MICROSTRUCTURE-CONDUCTIVITY RELATIONSHIPS IN SOLID ANISOTROPIC IONICALLY CONDUCTING MATERIALS

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ABSTRACT

In a randomly oriented polycrystalline ionically conducting material the total conductivity is reduced by the lengthening of the effective conduction pathway which is determined by the microstructure. It is, therefore, desirable to develop a better understanding of the relationship between the conductivity and the microstructure of the ceramic material.

This work focused on the quantification of the various contributions to the overall conductivity. Na- β " alumina ceramics with different microstructures but the same chemical composition were used as samples. Conductivity data were obtained by impedance spectroscopy measurements (IS) carried out in a temperature range from 350 to -30 °C at frequencies from 1 Hz to 500 KHz. An attempt has been made to calculate distinct geometric factors for the specific values of the grain and grain boundary contribution. These were inferred from the sample geometry, Laser Scanning Microscope (LSM) pictures, microstructural observations by image analysis, Transmission Electron Microscope (TEM) pictures, and considerations of the current pathways in the anisotropically conducting ceramic.

INTRODUCTION

With the application of complex plane analysis of AC impedance spectroscopy measurements on solid ion conductors, which had been first introduced by Bauerle in 1969 [1] it became possible to separate grain and grain boundary contributions to the total resistivity of a sample. Nevertheless, to compare the resistivities measured for different samples the absolute values obtained from impedance spectroscopy measurements need to be normalized. In the case of the grain contribution this can in a first approximation be done by multiplying the measured values for the grain resistivity by the macroscopic area over length factor given by the sample geometry. For two-dimensional conductors the pathway length for the Na-ion migration is longer than in ceramics with isotropic crystals. A tortuosity factor of 3/2 should be used to correct the measured values as suggested by Armstrong et al. [2].

In the case of the grain boundary contribution a normalization of the measured resistivities is more difficult, since the volume fraction of grain boundaries, and hence, the current pathway length across or along the grain boundaries changes dependent on the microstructure of the ceramic, and may not be simply approximated by the sample geometry.

The aim of this work is the quantification of the grain and grain boundary contributions to the overall conductivity. For this purpose, four ceramics with different microstructures but the same chemical composition were investigated. Laser Scanning Microscope (LSM) pictures of the

samples served as starting pictures for image analysis, which was used to characterize the ceramic microstructures. TEM investigations were performed of the grain boundary zone of the different microstructures. The total resistivity as well as the grain and grain boundary contributions were determined using impedance spectroscopy (IS).

EXPERIMENTAL ASPECTS

Sample preparation

Four samples with different microstructures were used for the investigations. Sample CE0 was a commercially available Na- β alumina with a chemical composition of 90.40 wt% Al_2O_3 , 8.85 wt% Na_2O , and 0.75 wt% Li_2O . The other samples were prepared from a commercially available powder of the same nominal composition which consisted mainly of α - Al_2O_3 and Na-aluminate, as could be confirmed by X-ray diffraction measurements (XRD).

The mean particle size of 0.61 μm has been determined using a laser beam particle sizer Model Galai CIS.

Prior to sintering, all powder samples were predensified by uniaxial pressing at 40 MPa and subsequent isostatic pressing at 200 MPa. The green bodies were then sintered in air. In order to obtain different microstructures, the sintering conditions were varied as follows:

6413:	$\xrightarrow{2^\circ/\text{min}}$	600°C, 1.5h	$\xrightarrow{4^\circ/\text{min}}$	1250°C	$\xrightarrow{15^\circ/\text{min}}$	1620°C, 15min
6428:	$\xrightarrow{2^\circ/\text{min}}$	600°C, 1.5h	$\xrightarrow{4^\circ/\text{min}}$	1250°C	$\xrightarrow{15^\circ/\text{min}}$	1650°C, 15min
6432:	$\xrightarrow{2^\circ/\text{min}}$	600°C, 1.5h	$\xrightarrow{5^\circ/\text{min}}$	1500°C	$\xrightarrow{2^\circ/\text{min}}$	1585°C, 15min

Sample preparation for LSM, IS, and TEM investigations

The samples which were used for the investigations in the Laser Scanning Microscope (LSM) were polished on one side to 1 μm using successive grades of diamond paste. Since Na- β alumina is sensitive to water [3], a lubricant based on ethanol was used. After each polishing step, the samples were thoroughly cleaned in an ultrasonic bath with isopropanol. After polishing, the samples were thermally etched at 1400 °C for 20 minutes. To enhance the reflection of the sample surface in the microscope, a 10 nm thick Au layer was sputtered onto the polished surfaces. LSM investigations were carried out using a ZEISS Laser Scanning Microscope.

Samples used for the impedance spectroscopy measurements were polished in the same way but on two opposite surfaces. After polishing, these samples were dried in an Ar atmosphere at 500 °C for at least 10 hours to remove residual moisture before ion blocking Al electrodes were deposited on the polished surfaces by evaporation in a Leybold evaporation equipment Model L560. Impedance measurements were carried out in the frequency range from 1 Hz to 500 kHz using a Zahner IM5e at temperatures from 350 to -30 °C in a dry Ar atmosphere. The Argon was dried by passing it over P_2O_5 -powder.

The samples used for the TEM investigations were first polished to a final thickness of about 100 nm before they were ion milled for about 10 hours. Using ion milling creates holes in the thin ceramic material. In the neighbourhood of the holes the samples are then thin enough to carry out High Resolution TEM investigations. A Philips TEM Model CM30 was used.

RESULTS AND DISCUSSION

Laser Scanning Microscopy

For microstructure analysis pictures were taken of the samples using the Laser Scanning Microscope in the confocal mode. In order to compare the results of the image analysis the different microstructures had to be photographed at the same magnification. This is difficult to do when grain sizes in the range of $< 1\text{ }\mu\text{m}$ to several $100\text{ }\mu\text{m}$ are present. With the magnification of about 1000 a representative picture of the microstructure could be obtained, in which grains of about $2\text{ }\mu\text{m}$ could still be resolved.

The automated image analysis requires a picture of the microstructure with maximum contrast between the features of interest, which is then converted into a binary picture using the threshold functions supplied by the image analysis software program. Comparisons of SEM and LSM pictures of the ceramic microstructures showed that the latter had a better contrast between grains and grain boundaries.

The microstructures of the four samples are shown in Figure 1. The microstructure of sample CE0 may be described as a duplex structure in which large grains form a network, and small crystals fill the wedges. Compared to the other samples, the content of crystals smaller than $1\text{ }\mu\text{m}$ is significantly higher. In contrast, the other samples do not have a duplex structure but are built up by crystals of a rather broad grain size distribution.

Image analysis

Image analysis programs offer the opportunity to measure certain geometric features which may be used to characterize microstructures such as the grain size distribution, shape factors of crystals, and aspect ratios. In order to be able to use time-saving automated measuring procedures binary pictures of the microstructures in which the grains are white and the grain boundaries are black or vice versa have to be provided. If the contrast in the original greyscale picture is high enough i.e. if there is a definite assignment of certain greylevels to certain features in the microstructure, an easy conversion into a binary picture using threshold functions or so-called watershed algorithms is possible. The threshold functions work in a way that all greyvalues in a given picture which are below a chosen threshold value are set as black, all others as white. Comparisons between LSM and SEM pictures of thermally and chemically etched samples showed that a maximum contrast between grains and grain boundaries could be achieved using LSM pictures of thermally etched samples. Nevertheless, dark structures in the grains, which had about the same greyvalue as most of the grain boundaries, and light parts of the latter made an application of thresholding functions impossible. Therefore, the grain boundaries were traced with a black pencil and the black and white pictures obtained this way were photo scanned into the computer. Crystals smaller than about $1\text{ }\mu\text{m}$ were painted black, and treated as a different phase.

In order to obtain reasonable results from the image analysis a sufficiently large number of grains has to be measured. In this work, ten pictures with together 800 to 1200 grains larger than about $1\text{ }\mu\text{m}$ were taken of each sample.

The most obvious difference between CE0 and the other samples was the large amount of small grains in the microstructure. The determination of the area fraction of black features which includes both, grain boundaries and small grains, gave values of 30% of small grains for CE0 compared to about 15 % for the other samples. This reflects the impression one obtains when first looking at the microstructure. For the calculation of the grain size distribution, the shape

factor and the maximum chord-to-average chord ratio, the small grains shown in black were neglected and only the white grains larger than about 1 μm were examined.

Fig. 1: Polished and etched microstructures of the samples a) CE0, b) 6413, c) 6428, and d) 6432.

The grain size distribution in the four samples is presented in Figure 2. All microstructures show a bimodal distribution with maxima at areas ranging from 1 to 10 μm^2 and 100 to 200 μm^2 . In the CE0 material the percentage of small grains is considerably higher than in all other samples. Sample 6432 which was sintered at the lowest temperature shows less pronounced maxima indicating that a more uniform grain growth has taken place.

In the evaluation of the grain size distribution only the areas of the crystals are considered. To obtain information about the grain shapes, the shape factor and the maximum chord-to-average chord ratio (MaxChord/AvChord) have to be calculated.

The shape factor can be calculated from two measured values. It is defined as

$$\text{shape factor} = 4\pi \cdot \text{area} / \text{perimeter}^2 \quad (1)$$

and gives 1 for spheres. Rectangular grains show decreasing values with increasing length to width ratios. Another parameter which provides information about the grain shape is the maximum chord-to-average chord ratio. The maximum chord length is defined as the maximum straight line which can be drawn in a crystal, and, therefore, gives the maximum elongation of a crystal independent on the orientation of the grain in the ceramic. The average chord can be calculated by deviding the area of the grain by the maximum chord, and give an average width. The ratio MaxChord/AvChord is larger the more elongated the crystals are. The distribution of both factors is given in Figures 3 and 4. Separate diagrams are given for area ranges of 1 to 10, 10 to 100, and exceeding 100 μm^2 .

Fig. 2: Grain size distribution in the four samples. The grains smaller than about 2 μm were treated as a second phase and are neglected in this diagram.

Fig.: 3 Shape factor distribution in the area ranges a) 1-10 μm^2 , b) 10-100 μm^2 , and c) 100-2633 μm^2 .

Fig. 4: Distribution of the maximum chord-to-average chord ratio in the area ranges a) 1-10 μm^2 , b) 10-100 μm^2 , and c) 100-2633 μm^2 .

The CE0 material shows a higher percentage of grains with small shape factors and large MaxChord/AvChord ratios in the area ranges 10-100 and larger than 100 μm^2 . This indicates that there is a higher amount of large and elongated crystals in this sample compared to the others.

In all considerations it was neglected that the crystals in a ceramic are generally not rectangularly shaped. Therefore, the diagrams can only show a trend.

Transmission Electron Microscopy

High Resolution TEM investigations of samples CE0 and 6413 were carried out to examine the grain boundaries of the different microstructures. The results are shown in Figures 5 and 6.

The grain boundaries used for the investigations were chosen in such a way that the a-c-plane of at least one of the two neighbouring crystals was perpendicular to the incident electron beam. In this orientation, a pattern of black and white lines can be observed which can be attributed to the stacking arrangement of the so-called spinel blocks and conduction layers in the Na- β'' alumina structure. A definite attribution of the black and white lines to the two structure elements can not be made, but from the crystal structure it is obvious that the thinner line must be attributed to the conduction layers (white lines in Fig. 6a-c and 7b, and black line in Fig. 7a). Each unit cell of Na- β'' alumina with a lattice constant in c-direction of about 34 Å contains three conduction slabs. As can be seen best in Figure 6a, which has been taken at the highest magnification, the stacking arrangement observed in these TEM pictures indeed repeats after three conduction slabs. The dark spots in every fourth line are at the same position.

The grain boundary structures in samples CE0 and 6413 are rather similar. An amorphous grain boundary phase or disturbed layer could not be observed. The disordered region which can be observed in Figure 6b is due to the fact that the spur of the grain boundary in the depth was not perfectly parallel to the incident electron beam. Imaging of the overlapping crystal lattices of the two neighbouring differently oriented crystals results in a apparently disturbed layer.

Both samples show a variety of different orientations of neighbouring grains. In most cases, angles between the conduction slabs of two neighbouring crystals ranging from nearly zero (see Fig. 6b) to 70 or 80° (see Fig. 5a and b) are observed. In all these cases, an easy hopping of Na-ions from one grain into the other can be expected. Nevertheless, due to the random orientation of the grains in the ceramic, a certain percentage of grains is oriented in such a way that the conduction layers of the two neighbouring crystals are perpendicular to each other (see Fig. 5c). These grain boundaries will be blocking for the Na-ion migration.

In sample CE0 it is important to note that no difference between grain boundaries between two large grains and grain boundaries between two small grains could be seen (see Figs. 5a-c and 5d, respectively).

Fig. 5: Grain boundaries in sample CE0 a)- c) between two large grains, and d) between two small grains

Fig. 6: Grain boundaries in sample 6413.

AC Impedance Spectroscopy

The behaviour of a polycrystalline ionically conducting ceramic in the AC-field measured with blocking electrodes is often described [4] using the equivalent circuit shown in Figure 7.

Fig. 7: Equivalent circuit used to describe the impedance behaviour of polycrystalline ion conductors measured with blocking electrodes.

The resulting ideal complex impedance spectrum shown in Figure 8 consists of two semicircles at high and medium frequencies which are due to the grain and grain boundary contributions to the total resistivity. Moreover, at the low frequencies a 90° spur is expected for the response of the electrode/electrolyte interface [5]. The total resistivity $R_{\text{tot}} = R_1 + R_2$ can be determined by extrapolation of the low frequency line to the real axis. Either the high frequency intercept of the first, or the low frequency intercept of the second semicircle with the real axis can be used to determine R_1 .

Fig. 8: Ideal impedance spectrum of a ceramic ion conductor measured with ion blocking electrodes.

Figure 9 shows the impedance spectra of the four samples at 30 °C.

Fig. 9: Impedance spectra of the samples a) CE0, b) 6413, c) 6428, and d) 6432 at 30 °C. The graphical extrapolation of the semicircles to the real axis is given by the dashed lines.

As can be seen, the spectra of all samples show part of a semicircle at the highest measured frequencies, and a nearly 90° spur at low frequencies. The graphical extrapolation of the semicircle to the real axis is given by the dashed lines. All samples but CE0 give intercepts at positive Z' -values, indicating that a second semicircle at higher frequencies exists which can not be resolved because of the limited frequency range. The graphical extrapolation of the semicircle in the spectrum of sample CE0 does not give a clear intercept at a positive Z' -value. This could either indicate that the grain semicircle is rather small compared to the grain boundary semicircle and therefore can not be resolved or that one semicircle indeed passes the origin and actually consists of two overlapping arcs. In this case, the relaxation times for the grain and grain boundary conductivity, and hence the specific resistivities and dielectric constants for both

contributions have to be very similar. To find out which case may apply, first the total resistivities measured for the four samples have to be compared. They were derived by graphical extrapolation of the low frequency line to the real axis. Fig. 10 shows the Arrhenius plot of the total conductivities. For the calculation of the specific conductivities the geometric factor of the samples A/l was used.

In all diagrams a change in the activation energy over the temperature range investigated can be observed. While both the high and low temperature activation energies of samples 6213, 6428, and 6432 are rather similar sample CE0 shows a higher activation energy at low temperatures. Moreover, the temperature at which the change in E_a is observed is lower for sample CE0. Comparing the total conductivities measured for the samples, CE0 with the highest amount of small crystals shows the highest conductivity over the entire temperature range. This is in contrast to the idea that the low conductivity values of polycrystalline Na- β " alumina compared to single crystals are to a large extent due to the contribution of the less conductive grain boundaries [7]. In this case, the finest grained ceramic or the one with the largest amount of small crystals should exhibit the highest total resistivity as has been shown by VIRKAR et al.[8].

Fig. 10: Arrhenius plot of the total conductivities of the samples a) CE0, b) 6413, c) 6428, and d) 6432. The activation energies are given in eV.

To determine the exact grain and grain boundary contributions, an equivalent circuit somewhat different from the one shown in Figure 8 was used to fit the measured data using a software supplied by Zahner. Constant Phase Elements (CPE) instead of simple capacities were used for the fitting procedures since all semicircles were slightly depressed. To describe the electrode/electrolyte interface behaviour more appropriately a double layer resistivity was added in parallel to the double layer capacitance.

The starting values of R_1 , R_2 , CPE_1 , R_{dl} and C_{dl} were derived from the measured spectra. CPE_{geo} was calculated using $\epsilon=30$ as had been suggested by Hunter [9]. It turned out that the impedance spectra of samples 6413, 6428, and 6432 could be fitted well using the modified

equivalent circuit. The results obtained for sample 6413, for which a series of low temperature data were available, are exemplified in Figure 11.

Fig. 11 Arrhenius plot for the grain and grain boundary contribution to the total conductivity in the temperature range 70 to -30 °C.

As can be seen from Figure 11, the activation energies for the grain and grain boundary contribution are similar in the temperature range from 50 to -30 °C. This indicates that the conduction mechanisms for grain and grain boundary conduction are similar. Considering the grain boundaries this appears to be reasonable. For sample CE0 the data obtained from fitting were too inaccurate to obtain reasonable results.

CONCLUSIONS

Based on comparisons of the results from microscopic investigations and conductivity measurements of samples CE0 and 6413 which have the same chemical composition but different microstructures, a model for the Na-ion conduction in both ceramics is proposed:

AC impedance spectroscopy measurements of both samples yield distinct differences in the impedance spectra. While for sample 6413 two semicircles could be resolved at low temperatures, indicating that there are two contributions to the total resistivity, only one semicircle was observed for sample CE0.

High Resolution TEM investigations were carried out to see whether this difference in the impedance spectra could be explained by different grain boundary structures. It could be shown that both samples have similar grain boundaries with neighbouring grains interconnected without any evidence of an amorphous film or trapped impurities in between. A variety of different orientations of neighbouring grains is observed in both samples. In most of the cases the orientation of the conduction slabs is such that an easy hopping of Na-ions from one grain into the other can be assumed. The specific resistivity for the migration across such a grain boundary will be similar to the specific resistivity for the migration in grains and substantial polarization effects are not likely to occur. Therefore, a resolution of distinct grain and grain boundary semicircles will be impossible provided that all grains are suitably orientated.

In every non-textured Na-β" alumina ceramic, however, a certain percentage of grains will be orientated in such a way that the conduction slabs of two neighbouring grains are perpendicular to each other. These boundaries will be blocking for the Na-ion migration and a transport along grain boundaries to the next suitably orientated crystal will be necessary. The specific resistivity for this process will be different from that of the grain conduction, and polarization effects are probable to occur giving rise to an additional grain boundary capacitance. A resolution of two semicircles should, therefore, be possible.

The phenomena described so far, hold true for both samples. Therefore, the differences in the impedance spectra have to be due to the different microstructures.

Sample CEO shows a duplex structure in which large grains form a network and small grains fill the wedges. In contrast, the microstructure of sample 6413 is built up by crystals with a rather broad grain size distribution. The most obvious difference, however, is the much higher content of grains smaller than about 1 μm in sample CEO, which makes up about 30 % of the total area compared to about 15 % in sample 6413.

Considering the pathways for Na-ions in both microstructures, distinct differences can be found. In sample 6413, it is very likely that the Na-ions will - after passing a number of suitably oriented grains - meet a blocking grain boundary where an easy hopping into the next crystal is not possible. Since the grains are fairly large migration along grain boundaries over a rather long distance has to occur. This will then give rise to the second semicircle which is found in the impedance spectrum of sample 6413.

A different situation occurs in sample CEO. Na-ions which approach a blocking grain boundary between two large grains may easily find smaller grains in the neighbourhood having orientations, which allow the easy hopping across the grain boundary. Since there is a large amount of small crystals, the probability to find one with a suitable orientation is very high. Therefore, a migration along grain boundaries will not be necessary in this kind of microstructure. Polarization effects are then of minor importance and a resolution of a distinct grain boundary contribution in the impedance spectrum will not be observed.

Provided, that the grain boundaries are free of amorphous phases or trapped impurities, an easy hopping of Na-ions from one grain into the other across the grain boundaries can take place if the grains are suitably oriented. Since hopping of Na-ions across grain boundaries adds a very minor contribution to the total resistivity, compared to migration of Na-ions along grain boundaries, fine grained ceramics with a high probability for non-blocking orientations of neighbouring crystals are likely to show better specific conductivities than coarse grained ceramics. In addition, fine grained ceramics can also provide improved mechanical properties.

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