SOLID STATE IONICS

Correlation between ionic radius and cation diffusion in stabilised zirconia

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Abstract

To get an insight into the mechanism of cation diffusion in stabilized zirconia, the diffusion of all stable lanthanides was measured simultaneously in zirconia stabilised with scandia (ScSZ), yttria (YSZ) and calcia (CSZ). It was possible to identify all lanthanides with SIMS and to obtain the bulk diffusion coefficients between 1400 and 2000 K from SIMS depth profiles.

For CSZ and YSZ, the lanthanide bulk diffusivities increase with increasing lanthanide ionic radius, while for ScSZ, they are nearly independent of the radius. The experimental activation enthalpies and pre-exponential factors are highest for two-valent CSZ and lower for the three-valent systems ScSZ and YSZ. They are not strongly affected by the type of the lanthanide for all systems investigated.
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1. Introduction

Stabilized zirconias (YSZ: $ZrO_2+Y_2O_3$; CSZ: ZrO_2+CaO; or ScSZ: $ZrO_2+Sc_2O_3$) are used as electrolyte materials in solid oxide fuel cells. Their long-term stability, in particular the slow degradation of the electrical conductivity at high temperatures, is governed by the slow diffusion of the cations, the mechanism of which is still not yet fully understood [1]. It is assumed that the relative ionic radius of the cations may have a strong influence [2], but also an effect of the charge of the migrating ions is discussed [3]. The use of lanthanides (elements are in the following abbreviated as Ln) as probe elements is therefore helpful for answering this question, since they are chemically similar to each other and also in comparison to the host cations, reflected by the fact that all lanthanides are to some extend soluble in cubic zirconia while their ionic radius varies gradually.

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2. Experimental

Single crystals of CSZ and YSZ were obtained from Swarovski, Austria, and Djevahirdjian, Switzerland. ScSZ single crystals were made by skull-melting starting from Sc_2O_3 and ZrO_2 powders of >99.99% purity [4]. In this system, a small amount (0.017 mol%) of Al_2O_3 has to be added in order to avoid the formation of the rhombohedral β-phase, which is stable in ScSZ containing 10–12 mol% Sc_2O_3 at temperatures below 850 K [5,6]. The crystals were cut into slabs (oriented along [100]), polished and heated at 1700 K for several days in order to release polishing stress. Sample compositions as determined by electron microprobe analysis are summarised in Table 1. An inductively coupled plasma (ICP) lanthanide standard containing all stable lanthanides as well as zirconium, yttrium and scandium (Alfa #23261; 100 μg/ml each in 5% HNO_3) was diluted first 1:10 with water and then 1:1 with ethanol. This solution was dropped onto the surface of the crystals and dried by subsequently heating to 90 °C. In the case of ScSZ, also a small amount of ^{96}Zr (2.78% natural abundance) was added to the solution. The layer thickness was estimated to be in

Table 1
Sample composition and parameters of diffusion anneal experiments

System	Stabilizer content	Diffusion anneal temperatures/K
CSZ	11.4 mol% CaO	1559–1733
ScSZ	10.1 mol% Sc_2O_3+0.17 mol% Al_2O_3	1404–1901
YSZ	11.1 mol% Y_2O_3	1543–1873

the range of 20–40 nm. For diffusion anneals, the dried samples were heated for various times in air at temperatures between 1400 and 2000 K, as indicated in Table 1.

The depth distributions of the cations were analysed using two different SIMS machines working in different modes (VG SIMSlab; 7 kV Ar^+ ions, analysis of positive secondary ions, charge compensation using flood gun; and Cameca ims 5f, 10 kV Cs^+, analysis of positive $LnCs^+$ clusters, charge compensation using a 10 nm Au layer [7]). There was no influence of the type of SIMS machine on the results observable. To measure the depth profiles, care was taken to select the appropriate mass in order to avoid mass interferences of the various lanthanides or LnO^+ fragments or, in the case of $LnCs^+$, also $Ln_1Ln_2^+$ clusters.

Sputter profiles were converted into depth profiles using the measured eroded depth (Tencor alphastep 500) and were analysed according to standard mathematical procedures assuming the layer to be of limited thickness [8].

3. Results

The SIMS spectrum in Fig. 1 shows the large number of mass peaks in the range of 130–200 amu for the Ln diffusion in YSZ. Beside the Ln^+ masses, also various LnO_n^+ fragments give rise to significant signal intensity, leading to interferences with other masses. Nevertheless, characteristic masses for each lanthanide cation could be selected unambiguously and were used for SIMS depth profiling.
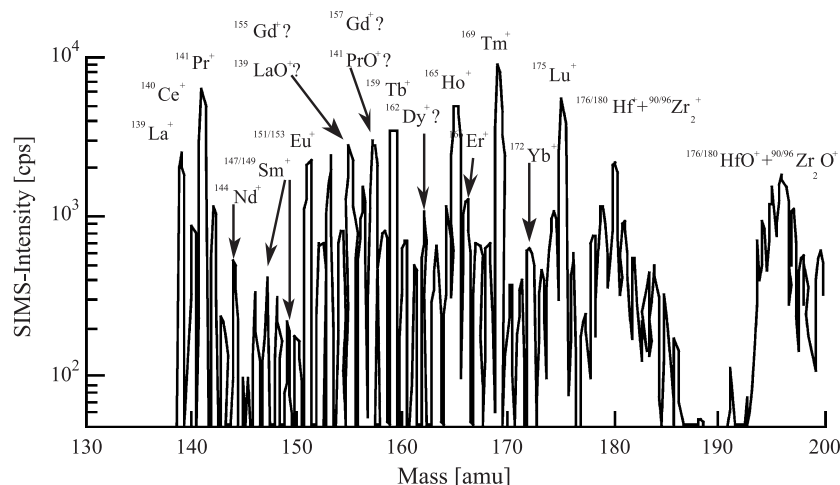
From a depth profile (Fig. 2, for holmium in ScSZ), the diffusion coefficient can be calculated and plotted as a function of temperature to give the activation enthalpies and pre-exponential factors of diffusion (Fig. 3, also for holmium). In Table 2, the results of the Arrhenius evaluations are summarised. The lanthanide diffusion coefficients are plotted in Figs. 4 and 5 as a function of the lanthanide ionic radius according to Shannon [9]. Here, it was assumed that the lanthanides are eightfold-coordinated, as it can be expected from the cubic fluorite structure. Furthermore, all lanthanides were taken to be present in the oxidation state +3 under the applied conditions (air).

In the case of ScSZ, the previously unknown self-diffusion coefficients of zirconium in single crystalline material were also measured in parallel to the lanthanide diffusivities by using the stable tracer ^{96}Zr. The activation enthalpy obtained was 4.7 eV with D_0=2 cm^2 s^{-1} (see Table 2).

The activation enthalpies for lanthanide diffusion fall in the range of 5–6 eV for CSZ, 4.5–5.5 eV for YSZ, and 4.0–4.5 eV for ScSZ. For each system, no significant dependence on the cation radius or cation mass could be detected. The pre-exponential factors are in the range 10^{-3}–10^3 cm^2 s^{-1}, also without any correlation to mass or radius of the lanthanides, but lowest for ScSZ and highest for CSZ, corresponding to the increasing activation enthalpies. The latter values correspond to activation entropies for diffusion ΔS in the range of 0–3k_B in the case of YSZ ($\Delta S/k_B$=ln($8D_0/a^2fv_0$); a=513 pm is the lattice constant of YSZ, f=0.653 is the correlation factor, and v_0=1.3×10^{13} s^{-1} is the Debye frequency [10]). For CSZ, activation entropies were in the range 10–20k_B, and for ScSZ, they were around 2–7k_B.

4. Discussion

It is possible to investigate the diffusion of all stable lanthanides in single crystalline cubic stabilised zirconia

Fig. 1. SIMS mass spectrum of lanthanides on YSZ-11 after annealing in air (24 h at 1673 K).
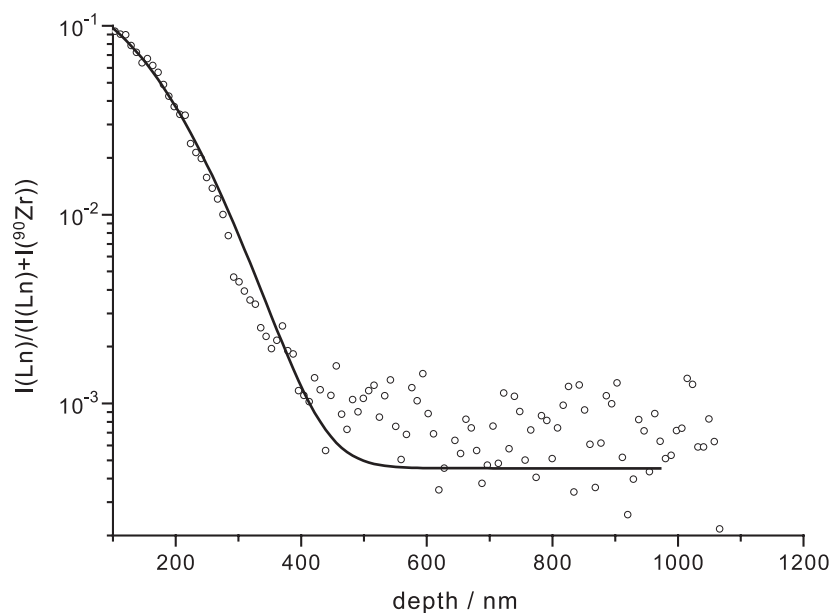
Fig. 2. Depth profile of Ho diffusion in ScSZ after annealing at 1620 K for 110 h in air.

simultaneously using SIMS analysis. For YSZ and CSZ, the lanthanide diffusion coefficients are slightly higher (by a factor of 2–10) than the self-diffusion coefficients of the host cations Zr, Y or Ca. It is remarkable that in ScSZ, the lanthanide diffusion and the zirconium self-diffusion are practically identical. Bak et al. [11] and Kowalski et al. [11,12] investigated the diffusion of Mg^{2+} [11], Ca^{2+} [12] and Ti^{4+} [13] in YSZ. They found that the cation diffusion of these elements is increased almost by a factor of 100 in comparison to the host cation diffusion [2], significantly

more than observed here. This difference is due to the fact that the lanthanides are more similar both by size and by charge to the host cations than the cations investigated by Bak and Kowalski.

For YSZ, the values of the activation enthalpy of diffusion correspond well to the values for self-diffusion of the constituent cations, which are in the range of 4.5–5 eV [1,2]. In contrast, for CSZ the activation enthalpies are slightly higher, by 1 eV, while for ScSZ, the activation energies of lanthanide diffusion are nearly identical to the
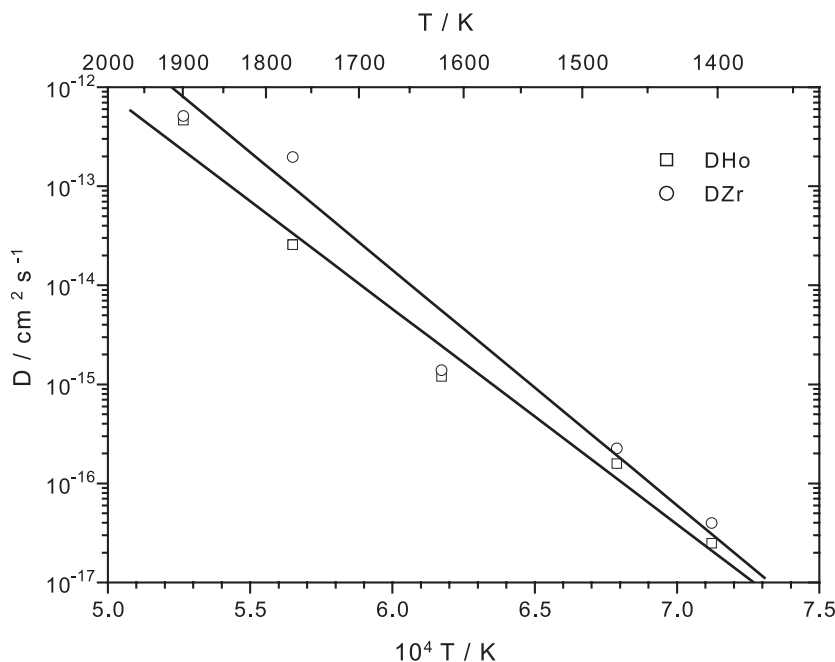

Fig. 3. Corresponding Arrhenius plot of the temperature dependence of the Ho diffusion in ScSZ. The resulting activation enthalpy and the pre-exponential factor are given in Table 2. Also included are the Zr self-diffusion coefficients in ScSZ measured in parallel.

Table 2
Results of Arrhenius fits for the different investigated systems

Ion	Ion radius/Å	Activation enthalpy/eV			$\ln(D_0/\mathrm{cm}^2\ \mathrm{s}^{-1})$		
		YSZ	CSZ	ScSZ	YSZ	CSZ	ScSZ
Lu^{3+}	0.977	4.9±0.2	6.2±0.5	4.6±0.4	0.2±0.2	9±3	−0.4±2.5
Yb^{3+}	0.985	4.9±0.3	6.0±0.6	4.6±0.4	0.0±1.7	8±4	−0.8±2.8
Tm^{3+}	0.994	5.1±0.1	6.1±0.8	4.1±0.3	1.2±0.8	8±5	−4.5±2.2
Er^{3+}	1.004	–	5.8±0.7	3.9±0.1	–	7±4	−5.4±0.8
Ho^{3+}	1.015	5.4±0.1	5.6±1.2	4.3±0.3	2.5±0.6	5±8	−2.8±2.2
Dy^{3+}	1.027	5.2±0.1	5.9±0.8	4.3±0.3	2.2±0.9	8±6	−2.8±2.5
Tb^{3+}	1.040	5.2±0.2	5.8±1.2	4.2±0.4	1.9±1.5	7±8	−3.5±2.5
Gd^{3+}	1.053	5.4±0.2	6.4±0.8	4.4±0.5	4.1±1.6	12±5	−1.8±3.2
Eu^{3+}	1.066	5.2±0.2	5.9±1.5	3.9±0.1	2.2±1.5	8±11	−6.0±0.7
Sm^{3+}	1.079	5.2±0.2	6.3±0.8	4.1±0.3	2.2±1.6	12±5	−4.5±2.1
Nd^{3+}	1.109	4.7±0.3	6.1±0.7	4.1±0.2	−0.4±1.8	10±5	−4.3±1.1
Pr^{3+}	1.126	5.3±0.2	5.7±0.7	4.0±0.1	3.6±1.4	8±7	−5.1±0.9
Ce^{3+}	1.143	5.1±0.3	6.6±0.9	4.0±0.2	2.4±2.0	14±6	−4.9±1.6
La^{3+}	1.160	5.0±0.4	5.6±0.6	4.0±0.1	1.3±2.7	7±4	−5.1±0.5
Zr^{4+}	0.840	4.7±0.2[1]	5.1±0.3[2]	4.7±0.5	−2.3[1]	1.7[2]	0.9±3.4
Sc^{3+}	0.870	5.0±0.2	4.1±0.9	–	0.6±1.4	−4±6	–
Y^{3+}	1.019	4.2±0.8[2]	5.2±0.5[2]	–	−3.7[2]	3.5[2]	–
Ca^{2+}	1.120	3.5±0.3[2]	5.6±0.1[2]	–	−5.6[2]	7.4[2]	–

Included are also some results of self- and tracer diffusion of host cations in the materials, taken from Refs. [1,2].

self-diffusion of zirconium [14]. It was concluded in Ref. [2] that in YSZ, the diffusion occurs via free cation vacancies V_{Zr}^{4+} formed by a Schottky reaction of ZrO_2. These vacancies should be not bound to oxygen vacancies despite their large charge. We assume that this mechanism should also govern the diffusion of the lanthanides in YSZ, both because of their similar activation enthalpy and their chemical similarities. In contrast, it was suggested for CSZ [2] that the cation diffusion goes via complex defects $[V_{Zr}^{4'},2V_O^{2\bullet}]^x$. In the case of ScSZ, it seems to be that cation diffusion might go via free vacancies like in YSZ. Since the lanthanide diffusion in ScSZ is almost independent of the type of lanthanide and also identical to the Zr self-diffusion, we think that there are no strong interactions between the host cations Sc^{3+} and Zr^{4+} with the lanthanides. This is consistent with results of Yokokawa who calculated the chemical interaction parameters of lanthanides in YSZ and CSZ and did not found a strong interaction [15].

With values of $0–7k_B$, the entropies of diffusion also support a diffusion mechanism going via free vacancies for YSZ and ScSZ [16]. According to the author, for simple vacancy diffusion processes, an entropy of $3k_B$ for migra-
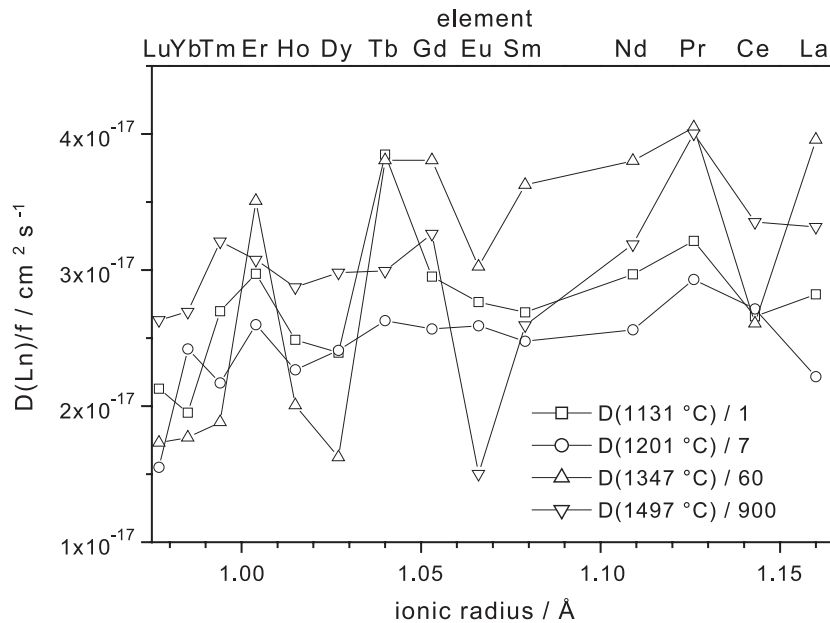

Fig. 4. Cation diffusion coefficient for the different lanthanides as a function of their ionic radius in ScSZ. To compare the data for different diffusion temperatures, diffusion coefficients were scaled for each temperature by a constant factor *f* indicated in the figure (*f*=1 for the lowest temperature). All lanthanides were assumed to be in the 3+ oxidation state.
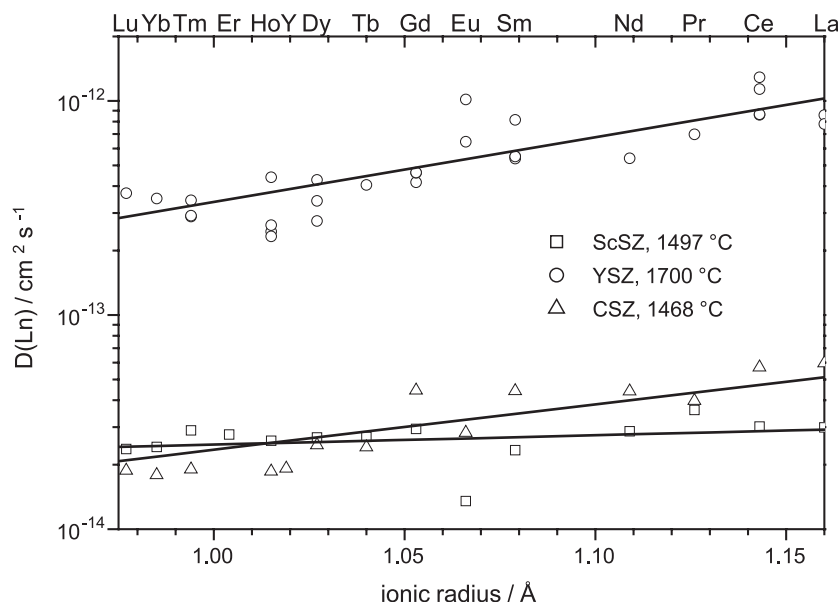
Fig. 5. Lanthanide diffusion coefficient for the systems ScSZ, CSZ and YSZ as a function of the lanthanide ionic radius at the indicated temperatures.

tion and $3k_B$ for formation of the vacancies are typical values for the two processes. Our values are in general slightly lower for YSZ, but since the determination of the activation entropy is more erroneous than the determination of the activation enthalpy they still support the diffusion via free vacancies. In contrast, the values for CSZ are in the range $10–20k_B$. For diffusion processes promoted by complex defects $[V_{Zr}^{4'}, 2V_O^{2\bullet}]^x$, the activation entropy should be higher and should include at least $9k_B$ for the formation of the defect complex.

Comparing the diffusion coefficients as a function of the cation radius, it can be seen that they are lowest when the radii of the cations are similar to the radius of the stabilizer elements yttrium or calcium, and they are higher in the other cases. This effect might be explained by the stress induced by the different ion size, similar to the arguments used for explaining the self-diffusion in YSZ and CSZ [2]. This is also proved in the ScSZ system, where the two host elements have the same ionic size, and therefore, the lanthanide diffusion in this system is nearly independent of the ionic radius. There is no evidence for the existence of different cation sublattices responsible for the transport of the zirconium or the stabiliser element as could be the case in highly doped systems, when the stabiliser content is above 20 mol% (40 mol% for CSZ) and long-range ordered phases are observed. Computer simulations have shown for these systems the transport properties might show some abnormalities [17].

In Ref. [2], also the role of the charge density, defined as C/r^2 was discussed. While the sizes of the two ions Sc^{3+} and Zr^{4+} are identical, their charges, and therefore their charge densities, are different. If the cation diffusion were governed by the charge density, one would expect a small dependence of the lanthanide diffusion on the lanthanide radius. The charge densities of Zr^{4+} and Sc^{3+} are higher than the charge densities of the lanthanides, and therefore, the lanthanide

diffusion should be expected to be higher than the diffusion of Zr^{4+}. For the data collected here, it does not seem that the ionic charge plays a major role in cation diffusion; mainly the size of the ions is responsible for cation diffusion.

5. Conclusions

The diffusion of all stable lanthanides into cubic stabilized zirconia containing yttria, calcia or scandia was measured simultaneously. It was possible to identify all lanthanides with SIMS and to perform depth profiling to obtain the bulk diffusion coefficients between 1400 and 2000 K.

For CSZ and YSZ, the lanthanide diffusion is increasing with increasing lanthanide radius, while for ScSZ, it is nearly independent of the lanthanide radius. The activation enthalpies, and correspondingly the pre-exponential factors, are increasing in the range CSZ>YSZ>ScSZ. Within one system, there is no strong dependence on the lanthanide cation radius. This behaviour can be explained by the size of the host and stabiliser cations, which are both smaller than the lanthanides in ScSZ. In CSZ and YSZ, Ca^{2+} and Y^{3+} are of similar size like the Ln^{3+} (see Table 2) and can therefore easily be replaced by a migrating lanthanide.

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