Low oxygen partial pressure increases grain boundary ion conductivity in Gd-doped ceria thin films

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Abstract
Grain boundaries play an important role in the transport properties of oxide ion conducting electrolytes and mixed ionic electronic conductors. Nevertheless, very little is known about the electrical grain boundary properties in thin films. In these, the separation of in-plane grain and grain boundary conductivity is more complicated due to the large capacitive effect of the insulating substrate. This can be overcome by using interdigitating electrodes with separation of few micrometres. By comparing grain and grain boundary conductivities of Gd-doped Ceria (GDC) thin films with 5 and 10 mol % Gd content, we can show that the much lower conductivity of 5% doped GDC is almost exclusively caused by a significantly higher grain boundary resistance. In reducing atmosphere, GDC becomes mixed ion and electron conducting and in such conditions, the employed Pt thin film electrodes are virtually blocking for oxygen anions and reversible for electrons. With impedance spectroscopy we can therefore simultaneously measure ionic and electronic conductivities under reducing conditions. Although the bulk vacancy concentration remains dominated by the extrinsic acceptor doping, the ionic conductivity of the films increases by up to one order of magnitude when going from oxidising to reducing atmosphere. This result is—although in such a clear manner not observed or predicted before—in line with the widely accepted grain boundary space charge model. It is concluded that an accumulation of Ce\textsuperscript{3+} in the space charge zone weakens the oxygen vacancy depletion and therefore increases the grain boundary conductivity. The results are of high relevance for understanding and optimising the properties of GDC in anodes and electrolytes for solid oxide fuel cells, and potential new uses such as electrostrictive and memristive devices, for which oxygen partial pressure dependent ionic conductivity is an important new aspect.

1. Introduction

Over the past decades, pure and doped ceria were extensively investigated and used for a variety of applications, which mostly rely on surface redox catalytic properties and ionic conductivity. Doped and pure ceria are thermally and chemically stable in harsh conditions such as automotive exhaust streams [1]. Also, a part of the Ce\textsuperscript{4+} ions is easily reduced to Ce\textsuperscript{3+}, especially at the surface and interfaces [2, 3]. This redox-activity is the reason for high surface catalytic activity for a variety of redox reactions [4]. Moreover, the presence of Ce\textsuperscript{3+} ions also causes electronic conductivity in reducing atmospheres [5, 6] by a small polaron hopping mechanism [7, 8], which is characterised by a very low and thermally activated mobility of electronic charge carriers. Acceptor doping e.g. with as Gd\textsuperscript{3+} or Sm\textsuperscript{3+}, additionally introduces formation of oxygen vacancies, which exhibit very high mobility at elevated temperatures [9]. This makes acceptor doped ceria a very good oxide ion conductor that is stable in oxidising and reducing conditions [9], and therefore applicable as an electrolyte [9, 10] or anode material constituent [11–13] in solid oxide fuel cells. Electronic and ionic conductivities of ceria were already well investigated and a number of studies deal with the grain and grain boundary conductivity of dense sintered
acceptor doped ceria polycrystals [14–17]. All of these studies conclude that the grain boundary resistance decreases and the bulk activation energy increases with higher acceptor doping levels, and that samaria and gadolinia doped materials with 10–20 mol% doping exhibit the highest conductivities in the temperature range of SOFC operation (500 °C–800 °C).

Also on a microscopic level, the origin of the grain boundary resistance [18] and the atomic structures of grain boundaries and other interfaces in doped ceria have been thoroughly investigated by TEM experiments [2, 15]. In line with the interpretation of the TEM images, computational results suggest that at the core of the grain boundary, the O:Ce ratio is below two, meaning that the grain boundary core is positively charged. This core charge is balanced by a negatively charged, oxygen vacancy depleted space charge region which extends few nm around the grain boundary core [19, 20]. Since oxide ion transport takes place by a vacancy hopping mechanism, this depletion of oxygen vacancies is thus concluded to be the main reason for the grain boundary resistance, at least for high purity materials. In accordance with this model, the grain boundary conductivity increases with Gd-doping level, while the capacitance of the grain boundary arc increases, indicating that the space charge zone becomes narrower [20]. However, significant scatter is found when comparing the grain boundary conductivities of equally doped polycrystals, which is probably caused by small amounts of SiO2 or maybe other impurities [16]. Already 200 ppm SiO2 can already increase the grain boundary resistance by a factor of ten [16, 21], which can be explained by a strong accumulation of impurities at the grain boundary. Not all impurities impede grain boundary conduction. Small amounts of Co [22] or Fe [23] also segregate to the grain boundary, where they act as sintering aid and increase the grain boundary conductivity. Also dopant ions significantly accumulate close to the grain boundary, which was e.g. observed for Gd [24], Pr [15] or Ca [25], and also predicted by numerical simulations [26]. Therefore, the composition of the space charge zone likely strongly differs from the bulk.

In literature, several authors calculate the grain boundary core potential \( \phi_{\text{GBC}} \) from the ratio of specific bulk and grain boundary conductivities [18, 20] (see results and discussion section for details), and values in literature are consistently reported to be in the order of 0.2–0.4 V. However, the vacancy concentration and effective grain boundary conductivity depends exponentially on \( \phi_{\text{GBC}} \), so small variations in the potential have a large effect on the grain boundary resistance. Also, several assumptions and simplifications are required for calculating \( \phi_{\text{GBC}} \) such as:

1. The resistance of the grain boundary core is small compared to the space charge zone.
2. The oxygen vacancy chemical potential depends only on the concentration and defect interactions are negligible.
3. There is no accumulation of dopants in the space charge zone.
4. There is no structural distortion in the fluorite lattice next to the grain boundary, which may have an additional effect on the Ceria reduction enthalpy [27] and ion mobility.

Apart from these assumptions, even treating the space charge zone as a continuum is an approximation, since the Debye length of GDC10 at 300 °C is only 0.15 nm, which is less than a single Ce–O bond distance. Although there are reasons to be sceptical about exact numbers for the space charge potential and width, the space charge model works excellently on a semi-quantitative scale to describe the ionic grain boundary resistance in high purity materials as function of doping level and temperature [20].

In contrast to the rather large amount of data for grain boundaries in sintered ceria polycrystals, the electrical properties of grain boundaries in ceria thin films are largely unknown. The measurement of the grain boundary resistance in thin films is not trivial and so some studies omit the separation of grain and grain boundary impedance and evaluate the total ionic conductivity of polycrystalline thin films [28–33]. However, from these measurements it is not easy to separate the effect of grain boundaries because also strain [32, 34–36] influences ion conduction in GDC thin films. Without being able to separate grain and grain boundary conductivities, measurement of the bulk conductivity and strain effects is experimentally challenging and only reliable on epitaxial films [35].

In this study we show that the difficulty of separating grain and grain boundary resistance can be overcome by photolithographic patterning of closely spaced interdigitating electrodes, which was already successfully demonstrated on YSZ thin films [37–39]. Also we compare the oxygen partial pressure and temperature dependence of the ionic grain and grain boundary conductivities of 5 and 10 mol% Gd doped ceria thin films to values for sintered polycrystals that were already extensively investigated in literature [14, 16–18].

In addition to separating grain and grain boundary impedance by fitting the dielectric high frequency arc, we also show that the contributions of ionic and electronic conductivities can be separated in reducing H2 + H2O atmospheres by evaluating the low frequency impedance arc, which is a characteristic for a mixed conductor that
is placed between two oxygen ion blocking electrodes. With such electrodes, electronic current is measured in DC-like conditions, whereas with a high frequency AC signal, electrons and oxygen anions are mobile and the total electronic plus ionic conductivity is measured. According to equivalent circuit models were derived in literature [6]. This technique was already successfully applied to SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ thin films [40]. For our GDC films, these measurements reveal that the ionic conductivity in reducing atmospheres is up to ten times larger than in oxidising conditions, although the bulk vacancy concentration is hardly affected by the atmosphere. Although the observation of this effect is new, we can show that it is a logical consequence of the grain boundary space charge model, and the defect chemistry of GDC.

1.1. Electrode designs and circuit models for separating grain and grain boundary impedance in thin films

Impedance spectroscopy can separate the dielectric relaxation of grains and grain boundaries due to their different capacitances and time constants. The dielectric relaxation frequencies for grains and grain boundaries follow the law $\omega = \sigma \varepsilon^{-1}$ where $\sigma$ and $\varepsilon$ are conductivity and permittivity, respectively. Since specific conductivities of grains and grain boundaries usually differ by at least 2–3 orders of magnitude, while the permittivity is approximately equal, two well separated arcs for grain and grain boundary can be usually observed in a Nyquist plot. However, capacitances caused by the electrical wiring (typically few picofarads) are always present and measured in parallel to the sample. These must be therefore smaller than the grain capacitance of the sample, in order to be negligible. For pellet shaped samples with electrode sizes of ~1 cm$^2$ and thickness of ~1 mm, the grain and grain boundary capacitances are typically ~100 pF and several nF, respectively, so the setup capacitance (typ. 1–5 pF) is virtually negligible. In this case, the impedance spectra are fitted with the classical brick layer model equivalent circuit sketched in figure 1(a). In thin films, however, the separation of in-plane grain and grain boundary conductivities is complicated, due to the small cross-sectional area, and thereby very small capacitance. In a classical in-plane conductivity measurement geometry, impedance is measured between two parallel electrodes which are separated by roughly 1 mm. In the case of a 400 nm thick GDC film, the in-plane bulk capacitance is then in the order of $10^{-15}$ F, and the grain boundary capacitance is also $\ll$1 pF. Such small capacitances are at the measurement limit even for high-end impedance analysers, such as the used Novocontrol alpha system and the setup stray capacitances are orders of magnitude larger. In such a case, only the total conductivity of the thin film can be measured.

To overcome this problem, photolithographic structuring of the electrodes in form of interdigitating fingers (see figure 2) can be used to decrease the distance and increase the effective length of the inter-electrode gap.

With an electrode gap of only 5 $\mu$m and a total of 24 fingers, each 1 mm long, a film bulk capacitance of about...
$4 \times 10^{-13} \text{ F}$ and a grain boundary capacitance of several $\text{pF}$ can be expected. The dielectric setup capacitance, caused by the insulating substrate and measurement wiring is measured in parallel. Also for this optimised design, the stray capacitance is much larger than the thin film bulk capacitance, and in the order of the grain boundary capacitance. This situation and the according equivalent circuit are sketched in figure 1(b). In order to avoid over-parametrisation during impedance fitting, the (very small) capacitance modelling the thin film bulk is removed from the circuit model, as sketched in figure 1(b). The appropriateness of this circuit model was already demonstrated in literature for YSZ thin films [37–39, 41]. Furthermore, instead of capacitors, constant phase elements (CPE) with $Z_{\text{CPE}} = 1/(Q \omega^p)$ were used in order to better describe the typically slightly depressed grain boundary arc in the impedance spectra [42]. The origin of this depressed arc is most probably the stochastic variability of different grain boundaries. With a $p$-value of 1, the CPE equals a perfect capacitor with $C = Q$, for $p$-values below 1 the capacitance of a parallel $R$CPE element can be approximated by [42]

$$C_{(R\text{CPE})} = (R^{1-p}Q)^{1/p}. \quad (1)$$

### 2. Experimental procedures

#### 2.1. Sample preparation

Polycrystalline 5 and 10 mol% Gd doped Ceria (GDC5 and GDC10) targets were prepared from commercially available powders of GDC10 (Treibacher AG, Austria 99.95% purity). For GDC5, a 1:1 molar mixture of GDC10 and CeO$_2$ (Sigma Aldrich, 99.95% purity) powders was used. Pellets were cold isostatically pressed at 3000 bar and sintered at 1400 °C for 10 h in air. Prior to the GDC thin film deposition, 5 nm Ti + 100 nm Pt films were sputtered on polished 0001-oriented Al$_2$O$_3$ single crystals. From those, interdigitating electrodes were produced by photolithography and Ar-ion beam etching of the Ti+Pt thin films. On the substrates with Pt electrodes, GDC thin films were then grown by pulsed laser deposition at 650 °C substrate temperature (measured by a Pyrometer) in 0.04 mbar O$_2$ atmosphere. Laser energy was 100 mJ per pulse in the chamber (400 mJ per pulse at laser exit), 7 cm substrate-target distance and 5 Hz laser repetition rate for 20 min. The resulting GDC5 and GDC10 films were 420 nm thick. The contacting pads visible in figure 2 were shadowed with ZrO$_2$ particle slurry to prevent deposition of GDC on the contacting pads. After GDC film deposition, the substrates were cleaned with ethanol p.a. and ultrasound to remove the ZrO$_2$ particles and reveal the bare contacting pads, which could be easily contacted by Pt–Ir tips. A microscope image of the resulting thin films with interdigitating Pt electrode structures is visible in figure 2.

#### 2.2. Impedance spectroscopy

Thin film conductivity was measured in a gas tight, homogeneously heated micro-contact setup (Huber Scientific, Austria), mounted in a tubular furnace. Impedance spectroscopy was carried out in 2-wire mode in a frequency range of 0.01–$10^6$ Hz and a temperature range of 120 °C–600 °C. 60 Ω offset resistance were subtracted from the measurements to account for wiring and sheet resistance of the Pt thin film electrodes. Only spectra measured above 500 °C were significantly (more than 10%) influenced by this correction.

For separation of grain and grain boundary impedance, samples were tested in synthetic air, whereas for reducing atmospheres dry 2.5% H$_2$ in Ar and humidified N$_2$ were mixed with mass flow controllers. H$_2$:H$_2$O
mixing ratios varied from 20:1 to 1:15. The reducing gas mixtures thereby cover about five orders of magnitude in equivalent \(\text{p(O}_2\text{)}\).

2.3. AFM measurements
AFM scans were performed with a Bruker NanoScope 8 Multimode AFM with Nanoworld NCH cantilevers in tapping mode. From the obtained images, the average grain size and rms roughness of the films were determined as shown in figure 3. The linear intercept method was used for determining average grain sizes.

2.4. X-ray diffraction
The GDC5 and GDC10 thin films that were used for electrical conductivity measurements were afterwards characterised by XRD in \(\Theta–2\Theta\) geometry with a Panalytical X’Pert PRO diffractometer with para-focussing Bragg-Brentano arrangement, equipped with a Cu tube, secondary sided Ni–K\(_\beta\) filter, and X’Celerator detector. The diffraction patterns in figure 4 show that both GDC films as well as the Pt current collectors growing on sapphire are almost exclusively \((111)\) textured. The GDC out-of-plane lattice parameter is \(5.42(6) \pm 0.01\text{ Å}\) for GDC5 and \(5.42(1) \pm 0.01\text{ Å}\) for GDC10, within experimental error, this value equals the bulk value of \(\sim 5.418\text{ Å}\) [43] for GDC10, so strain effects are expected to be negligible. The reflex assigned to TiO\(_2\) is explained by the thin oxidised Ti adhesion layer between Pt and Al\(_2\)O\(_3\). The asterisk denotes a tiny unidentified peak, which may also be related with the presence of TiO\(_2\) at the Pt/sapphire interface, but could not be assigned to a phase.

3. Results and discussion
3.1. Ionic grain and grain boundary conduction in GDC thin films
The thin film impedance spectra were recorded in a gas tight micro-contact setup, mounted in a homogeneously heated tube furnace. To illustrate the difference between the impedance of pellet and thin film samples, impedance spectra for both geometries measured at 200 \(^\circ\)C are plotted in figure 5(a). The pellet shaped sample shows two arcs for bulk (magnified in the inset) and grain boundary. The thin film spectrum does not show this clear separation of grain and grain boundary, but still a weak shoulder is observed in the inset. The onset of a low frequency arc for the thin film (black stars) is related to the oxygen ion blocking electrode and is not considered in the circuit model, so according data points were excluded from the fit. The thin film impedance spectra are similar to those obtained from polycrystalline YSZ thin films when a similar electrode pattern is used [37–39]. When instead of impedance, the complex permittivity \(\varepsilon = 1/(i\omega \varepsilon_{\text{r}})\) is plotted, a high frequency feature related to the grain boundary is much better visible also for the thin film sample, shown in figure 5(b). In a permittivity plot, a simple parallel resistor capacitor circuit \((R||C)\) would just deliver a straight vertical line with the real part being the relative permittivity \(\varepsilon_{\text{r}}\) of the capacitor dielectric. Solid lines in figure 5 represent the equivalent circuit fit, for which only the high frequency bulk and grain boundary relaxation features were considered. For
impedance fitting, the equivalent circuit from figure 1(a) was used for the pellet impedance, and the circuit from figure 1(b) for the thin film. For a reasonable fit, the dielectric grain boundary relaxation frequency must be significantly below 1 MHz (limit of the Novocontrol impedance analyser), which gives an upper temperature limit of 300–350 °C.

In order to prove the appropriateness of the physical interpretation of our measurements we first look at the ionic grain (bulk) conductivity. In literature, the reported GDC bulk conductivity is very similar among different authors, although purity and synthesis route differ and significant scatter is found in grain boundary conductivity [14, 16, 17, 44]. Also the few available studies on grain boundary free thin films of acceptor doped ceria report conductivity values that are very close to the bulk conductivity of polycrystals [35, 45, 46].

Also in the case of our results, the bulk conductivity plotted in the Arrhenius diagram in figure 6 (solid lines) matches very well with the literature values reported for high purity polycrystalline GDC samples by Zhang et al [16]. Note that the bulk conductivities of GDC5 and GDC10 differ by less than a factor of 2, due to slightly different oxygen vacancy mobilities, and the difference in total conductivity is almost entirely a grain boundary property. The measured grain boundary conductivities were corrected for the ratio of grain size and grain boundary thickness. The grain size was determined by AFM (see figure 3), and the grain boundary thickness was calculated by
where \( A \) and \( l \) are cross-sectional area and electrode distance, respectively, \( C_{gb} \) is the grain boundary capacity, and \( d_g \) is the average grain diameter determined by the AFM scans in figure 3. Since the bulk permittivity \( \varepsilon_r \) and the grain capacitance \( C_g \) are not accessible in the thin film impedance data, an \( \varepsilon_r \) value of 40 was determined from pellet shaped samples. When assuming the same permittivity for grain and grain boundaries, we calculate grain boundary widths of 2.1 nm for GDC10 and 3.1 nm for GDC5. For GDC10 and GDC5 pellets, grain boundary widths of 3 and 4 nm are reported, respectively [20], so the grain boundary width of our thin films agrees reasonably with literature. Among the many studies dealing with grain boundary conductivity in doped ceria, the values reported by Zhang et al [16] (30 ppm SiO\(_2\)) exhibit the lowest grain boundary resistances, probably due to the high sample purity. In our thin films, the specific grain boundary conductivity of our thin film samples is even about 10 times higher than in the best polycrystals. This difference may be a grain size effect, since also for Yttria-stabilised Zirconia the specific grain boundary conductivity was found to decrease with larger grain sizes [47]. However, also the growth mode of the grain boundary differs between thin film and polycrystal, and distribution of grain boundary angles is most likely non-random in the thin films, as we observe strong (111) texture of the GDC films by XRD (figure 4). Therefore, the relatively high grain boundary ion conductivity is not fully unexpected.

### 3.1.1. Origin of the grain boundary impedance

The grain boundary resistance in GDC polycrystals is often explained either by the grain boundary space charge or by the formation of a siliceous impurity phase due to the low bulk solubility of SiO\(_2\) in ceria [16, 18]. For high purity materials e.g. GDC with 30 ppm SiO\(_2\) [16] the total amount of silicon can only form 10% of a monolayer coverage at the grain boundaries of 2 \( \mu \)m grains, so impurities are very unlikely to play a big role in this case. Also our thin films were prepared from a high purity target (10 ppm SiO\(_2\)), and with a grain size of \( \sim 30 \) nm a SiO\(_2\) monolayer on each grain boundary would require impurity levels exceeding 20 000 ppm SiO\(_2\). Therefore, the grain boundary resistance must be a property of the pure material. In agreement with literature, we therefore suggest that oxygen vacancy depletion in the grain boundary space charge zone [19, 20, 47] is the reason for the grain boundary resistance of our GDC thin films, which also explains the strong dopant concentration dependence of the grain boundary resistance. Moreover, the applicability of the space charge model is further supported by the fact that the grain boundary ionic conductivity strongly increases in reducing conditions, which is elaborated in the following.

### 3.1.2. Oxidising versus reducing conductivity

GDC is a pure ion conductor in oxidising conditions, and becomes a mixed conductor in H\(_2\) + H\(_2\)O atmosphere. The onset of electron conduction increases the total conductivity and has a severe effect on the low frequency arc, which is associated to the ion blocking electrodes, which is visible in figure 7(a). The high frequency arc (associated with bulk and grain boundary conductivity) shrinks in H\(_2\) + H\(_2\)O atmosphere, due to...
an increase in total conductivity. Also the low frequency arc, which is so far not considered in the fit, shrinks dramatically. In oxidising atmosphere, the low frequency arc appears as an imperfect capacitor, and in reducing atmosphere, the spectrum meets the real axis at very low frequencies. From fitting the high frequency arc with the circuit displayed in figure 1(b), we can determine grain and grain boundary conductivities (this time not normalised to the grain boundary width), shown in figure 7(b) and observe increased conductivity in reducing conditions. In literature, this increase is entirely explained by additional electronic conductivity, while the ionic conductivity is assumed to remain constant as long as the amount of oxygen vacancies is primarily defined by the extrinsic dopant concentration [5, 17].

Although the ionic grain boundary resistance is not experimentally accessible in mixed conductors, the width of the grain boundary can be determined from the capacitance of the grain boundary arc, even in reducing conditions, by using equation (2). The grain boundary width determined with this method is shown as a function of oxygen partial pressure in figure 8. The solid horizontal lines represent the grain boundary thicknesses determined in oxidising atmosphere. GDC5 has a larger grain boundary thickness, probably due to its lower grain boundary space charge density, which is (in air) proportional to $\left[\text{Gd}^{3+}\right]$ (equation (9)). For both, GDC5 and GDC10, the grain boundary thicknesses decrease in reducing atmospheres. This result gives a first hint that the ionic grain boundary properties also depend on the oxygen partial pressure, which we experimentally verify in the following section.

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**Figure 7.** (a) Oxygen partial pressure dependent grain and grain boundary conductivities of a GDC10 thin film at 227 °C. (b) In-plane impedance spectra in oxidising and reducing atmospheres.

**Figure 8.** Grain boundary width of GDC5 and GDC10, calculated from the grain boundary capacitance. Symbols: reducing atmosphere, solid horizontal lines represent GB thickness in oxidising atmosphere.
3.2. Separation of ionic and electronic conductivity

At temperatures above 325 °C, grain and grain boundary impedances cannot be separated in thin films, because the dielectric relaxation of the grain arc is too fast to be resolved by the used impedance analyser, which measures not higher than 1 MHz. Nevertheless, we also get important information when we interpret the low frequency arc, which was not considered in the dielectric grain/grain boundary impedance modelling. A set of spectra recorded in different atmospheres at 370 °C is shown in figure 9(b). In the equivalent circuit model and further discussion, only the strongly pO₂ dependent low frequency arc, with a peak frequency of ~ few Hz is considered. Therefore, the high frequency axis intercept corresponds to the total conductivity of the film. When low frequency or DC current is applied, oxygen anions and electrons move with the electrical field. The electronic conductivity therefore scales with the low frequency real axis intercept and ionic in-plane conductivities. In oxidising atmosphere (N₂ + 100 ppm O₂) the electronic conductivity is almost zero, so the low frequency arc becomes very large. The equivalent circuit model of a mixed conductor between two metallic electrodes was already derived in literature [6, 48] and can be sketched as a transmission line shown in figure 9(a). Ion blocking electrodes are usually modelled with a capacitor that represents the double-layer capacitance at the interface [48]. Due to the in-plane geometry of the used electrodes, however, an ‘open Warburg’ impedance [49] better describes the actual situation as already elaborated in [40]. Although the circuit model appears complex, it has an analytical impedance function [6] and only 4 free fit parameters. The applicability of this circuit model to separate electron and ion conduction in thin films was already successfully proven for Fe-doped SrTiO₃ thin films in [40].

In figure 9(b), the solid lines represent the fit of the equivalent circuit fit and symbols are measured data. Already the very good fit with only four parameters indicates that the circuit model is appropriate. In addition to electronic and ionic conductivities, the equivalent circuit fit delivers the chemical capacitance of the GDC film, which contains information on the concentration of Ce³⁺ ions [50, 51]. It is worth noting that the circuit model is only appropriate when the rate of electrochemically driven oxygen exchange at the GDC surface is much lower than the current carried by electronic and ionic charge carriers. The validity of this assumption can be checked by geometric variations: when the distance between the electrode fingers is increased, the surface area for electrochemical oxygen exchange increases, thus increasing the surface exchange current, while ionic and electronic currents decrease, due to the lower applied electric field. Therefore, the assumption of ion blocking electrodes is only valid up to a certain electrode distance, and typically photolithographic electrode patterning is required to achieve sufficiently small distances. In order to prove that our electrode fulfil this condition, we measured spectra for different electrode distances of 5, 15 and 30 μm. In figure 10(a), such geometry normalised impedance spectra are shown. The corresponding fit values are plotted in figure 10(b) as a function of the electrode distance, and no systematic dependence of electrode finger separation on electronic and ionic conductivity as well as chemical capacitance can be found. Consequently, we then can experimentally confirm the assumption of negligible electrochemical oxygen exchange current at the surface. Therefore, we can reliably measure electronic and ionic conductivities of mixed conducting GDC thin films. This analysis of both conductivities was performed over a broad temperature range from 250 °C up to 600 °C, and in gas mixtures of either N₂ + 100 ppm O₂ or dilute H₂ + H₂O mixtures in Argon, with H₂:H₂O ratios of 20:1 to 1:15. In the
oxidising atmosphere, only the total ionic conductivity is measured (without grain/grain boundary separation due to too high temperature), whereas in reducing gas mixtures, ionic and electronic conductivities as well as chemical capacitance can be determined.

The results of these measurements are summarised in figure 11 for three selected temperatures. The electronic conductivity (squares) is relatively independent of the dopant concentration and increases in more reducing conditions, due to the increased concentration of electronic charge carriers. This behaviour is well known in literature [5, 17]. Please note, that electronic charge carriers in ceria are localised around Ce ions in form of small polarons. In literature, the notations $e^\prime$, Ce$^{3+}$ and Ce$^{4+}$ represent the same defect for this material. Also the chemical capacitance is a measure for the Ce$^{3+}$ concentration [50, 51]. Therefore, also the increase of chemical capacitance in more reducing atmospheres is also in line with the literature defect chemical models [6, 50, 51]. In case of relatively small Ce$^{3+}$ concentrations, the model of doped bulk ceria predicts that chemical capacitance and electronic conductivity are proportional to $p(O_2)^{-0.25}$ [5, 51]. This power law is sketched by the black triangles in figure 11, and the data almost meet these slopes at 600 °C, but significant deviations are observed at lower temperature, especially for the chemical capacitance. Weakly $pO_2$ dependent chemical capacitance at low temperature and water rich gas compositions and was observed already in literature and was linked to Ce$^{3+}$ enrichment at surfaces and interfaces in GDC thin films [3, 51, 52]. These surfaces and interfaces therefore have an additional, weakly $pO_2$ and temperature dependent chemical capacitance [51, 52]. Since the deviations from ideal behaviour is moderate above 500 °C, we can still reasonably estimate the Ce$^{3+}$ content from the chemical capacitance according to [5, 6]

$$[\text{Ce}^{3+}] = \frac{C_{\text{chem}} \cdot k_B T}{V},$$

where $V$ is the sample volume, $k_B$, $T$ and $e$ are Boltzmann’s constant, temperature and elementary charge, respectively. From the chemical capacitance of the thin films we therefore yield a Ce$^{3+}$ concentration not exceeding 1% even for the highest temperature and most reducing atmosphere in the experiment, which is also in accordance with thermogravimetric measurements from literature [53, 54]. The concentration of oxygen vacancies in GDC bulk is derived from the charge neutrality condition as

$$[V_O] = \frac{1}{2} [\text{Gd}^{3+}] + \frac{1}{2} [\text{Ce}^{3+}].$$

Since the approximation $[\text{Gd}^{3+}] \gg [\text{Ce}^{3+}]$ is certainly the case in our measurement conditions, the bulk vacancy concentration and therefore the bulk ion conductivity can be regarded rather independent of the oxygen partial pressure. In contrast to this, the measured ion conductivity increases drastically in reducing atmosphere, especially for 5% Gd doping and low temperature, see figure 11(a), green stars versus horizontal green line. In these conditions, also the grain boundary resistance has the largest impact on the total ion conductivity. Therefore, this unexpected behaviour is very likely a grain boundary phenomenon. Although never directly observed before, such an increase of the grain boundary ion conductivity in reducing conditions is even a logical consequence of the grain boundary space charge model, as we show in the following.

### 3.3. Oxygen partial pressure dependent space charge in GDC grain boundaries

The shown measurement results can be consistently explained with the space charge model, which is elaborated in [18, 20]. In this model, the O:Ce ratio is below 2 in the grain boundary core, which causes a positive charge and electric potential $\Delta \Phi_{\text{core}}$ at the grain boundary core. The core potential is claimed to be in the range 0.2–0.4 V for
flourite type oxide ion conductors [18, 20, 47], and higher values are found for weakly acceptor doped ceria. The positive core charge also induces a negatively charged space charge zone, in which the local potential \( \Delta \phi_{gb} \) depends on the distance from the grain boundary core. In a nutshell, the grain boundary resistance decreases with higher dopant content, due to a narrower space charge zone of higher charge density. For the effect of the oxygen partial pressure, we argue that also accumulation of \( \text{Ce}^{3+} \) ions is an additional factor that causes a narrower space charge zone with a lower potential only in reducing atmospheres, where the \( \text{Ce}^{3+} \) concentration is large enough to have an effect. The space charge model works very well to explain the different conductivities at high and low oxygen partial pressures, because effects that complicate the quantitative analysis, such as defect interactions and accumulation of dopant ions near grain boundaries [18, 25], are independent of oxygen the partial pressure, and can therefore be regarded as constant error terms.

In a mathematical picture, we first have to consider the effect of the space charge potential on charged point defects, which is given by [18, 20]

\[
\frac{c_{gb}}{c_{bulk}} = \exp \left( -\frac{z\phi_{gb}}{k_B T} \right),
\]

where \( z \) is the relative charge of the defect (+2 for oxygen vacancies), \( c_{gb} \) and \( c_{bulk} \) are grain boundary and bulk defect concentrations, respectively. Therefore, oxygen vacancies are strongly depleted by orders of magnitude in the space charge zone, which is sketched in figure 12(a). When assuming that oxygen vacancy depletion in the space charge zone is the main factor influencing the grain boundary conductivity, the grain boundary potential and (averaged) conductivity are connected by the relation [20]

![Figure 11. Oxygen partial pressure dependent ionic conductivity, electronic conductivity and chemical capacitance of GDC5 (closed symbols) and GDC10 (open symbols) thin films at three different temperatures: (a) 370 °C, (b) 510 °C, (c) 600 °C. Horizontal lines represent the ion conductivities of GDC5 (green) and GDC10 (grey) in oxidising atmospheres.](image-url)
where \( z \) is the charge number of oxygen vacancies and \( \sigma_{\text{gb}} \) and \( \sigma_{\text{grain}} \) are grain boundary and grain conductivities. From our conductivity data we can calculate grain boundary potentials of 0.16 and 0.23 V for GDC10 and GDC5, respectively. These values are slightly below the literature value for polycrystalline GDC10 and GDC5 (0.32 and 0.34 V, respectively) [20]. This difference may originate from somewhat different atomic structures of grain boundary cores in sintered and vapour deposited films.

For understanding the effect of the oxygen partial pressure on the space charge potential, the total charge and charge densities have to be considered. The charge of grain boundary core plus space charge region must be zero, so the width of the low conductive grain boundary space charge region depends on its charge density and the grain boundary core charge, according to

\[
\rho_{\text{sc}}^0 d_{\text{gb}}^0 + \rho_{\text{core}}^A = 0.
\]  

Therein \( \rho_{\text{sc}}^0 \) is the volumetric space charge density in the space charge zone, \( \rho_{\text{core}}^A \) is the area-specific charge density in the grain boundary core, and \( d_{\text{gb}}^0 \) is the total width of the space charge zone, not including the grain boundary core. This equation is already an approximation, because the concentrations of \( \text{Gd}^{3+} \) and \( \text{Ce}^{3+} \) ions may vary within the space charge zone, which was already proven by TEM imaging for \( \text{Ge}^{3+} \) [15, 18]. However, for a semi-quantitative discussion that focuses on the difference between oxidising and reducing conditions, we can work with average concentrations. When we express the space charge density as a function of charged point defect concentrations, equation (7) is converted to

\[
\varepsilon [\text{Ce}^{3+}] + [\text{Gd}^{3+} - 2[\text{V}_{\text{O,sc}}]) d_{\text{gb}}^0 = 2\varepsilon [\text{V}_{\text{O,core}}]^A.
\]  

Oxygen vacancies in the grain boundary core have a weakly \( p(\text{O}_2) \) dependent concentration due to the atomic grain boundary structure, whereas the oxygen vacancy and \( \text{Ce}^{3+} \) concentration in the space charge zone varies. Due to the strong depletion of oxygen vacancies in the space charge zone, their concentration is typically neglected when calculating the space charge density [20]. By solving for the grain boundary space charge thickness, we yield then

\[
d_{\text{gb}}^0 = \frac{2[\text{V}_{\text{O,core}}]^A}{[\text{Ce}^{3+}] + [\text{Gd}^{3+}]}.
\]  

Within a homogeneously charged space charge zone, Poisson’s equation yields a parabolic potential that depends on the distance from the grain boundary core, reading

\[
\Delta \phi_{\text{gb}}(x) = \left( x - \frac{d_{\text{gb}}^0}{2} \right)^2 \frac{\varepsilon [\text{Ce}^{3+}] + [\text{Gd}^{3+}]}{2\varepsilon\varepsilon_0}.
\]
Therein $\Delta \phi_{gb}(x)$ is the electric potential, and the position $x$ is zero in the grain boundary core. At $x = 0$ we therefore get

$$
\Delta \phi_{\text{core}} = \frac{e (\{V_{0, \text{core}}\}^4)}{2 \varepsilon_0 \varepsilon (\{Ce_{3+}\} + \{Gd_{3+}\})}, \tag{11}
$$

where $\Delta \phi_{\text{core}}$ is the potential perturbation at the grain boundary core (which is assumed to be very thin).

From this equation we can see that a higher space charge density, either realised through higher doping levels or accumulation of $Ce^{3+}$ ions decreases the potential and hence increases the conductivity of the grain boundary space charge. $Ce^{3+}$ ions are strongly accumulated in the space charge zone, due to their relative negative charge (equation (5)). Therefore, accumulation of $Ce^{3+}$, especially in reducing atmospheres, is very likely to increase the grain boundary conductivity.

Defect concentrations in the space charge zone are in figure 12 for (a) oxidising and (b) reducing conditions. In the reducing conditions, the $Ce^{3+}$ concentration, which scales with $p(O_2)^{-0.25}$ in the bulk, is much higher. The additional $Ce^{3+}$ concentration increase in the grain boundaries results in a significantly higher grain boundary space charge density, and therefore a lower potential, which explains the strong increase in ion conductivity observed in (figure 11). Another consequence of the space charge model is that the changes in the grain boundary conductivity are stronger for systems with lower doping. This is also observed for our thin films (compare GDC5 and GDC 10 in figure 11), which further supports the validity of our interpretation. Due to the exponential dependence, decreasing the core potential by 70 mV is sufficient for the observed factor 10 increase in ionic conductivity for GDC5 at 370°C. Since we cannot separately measure the ionic grain boundary conductivity in mixed conductors, the lowering of the space charge potential is observed as an increase of the total ionic conductivity.

The defect chemistry of bulk Gd-doped ceria is well investigated [51, 55, 56], and for low $Ce^{5+}$ concentration, a $p(O_2)^{-0.25}$ dependence of the $Ce^{3+}$ concentration is found. When going from oxidising to reducing atmospheres, the $p(O_2)$ changes by roughly 32 orders of magnitude, which causes an 8 orders of magnitude increase in the bulk $Ce^{3+}$ concentration. Still, literature measurements and our evaluation of the chemical capacitance give an estimate of 0.1% $Ce^{3+}$ in the bulk at 370°C and $p(O_2) = 10^{-36}$ bar. With a space charge potential of only 230 mV, as calculated by equation (6) for the GDC5 film, the concentration of $Ce^{3+}$ in the grain boundary is 60 times higher than in the bulk. This enhancement is sufficient to make the $Ce^{3+}$ concentration comparable to the extrinsic $Gd^{3+}$ concentration in the grain boundary, and so an increased space charge density and decreased grain boundary potential is even expected, according to equation (10). Thus, taking into account the well investigated GDC bulk defect chemistry, increased grain boundary conductivity in reducing atmospheres is an almost necessary consequence of the space charge model. Although the effects of doping, temperature and atmosphere are well explained by the space charge model, a mathematically exact grain boundary model is far from trivial. In addition to the electrostatic effect, also Gd accumulation, local lattice distortions and strain near grain boundaries may change the oxide ion mobility and $Ce$ reduction enthalpy [3, 27, 57]. Such effects are, however, out of the scope of the present study, and shall just highlight that the mathematical description of the grain boundary space charge works excellently on a semi-quantitative level, but exact numbers should be taken with care.

Although such a grain boundary related increase of ionic conductivity and decrease of the grain boundary width in reducing atmosphere was never clearly observed and interpreted before in GDC, it is actually a necessary consequence from the space charge model. The results on our GDC thin films thus add a further puzzle piece to the verification of the space charge model in mixed conducting oxides. Moreover, we have preliminary data that this effect is not restricted to thin films, but will probably also occur in polycrystalline sintered materials such as technologically used catalysts or anodes for solid oxide fuel cells.

4. Conclusions

Impedance spectroscopic measurements of the in-plane conductivity in GDC thin films on Sapphire substrates were performed with careful equivalent circuit fitting. A key experimental feature was electrical contacting by photolithographically patterned thin film electrodes with interdigitating finger shape and a small electrode separation of 5 μm. This advanced electrode geometry allowed the determination of the in-plane grain boundary impedance, as well as simultaneous measurement of ionic and electronic conductivities and $Ce^{3+}$ content in reducing atmospheres. From these measurements, we could show that:

1. Grain and grain boundary conductivities in 5 and 10 mol % Gd doped $CeO_2$ can be separated by impedance spectroscopy, if a proper electrode design and equivalent circuit model are used. The lower ionic conductivity of the GDC5 films is in accordance with literature, and explained by lower grain boundary
conductivity, while the grain interior conductivity is almost equal. Compared to sintered polycrystals of high purity, the specific grain boundary conductivity in GDC thin films is about ten times higher, while grain interior conductivities are almost equal.

(2) Under reducing conditions, where GDC becomes mixed conducting, the used electrodes are reversible for electrons and virtually blocking for oxide ions. From evaluating the low frequency ‘electrode arc’ of the impedance spectrum, separation of electronic and ionic conductivities as a function of oxygen partial pressure becomes possible. Due to the high acceptor doping, the bulk oxygen vacancy concentration changes negligibly in reducing atmospheres. Nevertheless the ionic conductivity of GDC5 increases by a factor of 10 when switching from oxidising to reducing atmospheres. Consequently, this increase must be a grain boundary effect.

(3) The higher ionic conductivity in reducing atmosphere is in line with the space charge model of the grain boundary resistance: The grain boundary core is positively charged, causing an oxygen vacancy depleted and Ce\(^{3+}\) enriched space charge zone around the grain boundary. Due to the space charge potential, Ce\(^{3+}\) is accumulated in the space charge zone, and in reducing conditions the grain boundary Ce\(^{3+}\) concentration can become comparable to or higher than extrinsic Gd\(^{3+}\) doping. This accumulation increases the space charge density, which causes a strong decrease of the space charge potential and therefore significantly lower ionic grain boundary resistance.

The obtained results are highly relevant for completing our knowledge on space charges at interfaces and grain boundaries of mixed conducting oxides. We could show that the ionic grain boundary resistance of acceptor doped ceria not only depends on temperature, doping and purity, but also on the oxygen partial pressure. From an application point of view, these results improve the current understanding of the electrochemical behaviour of GDC containing electrolytes and anodes for solid oxide fuel cells as well as ceria-based redox catalysts. Therefore, determination of the conductivity of GDC ceramics in oxidising atmosphere does not necessarily reflect the real ionic conductivity in the often reducing operating conditions. In addition, it is worth mentioning that analogous behaviour is anticipated in other mixed conducting materials with ion blocking grain boundaries, that are used e.g. in resistive switches and novel memory devices.

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