Effect of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ microstructure on oxygen surface exchange kinetics

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Abstract

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) is a mixed ionic-electronic conducting perovskite (ABO_3) material which has attracted significant research interest in recent years as a cathode for solid oxide fuel cell (SOFC) applications at intermediate temperatures (500–750°C). Fundamental understanding of the oxygen surface exchange kinetics and diffusion in LSCF cathodes is necessary to optimize the cell performance at the required operating temperatures. In this study, we controlled the surface microstructure and crystalline orientation of LSCF thin films on (100) Gd_2O_3 -doped CeO_2 thin films (GDC) prepared by pulsed laser deposition on yttria-stabilized zirconia (YSZ) single crystal substrates. Tailoring of the LSCF microstructure was achieved by modifying the underlying GDC thin film surface morphology and microstructure. To clarify the effect of the LSCF microstructure on its oxygen surface exchange kinetics, we employed the $^{18}\text{O}/^{16}\text{O}$ oxygen isotope exchange technique in conjunction with secondary ion mass spectroscopy (SIMS) depth profile analysis. Comparison of the qualitative features of the measured concentration of the ^{18}O profile and evaluation of the oxygen surface exchange coefficient k^* were performed and the results correlated to the LSCF microstructure.

Keywords

solid oxide fuel cells; thin films; pulsed laser deposition; $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$; oxygen surface exchange; Gd_2O_3 -doped CeO_2

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted significant attention over recent years due to their promising use as source of clean and efficient power generation. The efficiency of these devices, however, is influenced by several electrochemical processes which occur at the gas-solid interface, i.e., oxygen surface exchange reactions occurring at the solid cathode surface. Lanthanum strontium cobalt iron oxide (LSCF) is a mixed ionic-electronic conducting perovskite (ABO_3) material most commonly used as a cathode at intermediate temperatures (500–750°C) and has also been developed as a promising material for thin film SOFC applications [1-2]. Moreover, in order to elucidate the fundamental mechanisms governing the behavior of these cathode materials, a commonly employed method is to fabricate these into dense thin film structures, which have a well-defined geometry and crystalline orientation. Recently, studies have also shown that engineering of lattice strain in oxygen ion conductors via heterostructures could lead to significant increases in ionic conductivity [3-5]. Studies have further demonstrated enhanced oxygen diffusion mediated by grain boundaries, suggesting enhancement of mass and charge transport properties in such intrinsic interfaces [6-7]. However, systematic comparison from sample to sample is complicated by the fact that controlling the density and size of grains usually entails modifying the film deposition parameters which would invariably affect its corresponding properties.

In this study, first we explore a new approach for tailoring the microstructure of LSCF thin film cathodes through a simple method of modifying the surface morphology of the underlying layer on which it is epitaxially grown, viz. Gd_2O_3 -doped CeO_2 (GDC) films grown on yttria-stabilized zirconia (YSZ) single crystal substrates. Through this approach, we aim to make a systematic comparison of LSCF microstructures and study its effect on oxygen surface exchange kinetics.

2. Experimental

LSCF films having nominal composition of $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_{3-\delta}$ of $\sim 0.3 \mu\text{m}$ thickness were prepared using pulsed laser deposition technique on (100) YSZ single-crystal substrates buffered with $\sim 1 \mu\text{m}$ -thick epitaxial GDC thin films. Briefly, the films were prepared using the following conditions: 675°C deposition temperature, 200 mJ laser energy, 10 Hz laser repetition rate, and 10 Pa oxygen pressure. As-grown (100) GDC thin films are characterized by densely packed nanocolumnar structures terminated by sharp nanofacets. On the other hand, GDC thin films undergo drastic microstructural reconstruction by annealing in air at sufficiently high temperatures.

Further details of the effect of high-temperature annealing at 1300 °C for 5 h on the GDC microstructure were reported in [8]. LSCF thin films were consequently prepared on two types of GDC thin films, i.e., as-grown and annealed. Surface morphology of the films was evaluated using atomic force microscopy (AFM, SPA-300HV, Seiko Instruments) operated in dynamic mode in air. Detailed microstructural evaluation of the heterostructures was performed using transmission electron microscopy (TEM, FEI Tecnai Osiris) operated at 200 kV.

Oxygen isotope labelling technique in conjunction with depth profiling with dynamic secondary ion mass spectroscopy (SIMS, ims5f, Ametek/CAMECA) was employed to evaluate the oxygen surface exchange coefficient k^* and the diffusion coefficient D^* . Oxygen isotope exchange was performed at $T = 600$ °C, 20 kPa oxygen pressure, and exchange time of 5 min. Details of the method can be found in literature [8, 9].

3. Results and Discussion

Fig. 1 shows the representative AFM surface and 3D topography images of (100) GDC films (prior to the deposition of LSCF films), and the corresponding LSCF films after deposition. The corresponding surface area values were derived from the analysis of the AFM images. Fig. 1(a) depicts nanosized grains comprising the surface morphology of the as-grown GDC film, and an analogous surface morphology shown in Fig. 1(b) is also exhibited by the LSCF film consequently deposited on top of this GDC. Interestingly, the LSCF microstructure is likewise characterized by nanograins terminated by sharp facets on the surface, analogous to those of the GDC surface [8]. In contrast, as depicted in Fig. 1(c), a drastic reconstruction of the GDC surface had occurred as a result of the high-temperature annealing. The initial granular morphology was transformed into a surface characterized by relatively flat terrain interrupted by submicron-sized pores. In Fig. 1(d) we can observe that the overall surface morphology of the LSCF deposited on annealed GDC is characterized by valleys and troughs with appearances resembling those found on the GDC surface. There appears to be relatively flat, densely-packed nanograins of several tens of nm in size which uniformly cover the entire surface; however, as TEM images will later show, these nanograins are coherent and are not similar to the randomly oriented nanograins of LSCF on as-grown GDC. The obtained surface area for this film is also lower as a consequence of the relatively flat granular surface (Fig. 1(h)), in contrast to the nanofaceted granular surfaces of LSCF on as-grown GDC (Fig. 1(f)).

These images clearly indicate that the LSCF microstructure is highly tunable by simply modifying the surface morphology of the underlying GDC layer.

Fig. 1. AFM topography images of (a) as-grown GDC film, (b) LSCF film on as-grown GDC, (c) annealed GDC film, and (d) LSCF film on annealed GDC. (e) – (h): 3D topography images corresponding to (a) – (d), respectively. Scan area: $2.5 \mu\text{m} \times 2.5 \mu\text{m}$.

Fig. 2 shows typical cross-sectional TEM images of the two LSCF/GDC multilayers. As depicted in Fig. 2(a), the LSCF on as-grown GDC exhibits a granular microstructure, with grains of $\sim 30\text{-}40$ nm in width and terminated by sharp facets at the surface, corresponding to those observed in the AFM images (Fig. 1(b) and 1(f)). This type of microstructure is considered to have resulted from its growth on relatively rough GDC surface comprised of nanograins. On the other hand, the LSCF on annealed GDC exhibits a continuous, quasi-single-crystalline layer spanning the entire film thickness. Some threading dislocations (denoted by white arrows) can also be observed in the LSCF film, but is otherwise continuous. It can also be noticed that this microstructure emanated from an atomically flat interface, which resulted from the extremely flat surface of the annealed GDC thin film. **Insets show the selected area electron diffraction (SAED) patterns for both LSCF films. For the LSCF film on as-grown GDC, some diffraction spots are arranged in a ring pattern, suggesting a nanopolycrystalline microstructure [10]. On the other hand, it can be seen that the all diffraction spots for the LSCF on annealed GDC are uniformly arranged with well-defined positions, suggesting that the LSCF film has a quasi-single-crystalline microstructure. Furthermore, these results suggest that the nanograin-like morphology observed in the**

AFM measurements (Fig. 1(b)) can be ascribed to coherent nanograins and differ from those observed for LSCF on as-grown GDC with randomly oriented nanograins. As both LSCF films were deposited using the same deposition conditions, the origin of the difference in their microstructure can be unequivocally attributed to the modification of the underlying GDC surface.

Fig. 2. Cross-sectional TEM images depicting the microstructure of LSCF films deposited on two types of GDC layers, (a) as-grown and (b) annealed. In (b), examples of threading dislocations are indicated by white arrows. Insets show the corresponding SAED patterns along the LSCF/GDC cross-section.

Fig. 3. XRD $\theta/2\theta$ scans for the two types of LSCF/GDC multilayers. For both LSCF films, the dominant crystalline orientation is confirmed to be (100) (pseudocubic notation).

Fig. 3 shows the XRD $\theta/2\theta$ scans confirming that the heterostructures are comprised of highly oriented LSCF and GDC crystalline phases. The results further show that the dominant crystalline orientation is (100)_{p.c.} (here we utilize the pseudocubic notation for simplicity) for the LSCF films when epitaxially deposited on (100)-oriented GDC. No other peaks from other reflections are present. It can be noticed that the heterostructure with annealed GDC layer exhibited (*h*00) GDC peaks which are shifted to higher diffraction angles, suggesting lattice shrinkage. This may be due to the oxidation of Ce^{3+} to Ce^{4+} , resulting to reduction in the lattice constant [8]. On the other hand, the peaks attributed to the LSCF phase showed a shift to lower diffraction angles when grown on annealed GDC, indicating lattice expansion. The lattice constants shown in Table 1 were estimated from the corresponding peak positions in the XRD pattern and employing the Nelson-Riley extrapolation function. Assuming an ideal cubic system for both phases, and considering that lattice matching can be accommodated when the LSCF is rotated by 45° along the basal plane of GDC, the lattice mismatch would be $\sim 1.7\%$ for the LSCF on annealed GDC, whereas this would be only $\sim 0.05\%$ for the LSCF on as-grown GDC (see Table 1). The relatively higher value obtained for LSCF on annealed GDC suggests that the film could be under higher interfacial strain as

compared to the LSCF on as-grown GDC.

Table 1

Lattice constants derived from XRD measurements.

Sample	LSCF (Å)	GDC (Å)	GDC lattice at 45° rotation ÷ 2 (Å)	Lattice mismatch (%)
LSCF on as-grown GDC	3.87(2)	5.48	3.87(4)	-0.05
LSCF on annealed GDC	3.89	5.41	3.82	1.71

In order to evaluate the oxygen surface exchange properties of the two types of LSCF thin films, we utilized the oxygen isotope labelling technique and evaluated the concentration of ^{18}O in the films using SIMS depth profile analysis. Fig. 4 shows the plots of the corrected ^{18}O fraction as a function of depth, denoted as $c_{18\text{O}}$ (calculated using the measured ^{16}O and ^{18}O intensities as in the given equation). Here we can clearly see that the relative concentration of incorporated ^{18}O is different for the two types of LSCF films in this study, with a higher amount exhibited by the LSCF film having nanograined microstructure (i.e., on as-grown GDC). Next we extract the oxygen surface exchange coefficient k^* and diffusion coefficient D^* from the fitting of the ^{18}O profile using Crank's solution to the diffusion equation for a semi-infinite medium [11]. The fitting is performed by utilizing the ^{18}O profile for the LSCF region only. Comparison of the calculated k^* values shows more than three times higher k^* for LSCF on as-grown GDC as compared to the one on annealed GDC. This result indicates that the introduction of grain boundaries into LSCF could have enhanced its oxygen surface reactivity. Based on the microstructural comparison of the two samples it is reasonable to expect that the difference in oxygen surface exchange properties could be much more significant than what the derived k^* values indicate; this may be accounted for by a possible counter effect attributed to the Sr segregation phenomenon mediated by fast diffusion along grain boundaries [12, 13]. Significant diffusion of Sr to LSCF surfaces is known to occur even at relatively low annealing temperatures at short duration. As reported in earlier studies, segregated Sr would effectively inhibit oxygen reduction reaction on the cathode surface [14, 15]. Furthermore, there appears to be some discrepancy in the obtained D^* values, suggesting that the diffusion behavior may be much more complex than what is described by the current analysis. For instance, it would be instructive to perform analysis of the SIMS profiles using other alternative

solutions for diffusion under different boundary conditions (e.g. plane sheet) and then compare the derived k^* and D^* values to obtain more accurate quantitative results.

Fig. 4. SIMS depth profile of the corrected fraction of ^{18}O for the two LSCF films. The plot in (a) shows the ^{18}O profile across the LSCF/GDC/YSZ heterostructures, whereas the plot in (b) shows the magnified view of the ^{18}O profile within the LSCF region with the fitting results from which k^* and D^* were derived.

In addition, we can extract some qualitative differences with regards to the ^{18}O profile within each heterostructure. Specifically, the ^{18}O concentration appears lower for the LSCF on as-grown GDC near the surface region, exhibits an almost flat profile within the LSCF thin film, and the ^{18}O concentration does not drop significantly at the LSCF/GDC interface. In contrast, the ^{18}O concentration is relatively high for the LSCF on annealed GDC near the surface region, exhibits a gradual descent across the LSCF thin film, and finally exhibits a drastic drop at the LSCF/GDC interface. For the LSCF on as-grown GDC, the relatively low ^{18}O concentration near the surface is interpreted as a consequence of its more reduced condition, suggested by a reduction of Co valence state indicated by spatially resolved STEM-EELS (electron energy loss spectroscopy) analyses performed across the cross-section (data not shown). The relatively smooth transition at the interface may be due to the presence of a high concentration of defects which would facilitate ion transport and diffusion [6, 16]. Detailed analyses of the two types of LSCF microstructure are currently being performed and results will be reported in the future.

Lastly, as a comparison Fig. 5 shows the plot of measured k^* values for the LSCF thin

films in this study compared to those reported in literature for LSCF powders [17, 18]. At $T = 600\text{ }^{\circ}\text{C}$, the LSCF on as-grown GDC exhibited more than ten times higher k^* compared to bulk LSCF. XRD measurements of LSCF powder samples usually exhibit strong reflections of the (110) peak compared to (100), indicating a higher occurrence of this type of surface and thus merits further investigation. In succeeding studies we intend to examine LSCF thin films preferentially oriented along the (110) and compare with the (100) films presented here.

Fig. 5. Measured surface exchange coefficients k^* of LSCF thin films in this study (squares) compared to literature values (circles) [17, 18].

4. Conclusion

LSCF thin films of varied microstructures were prepared on $\sim 1.0\text{-}\mu\text{m}$ thick GDC layers deposited on (100)-oriented YSZ single crystal substrates. The obtained LSCF microstructure was nanograined when grown on a similarly nanograined GDC surface; conversely, a quasi-single-crystalline LSCF layer was obtained when grown on a similarly structured annealed GDC. Evaluation of the oxygen surface exchange

properties for the differently structured LSCF films was performed using oxygen isotope labelling technique in conjunction with SIMS depth profile measurements. The relative concentration of incorporated oxygen is higher for the LSCF with nanograined microstructure, and exhibited an almost flat ^{18}O profile, suggesting fast oxygen diffusion. This feature is possibly attributed to the presence of a high density of crystalline defects existing across the LSCF/GDC heterostructure. On the other hand, both LSCF films exhibited significantly higher k^* compared to reported values in literature for LSCF powder samples, indicating enhanced oxygen exchange kinetics as influenced by its microstructure and crystalline orientation. Further studies are envisaged to examine the oxygen exchange kinetics for other major types of LSCF film surfaces.

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