



Short communication

Interfacial stability and cation diffusion across the LSCF/GDC interface

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ABSTRACT

We have performed cation diffusion experiments within the framework of the evaluation of long-term stability of gadolinium doped ceria acting as a reaction barrier between cathode and electrolyte materials. Diffusion couples were prepared depositing $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_x$ (LSCF) thick films onto sintered $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) substrates by Pulse Laser Deposition (PLD). Interdiffusion across the LSCF/GDC interface was investigated by means of SIMS, at temperatures of 1000–1200 °C and times from 30 h up to 672 h. A significant diffusion of lanthanum into GDC and diffusion of cerium and gadolinium into LSCF were observed. In contrast, only shallow depth profiles for strontium, iron and cobalt into GDC were observed. X-ray diffraction (XRD) reveals the probable formation of lanthanum doped ceria (LDC) in the vicinity of the interface. Finally, the temperature dependence of lanthanum and strontium diffusion coefficients in bulk GDC is described by the following equations in the temperature range indicated:

$$\text{La in GDC: } D_{\text{bulk}}/\text{m}^2 \text{ s}^{-1} = 4.2 \times 10^{-5} \exp\left(\frac{-390 \text{ kJ mol}^{-1}}{RT}\right) \quad (1273 - 1473 \text{ K});$$

$$\text{Sr in GDC: } D_{\text{bulk}}/\text{m}^2 \text{ s}^{-1} = 1.1 \times 10^{-7} \exp\left(\frac{-320 \text{ kJ mol}^{-1}}{RT}\right) \quad (1373 - 1473 \text{ K}).$$

The grain boundary diffusion of lanthanum is, at least, five orders of magnitude faster than the bulk diffusion.

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1. Introduction

As a candidate for cathode material in solid oxide fuel cells (SOFC), lanthanum strontium cobalt iron oxides (LSCF) surpass the widely used lanthanum strontium manganese oxides (LSM) in catalytic activity for oxygen reduction. Nevertheless, extensive reactions occur at the interface between these perovskite cathode materials and the most important electrolyte to date: yttria stabilized zirconia (YSZ) [1]. The reactions render formation of $\text{La}_2\text{Zr}_2\text{O}_7$, SrZrO_3 and spinel phases [1]. In their seminal work, Uchida et al. [2] showed the effectiveness of coating the electrolyte with a samaria doped ceria (SDC) thin film to prevent reactions at the interface. As a natural development, the use of a thin film of rare-earth doped ceria, especially of gadolinium doped ceria (GDC), has been proposed as a reaction barrier between the LSCF cathode and the YSZ electrolyte. A main concern is still the chemical stability of this type of films after long time operations.

On the other hand, our group has been actively engaged in the evaluation of cation diffusion as a key process to understand long-term stability of electrolytes and related materials, as well as in the characterization of interface stabilities among dissimilar materials, which is a very common feature in SOFC technology. Recently, using the classical technique of diffusion couples in combination with measurements by secondary ion mass spectrometry (SIMS), we have reported on the interface stability of $(\text{La}, \text{Ca})\text{CoO}_3/\text{M}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ ($\text{M} = \text{Y}, \text{Gd}$) [3] and the reaction and interdiffusion characteristics at the interface of rare earth doped ceria ($\text{M}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$, $\text{M} = \text{Gd}, \text{La}$) and perovskite-type cathode materials ($\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$, and $\text{La}_{0.8}\text{Sr}_{0.2}(\text{Co}, \text{Fe})\text{O}_3$) [4]. Here, a significant diffusion of transition metals (cobalt or iron) and strontium from the perovskite phase into ceria was observed. In both set of experiments, it was recognized the necessity to produce diffusion couples of higher quality that guarantee an intimate contact among the parts to be evaluated, making a homogeneous large region suitable for analysis; a type of contact that is not always achievable by simple mating of mechanically polished surfaces.

This is our first report on the evaluation of cation interdiffusion in systems of technological interest using a strategy to

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produce the above described type of diffusion couples with well-defined interfaces. In this case in particular, the strategy consists of depositing $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_x$ (LSCF) thick films onto sintered $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) substrates by Pulse Laser Deposition (PLD), in which a high degree of intimate contact between the oxides is attainable. Inter-diffusion across the LSCF/GDC interface was mainly investigated by SIMS.

2. Experiments

2.1. Diffusion couples preparation and treatment

A primary requirement for diffusion studies is the preparation of suitable diffusion couples where a tight contact among the parts is a fundamental issue. We have used PLD to deposit thick films of LSCF onto substrates of GDC. Surprisingly enough, with exception of the work by Dohmen et al. [5] and a brief mention in a review paper by Kilo [6], to our knowledge, no report has been published on the use of PLD to produce high quality diffusion couples to evaluate diffusion coefficients.

Both target and substrate, were prepared from commercial powder: $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_x$ (AGC Seimi Chemical Co., Ltd., Japan) and $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (Anan Kasei Co., Ltd., Japan) by a similar recipe. The LSCF powder was shaped into a large disk (25 mm in diameter and 5 mm thick) and the GDC powder was shaped into small disks (15 mm in diameter and 1 mm thick). Uni-axially pressed disks were then cold isostatically pressed at 390 MPa. Sintering temperature was 1400 °C and sintering times were 5 and 50 h for LSCF and GDC, respectively. Sintering time was varied according to the sinterability of the powder to obtain specimens with a relative density above 96%. All sintered disks were ground down and polished to finish with 1 μm diamond slurry to render optical flat surfaces. A homogeneous single phase of the perovskite or fluorite structure was confirmed for all samples by X-ray diffractometry (XRD).

PLD experiments were performed as follows. In a vacuum chamber with 10 Pa of oxygen, a pulsed KrF ($\lambda = 248$ nm) excimer laser was focused onto a rotating polycrystalline target of LSCF. The laser pulse energy and the repetition rate were 200 mJ and 10 Hz, respectively. The ablated LSCF is emitted as a plume in direction normal to its surface, depositing onto the GDC substrate heated at 600 °C. The thickness of the LSCF film was approximately 1–2 μm.

The diffusion couples prepared by PLD were annealed in a home made high-temperature tubular furnace with flowing air (flux: 50 mL min⁻¹). Annealing was carried out in the temperature range 1000–1200 °C, for a time up to 672 h. After annealing, the diffusion couples were moved out of the heat zone to provide rapid cooling, which is estimated to be 50 °C min⁻¹. To provide suitable samples for obtaining diffusion profiles into the material of interest, GDC, and made comparison, a group of diffusion couples was rinsed in diluted nitric acid (HNO₃) to remove the LSCF thick film.

Needless to say that one of the main concerns in this kind of experiments is the accurate grasp of initial conditions. We have taken careful steps to ensure that we are properly measuring cation diffusion of the elements that constitute LSCF into GDC. We have evaluated the samples in the as-deposited condition and verify that diffusion has not taken place at the “as-deposited” condition. Only a background level for lanthanum, strontium, iron and cobalt, likely due to impurities in GDC, rather than diffusion profiles for these elements from the deposited LSCF film were observed.

2.2. Phase analysis and elemental distribution analysis

To investigate the quality of the contact between the LSCF film and the GDC substrate, as well as the morphology along the interface, cross-sectional studies were performed using Secondary

Electron Microscopy (SEM, VE-7800, Keyence Co., Japan). Crystalline phases involved in this study were identified by standard XRD procedure (Ultima IV, Rigaku Co., Japan).

Elemental distribution as a function of depth was obtained by depth profiling of both types of samples, with the LSCF film attached and with the LSCF film removed, using SIMS (IMS 5f, Cameca, France). The sample surface is impinged by a focused Cs⁺ ion (accelerating voltage = 10 kV) and the emissions from the surface are detected as negative secondary ions. The intensities of secondary ions ¹⁶O⁻, ¹⁸O⁻, M¹⁶O⁻ (where M = ⁵⁶Fe, ⁵⁹Co, ⁸⁸Sr, ¹³⁹La, ¹⁴⁰Ce, and ¹⁵⁸Gd) are collected as a function of etching time. The samples are coated with a gold thin film to avoid charging effects and the analysis is always performed under electron irradiation for the same purpose, especially when the profiles reach the insulator GDC. The crater depth of etched area was measured by a surface profiler (Ultra-deep Color 3D Profile Measuring Microscope, VK-9510, Keyence Co., Japan). In the calculation of depth, a constant sputtering rate is assumed.

2.3. Diffusion profiles fitting and diffusion coefficient evaluation

The apparent bulk diffusion (D_{app}) coefficients were determined from the diffusion profiles by fitting with the solution proposed by Crank [7]:

$$\frac{X - X_0}{X_s - X_0} = 1 - \operatorname{erf}\left(\frac{z}{2\sqrt{(D_{app}t)}}\right) \quad (1)$$

where X is the normalized intensity of the secondary ion, X_s is the intensity at the surface ($z = 0$), X_0 is the intensity at the background (normally $X_0 = 0$), z is the depth, and t is the annealing time. The normalized intensity $I(\text{M}^{16}\text{O}^-)/I(\text{O}^{16}\text{O}^-)$ was used.

In turn, grain boundary diffusion coefficients (D_{gb}) are calculated from the diffusion profiles fitted with the equation proposed by Le Claire [8].

$$dD_{gb} = -0.66 \times \left(\frac{\partial \ln X}{\partial z^{6/5}}\right)^{-5/3} \left(\frac{4D_{app}}{t}\right)^{1/2} \quad (2)$$

where d is the “width” of the grain boundary. For practical purposes d is assumed to be 1 nm.

3. Results

Fig. 1 shows images of cross-section SEM micrographs for some of the annealing conditions evaluated. Regardless of substrate heating at 600 °C during the LSCF film deposition, the film in the “as-deposited” condition consists of an amorphous phase of 2 μm in thickness (Fig. 1a). This result was confirmed by XRD analysis, as it will be indicated later. From this amorphous stage, and upon annealing at different conditions (as indicated by the arrows in the figure) different microstructures developed. A detailed analysis of the crystallization process and grain growth of this film upon annealing is out of the scope of this report. The important information here is the high quality contact at the flat LSCF/GDC interface obtained by the PLD method, which is crucial for the diffusion analysis. It is worth noticing that the interface remains flat upon annealing, a surprising result when considering the evident changes in microstructure observed during the crystallization of the LSCF film. No evidence in image contrast or morphology indicating the formation of a third phase along the interface was observed for the present annealing conditions. At this point, we will call this kind of interfaces “air-tight interface” in contraposition with the “air-leaky interface” that it is a common feature of classical diffusion couples made of mating polished surfaces of sintered bodies.

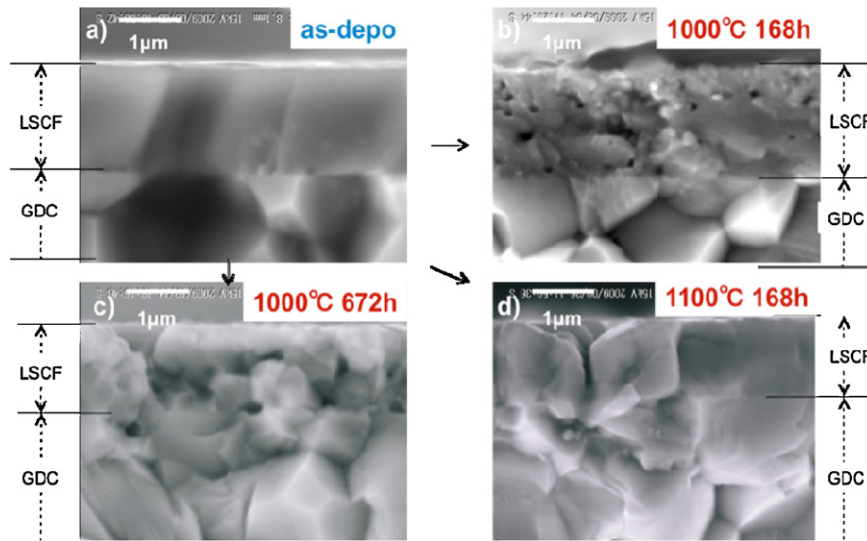


Fig. 1. Cross-section SEM micrographs of LSCF/GDC diffusion couples: (a) as-deposited; (b) annealed @1000 °C for 168 h; (c) annealed @1000 °C for 672 h; (d) annealed @1100 °C for 168 h.

The XRD patterns of the diffusion couples for all the conditions evaluated are shown in Fig. 2. The halo pattern of Fig. 2a confirms the amorphous nature of the LSCF film in the “as-deposited” condition. Reflections lines seen within this pattern correspond to the GDC substrate with fluorite structure. Upon annealing, the progressive crystallization of the LSCF film can be observed and, at the maximum annealing temperature of 1200 °C (Fig. 2d), a sharp and strong peak, indication of high crystallinity for this phase, can be observed around $2\theta = 33^\circ$. Moreover, in the pattern of Fig. 2d the presence of fluorite structure reflections (indicated by the inverse triangle) at $2\theta = 29^\circ$ and $2\theta = 57^\circ$, which correspond to a larger lattice parameter than corresponding to GDC is clearly observed. The same feature is observed for long time annealing at 1100 °C (Fig. 2c). Nevertheless, Fig. 2b shows a more complex XRD pattern for the sample annealed at 1000 °C for 168 h. A number of reflections that could be eventually associated to single oxide phases are present (probably existing at the surface of the film). Since no clear evidence of formation of a third phase along the interface was seen in the SEM analysis (for example, Fig. 1b), at this point, we have considered this information as being of no importance to the process of diffusion towards the GDC substrate.

Fig. 3 shows a typical SIMS depth profiles of $M^{16}O^-$ concentration for the LSCF/GDC diffusion couples where the LSCF has not been removed by acid rinse. In this case the sample was annealed at 1100 °C for 168 h. In the figure, the ion notation has been sim-

plified for the sake of clarity. Two important features need to be mentioned. Firstly, a notorious cation inter-diffusion takes place. Second, none of the profiles shows a concentration plateau typical of the presence of a third phase. Towards the GDC side, the high concentration signal for $^{139}La^{16}O^-$ describes a classical diffusion profile, which penetrates 1.5 µm from the interface before reaching a background level of 1000 wtppm. This indicates that a significant amount of lanthanum migrated into GDC. Other signals $^{88}Sr^{16}O^-$, $^{56}Fe^{16}O^-$ and $^{59}Co^{16}O^-$ show a less active behavior with a sharp drop in concentration close to the interface. Nonetheless, when comparing concentration levels with the $^{139}La^{16}O^-$, the shallow profiles for $^{88}Sr^{16}O^-$, $^{56}Fe^{16}O^-$ and $^{59}Co^{16}O^-$ concentrations show differences of two orders of magnitude, as in the case of $^{59}Co^{16}O^-$ at the background level. As for, cation diffusion from GDC into the

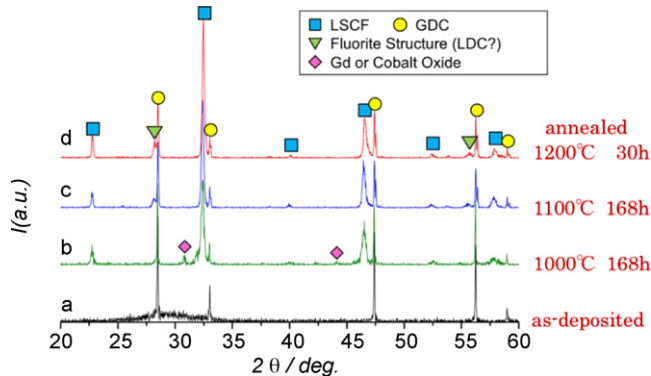


Fig. 2. XRD patterns of LSCF/GDC diffusion couples: (a) as-deposited; (b) annealed @1000 °C for 168 h; (c) annealed @1100 °C for 168 h; (d) annealed @1200 °C for 30 h.

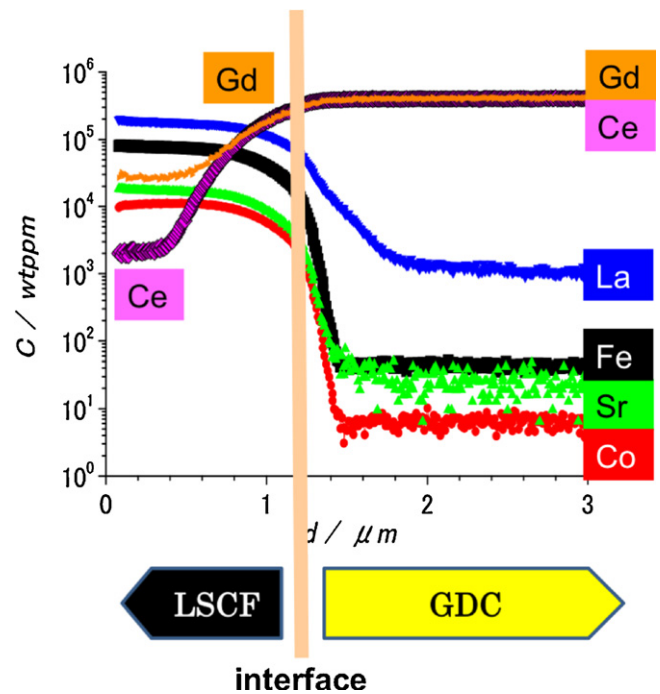


Fig. 3. Typical SIMS depth profile of LSCF/GDC diffusion couple when the LSCF has not been removed by acid rinse.

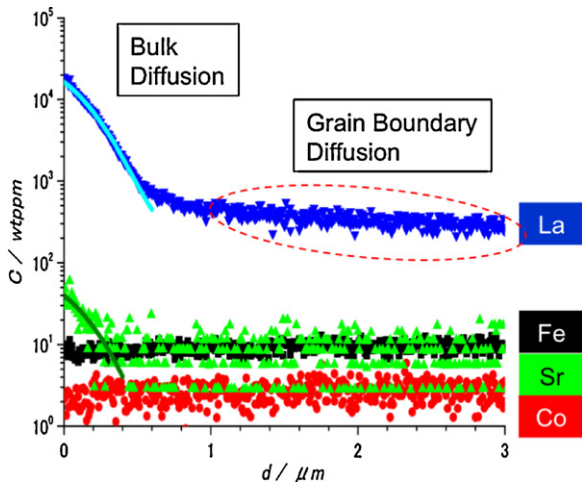


Fig. 4. SIMS depth profile of LSCF/GDC diffusion couple annealed @1100 °C for 168 h. In this sample the LSCF was removed by acid rinse. Notice the reduction in concentration level for Sr, Fe and Co species.

LSCF, $^{140}\text{Ce}^{16}\text{O}^-$ and $^{158}\text{Gd}^{16}\text{O}^-$ do also register classical diffusion profiles, with $^{158}\text{Gd}^{16}\text{O}^-$ presenting a concentration level one order of magnitude higher in the background level. This region is crucial of importance to completely understand the overall process of diffusion and substitution of lanthanum for cerium and gadolinium. However, we are not extending our analysis to diffusion towards LSCF in this report.

Fig. 4 shows the type of SIMS depth profiles used in the evaluation of cation diffusion coefficients into GDC. In this case the LSCF film was totally removed by rinse in dilute HNO_3 in a sample annealed at 1100 °C for 168 h. Thus, the comparison with Fig. 3 is direct. The principal reason for the LSCF removal is that only ions that could have migrated into GDC will be detected, without concerns about the contaminant effect (i.e., rising the background level) that the presence of the LSCF could have during SIMS analysis. The most important feature to be indicated is the noticeable reduction of concentration level observed for $^{88}\text{Sr}^{16}\text{O}^-$, $^{56}\text{Fe}^{16}\text{O}^-$ and $^{59}\text{Co}^{16}\text{O}^-$. For example, the 30 wtppm level seen in Fig. 3 for $^{88}\text{Sr}^{16}\text{O}^-$ decreases to the 10 wtppm level in Fig. 4.

Due to the above reason, the group of samples where the LSCF film was removed were used for the calculation of apparent bulk diffusion of lanthanum and strontium and grain boundary coefficients for lanthanum, the only elements for which was possible the fitting procedure using Eqs. (1) and (2).

4. Discussion

Our results revealed that the LSCF/GDC interface is very active in terms of inter-diffusion, which in turns offers the opportunity for evaluating cation diffusion in this system with a high level of accuracy. This statement on accuracy is presented in contrast to diffusion couples experiments where the “air-leaky” contact, mentioned above, is an important feature, and where formation of third phases at the interface creates concern in the determination of apparent diffusion coefficient (D_{app}). In those cases, a large uncertainty arises when the boundary conditions are changed by the formation of interfacial phases. Nevertheless, as the result of large amounts of lanthanum diffusing into GDC, and migration of gadolinium towards the LSCF film, a concurrent formation of lanthanum doped ceria (LDC) could be taking place in the vicinity of the interface, as it was suggested by the XRD results (Fig. 1d). A more detailed analysis is required to identify location, distribution and morphology of the newly formed phase.

The apparent inter-diffusion coefficients for lanthanum and strontium in GDC were determined using Eq. (1). The normalized intensity $I(M^{16}\text{O}^-)/I(^{16}\text{O}^-)$ ratio was used in the calculations. The fitting routine was carried out for the region where $^{140}\text{Ce}^{16}\text{O}^-$ intensity is constant. However, we were unable to obtain diffusion coefficients for the transition metals, iron and cobalt, due to the limited cation diffusion of these elements into GDC under the present experimental conditions, a fact that is in clear contradiction with results reported by Sakai et al. [4] and Sirman et al. [9]. In both reports, transition metal components of LSCF are regarded as being the main diffusing elements into GDC. Needless to say that differences in reaction mechanism at the interface translate into differences in diffusion behavior, and that basically those differences arise from the quality of the contact at the interface, in other words, the role of the air in its access to and from the interface. In a recent publication Uhlenbruck et al. [10] have clearly shown the effect of the material processing (i.e., porosity) on the diffusion of

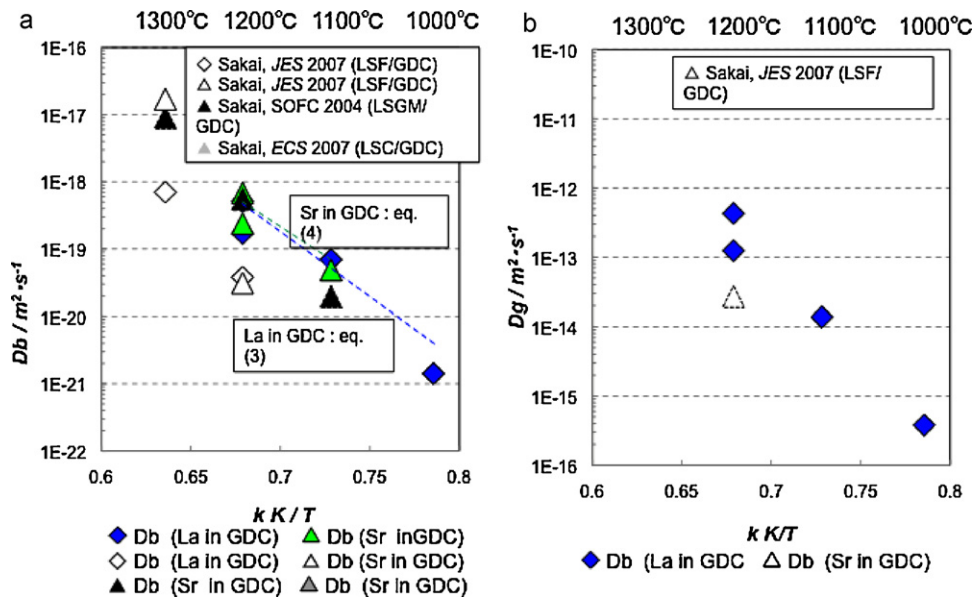


Fig. 5. (a) Apparent bulk diffusion coefficients of lanthanum and strontium in GDC and (b) grain boundary diffusion coefficient of lanthanum in GDC. For comparison, data obtained in the literature is also plotted [3,4,9].

chemical species. We will address in detail this issues in a separated publication [11].

The obtained bulk diffusion coefficients of lanthanum and strontium in GDC are shown in the Arrhenius plot of Fig. 5a, which contains also, for comparison, data reported in the literature. The apparent activation energy of lanthanum diffusivity was estimated to be 390 kJ mol^{-1} in the temperature range of $1000\text{--}1200^\circ\text{C}$. This value is slightly lower than the range of values reported by Kilo for diffusion of lanthanides in yttrium-stabilized zirconia (YSZ) [6]. The corresponding apparent activation energy of strontium diffusivity was estimated to be 320 kJ mol^{-1} in the temperature range of $1100\text{--}1200^\circ\text{C}$. Summarizing, the temperature dependence of diffusion coefficients in bulk GDC are described by the following equations:

La in GDC:

$$D_{\text{bulk}}/\text{m}^2 \text{ s}^{-1} = 4.2 \times 10^{-5} \exp\left(\frac{-390 \text{ kJ mol}^{-1}}{RT}\right) (1273 - 1473 \text{ K})(3)$$

Sr in GDC:

$$D_{\text{bulk}}/\text{m}^2 \text{ s}^{-1} = 1.1 \times 10^{-7} \exp\left(\frac{-320 \text{ kJ mol}^{-1}}{RT}\right) (1373 - 1473 \text{ K})(4)$$

Data obtained under ideal conditions of well-defined interface with an intimate contact between the interacting phases and taking special efforts to reduce levels of uncertainty, like reduction of background signal during SIMS analysis, has to be regarded as accurate. As it happens to be, data reported in the literature [3,4,12], which was obtained by classical diffusion couples, shows a reasonable agreement with our data, speaks well of the large amount of diffusion data collected thorough the years by different research teams. Our results, in this sense, validate the results obtained using classical diffusion couples.

As for grain boundary diffusion, the concentration of $^{139}\text{La}^{16}\text{O}^-$ exhibited a gradual linear slope in the depth region from 1 to $3 \mu\text{m}$ in GDC as shown in Fig. 4, which allows calculation of grain boundary diffusion coefficient (D_{gb}) using Eq. (2). The results are shown as a function of reciprocal temperature in Fig. 5b. The estimated D_{gb} of lanthanum in ceria at 1000°C was $3.0 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$, and at 1100°C was $0.5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, these values are 10^5 times larger than those for the apparent bulk diffusion of lanthanum reported in a previous paragraph.

On the other hand, and from a strictly pragmatic point of view, it is readily observed that bulk cation diffusion is rather limited in GDC, while grain boundary diffusion seems to be a dominant factor. Indeed, Sakai et al. [4] have determined that the actual migration

of strontium in GDC is much faster and in larger amount than that estimated by the bulk diffusion mechanism. Furthermore, in diffusion experiments for SrO/GDC couples, the $^{88}\text{Sr}^{16}\text{O}^-$ intensity in GDC was high and almost constant up to several microns in depth. They concluded that “anomalous fast diffusion” of strontium in GDC was taking place.

5. Summary

Ideal diffusion couples with tight contact were prepared for the system LSCF/GDC by pulsed laser deposition of a LSCF thick film onto GDC substrate. SIMS was used for the evaluation of inter-diffusion across the LSCF/GDC interface. Lanthanum, and in a lesser extent strontium, are the principal diffusing elements into GDC and X-ray diffraction (XRD) reveals the probable formation of LDC in the interface vicinity. Apparent bulk diffusion for lanthanum and strontium in GDC and the grain boundary diffusion coefficients of lanthanum into GDC were determined as a function of temperature. The grain boundary diffusion of lanthanum is, at least, five orders of magnitude faster than bulk diffusion.

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