Catalytic chemical potential shift on the surface of nonstoichiometric oxides under non-equilibrium gas atmosphere

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Abstract

Perovskite-type oxide, $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, has large oxygen nonstoichiometry and high electrical conductivity with a large carrier concentration. The oxygen nonstoichiometry, δ, of dense $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ was measured in the stream of $NO_x-O_2-N_2$ system at 873 to 1073 K by means of a thermogravimetric method. Small amounts of NO_2 caused large changes in oxygen nonstoichiometry. It seems probable that excessive amounts of oxygen can be incorporated into the bulk due to catalytic decomposition of NO_2, and as a result, oxygen potential on the surface of the sample seems to be much higher than that of gaseous phase. EMF measurements for dense $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ electrode also revealed that the oxygen potential is affected by NO_2. Thus, the gas sensing mechanism of this oxide was found to relate to the change of the bulk property, especially oxygen nonstoichiometry.
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1. Introduction

In order to prevent air pollution, the development of a toxic gas sensor is important to control exhaust gas from combustion engines. Attention has been paid to a solid oxide gas sensor, because it has the great advantages in terms of cost and ease of maintenance. To improve sensor performance, including selectivity, sensitivity and response time, it is necessary to clarify the gas sensing mechanism.

The mechanism of semiconductor sensors such as SnO_x has been intensively investigated. Most of them were explained by a surface adsorption model. In this model, adsorbed gaseous species trap charge carriers of a sensing material. Thus, the concentration change of test gas is detected as the variation of electrical conductivity. One should, however, note that this model can only be applied when the carrier concentration in bulk is small enough to be affected by gas adsorption. That is, the surface adsorption model does not hold in the case of a high carrier concentration system.

It was reported that doped $LnCoO_3$ (Ln: lanthanide) and La_2CuO_4 were sensitive to small amounts of the target gas, NO_2, although the carrier concentration of these material were high by aliovalent cation substitution [1,2]. The previous work proposed that small amount of the target gas induced the variation of electrical conductivity via change in oxygen nonstoichiometry of the bulk, which is to say, the bulk sensing mechanism. It was considered that, in this model, interaction of non-equilibrated gas with oxygen sublattice in the bulk caused the variation of the carrier concentration.

The perovskite type oxide, $La_{1-x}Sr_xCoO_{3-\delta}$, which has large oxygen nonstoichiometry [3] and a high oxidation catalytic activity [1,4], is well known material for gas sensors, SOFC electrodes, and catalysts, while the electrical conductivity has little dependence on oxygen

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partial pressure [5]. If the bulk sensing model is valid for $La_{1-x}Sr_xCoO_{3-\delta}$, the effect of non-equilibrated gas should cause not only the change in conductivity but the oxygen vacancy concentration, which can be detected directly as the weight change of the sample. In this study, an attempt was made to verify the bulk sensing model for $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) in NO_x (x = 1, 2) containing atmosphere with a thermogravimetric method and electrochemical measurement.

2. Experimental

2.1. Preparation of $La_{1-x}Sr_xCoO_{3-\delta}$ (x = 0.4, 0.5)

The powder of $La_{1-x}Sr_xCoO_{3-\delta}$ (x = 0.4, 0.5) was prepared by a citric acid method. Starting materials of lanthanum oxide, La_2O_3, strontium carbonate, $SrCO_3$, and cobalt oxide, Co_3O_4 were precisely weighed after drying process. Each powder was completely dissolved into diluted HNO_3. The concentration of each solution was determined from the weight of the dried powder and the volume of the solution. Then, these solutions were mixed together in proper ratios of the metal ions. An excess amount of citric acid was added to the mixed solutions. The precursors were obtained by heating the solution to remove water and nitric oxides. The dried powders were then fired in air at 1273 K for 5 h (x = 0.4) and at 1173 K for 3 h (x = 0.5), respectively. X-ray diffraction confirmed that the resultant powders were perovskite-type single phase.

2.2. Thermogravimetric (TG) measurement

The powder of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ were pressed into rods and sintered at 1373 K for 15 h, whose relative densities
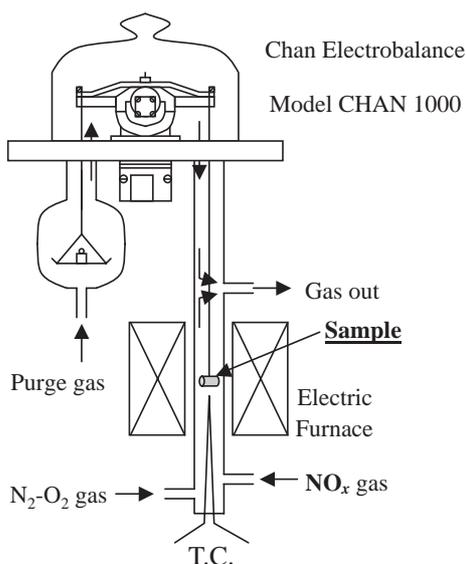
Fig. 1. A schematic view of apparatus for oxygen nonstoichiometry measurement.
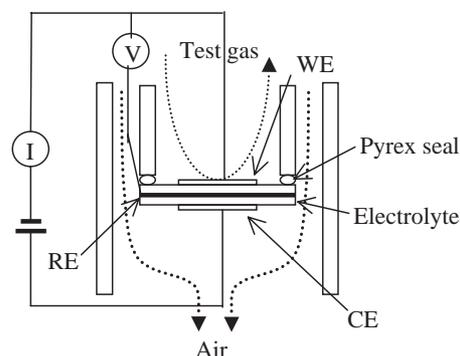
Fig. 2. A schematic view of electrochemical measurement setup.

were 99% of the theoretical one. The sample weight was 1.3 g. The oxygen nonstoichiometry, δ, was measured as the weight change of the sample by using a microbalance (CHAN model 1000). Fig. 1 illustrates an apparatus for thermogravimetric measurement. Gases were mixed to control oxygen partial pressure, $P(O_2)$, and nitric oxide partial pressure, $P(NO_x)$, then introduced into the lower side of the equipment at the flow rate of 100 cm^3/min in total, while the purge gas was fed into the microbalance at the same rate to avoid its damage caused by NO_x. The sample temperature, T, was monitored with a thermocouple placed just under the sample. Any material, which may have a catalytic activity for NO_x, was excluded from the measurement system to avoid equilibrating NO_x before reaching the sample. The measurements were conducted at 873 to 1073 K in NO_x–O_2–N_2 system, where $P(NO_x)$ was changed between 0 and 900 ppm. In order to minimize the experimental error, the difference in buoyancy, which depends on the various gas compositions and temperatures, was taken into consideration. As a result, the accuracy of the microbalance was in the range of 30 μg.

2.3. EMF measurement

The electrochemical cell was fabricated as following: the electrolyte powder of $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ was prepared by a coprecipitation method from cerium and gadolinium nitrate solutions. It was calcined at 1273 K for 5 h, and then pressed and sintered at 1873 K for 5 h. The relative density was higher than 98%. The dense film of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ was deposited on the electrolyte as a working electrode (WE) by a pulsed laser deposition technique. The deposition condition follows: oxygen partial pressure was ca. 1 Pa; temperature of the electrolyte substrate was 973 K; Xe–Cl laser was irradiated to $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ target at the power density of 200–230 mJ/cm^2; the repetition rate was 4 Hz. Platinum paste (Tanaka, TR7905) was painted and sintered at 1173 K for 1 h to form counter and reference electrodes on the back surface and the side surface of the pellet, respectively.

In electrochemical measurements, a two-compartment chamber was used to control gas composition at each