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Oxygen transport of A-site deficient $Sr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ ($x = 0$–0.3) membranes

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ABSTRACT

A solid-state reaction was used to prepare $Sr_{1-x}(Fe_{0.5}Co_{0.5})O_{3-\delta}$ ($x = 0$–0.3) mixed (electronic and ionic)-conducting oxides. An A-site cation deficiency in $Sr_{1-x}(Fe_{0.5}Co_{0.5})O_{3-\delta}$ ($x = 0.05$–0.1) causes the Sr-rich phase of grain and grain boundaries to disappear. It also enhances the stability of the perovskite structure and reduces thermal expansion at high temperatures in an Ar atmosphere. However, a further deficiency of Sr causes the segregation of a considerable amount of Co_3O_4 and FeO. As the Sr deficiency is increased, there is a slight decrease in the electrical conductivity in air and improvement of the oxygen permeation fluxes of slightly Sr-deficient membranes ($x = 0.05, 0.1$). The effect of Sr deficiency on the oxygen transport in the $Sr_{1-x}(Fe_{0.5}Co_{0.5})O_{3-\delta}$ membrane is discussed in terms of the microstructure and phase transition.

1. Introduction

Mixed oxygen-ionic and electronic conducting (MIEC) ceramics are very attractive for oxygen separation at high temperatures because they have the potential to permeate oxygen with high selectivity over other gaseous phases [1,2]. Of the MIEC materials, $(La,Sr)(Co,Fe)O_{3-\delta}$ systems have been researched for their transport properties, chemical and thermal stability, and performance in membrane applications [3–7]. Teraoka et al. reported that the substitution of Sr^{+2} for La^{+3} in the A-cation site raises the ionic conductivity due to the increase of the oxygen vacancy whereas the substitution of Fe for Co in the B-cation site preserves the perovskite structure with a high Sr content [8–11]. Other studies have shown that $Sr(Co,Fe)O_{3-\delta}$, whose A-sites are fully substituted with alkaline-earth metal (Sr), has a high level of oxygen permeability [8,12].

The oxygen-permeating properties of these MIEC materials are strongly correlated with the structure and chemical composition. $Sr(Co,Fe)O_{3-\delta}$ undergoes a phase transition from a perovskite structure to a brownmillerite structure, especially under low oxygen activity [7,13–16]. The phase transformation enhances the ordering of the oxygen vacancies, which degrades the ionic conductivity because the oxygen vacancy is trapped in a local cluster. The perovskite phase of $Sr(Co,Fe)O_{3-\delta}$ was reported to be thermodynamically unstable at low temperature under reduced oxygen partial pressure [16–18].

Because the perovskite structure (ABO_3) is flexible in its elemental composition, a modified A/B stoichiometry can be used as an alternative to enhance the properties of the oxygen membrane. The A-site cation deficiency in $Sr_{1-x}Fe_{0.8}Ti_{0.2}O_{3-\delta}$ ($x = 0$–0.06) suppresses the oxygen vacancy ordering and thereby enhances the oxygen ion conductivity and stability in the presence of CO_2 [19]. The A-site deficiency also helps the sintering of the $(Ba_{0.5}Sr_{0.5})_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane due to an increase in A-site cation mobility and enhances the oxygen permeation flux [20]. There is a discrepancy between the oxygen permeability results of the A-site deficient perovskite materials. The A/B cation nonstoichiometry in $(Ba_{0.5}Sr_{0.5})_{0.97}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [20] and $La_{0.5}Sr_{0.4}MnO_{3-\delta}$ [21] enhances their oxygen permeability. On the other hand, it has been reported that the ionic transport of the A-site cation-deficient $(La_{0.3}Sr_{0.7})_{0.97}CoO_{3-\delta}$ is lower than that of $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ [22].

In this study, we synthesized $Sr_{1-x}(Fe_{0.5}Co_{0.5})O_{3-\delta}$ ($x = 0$–0.3) by using a solid-state reaction; we also investigated the compositional effects on structural and microstructural stability, thermal expansion, and electrical conductivity. In addition, the oxygen permeation properties of Sr-deficient $Sr_{1-x}(Fe_{0.5}Co_{0.5})O_{3-\delta}$ membranes were analyzed in relation to the stability of the perovskite phase and microstructure.

2. Experimental

A solid-state reaction was used to synthesize $Sr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ ($x = 0$–0.3) oxides. Stoichiometric amounts of $SrCO_3$

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(99.9%, Aldrich Chemical), Fe_2O_3 (99.9%, Aldrich Chemical), and Co_3O_4 (99.9%, Grand Chemical & Material) were mixed by wet-milling for 24 h with isopropyl alcohol and zirconia balls. The mixed powders were dried with a rotary evaporator and calcined at 1100 °C for 2 h to synthesize the perovskite phase. Disk-type membranes were prepared by cold isostatic pressing at 300 MPa and sintering at 1240 °C for 5 h in ambient air. The relative density of the membranes measured by the Archimedes method was not less than 94% in this work.

The sintered disks were pulverized into powder and an X-ray diffractometer (XRD, Rigaku, Japan) was used to investigate the phase change in situ as the temperature increased. The high-temperature XRD experiments were conducted in ambient air and He at temperatures ranging from room temperature to 1000 °C. For analysis of the microstructure, a cross section of sintered disks was polished and thermally etched at 1100 °C in ambient air. The microstructure and local composition of the sintered membranes were investigated with a scanning electron microscope equipped with an energy dispersive X-ray spectroscope (SEM/EDX, Hitachi, Japan). The thermal expansion coefficient (TEC) of the sintered specimen (3 mm × 3 mm × 25 mm) was measured with a DIL 402C dilatometer at temperatures ranging from 25 °C to 900 °C at a heating rate of 5 °C/min under an Ar condition.

The electrical conductivity of the sample was measured by means of a four-probe DC method in O_2, air, 1% O_2 and Ar atmospheres ($pO_2 = 6.6 \times 10^{-4}$ atm). The bar specimens were painted with Pt paste (Engelhard, model no. 6082, USA) at specific intervals and cured at 900 °C for 30 min. Four Pt wires were wound around the bars as connection points for the probes from a source-measure unit (Keithley, K2400, USA). The current–voltage characteristics were measured in a current range of −0.05 mA to +0.05 mA. The measurements were conducted in a mode of decreasing temperature in the same atmosphere.

The oxygen permeation fluxes of the sintered membranes were characterized from 1000 °C to 700 °C. The polished membranes, which had a diameter of 20 mm and a thickness of 1.0 mm, were sealed with a Pyrex glass ring (inner diameter = 13.4 mm) at the end of an alumina tube. Thus, the effective area of membranes exposed to gas was 1.41 cm^2. The reactor was heated to 1000 °C at 2.0 °C/min in ambient air and maintained for 5 h for the glass ring to be softened. Synthetic air (0.21 atm) was fed into one side and high purity He (99.999%) was used as the sweep gas on the permeate side (3.2×10^{-4} atm). The gas flow rates were kept at 30 ml/min. The leaked oxygen flux due to incomplete sealing or open pores in the membrane was detected in a gas chromatograph (GC, ACME 6000, carboxen-1000 column) used to monitor the nitrogen concentration. The oxygen permeation flux was calculated as follows:

$$j_{O_2}(\text{mol cm}^{-2}\,\text{s}^{-1}) = \left[C_O - C_N\frac{0.21}{0.79}\right]\frac{F}{S},$$

where C_O is the oxygen concentration and C_N is the nitrogen concentration as measured at the permeate side; F is the flow rate of the sweeping gas, including the permeated gas; and S is the active area of the disk membrane. The amount of oxygen leak possibly from incomplete sealing was less than 0.015 μmol $cm^{-2}\,s^{-1}$, which was negligible compared with permeated oxygen flux by ionic diffusion in the specimen.

3. Results and discussion

3.1. Phase and microstructure of $Sr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (x = 0–0.3)

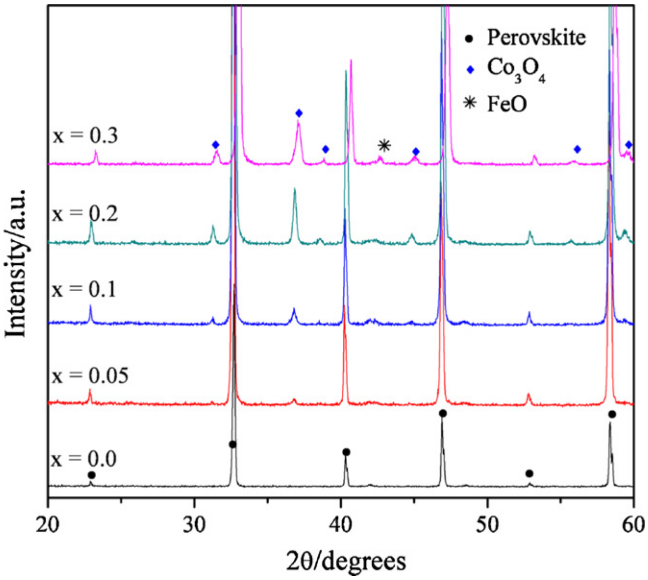

Fig. 1. X-ray diffraction patterns of $Sr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (x = 0–0.3) at room temperature.

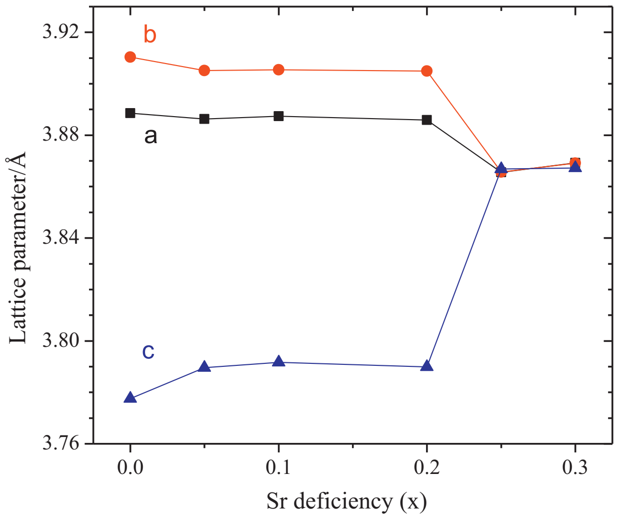

Fig. 2. Lattice parameters of $Sr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (x = 0–0.3) at room temperature in ambient air.

Fig. 1 shows XRD spectra of $Sr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (SFC) (x = 0–0.3) synthesized by a solid-state reaction of a carbonate and oxide mixture. The pulverized powder from the sintered disks (1250 °C) was placed on a quartz holder and heated from room temperature to 1000 °C. XRD patterns were obtained at room temperature after cooling in ambient air. The major peaks of SFC oxides were identified as a perovskite structure. With an increase of Sr-deficiency, the intensity of the peaks for the Co_3O_4 phase was strengthened at $x \geq 0.1$, and an FeO phase was detected at $x = 0.3$. This outcome suggests that the limit of Sr deficiency for the single perovskite phase is around $x = 0.1$; beyond that amount there is an increase in secondary phases. Fig. 2 shows the unit cell parameters of SFC as calculated from the plane distances of (1 1 0), (2 0 0), (2 1 1). The peak positions were calibrated using standard Si powder which was mixed with specimen. As the Sr deficiency increases within a range of $x \leq 0.2$, the lattice parameters of a and b remain almost constant whereas the lattice parameter of c is slightly increased. At room temperature, most of the specimen showed splits of peaks around $2\theta = 40°$, 47°, and 58°. The crystal structure of the $SrFe_{1-x}Co_xO_{3-\delta}$ with cobalt content $0 \leq x \leq 0.3$ was found to be tetragonal, space