

Defect Chemistry, Electrical Properties, and Evaluation of New Oxides $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ ($0 \le x \le 1$) as Cathode Materials for Solid Oxide Fuel Cells

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The perovskite series $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ ($0 \le x \le 1$) was investigated in the full compositional range to assess its potential as cathode material for solid oxide fuel cell (SOFC). The variation of transport properties and thus, the area specific resistances (ASR) are explained by a detailed investigation of the defect chemistry. Increasing the titanium content from x=0-1 produces both oxidation of Co^{3+} to Co^{4+} (from 0 up to 40%) and oxygen vacancies (from 6.0 to 5.7 oxygen atom/formula unit), although each charge compensation mechanism predominates in different compositional ranges. Neutron diffraction reveals

that samples with high Ti-contents lose a significant amount of oxygen upon heating above 600 K. Oxygen is partially recovered upon cooling as the oxygen release and uptake show noticeably different kinetics. The complex defect chemistry of these compounds, together with the compositional changes upon heating/cooling cycles and atmospheres, produce a complicated behavior of electrical conductivity. Cathodes containing Sr₂CoTiO_{6-ð} display low ASR values, 0,13 Ω cm² at 973 K, comparable to those of the best compounds reported so far, being a very promising cathode material for SOFC.

Introduction

Perovskites are very versatile materials that have been proposed as components of several electrochemical devices such as fuel cells,^[1] electrolyzers,^[2] and oxygen-transport membranes.^[3] For the former, not only cathodes but also anodes and even electrolytes based on perovskite-like compounds have been proposed and are considered presently the state-ofthe-art in such applications.^[4] Accommodation of cations of different size in different crystallographic sites produces structural

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distortions to lower symmetries when compared to the arystotype SrTiO₃, whereas different charges of these cations result in a variety of electrical and electrochemical properties. Moreover, perovskites show a quite flexible microstructure that influences their properties,^[5] including transport properties, oxygen conductivity, and electrochemical activity.^[6]

Among perovskites, the so-called "double perovskites" with general formula $A_2BB'O_6$ present a variety of compositions and properties related to the capability of the simple perovskite structure to accommodate different transition metal cations B and B' of different sizes and electronic structures. In addition, partial substitution of cations in the A-site opens new possibilities, including the induction of anionic vacancies through aliovalent substitution. The most investigated cathode material, $La_{1-x}Sr_xMnO_3$ (LSM), is obtained by substitution of La^{3+} by Sr^{2+} . Aliovalent substitution improves the electronic conductivity (owing to small polarons hopping related to the manganese mixed oxidation state, Mn^{3+}/Mn^{4+}) with respect to the parent LaMnO₃.

We have recently studied the La_{2-x}Sr_xCoTiO₆^[7] ($0 \le x < 1$) and La_{2-x}CoTiO_{6- δ} (0.05 < x < 0.20)^[8] series. In the former, La/Sr replacement produces a significant increase of electronic conductivity (from 3.6×10^{-2} Scm⁻¹ for the parent compound to 1.4 Scm⁻¹ for x = 0.4),^[8] in as much as the sole charge-compensation mechanism is the oxidation of Co²⁺ to Co³⁺ with the consequent increase of positive charge carriers. In the latter, La-deficiency is compensated through two main mechanisms: the oxidation of Co²⁺ to Co³⁺ on one hand, which is predominant at low *x*, and the creation of oxygen vacancies that pre-

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dominates at intermediate x values. At high x values both mechanisms operate. The existence of the two extrinsic defects, Co^{3+} and oxygen vacancies, explains the variation of the total electrical conductivity with oxygen partial pressure.

There is another related double perovskite $Sr_2CoNbO_{6-\delta r}$ in which the operating redox couple responsible for the electrical properties is Co³⁺/Co⁴⁺ instead of Co²⁺/Co³⁺; however, the reports on their possible applications are scarce.^[9] In addition, some structural characteristics have already been reported.^[10] Our own studies on this interesting double perovskite started with the investigation of the structure, microstructure, and magnetic properties of Ti-containing derivatives, $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ (0 $\leq x \leq$ 0.5).^[5] These materials present a complex microstructure consisting of domains of a double-cubic perovskite grown in a simple-cubic perovskite matrix. The size and number of domains of the double perovskite (with rock salt ordering of the B-ions) depend on the degree of substitution of Nb⁵⁺ by Ti⁴⁺. Note that it is well established that not only the structure but also the microstructure have a strong influence on the electrical properties.^[11] Aliovalent substitution of Nb⁵⁺ by Ti⁴⁺ produces the oxidation of Co^{3+} to Co^{4+} for low x values whereas a second mechanism, creation of oxygen vacancies, starts to operate at high x values.^[5] Thus, changing the Co^{3+}/Co^{4+} ratio as well as oxygen content with x may have a significant effect on both electrical and electrochemical properties of the title compounds. Therefore, here, we report on the potential use of the $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ (0 < x < 1) series compounds as SOFC electrodes. Note that, besides the mixed oxidation state and oxygen vacancies, the presence of small amounts of titanium may enhance the catalytic effect for oxygen reduction, improving their electrochemical performances.

Results and Discussion

Compositional and structural characterization

As determined by XRD and energy-dispersive spectroscopy (EDS), all the as-prepared samples $\text{Sr}_2\text{CoNb}_{1-x}\text{Ti}_x\text{O}_{6-\delta}$ ($0 \le x \le 1$) are single phase. Within the experimental error, their chemical compositions match with the nominal ones; even more, the distribution of all the constituting elements was confirmed to be homogeneous throughout the samples. Back-scattered electron (BSE) images and the corresponding element-distribution maps for different compositions are shown in Figures SI 1 to SI 3 (in the Supporting Information). Therefore, the Ti⁴⁺ substitution by Nb⁵⁺ ions can be considered effective and homogeneous for all samples.

Recently, Bashir and Shaheen^[9b] reported a structural model of tetragonal symmetry for Sr₂CoNbTiO_{6- δ} (space group *I*4/*m*). However, in a recent paper using XRD and neutron powder diffraction (NPD) data, we report a different average structure of Sr₂CoNb_{1-x}Ti_xO_{6- δ} (0 ≤ *x* ≤ 0.5) oxides. This structure can be described as a simple-cubic perovskite (space group *Pm3m*) with Sr located in 1b ($^{1}/_{2}^{1}/_{2}$), Co/Nb/Ti randomly distributed in the 1a (000), and oxygen in 3d ($^{1}/_{2}$ 00) sites.^[5] The fitting of the XRD data revealed that the rest of the series members (i.e., those with 0.5 < *x* ≤ 1.0) also present the ideal perovskite structure with no cationic ordering or octahedral tilting, in agreement with the tolerance factors close to one, which ranges from 0.989 to 1.010 (see Figures SI4 to SI13).

On the other hand, as Figure 1 shows, the lattice parameter presents an interesting dependence with titanium content.

For low degree of aliovalent substitution (ca. 10%) the cell expands, whereas from x > 0.1 it continuously contracts. The latter is the expected behavior considering both the sizes of Nb⁵⁺ (0.64 Å) and Ti⁴⁺ (0.605 Å) and the effect of the aliovalent substitution of Nb⁵⁺ by Ti⁴⁺ on the oxidation state of cobalt. In fact, two charge-compensating mechanisms operate be-



Figure 1. Lattice parameter (blue squares), oxygen content per formula unit (f.u.) (green diamonds), and Co^{4+} content (red circles), obtained by both TGA and redox titration, as a function of the level of aliovalent substitution Nb^{5+} by Ti^{4+} .



cause of this substitution: the oxidation of Co^{3+} (^{HS}r = 0.61 Å, $^{LS}r = 0.545$ Å) to Co⁴⁺ ($^{HS}r = 0.53$ Å) (HS and LS indicates high and low-spin states, respectively), which contributes to a cell contraction as well; and the creation of oxygen vacancies, which would induce a volume expansion owing to the loss of Madelung energy. It is clear from Figure 1 that in the present materials, the size effect owing to cobalt oxidation is the predominant one. In this connection, Rietveld analysis of the XRD patterns shown in Figures SI4 to SI13 suggests the existence of some amount of oxygen vacancies that increases as the degree of aliovalent substitution does. However, XRD is not the best technique to deal with structural features associated with light atoms such as oxygen; therefore, other complementary techniques were used to quantify the oxygen stoichiometry of the title oxides. Using redox titration and thermogravimetric analysis (TGA) independently, we confirmed the dependence of oxygen content per formula unit (f.u.) on the degree of substitution; the results are plotted in Figure 1.

The volume expansion for low levels of substitution may be associated to the evolution of the microstructure. Recently,^[5] we found that the $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ oxides present a flexible microstructure, which evolves with the Ti/Nb ratio. The parent material (x=0) presents domains of cubic double perovskite with rock-salt order on the B-sites grown in a matrix of cubic simple disordered material. As Nb is substituted by Ti, the size and number of domains with double-perovskite structure decrease, resulting in the increase of metal-metal repulsions as interactions between highly charged Nb⁵⁺ ions are more probable in the disordered perovskite in comparison with the ordered structure. Besides, a complex microstructure consisting of intergrowth of small domains will provide a mechanism to accommodate a large amount of anion vacancies (as those observed in Figure 1) in the domain walls.

Evolution of the structure and composition with temperature

The understanding of the electrical and electrochemical properties of a SOFC material requires the knowledge of its structure at operational temperatures as well as its thermal evolution, including thermal expansion. In addition, oxygen loss could occur, which may be relevant for the electrochemical properties. Thus, a representative sample of the series, $Sr_2CoNb_{0.10}Ti_{0.90}O_{6-\delta}$ (the same batch used in the X-ray absorption, XAS, experiments) was studied by NPD at different temperatures from room temperature (RT) to 1173 K. To avoid the effect of high vacuum used in the furnace, the powder sample was wrapped with a platinum foil and introduced into a sealed quartz ampoule filled with air. Figure 2 shows the graphic result of the fitting of the NPD pattern recorded at RT and 1173 K to a cubic simple perovskite structural model. This structure is kept within the whole temperature range, the only varying parameters being the unit cell size and the oxygen content; the thermal evolution of both parameters is depicted in Figure 3.

At RT, anion deficiency is detected since the oxygen content is 5.75, corresponding to $\delta\!=\!0.25$ and to 40% of Co^{4+}, which

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Figure 2. Experimental (red circles) and calculated (black continuous line) NPD patterns (and their difference, blue line at the bottom) for $Sr_2CONb_{0.10}Ti_{0.90}O_{6-\delta}$ at RT (a) and 1173 K (b). The vertical bars indicate the Bragg peaks of the perovskite oxide (first row) and Pt foil (second row).



Figure 3. Thermal evolution of the oxygen content per f.u. and unit cell volume for $Sr_2CoNb_{0.10}Ti_{0.90}O_{6-\delta}$ obtained from NPD.

nicely agrees with the results obtained by redox titration (Figure 1) and XAS (see below). Oxygen release starts around 450 K and continues up to 1173 K. On cooling, oxygen is partially recovered, but only at quite low temperature. In fact, the material remains highly deficient almost down to RT; this may be owed to kinetic reasons as along the thermodiffraction experiment the sample is, undoubtedly, far from equilibrium. In any case, the oxygen loss influences the electrical and electrochemical properties, as observed in other 3d-metal containing oxides, in the same way it induces changes of the oxidation state of metal ions.^[12]

On the other hand, the linear thermal expansion coefficient (TEC) for Sr₂CoNb_{0.10}Ti_{0.90}O_{6- δ} in the 600 to 1100 K temperature range is $\alpha_L = 21.4(3) \times 10^{-6} \text{ K}^{-1}$. This quite high value, compared to that of the electrolyte Ce_{0.90}Gd_{0.10}O_{2- δ} (CGO, $\alpha_L = 9.5(3) \times$

 10^{-6} K⁻¹),^[13] may be associated to the oxygen loss. To confirm this hypothesis we performed two kinds of experiments:

- XRD patterns of the x=0.9 oxide were collected during two heating/cooling cycles in a continuously evacuated chamber (this avoids reoxidation and consequently the second heating cycle was performed on a reduced sample);
- ii) the TEC for the Sr₂CoNb_{0.9}Ti_{0.1}O_{6- δ} member of the series, which presents cobalt in low-oxidation state and experiences much lower oxygen loss, was determined.

The TEC determined for Sr₂CoNb_{0.10}Ti_{0.90}O_{6- δ} in the first and second heating steps are similar and very close to that determined by NPD (see Figure SI 14); even more, the value obtained after reduction (2nd cycle) is slightly higher than that of the pristine material. This suggests that the large cell expansion of these oxides is not related to oxygen release. This is confirmed by the behavior of Sr₂CoNb_{0.9}Ti_{0.1}O_{6- δ} (Figure SI 15), for which the oxygen loss is negligible but its TEC is even higher than that of the *x*=0.9 oxide (the corresponding values of the volume expansion coefficients are $\alpha_{V=}64.3(1) \ 10^{-6} \ K^{-1}$ for the latter and $\alpha_{V=}67.8(1) \ 10^{-6} \ K^{-1}$ for the former. It is reported in the literature that high values of TEC are intrinsic to cobaltites as it is owed to a spin transition of Co³⁺;^[4b,14] thus, the higher the content of trivalent cobalt the higher the TEC. Our results fully agree with this hypothesis.

Cobalt oxidation state

As discussed in previous sections, for $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ oxides the concentration of oxygen vacancies continuously increases with x in the range $0 \le \delta \le 0.30$ (Figure 1). But the evolution of the cobalt oxidation states is slightly different: for low Ti contents ($0 \le x \le 0.20$), the decreasing of positive charge owing to replacement of Nb⁵⁺ by Ti⁴⁺ is mainly compensated by oxidation of Co³⁺ to Co⁴⁺ and therefore very few oxygen vacancies are created. In the compositional range 0.30 < x < 0.50, the cobalt oxidation state remains constant at approximately 15% of tetravalent cobalt whereas the concentration of oxygen vacancies noticeably increases (0.05 $\leq \delta \leq$ 0.17). From x = 0.6– 0.90, oxidation of cobalt dominates again as charge compensating mechanism, although anion substoichiometry keeps increasing (0.18 $\leq \delta \leq$ 0.25). At x=0.90, the amount of Co⁴⁺ reaches a maximum of 40% and the same value is observed for the end member of the series x = 1.00, which shows the highest amount of oxygen vacancies ($\delta \approx 0.30$).

Large amounts of oxygen vacancies and cobalt in average (mixed) high-oxidation state (Co^{3+} and Co^{4+}) may result in high ionic and electronic conductivities, both desirable properties in a SOFC cathode material. Notably, the title perovskites lose oxygen upon heating in air. This is more pronounced for those members of the series with cobalt in higher nominal oxidation state, that is, with high degree of aliovalent substitution (see Figure 3 for the x=0.9 member). This could be a drawback for real applications as decreasing of p-charge carriers and mechanical stress could be induced by long-term exposure under operational conditions.

A sample of composition $Sr_2CoNb_{0.10}Ti_{0.90}O_{6-\delta}$, with a high degree of aliovalent substitution, was studied by extended X-ray absorption fine structure (EXAFS). Figure 4a shows the Co K-edge spectra of this material together with the corresponding references for metallic Co and some relevant oxides.



Figure 4. XAS measurements of Sr₂CoNb_{0.1}Ti_{0.9}O₆₋₆: (a) XANES spectra of the pristine sample with corresponding references of Co and selected Co oxides and (b) module of the Fourier transform of the EXAFS spectrum of Sr₂CoNb_{0.1}Ti_{0.9}O₆₋₆ with the corresponding fit of the (Co–O) first coordination shell.

A clear shift in the edge position and differences in the edge shape are observed even by eye inspection. The variations in the electronic structure of Co are tightly related to the local environment and the X-ray absorption near to edge spectrum (XANES) shape is highly sensitive to subtle differences in the scattering atom environment, both structural and electronic.

According to the Kunzl's rule, the edge shift from the metallic state reference (with oxidation state nominally zero) is roughly proportional to the oxidation state in transition metal oxides.^[15] To give a reliable and quantitative estimation of the oxidation state of cobalt in the sample, for a precise edge position determination, the XANES spectra was fitted to a Boltzman sigmoidal function, as successfully applied in previous works:^[16]

$$y = \frac{A_1 - A_2}{1 + \exp((E - E_0)/E_d)}$$
(1)

where *y* is the normalized absorbance, E_0 is the edge position, E_d is the curve slope at the edge, and A_1 and A_2 are the extreme values of the sigmoidal function (respectively 1 and 0 in the usual XAS normalized spectrum). Through this calculation, we obtained an accurate value for the cobalt formal oxidation state of +3.4 for this highly Ti-substituted material (i.e., x = 0.90). This value can be interpreted, considering a bimodal population of Co^{III} and Co^{IV} cations, with 40% of tetravalent cobalt, which is in good agreement with the results obtained by chemical titration and TGA (Figure 1) as well as by NPD (Figure 3).



Regarding the shape of the spectra, we noticed a high intensity pre-peak feature, which in the K-edge of 3d metals is related to 1s-3d electric quadrupole transitions.^[17] This transition is dipole forbidden and in principle weak for O_h symmetries in the 3d-transition elements (see, for instance, the cobalt oxides references here shown: metal coordination in CoO is O_h and in Co_3O_4 are both T_d and O_h). The pre-peak becomes more intense for T_h symmetry as result of hybridization of the d-p orbital. Thus, in principle, the observed increase of the intensity can be assigned to a distortion of the local environment of Co, at least to a partial population of low symmetry sites in the structure. Another interesting feature is the double peak in the white line of the spectra (cusp of the edge or also known as main peak). This double peak is a very uncommon feature in oxides and is usually observed for fivefold coordination.^[18] These evidences strongly suggest a partial occupancy of Co in fivefold-coordinated sites (most probably as square pyramids).

To analyze the local structure of cobalt, the average structural model obtained by NPD was used as starting point. Thus, we considered an O_h-coordinated cation as a first approximation to model our experimental data. The fitting of the EXAFS spectrum in the real space is shown in Figure 4b. Owing to the complexity of the structure and considering we are only interested in the information from the first atomic shell (formed by oxygen anions) we have restricted our study to this range. Our calculations give average oxygen coordination in the first shell of 5.1(2) (86% of the fully occupied shell), suggesting a clearly anionic-deficient environment. This average coordination is compatible also with a partial population of cobalt in square pyramidal symmetry, in accordance with the double peak observed at the most intense maximum in the XANES spectrum and with our ab initio calculations. This is a relevant result because it suggests that the oxygen vacancies are mainly associated to cobalt ions, as corresponds to a metal that presents remarkable flexibility in both oxidation state and coordination number and geometry.^[19] Considering the titration and TGA results, which give a composition of $Sr_2CoNb_{0.10}Ti_{0.90}O_{5.76}$ ($\delta = 0.24$), there are two plausible arrangements to account for such a reduced coordination number of cobalt: the formation of cobalt clusters^[20] associated to oxygen vacancies and the preferred accommodation of cobalt and vacancies in the large domains walls observed by TEM in these materials.^[5]

On the other hand, the second shell at approximately 3.35 Å is formed by eight Sr atoms and is clearly distinguished. This shell is structurally stable and in a first approach is not expected to play an active role in the oxidation/reduction mechanism of these materials, however, recent results revealed an important role of the perovskite A-site ions in the electrical properties of this sort of materials.^[21]

Stability at different oxygen partial pressures and compatibility with electrolyte materials

The use of a given material as SOFC electrode depends on both its stability under operational conditions and on the chemical compatibility with the electrolyte. As the title compounds are prepared in air, their stability under oxidizing atmosphere is evident; it is worth to note that oxides $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ with low Ti content ($0 \le x \le 0.2$) are unstable under reducing conditions ($p_{O_2} \approx 10^{-21}$ atm) (see Figures SI16 and SI17), contrary to what was previously reported.^[22] Although not so evident, members with high level of aliovalent substitution are also unstable upon reduction, as the XAS spectrum shown in Figure SI18 demonstrates for a sample of composition $Sr_2CoNb_{0.10}Ti_{0.90}O_{6-\delta}$.

Chemical compatibility with yttria-stabilized zirconia (YSZ) and CGO, commonly used as electrolytes, was also evaluated. Oxides of the Sr₂CoNb_{1-x}Ti_xO_{6- δ} series present severe compatibility problems with YSZ under oxidizing atmosphere since they react (even under mild conditions: 1173 K/15 hours/air) to yield large amounts of SrZrO₃ (see Figure SI 19a). The extension of this reaction (i.e., the amount of SrZrO₃ produced) increases with *x*. On the contrary, the whole series is chemically compatible with CGO; Figure SI 19b does not show any reaction product after the same experimental conditions above mentioned.

Therefore, conductivity measurements were performed in either air or pure oxygen, and polarization measurements on symmetric cells were conducted in air using CGO as electrolyte.

Electrical and electrochemical characterization DC conductivity

Temperature dependence of conductivity measured by DC four-probe technique (σ_{DC}) for Sr₂CoNb_{1-x}Ti_xO_{6- δ} ($0 \le x \le 1$) in the 1173–350 K range is depicted as an Arrhenius plot in Figure 5. All samples are p-type semiconductors, as demonstrated by the increase of conductivity with temperature and its enhancement in pure oxygen compared to that in air (Figure 6); some deviations from this general behavior will be clarified in the following section.

A small-polaron-hopping mechanism has been proposed to operate in the parent compound $Sr_2CoNbO_{6-\delta}$.^[22a] However, the thermal dependence of conductivity of the whole series is more complex. Conductivity changes for every composition according to different activation energies in different temperature ranges and at high temperature saturation is observed. Two different behaviors were found depending on the compositional range, low or high Ti content.

For low Ti contents and temperatures below 600 K, the conductivity increases with the degree of substitution, (Figure 5 a). However, for temperatures higher than 600 K, deviation from Arrhenius behavior occurs and conductivity displays a nonclear dependence on Ti content. The finding is similar for the high Ti-containing members of the series ($x \ge 0.6$) at any temperature in the investigated range, (Figure 5 b). In these cases a maximum of conductivity is observed between 650 and 750 K. These findings are most likely owed to the complex defect chemistry and microstructure of these materials,^[5] which strongly affect their charge-transport mechanism.^[22a]

As it was shown in Figure 1, in the low Ti-content range, the main charge compensating mechanism of the aliovalent substitution is the oxidation of Co^{3+} to Co^{4+} that can be de-



Figure 5. Arrhenius representation of the total DC conductivity in air for the $Sr_2ONb_{1-x}Ti_xO_{6-\delta}$ ($0 \le x \le 1$) series in air (measurements performed on cooling from 1173 K to RT, see text): (a) $x \le 0.3$ and (b) $x \ge 0.6$.



Figure 6. DC conductivity on cooling under air (open black symbols) or pure oxygen (solid red symbols) for Sr₂CoNb_{0.9}Ti_{0.1}O_{6.0} (circles) and Sr₂CoNb_{0.1}Ti_{0.9}O₆₋₀ (stars).

scribed through [Eq. (2)]. However, some oxygen vacancies are also induced [Eq. (3)], as confirmed by NPD and other techniques (see Figure 3); indeed, the latter mechanism is more important for high values of x. Thus, progressive substitution of Nb⁵⁺ by Ti⁴⁺ induces the increase of p-type charge carriers, which are dominant for these semiconducting materials. Therefore, according to incremented extrinsic holes given by

[Eq. (2)], the conductivity at a given temperature below 600 K increases with x as observed in samples with low Ti contents $(0 \le x \le 0.3)$.

$$x \operatorname{TiO}_{2}(\operatorname{Sr}_{2}\operatorname{CoNbO}_{6-\delta}) \to x \operatorname{Ti}'_{\operatorname{Nb}} + x \operatorname{Co}^{\bullet}_{\operatorname{Co}}$$
 (2)

$$\operatorname{FiO}_{2}(\operatorname{Sr}_{2}\operatorname{CoNbO}_{6-\delta}) \to x \operatorname{Ti}_{\operatorname{Nb}}' + x/2 \operatorname{V}_{O}^{\bullet\bullet}$$
(3)

The sample with x = 0.3 deserves some comments. It follows the general behavior up to 600 K, but above this temperature a deviation from steady conductivity increasing occurs, and conductivities smaller than expected are observed. This reveals the activation of a second process that tends to decrease the number of charge carriers. One possibility is that above that temperature oxygen loss occurs in a significant extent producing n-type charge according to [Eq. (4)] that annihilates p-type carriers [Eq. (5)]:

$$O_{O}^{x} \rightarrow \frac{1}{2}O_{2} + V_{O}^{\bullet\bullet} + 2e'$$

$$\tag{4}$$

$$p + n = null$$
 (5)

Expressed in a localized formalism electrons are trapped by Co^{4+} that is reduced to Co^{3+} :

$$2 Co_{Co}^{\bullet} + O_{O}^{x} \to 2 Co_{Co}^{x} + V_{O}^{\bullet\bullet} + \frac{1}{2} O_{2}$$
(6)

Thus, above 600 K thermal activation of the remaining holes does not compensate the reduction of p-type charge carriers upon oxygen loss and conductivity tends to reach a constant value.

The p-type electronic conduction in the parent material $Sr_2CoNbO_{6-\delta}$ has been proposed to proceed through direct exchange among neighboring B cations (Co and Nb) with incomplete d shells.^[22a] In a cubic disordered perovskite such as the title compounds, two paths for holes hopping are possible; those indicated as P1 and P2 in Figure 7. The distance between the two 3d-cations is directly related to the difficulty of holes exchange and inversely to the probability of a single jump. Obviously, P1 provides a better conduction path than P2, as the distance between adjacent B-ions are a_p and $2^{\frac{1}{2}} a_p$ (a_p refers to the cubic perovskite unit cell), respectively. It is also clear that any structural or electronic effect hindering holes motion will result in a decrease of conductivity. Among the latter ones, any pathway involving Nb or Ti ions will be blocked since Nb⁵⁺ and Ti⁴⁺ can hardly be oxidized accepting a hole, to participate in charge transfer, as observed in other hole-conducting materials.^[23] As stated above, the title materials present a complex microstructure, likely including cobalt clustering, which may affect the transport properties. Therefore, these aspects will condition the mobility of charge carriers, and together with its concentration will determine the conductivity at each temperature.

The thermal evolution of conductivity for samples with high Ti content is depicted in Figure 5 b. Materials with x=0.6 and 0.7 present a behavior somewhat similar to that observed for x=0.3 with a change of conductivity regime at high tempera-



Figure 7. Schematic diagram of the conduction paths (P1 and P2) for small polarons hopping in Sr₂CoNb_{1-x}Ti_xO_{6-b}: small red balls represent oxygen atoms, blue spheres correspond to Co, Nb and Ti randomly distributes throughout B-sites and large green one represent Sr in A-sites.

ture and a clear tendency to reach saturation. However, for x=0.8, 0.9, and 1.0, a maximum of conductivity arises at the temperature for which oxygen release is significant (between 600 and 700 K, see Figure 3 for the sample with x=0.9); above the maximum, conductivity clearly declines up to 900 K to start rising at temperatures higher than this (see Figures 5 b and 6). The data presented in Figure 6 suggest that this behavior is again related to the release of oxygen. Thus, DC conductivity of the sample with x=0.9 (as a representative example) measured in pure oxygen reaches saturation but it does not clearly rise at high temperature as it does when treated under air. Besides, at high temperature the conductivity is lower in oxygen than in air. This can be explained as follows.

Above 900 K, oxygen loss still occurs and originates electrons according to [Eq. (4)] in such a way that, once holes have been annihilated, the extra electrons induce n-type conduction. Both concentration and mobility of these n-type charge carriers are thermally activated; as a result, conductivity rises upon heating.

Total annihilation of holes according to [Eq. (6)] implies that all cobalt ions are trivalent and the oxygen content must be lower that the value determined by electroneutrality to allow some extra n-type charge carriers in the material or in a localized approach, therefore some cation (Nb⁵⁺, Ti⁴⁺ or Co³⁺) must be reduced. In Figure 3, we can see that the oxygen content at 1173 K is about 5.48, which is clearly below the 5.55 that corresponds to total annihilation of holes. From the different electrical behaviors of samples with low Ti content (low Co⁴⁺ content) and sample with high Ti content (high Co⁴⁺ content), it seems that oxygen evolution is facilitated by high Co⁴⁺ concentration which is easily reducible. Thus, most likely at high temperature some Co²⁺ is formed rather than Ti³⁺ or Nb⁴⁺ according to [Eq. (7)]:

$$2 \operatorname{Co}_{\operatorname{Co}}^{\mathrm{x}} + \operatorname{O}_{\mathrm{O}}^{\mathrm{x}} \to 2 \operatorname{Co}_{\operatorname{Co}}' + \operatorname{V}_{\mathrm{O}}^{\bullet\bullet} + \frac{1}{2} \operatorname{O}_{2}$$
(7)

Some ionic conductivity might exist in these materials because they present a large amount of oxygen vacancies; however, its contribution to the total conductivity is negligible when compared to the electronic contribution.

The temperature of the maximum conductivity observed for x = 0.8, 0.9, and 1.0 is not likely to depend only on the thermodynamic aspects given by action mass law as, for example, those of Equations (6) and (7) but also on kinetics aspects of oxidation/reduction of metals and oxygen intake or releasing. To stress the influence of this aspect we come back to the data on Figure 3, which in addition to the thermal evolution of oxygen content on heating, shows additional data on cooling. Although data on cooling are limited, they clearly demonstrate that oxygen gain on cooling does not follow a steady variation contrary to what was observed for oxygen loss upon heating. However, the oxygen content at RT after one complete heating/cooling cycle is similar to that of the pristine material. Once the sample is heated up to 1173 K and a noticeable amount of oxygen is lost, the material remains under-stoichiometric down to a temperature as low as 600 K; below this temperature the material is reoxidized to reach an oxygen content close to the original one. This behavior is most likely owed to kinetics aspects and evidences that in these materials oxidation/reduction reactions may be slow and this could have some influence on conductivity measurements.

The effect of p_{O_2} and thermal history on conductivity was studied for two samples with high and low Ti contents, $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ (x=0.1 and 0.9). Figure 8a shows that for the sample with lower Ti content ($Sr_2CoNb_{0.9}Ti_{0.1}O_{6-\delta}$) there are no major differences regardless of whether the measurements were performed under heating or cooling, either in oxygen or in air. In the low temperature range (approximately up to 750 K), conductivities are almost the same in air and oxygen atmospheres. However, at higher temperatures, conductivities are slightly higher under oxygen, as corresponds to a p-type semiconductor.

On the other hand, the conductivity of the oxide $Sr_2CoNb_{0.1}Ti_{0.9}O_{6-\delta}$ presents hysteresis on heating/cooling cycles in air (Figure 8b), confirming the different kinetics of oxidation and reduction processes observed by NPD. Hysteresis diminishes at higher p_{O_2} because oxygen loss/gain plays a crucial role in the redox behavior of these materials. Regarding the dependence of conductivity at a given temperature with p_{O_2} , two regimes are observed: in the low-temperature region, conductivity increases with p_{O_2} , in full agreement with p-type semiconducting behavior displayed by the entire series. However, above the maximum, when holes have been annihilated [Eq. (6)] and n-type carriers [Eq. (7)] dominate, electrical conductivity is higher in air, which is a less oxidant atmosphere than pure oxygen.

Transport properties are the result of at least two factors: the concentration and nature of charge carries and their mobility. In the title oxides, the former are related to the oxygen content given by [Eq. (4)–(7)]; whereas the latter is related with conduction paths. The atmosphere and the thermal history can modify not only the oxygen content but also the microstructure, which has a strong influence on conduction paths.





Figure 8. (a) dc-conductivity on heating and cooling under air or pure oxygen for (a) of $Sr_2CoNb_{0.9}Ti_{0.1}O_{6-\delta}$ and (b) of $Sr_2CoNb_{0.1}Ti_{0.9}O_{6-\delta}$.

Thus, to draw a detailed explanation of the dependence of conductivity with temperature and p_{0_2} in these oxides is a difficult task.

Polarization tests on symmetrical cells

Figure 9 shows the area specific resistances (ASR) values determined from the impedance spectra in the range 823-973 K for composites made with oxides $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ (x=0, 0.1, 0.3, 0.5, 0.7, and 1.0) and CGO as previously described. Broadly speaking, the ASR values are lower for samples with increasing Ti contents. Notably, for these materials, ASR increases after being heated at 973 K, as we detected when measuring upon cooling from this temperature. This is shown in Figure 10, which compares the impedance spectra of Sr₂CoNb_{0.5}Ti_{0.5}O_{6-δ} and Sr₂CoTiO_{6- δ} in air at 923 K; the hysteresis observed in ASR may have an origin similar to that pointed for total conductivity ($\sigma_{\rm DC}$), that is, the different kinetics of oxygen release and uptake (Figure 3s and 8). Although we observe this behavior in the whole temperature range and for all samples, this worsening of the cathode performance is more important for high Ti contents. Nonetheless, the ASR values at intermediate temperature (973 K) range from 0.12 to 0.82 Ω .cm² for x=0 and 1.0, respectively; whereas the activation energies are in the range 1.1 to 1.4 eV, which are comparable to those of similar systems.^[23, 24]

To separate the different contributions of the electrochemical processes of the cell, the impedance spectra were fitted to



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Figure 9. Arrhenius plot of the ASR values obtained from the impedance spectra of the $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}/CGO$ symmetrical cells on heating in air.



Figure 10. Nyquist plot (after subtraction of the apparent electrolyte resistance and instrumental inductance) of the impedance spectra of symmetrical cells made using composites $Sr_2CoNb_xTi_{1-x}O_{6-\delta}/CGO$ (70:30 % wt, x=0.5 or 1.0), measured at 923 K in air. Solid red symbols correspond to the first measurement (on heating from RT) and open blue symbols to that on cooling (after heated).

equivalent circuits. The simplest model giving good fits consists of: an inductance (L) owing to the wires of the electrochemical cell and equipment, an ohmic resistance (R_s) mainly associated with the total ion transport in the electrolyte, and a number of parallel RQ elements connected in series, associated to processes at the electrolyte-electrode interface and at the electrode surface (R = resistance, Q = constant phase element with impedance $Q^{-1}(i\omega)^{-n}$, where $0 \le n \le 1$ gives how the real capacitor defers from an ideal behavior n = 1).^[25]

The Bode plot (dependence of the phase angle with frequency) provides useful information to determine the number of processes in complex systems such as composites or porous electrodes.^[26] In Figure 11, the Bode plot corresponding to the composite electrode containing $Sr_2CoTiO_{6-\delta}$ revealed the presence of three processes at low, intermediate, and high frequencies (denoted as LF, IF, and HF, respectively); a similar behavior is observed for all samples.

Although the LF and IF processes tend to collapse upon heating, they can still be separated at the highest temperature studied (973 K).





Figure 11. Bode plot of the impedance spectra of symmetrical cells made using composites $Sr_2CoTiO_{6-\delta}/CGO$ (70:30 %wt), measured in air at different temperatures.

Therefore, the equivalent circuit used to fit the impedance spectra can be denoted as $LR_s(RQ)_{HF}(RQ)_{IF}(RQ)_{LF}$ and is shown in the inset of Figure 12a. This figure shows the fits of the impedance spectra of $Sr_2CoTiO_{6-\delta}$ and $Sr_2CoNbO_{6-\delta}$ (the initial and end members of the series) upon heating and cooling at 873 K, to this equivalent circuit. For all the other cases the results are similar. The refined impedance parameters at different temperatures for these compounds upon heating and cooling are given in Tables SI1 to SI4. The (*RQ*) values are related to

the capacitance (*C*) and the relaxation frequency (*f*) (see Table S1), which can be calculated using Equations (8), (9), and (10).

$$C = \frac{(RQ)^{\frac{1}{n}}}{R} \tag{8}$$

$$f = \frac{\omega}{2\pi} \tag{9}$$

$$\omega = (RQ)^{-\frac{1}{n}} \tag{10}$$

The capacitance and relaxation frequencies for the HF process are in the range of 0.001–1000 μ F cm⁻² and 100–0.01 MHz, respectively, which can be associated with oxide-ion transfer through the electrolyte-electrode interface.^[25a, 27] Although as a general rule, the more vacancies there are, the faster oxygen can be absorbed by, and move through the material and the material-electrolyte interface; higher electronic conduction also favors faster oxygen exchange.^[25b] As in the title materials these two features are inversely related with oxygen content (higher degree of vacancies results in lower electronic conductivity), the dependence of the HF process with Ti content and oxygen vacancies concentration is not simple. In the heating cycle, the resistance associated to this process seems to be related to the degree of aliovalent substitution, that is, the value of x, in such a way that the higher the concentration of Ti the lower the resistance. This may be the result of both a higher



Figure 12. Impedance spectra, after subtraction of the apparent electrolyte resistance and instrumental inductance, of symmetrical cells made using composites $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}/CGO$ (70:30%wt). Impedance spectra for $Sr_2CoTiO_{6-\delta}$ in air at 873 K in heating (a) and cooling cycles (b); (c) and (d) Impedance spectra for $Sr_2CoNbO_{6-\delta}$ under the same conditions in heating and cooling cycles, respectively. The spectra are fitted to the equivalent circuit represented in the inset of (a). The solid lines are the fitting results whereas small circles represent experimental data.

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ionic conductivity owing to oxygen vacancies, created upon substitution of Nb⁵⁺ by Ti⁴⁺, and a higher electronic conduction.^[21] However, in the cooling cycle, once the samples lose some oxygen and the concentration of anionic vacancies has increased, the resistance and activation energies of this HF process slightly increase suggesting that the effect of a lower electronic conductivity is dominant (see Tables SI 1 to SI 4) since conductivity decreases upon reduction (Figure 8).

At intermediate frequencies (IF process) the capacitance and relaxation frequency are between $10^{-2}-10^{-5}$ F cm⁻² and $10^{1}-10^{2}$ Hz, respectively, which are both in the typical range for an electron charge transfer process.^[22,27] This process seems to be favored by a high electronic conductivity associated to samples with high degree of aliovalent substitution; thus, the resistance corresponding this process is lower for highly substituted samples.

Finally, at low frequencies, two main processes are usually observed: oxygen absorption/desorption associated with the oxidation/reduction reaction and diffusion. The latter case is characterized by *n* values smaller than 0.5;^[28] in our cases the *n* values are closer to 1, indicating a pseudo-capacitive behavior.

The capacitances of the order of 10^{-1} F cm⁻² independent on temperature are similar to the chemical capacitance that arises as a consequence of a reduction process and formation of bulk oxygen vacancies in (La_{0.6}Sr_{0.4})CoO_{3- δ}^[29] Moreover, the relaxation frequencies in the range 10^{-1} –10 Hz support this assignment. Therefore, these materials experience some degree of oxidation/reduction upon heating/cooling, respectively, as observed by NPD, much easier (lower resistance) for samples with higher Ti contents. The capacitance is similar for all samples because the microstructural and textural properties of the electrodes are the same as they were prepared in the same manner and consequently the fraction of the cathode involved in the reaction is similar in all cases.

The contribution of these three processes to the ASR is somewhat different depending on the degree of aliovalent substitution and temperature. Thus, for x = 0 (Sr₂CoNbO_{6- δ}), the resistances associated to the three processes are similar at all temperatures (Tables SI3 and SI4) as none of them clearly dominates the resistive behavior of the electrode. In other words, for x = 0 the oxidation/reduction reaction, the electronic-charge transfer and the oxide-ion migration across the electrode-electrolyte interface are similarly impeded. The ASR values determined for composite electrodes made of $Sr_2CoNbO_{6-\delta}/CGO$ (70:30 % wt) are highly limiting its use in real SOFCs. On the contrary, cathodes containing $Sr_2CoTiO_{6-\delta}$ display quite low ASR values at intermediate temperatures (Tables SI1 and SI2), comparable to those of the state-of-the-art materials. At 973 K, an ASR value of $0.12 \,\Omega \,\text{cm}^2$ is similar to those of the best compounds reported so far: SrNdCo_{0.75}Fe_{0.25}O_{4.08} and SrNdCo_{0.75}Mn_{0.25}O_{4.08} (ca. 0.18 $\Omega\,cm^2$ in both cases at 973 K),^[30] and similar values at 1073 K for $La_4Ni_{2.6}Co_{0.4}O_{10+\delta}{}^{[31]}$ and $NdSrCoO_{4+\delta}{}^{[32]}$ The better performance of the x=1 member of the series is mainly owing to higher conductivity, which favors both electronic-charge transfer and oxidation/reduction processes.

A cross-sectional view of an electrode of composition $Sr_2CoNb_{0.7}Ti_{0.3}O_{6-\delta}/CGO$ (70:30 wt%) after operation is presented in Figure 13. A good adherence between the electrode composite and the electrolyte surface is observed. However, the electrode microstructure needs further optimization, since it consists of large particles (of micron size) of the active material covered by submicron particles of the electrolyte.



Figure 13. SEM image of a cathode $Sr_2CoNb_{0.7}Ti_{0.3}O_{6-\delta}/CGO~(70:30\,\%wt)$ on CGO electrolyte after operation.

Conclusions

The perovskite series $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ exhibits a cubic perovskite structure (space group Pm3m) in the whole compositional range $0 \le x \le 1$. The effect of temperature on the structure and composition is studied in the room temperature-1173 K range, which includes the solar oxide fuel cell (SOFC) operational temperature. A sample case, one with high titanium content (x = 0.9) studied by neutron powder diffraction (NPD) reveals a significant and reversible oxygen loss above 600 K. Thus, in the pristine sample $Sr_2CoNb_{0.10}Ti_{0.90}O_{6-\delta}\text{,}$ the oxygen content is 5.75 ($\delta = 0.25$ and 40% of Co⁴⁺), which nicely agrees with the results obtained by redox titration and X-ray absorption (XAS). The sample loses oxygen continuously upon heating and at 1173 K reaches an oxygen content of 5.48. The structure is kept up to 1173 K and after cooling, the lost oxygen is again gained. However, a different kinetics for both reduction and oxidation processes is observed.

Defect chemistry of this series involves a two-charge compensating mechanism as the Ti content increases. Increasing Ti content from x=0 to 1 produces both oxidation of Co³⁺ to Co⁴⁺ and oxygen vacancies, although each mechanism predominates in different compositional ranges. The complex defect chemistry of the title compounds together with the compositional changes upon heating/cooling cycles and atmospheres produce a very complicated behavior of electrical conductivity that is explained satisfactorily.

Area-specific resistances (ASR) values were determined for composites of Sr₂CoNb_{1-x}Ti_xO_{6- ∂}/CGO (70:30 % wt) in air assessing its potential use as cathode components. Broadly speaking, ASR values are lower for samples with high Ti content owing to an increased amount of oxygen vacancies. For example, the



ASR value at 973 K in air determined for composite electrodes made of Sr₂CoNbO₆₋₀/CGO (70:30 %wt) is 0.82 Ω cm²; such a high value limits its use in real SOFCs. On the contrary, cathodes containing Sr₂CoTiO₆₋₀ display (under the same conditions) lower ASR values (0.12 Ω cm²), which are comparable to those of the best cathodes reported so far. Thus, oxides of the Sr₂CoNb_{1-x}Ti_xO₆₋₀ series with high Ti contens (x > 0.5) seem to be promising cathode materials for SOFC.

Experimental Section

The synthesis of these compounds was done according to previous reports by Azcondo et al. $\ensuremath{^{[5]}}$

XRD patterns were recorded on a Bruker D8 high-resolution X-ray powder diffractometer, equipped with LynxEye fast detector, using monochromatic CuK_{a1} ($\lambda = 1.5406$ Å) radiation obtained with a germanium primary monochromator. Data were collected in the range $2\theta = 10-150^{\circ}$ with a step width 0.015° (2θ) over a total exposure time period of 16 h. The powder diffraction data were analyzed by the Rietveld method, using the FullProf program.^[33]

NPD experiments were performed at D1B instrument at Institute Laue Langevin (ILL, Grenoble, France), using a monochromatic beam of 1.2902 Å. The contribution of the instrument to the peaks width was determined by the instrument resolution function built from the experiment on Na₂Ca₃Al₂F₁₄ standard sample whereas the wavelength was determined using a Si standard.

XAS measurements were performed at the Co K-edge (7709 eV) at the BM25A-Spline beamline in the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The monochromator is a pseudo channel-cut type with a double Si(111) crystal type refrigerated at 200 K by a homemade ethanol cooling system. The measurements were performed in fluorescence yield mode for the samples and at transmission mode for the references. Three scans were acquired for each sample to ensure reproducibility and to average the spectra and increase the signal-to-noise ratio. Both metallic Co and Co reference oxides references were measured under the same experimental conditions. Fluorescence signal was acquired with a 13-elements fluorescence detector SGX Sensortech. The XAS data were reduced applying standard procedures using the Demeter package^[34] and fits on EXAFS region for k3 weighted signals were performed in r space using theoretical path functions calculated with FEFF8 code.[35]

SEM experiments were performed on sintered pellets using a FEI XL30 apparatus equipped with an EDAX analyzer for EDS. Metal composition was determined by analyzing several microcrystals of every sample (typically, ca. 20 microcrystals were analyzed). In addition, these techniques were used to determine the morphology and microstructure of the electrodes after electrochemical characterization.

The cobalt oxidation state (Co³⁺/Co⁴⁺) and oxygen content (assuming charge neutrality) of the samples were determined by TGA using a D200 Cahn Balance under a reducing atmosphere and high temperature. For this purpose, typically ca. 70 mg of sample were weighed to a precision of ± 0.0005 mg at a total reduced pressure of 400 mbar containing 60:40 He/H₂ gas mixture to reach oxygen partial pressure (p_{O_2}) of 10⁻²⁸ atm. Afterwards, the sample was heated up to 1173 K (5 Kmin⁻¹). Moreover, independent determinations were performed by titration using potassium dichromate, as described in Ref. [7]

The DC conductivity (σ_{DC}) of the Sr₂CoNb_{1-x}Ti_xO_{6- δ} (0 \leq x \leq 1) compounds was measured by the four-probe technique on prismatic bars (\approx 4.5×4×3mm³). Powders with a small amount of an organic binder (poly(ethylene carbonate)) were pressed uniaxially at ca. 200 MPa. The green bodies were heated at 1173 K for 3 h to decompose the organic matter, at 1573 K for 12 h, and then cooled down to RT; the heating and cooling rates were 2 Kmin⁻¹. Platinum wires and paste were used to ensure electrical contact. Measurements were performed in air in the temperature interval from 1173 to 350 K every 25 K; a value was recorded after stabilization of conductivity within a \pm 0.1% fluctuation in one hour. To determine the effect of the thermal history of the samples on conductivity, samples of composition $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ (x=0.1 and 0.9) were measured under air and pure oxygen atmospheres upon heating (from the lowest to the maximum temperature in the aforementioned range) and then upon cooling. The chemical compatibility of the electrode materials $Sr_2CoNb_{1-x}Ti_xO_{6-\delta}$ (0 $\leq x \leq 1$) with powdered cerium gadolinium oxide, $Ce_{0.90}Gd_{0.10}O_{2-\delta'}$ (CGO) (Fuel Cells Materials Corp.) was evaluated by mixing both in a 1:1 by weight ratio. Mixtures were pelletized and heated at 1173 K for 15 h under air to simulate the electrode preparation conditions. Phase analysis was then performed by XRD.

ASRs associated to the total electrochemical processes at the electrodes were determined from impedance diagrams at different temperatures in air on symmetrical two-electrode configuration cells as described previously.^[6] Electrolyte pellets of commercial CGO were prepared by pressing the powder at 250 MPa and sintering in air at 1673 K for 12 h (heating/cooling rate of 2.5 Kmin^{-1}) to obtain discs of relative densities higher than 97% of 10 mm diameter and 1 mm thickness. Slurries were prepared by mixing $Sr_2CoNb_xTi_{1-x}O_{6-\delta}$ (0 $\leq x \leq$ 1) and commercial CGO composite (70:30 wt%) with Decoflux (WB41, Zschimmer and Schwarz) as a binder, and deposited onto both sides of the electrolyte pellet. Finally, the symmetric cells were fired at 1173 K for 3 h in air (heating/cooling rate of 2.5 Kmin⁻¹). Silver paste and silver mesh were used as current collectors. The measurements were performed in air upon heating and cooling cycles between 773 and 973 K using a frequency response analyzer and a dielectric interface (Solartron 1255 and 1296, respectively) in the frequency range 0.1 Hz to 1 MHz with an excitation voltage of 50 mV. The ASR values were determined from impedance spectra by fitting to equivalent circuits model and corrected considering the electrode surface area and the symmetrical configuration^[25] using ZView software.^[36]

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Conflict of interest

The authors declare no conflict of interest.

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