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## Observations on the Na- $\beta''$ -alumina/metal interface by impedance spectroscopy and scanning electron microscopy $\star$

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### Abstract

The quality of the electrode/electrolyte interface is important if impedance spectroscopy is used to separate the contributions of bulk and grain boundary regions to the electrical response of polycrystalline ionically conducting ceramics. This work focused on a number of parameters related to the sample preparation prior to impedance spectroscopy measurements. To evaluate the influence of the surface roughness samples with different surface roughnesses have been created by polishing them with successive grades of diamond paste down to 1, 6, or 15  $\mu\text{m}$ . Next, samples of all three surface roughnesses were coated with Pt and Au by sputtering and with Al by evaporation. Two samples polished down to 1  $\mu\text{m}$  were coated with Au by evaporation and Cr/Au by sputtering, respectively. The metal layers served as blocking electrodes in impedance spectroscopy measurements, which were carried out in a temperature range from 30 to 300°C and a frequency range from 1 Hz to 500 kHz. The results were discussed in terms of the various equivalent circuit elements inferred from complex impedance plots. SEM investigations were carried out to characterize optically the ceramic/electrode interface prior to and after measurement.

### 1. Introduction

The ideal complex impedance spectrum for Na- $\beta$ -alumina single crystals with ionically blocking electrodes is reported to consist of a semicircle at high frequencies which is related to the bulk conductivity, and a 90° spur at low frequencies derived from the double layer region of the electrode/electrolyte interface [1]. The high frequency semicircle goes through the origin, and the lower frequency intercept with the real axis gives the value for the bulk resistivity, which may also be determined by extrapolation of the 90°

spur to the real axis. Measured complex impedance spectra of single crystal material show close agreement with the theoretical value of 90° for the low frequency spur as reported by Armstrong et al. [2].

The ideal complex impedance spectrum for both polycrystalline Na- $\beta$ - and Na- $\beta''$ -alumina shows an additional semicircle at intermediate frequencies which is related to the grain boundary regions of the material [3].

Measured spectra of polycrystalline material often show deviations from this behaviour.

The frequency at which the maximum of the bulk semicircle appears may be calculated from  $\tau = 1/R_b C_{geo}$ , with  $R_b$  being the bulk resistivity and  $C_{geo}$  the geometric capacitance [4]. As the temperature in-

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creases,  $R_b$  decreases while  $C_{geo}$  is rather temperature independent. This results in a shift of the frequency spectrum to the right with the first semicircle being out of the frequency range [5]. At higher temperatures ( $> 100^\circ\text{C}$  for the material used in the investigations discussed here) also the medium semicircle which is related to the grain boundaries disappears. Good estimations of the total resistivity may nevertheless be given by extrapolation of the vertical line to the real axis.

Deviations from the ideal behaviour also occur at low frequencies, where a deviation of the vertical line from  $90^\circ$  or a curvature is observed. This is reported to be partly due to surface roughness of the polycrystalline samples [6] and the influence of moisture. Water is in a first step adsorbed on the electrolyte surface thus leading to a distortion in the capacity line. The much slower process of hydronium ion diffusion into the crystal lattice results in ion exchange processes and an increase in the resistivity [7].

To evaluate the influence of the quality of the electrode/electrolyte interface on the measured impedance spectroscopy data, samples with different surface roughnesses coated with different metals used as the blocking electrode were investigated. To evaluate the influence of moisture, measurements were carried out in both dry and humid atmosphere. An optical characterization of the interface was carried out with Scanning Electron Microscopy (SEM).

## 2. Experimental

The Na- $\beta''$ -alumina samples used in the present study were supplied by Ceramtec Inc. with a nominal composition of 8.85 wt%  $\text{Na}_2\text{O}$ , 0.75 wt%  $\text{Li}_2\text{O}$  and 90.40 wt%  $\text{Al}_2\text{O}_3$ . The Na-ion resistivity was given to be  $5.0 \Omega \text{ cm}$  at  $300^\circ\text{C}$ .

Samples with two different types of geometries were cut from the Na- $\beta''$ -alumina bars. Type I geometry with dimensions  $0.5 \times 1.0 \times 0.1 \text{ cm}^3$  was polished on the  $0.5 \times 1.0 \text{ cm}^2$  surfaces and served for the SEM investigations. Type II geometry with dimensions  $0.5 \times 0.5 \times 1 \text{ cm}^3$  was used for impedance measurements. These samples were polished on both  $0.5 \times 0.5 \text{ cm}^2$  surfaces.

To evaluate the influence of the surface roughness samples with different surface roughnesses were pre-

pared by polishing the corresponding surfaces with 15, 6, and  $1 \mu\text{m}$  diamond paste. After polishing, the samples were thoroughly cleaned in an ultrasonic bath with isopropanol, and dried in an argon atmosphere at  $500^\circ\text{C}$  for at least 10 h.

Next, samples of all surface roughnesses were coated with various metals, which are commonly used as blocking electrodes in impedance experiments [5,8]. Al and Au were deposited by evaporation in a Leybold evaporation equipment Model L560, while Pt, Au, and Cr/Au were sputtered using a Balzers sputtering device Model SCD 050.

Impedance measurements were carried out over a frequency range from 1 Hz to 500 kHz using a Zahner IM5E at temperatures from 30 to  $300^\circ\text{C}$  in both dry and wet argon atmosphere. Argon was dried by passing it over  $\text{P}_2\text{O}_5$ -powder. Wet argon atmosphere of a constant humidity of 70% was maintained by passing the argon through a saturated  $\text{CuSO}_4$  solution.

Simulations of the measurements were carried out using the Zahner fitting program which uses the complex nonlinear least squares fitting method (CNLS).

An optical characterization of the metal layer prior to and after measurement was carried out using a Philips scanning electron microscope model XL 40.

## 3. Results and discussion

### 3.1. SEM

Prior to SEM investigations the samples were mechanically fractured in order to investigate the Na- $\beta''$ -alumina/metal interface.

In Fig. 1 a laser scanning microscope picture of the microstructure of the Ceramtec material used for these investigations is shown.

Figs. 2–4 show SEM-pictures of the 1, 6, and  $15 \mu\text{m}$  polished surfaces coated with Au and Pt by sputtering, and with Al and Au by evaporation.

One feature common to all investigated metal layers is, that the surface morphology of the samples is perfectly copied by the metal layers. The best agreement between the macroscopic area to length factor measured from the sample's geometry and the real Al factor given by the microscopic structure of the ceramic surface seems to be achieved by a  $1 \mu\text{m}$  polish.

The microstructures of the sputtered and the evap-



Fig. 1. Microstructure of the Na-β'-alumina used in the investigations. The sample was polished to 1 μm and thermally etched.

orated blocking electrodes show distinct differences. While the evaporated Al and Au layers show a dense microstructure, the sputtered Au and Pt layers exhibit a columnar microstructure.

Heat treatments caused by temperature excursions up to 300°C during the impedance measurements caused changes in the structures of the sputtered Au and Pt layers, which both exhibit recrystallization phenomena as can be seen in Fig. 5.

The sputtered gold layer indicates interdiffusion of species from the columnar crystallites to the grain boundaries which are still visible but much less pronounced than after sputtering. The coating appears more uniform than before temperature excursions up to 300°C.

In the case of sputtered platinum a transport from the grain boundaries to the columnar crystallites seems to have occurred, which resulted in the formation of crystalline islands separated by deep channels throughout the entire layer thickness.

### 3.2. Impedance measurements

#### 3.2.1. Measurements in a dry atmosphere

From the ideal complex impedance spectrum for polycrystalline Na-β'-alumina described before a vertical line at low frequencies which is related to the

electrode/electrolyte interface would be expected over the whole low frequency range. Deviations from the ideal behaviour resulting in a deviation of the spur from 90° are reported to be due to surface roughness of the ceramic surface [6].

The results of this work indicate that there is little influence of the surface roughness on the shape of the complex impedance spectra, but significant differences are caused by the various metals and the deposition techniques.

Fig. 6 shows the complex impedance spectra for 1 μm polished samples coated with the various metals in the scale used for the evaluation of the total resistivity.

As can be seen a 90° spur could only be found for the Al coated samples. Significant deflections of 9 to 11° for the sputtered Au, Pt, and Cr/Au electrodes were observed. Differences in the values for the total resistivities ( $R_b + R_{pb}$ ) of the samples are due to small differences in the measuring temperatures as well as in the sample geometries. The normalized values show a good agreement.

Increasing the scale of the complex impedance plots into the kΩ scale showed that in no case a simple vertical line as expected from the electrode/electrolyte interface could be observed over the whole low frequency range. Samples sputtered with Au and Pt showed a further semicircle in addition to the more or less resolved first semicircle at high frequencies which upon extrapolation to the real axis gives the value for the total resistivity ( $R_b + R_{pb}$ ) of the sample. The additional semicircle is then again overlapped by a straight but not vertical line at the lowest measured frequencies as can be seen from Fig. 7.

Samples with evaporated Al electrodes exhibited a nearly straight line at low temperatures which curved into semicircle at higher temperatures as can be seen from Fig. 8. An increasing deviation of the spur from 90° with decreasing temperature as reported by Lilley et al. [5] could not be observed.

The additional semicircle in the case of sputtered Pt and Au electrodes as well as the curvature of the low frequency line in the case of evaporated Al electrodes is probably due to the formation of a highly resistive surface layer caused by a reaction of the sample and the electrode material. More detailed investigations of that surface layer will be the subject of an additional paper.

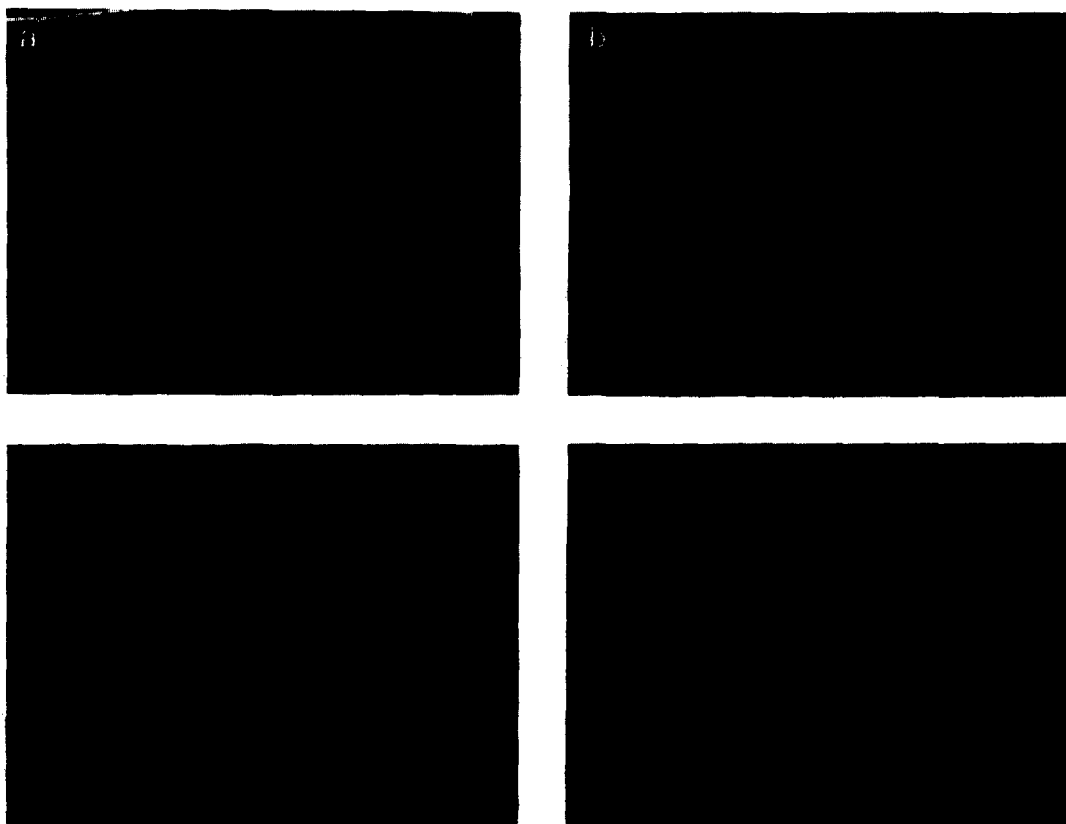


Fig. 2. Na- $\beta''$ -alumina polished to 1  $\mu\text{m}$  grade diamond paste and coated with (a) Al(ev), (b) Au(ev), (c) Pt(sp), and (d) Au(sp).

Figs. 9 and 10 describe the influence of surface roughness on the shape of the complex impedance spectra. In the case of the samples with evaporated aluminium electrodes there is little influence of the surface roughness on the complex impedance spectra (Fig. 9).

Au and Pt deposited by sputtering show no consistent trend in the curvature of the spur as can be seen from Fig. 10.

### 3.2.2. Influence of water vapour

It is well known that  $\beta$ - and  $\beta''$ -alumina are sensitive to moisture. Armstrong et al. [7] reported that two different effects which have different influences on the measured complex impedance spectra are conceivable.

The first effect, which rapidly occurs after exposure to moisture, is the physical adsorption of water on the electrolyte surface. This leads to the formation

of a water film between electrode and electrolyte, which influences the low frequency part of the complex impedance spectrum. In addition to the straight line at low frequencies, which is related to the double layer capacity, a semicircle at higher frequencies is observed which is caused by the water film [8].

The second effect starts with the fast penetration of water into micropores and cleavage planes of the ceramic. In a following step,  $\text{H}_3\text{O}^+$  ions in the water exchange against  $\text{Na}^+$  ions in the crystal lattice. This ion exchange proceeds with concurrent formation of NaOH. The influence of water on grain and grain boundary conductivities has been studied by Will [9]. He found that the slow diffusion of hydronium ions into the crystal lattice increases the grain boundary resistivity by more than an order of magnitude, while the bulk resistivity raises about 20%.

Water uptake in  $\beta$ - and  $\beta''$ -alumina has been investigated by different authors using various techniques.

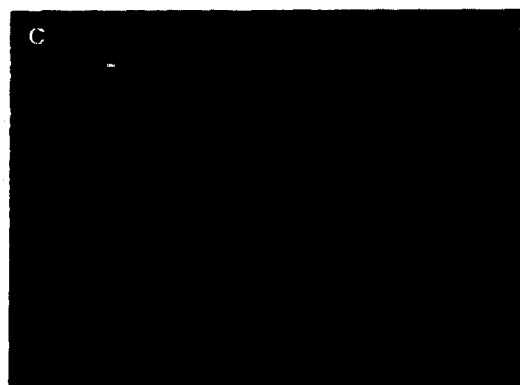


Fig. 3. Na- $\beta''$ -alumina polished to 6  $\mu\text{m}$  grade diamond paste and coated with (a) Al(ev), (b) Pt(sp), and (c) Au(sp).

Intercalation of water into the conduction planes is indicated by IR spectra [10], NMR studies [11–13], and lattice parameter measurements with X-ray diffraction techniques [14].

Surface layers several micrometers in depth, in

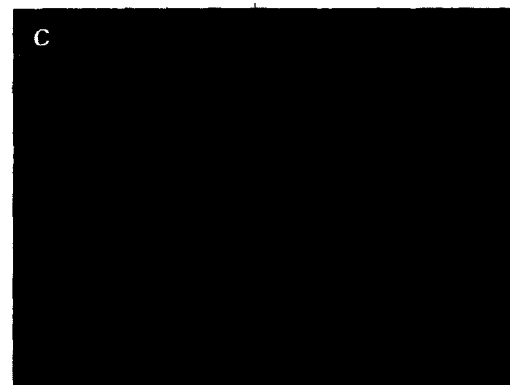


Fig. 4. Na- $\beta''$ -alumina polished to 15  $\mu\text{m}$  grade diamond paste and coated with (a) Al(ev), (b) Pt(sp), and (c) Au(sp).

which the  $c$ -axis expands, have been found to form after exposure of samples to moisture. Heavens [15] reported that this lattice expansion is the result of ion exchange between  $\text{Na}^+$  and  $\text{H}_3\text{O}^+$  following the reaction:

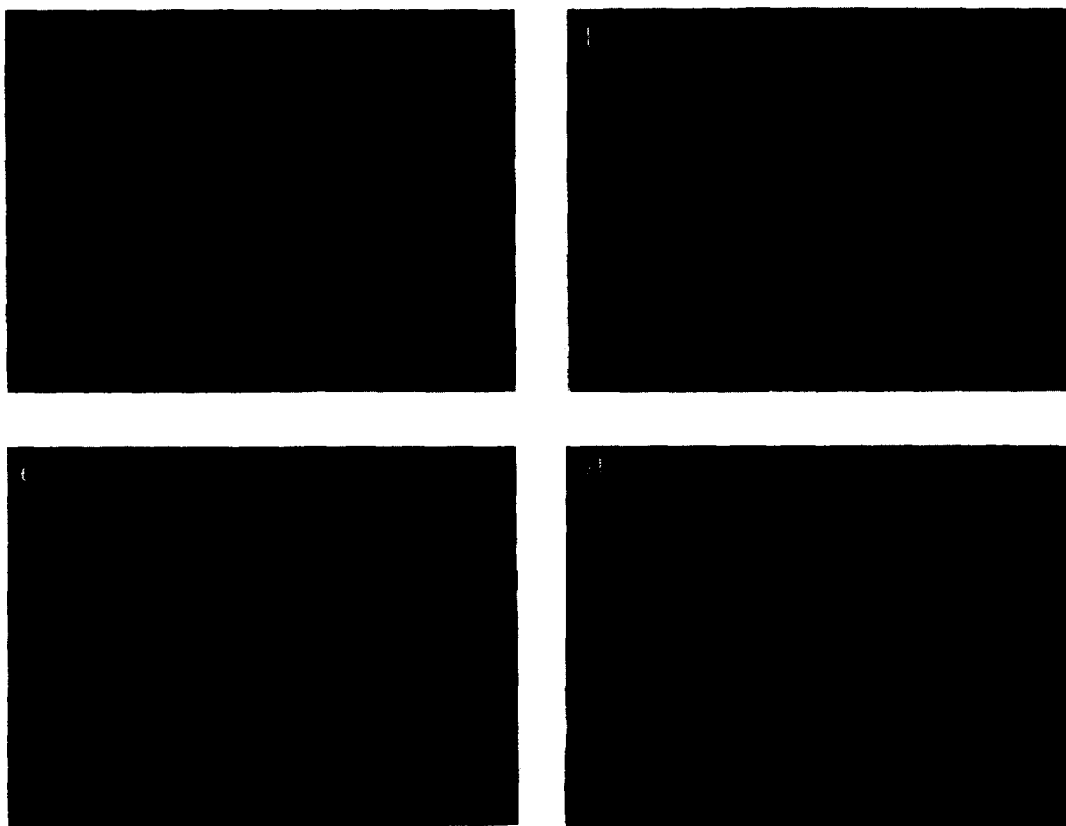


Fig. 5. Na- $\beta''$ -alumina polished to 1  $\mu\text{m}$  grade diamond paste and coated with (a) Al(ev), (b) Au(ev), (c) Pt(sp), and (d) Au(sp) after several temperature excursions in the 30 to 300°C range during impedance measurements.



Dunn [16] reported that the existence of such layers increases the room temperature resistivities of both  $\beta$ - and  $\beta''$ -alumina. Heating the samples up to 600°C reversibly restores the original resistivities.

Measurements of a sample with evaporated Al electrodes under a constant humidity of  $70 \pm 5\%$  showed significant changes in the low frequency part of the spectrum during the exposure to moisture. The slightly inclined low frequency line, which could be observed under dry conditions (see Fig. 11 (+)) and which was related to a surface layer, bent over. An additional semicircle at medium frequencies could be partly resolved. It is important to note that the high frequency intercept of the first semicircle with the real axis gives the value for the total resistivity ( $R_g + R_{gb}$ ) of the sample. The intercept of the second semicircle,

although in the same order of magnitude, is a moisture phenomenon and not related to the grain boundary resistivity of the sample. At the lowest measured frequencies a straight but not vertical line completed the spectrum as can be seen from Fig. 11.

A similar behaviour has been reported by Hunter et al. [17] during impedance measurements of single crystal Na- $\beta$ -alumina. They believe that the nearly vertical line which they observed under dry conditions at low frequencies must be regarded as the high frequency end of a large semicircle arising from a highly resistive surface layer. Exposure to moisture induces a large reduction in the resistivity of that layer.

This is in contrast to Armstrong et al. [1,2] who reported deviations from the vertical line at low frequencies to be due to the electrode/electrolyte interface.

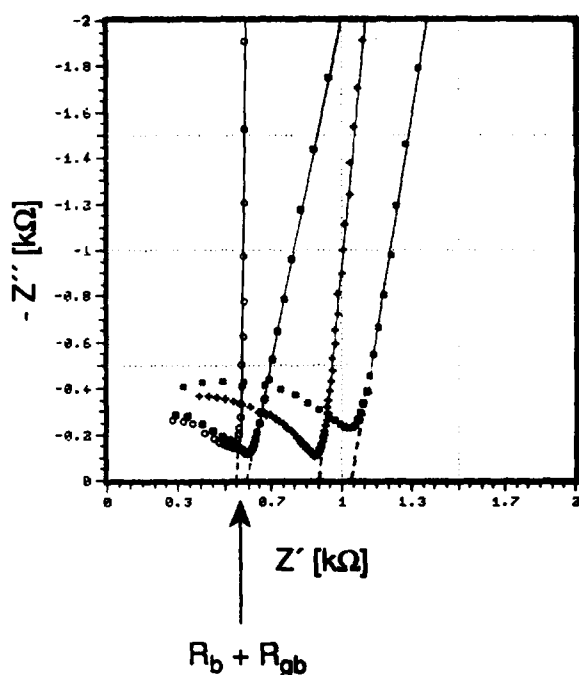


Fig. 6. Comparison of the complex impedance plots of four Na- $\beta'$ -alumina samples polished to 1  $\mu\text{m}$  with Al(ev) ( $\circ$ ), Pt(sp) ( $\bullet$ ), Au(sp) ( $\bullet$ ), and Cr/Au(sp) ( $+$ ) contacts at 50°C.

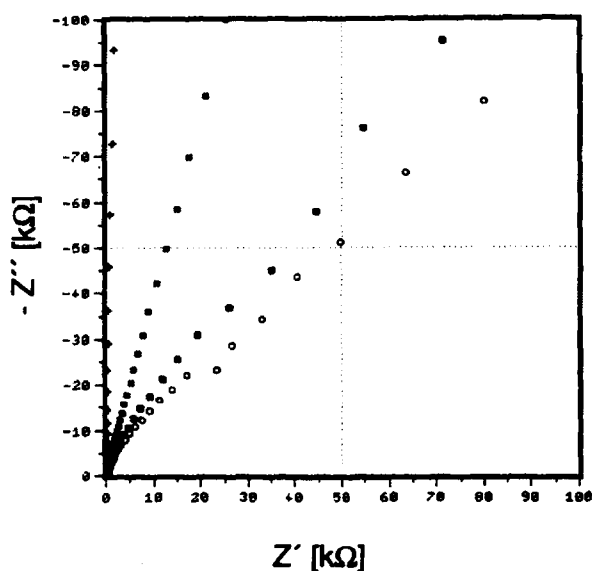


Fig. 7. Comparison of the complex impedance plots of Na- $\beta'$ -alumina polished to 1  $\mu\text{m}$  with Al(eV) ( $+$ ), Pt(sp) ( $\bullet$ ), Au(sp) ( $\circ$ ), and Cr/Au(sp) ( $\bullet$ ) contacts at 100°C.

Comparing the spectra of the sample with evaporated Al electrodes under controlled moisture with measurements carried out with a sample with sputtered Pt electrodes in moist laboratory atmosphere showed similarities. The sample was first heated up to 300°C, and measured with decreasing temperature in a dry Ar atmosphere. Fig. 12 shows the complex impedance spectrum measured at 63°C ( $+$ ).

As can be seen a small part of the high frequency semicircle, which is related to the  $\beta'$ -alumina sample is resolved, followed by a large semicircle at lower frequencies assumed to be caused by a surface layer. Switching off the Ar during the night resulted in a bending of the curved line (Fig. 12 ( $\circ$ )) similar to what had been observed for the Al evaporated sample after exposure to humidity of 70% for more than 20 h. This may result from the fact that the sputtered layers due to their columnar microstructure facilitate moisture uptake so that even short times of exposure of the samples to laboratory atmosphere are sufficient to cause changes in the resistivity of the surface layer.

After measurements in a moist atmosphere, the sample with the evaporated Al electrodes was baked out at 300°C in a dry Ar atmosphere. Measurements were made during the bake out procedure to see whether the moisture uptake was reversible. As can be seen from Fig. 13 the radius of the semicircle at medium frequencies increases with time but does not reach the original shape measured with an as received sample during the time of investigation. This is in agreement with the results of Dunn [16] who reported that heating out the samples at temperatures as high as 600°C was necessary to restore the original resistivity.

### 3.3. Equivalent circuits

#### 3.3.1. Dry conditions

The 1  $\mu\text{m}$  grade polished samples were taken for the simulation of the measured impedance data. From the results which were found by impedance measurements the following equivalent circuit has been chosen to describe the samples' behaviour.

The equivalent circuit was used to simulate the measured impedance data of all samples. Constant phase elements (CPE) instead of simple capacitances were used to take the depression of the semi-

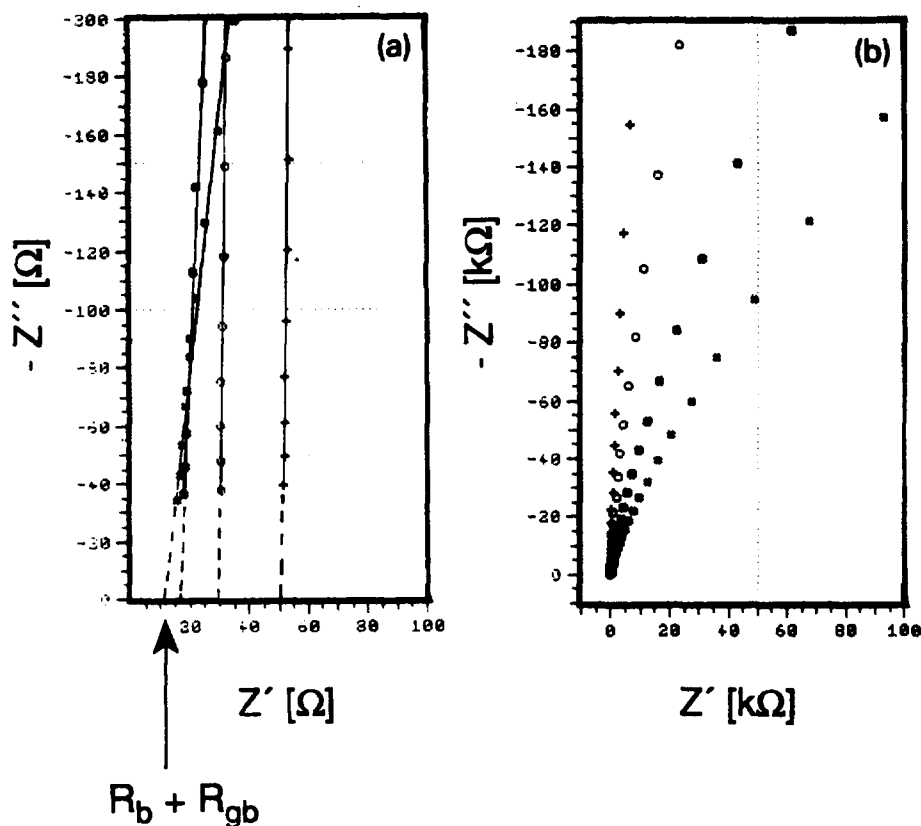
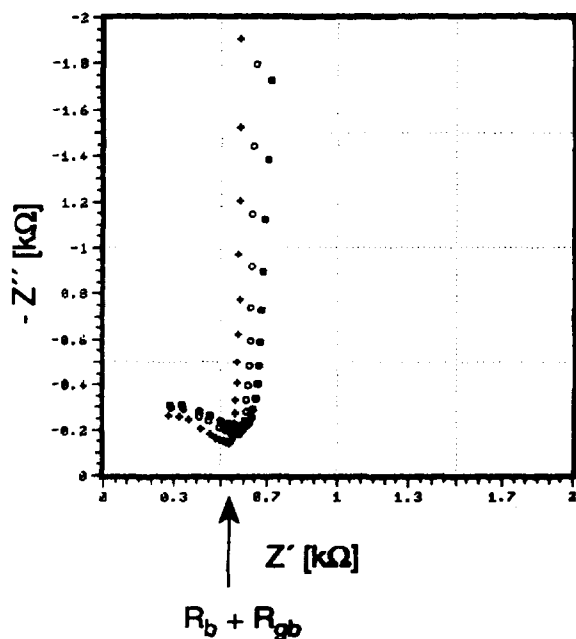


Fig. 8. Influence of temperature on the angle of the spur in the complex impedance plot of Na- $\beta$ -alumina coated with aluminium by evaporation. (a) Scale used for the evaluation, (b)  $k\Omega$  scale 155°C (+), 200°C (O), 250°C (\*), 300°C (#).



circles as well as the deviation of the double layer capacitance line from  $90^\circ$  into account. A depressed semicircle is observed if the relaxation time of the process is not single-valued but distributed continuously or discretely around a mean value. Such distributions of relaxation times are due to inhomogeneities of the material. In the case of the electrode/electrolyte interface the surface of the sample is inherently rough on a microscopic scale. The contributions of different places of the interface to the total current received as a response to an applied voltage are different. This results in a distribution of relaxation times which may be described using constant phase elements [18].

In the equivalent circuit shown in Fig. 14  $R_{el}$  and

◀ Fig. 9. Influence of the surface roughness on the complex impedance behaviour of Na- $\beta$ -alumina polished to 1  $\mu m$  (+), 6  $\mu m$  (O), and 15  $\mu m$  (\*) and coated with aluminium by evaporation. Temperature is 50°C.



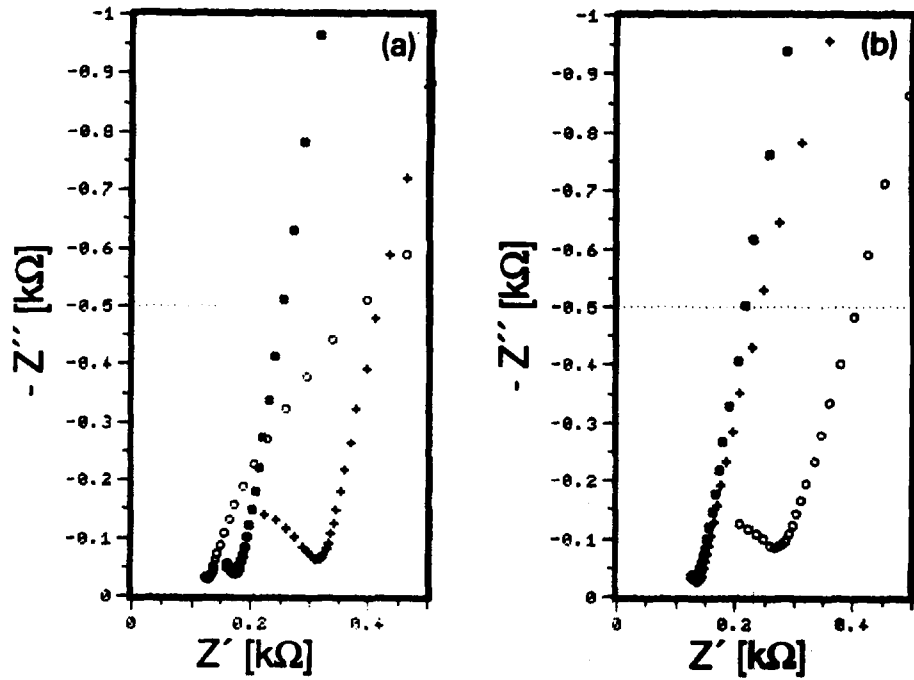


Fig. 10. Influence of the surface roughness on the complex impedance behaviour of Na- $\beta$ '-alumina polished to 1  $\mu\text{m}$  (+), 6  $\mu\text{m}$  (○), and 15  $\mu\text{m}$  (\*) and coated with (a) platinum by sputtering, (b) gold by sputtering. Temperature is 100°C. Differences in the total resistivities ( $R_b + R_{gb}$ ) are due to slight differences in the measuring temperature and the samples' geometry.

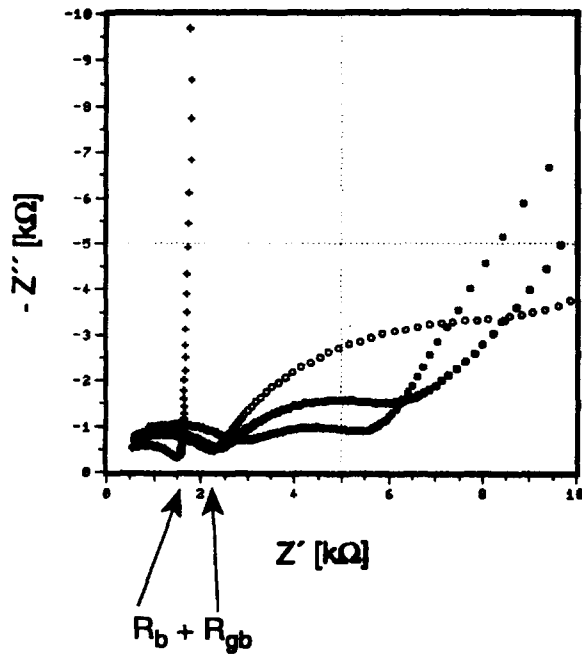


Fig. 11. Change of the complex impedance plot of a sample with Al(ev) electrodes after 22 (○), 28 (\*), and 55 (#) hours of exposure to 70% humidity. A measurement of the sample in dry atmosphere is shown for comparison (+). The total resistivities may not directly be compared, because the temperature slightly varied between the measurements.

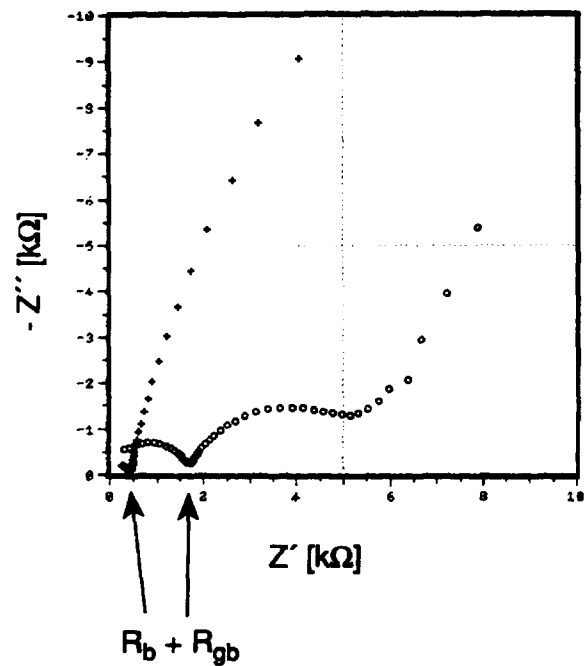


Fig. 12. Complex impedance plot of a sample with sputtered Pt electrodes exposed to laboratory atmosphere. (+): Spectrum of the sample measured in a dry Ar atmosphere at 63°C. (○): Spectrum after exposure to laboratory atmosphere over night at 27°C.

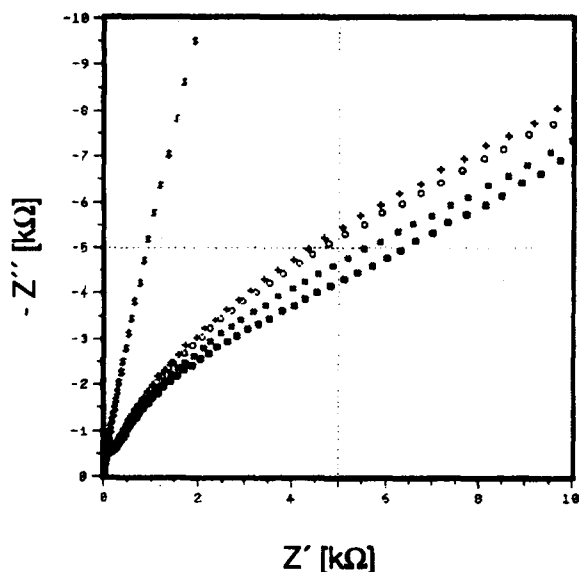


Fig. 13. Wet sample after heating to 300°C for 1 hour (\*), 5 hours (#), 29 hours (O), and 50 hours (+). Also a measurement on the dry sample before exposure to moisture is shown for comparison (\$).

$CPE_{dl}$  describe the behaviour of the highly resistive surface layer which was observed for all metals used as a blocking electrode. In addition a constant phase element (CPE) was added which is attributed to the straight, but not vertical line which could be observed in the  $k\Omega$  scale plot of the samples with sputtered Pt and Au electrodes. This line is probably due to the double layer capacitance. In the case of evaporated Al electrodes this capacitance could not be observed in the frequency range of investigation, but it is obvious that it should be visible at lower frequencies.

The starting values of  $R_b$ ,  $R_{gb}$ ,  $C_{gb}$ ,  $R_{sl}$ , and  $CPE_{dl}$

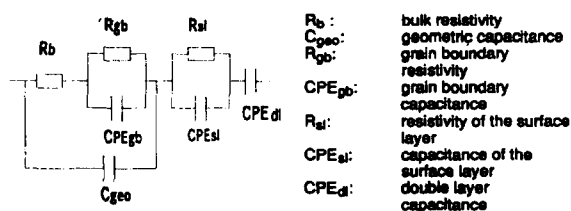


Fig. 14. Equivalent circuit used to simulate the measured data.

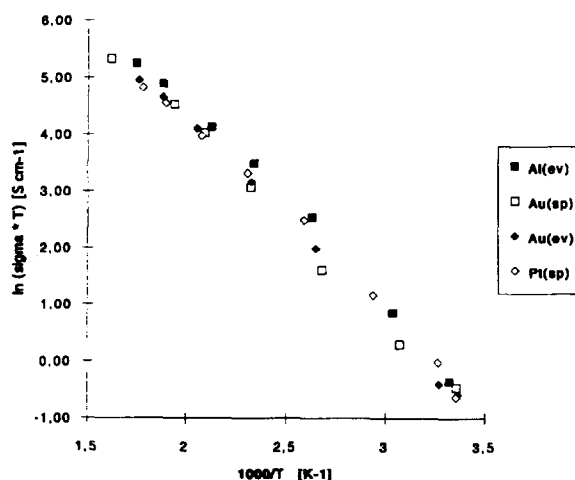


Fig. 15. Arrhenius plot of the total ionic conductivity.

for the simulation were estimated from the measured impedance plots.  $C_{geo}$  was calculated using  $\epsilon_{Na-\beta''-alumina} = 30$  as suggested by Hunter et al. [9].

The total resistivity ( $R_b + R_{gb}$ ) shows Arrhenius behaviour (Fig. 15) with an activation energy of 0.31 eV. As grain and grain boundary resistivities could not even be clearly separated at the lowest measured temperatures a calculation of the activation energies for each was omitted.

### 3.3.2. Moist atmosphere

To simulate the measured impedance data of the measurements in a moist atmosphere of the sample with evaporated Al electrodes the equivalent circuit described in Fig. 14 was used. Values for the various equivalent circuit elements are given in Table 1.

The values for the resistivities may not directly be compared because of slight differences in the measuring temperature.

## 4. Conclusions

Sample preparation plays an important role in impedance spectroscopy measurements.

The optical characterization of the electrode/electrolyte interface carried out with the SEM showed that

Table 1

Equivalent circuit elements for simulations of measurements in moist atmosphere. All resistivities in  $\Omega$ , capacities in F.

	$R_b$	$R_{gb}$	$R_{al}$	$C_{geo}$	$CPE_{gb}$		$CPE_{al}$		$CPE_{dl}$	
					$k$	$\alpha$	$k$	$\alpha$	$k$	$\alpha$
dry	30	1603	$1.1 \times 10^7$	$2.6 \times 10^{-12}$	$9.3 \times 10^{-10}$	0.893	$6.2 \times 10^{-8}$	0.937	$1.9 \times 10^{-6}$	0.916
after 22 h	189	1775	139600	$7.1 \times 10^{-12}$	$7.7 \times 10^{-10}$	0.895	$7.8 \times 10^{-8}$	0.579	$3.7 \times 10^{-6}$	0.822
after 28 h	259	1993	4077	$9.3 \times 10^{-13}$	$9.6 \times 10^{-10}$	0.872	$8.1 \times 10^{-8}$	0.701	$8.7 \times 10^{-7}$	0.621

all metals used as a blocking electrode perfectly copy the surface of the sample. Differences between layers made by the two deposition techniques were that sputtered Au and Pt both showed a columnar growth, while evaporated Al and Au formed closed layers. Sputtered Au and Pt layers also changed their structures after temperature excursions during impedance measurements, while the evaporated Au and Al layers remained unaffected.

Impedance measurements showed that there is little influence of the surface roughness between 1 and 15  $\mu\text{m}$  on the complex impedance spectra. The choice of the metal used as a blocking electrode, however, plays an important role. The highest reproducibility in the determination of the total resistivity could be achieved using evaporated aluminium electrodes on 1  $\mu\text{m}$  polished surfaces. In this case a simple extrapolation of the nearly 90° spur is sufficiently accurate.

Exposure of a sample with evaporated Al electrodes to moisture caused significant changes in the complex impedance spectra. The only slightly curved low frequency line which could be observed under dry conditions bent over and an additional semicircle at medium frequencies could be resolved. A similar behaviour could be observed during measurements on a sample with sputtered Pt electrodes after exposure to laboratory atmosphere over night. This indicates that the deep channels which formed in the sputtered platinum layers after temperature excursions facilitate moisture uptake.

Thorough baking out procedures of the samples, and a careful storing in a dry atmosphere prior to measurement are, therefore, recommended.

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