Oxygen deficiency, vacancy clustering and ionic transport in \((\text{La}, \text{Sr})\text{CoO}_3 - \delta\)

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1. Introduction

Lanthanum–strontium cobaltites with \(\text{ABO}_3\) perovskite-type structure, \((\text{La}, \text{Sr})\text{CoO}_3 - \delta\) possess very high levels of \(p\)-type electronic conduction, oxygen ion diffusivity, oxygen surface exchange rates and electrocatalytic activity in the reactions involving oxygen [1–10]. These properties, attracting great interest to the cobaltite-based systems for a variety of high- and low-temperature electrochemical applications, are all dependent on the oxygen stoichiometry and oxygen thermodynamics. Moderate additions of \(\text{Sr}^{2+}\) in \((\text{La}, \text{Sr})\text{CoO}_3 - \delta\) result in increasing hole concentration and delocalization, leading to maximum electronic transport at \(x \approx 0.3 - 0.4\). On further \(\text{Sr}^{2+}\) doping, the charge compensation mechanism via the oxygen vacancy formation starts to prevail; the partial ionic conductivity increases with strontium content up to \(x \approx 0.7\), and then exhibits a decrease due to extensive ordering processes in the oxygen sublattice and phase separation [1.6–8,10]. Although some aspects in \((\text{La}, \text{Sr})\text{CoO}_3 - \delta\) behavior can be successfully represented by the standard point-defect models [e.g. \(10,11\)], the essentially itinerant nature of \(p\)-type electronic charge carriers requires to avoid use of the ideal solution-based approaches for description of the cobalt sublattice. The oxygen nonstoichiometry in \((\text{La}, \text{Sr})\text{CoO}_3 - \delta\) is often analyzed using a simplified rigid-band approach assuming that oxygen release from the perovskite lattice results in gradual filling of the electronic states in a wide band, rising the Fermi level, whilst any nonidealities in the oxygen sublattice are neglected [3,4]. At the same time, numerous experimental data (see \([7,8,12,13]\) and references therein) indicate a significant role of short- and long-range ordering processes in the oxygen sublattice, particularly at \(x > 0.5\) and moderate oxygen chemical potentials.

The major purpose of this work was to evaluate effects of defect clustering phenomena in \((\text{La}, \text{Sr})\text{CoO}_3 - \delta\) on the oxygen deficiency variations and ionic transport, using the rigid-band model [3] for \(p\)-type electronic charge carriers. As the analysis of point-defect interactions leads to complex statistical models and, hence, requires large arrays of experimental data points, the equilibrium \(p(O_2)-T-\delta\) diagrams of lanthanum–strontium cobaltites were collected in wide ranges of temperature and oxygen partial pressure by thermogravimetric analysis (TGA) and coulometric titration (CT). The obtained parameters describing behavior of the perovskite lattice components were then used to model steady-state oxygen permeation through dense cobaltite membranes. The local structural features associated with vacancy ordering were also evaluated by Mössbauer spectroscopy (MS) of \((\text{La}, \text{Sr})\text{CoO}_3 - \delta\) doped with 1 mol% \(^{57}\text{Fe}\), where the isotope probe was selected close to possible minimum in order to minimize strains and structural changes in the host cobaltite matrix.
2. Experimental

Single-phase ceramics of La$_{1-x}$Sr$_x$CoO$_{3-x}$ (x = 0.3, 0.5 and 0.7) with >93% density were prepared via the glycine-nitrate synthesis route, calcination at 1073–1273 K, ball-milling, pressing at 180–250 MPa and final sintering in air at 1520–1650 K for 2 h. The powdered samples used for X-ray diffraction (XRD), CT and TGA were obtained by grinding of sintered ceramics. XRD showed the formation of single perovskite-type phases with rhombohedral (x = 0.3 and 0.5) or cubic (x = 0.7) structure. The overall cation composition was confirmed by the inductively-coupled plasma (ICP) spectroscopic analysis. The equipment and procedures used for materials characterization, including the oxygen permeation and total conductivity measurements, were described elsewhere ([5,8,11,14–16] and references cited). TGA was carried out in the regimes of temperature cycling at 293–1323 K and isothermal dwells at 873–1223 K in flowing dry air, with subsequent reduction in 10%H$_2$–90%N$_2$ mixture at 1373 K. The calculated values of total oxygen content (δ–δ) at atmospheric oxygen pressure were used as the reference points for the CT data arrays. The average reproducibility error of the δ values at 873–1223 K, estimated from 10 measurement cycles, was lower than ±0.004 atoms per formula unit. One example illustrating reproducibility of the TGA data is presented in Fig. 1A. The CT measurements were performed in isothermal regime, varying p(O$_2$) in the range 10$^{-5}$ to 1 atm, at 873–1223 K. An excellent reproducibility validated after each redox cycle, as illustrated by Fig. 1B, confirmed zero leakage in the coulometric titration cells. The same conclusion was drawn comparing the oxygen nonstoichiometry variations at atmospheric p(O$_2$), measured by the TGA and CT methods. For the Mössbauer spectroscopy studies a series of Fe-doped compositions, La$_{1-x}$Sr$_x$CoO$_{3.01}$Fe$_{0.01}$O$_{3-x}$ (x = 0.3, 0.5 and 0.7), was synthesized under conditions identical to those for the iron-free materials. After XRD, the samples were annealed in air or in flowing argon at 973–1223 K for 10 h, and then slowly cooled or quenched in liquid nitrogen. The Mössbauer spectra were collected at 4 and 290 K on a transmission constant-acceleration spectrometer with a $^57$Co (Rh) source as described elsewhere [14,15], and analyzed using MossWin software [17]. For all MS data, isomer shifts (IS) are given relative to metallic α-Fe at room temperature.

3. Results and discussion

3.1. Oxygen nonstoichiometry

In this work, all statistical-thermodynamic models for the equilibrium p(O$_2$)–T–δ diagrams (Fig. 2) included the hole contribution, described in framework of the rigid-band approach [3] and formulated as:

$$\mu(h) = \mu(h^0) + \frac{\[h^0] - \langle h \rangle}{g(\mu(h^0))}$$

(1)

where $\mu$ is the chemical potential consisting of concentration-dependent ($\mu'$) and concentration-independent ($\mu^0$) parts, $\mu(h^0)$ is the electron-hole concentration at zero $\delta$, and $g(\mu(h^0))$ is the electronic density of states at the Fermi level. Hereafter, the Kröger–Vink notation is used and all concentration-related terms are normalized to one formula unit. If the generation of p-type charge carriers is significantly contributed by intrinsic electronic disordering when Co$^+$ exists predominantly in the form of any clusters with oxygen vacancies, such as V(o)−Co$^{2+}$, the parameter $[h^0]$ is equal to [Sr$^{4+}$]. The concentration-dependent part of the vacancy chemical potential can be generally formulated as:

$$\mu'(V_o^0) = RT \ln \frac{[V_o^0]}{N(\delta) - \delta}$$

(2)

where $[V_o^0]$ is the concentration of mobile oxygen vacancies, $\delta$ is the total concentration of vacant oxygen sites measured by TGA and CT, and $N(\delta)$ is the corresponding number of states. In the simplest case when all oxygen sites are energetically equivalent and vacancies interaction can be neglected (Model 1), the latter quantity is equal to the number of oxygen sites: $N(\delta) = [O_2^0] = 3$. When the site-exclusion effects caused by coulombic repulsion between the vacancies are significant (Model 2), $N(\delta)$ is determined by the probability of complete occupation of $n$ neighboring oxygen sites:

$$N(\delta) = \left[O_2^0\right] \left(1 - \frac{\delta}{[O_2^0]}\right)^n$$

(3)

If no vacancy can be located in the first coordination sphere near a vacant site, $n = 8$.

Preliminary analysis of the p(O$_2$)–T–δ diagrams (Fig. 2) demonstrated that, since the average oxidation state of cobalt cations at relatively low p(O$_2$) and elevated temperatures becomes quite close to 3+, the electron-hole equilibrium and Co$^+$ formation cannot be neglected. For Models 1 and 2, the latter species were considered as polarons localized near oxygen vacancies, forming stable pair clusters (V(o)−Co$^0$):
In this case, the site-conservation and electroneutrality conditions can be expressed as

\[ \delta + [O_0^2] = [O_0^2] = 3 \text{ and } [\langle V_0 - Co_b^2 \rangle] + [V_0^2] = \delta \]  
\[ [h^+] + [\langle V_0 - Co_b^2 \rangle] + 2[V_0^2] = [Sr^\alpha] \]  

whilst the electron-hole recombination processes should be correlated to the oxygen nonstoichiometry:

\[ V_0^2 = h^+ + \langle V_0 - Co_b^2 \rangle \quad K_1 = \frac{a(V_0^2)}{a(h^+)a(\langle V_0 - Co_b^2 \rangle)} \]  

where \( a \) is the thermodynamic activity and \( K \) is the equilibrium constant.

One modification of this formalism, referred to as Model 3, was similar to Model 1 but presumed that clustering is governed by the cobalt sublattice:

\[ \mu'(\langle V_0 - Co_b^2 \rangle) = RT \ln \frac{[\langle V_0 - Co_b^2 \rangle]}{N(\langle V_0 - Co_b^2 \rangle)} \]  

where \( N(\langle V_0 - Co_b^2 \rangle) = (1 - \tfrac{1}{2})^n \) and \( n = 5 \), implying that no other vacancies may be located near \( \langle V_0 - Co_b^2 \rangle \) pair. Finally, Models 4 and 5 were based on Models 1 and 2, respectively, but were altered in order to account for cobalt disproportionation. This reaction shifts \( [h^0] \) and leads to the existence of free \( Co_b^2 \):

\[ Co_b^2 \rightleftharpoons h^+ + Co_b^0 \quad K_2 = \frac{a(h^+)}{a(Co_b^0)} \]  

with the concentration-dependent part of chemical potential expressed as \( RT \ln[Co_b^2/Co_b^0] \); the \( \langle V_0 - Co_b^2 \rangle \) formation should still be considered as an additional process:

\[ V_0^2 + Co_b^0 = \langle V_0 - Co_b^2 \rangle \quad K_3 = \frac{a(V_0^2)a(Co_b^0)}{a[\langle V_0 - Co_b^2 \rangle]} \]  

In the course of comparative fitting of the experimental data, more than 20 alternative models were tested, including the formulae [3,4] neglecting any deviations from ideal behavior in the oxygen sublattice. Model 1 was found to provide the best description of the oxygen nonstoichiometry dependencies on temperature and oxygen partial pressure; the fitting results are shown in Fig. 2 as solid lines. One representative example of the fitting residuals distribution is shown in Fig. 3. The residuals exhibit a clear correlation with \( p(O_2) \) and \( \delta \) values in all cases, except for Model 1. This confirms the relevance of clustering processes governing the concentrations of mobile oxygen vacancies and divalent cobalt cations in \( La_{1-x}Sr_xCoO_3-\delta \); at the same time, the introduction of variables describing other
processes, such as site-exclusion phenomena near the vacant sites, leads to the model over-determination. Another necessary comment is that attempts to account for higher-order defect clusters failed as the corresponding contributions to the oxygen chemical potential variations were modest compared to the electronic sublattice, disordered vacancies and simplest pair clusters. Although the formation of ternary and larger defect associates is very likely when \( \delta > 0.1 \), these cannot be distinguished using the statistical-thermodynamic analysis of the equilibrium \( p(O_2) - T - \delta \) diagrams, making it necessary to use complimentary methods. In fact, the importance of long-range ordering at \( x > 0.5 \) and \( p(O_2) \approx 10^{-5} \) atm was unambiguously revealed by Mössbauer spectroscopy; for the compositions with \( x = 0.3 - 0.5 \), no indication of long-range order was found, validating the use of defect cluster approach regardless of the associate sizes. These issues are briefly addressed below.

3.2. Ionic transport

In agreement with numerous literature data (e.g. [1-11]), strontium additions in La\(_{1-x}\)Sr\(_x\)CoO\(_{3-\delta}\) result in increasing oxygen deficiency (Fig. 2) and steady-state permeation fluxes (Fig. 4). However, the role of surface exchange kinetics evaluated from the oxygen flux dependencies on membrane thickness \( (L) \), also increases with \( x \) and becomes critical at \( x > 0.5 \). As an example, at \( x = 0.3 \) the permeation fluxes \( (j) \) are proportional to \( 1/L \); at \( x = 0.7 \) the permeation becomes almost thickness-independent, Fig. 4. The oxygen transport processes were hence modeled numerically, by splitting the overall oxygen chemical potential gradient into three parts corresponding to the membrane bulk \( (\Delta \mu_{\text{bulk}}) \), permeate-side \( (\Delta \mu_{\text{surf}}) \) and feed-side \( (\Delta \mu_{\text{fl}}) \). The bulk contribution determined by the partial ionic \( (\sigma_0) \) and electronic \( (\sigma_e) \) conductivities, was calculated by solving the Wagner equation

\[
j = \frac{1}{16F^2L} \int_{\mu_0}^{\mu_f} \frac{\sigma_0 \sigma_e}{\sigma_0 + \sigma_e} d\mu(O_2) = \frac{1}{16F} \frac{\sigma_0 \sigma_e}{\sigma_0 + \sigma_e} \cdot \mu_f(O_2).
\]

(11)

Since the electronic conductivity in lanthanum–strontium cobaltites is \( 10^4 - 10^5 \) times higher than ionic [1-6,8,9], \( \lim_{\alpha_0 = \sigma_0 \sigma_e / \sigma_0 + \sigma_e} = \sigma_0 \). Again, in the course of regression analysis, more than 10 alternative models were compared. The best fitting results were obtained neglecting the long-range ordering phenomena and coulombic repulsion:

\[
\alpha_0 = U_0 [V_0^{\sigma} O_0^{\sigma}]
\]

(12)

where \( U_0 \) is a temperature-dependent constant and the concentration of mobile oxygen vacancies, \( [V_0] \), is defined by Eq. (5). For the materials with \( x = 0.5 - 0.7 \) when the oxygen fluxes are surface-limited, oxygen transfer across the membrane/gas interfaces was simulated using phenomenological expressions:

\[
1 - \exp \left( \frac{\delta}{\Lambda_1 RT} \right), \quad \frac{\delta}{\Delta \mu_{\text{surf}}}, \quad \frac{\Lambda_1}{RT}
\]

\[
\frac{\delta}{\Delta \mu_{\text{surf}}}, \quad \frac{\Lambda_1}{RT}
\]

\[
1 - \exp \left( \frac{\Lambda_1}{RT} \right), \quad \frac{\Lambda_1}{RT}
\]

\[
1 - \exp \left( \frac{\Lambda_1}{RT} \right), \quad \frac{\Lambda_1}{RT}
\]

where \( \Delta \mu_{\text{surf}} / z \) is the driving force, \( z \) is the stoichiometric coefficient showing relationships between the fluxes of...
molecular O$_2$ and species involved in the rate-determining step, $f_1^0$ and $f_2^0$ are temperature-dependent constants, and the indices “1” and “2” correspond to the permeate- and feed-side surfaces, respectively. Eqs. (13) and (14) were selected from a number of alternative expressions, including the Butler–Volmer type models and various kinetic and thermodynamic equations [18,19], on the basis of fitting results. Both Eqs. (13) and (14) represent simplified solutions of the general thermodynamic formulae [18,19], where the transport coefficient $\kappa_i$ may comprise concentration of species involved in the rate-determining steps. Note also that the best fitting quality was obtained fixing $z=2$, in agreement with the conclusion [20] on limiting role of oxygen vacancies and/or adsorbed atomic species in the surface exchange of La$_{0.3}$Sr$_{0.7}$CoO$_3$. 

In the course of regression analysis of the oxygen permeation data, the set of Eqs. (11)–(14) was solved numerically for $x=0.5$–0.7; the relationships between $[V_{O}^0]$, $[O_2]$ and $\mu(O_2)$ were described using the fitting parameters for equilibrium $p(O_2)$–$T$–$\delta$ diagrams (Fig. 2). For $x=0.3$, Eqs. (13) and (14) were excluded as the oxygen transport is limited by the bulk ionic transport and, therefore, $\Delta \mu_{\text{eff}}^0=\Delta \mu_{\text{kin}}^0=0$. The results shown in Fig. 4 as solid lines are in a reasonable agreement with experimental data. Fig. 5 displays the calculated ionic conductivity and concentration of mobile vacancies at 1023 and 1173 K. When the concentration of Sr$^{2+}$ is moderate ($x=0.3$), increasing $\delta$ results in the generation of both free vacancies and their clusters. Consequently, the ionic conductivity exhibits a maximum at relatively low $\delta$ values; on further reduction, the defect associates become prevailing and ion diffusivity starts to decrease. This type of behavior, and shifting the maxima positions on heating, confirm the trends reported for La$_{0.3}$Sr$_{0.7}$CoO$_3$ [7,8]. In the case of La$_{0.3}$Sr$_{0.7}$CoO$_3$, the values of $\delta$, $[V_{O}^0]$ and $[[V_{O}^0]-C_{O2}]^{-1}$ are substantially higher; no maxima are visible in the experimentally studied $\delta$ range and the ionic conductivity tends to decrease on reduction.

3.3. Mössbauer spectroscopy

The local structures formed in oxygen-stoichiometric and deficient cobaltites were further assessed by the MS analysis of 1 mol% Fe-doped materials. At 4 K, the Mössbauer spectra of essentially oxygen-stoichiometric La$_{1-x}$Sr$_x$Co$_{0.99}$Fe$_{0.01}$O$_{3-\delta}$ equilibrated with atmospheric oxygen at low temperatures (Fig. 6A), display single sextets analyzed with a distribution of magnetic hyperfine fields ($B_{hf}$). The room-temperature spectra were fitted to a quadrupole doublet with low quadrupole splitting. Fig. 7 compares the estimated average IS and $B_{hf}$ values with literature data on other (La,Sr)Co$_3$–$\delta$ perovskites containing 1–5% Fe in the cobalt sites [21–23] and (La,Sr)FeO$_3$ [24,25]. Both Mössbauer parameters monotonically decrease with increasing $x$, indicating that the average oxidation state of iron increases. The fraction of Fe$^{4+}$ should still be significant in La$_{0.3}$Sr$_{0.7}$Co$_{0.99}$Fe$_{0.01}$O$_{3-\delta}$ and even in La$_{0.3}$Sr$_{0.7}$Co$_{0.95}$Fe$_{0.05}$O$_{3-\delta}$; the observed IS of La$_{0.3}$Sr$_{0.7}$Co$_{0.99}$Fe$_{0.01}$O$_{3-\delta}$ is slightly higher compared to SrFeO$_3$ [24,25] and SrCo$_{0.99}$Fe$_{0.01}$O$_3$ [22], which suggests that a part of iron remains trivalent. Consequently, Fe cations incorporated into the cobalt sublattice of these perovskites possess an average oxidation state between 3+ and 4+, a result of high delocalization of the p-type electronic charge carriers. Another important comment is that the electronic states of B-site cations remain cationized down to 4 K. An absence of low-temperature charge disproportionation, that occurs in La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ ($0 \leq x \leq 0.9$), seems therefore typical for the perovskites where most B sites are occupied by cobalt.

For $x \leq 0.5$, the spectra of moderately reduced La$_{1-x}$Sr$_x$Co$_{0.99}$Fe$_{0.01}$O$_{3-\delta}$ annealed in flowing Ar at $p(O_2) \approx 10^{-5}$ atm and 973 K (Fig. 6B), are very similar to those of the oxidized samples. This implies, in particular, ...
that no structural changes occur on reduction, in agreement with XRD. 
In the case of reduced La$_{0.3}$Sr$_{0.7}$Co$_{0.99}$Fe$_{0.01}$O$_{3}$, where $\delta$ is close to 0.37, two distributions of $B_{hf}$ with different IS were however necessary to analyze the 4 K spectrum. The estimated IS (0.45 and 0.41 mm/s) and $B_{hf}$ (50.6 and 46.2 T) are characteristic of hexa- and penta-coordinated Fe$^{3+}$, respectively [14,15]; their concentration ratio is 57/43. The XRD analysis revealed transition from cubic perovskite to the tetragonal structure (space group $I4/mmm$), as for oxygen-deficient La$_{0.3}$Sr$_{0.7}$Co$_{0.99}$CoO$_{2.7}$ [8,12]. In accordance with Refs. [12,26], this structure may be visualized as a partially oxidized A$_2$B$_3$O$_6$ brownmillerite lattice where the extra oxygen anions are incorporated into 8j positions in the layer formed by BO$_4$ tetrahedra, thus leading to the appearance of pyramids and/or octahedra. For La$_{0.3}$Sr$_{0.7}$Co$_{0.99}$Fe$_{0.01}$O$_{3+\delta}$ a transition would be accompanied by increasing concentrations of the octa- and penta-coordinated B-site cations up to 63% and 26%, respectively; in the spectra, the remaining FeO$_4$ tetrahedra signal may overlap with the pyramids signal. It should be mentioned that no evidence for another vacancy-ordered superstructure with square pyramidal coordination of cobalt [13] was revealed from the MS and XRD data; the structures known for LnBa$_2$Mo$_3$O$_{9+\delta}$ (M = Co, Fe; Ln = Pr–Lu, Y) double perovskites [27,28] require A-site cation ordering and are therefore unlikely in the present case.

The 4 K spectrum of La$_{0.3}$Sr$_{0.7}$Co$_{0.99}$Fe$_{0.01}$O$_{3+\delta}$ with $\delta$ = 0.48, partly reduced at 1223 K, consists of six broad absorption peaks and can only be analyzed with four sextets (Fig. 6B). Two main contributions with equal areas are related to the same tetragonal phase as observed after annealing at $p$(O$_2$) $\approx$ 10$^{-5}$ atm and 973 K. This agrees with XRD results, which showed the co-existence of ordered tetragonal and disordered perovskite phases. The IS values of the two remaining sextets (0.53 and 0.34 mm/s) were ascribed to the penta- or tetra-coordinated iron cations, the higher IS suggesting the presence of Fe oxidation state lower than 3+, in the highly-deficient perovskite phase [28]. In summary, the MS analysis of 1 mol% Fe-doped La$_{1-x}$Sr$_x$Co$_3$O$_{4-\delta}$ ($x$=0.3–0.5) clearly indicates an absence of long-range ordering at 973–1223 K and oxygen partial pressures higher than 10$^{-5}$ atm. This validates the hypotheses regarding relatively small point-defect clusters, used for the statistical-thermodynamic analysis of oxygen incorporation and ion diffusion processes. Notice, however, that there is a high probability of forming trimers and higher-order clusters as the vacancy concentration increases. The models dealing with the pair clusters are simplest from the statistical point of view and thus provide minimum errors in the entire $p$(O$_2$) range; identification of the cluster size and configuration requires the use of complementary spectroscopic and diffraction methods. Nonetheless, the results unambiguously show significant influence of the vacancy association phenomena on oxygen thermodynamics and ionic conductivity of (La$_x$Sr$_{1-x}$)CoO$_3$−δ. This influence becomes critical on reduction and should be taken into account when analyzing the defect chemistry of lanthanum–strontium cobaltites and related systems. In particular, the formation of stable defect clusters involving Co$^{4+}$ and V$_G$ may explain the almost negligible contribution of n-type electronic charge carriers to total conductivity at moderately low oxygen pressures [1,5,10]. Although the relationships between mobile vacancy concentration and surface exchange kinetics require further investigations, the modeling results indicate their direct correlation, which may be relevant for the rising role of surface exchange as the oxygen permeation-determining factor when Sr$^{2+}$ content increases. The same correlation may contribute to the increase of interfacial exchange rates with increasing $p$(O$_2$), known for most cobaltite-based systems (e.g. [6,20]). Finally, the transition into vacancy-ordered tetragonal phase in La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ ($x$=0.5) makes it necessary to assess equilibrium phase relationships in moderately reducing atmospheres. At oxygen partial pressures higher than 10$^{-3}$ atm, the $p$(O$_2$)–$T$–$\delta$ diagrams exhibit no anomalies characteristic of phase boundaries (Fig. 2), thus providing an additional argument in favor of the mechanism based on vacancy-ordered microdomain formation [7]. Similar mechanisms are well known for the perovskite-like ferrites, where the overall oxygen stoichiometry variations on reduction are essentially governed by the perovskite phase defect chemistry.

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References


