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ABSTRACT

Powder compositions in the series $La_{1-x}A_xCo_{1-y}Fe_yO_{3-\delta}$ (A=Sr, Ca) have been prepared by a combustion synthesis method. Sintering of pressed powders produced high-density test specimens with the perovskite structure. The specimens exhibited high electrical conductivities with appreciable oxygen-ion conductivity that increased with Co content for the compositions studied. Oxygen permeation studies showed a significant flux of oxygen that increased with temperature for specimens in a $P(O_2)$ gradient with no applied field. Thermogravimetric studies of the $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-\delta}$ system indicated a reversible mass loss with increasing temperature that increased with Sr content.

INTRODUCTION

Mixed ionic-electronic conductors exhibit appreciable ionic and electronic conductivities at elevated temperatures. Mixed-conducting oxides with high oxygen-ion conductivity are promising candidate materials for a wide range of attractive applications, such as cathodes for solid oxide fuel cells, oxygen-separation membranes, catalytic materials, and oxygen sensors [1,2]. The utilization of mixed conducting oxides in these applications will require a detailed understanding of processing behavior as well as electrical properties, oxygen stoichiometry, and phase stability as a function of temperature, oxygen partial pressure, and composition.

Oxides with the ABO_3 perovskite-type structure represent an important class of electroceramics that are receiving increased attention. The perovskite-type oxide, $LaCoO_3$, exhibits very high p-type electronic conductivity [3]. Recent studies [4-11] have demonstrated that the substitution of acceptor dopants onto the A or B sites of $LaCoO_3$ can introduce high concentrations of oxygen vacancies that give rise to oxygen-ion conductivity. Perovskites in the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ system have received particular attention recently [4-9] due to their high oxygen-ion conductivity. Although the ionic transference number may be quite small (<0.01), the magnitude of the ionic conductivity can be quite large. At 800°C, the oxygen ion conductivity of $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is reported to be an order of magnitude higher than for yttria-stabilized zirconia [4,5]. One of the important issues regarding compositions in these systems is structural stability.

In this study, compositions in the series $La_{1-x}A_xCo_{1-y}Fe_yO_{3-\delta}$ (A=Sr, Ca) with the perovskite structure were prepared by a combustion synthesis method. Phase development and densification of dry pressed samples were studied by X-ray diffraction and SEM analysis. Electrochemical properties were determined by electrical conductivity measurements, oxygen permeation studies, and thermogravimetric analysis.

EXPERIMENTAL PROCEDURES

Sample powders of the general composition, $La_{1-x}A_xCo_{1-y}Fe_yO_{3-\delta}$, where A = Sr and Ca, were synthesized using a glycine-nitrate process [12]. In this process, metal nitrate solutions were mixed in appropriate proportions, then glycine was added as a fuel and complexant. This glycine-nitrate mixture was heated until combustion occurred, producing a fine ash powder of the desired stoichiometry. These fine powders were calcined in air at 850°C for 12 hours. The powders were then passed through a 200-mesh sieve and pressed into rectangular bars for conductivity measurements or discs for permeation measurements. The powders were uniaxially pressed at 10,000 psi and subsequently cold isostatically pressed at 20,000 psi. The samples were sintered in air for 2 to 4 hours at temperatures ranging from 1150 to 1250°C. Bulk densities of the sintered specimens, which were measured using an immersion technique in ethanol, were 90-95% of the theoretical density.

Electrical conductivities were measured in air using a four-probe, pulsed dc technique on specimens in the form of rectangular bars, nominally 3 mm by 3 mm by 38 mm. Specimens were positioned in a resistance-heated furnace with Pt knife-edge contacts, set at predetermined distances, and Pt lead wires. The contacts were coated with Pt paste to reduce contact resistance, and the temperature of each specimen was measured with two calibrated Pt-Pt10%Rh thermocouples in contact with the specimens. The electrical conductivity instrumentation and temperature measurements were computer interfaced for automated data collection and storage. Measurements were made both on heating and cooling over the temperature range from 25 to 1200°C.

Thermogravimetric analysis (TGA) was carried out over the temperature range from 25 to 1250°C using a Cahn Model TG-171 instrument. Measurements were performed with an air atmosphere on single-phase powders that were calcined at 850°C. The rate of heating during the measurements was 5°C/min, and the rate of cooling was 2°C/min.

Oxygen permeation measurements were carried out using disc specimens (2.5 mm thick and 25 mm diameter). Each specimen was sealed in an alumina cell with gold gaskets. During the measurements, one side was exposed to a stream of O_2 (1 atm), while the other side was exposed to a N_2 stream. The oxygen/nitrogen $P(O_2)$ gradient (~10) across the specimen provided a driving force for oxygen transport from the oxygen side to the nitrogen side. Due to the mixed conductivity in these perovskite systems, the specimens responded to the $P(O_2)$ gradient by spontaneously reducing O_2 to anionic oxygen at the high $P(O_2)$ surface, transporting the anionic oxygen through the material via an oxygen-vacancy mechanism, and oxidizing the anionic oxygen to O_2 at the low $P(O_2)$ side. The passive (i.e., no applied electric field) flux of oxygen through the specimens was measured as a function of temperature with a mass spectrometer.

RESULTS AND DISCUSSION

X-ray diffraction

X-ray diffraction analysis showed that all compositions in the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ system were phase-pure perovskites, while compositions in the $La_{1-x}Ca_xCo_{1-y}Fe_yO_{3-\delta}$ were 95% phase-pure perovskites. Compositions sintered in air with high Sr content exhibited high densities; however, the sintered specimens tended to be extensively microcracked. Processing techniques that successfully reduce the microcracking will be reported at a later date.

Electrical conductivity

The dependence of electrical conductivity, σ, on absolute temperature, T, for specimens in the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and the $La_{1-x}A_xCo_{1-y}Fe_yO_{3-\delta}$ systems is shown in Figs. 1 and 2,

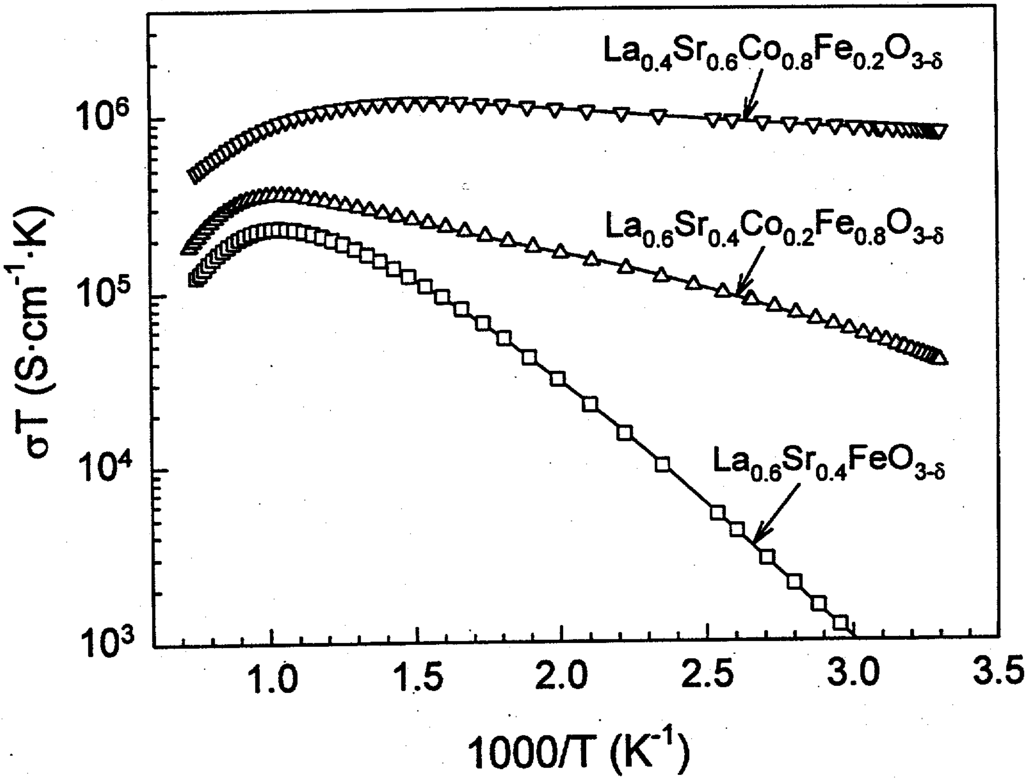

Fig. 1. Log(σT) versus 1/T for compositions in the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ system.

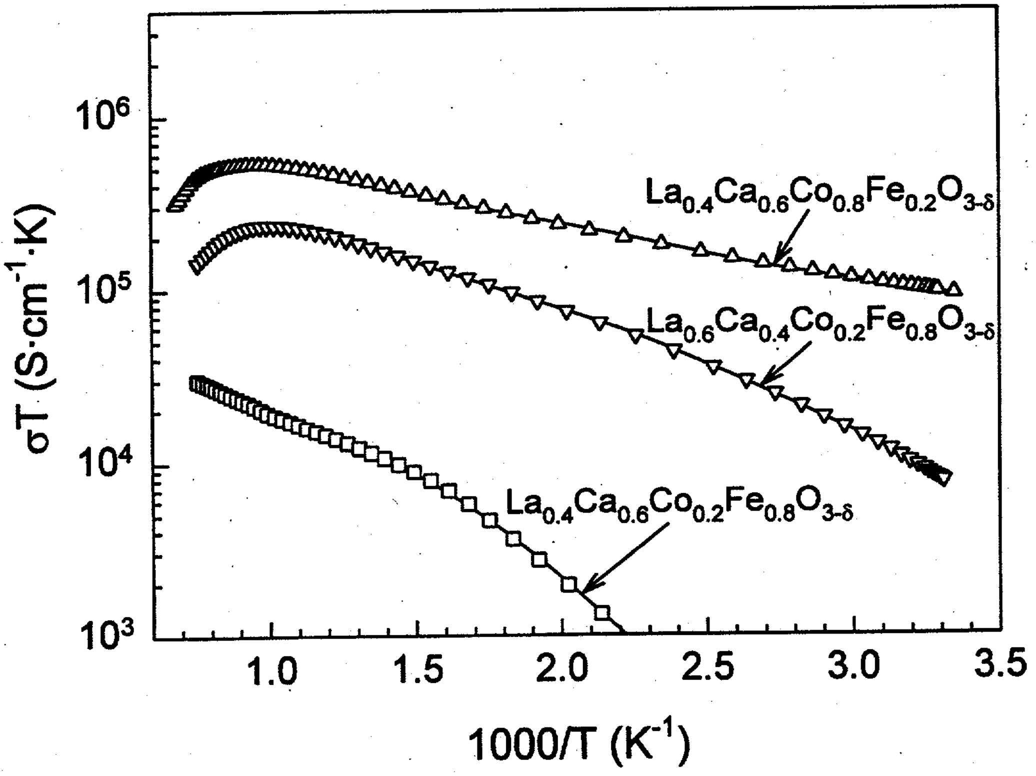

Fig. 2. Log(σT) versus 1/T for compositions in the $La_{1-x}Ca_xCo_{1-y}Fe_yO_{3-\delta}$ system.

respectively. At lower temperatures, σT follows the behavior expected for small polaron conduction in these materials that is given by the expression [13,14]:

$$\sigma T = C \exp(-E_a/kT) \tag{1}$$

where the pre-exponential C is both a charge carrier and material dependent constant, E_a is the activation energy, and k is the Boltzmann constant. Activation energies measured below 650°C are less than 0.2 eV, consistent with a small polaron hopping mechanism. The highest conductivities are observed in the high-Co, high-(Sr,Ca) specimens, $La_{0.4}(Sr,Ca)_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$. The decrease in conductivity at temperatures above about 900°C can be attributed to a decrease in electronic charge carriers as a result of oxygen loss observed by TGA (below). This decrease in electron holes is described by the defect equation:

$$2h^{\cdot} + O_O \Rightarrow V_O^{\cdot\cdot} + \tfrac{1}{2}O_2. \tag{2}$$

Thus, the decrease in oxygen stoichiometry with increasing temperature decreases the concentration of the dominant charge carriers (electron holes) and increases the concentration of ionic charge carriers (oxygen vacancies), which results in an increased oxygen-ion conductivity (oxygen permeation rate), as discussed below.

Thermogravimetric analysis

The TGA results for specimens in the $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-\delta}$ system are shown in Fig. 3. The decrease in mass from oxygen loss increases with increasing temperature and with Sr content. The most stable compound of this group, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, has the lowest Sr content. The mass loss from oxygen creates additional vacancies in the lattice, which increases the oxygen-ion conductivity and decreases the small polaron concentration. Continued TGA measurements as a function of oxygen partial pressure are in progress, and analysis of additional compositions is planned, particularly those corresponding to the electrical conductivity data in Figs. 1 and 2.

Oxygen permeation

The passive rates of oxygen permeation through 2.5 mm thick disc specimens of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$ in an oxygen/nitrogen $P(O_2)$ gradient of ~10 are shown in Fig. 4 as a function of temperature. The steep temperature gradient is due to the thermally-activated diffusion of oxygen and the increase in oxygen vacancies at elevated temperatures. From the flux measurements, it is possible to calculate the oxygen-ion conductivity. At 900°C, the ionic conductivities are 0.194 and 0.499 $S \cdot cm^{-1}$ for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$, respectively. Based on the ionic conductivity and the total electrical conductivity (Fig. 1), the ionic transference number for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ at 900°C is 7.7×10^{-4}, which is similar to that found by others [8]. The ionic conductivities deduced from Fig. 4 indicate an increasing ionic conductivity with temperature, in agreement with the results of others [5,8]. Consequently, the decrease in total electrical conductivity observed in Fig. 1 is due to a decrease in electronic conductivity (i.e., a decrease in the electronic carrier concentration).

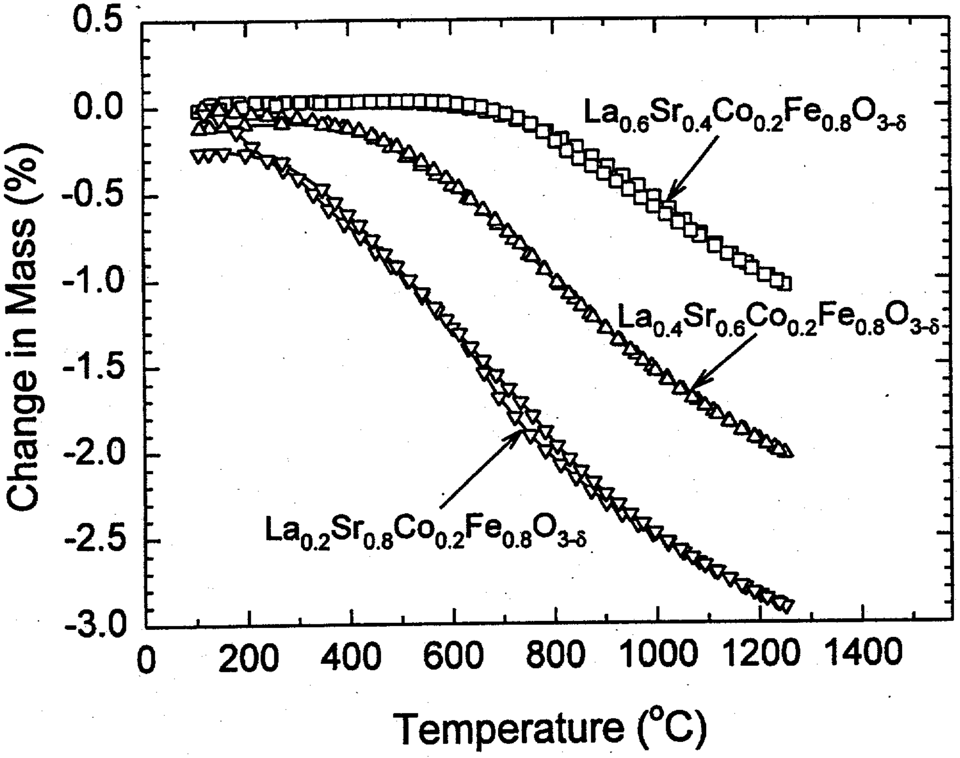

Fig. 3. TGA results for specimens in the $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-\delta}$ system.

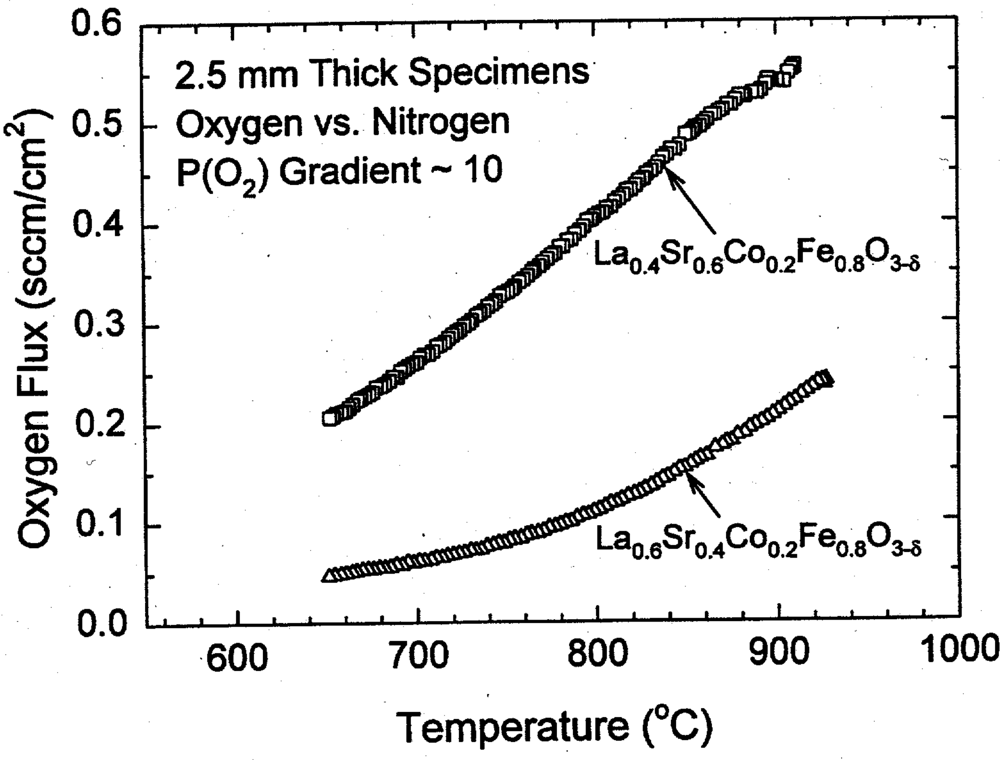

Fig. 4. Passive oxygen flux through $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{1-\delta}$ in a gradient established by oxygen versus nitrogen.

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