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High surface reactivity of La/Sr–Co perovskite based cathode with cation nonstoichiometry

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ABSTRACT

The effect of cation nonstoichiometry on the surface reactivity of mixed ionic and electronic conducting $(La,Sr)CoO_3$ (LSC113)-based bi-layer thin film cathodes is investigated by ac impedance method as a function of thin film surface composition. The bi-layer thin film cathodes are fabricated by an RF-sputtering method. The results of X-ray diffraction and transmission electron microscopy observation prove that LSC thin films of A-site and B-site deficient composition crystallize in a perovskite structure, which is attained by retained supersaturated metastability from the fabrication process. Both A-site and B-site deficient LSC113 phases have surface reaction performance significantly higher than the cation-stoichiometric LSC113 phase, which is attributed to the increase of oxygen vacancy in charge-compensation for cation vacancy. The "cation nonstoichiometry" is one of high surface reaction models to improve solid oxide fuel cells' performance.

1. Introduction

For realization of intermediate temperature solid oxide fuel cells (IT-SOFCs), which have advantages of long lifetime and wide variety of material selection, one of core issues is further improvement of conversion efficiency by reduction of internal resistance. Among various sources of internal resistance, a marked deterioration of cathode reaction kinetics at lower temperatures is one of major problems. For cathode materials, mixed ionic and electronic conducting (MIEC) oxides like perovskite-type oxide of $(La,Sr)CoO_3$ have been extensively studied. From the research of MIEC electrodes, the surface reaction is reportedly the rate-determining step in the cathode reaction process [1]. Improving the surface reactivity is, therefore, a key to make high-performance materials for IT-SOFC cathode.

Recently, it was observed through oxygen isotope exchange experiments that the hetero-interface of $(La,Sr)CoO_3$ (LSC113) and $(La,Sr)_2CoO_4$ (LSC214 with K_2NiF_4-type structure) shows high surface exchange rate of oxygen, which is estimated as ca. 1000 times higher than single-phase LSC113 [2,3], while the mechanism of the enhancement has not been well understood to date [4,5]. Attempts to utilize the enhancement phenomenon for achieving high-performance cathode, however, have not been enough successful. For instance, the performance of LSC113–LSC214 composite electrodes reported so far is not sufficiently high [6].

Considering the microscopic situation around the LSC113/LSC214 interface, one may expect that the two regions are not perfectly discrete, involving a transitional region between them. For example, in the reported LSC113/LSC214 dense film specimen fabricated via pulsed laser deposition [3], the LSC214 film deposited on the partially masked LSC113 film may be accompanied with a very thin region around the boundary, which arises from possible penetration of ablation plume behind the stencil mask. It can be supposed that the very thin region deposited with the LSC214 target forms in a phase different from the normal LSC214 phase, which is possibly a perovskite phase with a significant A-site deficiency.

It can be thus hypothesized that a cation deficiency on the A- or B-site of LSC113 improves the surface reaction kinetics and cathode performance. In this study, we have prepared and examined various LSC113-based bi-layer thin film electrodes that consist of the cation-nonstoichiometric surface layer and the cation-stoichiometric under layer. It will be demonstrated that the electrode performance, which is controlled by surface reaction kinetics, is improved by cation nonstoichiometry of the surface layer.

2. Experimental

The dense electrode thin films are deposited on the electrolyte substrates by an RF-sputtering method (Sanyu, SVC-700RFII, Japan). The sputtering target materials of La/Sr–Co perovskite-based oxides are synthesized via Pechini method. The appropriate amounts of $La(NO_3)_3 6H_2O$, $Co(NO_3)_2 xH_2O$ and $SrCO_3$ are dissolved into deionized water with citric acid. The solution is gradually heated up to form gel, which is subsequently dried and burned into ash-like solids. The powder is calcined at 873–1173 K, followed by grinding with a mortar. The obtained powders are pressed at ca.100 MPa into pellets of 24.5 mm diameter, and then

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sintered at 1373–1473 K to be used as sputtering targets. The sputtering process is carried out under chamber pressure of 2 Pa with Ar as process gas at applied RF power of 150 W.

The compositions of La/Sr–Co perovskite-based dense thin films are evaluated by energy dispersive X-ray spectrometry (EDS) (JEOL, JSM 7001F, Japan). The characterization with X-ray diffraction (XRD) (Rigaku, Ultima III, Japan) and transmission electron microscopy (TEM) (JEOL, JEM 2010HC, Japan) is made on the thin films fabricated on sintered polycrystalline Gd-doped CeO_2 (GDC) pellets. For the fabrication of the GDC pellets, powder of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (Anan Kasei, Japan) is pressed and sintered at 1873 K for 10 h. The surface of the pellets is polished with diamond paste.

Three-terminal cells (Fig. 2) are constructed for ac impedance measurements on La/Sr–Co perovskite-based dense thin film electrodes fabricated as described above. The electrolyte is 10% YSZ single-crystal (10 mm square, 0.5 mm thick) with polished (100) surface. Pt counter electrode, a thin Gd-doped CeO_2 (GDC) layer between electrolyte YSZ and working electrode, and La/Sr–Co thin film as working electrode are prepared by an RF-sputtering method. The La/Sr–Co thin as-sputtered films in amorphous structure are subsequently heat-treated at 873 K for 1 h in oxygen atmosphere (oxygen partial pressure (P_{O2}) = 1 atm) for crystallization.

An ac impedance spectroscopy measurement on the three terminal cells is conducted with a frequency response analyzer (Ivium technology, Compactstat, The Netherlands) in a frequency range of 0.01 Hz to 1 MHz with voltage amplitude of 10 mV. Electrical contact to the working electrode is made with an Au net, whereas those to the counter and reference electrodes are made with Pt mesh and wire. Electrochemical impedance spectroscopy (EIS) data are collected in the oxygen partial pressure of 1 atm at 673–873 K.

In this work, the authors examined a dense single-layer thin film electrode of $(La,Sr)CoO_3$ (termed LSC113 hereafter) and some dense bi-layer thin film electrodes, which are prepared by depositing onto the LSC113 film a thin surface layer of $(La,Sr)CoO_3$ with A-site and B-site deficiency (termed A-deficient LSC113 and B-deficient LSC113, respectively).

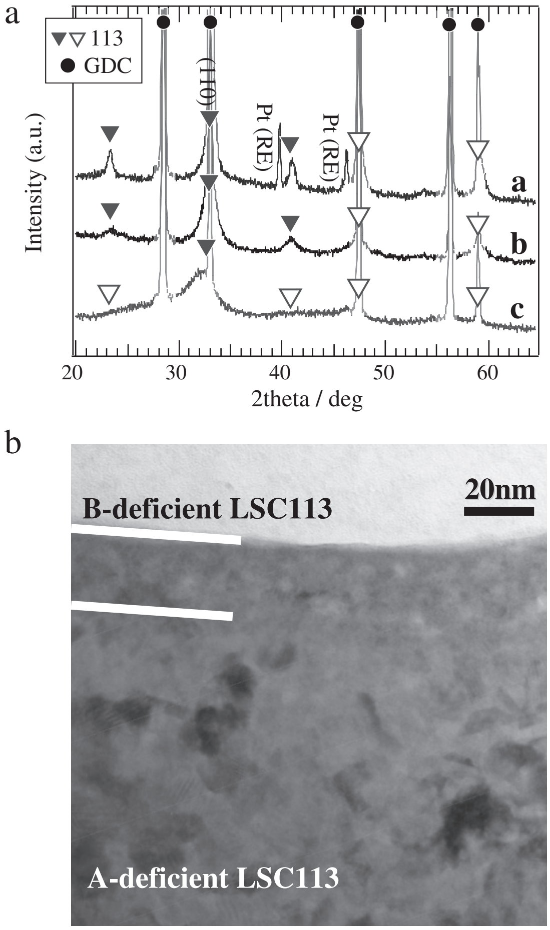

Fig. 1. a: X-ray diffraction spectra of thick single-layer thin films on polycrystalline GDC pellets, (a) A-deficient LSC113, (b) LSC113 and (c) B-deficient LSC113. b: TEM micrograph of bi-layer thin film: B-deficient LSC113/A-site deficient LSC113 on polycrystalline GDC pellet.

3. Results and discussion

Fig. 1a shows XRD patterns of a thick single-layer of LSC113, A-deficient LSC113 and B-deficient LSC113. These thick single-layer films are prepared onto polycrystalline GDC pellets. LSC113 crystallizes in pseudocubic after the post-annealing at 873 K for 1 h. The XRD patterns of LSC113, A-site deficient LSC113 represent the peaks of perovskite-type $(La,Sr)CoO_3$. It is noted that for A-site deficient LSC113 film, a signature of Co_3O_4 coexistence is observed in the Raman spectrum (not shown). On the other hand, the XRD pattern of B-deficient LSC113 is less distinctive, except for a broad peak centered at about 32°. Although the *d*-spacing for this peak is rather large compared with typical $(La,Sr)CoO_3$, this peak can be ascribed to a perovskite (110) peak, which is also inferred by electron diffraction analysis (not shown) combined with TEM. This result suggests that, under oxidizing atmosphere (P_{O2} = 1 atm) at 873 K, B-deficient LSC113 crystallizes in the perovskite structure with low crystallinity, not in the K_2NiF_4 structure.

TEM observation of the bi-layer B-deficient LSC113/A-deficient LSC113 film, which is fabricated onto polycrystalline GDC pellets, is conducted in order to investigate the cross section morphology of the bi-layer film. The preparation method of bi-layer B-deficient LSC113/A-deficient LSC113 is the same as that of single- and bi-layer electrode for ac impedance measurements. From the results of TEM observation as shown in Fig. 1b, a dense and compact surface layer is fabricated on the A-deficient LSC113 under layer. This result suggests that surface oxygen adsorption and dissociation in the electrode reaction occur at the two-phase boundary of gas phase and surface layer.

From the impedance measurements carried out in the temperature range from 673 K to 873 K under pure dry oxygen atmosphere (P_{O2} = 1 atm), the total resistance of the electrode reaction, which is considered to originate mostly from the reaction at electrode surface, is extracted, and converted into the electrode interfacial conductivity (σ_E) as a measure of electrode performance. It is noted that σ_E is equivalent to the inverse of area specific resistance (ASR). The σ_E values obtained just after attaining the sample temperature stabilization are shown in Fig. 2, which includes the four types of LSC thin film electrodes fabricated on YSZ single-crystals with GDC buffer layers as follows: (1) single-layer “LSC113”; (2) and (3) “B-deficient LSC113/LSC113” bi-layer thin film consisting of thick LSC113 under layer and thin (20 nm) B-deficient LSC113 surface layer; and (4) “A-deficient LSC113/LSC113” bi-layer thin film consisting of thick LSC113 under layer and thin (20 nm) A-deficient LSC113 surface layer. The compositions of the surface and under layer are summarized in Table 1. Fig. 2 suggests that the bi-layer electrode with highly cation-nonstoichiometric surface layer, shows higher σ_E than the single-layer LSC113 at 873 K.

The results of Figs. 1 and 2 suggest that A-deficient and B-deficient LSC113 crystallize as a cation-nonstoichiometric perovskite phase, which is a metastable state retaining a certain extent of supersaturation from the initial amorphous state of as-sputtered film via stabilization by a short-term post-annealing for crystallization. This is a possible origin of the cation-nonstoichiometric surface layer with highly enhanced reaction kinetics. The fast reaction kinetics of A-deficient and B-deficient LSC113 can be attributed to increased concentration of oxygen vacancy formed specifically for the charge-compensation of the A-site and B-site deficiency. The relationship of cation

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