Stability and oxygen transport property of $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$

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A B S T R A C T

The stability of $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCrF) in reducing atmosphere was investigated by examining the extent of its reaction with hydrogen at elevated temperature. LSCrF powder exposed to diluted hydrogen was found to loss a weight of only ~0.5%, corresponding to the formation of oxygen vacancies in the lattice. LSCrF powder exposed to flowing concentrated hydrogen for 30 h was found to decompose partially. The decomposition oxygen partial pressure of LSCrF at 950 °C was estimated to be 6.3×10^{-28} atm from thermodynamic calculations. The stability of LSCrF under an oxygen chemical potential gradient was also examined by exposing a disk-shaped dense sample to air at one side and to reducing atmosphere (CO) at the other side at elevated temperatures. A thin, porous layer was found to form on the CO side surface. An oxygen permeation flux of 2.5×10^{-7} mol cm^{-2} s^{-1} was observed at 950 °C under given air/CO gradient. The occurrence of oxygen permeation revealed the presence of mixed oxygen ionic and electronic conductivity. The oxygen ionic conductivity was estimated to be ~0.01 S/cm at 950 °C.

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1. Introduction

Perovskite-structured transition metal oxides have been explored for applications as electrodes in solid oxide fuel cells (SOFCs), oxygen separation membranes and oxidation catalysts [1–12]. In particular, $LaCrO_3$-based oxides have been investigated as anode materials in SOFCs as well as oxidation catalysts [4–7]. The composition $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ has been reported to exhibit good stability and catalytic properties for oxidation of CH_4 [7]. It has also been used to form dual-phase composite membranes for oxygen separation [13, 14], in which oxide ions and electrons are transported through different phases.

Perovskite-structured oxides with potential applications as electrodes in SOFCs and oxidation catalysts usually exhibit mixed oxygen ionic and electronic conductivity. In these materials, oxide ions are transported via jumping of oxygen vacancies while electrons via polaron mechanism. In most cases, their electronic conduction is dominant over the oxygen ionic conduction. Therefore, the conventional electrical conductivity measurement gives the electronic conductivity of the materials. The oxygen ionic conductivity in pre-dominantly electronic conductors can be measured via using a special electrode which allows oxide ions to pass through while blocking electrons. However, this blocking electrode method has its own limitation [15]. The oxygen ionic conductivity can also be derived from oxygen permeation measurements in combination with total conductivity measurements [16]. In the present study, this method was used to measure the oxygen ionic conductivity of LSCrF.

The chemical stability and the structural integrity of the materials are essential for applications as SOFC anodes or oxidation catalysts. LSCrF was reported to be at its stability limit under the operation conditions for SOFC anode [7]. In the present study, the stability of LSCrF in reducing atmosphere was investigated by examining the extent of its reaction with hydrogen. In addition, the decomposition oxygen pressure of LSCrF was obtained from thermodynamic calculations. The structural integrity of LSCrF was also examined under a large oxygen chemical potential gradient with one side of a disk-shaped dense sample exposed to air and the other side to reducing atmosphere (CO).

2. Experimental

2.1. Sample preparation and characterization

Perovskite LSCrF powders were synthesized via a conventional solid-state reaction route. Appropriate amounts of $SrCO_3$ (AR, Sinopharm Chemical Reagent Co.), La_2O_3 (AR, Sinopharm Chemical Reagent Co.), Cr_2O_3 (AR, Sinopharm Chemical Reagent Co.) and Fe_2O_3 (AR, Sinopharm Chemical Reagent Co.) were weighed and ball-milled. The mixture was calcined at 1200 °C in air for 10 h to yield the perovskite structure. The phase purity was verified by X-ray powder diffraction (XRD) (X'Pert Pro, Phillips) using CuKα (with an output power 40 kV × 100 mA) radiation in a 2θ range of 20°–80° with a scan step of 0.02°.

Disk-shaped samples of LSCrF were also prepared from the as-synthesized powder. The LSCrF powder was ground and pressed into discs under a pressure of 100 MPa and then subjected to sintering at 1550 °C in air for 10 h. The density of as-prepared samples was measured to be above 90% of the theoretical density using Archimedes

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method in mercury. The microstructures of the sintered bodies were examined by scanning electron microscopy (JSM-6700 F, JEOL).

The stability of LSCrF was characterized by the extent of its reaction with hydrogen at 950 °C. A powder sample was exposed to diluted flowing hydrogen (2% H_2/N_2) at that temperature, and the weight change was recorded. Another powder sample was annealed in pure flowing hydrogen for 30 h. The heat-treated powders were analyzed by XRD. The decomposition oxygen partial pressure for LSCrF was obtained via thermodynamic calculations using the software Thermo-Calc [17] together the thermodynamic databases (E. Povoden-Karadeniz, unpublished data) [18].

2.2. Oxygen permeation measurement

Experimental details on oxygen permeation measurements are referred to Ref. [19]. Disk-shaped samples were machined to 1 mm thick, ultrasonically cleaned in ethanol and then sealed to the end of an alumina tube at 1050 °C using a glass ring to form a permeation cell. After sealing, the temperature was lowered to measurement temperatures. Air was fed at one side of the sample, while CO was led over the other side at fixed rate of 20 mL/min to react with the oxygen permeated from the air side. The gas composition in the effluent was analyzed by gas chromatographs (GC9750, FuLi), and the oxygen permeation flux was calculated from the formation rate of CO_2 at the CO side ($CO + 1/2O_2 = CO_2$). Any leakage of oxygen gas due to imperfection in the glass sealant or the membrane was monitored by measuring the nitrogen concentration in the effluent stream, and the oxygen permeation rate was corrected for the oxygen leakage using the corresponding nitrogen concentration [20].

3. Results

3.1. Reduction tolerance of LSCrF

Fig. 1 shows the TGA result of LSCrF powder in diluted flowing hydrogen (2% H_2/N_2). The total weight loss was ~0.5%. The powder sample after TGA analysis was examined with XRD (Fig. 2). It was found that the perovskite structure was retained. Therefore, the weight loss observed in TGA analysis was attributed to the release of oxygen and formation of oxygen vacancies: $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ $\rightarrow La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta-x} + x/2O_2$. The total weight loss of 0.5% corresponded to an increase of 0.072 in oxygen deficiency (δ).

The air-calcined LSCrF powder was also annealed in undiluted flowing hydrogen. XRD analysis shows that the LSCrF had partially decomposed into metallic iron and some unknown phases (Fig. 2). In light of the XRD analysis, thermodynamic calculations were further carried out to determine the decomposition oxygen partial
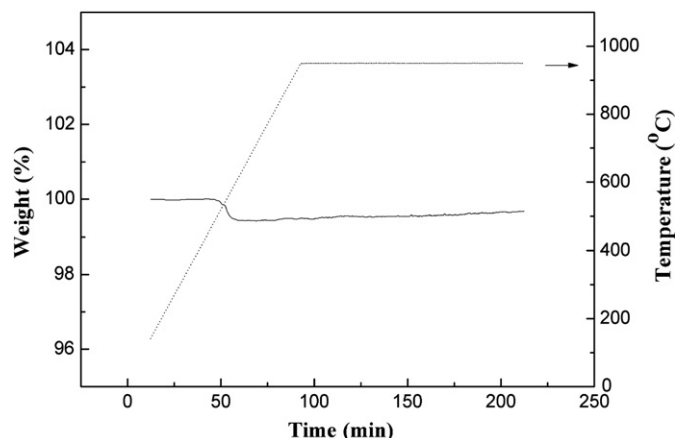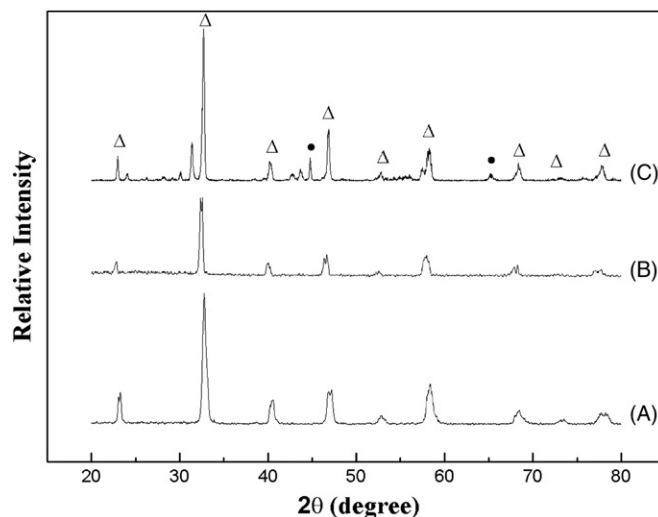
Fig. 2. The XRD patterns of LSCrF powders. (A) as-prepared, (B) after TGA in diluted H_2, (C) after thermal treatment in undiluted H_2, ($\triangle$) LSCrF and ($\bullet$) Fe.

pressure $P(O_2)$ of LSCrF, assuming that it decomposes into metallic Cr and Fe and oxides of La and Sr, i.e. $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ $\rightarrow La_2O_3 + SrO + Cr_{0.5}Fe_{0.5} + O_2$. The decomposition $P(O_2)$ was calculated to be 6.3×10^{-28} atm at 950 °C. Apparently, the $P(O_2)$ in flowing pure hydrogen is lower than that value; thus, LSCrF decomposes at that temperature. Fig. 3 plots the decomposition $P(O_2)$ as a function of temperature. Clearly, decomposition $P(O_2)$ decreases rapidly with decreasing temperature, showing that the material exhibits better stability at lower operation temperatures.

3.2. Oxygen transport of LSCrF under a large oxygen chemical potential gradient

Fig. 4 shows that when a disk-shaped sample was placed under air/CO gradient at 950 °C, an appreciable oxygen permeation flux of 1.25×10^{-7} mol cm^{-2} s^{-1} appeared and gradually increased to ~2.5×10^{-7} mol cm^{-2} s^{-1} over a period of ~90 h. The occurrence of oxygen permeation reveals that the LSCrF possesses mixed ionic and electronic conductivity at elevated temperatures. Under an oxygen chemical potential gradient, oxide ions transport from the high to the low PO_2 side, whereas electrons moves in the opposite direction. The increase of permeation flux with time observed for LSCrF may be explained as follows. Since the sample had been sintered in air ($PO_2 = 0.209$ atm),
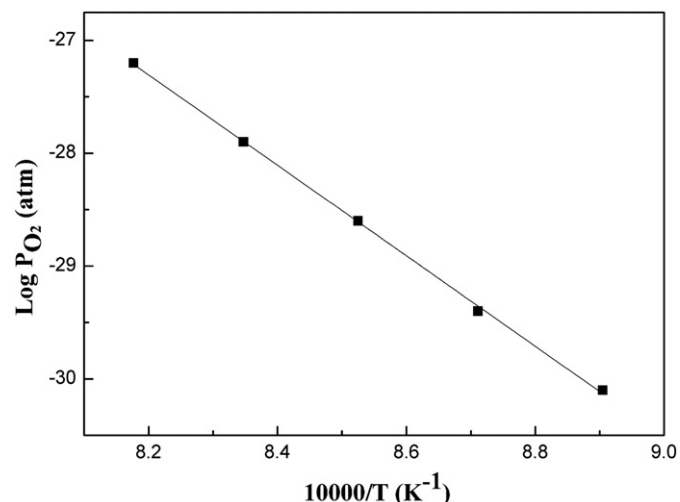
Fig. 1. TG curves of the LSCrF in a flowing 2% H_2/N_2 stream at 950 °C.

Fig. 3. The calculated decomposition oxygen partial pressure of LSCrF.