assurance, without detailled theoretical analyses of both processes, that ω_p or ω_{pm} is the same quantity as that obtained from mechanical relaxation peaks or that either of the rates derived from electrical or mechanical measurements is exactly equal to ν_H. Since longitudinal ultrasonic waves are coupled to the Na β-alumina lattice and to the conducting ions in an entirely different fashion than are alternating electrical currents, which are directly associated with ionic motion, it would indeed be quite surprising if both processes involved ν_H (an intrinsically conducting, ionic quantity) directly in such a fashion that it could be obtained directly from either mechanical or electrical measurements of the kind discussed above. At the present time, it thus appears that even if all electrical rate estimates were found to be closely equal to the mechanical ones, a situation still in limbo, the results would be unlikely to equal ν_H.

NEW FITTING RESULTS

Since A/W have directed special attention [1] to our $T = 151$ K fitting results, we started our re-analysis of the A/W data with the original 151 K data set. A complex plane impedance plot of this data set is presented in Fig. 3. In order to obtain a meaningful CNLS fit to data having such irregularity, we eliminated three points: the lowest frequency one, one in the glitch region, and the next to the last one at the highest frequency end of the curve. Our initial CNLS fitting results suggested that it would be desirable to refit all nine A/W data sets, not just the three highest,those where we previously used extrapolated A_1 values [2]. Therefore, we plotted all nine sets like that in Fig. 3 and eliminated the worst irregular and outlying points before fitting. The number of points eliminated varied from zero to five.

Our new fitting to the 151 K, 141 K, and 132 K data sets was found to be possible without using extrapolated, fixed values of A_1 as in the earlier work. All parameters were taken free to vary, and we obtained σ_f values roughly three times smaller than those of the original fits! Here σ_f is the estimated standard deviation of the data fit residuals. Evidently, our earlier higher-temperature results were not true

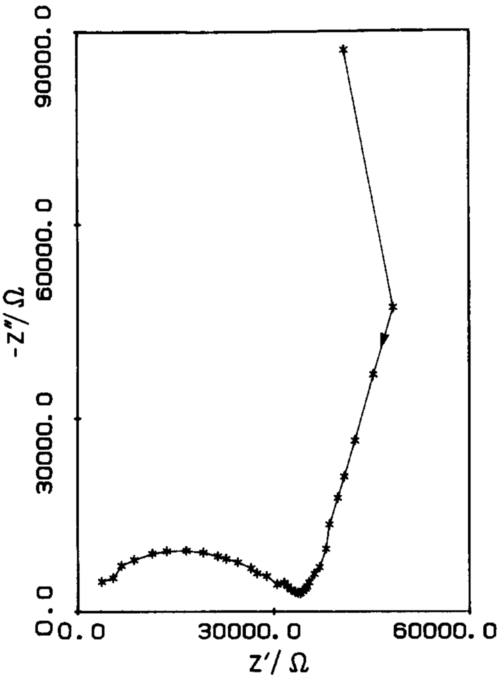

Fig. 3. Complex plane impedance plot of the original A/W 151 K data.

least square ones but involved local rather than absolute minima. This possibility, always a danger in iterative *nonlinear* least squares fitting, is much less likely when all parameters are free as above and when good fits are obtained. Thus, we believe that our current results are all *least* squares ones. We wish to thank A/W once more for stimulating us to re-examine and improve our earlier fitting results. We believe our current results are the most objective ones currently available for the A/W data. Further, as we shall see, they are usually much closer to the subjective-fit ones obtained earlier by A/W.

Before discussing the complete fitting parameter estimate results in some detail, it is worthwhile comparing some of the results of our new 151 K fit with those obtained using A/W's estimated parameter values for this temperature [9,10]. Such comparison is carried out in Figs. 4–6. Where there are very large discrepancies between the A/W predictions and the data, these arise because A/W did not include the CPE_2 element of Fig. 2 in their analysis. When it is included, as in our results, one sees excellent agreement between the data and the fit results over virtually the entire frequency range. Although the results of Fig. 5 are included in the projection planes of Fig. 4, we have presented them here, over the limited frequency range where the A/W fit applies, in order to illustrate on a larger scale the differences between the A/W and M/C fits. Figure 6, which should be compared to Figs. 3 and 4 of the A/W comments [1], shows the comparison at the log admittance

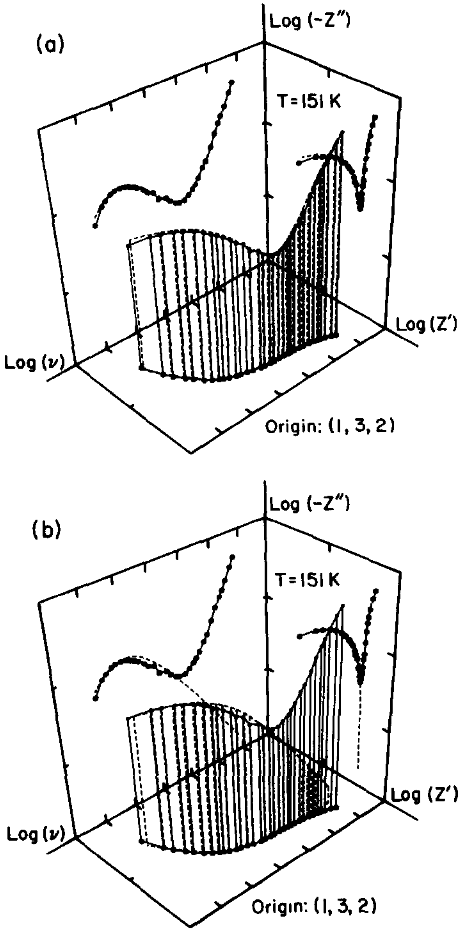

Fig. 4. Three-dimensional perspective plots of the 151 K data and fits. Data points and fitted lines shown. (a) Comparison of data with the new M/C fit. (b) Comparison of data with a fit produced using A/W parameter estimates.

level for the full frequency range. It is evident from these results that in the range where the A/W fits apply, they are reasonably good but not as accurate as the M/C ones. Similar conclusions apply for the other lower temperature fits.

Because Na β-alumina is an important material and because the A/W data sets are virtually the only ones currently available in the relatively low temperature region, we have decided to present our complete results for all parameter values estimated directly from the data by CNLS fitting. These results thus become available for direct comparison with those obtained earlier by A/W, where overlap exists, and, more importantly, may be used in the future to compare with fitting results obtained from new and improved low temperature Na β-alumina data.

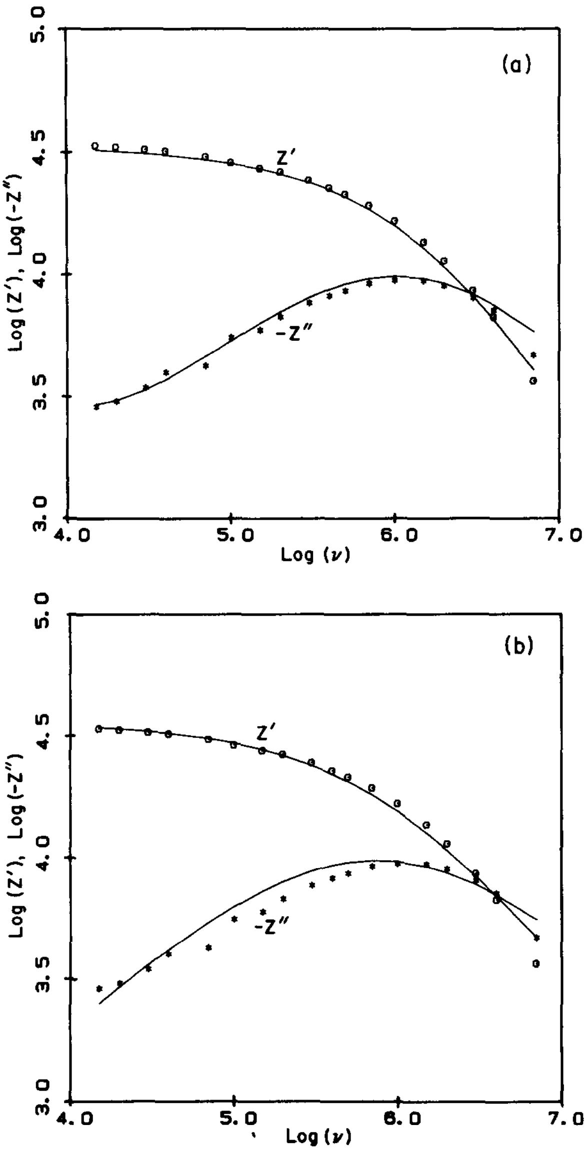

Fig. 5. Log–log impedance-frequency plots for $T = 151$ K. (a) Comparison of our results with the data over a limited frequency range. (b) Comparison of A/W results for the same range.

Direct fitting results are presented for the nine available temperatures in Table 1, and quantities of interest derived from them in Table 2. For easier comparison with future results, we have presented all present quantities in such a way that they are independent of the original A/W measuring cell dimensions. Thus ε_g is the effective

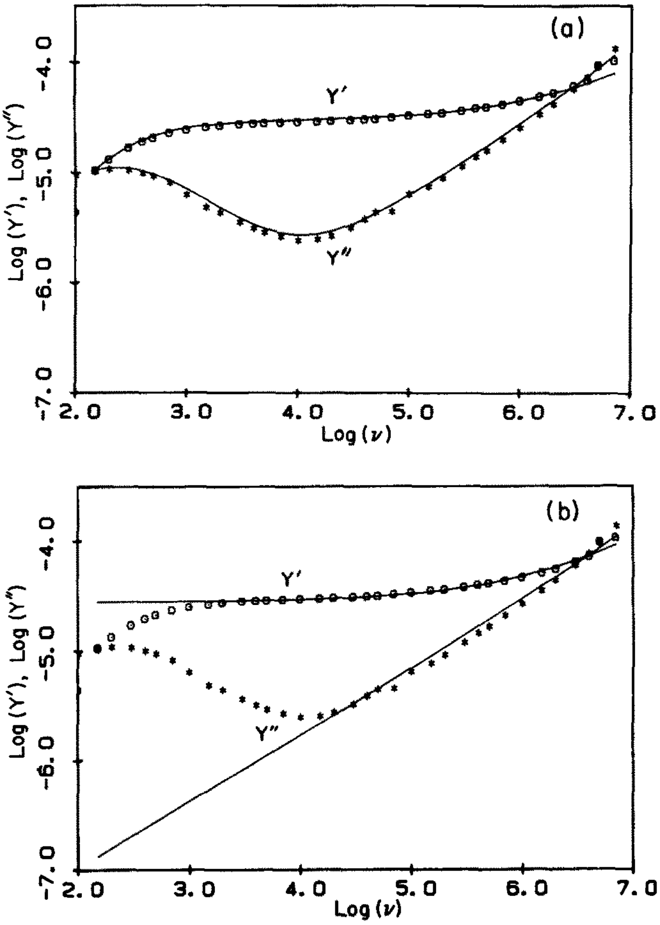

Fig. 6. Log–log admittance–frequency plots for $T = 151$ K. (a) Comparison of our results over the full frequency range. (b) Comparison of A/W results for the same range.

dielectric constant associated with C_g, and gA_2 is presented rather than A_2, a quantity which does depend on cell dimensions. Here the A/W g factor is 2.53 cm^{-1}. Incidentally, the dimensions of the quantity A_{OB} of the earlier work, here A_1, are given incorrectly there [2]. The dimensions of A_1 are $[\Omega^{-1}\text{rad}^{-n}]$. The results in Table 1 are presented in the form Q/σ_r, where Q is the estimated value of the parameter and σ_r is its estimated relative standard deviation, a quantity which gives some information on how well Q is determined by the CNLS fitting.

It will be noted from Table 1 that σ_r for gA_2 increases as T decreases. A fitting run for $T = 121$ K with A_2 free yielded $gA_2 = 4.90 \times 10^{-8}/0.65$. Although the very large value of σ_r shows that the 4.90×10^{-8} value is very uncertain, it is evidently very little biased since it agrees closely with the value shown in the table, a value

TABLE 1

Direct CNLS fitting results. The notation Q/σ_r is used, where Q is the estimated value and σ_r is its estimated relative standard error. When $\sigma_r = F$, Q was taken fixed and not free to vary

T/K	ε_g	$T\sigma_0/\Omega^{-1}\text{cm}^{-1}\text{K}$	τ_1/s	n_1	$gA_2/\Omega^{-1}\text{cm}^{-1}\text{rad}^{-n_1}$	n_2
151	29.7/0.21	1.14×10^{-2}/0.01	1.33×10^{-7}/0.09	0.600/0.04	1.90×10^{-7}/0.13	0.823/0.02
141	32.9/0.09	3.54×10^{-3}/0.01	3.10×10^{-7}/0.06	0.609/0.03	1.40×10^{-7}/0.15	0.827/0.03
132	34.9/0.02	9.53×10^{-4}/0.01	1.36×10^{-6}/0.04	0.551/0.02	8.56×10^{-8}/0.24	0.869/0.04
121	31.7/0.007	1.37×10^{-4}/0.006	1.07×10^{-5}/0.02	0.556/0.007	$4.96\times10^{-8}/F$	0.884/0.007
113	30.4/0.01	3.68×10^{-5}/0.01	4.20×10^{-5}/0.05	0.568/0.01	$3.03\times10^{-8}/F$	0.869/0.03
110	29.8/0.009	1.49×10^{-5}/0.01	9.49×10^{-5}/0.04	0.585/0.009	$2.47\times10^{-8}/F$	$1/F$
102	30.4/0.01	1.36×10^{-5}/0.01	8.73×10^{-5}/0.05	0.598/0.01	$1.36\times10^{-8}/F$	$1/F$
92	28.6/0.008	1.46×10^{-6}/0.04	5.45×10^{-4}/0.09	0.653/0.009	$5.53\times10^{-9}/F$	$1/F$
83	27.0/0.07	1.22×10^{-7}/0.07	3.05×10^{-3}/0.11	0.732/0.006	$2.05\times10^{-9}/F$	$1/F$

TABLE 2

Quantities calculated from Table 1 results

T/K	$A_{cl}/\Omega^{-1}\ \text{cm}^{-1}\ \text{rad}^{-n_1}$	$\omega_{pm}/\text{s}^{-1}$	ω_p/s^{-1}	$K_0/\Omega^{-1}\ \text{cm}^{-1}\ \text{s K}$
151	3.34×10^{-9}	7.53×10^{6}	1.83×10^{7}	6.25×10^{-10}
141	1.58×10^{-9}	3.22×10^{6}	7.97×10^{6}	4.45×10^{-10}
132	2.75×10^{-9}	7.35×10^{5}	1.61×10^{6}	5.91×10^{-10}
121	1.26×10^{-9}	9.37×10^{4}	2.08×10^{5}	6.62×10^{-10}
113	6.69×10^{-10}	2.38×10^{4}	5.40×10^{4}	6.81×10^{-10}
110	3.65×10^{-10}	1.05×10^{4}	2.47×10^{4}	6.03×10^{-10}
102	2.96×10^{-10}	1.15×10^{4}	2.76×10^{4}	4.93×10^{-10}
92	6.06×10^{-11}	1.83×10^{3}	5.02×10^{3}	2.91×10^{-10}
83	8.68×10^{-12}	3.28×10^{2}	1.11×10^{3}	1.10×10^{-10}

obtained by fitting the three higher-T gA_2 results to an exponential law of the form $Q\exp(-\lambda_a/T)$ and extrapolating to $T = 121$ K. The value of λ_a obtained was about 844 K, corresponding to a 0.073 eV activation enthalpy. The first three A_2 estimates were found to lie very closely on the above exponential response curve. Since the fourth value also was very close to that predicted from the fit of the first three, it seemed reasonable to conclude that A_2 followed this behavior over the full temperature range. Since the data were inadequate to determine A_2 values to any reasonable degree of accuracy below 121 K, we have used fixed, extrapolated values of A_2 for $T = 121$ K and below in the CNLS fittings for these temperatures. The symbol "F" in Table 1 indicates a fixed, rather than free parameter. Further, we have followed our earlier approach in setting $n_2 = 1$, fixed, for the lower temperatures. A value of about 0.9 might be suggested by the results in the table for higher temperatures but the actual values of A_2 and n_2 are only of secondary importance to the fit anyway at the lower temperatures [2].

It will be noted that Table 1 gives τ_1 values rather than A_1 ones. It was found that fitting with the ZARC impedance of eqn. (1) was generally superior [25] to using the parallel R_B and CPE approach of Eq. 2, the one used in our earlier work [2]. Specifically, σ_r for τ_1 was generally two to four times smaller than the σ_r of A_1 obtained in a separate fit. Further, the correlations of τ_1 with the other parameters were generally smaller than those involving A_1. Of course σ_f, the standard deviation of the overall fit, and the other parameter estimates were identical whether τ_1 or A_1 was determined. Further, values of A_1 obtained from direct fitting and from $A_1 = \tau_1^{n_1}/R_B$, using fitting estimates of τ_1, n_1, and R_B, were usually very close to each other. But note that although τ_1 shows monotonic temperature dependence for the 110 K–151 K range, the A_{c1} values in Table 2 calculated using eqn. (12) do not. This behavior was also reflected in calculated or estimated A_1 values and is a further justification for the use of τ_1 as a fitting parameter rather than A_1.

It is also clear from Table 1 that the higher-temperature estimates of n_1 differ appreciably from our earlier values and agree rather closely with the A/W estimates [1]. For 110 K $\leqslant T \leqslant$ 151 K it appears that n_1 is nearly temperature independent, but it seems to increase as T decreases from 102 K. Both types of temperature dependence are in agreement with the predictions of a recent distribution-of-activation-energies theory [28] which can lead to response very like that of eqn. (1) over a wide frequency range.

It remains to discuss the results for $T\sigma_0$, ω_p, and K_0. The one principal issue remaining between ourselves and A/W is whether the data indicate the possible presence of a glass-like transition in Na β-alumina between 102 K and 110 K or not. We believe that the evidence is clear for such a process, while A/W believe that there is no real discontinuity in $T\sigma_0$ and ω_p results above and below these temperatures. They ascribe any apparent discontinuity to "variations" in the data. Further, in their Figs. 1a and 1b they omit our separate fitting lines for the upper and lower temperatures and draw a single line through all the results, thus obscuring our evidence for discontinuities.

Figure 7 shows data (points) and fitting results (lines) for our new $T\sigma_0$ and ω_p results. Here ω_p was calculated with eqn. (7) using τ_1 and n_1 estimates. Fitting was carried out using weighted nonlinear least squares to avoid the bias introduced by fitting, say $\log(T\sigma_0)$ with linear least squares. Clearly all the results are well fit by exponential dependence of the form $Q \exp(-\lambda/T)$. Further, the presence of discontinuities seems self-evident. Although the discontinuities and different slopes could have arisen from systematic temperature errors, this seems somewhat unlikely. The upper and lower temperature lines for $\log(T\sigma_0)$ involve λ values of about 0.23 eV and 0.18 eV, respectively. The corresponding values for the $\log(\omega_p)$ lines are about 0.24 eV and 0.12 eV, not very different from our earlier results [2]. Also the ω_e estimates, $(3.14 \pm 3.50) \times 10^{10}$ s^{-1} and $(1.60 \pm 1.00) \times 10^{15}$ s^{-1} for the lower and upper ω_p lines, respectively, are in the same ranges as found earlier, are not close to the hopping value, and are still too uncertain to be particularly meaningful. Almond and West state that our $T\sigma_0$ activation energies are anomalously high when compared with results obtained from conductivity measurements at much higher temperatures, i.e. an activation energy of 0.16 eV or slightly less. But there is no assurance that indeed λ should be the same at room temperature and above and in the low

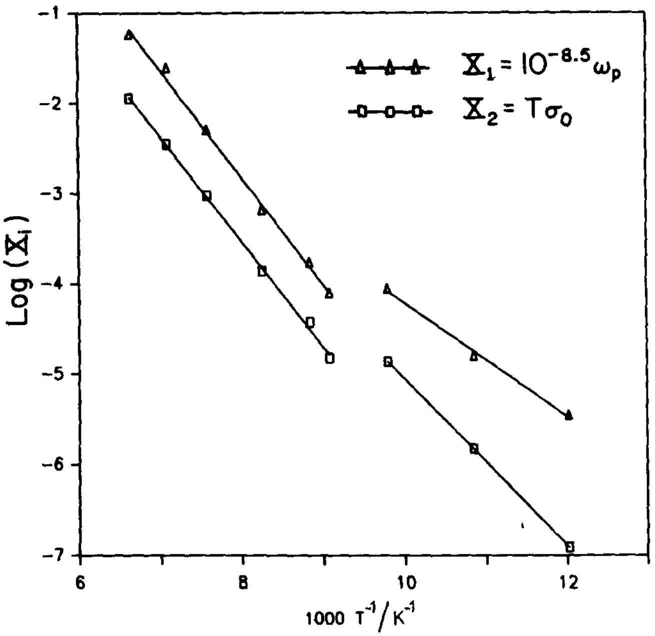

Fig. 7. Dependence of $\log(10^{-8.5}\omega_p)$ and $\log(T\sigma_0)$ on $10^3/T$ for the new M/C results.

temperature region. If the conduction process is actually the same at low and high temperatures, we can only conclude that the A/W data are too inaccurate to establish the matter adequately.

When one follows A/W and fits the $T\sigma_0$ data with a single exponential over the entire temperature range, but here using weighted nonlinear least squares, the A/W values of $T\sigma_0$ lead to a λ value of about 0.17 eV/0.07 and an estimated mean square error (mse) of fit of 0.23. The corresponding results obtained using our $T\sigma_0$ estimates are about 0.17 eV/0.11 and a mse of 0.34. Thus our results fit a single line somewhat less well even than do those of A/W. But even a mse of 0.23 is very poor indeed. For comparison, the mse's for the worst of the four individual fits of Fig. 7 is about 0.03 and most of them are about 0.01 or less, far better fits.

In Table 2 we have presented both ω_{pm} and ω_p values for comparison and possible later use. Also given are K_0 values calculated using eqn. (8) with the assumption $\nu_H = \omega_p$. In order to allow comparison with the A/W results [1] for K_0 shown in their Fig. 1c, our values are presented in semi-log form in Fig. 8. We see that above the transition K_0 might almost be taken constant at its average value of about 6×10^{-10} Ω^{-1} cm^{-1} s K. Clearly below the transition it decreases. If one assumes an exponential decrease, possibly associated with thermal activation of the carrier concentration, one finds a reasonable fit with an activation parameter of about 0.06 eV/0.13 and a mse of 0.02. When one converts the above average K_0 value to the K_{00} parameter of the earlier work [2], one finds $K_{00} = 3.4 \times 10^{-9}$ Ω^{-1}

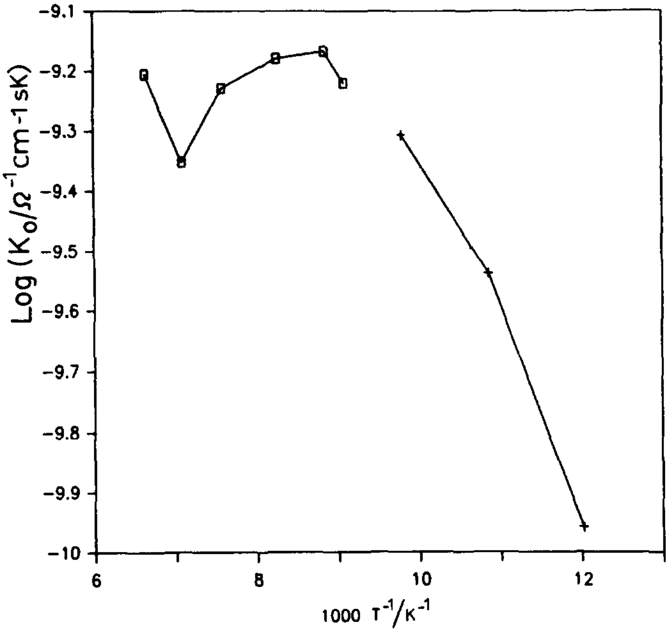

Fig. 8. Dependence of $\log(K_0)$ on $10^3/T$ for the new M/C results.

cm^{-1} s K, if one assumes full activation of all available carriers (above the transition) and a non-stoichiometry factor x of 0.227. The value of K_{00} calculated independently of the fitting results in the earlier work [2] from the random-walk diffusion formula was about $4.8 \times 10^{-9}\ \Omega^{-1}$ s K, not substantially different from that above. It is this fairly good agreement that seems to be the only plausible evidence so far that ω_p and ν_H may indeed be closely related if not identical. But one should remember that the present K_0 estimates are all quite uncertain.

It would certainly be useful to apply this same test and that for ω_e to further more accurate data for the temperature range from $T = 110$ K and above. Preliminary fits carried out by one of us (J.R.M.) on two-point single crystal Na β-alumina data of Bates [29] at $T = 139$ K to 162 K show quite different n_1 behavior than that found for the A/W data. Instead of n_1 values near 0.6, these fits yield results near 0.93, but, according to Bates, such high values are associated with stray capacity present in his measurements. On the other hand, Bates has found little or no frequency dispersion of Z' in four-point probe measurements on the same material at room temperature and above. [29] It thus remains somewhat uncertain as to how much bulk dispersion one might expect for the low-temperature region covered by the A/S data. We look forward to the future when objective fitting of new, more accurate Na β-alumina data may allow the various uncertainties discussed in the present work to be resolved.

ACKNOWLEDGEMENTS

We are grateful to the U.S. Army Research Office for support of the work and to Dr. J.B. Bates for kindly sending us some of his unpublished data.

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