

Electrochemical Properties of Mixed Conducting Perovskites $\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (M = Sr, Ba, Ca)

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Electrochemical Properties of Mixed Conducting Perovskites

$\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($\text{M} = \text{Sr}, \text{Ba}, \text{Ca}$)

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ABSTRACT

Perovskite compositions in the system $\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($\text{M} = \text{Sr}, \text{Ba}, \text{Ca}$) exhibited high electronic and ionic conductivity. Substantial reversible weight loss was observed at elevated temperatures as the materials became increasingly oxygen deficient. This loss of lattice oxygen at high temperatures, which tended to increase with increasing acceptor content, resulted in a decrease in the electronic conductivity. In an oxygen partial pressure gradient, oxygen flux through dense sintered membranes of these materials was highly dependent on composition and increased with increasing temperature. The increase in oxygen flux with increasing temperature was attributed to increases in the mobility and concentration of lattice oxygen vacancies. The calculated ionic conductivities of some compositions exceeded that of yttria-stabilized zirconia.

Introduction

In recent years, compositions in the $(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_{3-\delta}$ system (ABO₃ perovskite structure) have been investigated because of their mixed conducting behavior.¹⁻¹⁸ At elevated temperatures, these solid-solution compositions exhibit substantial ionic and electronic conductivity, making them attractive candidate materials for several important applications, including solid oxide fuel cell cathodes, oxygen separation membranes, and membrane reactors for syngas production and the partial oxidation of hydrocarbons. Although the ionic conductivity in these materials frequently accounts for less than 1% of the overall electrical conductivity, the magnitude of that conductivity can be quite large relative to other oxygen ion conductors, such as yttria-stabilized zirconia (YSZ). This mixed conducting behavior results in a spontaneous flux of oxygen through dense sintered specimens when they are placed in an oxygen partial pressure [$P(\text{O}_2)$] gradient at elevated temperatures. Under these conditions, gaseous oxygen on the high $P(\text{O}_2)$ side of the material is spontaneously reduced to anionic oxygen at the surface and then transported through the material (via a lattice vacancy diffusion mechanism) to the low $P(\text{O}_2)$ side, where the oxygen anions are reoxidized. The ionic current resulting from this flux of oxygen ions is compensated internally by an electronic current, so that no electrodes or external circuitry are required for the oxygen flux through the membrane to occur.

Teraoka *et al.*⁴ studied the electronic and ionic conductivities of a number of $(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_{3-\delta}$ compositions using oxygen permeation and four-probe dc techniques. At 800°C, ionic conductivities were on the order of 0.01 to 1.0 S/cm, while electronic conductivities exceeded 100 S/cm. Ionic conductivity increased steeply with increasing Sr content and decreased slightly with increasing Fe content. The increase in ionic conductivity with increasing Sr con-

tent was attributed to ionic charge compensation (*i.e.*, the formation of lattice oxygen vacancies) as trivalent La cations were replaced by divalent (acceptor) Sr cations. Although the oxygen flux tends to be highest in materials having high Sr and Co contents, other factors need to be considered. In particular, compositions high in Sr and Co exhibit very limited chemical and structural stability in reduced $P(\text{O}_2)$ environments. For example, tubular $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membrane reactors fractured as a result of an approximately 2% increase in the lattice volume for the inner wall exposed to a reducing environment relative to the outer wall that was exposed to air.⁷ In addition, Kruidhof *et al.*¹² reported that, at intermediate temperatures (*e.g.*, 750°C), the oxygen flux through several compositions high in Sr and/or Co (*e.g.*, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ and $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$) decreased substantially with time. This degradation in behavior was attributed to an order-disorder phase transition from a high-temperature structure in which the vacancies were disordered (and therefore mobile) to a low-temperature structure in which the oxygen vacancies were highly ordered and, therefore, essentially immobile. Values reported for the composition-dependent transition temperature ranged from 790 to 940°C.

For relatively thick specimens, the oxygen permeation is limited by the bulk diffusion of oxygen anions through the material. Under these conditions, the observed flux should be inversely proportional to the thickness.¹⁹ Thus, to maximize the flux through the material, it is desirable to minimize the specimen thickness. At some point, however, the surface exchange kinetics will become rate limiting, so that any further reduction in specimen thickness will not result in an increased flux. Bouwmeester *et al.*¹⁴ calculated the "characteristic thickness" (below which oxygen permeation is controlled by the surface exchange reactions) for Sr-doped $\text{LaCoO}_{3-\delta}$ and $\text{LaFeO}_{3-\delta}$ to be in the 20 to 500 μm range at 900°C.

The purpose of this study was to increase the understanding of the synthesis and electrochemical properties of perovskite compositions within the $\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$

* Electrochemical Society Active Member.

(M = Sr, Ba, Ca) oxide systems to facilitate their successful use in electrode and oxygen separation applications.

Experimental

Compositions within the system $\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (M = Sr, Ba, Ca; $0.4 \leq x \leq 0.8$; $0.2 \leq y \leq 0.8$) were prepared using the glycine-nitrate combustion synthesis technique.²⁰ After mixing La, Sr, Ba, Ca, Co, and Fe nitrate solutions in the appropriate proportions, glycine was added as a fuel and complexant. The resulting mixtures were then heated in stainless steel beakers on a hot plate to the point of combustion. The resulting ash was calcined at 850°C for 12 h in air. The calcined powders were compacted in a rectangular die using uniaxial pressure (55 MPa) and then pressed isostatically (138 MPa). The pressed compacts were sintered in air in a MoSi₂ furnace using a heating rate of 5°C/min and a cooling rate of 2°C/min; typical sintering conditions to achieve relative densities $\geq 90\%$ were 1150 to 1250°C for 2 to 4 h. The densities of the sintered specimens were determined by the Archimedes method using ethanol.

Phase development was determined by x-ray diffraction analysis using Cu K α radiation (XRG 3100, Philips Electronic Instruments, Mahwah, NJ). Semiquantitative analysis of phase concentrations was based on comparison of observed peak heights after background subtraction. At least one peak for each phase present, typically the 100% peak, was selected for this comparison. In cases where superposition obscured the 100% peak, the strongest, lowest angle resolved peak was selected and then normalized to 100%. The sum of the heights of the selected peaks for all phases present in any given specimen was taken as the total diffracted intensity. For all cases studied, the reported semiquantitative phase concentrations were equal to the ratio of the height of the selected peak for each individual phase *vs.* the total diffracted intensity.

Electrical conductivity of sintered bars (nominal dimensions: $30 \times 2 \times 2$ mm) was measured as a function of temperature (25 to 1100°C) in air by a four-point pulsed dc method using platinum electrodes and a heating and cooling rate of 1.6°C/min. Thermogravimetric analysis (TGA, Cahn TG-171, Cerritos, CA) was performed on calcined powder specimens using a heating rate of 5°C/min and a cooling rate of 2°C/min. Buoyancy corrections were performed using a platinum standard. The TGA measurements were performed in several different atmospheres (dry air; 10,000, 1,000, and 100 ppm O₂ in N₂). Passive (*i.e.*, no applied field) oxygen permeation measurements were performed between 750 and 950°C using sintered disk specimens (nominal dimensions: 20 mm diam $\times$ 2 mm thick) sealed in an alumina test cell with gold gaskets. Oxygen was used as the source gas with nitrogen as the carrier gas. The oxygen permeation was measured as a function of temperature using heating and cooling rates of 0.7°C/min and gas flow rates of 25 to 30 sccm. An oxygen sensor and mass spectrometer were used in calculating the oxygen fluxes.

Room temperature oxygen stoichiometries of calcined powder specimens were determined by iodometric titration using a modified version of Nadalin and Brozda's oxidizing power method No. 3.²¹ The powder was placed in a sealed flask through which a carrier gas (nitrogen) was passed. Upon exiting the flask, the carrier traveled through a condenser into a bank of gas washing bottles (with fritted dispersion disks) containing KI solution. The powder specimen was dissolved by introducing concentrated HCl into the flask through a rubber septum and applying heat. The chlorine gas liberated by the redox reaction with the transition metal cations in the powder was transported by the carrier gas to the KI solution where it oxidized iodide to iodine, which was titrated using a standardized sodium thiosulfate solution. This result, combined with electroneutrality and mass balance constraints, allowed for calculation of the oxygen stoichiometry of the powder.

Results and Discussion

In this paper, $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ compositions are designated by the abbreviation LSCF. Numerals following the abbreviation refer to the relative proportions of each cation. For example, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ is designated LSCF-6428, $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ is LSCF-2882. Similarly, $\text{La}_{1-x}\text{Ca}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ and $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ compositions are designated as LCCF and LBCF, respectively, followed by the numerical code.

Phase development.—Phase development (as determined by XRD analysis) after calcination in air at 850°C and sintering in air at 1200°C is summarized in Table I. The LSCF compositions were essentially single-phase perovskite solid solutions after calcination at 850°C, while the LCCF and LBCF compositions typically required higher temperature treatment to yield a high proportion [≥ 95 weight percent (w/o)] of the desired perovskite phase. In the LCCF materials, additional phases observed included $\text{Ca}_2\text{Fe}_2\text{O}_5$, $\text{Ca}_2\text{Co}_2\text{O}_5$, CaFe_2O_5 , and CoO . One composition (LCCF-2882) contained only 75% perovskite after the 1200°C treatment and, therefore, was not studied further. LBCFs with a Ba content ≥ 0.6 mole fraction contained multiple perovskite-type phases, as well as other phases (*e.g.*, $\text{Ba}_5\text{Fe}_{14}\text{O}_{26}$, BaCO_3), after the 850°C calcination. After heat-treatment at 1200°C, they were nearly single-phase perovskites, with small quantities of additional phases (*e.g.*, BaFe_2O_4 , $\text{Ba}_2\text{Fe}_2\text{O}_5$, and $\text{Ba}_3\text{Fe}_2\text{O}_6$).

Thermogravimetric measurements.—All of the materials studied exhibited a substantial reversible weight loss when heated in air. The results for the LSCF, LBCF, and LCCF compositions are shown in Fig. 1, 2, and 3, respectively. This weight loss upon heating was due to a partial loss of lattice oxygen, so that the oxygen stoichiometry, $3-\delta$, decreased with increasing temperature. The magnitude of the oxygen loss during heating was highly dependent on composition, and tended to increase with increasing acceptor (Sr, Ba, Ca) content. The temperature at which oxygen loss began to occur was also highly dependent

Table I. Effect of heat-treatment (in air) on phase development.

Composition	850°C, 12 h	1200°C, 2 h
LSCF-6428	Single-phase perovskite	Single-phase perovskite
LSCF-4628	~99% perovskite	~98% perovskite
LSCF-4682	Single-phase perovskite	~99% perovskite
LSCF-2828	Single-phase perovskite	Single-phase perovskite
LSCF-2855	~99% perovskite	Single-phase perovskite
LSCF-2882	Single-phase perovskite	~99% perovskite
LCCF-6428	~95% perovskite	Single-phase perovskite
LCCF-4628	~85% perovskite	~95% perovskite
LCCF-4682	~80% perovskite	~95% perovskite
LCCF-2882	~35% perovskite	~75% perovskite
LBCF-6428	~93% perovskite	Single-phase perovskite
LBCF-4628	Multiple perovskite phases	~98% perovskite
LBCF-4682	Multiple perovskite phases	~98% perovskite
LBCF-2828	Multiple perovskite phases	~99% perovskite
LBCF-2882	Multiple perovskite phases	~99% perovskite

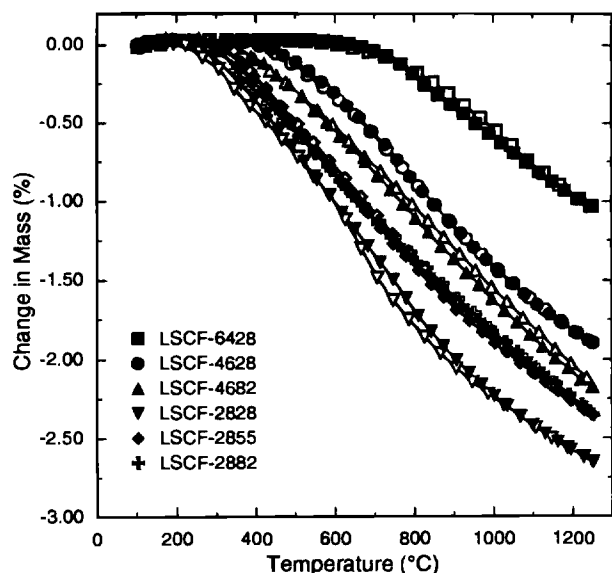


Fig. 1. Change in mass as a function of temperature for the indicated LSCF compositions. Measured in air. Open symbols refer to heating data; closed symbols refer to cooling data.

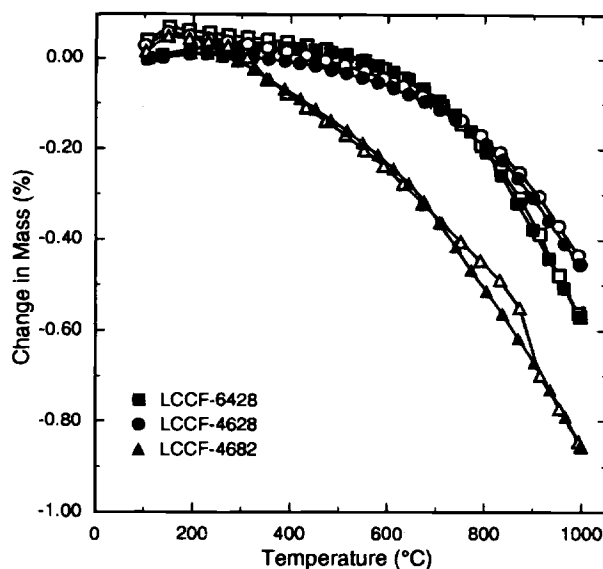


Fig. 3. Change in mass as a function of temperature for the indicated LCCF compositions. Measured in air. Open symbols refer to heating data; closed symbols refer to cooling data.

dent on the composition, with oxygen loss beginning to occur at lower temperatures as the acceptor content increased. Tai *et al.*^{17,18} observed similar behavior in a study focusing on LSCF compositions having a Sr content ≤ 0.4 mole fraction.

Iodometric titration was used to determine the oxygen stoichiometry ($3-\delta$) of the LSCF and LBCF compositions at room temperature (the limited solubility of the LCCF compositions in hydrochloric acid prevented an accurate determination of their room temperature oxygen stoichiometry). This reference point, in combination with the weight loss information from the TGA measurements, was used to determine the oxygen stoichiometry as a function of temperature. While it must be noted that the TGA measurements were dynamic (rather than static) measurements, the absence (or near absence) of hysteresis during heating and cooling at different rates indicates that the materials were close to their equilibrium oxygen contents

during the measurements. Figure 4 shows oxygen stoichiometry in air as a function of temperature for the LSCF compositions. LSCF-6428 was essentially stoichiometric at low temperatures, while the other compositions were oxygen deficient even at low temperatures. The magnitude of the initial oxygen deficiency increased with increasing Sr and/or Co content and was quite substantial ($\delta = 0.17$) for the composition highest in Sr and Co (LSCF-2882). The fact that ionic compensation became more prevalent as the Co content increased suggests that, in the perovskite structure, Co is more resistant to oxidation from the trivalent state than Fe. Similar trends were observed in the LBCF compositions (Fig. 5), with the LBCF compositions exhibiting greater oxygen deficiency than comparable LSCF compositions.

TGA measurements were also performed (on the LSCF compositions) in various atmospheres for studying the effect of ambient $P(\text{O}_2)$ on the weight loss behavior. Figure 6 shows the behavior of a high-Sr, high-Co composition (LSCF-2882) in a variety of oxygen partial pressures. The

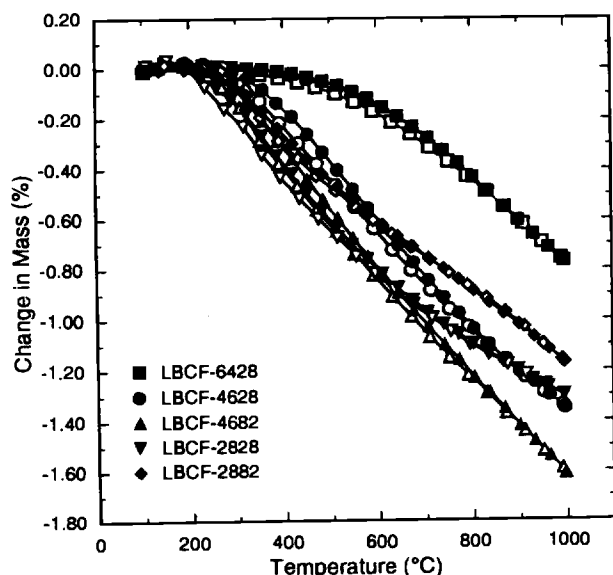


Fig. 2. Change in mass as a function of temperature for the indicated LBCF compositions. Measured in air. Open symbols refer to heating data; closed symbols refer to cooling data.

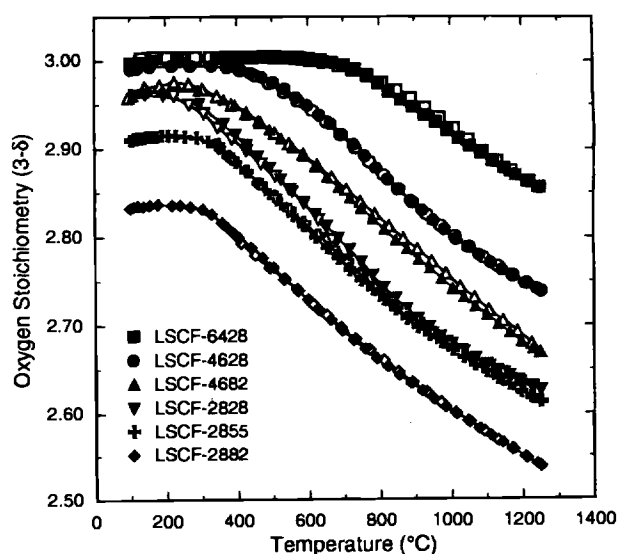


Fig. 4. Oxygen stoichiometry as a function of temperature for the indicated LSCF compositions. Measured in air. Open symbols refer to heating data; closed symbols refer to cooling data.

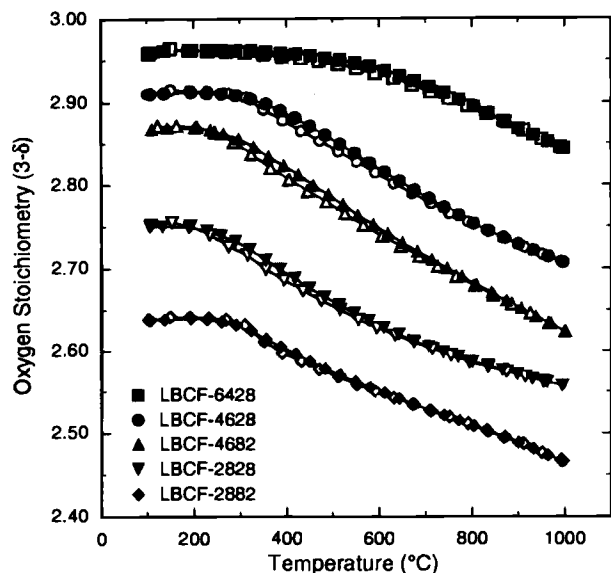


Fig. 5. Oxygen stoichiometry as a function of temperature for the indicated LBCF compositions. Measured in air. Open symbols refer to heating data; closed symbols refer to cooling data.

magnitude of the oxygen loss during heating increased only slightly as the ambient $P(\text{O}_2)$ was reduced. In a $P(\text{O}_2)$ of 10^{-2} atm, full reoxidation was observed upon cooling (as in air), but reoxidation did not occur in lower oxygen partial pressures (10^{-3} , 10^{-4} atm). Compositions containing less Co did not experience full reoxidation in the 10^{-2} atm O_2 environment.²² The observed irreversibility of the oxygen loss behavior during thermal cycling in reduced oxygen atmospheres is an indication of the limited phase stability of high Sr, high Co compositions in those atmospheres; this issue is addressed in more detail in the Oxygen permeation section of this paper.

Electrical conductivity.—Results of four-probe dc electrical conductivity measurements on several LSCF and LBCF compositions are plotted (as $\log \sigma T$ vs. $1000/T$, where σ is conductivity in $(\Omega\text{-cm})^{-1}$ and T is absolute temperature) in Fig. 7 and 8. Results for LCCF compositions were reported previously.²² Because the ionic transport

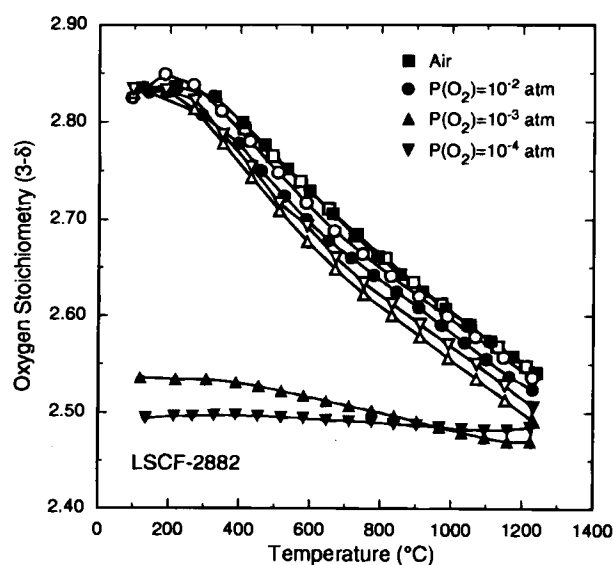


Fig. 6. Oxygen stoichiometry as a function of temperature for LSCF-2882 in the indicated atmospheres. Open symbols refer to heating data; closed symbols refer to cooling data.

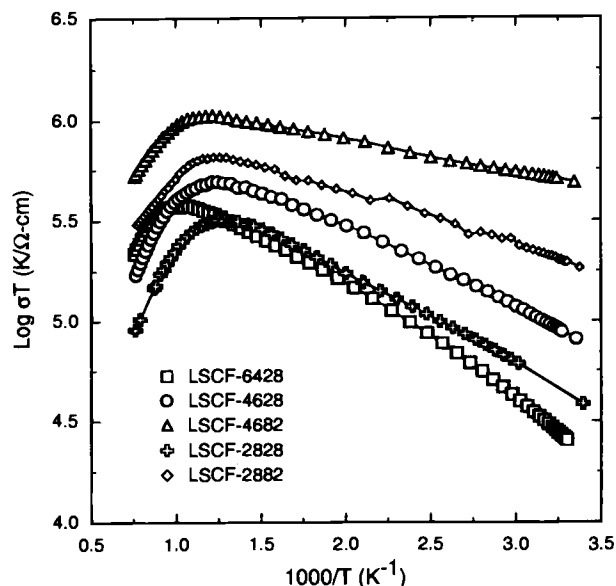


Fig. 7. $\log \sigma T$ vs. $1/T$ for the indicated LSCF compositions; σ is electrical conductivity in $(\Omega\text{-cm})^{-1}$, T is absolute temperature. Measured in air; heating and cooling rate: $1.6^\circ\text{C}/\text{min}$.

number in these compositions is low (typically less than 1%), the bulk conductivities obtained by these dc four-probe measurements were representative of the electronic conductivity of the materials. The conductivity was enhanced by increasing the Co content; this result is consistent with previous studies on acceptor-doped LaFeO_3 and LaCoO_3 .^{23,24} At lower temperatures, the plots are nearly linear, with the conductivity increasing with increasing temperature. The activation energies for the LSCF, LCCF, and LBCF compositions ranged from 0.03 to 0.29 eV (Table II). As shown in Table II, these values are similar in magnitude to previously reported activation energies for other compositions in the LSCF system and other electronically conducting perovskite systems. This behavior is consistent with small polaron conduction (*i.e.*, localized electronic carriers having a thermally activated mobility). If the carrier concentration is constant, the Arrhenius

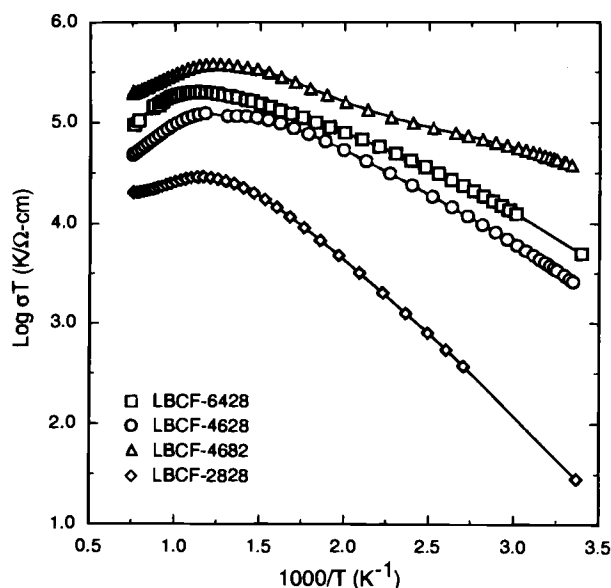


Fig. 8. $\log \sigma T$ vs. $1/T$ for the indicated LBCF compositions; σ is electrical conductivity in $(\Omega\text{-cm})^{-1}$, T is absolute temperature. Measured in air; heating and cooling rate: $1.6^\circ\text{C}/\text{min}$.

Table II. Activation energies for electronic conduction.

Composition	Activation energy (eV)	Ref.
LSCF-6428	0.08	This study
LSCF-4628	0.08	This study
LSCF-4682	0.03	This study
LSCF-2882	0.05	This study
LSCF-2828	0.09	This study
LCCF-6428	0.11	This study
LCCF-4628	0.16	This study
LCCF-4682	0.07	This study
LBCF-6428	0.12	This study
LBCF-4628	0.18	This study
LBCF-4682	0.11	This study
LBCF-2828	0.29	This study
(La,Sr)(Co,Fe)O ₃	0.10 to 0.18	18
(Y,Ca)MnO ₃	0.04 to 0.23	25
(La,Ca)MnO ₃	0.08 to 0.15	25
(La,Sr)MnO ₃	0.09 to 0.19	26
(La,Sr)CrO ₃	0.11 to 0.19	27

plots of $\log \sigma T$ vs. $1000/T$ should be linear, as the small polaron conduction mechanism follows the relation²⁷

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

where E_a is the activation energy, and k is the Boltzmann constant. The pre-exponential constant C includes the carrier concentration as well as other material-dependent parameters.

At higher temperatures, the plots show a significant negative deviation from linearity, due to a substantial decrease in conductivity with increasing temperature. For example, Fig. 9 shows the observed behavior for LSCF-6428. The dashed line shows the behavior which would be expected (as extrapolated using Eq. 1) at high temperatures if the concentration of charge carriers remained constant. It is obvious that the high temperature behavior is not consistent with that assumption.

When a divalent acceptor (e.g., Sr) is substituted for trivalent La, electroneutrality requires that the effective negative charge of the Sr cations be compensated by an increase in valence of some of the B-site cations (electronic compensation) and/or the formation of oxygen vacancies (ionic compensation)

$$[\text{Sr}'_{\text{La}}] = [\text{B}^{\bullet}_{\text{B}}] + 2[\text{V}^{\bullet\bullet}_{\text{O}}] \quad [2]$$

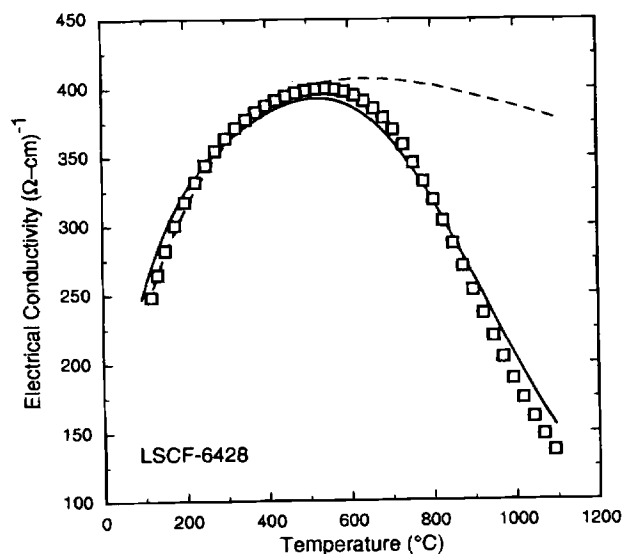
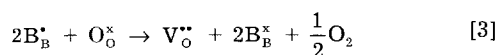


Fig. 9. Electrical conductivity in air as a function of temperature for LSCF-6428. Symbols represent experimental data, dashed line represents calculated conductivity assuming constant charge carrier concentration, solid line represents conductivity calculated using Eq. 4.

(In the above Kroger-Vink notation,²⁸ the brackets refer to the concentration of the enclosed species expressed as a mole fraction, " ' " represents unit negative charge with respect to the host lattice, " • " represents unit positive charge with respect to the lattice, and V_{O} refers to oxygen vacancies). Thus, electronic compensation results in an increase in the average valence of the transition metal cations, while ionic compensation reduces the oxygen stoichiometry.

At low temperatures, the charge compensation for LSCF-6428 is primarily electronic, with a substantial fraction of B-site cations being converted from the trivalent to the tetravalent state due to the presence of the acceptor cations. Because LSCF-6428 exhibits a positive Seebeck coefficient,¹⁸ consistent with p-type (electron hole, $h^{\bullet}$) conduction, electronic conduction occurs through the migration of electron holes (associated with the tetravalent cations, $\text{B}^{\bullet}$) to adjacent trivalent cations. At higher temperatures, ionic compensation becomes significant as the oxygen content of the material decreases, as shown in the TGA results. The exaggerated decrease in conductivity at high temperatures occurs in the same temperature region in which the loss of lattice oxygen occurs, and can thus be related to a decreasing concentration of electron holes as the concentration of oxygen vacancies in the material increases



where "x" refers to neutrality with respect to the lattice.

Because two electron holes are eliminated for each oxygen ion leaving the lattice, the conductivity model required modification to account for a variable carrier concentration. Accordingly, the conductivity model was modified to allow for a variable carrier concentration

$$\sigma = \{[(A' - 2\delta) C'] / T\} \exp(-E_a/kT) \quad [4]$$

The new term included in the pre-exponential factor represents the temperature-dependent carrier concentration. As temperature increases, each new oxygen vacancy eliminates two electron holes, so that the initial concentration of carriers (A') created by the acceptor (e.g., Sr) doping on the A site is reduced by 2δ , where δ is the temperature dependent oxygen vacancy concentration (see Fig. 4 and 5).

The solid lines in Fig. 9 and 10 represent conductivities calculated for several compositions using Eq. 4 and the oxygen vacancy concentrations obtained from the TGA measurements. The calculated values represent a reasonably good fit to the experimental data, supporting the conclusion that the substantial decrease in conductivity at high temperatures is largely due to the mechanism described in Eq. 3. The lack of perfect agreement between the calculated and experimental values suggests that other factors, such as the formation of defect clusters, may also play a significant role in the defect structure of these materials. Further investigations are planned.

Oxygen permeation.—Oxygen permeation rates (in an oxygen vs. nitrogen gradient) through sintered specimens of several LSCF, LCCF, and LBCF compositions are shown as a function of temperature in Fig. 11 and 12. Specimen thickness ranged from 2.3 to 3.1 mm. Oxygen [$P(\text{O}_2) = 1$ atm] was the source gas on the high $P(\text{O}_2)$ side, with nitrogen being used as the carrier gas on the low $P(\text{O}_2)$ side; the $P(\text{O}_2)$ on the low side, which varied as a function of composition and temperature, was measured continuously during the permeation trials and ranged between 2×10^{-4} and 9×10^{-1} atm. In the LSCF compositions, the oxygen flux increased significantly with increasing Sr content. This was consistent with the TGA results, which showed an increase in oxygen deficiency with increasing Sr content at high temperatures. Oxygen flux increased with increasing temperature; this increase can be attributed to an increase in the mobility of the lattice oxygen vacancies (the hopping of vacancies from site to site is

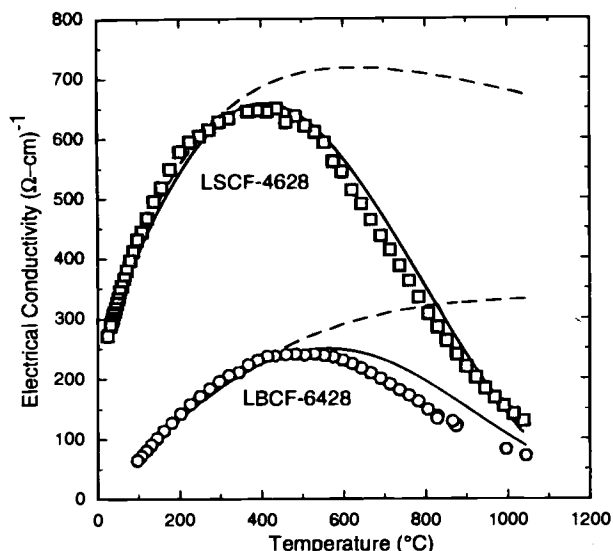


Fig. 10. Electrical conductivity in air as a function of temperature for LSCF-4628 and LBCF-6428. Symbols represent experimental data, dashed lines represent calculated conductivity assuming constant charge carrier concentration, solid lines represent conductivity calculated using Eq. 4.

thermally activated), as well as the increase in the concentration of lattice oxygen vacancies. Fluxes for the LCCF compositions were much lower than for the LSCF compositions. LBCF-6428 also exhibited a very low oxygen flux, while fluxes through LBCF-4628 and LBCF-2828 were on the same order as, but still lower than, fluxes observed through the corresponding LSCF compositions.

If a material is to be a successful candidate for oxygen membrane applications, it must exhibit long-term phase stability under the membrane operating conditions. In general, the perovskite systems evaluated in this study do not exhibit high stability toward reducing atmospheres at elevated temperatures. For example, room temperature XRD analysis of the LSCF compositions after being cooled at 2°C/min from 1200°C in a $P(\text{O}_2)$ of 10^{-5} atm revealed that several of those compositions had decomposed into mixtures containing additional phases [e.g., $\text{A}_2\text{B}_2\text{O}_5$ (brownmillerite) and AB_2O_4 (spinel) solid solutions] as well as the desired perovskite solid solution. It is important, however,

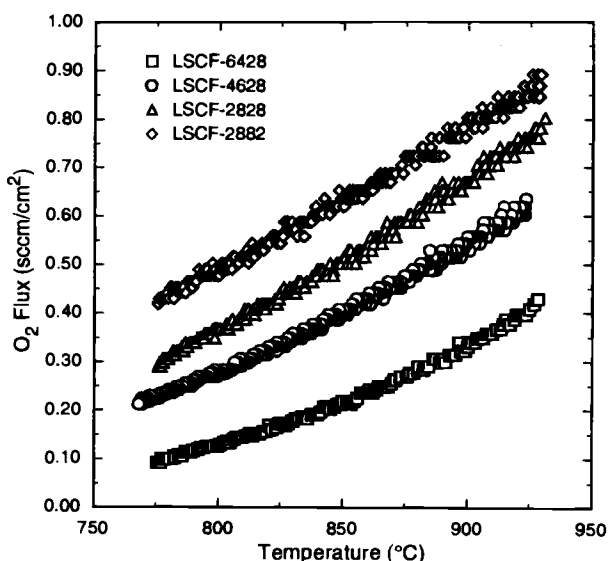


Fig. 11. Oxygen permeation as a function of temperature through sintered specimens of the indicated LSCF compositions in an oxygen vs. nitrogen gradient.

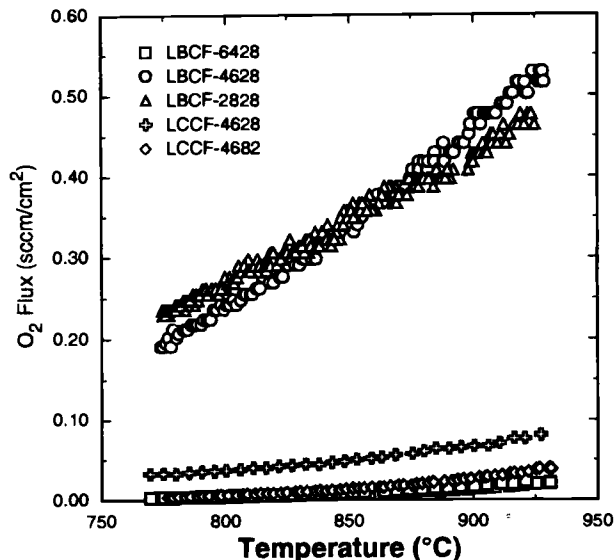


Fig. 12. Oxygen permeation as a function of temperature through sintered specimens of the indicated LBCF and LCCF compositions in an oxygen vs. nitrogen gradient.

to distinguish phase stability (or instability) when a specimen is completely exposed to a given atmosphere from stability when the two sides of the specimen are each exposed to a different atmosphere. For example, LSCF-2882, when cooled as described above in a uniform $P(\text{O}_2)$ of 10^{-5} atm, decomposed; at least one other (unidentified) phase was present in addition to the perovskite phase. Nevertheless, a membrane of this same composition operated for 340 h in an oxygen/nitrogen gradient at 775°C with minimal decrease in oxygen flux (<5 %), suggesting that, under these conditions, phase stability is adequate for that membrane application (see Fig. 13). Figure 13 also shows data from a study by Kruidhof *et al.*¹² for a related composition ($\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$) at a slightly lower temperature, 750°C. The substantial degradation of flux observed in that composition was attributed to an order-disorder phase transition in which oxygen vacancies within the structure became ordered and, therefore, immobile. Because, in the present study, a drastic decrease in flux was not observed in LSCF-2882, it is apparent that LSCF compositions can be considered to be viable candidate materials for oxygen permeation applications in the inter-

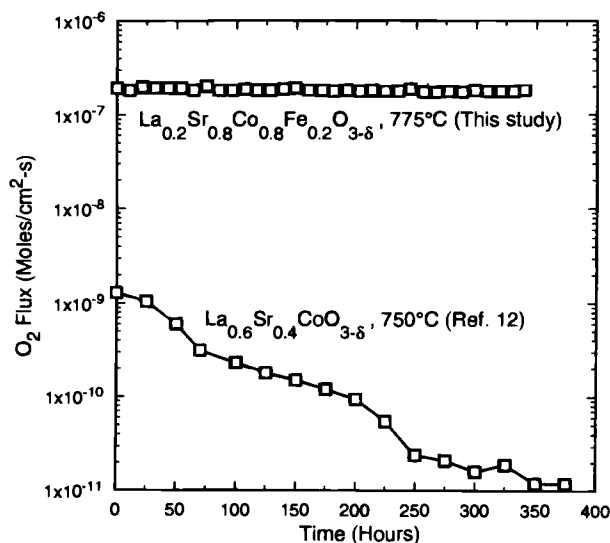


Fig. 13. Oxygen permeation as a function of time through LSCF-2882 (this study) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (Ref. 12).

mediate temperature range (e.g., 750 to 800°C). The observed long-term stability also indicates that the oxygen fluxes measured during the oxygen permeation trials in this study were true fluxes through the membrane rather than false transient fluxes resulting from oxygen depletion of the perovskite lattice.

Ionic conductivity.—Ionic conductivities (σ_i) were calculated from the measured flux rates, using the following relation¹⁹

$$\sigma_i = (4FJt)/(RT \ln [P(O_2^I)/P(O_2^II)]) \quad [5]$$

where F is Faraday's constant, J is oxygen flux (in A/cm²), t is specimen thickness, R is the gas constant, T is absolute temperature, and $P(O_2^I)$ and $P(O_2^II)$ are the oxygen partial pressures at each surface of the specimen. Given the substantial flow rates used (25 to 30 sccm) and the absence of electrodes (so that the surface was directly exposed to the gas flow), it was appropriate to assume that the oxygen activity at the surface was equivalent to the oxygen activity in the gas phase. This equation also requires the assumption that the oxygen flux was dominated by the bulk ionic conductivity rather than surface exchange kinetics. This assumption appears to be valid (at least for the Sr-doped compositions), because the specimen thicknesses (>2 mm) were considerably greater than the "characteristic thicknesses" reported by Bouwmeester *et al.*¹⁴ for Sr-doped LaCoO_{3-δ} and LaFeO_{3-δ}. The calculated ionic conductivities are shown in Table III. Conductivities of the LSCF and LBCF compositions (except LBCF-6428) at 900°C were higher than the conductivity of YSZ at that temperature [approx. 0.1 (Ω-cm)⁻¹]. The LSCF values are similar in magnitude to four-probe dc measurements reported by Teraoka *et al.*⁴ Approximate ionic transport numbers in Table III were obtained by dividing the ionic conductivity by the total conductivity. (These numbers must be considered approximate because the ionic conductivities were measured in an oxygen gradient of several orders of magnitude, while the electronic conductivities were measured in air.)

Activation energies for ionic conduction (obtained from the slopes of plots of $\ln \sigma_i T$ vs. $1/T$) are shown in Table IV. The LSCF energies are similar in magnitude to other reported results. For example, Teraoka *et al.*⁴ reported values between 0.67 and 0.89 eV for a similar set of LSCF compositions. Chen *et al.*¹⁶ obtained an activation energy of 1.1 eV for LSCF-6428. As noted above, two factors are expected to contribute to the increase in ionic conductivity with temperature: increasing vacancy mobility and increasing vacancy concentration. Therefore, the calculated activation energies for ionic conduction are a sum of two terms: (i) the activation energy for vacancy migration (or diffusion) within the lattice, ΔH_m , and (ii) a second term related to the enthalpy of formation of oxygen vacancies (ΔH_f).

It should be emphasized that the second term is not equivalent to ΔH_f . For example, in the case of undoped oxygen deficient oxides, the second term can be shown to be $\Delta H_f/3$, so that the total activation energy for ionic conduction is $(\Delta H_m + \Delta H_f/3)$.²⁸ For doped oxides, however (as in the present study), the second term cannot be expressed as a simple function of ΔH_f .

Table III. Ionic and electronic conductivities at 900°C.

Composition	Ionic conductivity (Ω-cm) ⁻¹	Electronic conductivity (Ω-cm) ⁻¹	Ionic transport number
LSCF-6428	0.23	252	9×10^{-4}
LSCF-4628	0.40	219	2×10^{-3}
LSCF-2828	0.62	120	5×10^{-3}
LSCF-2882	0.87	310	3×10^{-3}
LCCF-4628	0.03	52	6×10^{-4}
LCCF-4682	0.01	296	3×10^{-5}
LBCF-6428	0.01	123	8×10^{-5}
LBCF-4628	0.33	57	6×10^{-3}
LBCF-2828	0.37	19	2×10^{-2}

Table IV. Activation energies for ionic conduction.

Composition	Activation energy (eV)
LSCF-6428	1.30
LSCF-4628	0.95
LSCF-2828	0.85
LSCF-2882	0.66
LCCF-4628	0.70
LCCF-4682	1.80
LBCF-6428	1.64
LBCF-4628	0.90
LBCF-2828	0.65

Because ionic conductivity is the product of three terms [carrier concentration (*i.e.*, oxygen vacancies per unit volume, n_v), carrier charge ($2e$), and carrier mobility (μ_v)], it was possible to estimate the oxygen vacancy mobility

$$\mu_v = \sigma_i / n_v (2e) \quad [6]$$

For these calculations, the oxygen vacancy concentrations were based on the observed oxygen deficiencies in air (Fig. 4 and 5); unit cell volumes were corrected for thermal expansion assuming a TEC value of 15×10^{-6} .¹⁰ The temperature dependence of the vacancy mobility takes the form²⁸

$$\mu_v = (A/T) \exp(-\Delta H_m/kT) \quad [7]$$

where A is a constant. Accordingly, the activation energies for vacancy diffusion were obtained from plots of $\ln \mu_v T$ vs. $1/T$. These values are listed in Table V. Ishigaki *et al.*³ determined the activation energies for vacancy diffusion in La_{1-x}Sr_xCoO₃ and La_{1-x}Sr_xFeO₃ ($0 \leq x \leq 0.25$) to be between 0.78 and 0.88 eV. Those activation energies are higher than those obtained for the more highly acceptor doped, mixed B-site compositions characterized in the present study.

Table V also contains empirical expressions for the oxygen vacancy mobility as a function of temperature. Expressions for the vacancy diffusion coefficient, D_v , as obtained from the Nernst-Einstein relation

$$\mu_v = (2e D_v)/kT \quad [8]$$

are also shown in Table V. As expected from the discussion above, the activation energies for vacancy diffusion are less than the activation energies for ionic conduction, with the difference between the two representing the term related to the formation of oxygen vacancies.

Table V. Activation energies, mobilities, and diffusion coefficients for oxygen vacancy diffusion; T is absolute temperature.

Composition	Activation energy (eV)	Mobility (cm ² /V-s)	Diffusion coefficient (cm ² /s)
LSCF-6428	0.55	(209/T) exp (-0.55/kT)	0.009 exp (-0.55/kT)
LSCF-4628	0.63	(269/T) exp (-0.63/kT)	0.012 exp (-0.63/kT)
LSCF-2828	0.69	(436/T) exp (-0.69/kT)	0.020 exp (-0.69/kT)
LSCF-2882	0.56	(129/T) exp (-0.56/kT)	0.005 exp (-0.56/kT)
LBCF-6428	1.36	(10700/T) exp (-1.36/kT)	0.462 exp (-1.36/kT)
LBCF-4628	0.77	(551/T) exp (-0.77/kT)	0.024 exp (-0.77/kT)
LBCF-2828	0.59	(78/T) exp (-0.59/kT)	0.003 exp (-0.59/kT)

There is no obvious explanation for the superior ionic conduction observed in the Sr-doped compositions, but it is apparent that the higher ionic conductivity of LSCF compositions relative to LBCF compositions is attributable to a higher mobility of oxygen vacancies, rather than a higher concentration of vacancies (see Fig. 4 and 5, and Table V). Because Ca^{2+} , Sr^{2+} , and Ba^{2+} are all divalent alkaline earth (Periodic Table Group IIA) cations, the most apparent difference between them is their size. The geometrically derived Goldschmidt tolerance factor, t , is a useful measure of the degree of "misfit" between the constituent ions in a perovskite material. This factor is given by²⁹

$$t = (r_A + r_O) / \sqrt{2}(r_B + r_O) \quad [9]$$

where r_A , r_B , and r_O are the ionic radii of the A-site cation, B-site cation, and oxygen anion, respectively; t is equal to 1 for an ideal cubic perovskite. Tolerance factors calculated using Shannon and Prewitt ionic radii³⁰ range between 0.97 to 0.98, 0.99 to 1.02, and 0.95 to 0.96, respectively, for the LSCF, LBCF, and LCCF compositions through which oxygen fluxes were measured. These results suggest that a slight negative deviation from ideality in the tolerance factor may enhance oxygen ion vacancy mobility. It is likely, however, that other nongeometric factors (such as ionic polarizability and defect interactions) also play a role in the behavior of these complicated systems. It is hoped that future work will provide a definitive explanation for the superiority of Sr as an A-site dopant.

Conclusions

Perovskite compositions in the system $\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($M = \text{Sr}, \text{Ba}, \text{Ca}$) exhibited a substantial reversible weight loss at elevated temperatures resulting from a decrease in oxygen stoichiometry. This loss of lattice oxygen, which resulted in a decrease in the electronic conductivity at high temperatures, also increased the oxygen vacancy concentration within the material. As acceptor content increased, the oxygen loss began at lower temperatures, and the magnitude of the oxygen loss increased. Electronic conduction behavior was consistent with the small polaron mechanism. A substantial decrease in electronic conductivity was observed at elevated temperatures because of the decrease in oxygen stoichiometry. In an oxygen partial pressure gradient, the oxygen flux through dense sintered membranes of these materials was highly dependent on composition and increased with increasing temperature. The increase in oxygen flux with increasing temperature was attributed to two factors: an increase in the mobility of the lattice oxygen vacancies, and an increase in the concentration of lattice oxygen vacancies. The ionic conductivities (calculated from oxygen flux data) of the high-Sr compositions exceeded that of yttria-stabilized zirconia by nearly an order of magnitude.

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