Ionic conductivity and activation energy for oxygen ion transport in superlattices — The multilayer system CSZ (ZrO₂+CaO)/Al₂O₃

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Abstract

In multilayer systems consisting of an ionic conductor and an electric insulator the ionic current can flow both across the bulk phase and along the heterophase boundaries. Here we report the results of a study on CSZ (ZrO₂+8.7 mol.% CaO)/Al₂O₃ multilayer systems, representing a system with incoherent interfaces as shown by HRTEM (high resolution transmission electron microscopy). In order to separate the interface contribution of the total conductivity from the bulk contribution, the thickness of the CSZ and Al₂O₃ layers have been varied systematically, and the oxygen ion conductivity was measured parallel to the interfaces as a function of temperature. The total conductivity of the CSZ increases by two orders of magnitude when the thickness of the individual CSZ layers is decreased from 0.78 μm to 40 nm. It depends linearly on the reciprocal thickness of the individual layers, i.e. on the number of CSZ/Al₂O₃ interfaces, indicating a parallel connection between individual conduction paths in the bulk and the interfacial regions. The activation energy for the ionic conductivity measured in the temperature range between 350 and 700 °C decreases from about 146 kJ mol⁻¹ to 104 kJ mol⁻¹ by reducing the CSZ layer thickness. The activation energy for the interfacial transport is evaluated as 70 kJ mol⁻¹, suggesting a much higher ionic mobility in the disordered core regions of incoherent interfaces than in the bulk.

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1. Introduction

Layered, multilayered or composite oxide ceramics are often key elements of solid state electrochemical devices, e.g. sensors made from semiconducting oxides, capacitors (high-k-materi- als) or solid oxide fuel cells. As a consequence of the increasing miniaturisation of these devices, interfaces gain more influence on the device properties. The transport in interfaces is usually faster compared to the bulk (higher transport or diffusion coefficient), and it turned out that by using functional ceramics at elevated temperatures, interfacial transport can lead to premature degradation or failures in devices by unexpected ionic conduction or solid state reactions. Improved transport properties of interfacial regions are utilised in so-called “artificial ionic conductors”, prepared by heterogeneous doping of an ionic conductor with an insulator, e.g. in LiI/Al₂O₃ as one of the prototype materials [1]. In recent years this heterogeneous doping was intensively studied because of the great interest in the increase of ionic conductivity at low temperatures [2–10].

Driven by the results on the heterogeneous doping effect in solid dispersions with their irregular microstructure, the need for thin films and multilayers as two-dimensional systems with a well-defined geometry grew on one hand [11–16]. In addition, detailed models for percolation phenomenon in disperse materials have been developed [17,18]. Parallel to this development Maier and his coworkers extended the space-charge concept as one of the possible origins of a higher conductivity along interfaces to the study of nano- and meso-scaled materials, suggesting non-trivial size-effects for systems being confined to lengths in the order of the Debye length [19,20].

The starting point of our experimental study was the lack of experimental data for microstructurally and geometrically well
defined oxide model systems. Despite the enormous interest in the properties of stable nanoscale ionic conductors, only few experimental investigations had been published and still to date the number of references is small. Kosacki [21,22] studied single zirconia and ceria films on magnesia substrates, finding significant interface contributions to the ionic conductivity of the films. However, as these studies always employ open films, the analysis is hampered by the fact that two different interfaces (one solid/solid and one solid/gas interface) contribute. Azad et al. studied ceria/zirconia multilayer systems on alumina substrates, i.e. multilayer systems composed of two ionic conductors [23]. He also reports on an increase of the total ionic conductivity with an increasing number of interfaces, but does not specify the origin of this effect. He assumes that lattice strain and extended defects due to lattice mismatch between the two adjacent phases might be responsible.

As part of a more systematic study of the influence of different types of interfaces on the ionic conduction in spatially confined solid electrolytes, we present here the results of experiments on incoherent interfaces in CSZ/alumina multilayers. The results of experiments on a semicoherent interface are subject of a forthcoming paper.

2. Formal considerations

It is well known that the physical and chemical properties of condensed matter differ at surfaces or interfaces significantly from the volume phase. Heterophase interfaces like surfaces and phase boundaries or homophase interfaces like grain boundaries exhibit often a much higher diffusivity for atomic transport than the volume phase. In the case of ionic materials this may lead to a higher conductivity with decreasing grain size. In general, this increase in conductivity for interfacial regions can be based on two effects: Firstly, the existence of a region with a more defective lattice structure caused by the structural mismatch between two different phases or strong misorientation between two grains of the same phase can be responsible. Secondly, the formation of a space charge region with an increased concentration of mobile point defects may play a role.

2.1. Structural effects

An inner interface between different phases of different crystallographic orientations of the same phase (grain boundary) is often a region with a lower packing density and increased lattice strain. As illustrated in Fig. 1b in such a region two lattices with diverse spacings of the lattice planes and different symmetries merge. Depending on the degree of the mismatch this leads to coherent, semicoherent or completely incoherent interfaces:

a) In the case of a coherent interface the ionic mobility can only be affected by the residual lattice strain in the interface region. This will change the activation energy for atomic jumps in the strained region and thus the interfacial ionic conductivity.

b) In semicoherent interfaces a network of mismatch dislocations exists. These can act as fast diffusion paths because of the lower packing density and the strain field in and around the dislocation core. The effect on the ionic migration should be more pronounced compared to coherent interfaces.

c) In completely incoherent interfaces often structurally highly disturbed or even partially amorphous interface regions can be found. In such regions with significant lower packing density and different atomic interaction compared to the bulk also a significant lowering of the activation energies for the atomic transport is expected. Thus, the effect of a continuous structurally disturbed interface region might result in an even more increased ionic conductivity compared to the cases of a coherent or semicoherent interface.

The strain caused by the lattice mismatch in the interface region may also lead to the stabilisation of another polymorphic phase of the ionic conductor. This may also cause a modified interfacial conductivity [5,6].

All of these structural effects should dominate at interfaces between materials with incommensurate lattice parameters, completely different lattice symmetries and rather short Debye lengths, i.e. materials with a high concentration of mobile point defects (extrinsic point defects, highly doped materials). In this case, space charge effects as described in the next paragraphs can be completely neglected. As an opposing effect the segregation of dopands or impurities at the interfaces may cause a blocking effect.

2.2. Effects of a space charge region

Mobile point defects in an ionic solid can be adsorbed at inner and outer interfaces. This is accompanied by the build up of a space charge region in the interfacial region to accommodate the counter charge. According to the point defect
equilibria of the material, the concentration of opposite charged mobile point defects is increased in the space charge region, e.g. for a oxygen ion conductor with a Frenkel equilibrium for the anionic sublattice has to be taken into account:

$$\text{O}^n_\text{O} + \text{V}^k_i = \text{O}^+ + \text{V}^-_\text{O}$$

If we assume the segregation of oxygen interstitials $\text{O}^{n}_\text{O}$ at the phase boundary, a positive space charge region with an increased concentration of oxygen vacancies $\text{V}_\text{O}$ will be formed as depicted in Fig. 1b.

The boundary region with a significantly higher ionic conductivity compared to the undisturbed volume phase has an extension in the order of the Debye length $\lambda_D$ [15,19,20].

$$\lambda_D = \sqrt{\frac{e^2 kT}{2N_A e^2 I}} \quad \text{with} \quad I = \frac{1}{2} \sum_i z_i^2 c_i$$

Here $I$ denotes the ionic strength with $z_i$ as the number of the excess charge carriers and $c_i$ as their molar concentrations.

However, this picture is only applicable to systems with low defect concentrations, small surface charges and small space charge potentials. For large space charge potentials and significant space charges, the linearised Poisson–Boltzmann equation does not apply. Solving the Poisson–Boltzmann equation for large space charge potentials, one finds that the space charge region is much narrower than estimated by $\lambda_D$ in Eq. (1).

Thus, space charge effects will be pronounced only in materials with a large Debye length $\lambda_D$, i.e. in materials with low concentrations $c_i$ of mobile point defects (only intrinsic point defects). For highly doped systems like yttria stabilised zirconia, YSZ (ZrO$_2$ + Y$_2$O$_3$) or calcia stabilised zirconia, CSZ (ZrO$_2$ + CaO), the system of our present investigation, bulk concentrations of dopand ions and oxygen vacancies are very high [24]. This results in a diminutive Debye length ($\lambda_D \approx 1 \text{ Å}$) and implies negligible space charges.

In order to observe a true space charge effect, one has to prepare multilayers of preferably undoped ionic conductors with low intrinsic defect concentrations. As these undoped ionic conductors show much higher resistivities than conventional ion-conducting ceramics, this requires high-ohmic measurements and may lead to experimental problems at low temperatures.

2.3. Conduction paths in a layered composite

To derive a simple formal expression for the ionic conductivity of multilayers, we consider a system consisting of $n+1$ insulating layers and $n$ conducting layers. The total thickness of each conducting layer is $d$, the length is denoted as $l$ (parallel to the current) and the width as $b$ (perpendicular to the current). We consider two independent conduction paths in the system, a) the volume regions, each with a thickness $d = 2\delta$ and b) the interfacial regions at each conductor/insulator boundary with a thickness $\delta$. We obtain for the total square sectional area of the individual paths:

$$A_{\text{vol}} = n(d-2\delta)b$$

Here $A_{\text{vol}}$ and $A_{\text{int}}$ represent the total cross sectional areas of the volume phase and the interface region ($A_{\text{tot}} = A_{\text{vol}} + A_{\text{int}}$), respectively. The parallel connection of all conduction paths across the system yields the total current:

$$I = \frac{(\sigma_{\text{vol}} A_{\text{vol}} + \sigma_{\text{int}} A_{\text{int}}) U}{T}$$

Thus the total conductivity $\sigma_{\text{tot}}$ of the solid electrolyte phase can be equated as:

$$\sigma_{\text{tot}} = \frac{1}{A_{\text{tot}}} \frac{I}{U}$$

$$\sigma_{\text{tot}} = \sigma_{\text{vol}} + 2\delta(\sigma_{\text{int}}-\sigma_{\text{vol}}) \frac{1}{d}$$

$\sigma_{\text{vol}}$ and $\sigma_{\text{int}}$ are the partial conductivities of the volume and the interfacial regions of the solid electrolyte phase, and $U$ is the voltage drop across the sample. The volume of the insulator is not taken into account, thus the total conductivity $\sigma_{\text{tot}}$, including the non-conducting volume of the insulating layers, is always lower than $\sigma_{\text{tot}}$, i.e. $\sigma_{\text{int}} < \sigma_{\text{tot}}$.

A plot of the total conductivity $\sigma_{\text{tot}}$ of the solid electrolyte component of the multilayer system versus the reciprocal thickness of the conducting layers yields a linear relation with the slope $2\delta(\sigma_{\text{int}}-\sigma_{\text{vol}})$. The intercept with the $\sigma_{\text{tot}}$ axis is identical to the conductivity of the volume phase $\sigma_{\text{vol}}$ (see Fig. 2, interval $0 \leq 1/d \leq 1/2\delta$). If the conductivity of the interfacial regions is much higher than of the volume phase ($\sigma_{\text{int}} \gg \sigma_{\text{vol}}$), the product of the interfacial conductivity and its thickness $\delta \sigma_{\text{int}}$ can be evaluated directly from the slope ($\sigma_{\text{tot}} \approx \sigma_{\text{vol}} + 2\delta \sigma_{\text{int}}/d$).

Eq. (5) is only valid for $d \geq 2\delta$. For $d < 2\delta$ the total conductivity $\sigma_{\text{tot}}$ is equal to the conductivity of the interfacial regions $\sigma_{\text{int}}$ solely. As shown in Fig. 2, branches a) and b), the thickness dependence of $\sigma_{\text{tot}}$ in this region can only be

![Fig. 2. Total conductivity $\sigma_{\text{tot}}$ of an ionic conducting multilayer as a function of the reciprocal thickness $1/d$. The direction of the ionic (O$^+$) current densities $i_{\text{vol}}$ and $i_{\text{int}}$ is parallel to the internal interfaces. For $d < 2\delta$ the conductivity of the interface region is $\sigma_{\text{int}} = \sigma_{\text{int}}$ according to a space charge model a) or for structural disorder b).](image-url)
described by assuming a specific model for the prevailing conduction mechanism in the interfacial region:

a) Assuming the formation of space charge regions within the solid electrolyte at the interfaces, the thickness $\delta$ correlates with the Debye length $\lambda_D$ in Eq. (1) for diluted electrolytes. For concentrated electrolytes $\delta$ is smaller than $\lambda_D$. If the thickness $d$ is decreased below $\delta$, the space charge regions overlap. This will result in an additional increase of the average charge carrier density compared to those of the non-overlapping space charge regions [15,19,20]. The ionic conductivity will further increase beyond the value reached at $d=2\delta$.

b) If we neglect space charges and only assume the existence of structural disorder in an interfacial region with a thickness $\delta$, a further decrease of the total thickness $d$ should not necessarily lead to a modification of the conductivity.

A second polymorphic phase of the ionic conductor, formed at the phase boundary would also not lead to a further increase of the conductivity $\sigma_{\text{tot}}$ below $d<2\delta$. If we assume a structurally disordered region, which also accommodates some elastic strain, one may find a slightly changing conductivity upon further reduction of $d$.

3. Experimental

3.1. Sample preparation

We used single crystalline alumina substrates with the surface orientation (random, orientation (2243) determined by XRD and SAED) for the preparation of geometrically well defined samples. A final polish of these substrates was achieved by the use of 0.05 $\mu$m diamond paste. The polycrystalline bulk targets for the PLD were supplied by Friatec–Degussit (Mannheim, Germany) as Degussit AL 23 ($\text{Al}_2\text{O}_3$) and Degussit ZR 23 (CSZ, $\text{ZrO}_2 + 10.4$ to 12.3 mol.% CaO$^1$). Contrary to the data given by Friatec–Degussit, we measured a lower degree of doping for the utilized CSZ target material. From EDX investigations the chemical composition was determined as $\text{ZrO}_2 + 8.7$ mol.% CaO ($\pm 0.8$ mol.%). The lattice constant from the target material measured by XRD yields to 5.115 Å, which is also consistent with the lower dopant concentration [25].

All specimens of CSZ/Al$_2$O$_3$ multilayers were prepared by pulsed laser deposition. During deposition the temperature of the sapphire substrate was kept at 873 K while the background pressure of oxygen in the deposition chamber was adjusted to 2 Pa. For the ablation a KrF excimer laser was used (Lambda-Physik ComPEX 201, $\lambda=248$ nm). The layers were prepared at a repetition rate of 10 Hz and a pulse energy of 200 mJ.

From the as-deposited samples we cut rectangular specimen and equilibrated them by heat treatment at 1073 K in air for at least 12 h. This treatment was necessary to reduce the oxygen deficiency introduced during PLD and to avoid an electronic contribution to the total conductivity.

3.2. Microstructural characterisation by XRD, SEM and TEM/HRTEM

To obtain a first overview on the crystallinity and orientation/texture of the multilayer structures all samples were investigated by X-ray diffraction (Siemens D500), using Cu–K$_\alpha$ radiation in Bragg–Brentano geometry.

For the determination of the individual layer thicknesses the samples were investigated by scanning electron microscopy (LEO Gemini 982). A more detailed microstructural

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$^1$ 5 to 6 wt.% CaO.
characterisation was achieved by transmission electron microscopy (Philips CM20T and JEOL 4010). For SEM the samples were cross-sectioned and polished. The final polish was improved by the use of colloidal SiO$_2$ (0.01 μm). Micrographs were recorded in backscattered electron (BSE) mode at 10 kV accelerating voltage.

For TEM, the same samples used for SEM were firstly mechanically thinned and then further thinned with a proximate ion beam down to electron transparency (grinding and dimple grinding, Ar$^+$-beam thinning at 5 kV and 1 mA). The high resolution images were collected at an accelerating voltage of 400 kV.

3.3. Conductivity measurements

To complete the conductivity cell, two opposite face sides of each specimen were contacted with silver paste and platinum nets as electrodes. This permitted free exchange of oxygen with the surrounding and provided reversible electrodes, as we checked by a comparison of DC and AC measurements (see Section 4.2, Results/Oxygen ion conductivity).

All conductivity measurements were carried out in air in a high temperature furnace. For the DC measurements of the ion conductivity a potentiostat (Potentiostat/Galvanostat, Model 263A, EG&G Instruments, Princeton Applied Research) and a high-impedance digital voltmeter (Keithley DMM 2001) were used. For the schematic arrangement see Fig. 3a. AC measurements were performed with an impedance analyser (Frequency Response Detector, Model 1025, EG&G Instruments, Princeton Applied Research) within a frequency range between 0.1 Hz and 5 MHz.

4. Results

4.1. Microstructural characterisation by XRD and TEM/HRTEM

Directly after preparation, only reflections of CSZ have been identified by XRD as shown in Fig. 4a. Using TEM it turned out that all CSZ layers of the layered composites were crystalline and show a columnar microstructure (average column diameter of about 20 nm). Thus, no grain boundaries in the CSZ layer parallel to the CSZ/Al$_2$O$_3$ interface have been found. In contrast to the CSZ most of the Al$_2$O$_3$ layers were amorphous as to be seen in Fig. 4b. Only small regions of the Al$_2$O$_3$ layers starting from the CSZ/Al$_2$O$_3$ interfaces were crystalline. This explains why no Al$_2$O$_3$ reflexes were found by XRD. Even an increase of the substrate temperature up to 1000 °C during the PLD preparation could not enforce the deposition of crystalline Al$_2$O$_3$.

![Fig. 4. a) XRD (Bragg–Brentano, Cu–Kα) and b) TEM dark field micrograph of a CSZ/Al$_2$O$_3$ multilayer system directly after preparation by PLD (in the field of view: 4 layers CSZ and 3 layers Al$_2$O$_3$). In the XRD all reflections for CSZ are indexed. Reflections from the Al$_2$O$_3$ substrate are marked with an asterisk.](image-url)
Only after a long heat treatment the complete crystallisation of the Al₂O₃ layers took place. For the results of a heat treatment at 800 °C for about 100 h see the TEM micrograph in Fig. 5a. The grain structure of the recrystallised Al₂O₃ layers (average grain size of about 40 nm) is distinctly coarser compared to the CSZ layers. SAED investigations show that there is no orientation relation between the individual CSZ and Al₂O₃ layers, i.e. the CSZ columns and the Al₂O₃ grains are randomly orientated. As depicted in Fig. 5b), the reflexes from CSZ forms continuous "rings" and the reflexes from Al₂O₃ are randomly distributed single "spots". From additional tilting series it turned also out that there is no orientation relation between the Al₂O₃ substrate and each subsequent CSZ layer.

The transition region between the adjacent phases CSZ and Al₂O₃, as depicted in Fig. 6, is difficult to resolve. However, from HRTEM we conclude that the transition between both lattice structures takes place in a disordered interface core region with a thickness of less than 1 nm. In many regions of the Al₂O₃ layers, close to the CSZ/Al₂O₃ interfaces, pores of approximately 2 nm width can be identified (see Fig. 6, right inset). These cavities along the boundary are arranged in chains and are partially connected. According to the HRTEM results, these pores are not in direct contact to the phase boundary. The average distance to the interface is about 3 nm.

4.2. Oxygen ion conductivity

The conductivity of all specimens has been determined in the temperature range between 475 °C and 675 °C by DC and AC (impedance) measurements. Additionally, samples were measured twice with freshly prepared silver electrodes in order to check the influence of the electrode preparation. When the...
recrystallisation of the Al₂O₃ layers was finished completely (after the additional heat treatment at 800 °C for about 100 h), no further change (increase) of the resistance with time was observed.

The impedance (Nyquist) plots show in the measured range from 5 MHz to 0.1 Hz a single, almost ideal semicircle, as it is exemplified in Fig. 3b). The resistance data determined by the DC and AC (impedance) conductivity measurements do not differ significantly, the deviation is about 1%. Calculating the capacity from the angular frequency \( \omega \) at the apices of the semicircles, we obtain a temperature independent value of about 40 pF (for a system with 5 layers CSZ/5 layers Al₂O₃).

A series of measurements at a constant temperature shows clearly an increasing total ionic conductivity \( \sigma_{\text{tot}} \) of the heterolayered systems with decreasing thickness \( d \) of the CSZ layers, i.e. with an increasing number of CSZ/Al₂O₃ interfaces. The results for 575 °C (848 K) are presented in Fig. 7. By decreasing the thickness of the individual CSZ layers from 780 nm (1 layer CSZ/1 layer Al₂O₃) to 40 nm (5 layers CSZ/5 layers Al₂O₃), the total conductivity \( \sigma_{\text{tot}} \) was increased approximately by two orders of magnitude (factor of 60).

Due to the scattering of the data the relatively small bulk conductivity \( \sigma_{\text{vol}} \) can not be determined from the intercept with \( \sigma_{\text{tot}} \) axis by linear regression with an acceptable error. The conductivity of a single CSZ layer with a thickness of about 780 nm agrees well with data reported in the literature[26].

From the conductivity data in Fig. 7 we can assume that \( \sigma_{\text{vol}} \) is at least one order of magnitude smaller than \( \sigma_{\text{int}} \). Further, from the slope \( 2\delta(\sigma_{\text{int}} - \sigma_{\text{vol}}) \) we can estimate an interfacial conductance \( \delta\sigma_{\text{int}} \) of 1.32 \( \times \) 10\(^{-9}\) S at 575 °C (see Fig. 8 for \( \ln(\delta\sigma_{\text{int}}) \) at other temperatures \( T \)).

4.3. Activation energy for ionic transport parallel to the CSZ/ Al₂O₃ multilayer

Measurements on three selected multilayer systems as a function of temperature in an interval from 350 °C to 700 °C indicate consistently a decrease of the average activation energy \( E_{a,\text{tot}} \) for the total oxygen ion conduction \( \sigma_{\text{int}} \) with an increasing number of CSZ/Al₂O₃ interfaces (respectively with decreasing \( d \), see Arrhenius plot in Fig. 8). The numerical results for these specimens are shown in Table 1.

The interfacial conductances \( \delta\sigma_{\text{int}} \) calculated from the slopes of the total conductivity \( \sigma_{\text{tot}} \) vs. \( 1/d \)-plots can be used for an Arrhenius plot (see Fig. 9) to evaluate the activation energy \( E_{a,\text{int}} \) of the interfacial transport. The activation energy \( E_{a,\text{int}} \) results from the slope as (70± 10) kJ mol\(^{-1}\) (0.72 eV).

5. Discussion

5.1. Microscopic structure of the CSZ layer

Directly after preparation by PLD the Al₂O₃ layers were partially amorphous. Only a long heat treatment (in air) enforced the complete recrystallisation of the alumina layers. When complete recrystallisation is attained also the measured total conductivity \( \sigma_{\text{tot}} \) became constant. No further change in the interfacial and grain structure of the conducting layers was observed with the time period of the experimental investigations. The cavities in the Al₂O₃ layers observed by TEM are most probably the result of the recrystallisation process. It is not possible to determine whether these cavities are the consequence of a lattice relaxation in the vicinity of the phase boundaries or of a volume contraction during the crystallisation.

Table 1

<table>
<thead>
<tr>
<th>d/nm</th>
<th>No. of CSZ layers</th>
<th>( E_a/kJ \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>780</td>
<td>1</td>
<td>155 (1.60 eV)</td>
</tr>
<tr>
<td>160</td>
<td>3</td>
<td>129 (1.34 eV)</td>
</tr>
<tr>
<td>51</td>
<td>5</td>
<td>87.8 (0.91 eV)</td>
</tr>
</tbody>
</table>

The measurement for each multilayer system was performed twice, (1) and (2).
process. However, no pores are formed in the bulk of the crystallised Al₂O₃ films.

The CSZ layers are composed of columnar grains and grain boundaries parallel to the CSZ/Al₂O₃ interface. As depicted in Fig. 10, these grain boundaries in the CSZ layers perpendicular to the CSZ/Al₂O₃ interface and parallel to the current might also represent additional fast diffusion paths for ionic transport. However, it is obvious that their contribution to the total conductivity σtot does not depend on d.

The multilayer conduction model can be easily extended by an additional cross section Agb for the transport in grain boundaries within the CSZ layers (perpendicular to CSZ/Al₂O₃ interfaces), i.e. splitting up Aint = Avol + Aint + Agb. Denoting the average density of the CSZ grain boundaries with c_gb (number of grain boundaries per length l of the cross section), the thickness of the regions with increased ionic transport around the grain boundaries with δ and their increased conductivity with σ_gb, we obtain the following expression¹:

\[ \sigma_{tot} = \sigma_{vol} + \frac{2\delta(\sigma_{int} - \sigma_{vol})}{d} + 2\delta'c_{gb}(\sigma_{gb} - \sigma_{vol}) - 4\delta\delta'c_{gb}\left(\frac{1}{2}(\sigma_{int} + \sigma_{gb}) - \sigma_{vol}\right) \frac{1}{d}. \]

(9)

Compared to Eq. (5) we get two additional terms. The first term, \(2\delta'c_{gb}(\sigma_{gb} - \sigma_{vol})\), represents the additional grain boundary transport due to the columnar structure of the CSZ. It does not depend on the reciprocal thickness 1/d. When plotting σtot against 1/d it will only change the intercept with the ordinate, i.e. it will influence the estimation of the volume conductivity σvol (compare to Fig. 2). The second additional term, \(4\delta\delta'c_{gb}\left(1/2(\sigma_{int} + \sigma_{gb}) - \sigma_{vol}\right)/d\), takes the intercepts of the perpendicular grain boundaries with the CSZ/Al₂O₃ interfaces into account. Like the term 2δ(σint - σvol)/d it also depends on 1/d.

Carefully estimating δ and δ' in the order of 1 nm (10⁻⁷ cm) and using an average grain boundary density c_gb ≈ 5·10⁵ cm⁻¹ (20 nm average column size), this term is about two orders of magnitude smaller, because of the small intercept area 4δδ'. Hence, it can be safely neglected.

If we assume that both interfacial conductivities, σ_int and σ_gb, are much higher than the conductivity of the volume phase σvol, Eq. (9) can be approximated by:

\[ \sigma_{tot} = \sigma_{vol} + 2\delta c_{gb}\sigma_{gb} + 2\delta\sigma_{int}\frac{1}{d}. \]

(10)

Thus, we can assume that the observed change in total conductivity σtot with increasing periodicity of the CSZ and Al₂O₃ layers is primarily due to an increased conductivity σ_int of the CSZ/Al₂O₃ interfaces.

5.2. Oxygen ion conductivity

The resistance data determined by the DC and AC (impedance) conductivity measurements agree, which indicates a negligible polarisation resistance of the porous silver electrodes compared to the total resistance of the multilayer systems. The observation of a single semicircle in the Nyquist plots is in accordance with similar experimental results by Kosacki et al. [22], performing impedance measurements on single layered asymmetric thin film systems (YSZ on MgO). The only occurring single semicircle can be explained by the thin film geometry of the system. The capacity of the multilayered thin film system (with grains, interfaces, phase boundaries) is negligible compared to the purely geometric capacity of the much thicker Al₂O₃ substrate (factor of 10⁴ =1 µm/µm). As the ionic conductance of the multilayered thin film is much higher compared to the much thicker insulating substrate, this results in a single parallel RC circuit with the geometric capacitance of the substrate and a resistance only determined by the multilayer thin film system as an equivalent circuit.

The total (ionic) conductivity σ_int in CSZ/Al₂O₃ multilayer systems is increased significantly in comparison to the bulk...
electrolyte CSZ (for a system with 5 layers CSZ/5 layers Al₂O₃ layers by a factor of 60, see Fig. 2). A linear correlation between the total ionic conductivity \( \sigma_{\text{tot}} \) of the multilayer systems and the reciprocal thickness \( 1/d \) of the CSZ layers (respectively the number of interfaces) is observed, as described by Eq. (5) or Eq. (10).

In the TEM images no distinct transition region between the two lattice structures can be identified. By assuming the thickness \( \delta \) of an interfacial region in the order of 1 nm, we estimate that the oxygen ionic conductivity \( \sigma_{\text{int}} \) of the interfacial region is about 3 to 4 orders of magnitude higher than the conductivity \( \sigma_{\text{vol}} \) of the bulk phase (\( \sigma_{\text{vol}} \approx 1.3 \times 10^{-2} \text{ S cm}^{-1} \) for \( \delta = 575 \) °C and \( \delta \approx 10^{-9} \text{ m} \), from literature \( \sigma_{\text{vol}} = 6.0 \times 10^{-6} \text{ S cm}^{-1} \) [26]).

In principle, it cannot be ruled out that the increase of the total conductivity \( \sigma_{\text{tot}} \) is due to an increased equilibrium electronic conductivity caused by any kind of size or interface effects. This effects can only be investigated by an additional measurements of the electronic partial conductivity, e.g. with the Wagner–Hebb method. To our knowledge, all comparable studies to date suffer from the same basic problem. There exist no published reports on measurements of the partial electronic conductivity caused by any kind of size or interface structure.

5.3. Activation energy

The average activation energy \( E_{a,\text{tot}} \) for the total ionic transport in the multilayer systems is significantly decreased by increasing the number of interfaces (see Fig. 8 and Table 1). For a 5 layers CSZ/5 layers Al₂O₃ system the average activation energy \( E_{a,\text{tot}} \) is about 0.5 eV smaller compared to a 1 layer CSZ/1 layer Al₂O₃ system with almost bulk character. The activation energy of 1 layer CSZ/1 layer Al₂O₃ system of 1.47 eV corresponds to the activation energy of the used CSZ target material, determined as 1.44 eV. This is consistent with the data found in the literature for a system containing 8.7 mol.% CaO (taken from [26,27], see data from literature in Table 2).

This result agrees with the chemical composition measured by EDX, which differ significantly from the composition given by Friatec–Degussit (ZrO₂ +10.4 to 12.3 mol.% CaO). As the literature data indicate, calcia-stabilised zirconia with 12 mol.% CaO dopant concentration has a lower activation energy of only 1.20 eV [26]. This obviously differs from the measured conductivity data.

The measured average activation energy \( E_{a,\text{tot}} \) is a weighted average of the activation energies for each of the possible conduction paths:

\[
E_{a,\text{tot}} = f(E_{a,\text{int}}, E_{a,\text{vol}}, E_{a,\text{gb}})
\]

(11)

The activation energy \( E_{a,\text{int}} \) for interfacial transport, determined from the interfacial conductances \( \delta \sigma_{\text{int}} \) can be estimated to 0.7 eV (see Fig. 9, about 0.8 eV smaller compared to bulk CSZ). We assume that this is the lower limit for the average activation energy \( E_{a,\text{tot}} \) for multilayered systems with even thinner conducting layers. Thus, the total conductivity of CSZ/Al₂O₃ multilayer systems should further increase when the thickness of the CSZ layers is decreased below 51 nm (sample with 5 layers CSZ/5 layers Al₂O₃).

Our results for the activation energies agree very well with the experimental studies on single YSZ thin films on MgO (100) reported by Kosacki et al. [22]. Kosacki attributes a higher oxygen ion conductivity to a much lower activation energy for the ionic transport at the YSZ/MgO interface. However, the interpretation of the data in [22] is slightly hampered by the simultaneous effect of both the free YSZ surface and the YSZ/MgO heterostructure boundary. Therefore, Kosacki et al. conclude that superlattice studies are required in order to extract precise information on the effect of inner phase boundaries — as presented in this paper.

The Debye length of stabilised zirconia is very small because of the high concentration of mobile charge carriers. For CSZ with 8.7 mol.% CaO the concentration of oxygen vacancies \( c_{\text{V}} \), and calcium ions \( c_{\text{Ca}^2+} \) can be calculated as \( 6.0 \times 10^{-7} \text{ mol cm}^{-3} \) which corresponds to a Debye length \( \lambda_{\text{D}} \) of 0.6 Å (\( T = 773 \text{ K} \), [28,29]). As the Debye–Hückel theory is a priori not applicable to such a concentrated electrolyte, \( \lambda_{\text{D}} \) has here no real physical relevance. Thus, space charge effects will definitely play no role in multilayers or superlattices of solid electrolytes with large concentrations of charge carriers, allowing measurements of structural interface effects.

Al₂O₃ and CSZ have quite different lattice symmetries and lattice spacings:

| CSZ: Fm3m, \( a = 5.115 \text{ Å} \) |
| Al₂O₃: R3c, \( a = 4.754 \text{ Å} \) and \( c = 12.990 \text{ Å} \) |

We found no commensurate lattice spacings for low indexed lattice planes and — as confirmed by TEM, HRTEM, SAED and XRD — this multilayered system has high lattice misfits. As a consequence, no orientation relation between the crystallites in adjacent layers of the multilayer system exists. Thus, it is very likely that the strong change in conductivity and activation energy, which we found for the CSZ/Al₂O₃ multilayer system, can be completely attributed to a high ionic mobility in the interface core regions due to the strong structural mismatch between CSZ and Al₂O₃.

Further measurements on specimens with CSZ layers down to a thickness of 5 nm will possibly reveal whether a nonlinear size effect, even though not expected at this point, exists.

Further measurements on multilayered systems with other insulating oxides, showing different lattice mismatches, could clarify a possible dependence of transport properties on the interface structure.
6. Summary

The ionic conductivity of CSZ/Al₂O₃ multilayers parallel to the heterophase boundaries is increased by the number of internal interfaces. The activation energy for the ionic migration in these multilayers (superlattices) is decreased considerably in comparison to the CSZ bulk phase. We assign the observed effects to a structural effect within the boundary core. A correlation between the degree of interface structural disorder/misfit and a lowering of the interfacial activation energy is assumed.

For a layer thickness down to 40 nm no contribution of a space charge region to the total multilayer conductivity was found. However, by virtue of the short Debye length in this material a space charge effect is not expected.

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References