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The separability of inter- and intragranular resistivities in sodium beta-alumina type ceramics

R. W. POWERS
General Electric Corporate Research and Development, PO Box 8, Schenectady, NY 12301, USA

The intergranular and intragranular resistivity components in β-alumina ceramics cannot be separated quantitatively by impedance analysis, it was concluded a few years ago in a previous article in this journal. This conclusion was based on use of the so-called parallel multi-element equivalent circuit to model the electrical properties of polycrystalline electrolytes. However, this model is shown to be inconsistent with the observation that the activation energy for the intergranular resistivity is independent of the size of that component for many compositions – both β- as well as β''-alumina. From this finding and others, the author infers that the separation of intra- and intergranular resistivities in sodium beta-alumina type ceramics is clean. Consideration of the separability question is greatly facilitated by an unconventional method of resistivity analysis. This alternative method involves essentially d.c. measurements on a set of specimens of the same composition but with different microstructures and resistivities. The method is described and its use illustrated.

1. Introduction

A few years ago, DeJonghe [1] published in this journal a sophisticated study of β-alumina grain boundary morphology and structure using transmission electron microscope lattice imaging. Every grain, it appears, is bounded by boundaries that have a wide spread in intergranular resistivities. The ionic current flow in polycrystalline electrolyte is not homogeneous. This study contributes significantly in providing a better mechanistic understanding of the often noted observation that the variation of impedance with frequency for well conducting polycrystalline electrolytes cannot be described by a single time constant (intergranular resistance × intergranular capacitance) but requires instead a wide distribution of such response times.

As one part of this study, DeJonghe modelled these current heterogeneities using the parallel multi-element equivalent circuit shown in Fig. 1. This circuit comprises parallel units of that simplified equivalent circuit normally used as the model of the electrical properties of polycrystalline electrolytes. In the simplified circuit, r_c is the specific resistivity associated with the interior of the grains and will frequently be referred to as the crystal or intragranular resistivity. It is in series with r_b, the intergranular resistivity, the extra resistivity in polycrystalline specimens arising mainly from the presence of grain boundaries. C_b represents the specific capacitance associated with these grain boundaries. DeJonghe carried out computations on a model with 100 parallel units. Resistors representing r_c were made identical in each unit. All had the same activation energy E_c, assumed to be 4 kcal mol^{-1}. On the other hand, values of the grain boundary resistivity were made widely different in the parallel units. Each was given the same activation energy, E_b, of 8 kcal mol^{-1} however. The apparent lumped grain boundary resistivity was calculated and compared with a true value obtained by setting r_c to zero. The ratio of the two was usually greater than one. The discrepancy arises because the apparent lumped grain boundary resistivity contains contributions from the crystal resistivity. The apparent value equals the true one

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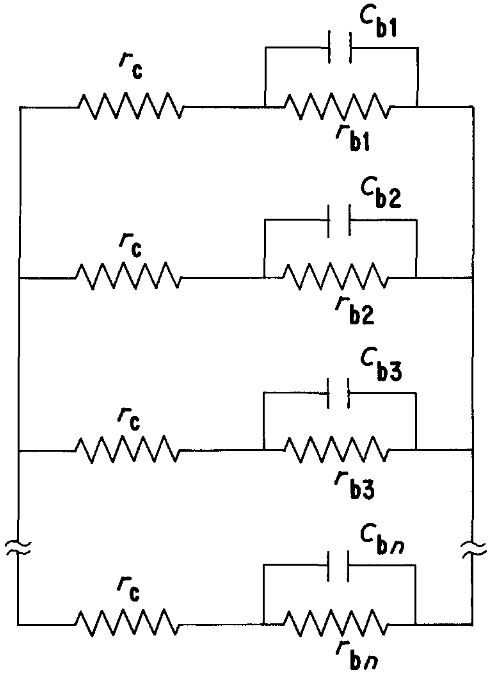

Figure 1 Parallel multi-element equivalent circuit.

only when the grain boundary resistivity is very much larger than the crystal resistivity, a situation usually occurring at lower temperatures. From such results, DeJonghe concluded that impedance analysis does not yield data of fundamental significance for polycrystals. An important question was thus raised about the real worth of impedance analysis. Can intragranular resistivities be separated from the intergranular or are these components hopelessly entangled?

This question is the main concern of the present paper. The author has found that consideration of this problem can be facilitated by use of a scheme of resistivity analysis different from the conventional one. The experimental procedures used in this study will be stated, the analytical method described, and its use illustrated to show its validity before the separability question is discussed.

2. Experimental procedures

The β- or β''-alumina specimens used in this work were fabricated in the form of cylindrical tubes about 10 cm long, 1 cm in outer diameter, and 0.1 cm wall thickness. Two different starting powders were used. One was Alcoa XB-2 β-alumina powder [2]. Work with nearly phase-pure β-alumina specimens was greatly facilitated by use of this powder because of its stability against transformation to β''-alumina [3]. Ceramics of high β''-alumina content were made using another Alcoa starting powder containing approximately 65% β''-, the balance being β-alumina. Specimens were formed by electrophoretic deposition and were sintered using a fast firing method [4–6].

The four-point impedance measuring technique employed has also been described previously [7]. With the method of resistivity analysis described in this paper, the geometric constant must be very accurately known for every specimen. The accuracy of this constant, the ratio of the cross-sectional area to the distance between the voltage probes, can be severely limited by wall thickness measurements on tubular specimens. In the present work, the cross-sectional area was obtained from the specimen mass, density, and overall length.

3. The temperature comparison method of resistivity analysis

Impedance analysis of well conducting polycrystalline electrolytes conventionally makes use of measurements carried out over a wide range of frequencies. Unless the electrolyte contains an additive such as yttria, which greatly increases the intergranular capacitance, measurements well into the megahertz range are required. The increasing difficulty of impedance measurements at higher frequencies supplied much of the motivation for developing the analytic method described in this paper.

This technique, called the temperature comparison method, involves only d.c. or low frequency a.c. measurements. Its basis is the fact that the parameter r_b varies with the grain size. Resistivity measurements are made on a set of specimens of the same composition but sintered at different temperatures to display a range of microstructures and consequently different resistivities. An extrapolation is carried out to zero contribution from r_b to obtain r_c, the crystal resistivity component. The extrapolation does not involve explicit knowledge of the grain size. No information is obtained about the grain boundary capacitance since only d.c. or low frequency a.c. measurements are used.

Full use of this method can be made only if four conditions are fulfilled. These are as follows:

1. that $r = r_b + r_c$;
2. that all specimens in the set have the same r_c value at a given temperature;
3. that the form of the variation of r_c with

temperature be known, the Arrhenius relation, $T/r_c = \sigma_0 \exp(-E_c/RT)$, being most commonly used; and

4. that, whereas r_b values will vary from specimen to specimen in the set, all have the same temperature variation.

Here T is the absolute temperature; σ_0 the pre-exponential constant; E_c the activation energy for the crystal resistivity component; and R is the gas constant. Previous experimental findings show these conditions are met in a number of β-alumina ceramics [7, 8].

The first condition, that the measured specific resistivity can be equated to the sum of the crystal and grain boundary resistivities, is equivalent to the statement that the simplified equivalent circuit is an adequate representation of the electrical properties of polycrystalline β- or β''-alumina. Discussions of previous use of this equivalent circuit and the basis of its validity have been given elsewhere [7, 8].

The second condition is the most important one in the application of the temperature comparison method and furthermore illustrates the utility of the simplified model. In general, while the grain boundary resistivity depends sensitively on the processing history, in contrast the crystal resistivity at a given temperature remains the same for specimens in the set. Members of a set must share a common crystal structure, chemical composition, and degree of preferred orientation. However, there are situations where this second condition is not valid such as when the crystal resistivity becomes a sensitive function of processing history. In this event, the temperature comparison method cannot be applied and the simplified model is reduced almost to an empty formalism. A commonplace example occurs with β,β''-alumina ceramics containing relatively low concentrations of stabilizers for the β''-alumina phase, usually lithia or magnesia. The ratio of β- to β''-alumina, and consequently the crystal resistivity, can change significantly with sintering conditions.

While a simple Arrhenius equation usually suffices to describe the variation of crystal resistivity with temperature, exceptions do occur. For example, large deviations from this relationship have been noted with single crystals of β''-alumina. This behaviour was first observed by R. H. Radzilowski and has been confirmed more recently by Briant and Farrington [9, 10].

The fourth condition, that the temperature variation of the grain boundary resistivity be the same for all members of the set, is of a sort rather different from the third. It is not necessary that the activation energy, E_b, remains invariant with temperature, and indeed it usually does change somewhat as shown below.

The extrapolation of experimentally determined resistivity values for a set of specimens to zero contribution from r_b involves use of plots of resistivities determined at various higher temperatures, for example at 250° C or 400° C, against the corresponding value at a reference temperature, taken for convenience to be 26.8° C (300.0 K). An annotated plot of this sort for 250° C is illustrated in Fig. 2 for a set of six β-alumina ceramic specimens containing 8.4% Na_2O. The individual specimens were sintered at different maximum temperatures between 1675 and 1775° C, as shown near the bottom of the figure, and therefore exhibited different microstructures. The linearity of the plot is an indication that the determined resistivity values can be viewed as the sum of two components, one of which is common to all the members of the data set and another component for which the ratio of the value at 250° C to that at 26.8° C is common. This ratio, or more accurately the slope b of such plots, is readily shown to be related to the grain boundary activation energy, averaged in reciprocal absolute temperature between 300 K and the higher measurement temperature TK, by the expression

$$E_b = R \ln(300b/T)/(1/T - 1/300). \qquad (1)$$

The slope b can be determined most accurately by linear regression analysis. Thus the linearity of a plot, such as shown in Fig. 2, shows that the first, second, and fourth conditions are satisfied for resistivity data obtained with the set of specimens under consideration.

Furthermore, Fig. 2 illustrates the point that, if an r_c value is known or can be determined at one temperature, for example, at the reference temperature 26.8° C, then r_c values can also be obtained at other temperatures for which plots are available. The value of $r_{c250^\circ C}$ is determined simply by the intersection of the line of slope b with the dashed vertical line, $r_{26.8^\circ C} = r_{c26.8^\circ C}$. Plots as shown on Fig. 2 are called resistivity distribution plots since they indicate at a glance the distribution of r_T, the determined resistivity at a temperature T, between its components r_{cT} and

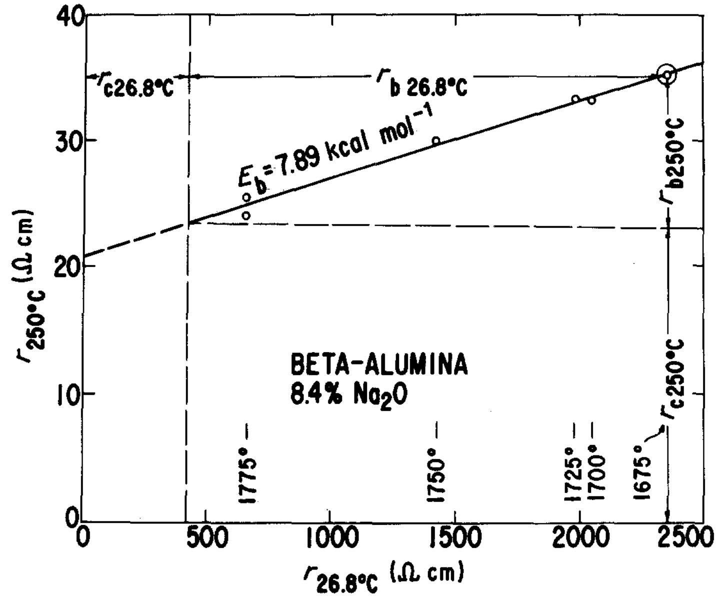

Figure 2 Annotated resistivity distribution plot at 250° C.

r_{bT}. For example, for the specimen whose (r_T, r_{300K}) values are encircled on Fig. 2, $r_{250°C}$ amounts to 35.1 Ω cm, of which the r_c component is 23.3 Ω cm and the r_b component, 11.8 Ω cm. At 26.8° C, r amounts to 2350 Ω cm, of which the r_c component is 418 Ω cm, and the remainder, r_b, 1932 Ω cm.

It is still more useful to display on the same figure resistivity distribution plots for several temperatures, e.g., 400° C, (673.2 K), 350, 300, 250, 200 and 150° C as shown on Fig. 3. E_b values can be calculated from the slope at each temperature. Actually, resistivities are measured near room temperature, 75, 125, 175, 225, 275, 325, 375 and 420° C, and linear interpolations are carried out on $\ln T/r$ against $1/T$ plots to obtain values at the stated temperatures.

It was assumed above that an r_c value for the reference temperature is known. Actually a best value is derived using a minimum variance principle. A trial value for r_{c300K} is assumed and a set of (r_{cT}, T) pairs is derived as described above for other temperatures for which resistivity distribution plots are available. The assumed value of r_{c300K}, along with $T = 300$ K, is also taken as a member of the set of data points. These values are fitted to the equation

$$T/r_c = \sigma_0 \exp(-E_c/RT),$$

or more accurately to its equivalent, the straight line

$$\ln(T/r_c) = I + M(1/T),$$

where $E_c = -RM$ and $\sigma_0 = \exp I$, using a least-square deviation procedure. The variance is computed. It is obtained for different trial values of

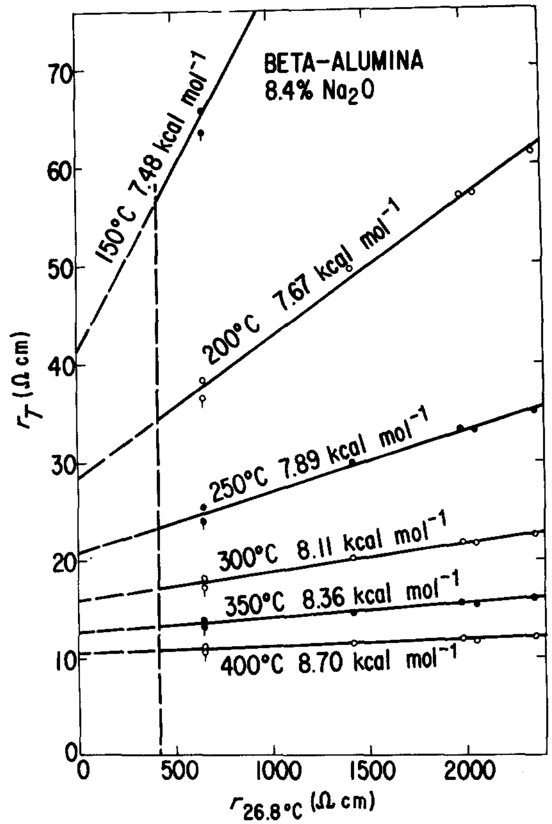

Figure 3 Resistivity distribution plots at various temperatures for β-alumina ceramic containing 8.4% Na$_2$O.

r_{c300K}. The best value of r_{c300K} is taken to be that corresponding to the minimum variance. Using these assumptions, E_c amounts to 4.81 kcal mol^{-1} and σ_0 to 2.29×10^3 K Ω^{-1} cm^{-1} for the ceramic composition under consideration. A value of r_c of 418 Ω cm is obtained for 26.8° C.

Parameter values for a β-alumina ceramic containing 7.2% Na_2O, 1.0% ZrO_2, 0.5% Y_2O_3, and the balance Al_2O_3 determined by this method of analysis agree well with others obtained by the impedance frequency method [7]. In fact, parameter values which are physically reasonable have been obtained this way in everyone of over a dozen different β-alumina compositions studied in this laboratory.

"Physical reasonableness" is a useful notion that can be used to restrict the permissible range of crystal resistivity values. For example, the notion that grain boundary resistivity values should always be positive quantities restricts r_c values to those less than any determined resistivity value at a given temperature for a given composition and crystal structure. Thus on Fig. 2, $r_{c26.8°C}$ must be less than 656 Ω cm, the lowest measured resistivity. Similarly the notion that crystal resistivity values should increase monotonically with decreasing temperature can be used to set a lower bound. Thus inspection of Fig. 3 indicates that crystal resistivity values must be greater than the ordinate values – 10.4 Ω cm at 400° C, 15.8 at 300° C, 28.4 at 200° C, and 41.2 at 150° C. It is assumed on this basis that r_c must be greater than about 75 Ω cm at 26.8° C. The upper and lower limiting r_c values at 26.8° C give rise to a permissible range of r_c values at other temperatures indicated by the unshaded area of the $\ln T/r_c$ against $1/T$ plot shown in Fig. 4. The upper limit for r_c gives rise to a boundary which is shaped slightly concave downward while the lower limit gives a boundary shaped concave upward. A value of 418 Ω cm at 26.8° C yields other r_c values which fall along a straight line with minimum variance.

4. Relaxation of conditions underlying the temperature comparison method

All four conditions or hypotheses on which the temperature comparison method is based have considerable experimental support with many β-alumina compositions. Use of these hypotheses has been very helpful in understanding the apparent complexity of the electrical behaviour of some polycrystalline electrolytes [8]. However, exceptions occur. Further understanding of electrolyte behaviour can be obtained from information about situations under which certain hypotheses do not hold. This information also helps define better the strengths and limitations of this resistivity analysis technique.

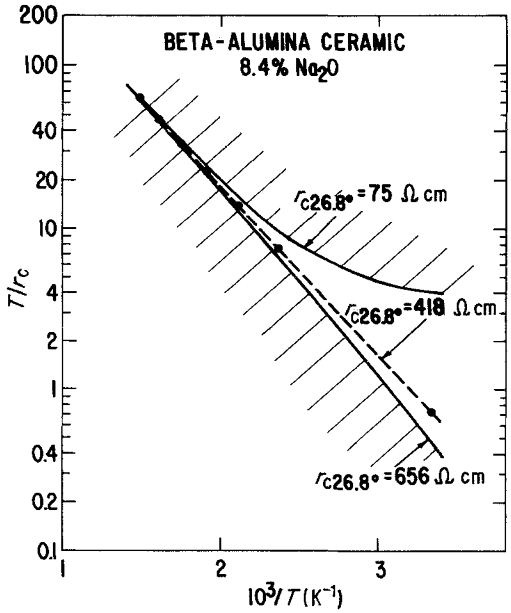

Figure 4 Ln T/r_c against $1/T$ plots showing application of minimum variance principle.

One such situation occurs with ceramics of high β″-alumina content. A good example was found with a ceramic with 9.6% Na_2O containing in addition 0.4% Li_2O and 3.0% MgO as the β″-alumina stabilizer. As shown in Fig. 5, resistivity distribution plots are linear to a good approximation. However, when an attempt was made to fit trial crystal resistivity values to an Arrhenius equation, no minimum variance was noted. The reason is apparent from Fig. 6.

Upper and lower limits on r_c at 26.8° C are estimated to be about 340 and 100 Ω cm, respectively. These are used to generate curves which define the limits of r_c which are physically reasonable at other temperatures. Both the upper and lower limiting curves are shaped concave downward for this ceramic. As a result, there can be no set of r_c values which fall along a straight line on this type of plot. Stated otherwise, the Arrhenius relationship does not describe the temperature variation of r_c. The activation energy is not a constant but varies with temperature. The third condition is not satisfied for this β″-alumina composition, nor for

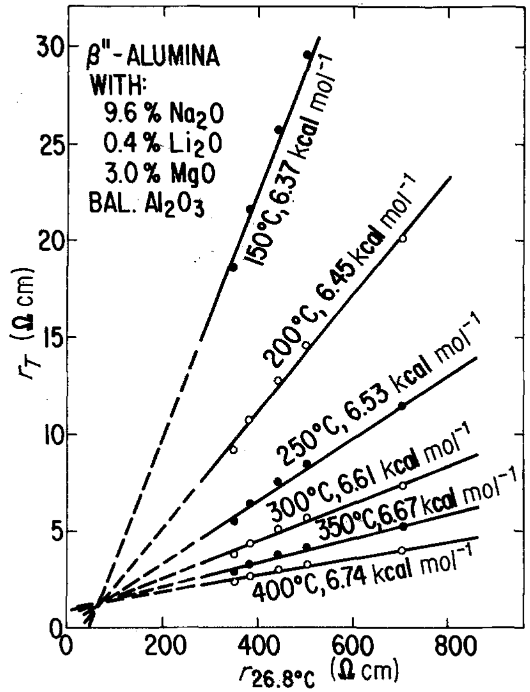

Figure 5 Resistivity distribution plots at various temperatures for mainly β''-alumina ceramic containing 9.6% Na_2O, 0.40% Li_2O, 3.0% MgO, the balance, Al_2O_3.

any other to this author's knowledge, with a β''-alumina content in excess of 90% as determined by X-ray diffraction analysis. The deviation from Arrhenius behaviour for r_C with β''-alumina ceramics is completely in agreement with measurements on β''-alumina single crystals as mentioned above. It contrasts sharply with the behaviour of ordinary β-alumina, both single crystal and polycrystalline ceramic, in which $\ln T/r_c$ varies linearly with $1/T$K to a very good approximation [7, 11].

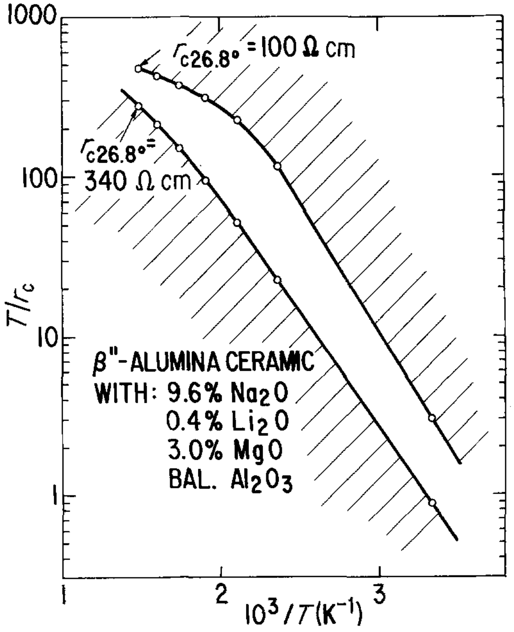

Figure 6 Ln T/r_c against $1/T$ plots indicating departure of crystal resistivity component from Arrhenius behaviour.

This breakdown of the third hypothesis for β''-alumina ceramics imposes limits on our ability to determine r_c. As a consequence of this more complex variation of r_c with temperature, precise values for r_c cannot be obtained by the temperature comparison method although upper and lower bounds can be set.

The fourth condition for full usage of the temperature comparison method, that the grain boundary activation energy not depend on the magnitude of r_b, is crucial to the question of the separability of r_c and r_b, as discussed below. The linearity of a resistivity distribution plot shows that this condition is satisfied. On the other hand, non-linearity does not necessarily indicate breakdown of this condition. The author is aware of only two situations giving rise to non-linear resistivity distribution plots. In each case, a cause other than breakdown of the fourth condition has been identified.

As discussed above in another context, one case occurs with β,β''-alumina ceramics containing relatively low concentrations of β''-alumina phase stabilizers. The ratio of β- to β''-alumina, and thus the crystal resistivity, can vary with the sintering temperature. This case is really a breakdown of the second condition and is detected by X-ray diffraction analysis.

The other case is related to an important mechanism of electrical degradation of both β- and β''-alumina ceramics in sodium–sulphur cells [12]. The parameter r_b can be increased very much in some ceramics by absorption of very small quantities of water at grain boundaries [13, 14]. With some specimens, this ageing process takes place to a significant extent during the course of carrying out measurements in the ambient atmosphere at higher measuring temperatures. Its occurrence is detected by an increase in the 26.8° C resistivity following a series of higher temperature measurements.

5. The separability of r_c and r_b by resistivity analysis

There is another aspect of the parallel multi-element model shown in Fig. 1 that deserves consideration. If the apparent lumped grain boundary

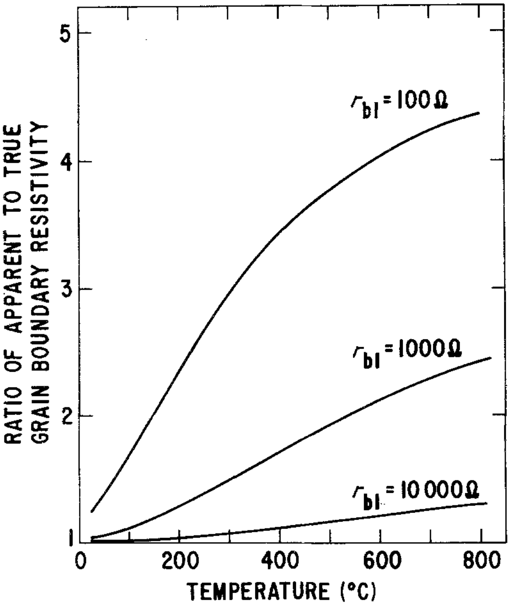

Figure 7 Ratio of apparent lumped grain boundary resistivity to true value for different "specimens" at various temperatures.

resistivity is contaminated by the crystal resistivity, then one might expect the apparent lumped grain boundary activation energy to be contaminated by the crystal activation energy. Consequently, in specimens of the same crystal resistivity but different grain boundary resistivities, the apparent lumped grain boundary activation energy at a given temperature might be expected to vary from specimen to specimen and would approach the true value only when the grain boundary resistivity is much larger than the crystal resistivity.

Consequently, computations were made by this author on a parallel multi-element equivalent circuit model with 100 parallel units using parameter values rather similar to those used previously by DeJonghe. r_c in each parallel unit was taken to be $100\,\Omega$ at 26.8°C and E_c, $4\,\text{kcal}\,\text{mol}^{-1}$. E_b was assumed to be $8\,\text{kcal}\,\text{mol}^{-1}$. In one series of calculations, the sizes of the grain boundary resistors formed a geometric progression with a common ratio of 1.05 at 26.8°C. Various "specimens" were considered which differed in the size of the smallest grain boundary resistor. The results of computations are given in Fig. 7 for three "specimens" at different temperatures in which the smallest resistors were either 100, 1000, or $10\,000\,\Omega$ at 26.8°C. The ratio of the apparent lumped grain boundary resistivity to the true value is larger than one, with deviations greater with "specimens" of smaller grain boundary resistivity, just as reported by DeJonghe. However, as shown in Fig. 8, the corresponding apparent grain boundary activation energies are less than the true value of $8.0\,\text{kcal}\,\text{mol}^{-1}$. These data were computed from the ratio of the apparent grain boundary resistivity at the temperature under consideration to that at 26.8°C in order to make a direct comparison with information from resistivity distribution plots. At any given temperature, the intergranular activation energy varies from specimen to specimen depending on the magnitude of r_b. Deviations from the true value of the activation energy are also greater in those specimens with the smaller grain boundary resistivity. Qualitatively similar conclusions were reached for an array in which the sizes of the grain boundary resistors formed an arithmetic progression.

The variations in the lumped grain boundary activation energies shown on Fig. 8 are much greater on the whole than uncertainties in measured activation energies determined from the slope of resistivity distribution plots. For example, the errors in the measured activation energies shown on Fig. 3, corresponding to one standard deviation in the slope value, amount to 0.8% at 200°C and 2.6% at 400°C. For Fig. 5, they are 1.2% at 200°C and 1.4% at 400°C.

Thus the fourth condition or hypothesis required for effective use of the temperature comparison method is not satisfied for "specimens" whose electrical properties can be described by the parallel multi-element model. They differ substan-

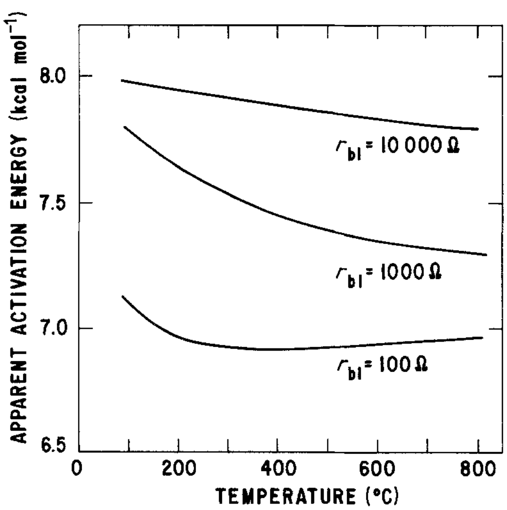

Figure 8 The apparent lumped grain boundary activation energy for different "specimens" at various temperatures.

tially then from real polycrystalline β- or β″-alumina specimens whose behaviour is well described by this hypothesis, as shown by the linearity of resistivity distribution plots. Linear resistivity distribution plots have been observed with dozens of compositions – both β- and β″-alumina. Examples of but two such compositions are given on Figs. 3 and 5. Also, it seems worthwhile to point out that the fourth condition was formulated initially as a generalization of a limited quantity of grain boundary activation energy data obtained by an impedance-frequency analytic method [8]. Since the parallel multi-element model is not a valid representation of current heterogeneities in polycrystalline electrolytes, it appears that the intergranular resistivity does not include substantial contributions from the crystal component. Neither does the inverse kind of contamination, that of the crystal component by the intergranular, seem to occur since the activation energy measured on β-alumina single crystals agrees very well with values for the intragranular component in ceramic of comparable composition [8]. The separation of inter- and intragranular resistivity components by resistivity analysis is clean.

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