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# Impedance studies of the cell Pt/(Na, Sr) β″-alumina/Pt

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The present work confirms that the temperature range in which the conductivity of polycrystalline (Na, Sr) β″-aluminas can be obtained by two- probe or four-probe measurements depends upon the composition. A separate determination of the inter- and intragranular resistance is feasible in a limited temperature range for each of the compositions. The intragranular resistivity of the polycrystalline material is considerably smaller than the total resistivity. The activation energy of the intragranular conductivity is lower than that of the total conductivity and shows an increase with the Sr content. The activation energy of the total conductivity increases strongly with the Sr content and passes through a maximum.

## 1. Introduction

When comparing the specific conductivity of a single crystal of a β″ alumina isomorph with that of the polycrystalline material, containing the same conducting cation, it is usually found that the conductivity of the single crystal [1] is larger. The magnitude of the said difference varies considerably with the system. Several orders of magnitude may be involved in the case [2] of bivalent cations. It can be concluded in a qualitative fashion that the so-called intergranular impedance, also called grain boundary impedance or inter-particle impedance [3], determines fully or partially the measured total impedance of the polycrystalline material. The intergranular impedance may be due to a "constriction resistance", as outlined in the early work [4] on this subject, or to the small area of contact and an associated voidance between the grains or to a transfer hindrance of the ion between particles.

Impedance spectroscopy was mainly used [3–7] in the attempt to divide the measured total impedance into contributions from the interior of the grains (intragranular or crystal impedance) and the grain boundaries. The interpretation of the impedance data was initially based on relatively simple analogue circuits [3–5] yielding in a first approximation the observed frequency dependence for certain systems. More complicated circuits, incorporating also constant phase elements, were chosen subsequently [8,9] for the simulation of the frequency dependence. The values of the parameters in these circuits are obtained by optimization programs with the aid of PCs.

As demonstrated by a comprehensive study [8] of the grain boundary morphology in Na β-alumina by transmission electron microscopy, the ionic flow in the polycrystalline material is not homogeneous. A similar situation exists for β″-aluminas. The ionic current can be assumed to flow through separate channels. Each of the channels starts in a crystallite with suitable orientation on one of the two surfaces which are covered by a metallic contact and ends in a crystal with the right orientation at the other surface. For simplicity the possibility of interconnecting channels is not considered. The impedance of polycrystalline β″-aluminas may be simulated by a three-dimensional array of the one-dimensional network shown in fig. 1. Here CPE denotes a constant phase element describing the interfacial impedance on the left side. $C_g$ is the geometric capacitance parallel to each of the intragranular resistances $R_c$. $C_b$ and $R_b$ denote the capacitance and the resistance of each of the grain boundaries. If the values of the sets of the latter four parameters are appropriate, measurements of the cell impedance at high frequencies will extrapolate to an ohmic value representing a lumped

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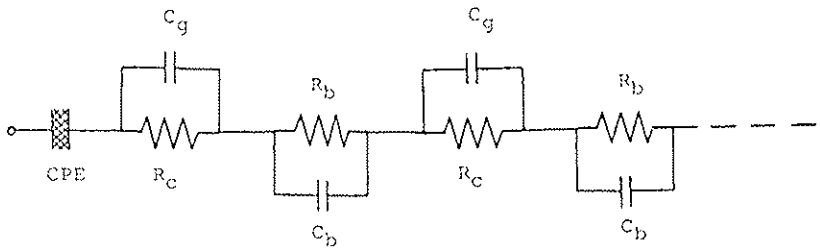


Fig. 1. Analogue network for a single path.

intragranular resistance. The extrapolation need not always be possible as the example of polycrystalline Na β″-alumina shows [10]. The extrapolation at small frequencies, if feasible because of appropriate values of the CPEs in fig. 1, will yield the sum of the lumped intragranular and intergranular resistances. As it is usually done for polycrystalline materials, the word "lumped" is dropped for simplicity in the subsequent text.

Two additional restrictions result from an experimental point of view: The cell impedance can only be determined in a sufficiently large frequency range if it is (a) not very small or (b) not very large. The above restrictions are imposed by the design of the impedance meter and should be kept in mind before selecting a system for studies.

The purpose of the present work was to investigate the possibility of a separation of the bulk impedance into the contributions from the crystal and the grain boundary. Polycrystalline (Na, Sr) β″-aluminas were chosen. This system is free of the restrictions (a) or (b) in certain temperature ranges. In addition it allows to follow in a systematic fashion the changes due to increasing Sr content of the samples. Comparative conductivity measurements by two-probe and four-probe techniques were previously carried out [11] for 10% and 70% exchanged (Na, Sr) β″-alumina. The present study covers the whole composition range of (Na, Sr) β″-alumina in a wider temperature range, and the two-probe measurements are made in a considerably larger frequency range than before [11].

## 2. Experimental

Thin slices (0.1 cm × 0.5 cm × 1 cm) were cut from bars of polycrystalline Na β″-alumina purchased as "Betalyte" from Ceramatec Inc. The samples were converted to (Na, Sr) β″-alumina in the way described previously [12]. This technique yields materials with a homogeneous distribution of $Na^+$ and $Sr^{2+}$. The composition of the exchanged material is known from the equilibrium distribution curve (fig. 2 in ref. [12]). Pt electrodes were sputtered onto two opposite surfaces of the rectangular pieces. The leads to the impedance meter were attached by silver paint to the Pt films.

The impedance of the symmetric cell Pt/(Na, Sr) β″-alumina/Pt was measured from room temperature to 800°C between $10^{-2}$ to $10^7$ Hz. Two automated impedance meters were employed. The IM 5E meter of Zahner-elektrik was used between $10^{-2}$ and $10^4$ Hz. The Hewlett Packard 4192 LF impedance analyzer in conjunction with an XT computer covered the range 5 to $10^7$ Hz. The measurements were made from high to low temperatures and subsequently from low to high temperatures. Such a procedure is necessary since the sputtered Pt film recrystallizes during the initial heat-up.

The arrangement of the cell, of the leads and thermocouples in the furnace is shown in fig. 2. There are separate leads for the ac current and the measurement of the ac voltage across the cell, done at constant temperature. The aluminum oxide tube is flushed by nitrogen. The furnace is heated by dc current to minimize stray signals affecting the impedance measurement. Both the temperature and frequency range can be set by the programme for measurements with the Hewlett Packard instrument. The data are stored on a disc and can be processed by separate AT computers. Plots of the data in the raw or processed form are obtained by printer or plotter. A schematic diagram of the set-up is shown

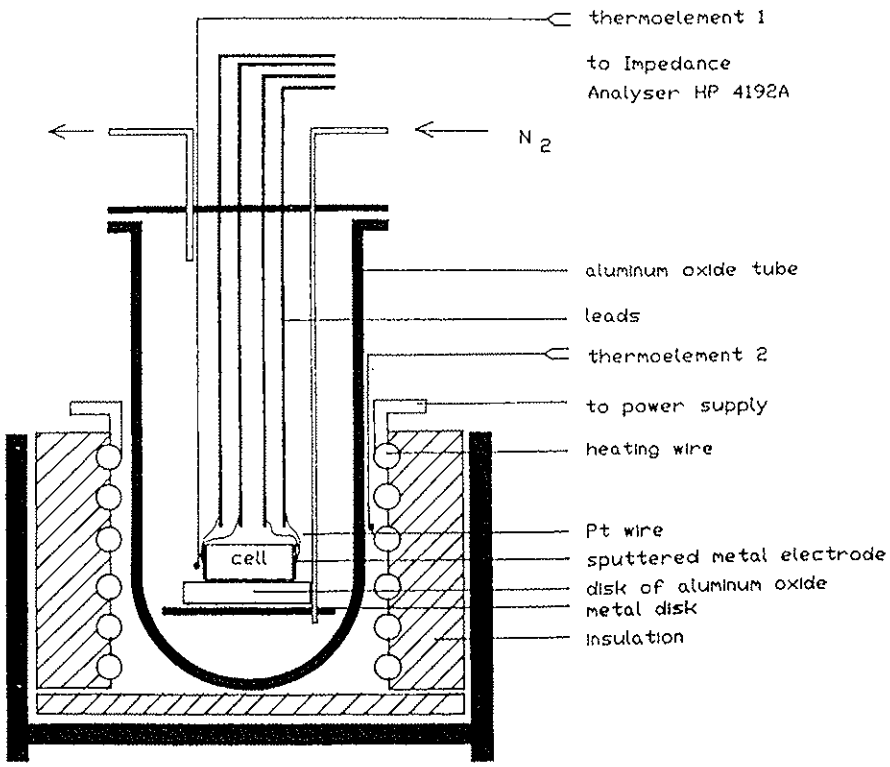


Fig. 2. Schematic diagram of furnace with cell.

in fig. 3. Complete automatization of the measurements with the other impedance meter is difficult because the memory of the PC, incorporated into the instrument, is too small for the programme. At present the temperature has to be set manually. The impedance measurements themselves are automated. Work is in progress to achieve complete automatization by the aid of an additional XT.

## 3. Results

Numerous plots of the negative values of the capacitative component of the impedance versus the ohmic component were obtained for the different compositions and temperatures. The plots look either similar to that in fig. 2 (initial portion of a deformed semicircle) or in fig. 3 (one depressed semicircle followed by a different curve at low frequencies) of ref. [11]. Therefore examples are not shown here.

It was attempted to simulate the frequency dependence of the impedance at constant temperature, using suitable analogue circuits and determining the parameters by the optimization programme FIRDAC [13]. Although a satisfactory approximation of the frequency dependence of the impedance could be frequently achieved, the circuits proved too complicated to distinguish between contributions from the crystal and the grain boundary in an unambiguous way. The previous results with 10 and 70% exchanged material are confirmed and extended to the whole composition range. The simpler approach of a graphical extrapolation was adopted. The extrapolation of the first portion of the impedance plot at high frequencies yielded the value of the intragranular resistance. A few data points at the highest frequencies had to be discarded in the extrapolation procedure sometimes. This was easily recognizable because the impedance plot begins to display a reversal of the previous trend or the points are distinctively separate from the other ones. Finally the extrapolation at the other side of the first depressed

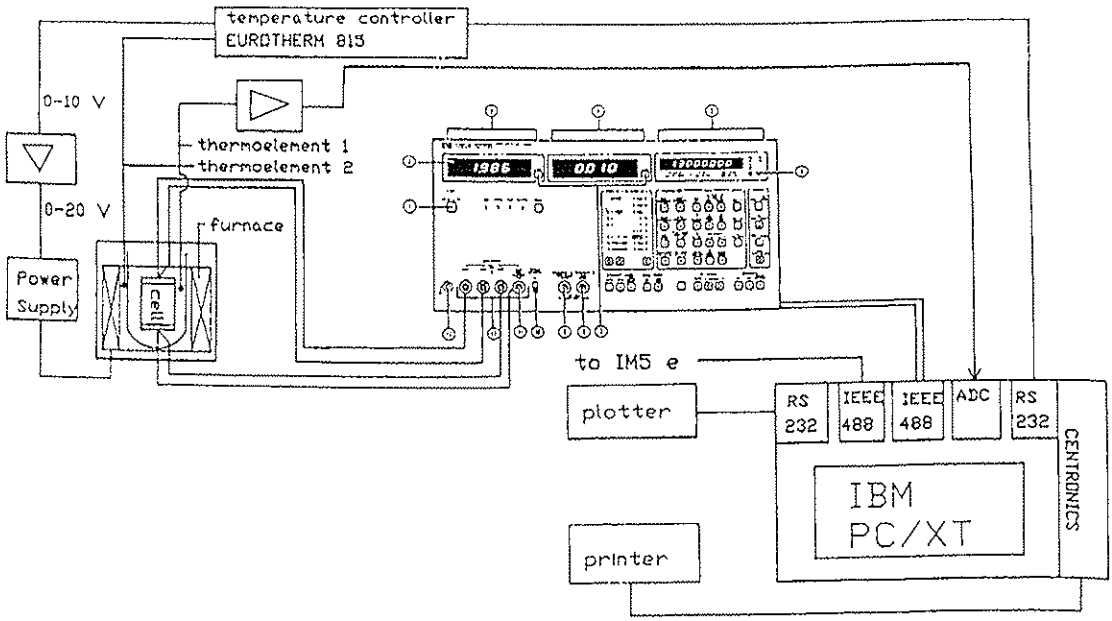


Fig. 3. Schematic diagram of set-up for the automated measurements of the cell impedance at constant temperature.

semicircle at intermediate frequencies yielded the total resistance. If the impedance plot was nearly linear at low frequencies, the linear portion was also extrapolated. Usually the intersection of this linear portion with the abscissa is close to the value extrapolated from the depressed semicircle. It should be pointed out here that the shape of the impedance curves did not always allow the latter extrapolation.

Examples for the results of the described extrapolation procedure are shown for an 11% exchanged sample in fig. 4 and for a 95% exchanged material in fig. 5. The product of conductivity and temperature is plotted in a semilogarithmic scale versus $1000/T$. The data obtained by a four-probe measurement in a set-up, described previously [14], are plotted for comparison. In addition the respective values for a Na single crystal and a Sr single crystal, taken from ref. [15], are given by solid lines in figs. 4 and 5.

The activation energies were determined from the slope of the plots in the linear regions (compare fig. 4 and fig. 5). They are plotted as a function of the extent of exchange in fig. 6.

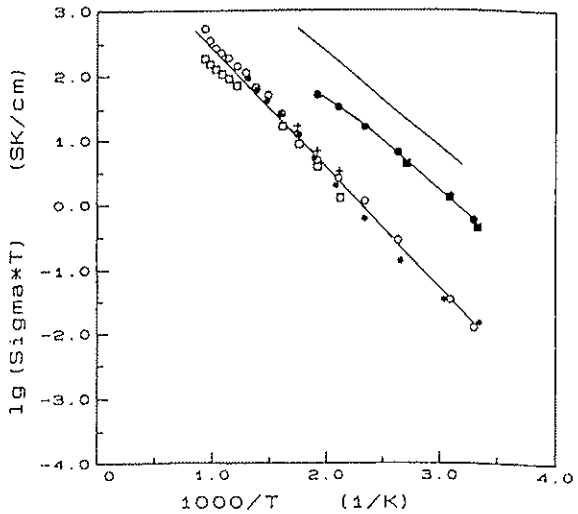


Fig. 4. Plots of total conductivity (*, ○, □, +) and of crystal conductivity (●, ■) as a function of temperature for 11% exchanged specimen. (*) four-probe technique; (○, ●, □, ■) HP 4192; (+) IM 5e.

## 4. Discussion

It has been observed previously that the total con-

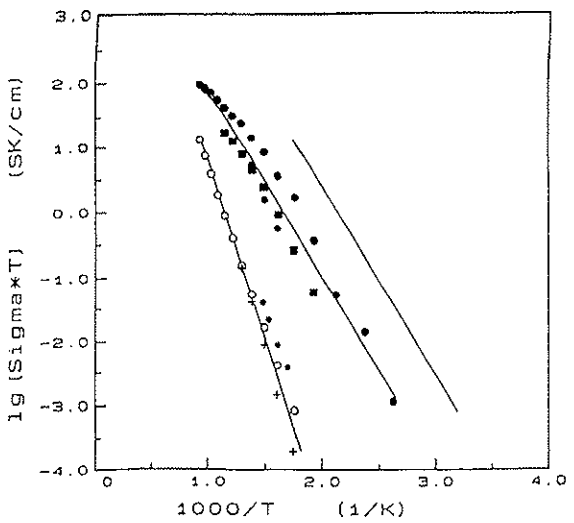


Fig. 5. Plots of total conductivity (•, o, +) and crystal conductivity (●, ■, ⋆) as a function of temperature for 95% exchanged specimen. (+, ⋆) four-probe technique; (o, ●, ■) HP 4192.

ductivity could not be determined over the whole temperature range by the four-probe technique for all the compositions (see fig. 1 in ref. [11]). The two-probe measurements reported here lead to a similar conclusion. The impedance plots do not allow an extrapolation of the total conductivity at low or intermediate frequencies for those compositions in the same temperature range in which the four-probe technique did not work.

The data in fig. 4 and fig. 5 demonstrate that the agreement between the values of the total conductivity from four- and two-probe measurements is satisfactory in the temperature ranges where the measurements overlap. The present measurements extended the temperature range from about 500°C in ref. [11] and to 800°C in ref. [12]. The intragranular conductivities could be determined in certain temperature ranges which did not always coincide with the temperature ranges for the determination of the total conductivity of a material with a given composition.

The curves of the intragranular conductivity lie by about an order of magnitude lower than those for single crystals in fig. 4 and fig. 5. The curve for a single crystal of Na β"-alumina had to be taken since data for a 10% exchanged crystal were not available. In fig. 5 the results for a fully exchanged single crystal are compared with those of 95% exchanged polycrystalline material because it is difficult to obtain a 100% exchange of polycrystalline samples. Thus materials of exactly the same composition in the single and polycrystalline state could no be compared. A difference of the reported crystal conductivities was to be expected alone on the basis of the different

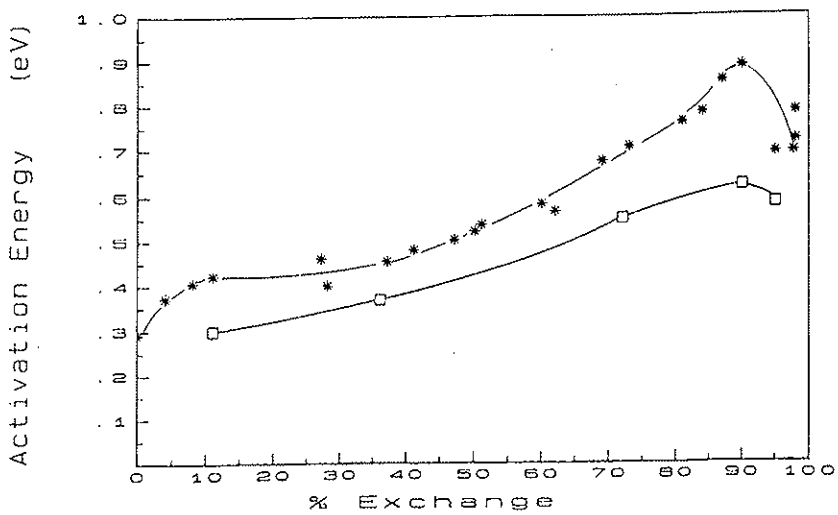


Fig. 6. Plots of activation energies versus extent of exchange: (•) total conductivity; (□) crystal conductivity.

composition. However, there are several other factors which may also be responsible: (c) the crystal conductivity need not be the same in the single and polycrystalline state for β″-alumina isomorphs of the same composition; (d) the polycrystalline material is stabilized by lithia and the single crystals by magnesia. There is not enough experimental information available to make an estimate of the contributions of factors (c) and (d).

The curves of the intragranular conductivity lie considerably above the curves for the total conductivity (see figs. 4 and 5). This statement holds for all the compositions. The grain boundary contribution to the impedance of the solid electrolyte is predominant.

The activation energies were computed from the slope of the linear portions of curves like those in figs. 4 and 5. This procedure is only valid in a restricted temperature range. Considering the whole temperature range of this study, the activation energy is not constant but changes at high temperatures. The said activation energies are plotted as a function of the extent of exchange in fig. 6 for the whole composition range. The activation energy of the crystal conductivity increases with the Sr content and reaches a broad maximum between 70 and 95% exchange. As is expected this curve lies lower than the respective curve for the total conductivity. The two curves display the same trend and are nearly parallel between 10 and 50% exchange. Then they deviate considerably. The effect of increasing $Sr^{2+}$ content on the grain boundary resistance becomes larger than that on the crystal resistance. It is concluded that the behavior of the grain boundary is responsible for the transport involving predominantly $Sr^{2+}$ at exchanges above about 85%.

## 5. Conclusions

The results, reported and discussed in this communication, yield important information on the properties of grain boundaries in polycrystalline (Na, Sr) β″-aluminas. It is understood that the applicability of impedance spectroscopy is limited to systems for which the conditions (a) and (b) of the Introduction are fulfilled. Thus systems with relatively high conductivity like Na and Ag β″-alumina will have to be studied at intermediate and low temperatures because of condition (a). In contrast, systems with relatively low conductivity like polycrystalline isomorphs with bivalent cations need to be investigated at higher temperatures.

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