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Oxygen nonstoichiometry and chemical expansion of mixed conducting $La_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$

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ABSTRACT

The chemical diffusivity and surface exchange constant of $La_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF1982) were successfully extracted by using the chemical expansion relaxation method, and the oxygen nonstoichiometry was determined by electrochemical coulometric titration as a function of oxygen partial pressure (pO_2) and temperature. The oxygen chemical diffusivity and surface exchange constants were 3.16×10^{-4} cm^2/s and 6.31×10^{-3} cm/s at 1000 °C in air, respectively. These values and the activation energies for oxygen diffusion were in good agreement with our own previously reported values determined from the 4-probe D.C. conductivity relaxation method. The oxygen nonstoichiometry was increased with decreasing pO_2 and increasing temperature, due to the thermal and chemical release of lattice-site oxygen from the lattice sites. The oxygen self-diffusion coefficient and ionic conductivity were successfully extracted from the relation between the oxygen nonstoichiometry and the chemical diffusion coefficient, and are best expressed by the following equations:

$$D_O/\mathrm{cm}^2/\mathrm{s} = (1.75\pm0.05)\times10^{-4}\exp\left(-\frac{0.68\pm0.10\,\mathrm{eV}}{kT}\right)\Bigg|_{pO_2=0.21\,\mathrm{atm}}$$

$$\sigma_{ion}T/\mathrm{cm}^2/\mathrm{s\,K}^{-1} = (4.01\pm0.02)\times10^{5}\exp\left(-\frac{0.65\pm0.04\,\mathrm{eV}}{kT}\right)\Bigg|_{pO_2=0.21\,\mathrm{atm}}.$$

1. Introduction

Over the decades, mixed-ionic–electronic conducting (MIEC) oxides have been investigated as an oxygen separation membrane [1–3], cathode for solid oxide fuel cells (SOFC), or reactor for partial oxidation of methane to syngas because of their higher ionic and electronic conductivities with higher surface catalytic effects [4,5]. Among MIECs, ABO_3 perovskite structure-type oxides have been widely investigated due to their superior performance compared to other structure-type oxides, which can be directly attributed to the partial substitution of both A- and B-site cations in the structure and its effect in accelerating the generation of oxygen vacancies via defect reaction [6–8].

The $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) series has been intensively studied for various commercial applications [6,7]. Teraoka's group [10] studied the oxygen permeability of several LSCF series and confirmed that perovskite-type oxides with two or more types of transition metal ion in the B-site are always more reactive than those with only one type of transition metal ion, and, furthermore, that the oxygen ionic conductivity was increased with increasing Sr and Co contents in the LSCF series [6,10]. Matsumoto et al. [9] also reported the higher catalytic effects of LSCF as an electrode for oxygen evolution in alkaline solution.

Recently, $La_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF1982) was reported as an excellent surface catalyst [11,12]. This can be explained by the action of Sr on the A-site lattice of LSCF in effectively presenting a negative charge and thus acting as an acceptor, giving rise to the formation of oxygen vacancies and changing the mobility of oxygen in the bulk, although A-site cations are not catalytically active. In the case of Co ions on the B-sites, because of their smaller binding energy for oxygen compared to Fe ions, the oxygen nonstoichiometry is expected to be larger in those LSCF compositions with a higher Co ion content [6,12]. Furthermore, the thermal reduction of Co^{3+} to Co^{2+} above 800 °C also contributed to the electronic conductivity unless it was exposed to a reducing environment. Defect chemistry is expected to change according to the cation-doping strategy. Therefore, quantitative defect analysis is very important because several of the oxide's transport properties are directly

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connected with the defect structure in the given thermodynamic condition. However, the oxide's transport properties have not yet been fully analyzed quantitatively. Therefore, we reported the fundamental properties, including the oxygen ionic conductivity and the chemical diffusion coefficient, of LSCF1982 that were successfully derived in our previous work by oxygen permeability study and the 4-probe D.C. conductivity method [13]. In the present work, the oxygen nonstoichiometry and the oxygen self-diffusion coefficient are measured by the electrochemical coulometric titration method and the chemical expansion relaxation technique under a range of thermodynamic conditions ($700 \leq T/°C \leq 1000$ and $10^{-6} \leq pO_2/atm \leq 0.21$).

2. Experimental

2.1. Sample preparation

The perovskite-type, LSCF1982 powders were synthesized by solid state reaction method. Highly pure La_2O_3 (Aldrich, 99.9%), $SrCO_3$ (Aldrich, 99.9%), Co_3O_4 (Aldrich, 99.9%), and Fe_2O_3 (Aldrich, 99.99%) were used as starting materials. The components at stoichiometric amounts were weighed and then mixed in a ball mill. The powder was calcined at 1000 °C in air for 10 h and then ground in a planetary mill with a zirconia jar for 5 cycles of 30 min at 320 rpm to finally afford a particle size of 1–3 μm. The X-ray diffraction (XRD) measurements were performed with a Rigaku diffraction device (D/Max Vitina III) in the 2θ range of 20–80°. The XRD pattern showed a single phase cubic perovskite ($P3\overline{m}3$) LSCF1982 structure, as shown in Fig. 1. For the measurements, the obtained powders were mono-axially pressed, and then cold isostatically pressed at 150 MPa. The obtained green pallets were sintered at 1200 °C in air for 10 h, and then cut and polished.

2.2. Thermal and chemical expansion properties

The thermal and chemical expansion properties of the LSCF1982 samples (≈95% of theoretical density) prepared in a rectangular shape (1.7 × 1.7 × 15 mm) were measured using a dilatometer (Netzsch L75 PT1600) under a range of thermodynamic conditions. The chemical expansion transitions were measured over a wide temperature range ($700 \leq T/°C \leq 1000$; heating rate-2 °C/min) and oxygen partial pressure range ($10^{-3} \leq pO_2/atm \leq 0.21$). The dilatometer was calibrated using standard alumina rod for the accuracy of data, under the air and nitrogen gas atmosphere. In the chemical expansion relaxation measurement, 250 sccm total gas was flowed to change the surrounding-atmosphere of sample at isothermal conditions. The pO_2 was controlled by air and nitrogen gas mixture and was monitored using a YSZ electrochemical sensor. Finally, the chemical diffusion coefficient and the surface exchange constant were extracted by non-linear equation fitting, as detailed in the literature [13–16].

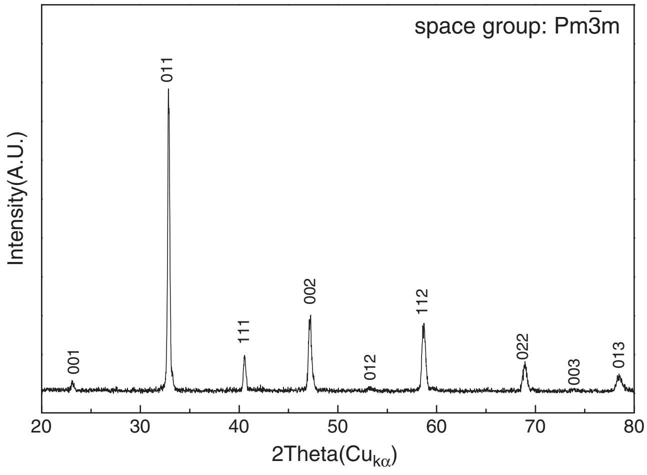

Fig. 1. Room temperature XRD patterns of calcined LSCF1982 at 1000 °C in air.

2.3. Oxygen nonstoichiometry

The oxygen nonstoichiometry of LSCF1982 was determined by the electrochemical coulometric titration method used in our previous study [17] and the absolute oxygen nonstoichiometry by the thermogravimetric full reduction method with Cahn D-200 microbalance [18,19]. The electrochemical coulometric titration cell was configured as illustrated in Fig. 2(a). The electrolyte, consisting of an 8 mol% YSZ disk, was used for the oxygen pumping and sensing. Mechanical leakage was prevented by sealing with borosilicate glass ($Al_2O_3/BaO/SiO_2/B_2O_3$: ratio of wt.% 10/25/49/16) [17]. For the leak test, the pO_2 inside the cell was measured according to time after the abrupt change of pO_2 outside the cell while a constant pO_2 was maintained, meaning no oxygen leakage flux as shown in Fig. 2(b). The measurement was conducted using a LabVIEW control system consisting of a programmable current source (Keithley 6210) and digital multimeter (Keithley 2700). The relative oxygen nonstoichiometry (Δδ) was calculated using Eq. (1) [17]

$$\Delta\delta = \delta - \delta^* = \frac{It}{2F}\frac{M}{m_0} \tag{1}$$

where, δ^* is the absolute oxygen nonstoichiometry, and I, t, F, M and m_0 represent a constant current flow through the electrochemical

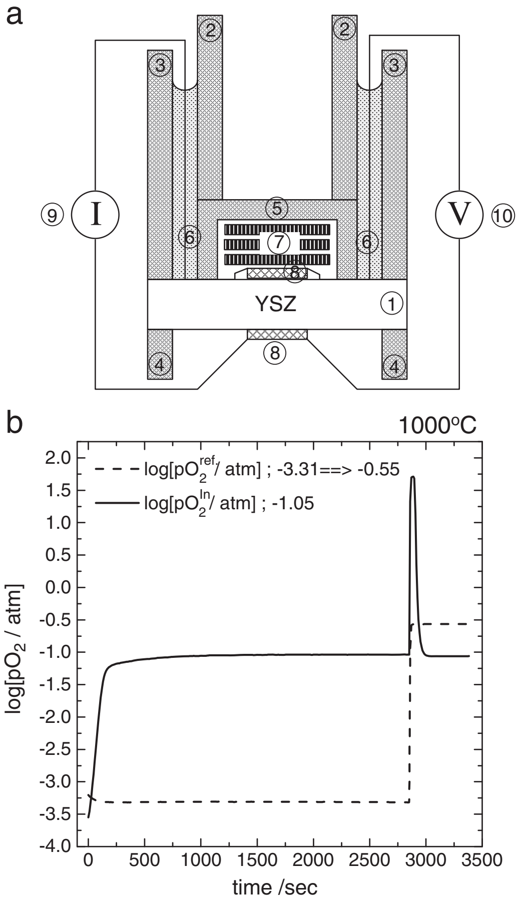

Fig. 2. (a) Illustration of configured electrochemical titration cell: 1 YSZ electrochemical electrolyte, 2–4 alumina tubes, 5 alumina cup, 6 borosilicate glass, 7 sample, 8 reversible Pt electrode, 9 programmable current source, and 10, digital multi meter, (b) Oxygen partial pressure change of the coulometric titration cell according to time during the leak test.