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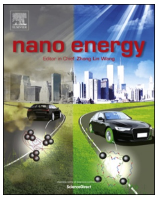

Full paper

Multilayered LSC and GDC: An approach for designing cathode materials with superior oxygen exchange properties for solid oxide fuel cells

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ABSTRACT

Cathode materials with significantly enhanced oxygen exchange properties are required to achieve high-performance solid oxide fuel cells (SOFCs). Here, it is shown that in multilayer heteroepitaxial films prepared by alternately stacking conventional mixed ionic and electronic conductors of $(La_{0.6}Sr_{0.4})CoO_{3-\delta}$ (LSC) and gadolinia-doped ceria (GDC), extremely fast oxide ion incorporation and transport can be achieved at relatively lower temperatures. Multilayer LSC and GDC heteroepitaxial films prepared on YSZ electrolytes exhibit enhanced oxygen surface exchange coefficient (k^*) values as compared to single LSC thin films. This is attributed to the existence of Ce^{3+} induced by the LSC-GDC interface, implying the presence of a relatively high density of oxygen vacancies which facilitate oxide ion incorporation and transport. Accordingly, unprecedented values of k^* in the order of 10^{-5} cm/s were obtained for LSC-GDC multilayer thin film cathodes even at a relatively low temperature of 500 °C. The results here conclusively show that leveraging the effect of heterointerfaces through multilayering can be a viable approach to achieving superior cathode materials with enhanced oxygen exchange properties.

1. Introduction

Solid oxide fuel cells (SOFCs) are novel devices used for the conversion of chemical energy directly into electrical energy with high efficiencies, and are currently being developed as a viable solution towards reducing carbon emissions and other pollutants associated with rapid consumption of fossil fuels [1]. In recent years, SOFCs have steadily entered the commercial market in the form of stationary applications (e.g. combined heat and power generation units) but largely their potential remains limited due to the required high operation temperatures (usually 750–800 °C). Some of the crucial issues currently facing SOFC development are the high cost and degradation of performance over time due to the typically high temperatures required for the operation of these devices [2]. To circumvent these issues, it is necessary to select and design cell components which can maximize performance at much lower temperatures [3,4]. Some of the approaches explored over the years include: reducing the electrolyte thickness, which has been shown to significantly lower the ohmic resistance [5,6], use of proton-conducting electrolytes to improve the power efficiency [7], and development of electrodes with high activity of oxygen reduction (cathode [8,9]) or fuel oxidation (anode [10,11]). A major problem that must be overcome at lower operating temperatures is the sluggish oxygen exchange kinetics at the cathode. Hence, fast oxygen reduction reactivity in electrodes has been identified as the key to implementing intermediate-temperature SOFCs in practical applications. [12]

One of the most promising materials being developed for SOFCs is the perovskite oxide $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC), a mixed ionic and electronic conductor (MIEC) as a cathode for cell operation at intermediate temperatures (500–700 °C) [13–15]. Studies have shown that combining cathode perovskites such as LSC with an excellent ionic conducting material such as gadolinia-doped ceria (GDC) in composite structures leads to significant improvements in performance [4,16,17]. Moreover, a significant enhancement in electrical conductivity has been demonstrated for vertically aligned nanostructures comprising LSC and GDC [18]. However, the exact mechanism for this enhancement is still not clear, and it is difficult to elucidate the intrinsic properties of interfaces in nanocomposites due to the randomness of structures in nanometer scale. Nevertheless, nanostructuring appears to induce significant effects which invariably change the macroscopic electrochemical properties of ionic conducting materials [8,19], and study of these nanostructures offer valuable and interesting insights into

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understanding and controlling the ionic conductivity of materials. This has been successfully demonstrated for nanograined oxide ion conductors fabricated into thin films [9], nanoscaffolds, [20,21] as well as multilayers [22].

In this study, we adopt the multilayering approach by alternately growing LSC and GDC layers to form a multitiered nanostructure. Multilayer films offer several advantages over conventional nanocomposites. First, chemical reaction occurs across heterointerfaces, and this becomes more pronounced for nanostructured composites. This is likely due to the fast cation diffusion promoted across heterointerfaces and along grain boundaries [23]. For multilayers, some diffusion occurs but this is limited to the vicinity of the planar interface of two materials. Second, granular growth at elevated temperatures inevitably occurs, and consequently nanocomposites tend to lose their original nanostructures. For multilayers, even with the loss of nanostructures due to sintering, the original interfaces are still maintained. Third, fabrication of vertically aligned nanocomposites with the correct distribution of phases has only been successfully implemented using physical vapor deposition techniques, specifically pulsed laser deposition (PLD). Furthermore, this seems to be achievable only within a very narrow window of PLD parameters and target composition. In comparison, multilayers can be fabricated over a wide range of deposition parameters because the interfaces are created by simply switching the source material (i.e., PLD target). In addition, because the interfaces are easily controlled, in principle this approach can be adapted to other types of film deposition methods (such as sputtering, liquid phase epitaxy, etc.). Therefore, the multilayering scheme essentially provides a more flexible route for processing. Lastly, sequentially grown multilayers result to well-defined heterointerfaces which can be accurately investigated by spatially resolved characterization techniques such as secondary ion mass spectrometry (SIMS) depth profiling and transmission electron microscopy (TEM). This will enable the elucidation of nanometer-scale effects which consequently arise from the heterointerfaces of dissimilar materials.

The goal of this work is twofold: 1) to enhance oxygen exchange properties of cathode materials by implementing a multilayer structure of LSC and GDC thin films to achieve superior performance; and 2) to clarify the nature of interfaces between LSC and GDC thin films fabricated in multilayer structures and its correlation to the enhancement of oxygen exchange properties. Ionic transport was evaluated using the isotope exchange depth profile technique which offers the advantage of high spatial resolution required for complex nanostructures. Detailed microstructural analyses were also performed to obtain complementary information for understanding the effect of interfaces created with LSC and GDC on ionic diffusion and transport. Lastly, the electrochemical properties of cells utilizing the multilayer cathodes were evaluated using electrochemical impedance spectroscopy. Results show that the multilayering approach is an effective method for obtaining superior performance of cathode materials suitable for intermediate-temperature SOFC applications.

2. Experimental

2.1. Pulsed laser deposition

Single layers of LSC on GDC (10 mol% $GdO_{1.5}$-doped CeO_2) thin films were prepared using pulsed laser deposition (PLD) technique on as-received (100)-oriented yttria-stabilized zirconia (YSZ) single crystal substrates using a KrF (248 nm, COMPexPro 102, Coherent) excimer laser source operated at 200 mJ laser energy. To investigate the effect of multilayering, additional layers were sequentially grown by switching targets starting with GDC, LSC, GDC, and LSC, while keeping the same deposition conditions. Two sets of samples were prepared: LSC single layer I and LSC-GDC multilayer I were deposited using identical conditions as listed in Table 1; LSC single layer II and LSC-GDC multilayer II were likewise deposited under identical conditions but different to those of the first set. A notable difference is the lower thickness obtained for the second pair of samples due to the reduced deposition rate. The average thickness for each layer was estimated from cross-sectional SEM observations of fractured samples.

2.2. Characterization

The properties of the films were evaluated using various characterization techniques including *X*-ray diffraction (XRD, Rigaku Ultima III) in the Bragg-Brentano geometry, scanning electron microscopy (SEM, NovaNanoSEM450, FEI)/energy dispersive *X*-ray spectroscopy (EDS, EDAX), and scanning/transmission electron microscopy (S/TEM, Tecnai Osiris, FEI) coupled with electron energy loss spectroscopy (EELS) operated at 200 kV. Samples for cross-sectional TEM analysis were prepared using a dual-beam SEM-FIB (focused ion beam, Scios, FEI) utilizing a Ga^+ ion source with a maximum acceleration voltage of 30 kV. $^{18}O/^{16}O$ oxygen isotope exchange was performed at various temperatures of 500, 600 and 700 °C, at $p(O_2) = 20$ kPa for 5 min. Details have been reported elsewhere [24]. Secondary ion mass spectrometry (SIMS, AMETEK-Cameca ims 5f) was used to obtain elemental depth and line scan profiles. The primary ion beam utilized was Cs^+, using an acceleration voltage of 10 kV, beam current of 10 nA, and raster area of 100 µm × 100 µm. Secondary ions were detected within an area defined by a diameter of 8 µm. For SIMS line scan analysis, the samples were first embedded in resin and then cut across using a diamond-tipped wire saw. Cross-sectional surfaces were further polished using diamond slurry and coated with a thin layer of evaporated Au to avoid charging effects. The beam current was adjusted to 5 nA and the raster area was set to 50 µm × 50 µm.

2.3. Electrochemical impedance measurement

To study the effects of multilayering on the cathode polarization resistance, symmetrical cells were prepared by depositing LSC-GDC multilayers on both sides of 0.5-mm-thick YSZ (100) substrates. Here, the same the deposition conditions as those for LSC-GDC multilayer II were employed. Prior to the characterization, a current collecting layer comprising a PLD-deposited LSC film of ∼ 1.0 µm thickness (deposited at room temperature) and an unsintered ∼ 30-µm-thick screen-printed layer of µm-scaled LSC particles were prepared to ensure homogeneous contact with the PLD-grown multilayers. Gold mesh was pressed onto the screen-printed LSC as contact. The active electrode area was 0.785 cm^2. Electrochemical impedance spectra were recorded with a Versastat4 (Princeton Applied Research, USA) frequency response analyzer in a frequency range of 10^{-2} Hz to 10^6 Hz from 500 to 700 °C in flowing air (50 ml/min). The impedance data was analyzed and fitted using the Zview software.

3. Results and discussion

3.1. Oxygen exchange properties as evaluated using the isotope exchange depth profile method

Fig. 1 shows the typical SIMS depth profiles obtained for the two pairs of samples in this study: LSC single layer I and LSC-GDC multilayer I, and LSC single layer II and LSC-GDC multilayer II; all samples were isotopically exchanged at 600 °C for 5 min. Each pair was prepared using identical PLD conditions, with multilayers having two LSC and two GDC layers each. The measured intensities of metal cations were normalized using the ^{16}O intensity (primary *y*-axis), whereas the corrected fraction of the ^{18}O concentration (c_{18O}, secondary *y*-axis) was obtained using the following equation:

$$c_{18O} = \frac{I_{18O}(x)}{I_{18O}(x) + I_{16O}(x)} \tag{1}$$

where $I_{18O}(x)$ and $I_{16O}(x)$ are the measured intensities of ^{18}O and ^{16}O