REVIEW OF THE STRUCTURAL AND ELECTRICAL PROPERTIES OF THE (La,Sr)(Co,Fe)O₃ SYSTEM

H.U. Anderson, L-W. Tai, C.C. Chen, M.M. Nasrallah & W. Huebner
University of Missouri-Rolla
Department of Ceramic Engineering
Rolla, MO 65401

ABSTRACT

The (La,Sr)(Co,Fe)O₃ LSCF system has been extensively studied because of its potential use as oxygen permeable membranes and cathodes for solid oxide fuel cells. This paper reviews the results of some of these studies and describes the thermochemical and electrical conductivity behavior of this system as functions of composition, temperature (600 to 1200°C) and oxygen activity (10⁻¹⁹ to 1 atm). The oxygen stoichiometry was measured thermogravimetrically. The results show that at 1000°C for the composition of La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃ as many as 20% of the oxygen sites can become vacant upon reduction before dissociation occurs. The total electrical conductivity show that at 1000°C in air the electrical conductivity is about 200 S/cm for La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃, but decreases with reduction as the oxygen vacancies reduce the number of carriers. Upon reduction, these oxides did not dissociate into binary oxides and metal in a simple step, but they formed transient compounds which with further reduction dissociated to La₂O₃, SrO, Co, and Fe.

INTRODUCTION

Perovskite-type oxides (ABO₃), with rare earth elements on the A sites and transition metals on the B sites, are well known for their refractory properties, catalytic activities, and wide range of electrical properties. Among them, the acceptor-doped A³⁺B³⁺O₃ (A = La, Y, Sr, Ca; B = Mn, Fe, Co, Ni) compositions have been evaluated as the cathode in solid oxide fuel cells (SOFC) (1).

There has been growing interest in utilizing perovskite-type La₀.₄Sr₀.₆Co₁.₆Fe₂O₇ (LSCF) for electrochemical applications. Among the various studies on LSCF compositions, Matsumoto et al. (2) found that La₀.₂Sr₀.₈Co₀.₈Fe₀.₂O₃ has the highest catalytic activity as an electrode for oxygen evolution in alkaline solution. Teraoka et al. have investigated the oxygen adsorption (3), and the oxygen permeation properties (4,5) of La₁₋₄SrₓCo₁₋₄FeₓO₃. Our recent studies have shown that at 800°C compositions...
in the LSCF system have oxygen ion conductivity 10 to 50 times larger than that observed in ZrO₂ containing 8 m% Y₂O₃.

Understanding the oxygen nonstoichiometry, thermochemical stability and electrical conductivity of the LSCF, under SOFC or oxygen-separation membrane operating conditions, is of importance for practical applications. Most of the reported studies were limited to either LaCo₁ₓFe₁₋ₓO₃ (6-9), or to LSCF compositions with high Sr and Co contents (10,11,12). In spite of all the interest in these LSCF compositions, there is little published information relating the structural, thermal, and electrical properties of these materials, particularly for compositions with low Sr and Co contents.

The purpose of this paper is to review the crystalline structure, thermal-expansion behavior, oxygen content, and electrical conductivity of LSCF compositions with low Sr content (La₀.₈Sr₀.₂Co₁₋ₓFeₓO₃), and low Co content (La₁₋ₓSrₓCo₀.₂Fe₀.₈O₃).

EXPERIMENTAL

Oxide powders of compositions LaₓSrₓCo₁₋ₓFe₀.₈O₃ (x = 0, 0.2, 0.4) and La₀.₈Sr₀.₂Co₁₋ₓFeₓO₃ were either prepared by the Liquid-Mix process (13) or obtained from Seattle Specialty Ceramics, Seattle, WA. Phase purity and crystalline structure of each composition were examined by X-ray powder diffraction (XRD) using Cu-Kα radiation. Lattice constants and the theoretical density for each composition were calculated from XRD data with an external standard of Si. Crystalline phases in sintered LSCF were determined by XRD (XRD-2000, Scintag Inc.)

Phase stability and the dissociated products of LSCF compositions in reducing atmospheres were studied by using quench experiments. Five to seven grams of powder samples were placed in an alumina boat and equilibrated at a given temperature and oxygen activity for 2 to 4 weeks in a muffle furnace. The samples were then quenched by pulling the crucible to the cool zone of the furnace (≈ 50°C) under the same atmosphere in about 10 sec to preserve the high temperature phase(s). The as-quenched powder samples were immediately weighted to determine weight loss and examined by XRD using a Scintag XRD-2000 diffractometer.

The powder samples used for thermogravimetry (TG) measurement were annealed in air at 1250°C for 24 hours to ensure removal of volatile matter.

The TG runs were initiated after equilibrating the LSCF sample in a pure oxygen atmosphere at 1200°C. When the sample weight remained unchanged for a period of 24 hours, the oxide was considered to be in equilibrium with the given oxygen activity and the sample weight was recorded. The oxygen activity was then reduced in about one order of magnitude intervals to 10⁻¹⁹ atm, by using a flowing gas
mixture of either O₂/N₂ or CO₂/H₂. Finally, to confirm reversibility, re-oxidation of the fully reduced sample to its original state was done by introducing oxygen. This is required since the presence of any volatile species other than oxygen will cause irreversible weight loss and makes the analysis of oxygen content impossible.

For electrical conductivity and thermal expansion measurements dense rectangular bars of LSCF were prepared by isostatically pressing powders at 207MPa, followed by sintering between 1250°C and 1350°C in air for 4 to 6 hours.

Electrical conductivity of sintered samples were measured using a computer-driven apparatus capable of carrying out the two-point, four-wire Kelvin technique electrical conductivity and the thermoelectric power measurements simultaneously on the same sample (14). To verify the reliability of the measured dc conductivity, a four-probe ac measurement was also performed at a frequency of 100 Hz on selected samples. The atmosphere control was provided by the same type of gas flow system used in the TG and annealing-quenching experiments. The sample resistance was monitored at 30 minutes intervals until equilibration was attained at a given oxygen activity.

Thermal expansion coefficients (TEC) of sintered LSCF samples were measured in air using an Orton dilatometer at a heating/cooling rate of 3.3°C/min (at least 3 measurements for each specimen).

RESULTS AND DISCUSSION

XRD Crystallography

X-ray diffraction showed that all of the as-calcined powders for all the compositions were single phase. However, EDS analyses on the sintered samples revealed that second phases containing Co/Fe oxide(s) existed in compositions with Sr content ≥ 0.6. To illustrate the effect of Sr substitution on the lattice parameters, the cube root of unit cell volume per ABO₃ (a’) was calculated. As shown in fig. 1, the pseudo-cubic lattice constant decreases with increasing Sr content, while the crystal structure gradually changes from orthorhombic to rhombohedral then to cubic. This behavior is similar to that observed for the LaFeO₃-SrFeO₃₄ system (15).

The influence of Fe content is shown in fig. 2 which shows that the pseudo-cubic lattice content a’ gradually increased with Fe content suggesting that La₀.₈Sr₀.₂CoO₃ and La₀.₈Sr₀.₂FeO₃ are miscible in each other.

Oxygen Stoichiometry and Phase Stability

The room temperature oxygen content for each composition was determined
using weight loss data from the TG and quenching experiments. A reference point was established by fully reducing LSCF into its components of La$_2$O$_3$, SrO, Co, and Fe at 1200°C. The dissociated sample was then quenched (under reducing atmosphere) and the final weight was quickly measured. It was assumed that the cation contents did not change after being dissociated, plus the fact that La$_2$O$_3$ and SrO still remained stoichiometric under the most reducing condition applied (oxygen activity = $10^{19}$). Using this reference point and TG weight loss data the compositions both at elevated and room temperature were calculated. Table I lists the oxygen contents for compositions with Sr = 0, 0.2, and 0.4 at the specified temperature and ambient atmosphere.

The weight loss of LSCF compositions as function of oxygen activity was measured at 1200°C, and the calculated oxygen content is shown in fig. 3. As can be seen in fig. 3, all three compositions show a significant decrease in oxygen content at oxygen activity of $10^{13}$, with a minimum in the $10^{15}$ to $10^{16}$ region. No further weight change was detected for oxygen activity $\leq 10^{16}$.

XRD analyses showed that (at 1200°C) both undoped and Sr-doped LaCo$_{0.2}$Fe$_{0.8}$O$_3$ fully dissociated into La$_2$O$_3$, SrO, plus Co and Fe for oxygen activity $\leq 10^{16}$.

Table I

| Oxygen Content (3-δ) | Room Temp in air | 1000°C in oxygen | 1200°C in oxygen |
|----------------------|------------------|------------------|------------------|
| LaCo$_{0.2}$Fe$_{0.8}$O$_{3.5}$ | 3.005±0.010 | 3.005±0.015 | 3.003±0.010 |
| La$_{0.8}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_{3.5}$ | 2.999±0.003 | 2.992±0.005 | 2.972±0.003 |
| La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3.5}$ | 2.948±0.009 | 2.908±0.005 | 2.849±0.006 |

XRD analyses on La$_{0.4}$Sr$_{0.6}$Co$_{0.2}$Fe$_{0.8}$O$_{3.4}$, equilibrated at 1000°C as a function of oxygen activity, showed that the perovskite phase was stable over a wider oxygen activity range than at 1200°C, and the final dissociation of the complex oxide occurred under more reducing conditions. The main difference between 1200°C and 1000°C was the coexistence of both the perovskite phase and the transient phases of (La,Sr)$_2$(Fe,Co)O$_4$ in the oxygen activity range from $10^{16}$ to $10^{-11}$ atm at 1000°C. The perovskite phase disappeared at oxygen activity = $10^{17}$ atm which is consistent with the results reported by Nakamura et al. (16). The La$_{0.8}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ compositions appears to be more stable than either acceptor doped LaMnO$_3$ or YMnO$_3$. (1,17). The thermochemical properties of LSCF in reducing atmosphere seem to follow the boundaries set between the two end members, LaFeO$_3$ and LaCoO$_3$. Although not shown here, the phase stability of compositions containing no Sr or Sr = 0.2 when compared to that shown for Sr = 0.4 suggested that Sr content has little influence on the high temperature phase stability.
Electrical Conductivity

The electrical conductivity as functions of temperature and composition measured in air is shown in figs. 4 & 5. As can be seen, a maximum conductivity is observed which depends both upon Sr and Fe content.

Positive Seebeck coefficients were observed for all compositions except in the extreme reducing regions where dissociation occurred. Within the single phase regions and in temperature regions below that of maximum electrical conductivity the Seebeck coefficients were constant suggesting that the electrical conductivity followed the relationship for the adiabatic small polaron hopping mechanism (18),

\[ \sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right) \]

where \( \sigma_0 \) is a constant, \( T \) is absolute temperature and \( k \) is Boltzmann's constant. The calculated activation energies for electrical conductivity are listed in Tables II and III.

| LSCF (moles) | Temperature Range (°C) | Activation Energy \(^1\)(eV) |
|--------------|------------------------|-----------------------------|
| \( x = 0 \)  | 500-900                | 0.62                        |
|              | 100-400                | 0.32                        |
| 0.1          | 400-900                | 0.18                        |
| 0.2          | 200-800                | 0.14                        |
| 0.3          | 100-600                | 0.13                        |
| 0.4          | 100-500                | 0.10                        |

\(^1\)Uncertainty \( \pm 0.004\) eV.

The oxygen activity dependence of the electrical conductivity of LSCF is illustrated in fig. 6 which shows the behavior of composition \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8} \text{O}_3 \) as function of temperature and oxygen activity. These data are typical of all LSCF compositions, with the conductivity minimum correlating with the dissociation of the single phase LSCF into its components.

The dependence of the oxygen ion conductivity upon composition and oxygen activity has been previously reported (19,20). These data show that the ionic conductivity increases from \( 10^2 \) S/cm at 1 atm \( \text{O}_2 \) to a maximum of 0.3 S/cm in oxygen activity range \( 10^{-12} \) to \( 10^{-5} \) atm at 800°C.
Table III

Calculated activation energies for the electrical conductivity of La$_{0.8}$Sr$_{0.2}$Co$_{1-y}$Fe$_y$O$_{3}$, assuming the adiabatic small polaron mechanism

| LSCF (moles) | Temperature Range (°C) | Activation Energy (eV) |
|--------------|------------------------|------------------------|
| y = 0        | 200-800                | 0.04                   |
| 0.1          | 200-800                | 0.06                   |
| 0.2          | 200-800                | 0.08                   |
| 0.3          | 200-800                | 0.09                   |
| 0.4          | 200-900                | 0.12                   |
| 0.5          | 200-900                | 0.12                   |
| 0.6          | 200-900                | 0.13                   |
| 0.7          | 200-900                | 0.14                   |
| 0.8          | 200-800                | 0.14                   |
| 0.9          | 300-800                | 0.13                   |
| 1.0          | 400-800                | 0.09                   |

*Uncertainty = ± 0.004eV.

Thermal Expansion

The thermal expansion was measured in air as functions of both Sr and Fe content. Tables IV and V summarize the results. As can be seen the rhombohedral-orthorhombic phase transformation is very dependent upon Sr content (below room temperature for Sr ≥ 0.3) with little dependence on Fe content. The upper temperature of the TEC measurement correlates with the loss of oxygen from the LSCF lattice which caused lattice expansion and nonlinearity of the TEC.

CONCLUSIONS

1. Compositions within the LSCF system show a wide oxygen activity range of stability. Upon reduction, these oxides do not dissociate into binary oxides and metal in a simple step, but form a series of transient compounds.

2. All compositions in the La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ (x = 0.2, 0.4) system had a perovskite-type structure. Both the thermal expansion coefficient and the p-type electrical conductivity increased with Co content. Oxygen vacancies formed in these oxides at high temperatures resulted in a lattice expansion and a reduction in the concentration of electronic charge carriers. As a result maxima in the electrical conductivities ranging from 200-330 S/cm were observed for compositions with x = 0.2-0.4 and Fe = 0.8 in the temperature range of 600-800°C, in air.
Table IV
Thermal-expansion data on La$_{0.8}$Sr$_{0.2}$Co$_{1-y}$Fe$_y$O$_3$

| LSCF (moles) | Temp. Range (°C) | TEC$^1$ (x 10$^{-6}$/°C) | Remarks |
|--------------|------------------|--------------------------|---------|
| $y = 0$      | 100-900          | 19.7                     |         |
| 0.1          | 100-900          | 20.1                     |         |
| 0.2          | 100-900          | 20.7                     |         |
| 0.3          | 100-900          | 20.3                     |         |
| 0.4          | 100-900          | 20.0                     |         |
| 0.5          | 100-900          | 18.7                     |         |
| 0.6          | 100-900          | 17.6                     |         |
| 0.7          | 100-900          | 16.5                     |         |
| 0.8          | 100-800          | 15.4                     |         |
| 0.9          | 200-900          | 14.5                     |         |
| 1.0          | 300-900          | 12.6                     |         |

For compositions with $0 \leq y \leq 0.7$, rhombohedral perovskite is the only phase existing between R.T. and 1000°C, no orthorhombic-rhombohedral phase transition.

The uncertainty of TEC data is about 2%.

Table V
Thermal-expansion coefficient on La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_3$

| LSCF (moles) | Temp. Range (°C) | TEC$^1$ (x 10$^{-6}$/°C) | Remarks |
|--------------|------------------|--------------------------|---------|
| $x = 0$      | 100-500          | 13.1                     |         |
|              | 600-900          | 17.5                     | orth. phase, rhom. phase, (orth.-rhom. transition at ≈ 520-580°C) |
| 0.1          | 300-900          | 16.0                     | rhom. phase, (orth.-rhom. transition at ≈ 170-250°C) |
| 0.2          | 100-800          | 15.4                     | rhom. phase, (orth.-rhom. transition below 60°C) |
| 0.3          | 100-700          | 14.6                     |         |
| 0.4          | 100-600          | 15.3                     |         |
| 0.6          | 100-400          | 16.8                     |         |

For compositions with $0.3 \leq x \leq 0.6$, samples with $x \geq 0.2$ started to expand at high temp. (due to the formation of oxygen vacancies).

The uncertainty of TEC data is about 2%.

3. Upon reduction the perovskite La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_3$ (0 $x < 0.4$):

(a) remains single phase even when 20% of its oxygen sites are vacant;
(b) the total electrical conductivity decreases from about 10$^2$ S/cm at 1 atm

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O₂ to about 1 S/cm at 10⁻¹³ atm O₂ in the temperature range of 800-1200°C.

(c) at 800°C has a maximum in its ionic conductivity of about 0.3 S/cm in the oxygen activity range of 10⁻¹² to 10⁻⁵ atm.

ACKNOWLEDGEMENT

This research was supported by the Gas Research Institute, British Petroleum of America, and the Basic Energy Science Division of the U.S. Department of Energy.

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Fig. 1. Cube root of lattice volume (per ABO₃) for LaₓSrₓCo₀₂Fe₀₈Oₓ as a function of Sr content (moles).

Fig. 2. Cube root of lattice volume (per ABO₃) for LaₓSrₓCo₀₂Fe₀₈Oₓ as a function of Fe content (moles).

Fig. 3. Oxygen content (moles) of LaₓSrₓCo₀₂Fe₀₈Oₓ as a function of oxygen activity and Sr content (moles) at 1200°C.

Fig. 4. Electrical conductivity of LaₓSrₓCo₀₂Fe₀₈Oₓ as a function of temperature and Sr content (moles) in air.
Fig. 5. Electrical conductivity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ as a function of temperature and Sr content (moles) in air.

Fig. 6. Electrical conductivity of $\text{La}_{0.8}\text{Sr}_{0.4}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_3$ as a function of oxygen activity equilibrated at different temperatures.