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Space–charge theory applied to the grain boundary impedance of proton conducting BaZr$_{0.9}$Y$_{0.1}$O$_3$ – δ

Christian Kjølseth a, Harald Fjeld a, Øystein Prytz b, Paul Inge Dahl c,1, Claude Estournès d, Reidar Haugsrud a, Truls Norby a,*

a Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, FERMI0, Gaustadalleen 21, NO-0349 Oslo, Norway
b Department of Physics, University of Oslo, POB 1048 Blindern, NO-0316, Oslo, Norway
c Department of Materials Technology, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway
d CNRS, Institut Carnot Cirimat and Plateforme Nationale de Frittage Flash (PNF2-CNRS), F-31062 Toulouse Cedex 09, France

A B S T R A C T

The specific grain interior and grain boundary conductivities, obtained from impedance spectroscopy and the brick layer model, are reported for BaZr$_{0.9}$Y$_{0.1}$O$_{3−δ}$ as a function of $p_\text{O}_2$ and temperature. $p_\text{O}_2$-dependencies were indicative of dominating ionic and p-type electronic conduction for the grain interior under reducing and oxidizing conditions, respectively, while the grain boundaries showed an additional n-type electronic contribution under reducing conditions. Transmission electron microscopy revealed enrichment of Y in the grain boundary region. These findings indicate the existence of space–charge layers in the grain boundaries. A grain boundary core–space–charge layer model is therefore applied to interpret the data. Using a Mott–Schottky approximation, a Schottky barrier height of 0.5–0.6 V and an effective grain boundary width of 8–10 nm (= 2× space–charge layer thickness) is obtained at 250 °C in wet oxygen. Finite-element modelling of the complex impedance over a grain boundary with a space–charge layer depletion of protons yields a distorted semicircle as observed in the impedance spectra.

1. Introduction

High electrical resistance in the grain boundaries is observed for several types of conductors such as the oxide ion conducting Y-doped ZrO$_2$ (YSZ) [1] and Gd-doped CeO$_2$ (CGO) [2], the mixed electron-oxide ion conducting Fe-doped SrTiO$_3$ [3] and the proton conducting Gd-doped BaCeO$_3$ [4], Y-doped BaZrO$_3$ [5,6] and Ca-doped LaNbO$_4$ [7]. BaZr$_{0.9}$Y$_{0.1}$O$_3$ – δ has one of the highest reported grain interior proton conductivities of the perovskite oxides, 6.5 × 10$^{-3}$ S cm$^{-1}$ in wet air at 600 °C [5] and a better chemical and mechanical stability than the corresponding barium and strontium cerates [8] under conditions with acidic gas impurities, e.g. CO$_2$. Possible applications as electrolyte in fuel cells and steam electrolysers may however be limited because of dominating grain boundary resistance.

The high grain boundary resistance in ionic conductors has commonly been attributed to highly resistive or blocking impurity phases at the grain boundaries. However, studies on high-purity materials have shown that there also exists an intrinsic grain boundary resistance in high-purity materials. Both extrinsic and intrinsic grain boundary resistances have been thoroughly investigated for oxide ion conductors [9–16], but for proton conductors little has been reported so far, see for instance [17,18]. In the present work we study the grain boundary resistance of BaZr$_{0.9}$Y$_{0.1}$O$_{3−δ}$ samples sintered for oxide ion conductors [1,14,19,20] using BaZr$_{0.9}$Y$_{0.1}$O$_{3−δ}$ applying models for the intrinsic grain boundary properties used for oxide ion conductors [1,14,19,20] and limitations of the BLM have been elaborated by Fleig et al. [21,22], treating effects such as constricted current paths from imperfect contacts between the grains and influence of inhomogeneous microstructures on the analysis of grain boundary impedances. The
present work discusses the influence of such deviations on the complex impedance.

Investigations of the intrinsic grain boundary conductivity of nominally impurity-free oxide ion conductors have given indications on the existence of space–charge layers which govern the grain boundary resistance. In the present work we apply similar approaches to evaluate the role and properties of space–charge layers in the grain boundaries of proton conducting ceramics, with BaZr$_{0.9}$Y$_{0.1}$O$_3$ as the experimental example.

2. Grain boundary core–space–charge layer model

The intrinsic grain boundary properties of the oxide ion conductors Y-doped ZrO$_2$ (YSZ) and Gd-doped CeO$_2$ (CGO) have been successfully interpreted by a grain boundary core–space–charge layer model [14,23–26]. A general solution of the space–charge theory has been given by Kim et al. [25] in which the case for singly charged carriers such as protons is included. The model describes a grain boundary in electrical terms as consisting of a core with two adjacent space–charge layers as depicted in Fig. 1. For these oxide ion conductors, it has been observed experimentally that divalent and pentavalent solutes are enriched in the grain boundary zone and not only in the grain boundary core, while there is no enrichment of tetra- and pentavalent solutes. This indicates a positive grain boundary core with adjacent negative space–charge layers [27], in which the enrichment of the lower-valent solutes makes up part of the net negative charge of the space–charge layer. The charge of the core was concluded to be an inherent materials property. Likewise, segregation of acceptor solutes in the grain boundaries has been observed for proton conductors in BaZr$_{0.85}$Y$_{0.15}$O$_3$ [28], which as for the oxide ion conductors indicates that the grain boundary core is positive and the space–charge layers negative.

In the following we will derive the grain boundary core–space charge model for the case of proton conductors. The important factor governing the defect concentration profile in the space–charge layer is the electrochemical potential of the defect through the grain boundary and grain interior. First we define the intercept between the grain boundary core and the space–charge layer, shown in Fig. 1, as position $x = 0$ and the grain interior as $x = \infty$. The electrochemical potential of a mobile proton as a function of distance $x$, is then ideally (assuming unity activity coefficient) given by

$$\eta_H^e(x) = \mu_H^0 + k_B T \ln c_H^e(x) + e \varphi(x)$$

where $\mu_H^0$ is the standard chemical potential of protons, $c_H^e(x)$ the proton concentration, $\varphi(x)$ the electrostatic potential, and $e$, $k_B$ and $T$ have their usual meanings. In the grain interior, the electrochemical potential of the proton is then given by

$$\eta_H^e(\infty) = \mu_H^0 + k_B T \ln c_H^e(\infty) + e \varphi(\infty).$$

At equilibrium, where $\eta_H^e(x) = \eta_H^e(\infty)$, the difference in electrostatic potential relative to grain interior, $\Delta \varphi(x) = \varphi(x) - \varphi(\infty)$, is then

$$\Delta \varphi(x) = \frac{k_B T}{e} \ln \frac{c_H^e(\infty)}{c_H^e(x)}$$

and, consequently,

$$\frac{c_H^e(x)}{c_H^e(\infty)} = \exp \left( - \frac{e \Delta \varphi(x)}{k_B T} \right).$$

From the Poisson equation we have

$$\frac{d^2 \Delta \varphi(x)}{dx^2} = -\frac{1}{\varepsilon} Q(x),$$

where $\varepsilon$ is the dielectric constant and $Q(x)$ the net charge density in the space–charge layer.

Onwards we assume that temperatures and water vapour pressures are such that protons are the dominating positive charge compensating defect. If we consider that protons are strongly depleted in the negative space–charge layer, the net charge density, $Q(x)$, can be considered to be governed only by the acceptor concentration:

$$Q(x) = e[c_H^e(x) - c_Y^e(x)] \approx -e c_Y^e(x).$$

At temperatures where cations can be considered frozen-in, we can apply the Mott–Schottky approximation, which assumes that the

Fig. 1. Schematic grain boundary consisting of a positive core charge compensated by two adjacent space–charge layers. Values of $x$ are defined such that $x = 0$ at the interface between the space–charge layer and the grain boundary core, while far into the grain interior $x = \infty$. The dotted lines represent concentration profiles in the space–charge layer for the protons and the acceptor dopant under the Mott–Schottky approximation, while the unbroken line represents the potential profile. The Schottky barrier height potential difference is also indicated.
speciﬁcally, and in order to approach this we address the ratio of the interior, and is called the Schottky barrier height. It can be calculated from the intercept between core and space-charge layer, relative to grain size. The grain boundary conductivity \( \sigma \) and the effective space-charge layer width, \( \lambda^* \) (Fig. 1) as

\[
\lambda^* = 2 L_0 \left( \frac{e\Delta \psi(0)}{k_B T} \right)^{\frac{1}{2}} \left( \frac{2 \varepsilon c \psi(\infty)}{k_B T} \right)^{\frac{1}{2}},
\]

one can derive an expression for the normalized proton concentration, in the space-charge layer at position \( x \) (Fig. 1),

\[
\frac{c_{fi}(x)}{c_{fi}(\infty)} = \exp \left[ -\frac{1}{4} \left( \frac{x - \lambda^*}{L_0} \right)^2 \right].
\]

For \( x > \lambda^* \), we obviously have \( \frac{c_{fi}(x)}{c_{fi}(\infty)} = 1 \).

The term \( \Delta \psi(0) = \psi(0) - \psi(\infty) \) in Eq. (9) is the potential at the intercept between core and space-charge layer, relative to grain interior, and is called the Schottky barrier height. It can be calculated numerically, and in order to approach this we address the ratio of the specific proton conductivity \( \sigma_{gi} \) in the grain interior and the experimentally accessible effective apparent specific proton conductivity \( \sigma_{gb} \) (hereby denoted only as the grain boundary conductivity) in the space-charge layer of the grain boundary. The local proton conductivity in the grain boundary region depends on the distance from the core. The grain boundary conductivity \( \sigma_{gb} \) is therefore the effective property for the entire boundary obtained from integrating the resistance over the thickness of the boundary. Assuming equal mobility of protons in the grain interior and in the grain boundaries, the concentrations in Eq. (4) can be substituted with specific conductivities through the relation \( c_{fi} = c_{gb} \rho \). In order to obtain an expression containing apparent effective grain boundary conductivity over the entire space-charge layer, we first invert Eq. (4) and, in turn, invert the grain boundary conductivity into resistivity,

\[
\frac{c_{fi}(x)}{c_{fi}(\infty)} = \frac{\sigma_{gi}(x)}{\rho(x)} = \sigma_{gb}(x) = \exp \left( \frac{e\Delta \psi(x)}{k_B T} \right).
\]

where \( \sigma(x) \) and \( \rho(x) \) are the proton conductivity and resistivity, respectively, at position \( x \) in the space-charge layer. In order to get the apparent effective specific resistivity over the whole space-charge layer thickness we integrate and divide by its thickness to remain with a specific value:

\[
\frac{\sigma_{gb}}{\sigma_{gb}} = \frac{\sigma_{gb}(x) dx}{1} = \frac{1}{N_0} e^{x} \exp \left( \frac{e\Delta \psi(x)}{k_B T} \right) dx.
\]

We substitute to get an expression for \( \Delta \psi(x) \) and assume a Mott–Schottky approximation. The further derivation has been shown in [12], and gives the following solution for the case of proton conduction:

\[
\frac{\sigma_{gb}}{\sigma_{gb}} = \frac{\exp \left( \frac{e\Delta \psi(0)}{k_B T} \right)}{\exp \left( \frac{e\Delta \psi(0) - e\Delta \psi(\infty)}{k_B T} \right)}.
\]

For each of the specific grain interior and grain boundary conductivities we can derive activation energies through \( E_A = -\frac{\partial \ln \sigma}{\partial (1/T)} \). The difference in grain interior and grain boundary activation energy can, through differentiating Eq. (13), be obtained as:

\[
E_{A,gb} - E_{A,gi} = \frac{(e\Delta \psi(0) - k_B T)}{1 + \frac{d \Delta \psi(0)}{d (1/T)}}.
\]

From this we see that the activation energy of the grain boundary conductivity, \( E_{A,gb} \), has a contribution from the mobility, i.e., \( E_{A,gb} \) and terms that are related to the variation of the concentration of charge carriers in the space–charge layer. These terms contain both the Schottky barrier height itself and the temperature dependence of the Schottky barrier height.

3. Experimental

BaZr2Y3O12–x powder was produced by spray-pyrolysis according to a method described elsewhere [29] with starting materials Ba(NO3)2, ZrO(NO3)2·3H2O and Y(NO3)3·6H2O. A sample denoted BZY10-HP was sintered by uni-axial hot pressing (HP) at 1650 °C for 1 h under 50 MPa while the sample denoted BZY10-SPS was sintered in a carbon die by spark plasma sintering (SPS), at 1600 °C for 5 min under 100 MPa in vacuum. Both sintering methods yielded relative densities > 95%. The very short sintering time enabled by SPS was intended to prevent possible evaporation of BaO. After SPS, the disc was annealed in air at 700 °C for 2 h to remove surface contamination of carbon. Following sintering, the samples were investigated by scanning electron microscopy (FEG-SEM, FEI Quanta 200 with energy dispersive X-ray spectroscopy (EDS, EDAX)) without detecting any sign of impurities. After electrical measurements, the samples were investigated with respect to microstructure and impurities by transmission electron microscopy (TEM, JEOL 2010F with EDS (Noran Vantage DI+)). Neither the grain interior nor grain boundaries showed any sign of impurities, as investigated by means of EDS with a spot size of about 5 nm. However, the EDS analysis revealed a higher concentration of dopant in the grain boundary region compared to the grain interior. Based on TEM characterization, Fig. 2a, the grain size of BZY10-HP was estimated to be 280 nm, while that of BZY10-SPS, Fig. 2b, is bimodal showing grain sizes mostly above ~450 nm and below ~50 nm.

The thicknesses of the samples were 1.85 mm for BZY10-SPS and 2.55 mm for BZY10-HP. Circular Pt electrodes of diameter ~1 cm were attached to each side of the specimens by ﬁrst painting one layer with Pt ink (Metalor, Pt A3788A) and then adding a Pt net, followed by painting of 3 new layers of ink. To burn off the residual organic from the Pt ink the samples were annealed at 1000 °C for 1 hour. Finally, the samples were mounted in a ProboStat™ (NorECs, Norway) measurement cell for electrical characterization, using 4 wires connected in pairs to the two electrodes.

Electrical characterization was performed in the frequency range 10 MHz to 0.1 Hz, with an oscillation voltage of 0.5 V RMS, using a Novocontrol alpha-A impedance spectrometer with a Z4G interface. This was done as a function of the oxygen partial pressure, which was controlled by mixing of O2, Ar, and H2O for oxidizing conditions, and
order to have reproducible oxygen activities in the \( \text{H}_2 + \text{H}_2\text{O} \) mixtures at the measurement partial pressures reported under reducing conditions are the 300\(^\circ\)/h to the temperature of measurements (at or below 300 \(^\circ\)C). The samples were in our study equilibrated at 700 \(^\circ\)C and then cooled at the size of BZY10-HP showing a relatively homogeneous grain structure with grain size of ∼280 nm, and b) of BZY10-SPS showing a bimodal grain size distribution with grain size of ∼450 and ∼50 nm.

\( \text{H}_2, \text{Ar}, \text{and H}_2\text{O} \) for reducing conditions. The water vapour partial pressure in wet gases was fixed by bubbling the gas mixture first through de-ionized water and then through a saturated KBr solution, both at room temperature, yielding 80% relative humidity.

Measurement temperatures were chosen so that impedance spectra showed both the grain interior and grain boundary arcs in a Nyquist plot, as parameters for the grain interior arc is a prerequisite to calculate specific grain boundary conductivities through the BLM [4]. These temperatures were typically between 150 and 300 \(^\circ\)C. The impedance spectra were deconvoluted using the “EqC for Windows” software [30] yielding capacitance and conductance parameters for both grain interior and grain boundaries.

The slow kinetics in the temperature regime for measurements lead to “frozen-in” conditions as seen in studies by Bohn and Schober [5,8] in which thermogravimetry of Ba\( \text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{3} \) showed that protons are “frozen-in” below ∼300 \(^\circ\)C and that the material by heating in dry surroundings dehydrates only above ∼300–350 \(^\circ\)C. In order to have reproducible “frozen-in” concentration of defects, the samples were in our study equilibrated at 700 \(^\circ\)C and then cooled at 300\(^\circ\)/h to the temperature of measurements (at or below 300 \(^\circ\)C). The oxygen partial pressures reported under reducing conditions are the oxygen activities in the \( \text{H}_2 + \text{H}_2\text{O} \) mixtures at the measurement temperature. This represents a coarse approximation since the defect situation freezes at a higher temperature, but trends in the oxygen activity dependence should still be valid. With respect to hydration, the data should represent a stable (frozen-in) defect situation corresponding to higher temperatures, with a somewhat lower proton concentration than the equilibrium concentration at the actual temperature of the measurement. This “frozen-in” state is mainly a result of the low mobility of oxygen vacancies; as they are considerably slower than protons and limit the chemical diffusion of water needed to reach equilibrium. The difference in mobility also allows us to assume that the material is mainly a proton conductor in the measured temperature range. Finally, it may be noticed that we later on will assume that protons may redistribute in and close to the space-charge layer as a function of temperature in the otherwise “frozen-in” temperature regime.

4. Results and discussion

4.1. Considerations on deconvolution of impedance spectra

Fig. 3 shows Nyquist plots of impedance spectra for (a) BZY10-SPS in wet hydrogen at 250 \(^\circ\)C, (b) BZY10-SPS in wet oxygen at 250 \(^\circ\)C and (c) BZY10-HP in wet oxygen at 350 \(^\circ\)C. For BZY10-SPS under reducing conditions (a) it is possible to see a small grain interior contribution at high frequencies followed by the grain boundary and electrode responses at lower frequencies. Also under oxidizing conditions, a small grain interior contribution is observed (b-I), which is magnified in (b-II) and showing a well-defined semicircle. The same features are observed for BZY10-HP showing the dominant grain boundary semicircle (c-I) and the magnified high frequency part showing the grain interior semicircle (c-II).

All the impedance spectra were deconvoluted after subtraction of a parasitic parallel capacitance, \( C_{\text{par}} \), originating from the measurement setup. The equivalent circuit used for the deconvolution is shown in Fig. 4. The samples’ relative dielectric constants, calculated from the grain interior capacitance, are fairly constant with temperature and estimated to ∼90 for BZY10-HP and ∼70 for BZY10-SPS. The values are somewhat larger than the value 46 reported for BZY20 by Babilo et al. [31]. Due to a distortion in the grain boundary semicircle observed for both specimens, this semicircle was deconvoluted with two (RG) sub-circuit elements, as shown in Fig. 4, reflecting the possibility of two grain boundary series contributions to the impedance. Distortions in the grain boundary semicircle have been observed also for other polycrystalline materials and suggested to reflect that there are inhomogeneities in terms of microstructure or composition [32]. In BZY10-SPS the non-uniform grain size distribution, as observed in Fig. 2, can be the origin of the distortion, resulting from a frequency dependence of the current paths as shown by a finite-element study by Fleig [33]. In our BZY10-HP sample the microstructure is however more uniform, but we still see a distorted grain boundary semicircle. This therefore suggests that the distortion may have other origins or contributions.

To investigate whether the distortion in fact can originate from the existence of space-charge layers we have simulated (using ZView, Scribner Associates Inc.) an impedance spectrum based on a series of space-charge layer elements through the boundary. The simulated spectrum, presented in Fig. 5, is based on normalized defect concentrations in the space-charge layer profile and on the grain interior conductivity from the BZY10-HP sample at 250 \(^\circ\)C in wet O\(_2\). The space-charge layer defect profile will be discussed later on. The impedance of the grain boundary was derived as a series of apparent resistivities (using the BLM backwards) representing finite parts of the space-charge layer profile, \( R_{\text{gb}} \), each in parallel with a capacitance, \( C_{\text{gb}} \), which was held constant at the value from the deconvoluted experimental spectrum. Finally, the grain interior impedance from the original spectrum was added in the total simulation. As can be seen in Fig. 5 the simulated arc is somewhat smaller than the experimental one, due to the use of a predetermined set of parameters chosen for the modelling, instead of fitting them to the experimental spectrum. These parameters include the doping concentration, the Schottky barrier height and the relative dielectric constant. A spectrum simulated with an effective dopant concentration of 7.5% fits better to the experimental spectrum, see Fig. 5. A somewhat lower dopant concentration has indeed been indicated by EDS analyses. Regardless of the exact magnitude of the arcs, the simulated spectra are seen to exhibit a clear distortion similar to the experimental
spectrum. Based on a simple fractal model, Branković et al. [34] showed that the existence of an inhomogeneous distribution of charge carriers in the vicinity of the grain boundary core results in a similarly distorted grain boundary arc. We conclude therefore that the distortion in the grain boundary arc for both the BZY10-SPS and BZY10-HP sample can originate from the distribution of impedance over the space–charge layers adjacent to a charged grain boundary core.

4.2. Yttrium distribution

Elemental distributions of Ba, Zr and Y in the grain interior and grain boundaries were investigated by TEM EDS spot analysis with a spot size of ~5 nm. In both samples the concentration of yttrium was higher in the grain boundaries compared to the grain interior as shown by the Y/Zr ratio reported in Table 1. A similar observation was made by Groß et al. [28] on BaZr_{0.85}Y_{0.15}O_{2.925}. Yttrium can segregate into the grain boundary core because of elastic strain due to the size mismatch of the cations (1.01 Å for Y^{3+} and 0.84 Å for Zr^{4+}). This would counteract the positive charge of the core. However, an increase in yttrium concentration at the grain boundary region is also in agreement with the overall picture that defects with effectively negative charge such as YZr accumulate in the space–charge layers to compensate the effectively positive core. This would counteract the depletion of protons. Here, we recall that the cation distribution

![Fig. 3. Nyquist plots of a) BZY10-SPS under wet H2 at 250 °C where the grain interior, grain boundary and electrode arcs are visible, b-I) BZY10-SPS under wet O2 at 250 °C where the grain interior and grain boundary arcs are visible, b-II) high frequency range of b-I which magnifies the grain interior arc, c-I) BZY10-HP under wet O2 at 350 °C showing a distorted grain boundary arc, and c-II) high frequency range of c-I magnifying the grain interior arc.](image1)

![Fig. 4. Schematic equivalent circuit used for deconvoluting the impedance spectra. See text for details.](image2)

![Fig. 5. Nyquist plot consisting of two simulated impedance spectra, with effective dopant concentrations of 10 and 7.5% and a spectrum obtained from the BZY10-HP sample at 250 °C in wet O2. Only the grain boundary response is shown. See text for details.](image3)
profile is “frozen-in” below 1000 °C, the profile has most probably been set during sintering. Based on accumulation of acceptor dopants both in the grain boundary core and space-charge layers, it becomes apparent that one may decrease the grain boundary resistance by increasing the dopant concentration. This has been shown for CeO2 doped with various amounts of Y2O3 [20]. Indications of similar behaviour for Y-doped BaZrO3 will be discussed later.

4.3. $p_{O_2}$ dependencies

Fig. 6 shows the $p_{O_2}$-dependencies of the specific grain interior and grain boundary conductivity BZY10-SPS at 250 °C. Under oxidizing conditions protons dominate the conductivity, and the conductivity is thus independent of $p_{O_2}$. Under reducing conditions, the grain interior conductivity is independent of $p_{O_2}$, reflecting dominating ionic conduction, whereas the grain boundary conductivity increases weakly with decreasing $p_{O_2}$, indicating mixed ionic and n-type electronic conduction. The difference between grain interior and grain boundary conductivity under reducing conditions may be attributed to an accumulation of electrons in the space-charge layer due to a positive grain boundary core. A similar accumulation of electrons under reducing conditions has been demonstrated for acceptor doped CeO2 [20].

4.4. Schottky barrier heights

Calculated Schottky barrier heights are given in Table 2. The observed difference in Schottky barrier height under wet conditions of ~0.1 V between BZY10-HP and BZY10-SPS reflects most probably the sensitivity of sample preparation of BZY which has been shown to give variations in the electrical properties (see e.g. overview by Babilo et al. [31]).

If the grain boundary core and the dopant concentration are constant and we assume a Mott–Schottky approximation, the Schottky barrier height, $\Delta \varphi(0)$ and the space–charge layer width, $\lambda$, should be independent of type of charge carrier. If we furthermore assume that the grain boundary core is unchanged going from wet to dry conditions, $\Delta \varphi(0)$ should be constant as a function of water vapour pressure. In Table 2 we see however that $\Delta \varphi(0)$ comes out smaller under dry compared to wet conditions (the analysis assumes that oxygen vacancies dominate under dry and protons under wet conditions). If oxygen vacancies do not dominate, and instead protons or electron holes dominate under dry conditions, the calculated $\Delta \varphi(0)$ would be 0.41 V, closer to, but still lower than that calculated under wet conditions, 0.50 V. A difference in $\Delta \varphi(0)$ and $\Delta \varphi(\lambda)$ may therefore instead originate from a change in the core charge. The following possible hydration reaction of the core is suggested (in Kröger–Vink notation):

$$H_2O(g) + V^\circ_{O_2} + 2O^\circ_{core} = O_{O_2}^\circ + 2OH^\circ_{core}.$$  

If we assume that oxygen vacancies are stabilised in the grain boundary core in order to decrease its mismatch energy, these vacancies will not be easily filled, and grain interior vacancies are then selectively filled during hydration. For the protons from the dissolved water it is, however, probably favourable to settle in the grain boundary core where they can terminate mismatched oxygen ions and further contribute to a decrease of the mismatch energy. Such a grain boundary core hydration would explain the observed difference in Schottky barrier height under wet and dry conditions.

Table 2 shows estimated Schottky barrier heights based on specific grain interior and grain boundary conductivities reported by Duval et al. [35] on a BZY10 sample and by Babilo et al. [31] on a 20 mol% Y-doped BaZrO3 (BZY20). The latter conductivity data are re-plotted in Fig. 8. The scattering of the Schottky barrier height for the BZY10 samples reflects the variations of conductivity reported in literature due to differences in preparation. The lower Schottky barrier height of the BZY20 sample indicates a decreasing height with increasing dopant concentration, which is in accordance with results obtained for Y2O3-doped CeO2 [20].

Our values for the Schottky barrier height (Table 2) are comparable with values reported for 1 mol% Y2O3-doped CeO2 (~0.5 V) [20] and higher than those reported for 8 mol% Y2O3-substituted ZrO2 [1] (~0.3 V). The relatively large value of the Schottky barrier height is

### Table 1

<table>
<thead>
<tr>
<th>Grain interior (Y/Zr)</th>
<th>Grain boundary (Y/Zr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZY10-HP 0.10 ± 0.01</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td>BZY10-SPS 0.07 ± 0.01</td>
<td>0.13 ± 0.04</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>$\Delta \varphi(0)$ (V)</th>
<th>Activation energy, $E_a$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Grain interior</td>
</tr>
<tr>
<td>BZY10-HP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet O$_2$</td>
<td>0.62</td>
<td>47 (±1)</td>
</tr>
<tr>
<td>(550–200 °C)</td>
<td></td>
<td>(350–200 °C)</td>
</tr>
<tr>
<td>Dry O$_2$</td>
<td></td>
<td>45 (±1)</td>
</tr>
<tr>
<td>(500–150 °C)</td>
<td></td>
<td>(350–150 °C)</td>
</tr>
<tr>
<td>BZY10 Duval et al. [35]</td>
<td></td>
<td>72 (±2)</td>
</tr>
<tr>
<td>Wet O$_2$</td>
<td>0.46</td>
<td>(500–150 °C)</td>
</tr>
<tr>
<td>BZY20 Babilo et al. [31]</td>
<td></td>
<td>(300–150 °C)</td>
</tr>
<tr>
<td>Wet O$_2$</td>
<td>0.44</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Fig. 6. $p_{O_2}$-dependency of specific conductivities for BZY10-SP5 under wet conditions at 250 °C.
reflected in the dominating grain boundary resistance of Y-doped BaZrO$_3$.

A Schottky barrier height cannot be calculated from the total grain interior and grain boundary conductivities when different species dominate the grain interior and grain boundary conductivity (knowledge of the partial conductivities would be needed). This is the case for BZY10-SPS under reducing conditions, where it has an additional electronic contribution besides the protonic grain boundary conduction. It is, however, interesting to point out the difference between the grain interior and grain boundary conductivities under reducing and oxidizing conditions in Fig. 4. Under oxidizing conditions, the grain boundary conductivity is approximately 4 orders of magnitude below the grain interior conductivity, while the difference is only 2 orders of magnitude under reducing conditions. This difference may reflect an increased concentration of electrons in the space-charge layer as part of the accumulation of negative defects, and therefore indeed supports the existence of space-charge layers.

4.5. Defect concentration profile in the space-charge layer

In the temperature interval measured it is reasonable to assume that the acceptor dopant is “frozen-in”. If we, to a first approximation, assume that the yttrium concentration is uniformly distributed throughout the sample, the Mott–Schottky approach can, as discussed above, be applied. Fig. 7 shows normalized defect concentration profiles estimated at 200, 250 and 300 °C in wet oxygen based on conductivity data of BZY10-SPS. The data for BZY10-HP give analogous profiles (not included). The calculated space-charge layer widths for the two samples are 4.3 nm for BZY10-SPS and 4.0 nm for BZY10-HP, i.e., equal within experimental uncertainty. The normalized concentration of protons in the space-charge layer decreases with decreasing temperature (Eq. (10)), while the space-charge layer width is independent of temperature (Eq. (9)) taking into account the experimentally observed temperature independent Schottky barrier height. From this, one may conclude that it is only the temperature dependency of the Debye length that determines the change in the concentration profile with temperature. The Debye length has a $T^{1/2}$ dependence (Eq. (8)) and is furthermore dependent on the concentration of charge carriers, $c_p$, which is, however, assumed independent of temperature.

4.6. Activation energies

Activation energies of specific conductivities are given in Table 2. The activation energies for grain interior under wet conditions (i.e. for the proton mobility) are 47 (±1) kJ mol$^{-1}$ for BZY10-HP and 45 (±1) kJ mol$^{-1}$ for BZY10-SPS and the grain boundary activation energy for BZY10-SPS is 81 (±5) kJ mol$^{-1}$, and these are comparable with the grain interior activation energy, 45 (±1) kJ mol$^{-1}$, and the grain boundary activation energy, ~68 kJ mol$^{-1}$, reported by Bohn and Schober [5] in the same temperature interval. The higher grain boundary activation energy for BZY10-HP, 110 (±1) kJ mol$^{-1}$ is reflected in the higher Schottky barrier height calculated for this sample, as mentioned above.

4.7. Implications for overall conductivity

Available literature on substituted BaZrO$_3$ materials tends to report the total conductivity without delineation into grain interior and grain boundary conductivities (see e.g. [36–38]). Few have reported grain boundary specific conductivities or resistivities (see e.g. [31,35]) which are needed to compare grain boundary properties. Fig. 8 shows collected literature results on grain interior and specific grain boundary conductivities of acceptor doped BaZrO$_3$ compared with the samples measured in this work. The grain interior conductivities of BZY10 samples are in the same range, and deviations can probably be ascribed to the different sintering routes which lead to structural deviations as discussed by Azad et al. [39]. A higher

![Fig. 7. Normalized concentration of protons in the space-charge layer relative to the concentration in the grain interior calculated on basis of data from BZY10-SPS at 200, 250 and 300 °C.](image-url)
do not rotate.

5. Summary and conclusions

(1) Impedance spectroscopy was used to investigate the grain boundary electrical properties of 10% Y-doped BaZrO3. Spark plasma sintering (BZY10-SPS) and hot pressing (BZY10-HP) were applied to achieve reasonable densities without loss of barium. Specific grain boundary conductivities were obtained using the brick layer model.

(2) \( p_0 \)-dependencies for the BZY10-SPS sample were indicative of proton conduction in the grain interior and a reduced proton conductivity across the grain boundaries, while under reducing conditions the grain boundaries showed an additional n-type contribution. All this supports the prevailing view of positively charged grain boundary cores with depletion of positive defects and accumulation of negative negatively charge defects in the adjacent space–charge layers.

(3) Schottky barrier heights were calculated from specific proton conductivities. By way of example, the Schottky barrier height at 250 °C was 0.5–0.6 V.

(4) With the obtained Schottky barrier heights, space–charge defect profiles were calculated. The model implies that the concentration of protons in the space–charge layer decreases while the space–charge layer width is constant with decreasing temperature. The space–charge layer width was around 4 nm in both BZY10-SPS and BZY10-HP. A difference in Schottky barrier height under wet and dry conditions was proposed due to a hydration process where the grain boundary core oxide ions were preferentially protonated but while grain interior oxygen vacancies were preferentially consumed.

(5) A simulated impedance spectrum based on the space–charge layer defect concentration profile gave a distortion in the grain boundary arc similar to that observed experimentally.

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