Effects of Nb and Sn co-doping on the structure and properties of SrCoO$_{3-\delta}$

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**ABSTRACT**

The structure and oxygen permeability of SrCo$_{0.9-x}$Nb$_{0.1}$Sn$_{0.3}$O$_{3-\delta}$ ($x = 0, 0.03$, and $0.05$) perovskite membranes were systematically investigated by co-doping the B-site of SrCoO$_{3-\delta}$ oxide with Nb and Sn. Combined X-ray and neutron diffraction experiments showed that all materials crystallized in the tetragonal $P4/mmm$ space group and that the crystal structures approached the ideal cubic perovskite structure with increasing Sn concentration. In addition, X-ray photoelectron spectra confirmed that Sn-doping increases the (Co, Nb, Sn)-O bond strengths. The impact of Sn-doping on the oxygen transport of dense SrCo$_{0.9-x}$Nb$_{0.1}$Sn$_{0.3}$ membranes was also investigated, under air/He gradient, as a function of both temperature and membrane thickness. The results showed that the oxygen transport of SrCo$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$ is governed by oxygen ion diffusion, while the oxygen surface exchange reaction is the limiting process for the Sn-doped membranes, SrCo$_{0.87}$Nb$_{0.1}$Sn$_{0.05}$O$_{3-\delta}$ and SrCo$_{0.85}$Nb$_{0.1}$Sn$_{0.05}$O$_{3-\delta}$.

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1. Introduction

Mixed ion-electron conducting perovskite oxides are receiving increasing attention for their application as electrodes for solid oxide fuel cells (SOFCs) and oxygen separation membranes [1–3]. The transport properties (i.e., ion diffusivity and surface exchange kinetics) of perovskite oxides (ABO$_3$) can be significantly influenced by A- and B-site cation substitutions, making them attractive for a variety of functional applications [4–10]. Among the numerous perovskite oxides that have been studied, Ba$_{0.5}$Sr$_{0.5}$Co$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$ exhibits low area specific resistance and high oxygen permeation flux due to high oxygen ion conductivity and oxygen surface exchange kinetics [11–14]. However, it undergoes a phase transition from cubic perovskite to oxygen vacancy-ordered non-perovskite at operational temperatures and pressures, effectively limiting its usefulness for many applications [15–19]. In addition, Ba-containing perovskite oxides are susceptible to acidic CO$_2$ in ambient air [20]. Hence, Sr$_{0.9}$Fe$_{0.1}$, which has a lower basicity than Ba$_{2+}$, is the preferred A-site cation and past research has often focused on B-site cation substitution and/or doping strategies for SrCoO$_{3-\delta}$-based oxides. B-site cations play a crucial role for both phase stability and oxygen transport properties [21]. It was found that 10 mol% Nb-doped SrCoO$_{3-\delta}$ (i.e., SrCo$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$) shows promising oxygen permeability and low area specific resistance comparable to that of the Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ stabilizing oxygen vacancy-disordered perovskite structure at operational conditions [22–30]. Similarly, Sn has been recognized as an effective B-site dopant for stabilizing oxygen vacancy-disordered structures. Furthermore, it improves the oxygen/proton transport properties for perovskite-type oxides [31,32]. Despite the low solubility (less than 5 mol%) of Sn in SrCoO$_{3-\delta}$-based perovskite oxides, the oxygen vacancy-disordered material, SrCo$_{0.95}$Sn$_{0.05}$O$_{3-\delta}$, also exhibits excellent cathode performance for SOFCs [33]. In recent studies, Nb/Fe (SrCo$_{0.9-\delta}$Nb$_{0.1}$Fe$_{0.9}$O$_{3-\delta}$) [4,34], Fe/Sn (SrCo$_{0.9}$Fe$_{0.3}$Sn$_{0.4}$O$_{3-\delta}$) [35–37], and Nb/Ta (SrCo$_{0.8}$Nb$_{0.2}$Ta$_{0.4}$O$_{3-\delta}$) [38] co-doping strategies for the B-site of SrCoO$_{3-\delta}$ have been reported to improve both phase stability and oxygen transport properties. However, there is little information on the change in structure and oxygen transport properties of Nb and Sn co-doped SrCoO$_{3-\delta}$ membranes.

In this study, the crystal- and surface structures of SrCo$_{0.9-x}$Nb$_{0.1}$Sn$_{0.3}$O$_{3-\delta}$ ($x = 0, 0.03$, and $0.05$) were investigated using X-ray and neutron powder diffraction, as well as X-ray photoelectron spectroscopy (XPS). Furthermore, the effect of Sn-doping on the oxygen transport properties was characterized using oxygen permeation measurements, as a function of temperature and membrane thickness. To the best of our knowledge, this is the first study on the effect of
small amounts of Sn-doping on $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$-based oxygen transport membranes.

2. Materials and methods

2.1. Synthesis of $\text{SrCo}_{0.9-x}\text{Nb}_{0.1}\text{Sn}_{x}\text{O}_{3-\delta}$ ($x = 0, 0.03,$ and $0.05$) membranes

$\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (SCN), $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{Sn}_{0.03}\text{O}_{3-\delta}$ (SCNT3), and $\text{SrCo}_{0.85}\text{Nb}_{0.15}\text{Sn}_{0.05}\text{O}_{3-\delta}$ (SCNT5) powders were synthesized by a solid state reaction [30], where stoichiometric amounts of the precursors, $\text{SrCO}_3$ (Sigma Aldrich, ≥ 99.9 %), $\text{Co}_3\text{O}_4$ (Alfa Aesar, ≥ 99%), $\text{Nb}_2\text{O}_5$ (Sigma Aldrich, ≥ 99.9 %), and $\text{SnO}_2$ (Sigma Aldrich, ≥ 99.9%), were processed by ball milling in ethanol for 48 h. Then, the powders were calcined at 1100°C for 5 h in air, followed by uniaxial pressing at 100 MPa and isostatic pressing at 400 MPa to form green disks. The discs were sintered at 1200°C for 5 h in air. The relative density of the sintered pellets, measured by the Archimedes method, was in excess of 95%. The phase composition of the calcined powders was studied by X-ray diffraction (XRD, Bruker D8) with Cu Ka radiation at ambient temperature. Transmission electron microscopy (TEM, FEI Tecnai G2 F30) was used to investigate the crystallinity of the prepared powder. Scanning electron microscopy (SEM, Hitachi S-4700) was used to analyze the microstructure of the sintered ceramics.

2.2. Crystal structure and oxygen content determination

In order to determine the crystal structure and oxygen content of SCNT3 and SCNT5, neutron powder diffraction measurements were carried out using the High-Resolution Powder Diffractometer (HRPD) of HANARO (Korea Atomic Energy Research Institute, Republic of Korea). Approximately 5 g of the sample was loaded in a vanadium container. The sample was exposed to the incident neutron beam with a wavelength of 1.834 Å and the diffraction pattern was measured over the range of $10^\circ \leq 2\theta \leq 150^\circ$ with a step size of 0.05° at 25°C. The neutron diffraction data were analyzed by the Rietveld method, using FullProf software [39] and employing a pseudo-Voigt peak shape function with a manual background correction. The occupancy of the oxygen sites was refined to evaluate the oxygen stoichiometry, while the occupancy of the cation sites was fixed at the same atomic displacement parameters. In the final refinement run, the following parameters were refined to convergence: zero shift, width/shape/asymmetry of peak, scale factor, and crystal structure parameters (lattice parameters, atomic positions, anisotropic atomic displacement parameters, and occupancy factors for oxygen).

2.3. Investigation of the chemical nature and oxygen stoichiometry

The chemical nature of SCN, SCNT3, and SCNT5 was examined by XPS (Thermo VG Scientific K-alpha) and the obtained spectra were analyzed using the Fityk program [40], where the spectral background was removed using the Shirley function. All peaks were adjusted to a binding energy of 285 eV for the aliphatic carbon. The absolute oxygen stoichiometry value at 25°C was also characterized by redox titration. For the titration, approximately 0.1 g of the powder was dissolved in 1 M HCl (Sigma Aldrich, 37%) and 2 M KI (Sigma Aldrich, ≥ 99%) was added. This solution was titrated against a 0.01 M Na$_2$S$_2$O$_3$ solution (Sigma Aldrich, ≥ 99.99%) using starch indicator under flowing nitrogen gas [41]. The titration was repeated three times and averaged to estimate the oxygen stoichiometries of SCN, SCNT3, and SCNT5. The changes in the oxygen stoichiometries of SCN, SCNT3, and SCNT5 were determined by thermogravimetry (SDT 2960, TA Instruments) in the temperature range from 25°C to 950°C. A heating rate of 2°C·min$^{-1}$ was employed in dry air with a flow rate of 100 mL·min$^{-1}$.

2.4. Oxygen permeation measurements

Oxygen permeation experiments were performed in the temperature range of 700°C to 850°C. The sintered SCN, SCNT3, and SCNT3 membranes were polished to thicknesses of 1 mm, 1.2 mm, and 1.4 mm using SiC sandpaper (100–1200 grit). The membranes were sealed to the reactor, using glass sealant, by holding the temperature at 870°C for 1 h. After sealing, oxygen permeation measurements were carried out under an oxygen partial pressure gradient, supplying synthetic air (99.9%) and He (99.999%) with flow rates of 300 mL·min$^{-1}$ to the feed and sweep sides, respectively. The oxygen concentration in the effluent He gas was measured using a gas chromatograph (ACME 6000, YoungLin). The oxygen permeation flux was corrected for gas leakage using the flowing equation, as described in our previous studies [42,43]. $J_O = \left(\frac{x_{O_2} - x_{H_2}}{75}\right) \times F$, where $J_O$ is the oxygen flux, $x$ the oxygen or nitrogen molar fraction, $F$ the volumetric flow rate, and $a$ the membrane area. The leakage was typically less than 0.5 % for these experiments.

3. Results and discussion

Figure 1(a) shows the XRD patterns of the synthesized SCN, SCNT3, and SCNT5 powders, which confirmed the formation of perovskite-type oxide phases. The obtained XRD patterns are typical for perovskite-type oxide phases reported in the literature [23–
No evidence of secondary phases was observed, thus indicating that both Nb and Sn are incorporated into the perovskite lattice. Furthermore, it was observed that the diffraction peaks shifted to lower angles, as the Sn concentration increased. Next, the crystal structures and oxygen content of SCN, SCNT3 and SCNT5 were analyzed by neutron powder diffraction. Figure 1(b–c) shows the high-resolution TEM images of SCNT3 and SCNT5, which confirm the polycrystalline nature of the prepared samples.

Many literature sources report a conventional cubic perovskite structure (space group $Pm\bar{3}m$ and a $\sim$ 3.8 Å) for SCN [23–25,27,28], however, the crystal structure obtained from the neutron diffraction study of SCN exhibited a tetragonal perovskite structure (space group $P4/mmm$, a $\sim$ 3.8 Å and c = 7.6 Å) [30]. The crystal structures of SCNT3 and SCNT5 were investigated further by employing the Rietveld refinement to analyze the neutron diffraction patterns at 25°C. Figure 2 illustrates the observed, calculated, and difference profiles of SCNT3 and SCNT5 from the Rietveld refinement. Both SCNT3 and SCNT5 crystallized in the tetragonal space group $P4/mmm$, which is isostructural to SCN [30]. As shown in Figure 2(b,e), the characteristic (1 0 5) (2 1 3) and (1 1 5) (2 2 1) peaks at $\sim$79° and $\sim$85° confirm the formation of tetragonal perovskite because these peaks are absent in the cubic perovskite. Statistically, Sr ions are located at the 2h-site (0.5,0,0.5,z) and Co, Nb, and Sn ions are distributed at the 1a-site (0,0,0) and the 1b-site (0,0,0.5). Three distinct sites were found for oxygen ions, 2f-site (0.5,0,0), 2g-site (0,0,z), and 2e-site (0.5,0,0.5). The oxygen site occupancies were refined in order to calculate the oxygen stoichiometry of SCNT3 and SCNT5. The refined oxygen occupancy is close to 1 for the 2f-site, while the values for the 2g- and 2e-sites were in the range of 0.77–0.97. This observation indicates that the formation of oxygen vacancies at the 2g- and 2e-sites occurs with large thermal parameters compared to the 2f-site. The corresponding structural parameters, residual indices, and bond distances from the refinements of neutron diffraction patterns are summarized in Tables 1 and 2. The observed increase in the lattice volume correlated with an increase in the Sn concentration (116.3 Å$^3$ for SCN, 117.1 Å$^3$ for SCNT3, and 117.7 Å$^3$ for SCNT5) and the lattice parameter ratio of c/a was close to 2 (2.007 for SCN and 2.004 for both SCNT3 and SCNT5), indicating that SCNT3 and SCNT5 are close to the ideal cubic perovskite structure.

Figure 3 shows the refined crystal structures of SCNT3 and SCNT5. The anisotropic thermal vibrations using ORTEP (Oak Ridge thermal-ellipsoid plot) diagrams with 90% probability level were used to describe the thermal motions of all atoms. It can be clearly seen that the (Co1/Nb1/Sn1)O$_6$ octahedron shares the O1 atoms (2f-site), whereas the (Co2/Nb2/Sn2)O$_6$ octahedron shares the O3 atoms (2e site). Both octahedra share the O2 atoms (2g-site). The elongated (Co2/Nb2/Sn2)O$_6$ octahedron layers alternating with the flattened (Co1/Nb1/Sn1)O$_6$ octahedron layers results in the doubling of the primitive unit cell along the c-direction. It is remarkable that the graphs of the thermal displacements of O1, O2, and O3 exhibit compressed ellipsoids perpendicular to their bonding direction with the B-site cations. This suggests that the shortening and stretching of the O-O distances due to the thermal displacement of the oxygen ions are in agreement with the conduction paths of the oxygen ions [44].

The redox titration measurements at 25°C also confirmed the absolute oxygen stoichiometries of SCNT3 and SCNT5 as SrCo$_{0.87}$Nb$_{0.1}$Sn$_{0.03}$O$_{2.74}$ and SrCo$_{0.85}$...
Figure 2. Neutron diffraction patterns of (a) SCNT3 and (c) SCNT5 powders at 25°C. The observed data are presented as circles, and the solid lines are the result of Rietveld refinements. The difference profile is also shown (lower line) and the tick marks indicate the Bragg positions. Magnified region from 78° to 88° for (b) SCNT3 and (d) SCNT5.

Table 1. Structural parameters and bond distances from Rietveld refinements of neutron powder diffraction data at 25°C for SCNT3.

| Atom          | Site | Occupancy | x   | y   | z     | U(100Å²) | U₁₁  | U₂₂  | U₃₃  |
|---------------|------|-----------|-----|-----|-------|----------|------|------|------|
| Sr1           | 2h   | 1         | 0.5 | 0.5 | 0.255(1) | 2.7(2)   | 2.7(2) | 0.6(1)|
| Co1/Nb1/Sn1   | 1a   | 1         | 0.0 | 0.0 | 0.0   | 3.5(7)   | 3.5(7) | 1.2(2)|
| Co2/Nb2/Sn2   | 1b   | 1         | 0.0 | 0.0 | 0.5   | 1.8(6)   | 1.8(6) | 0.4(1)|
| O1            | 2f   | 1.00(3)   | 0.5 | 0.0 | 0.0   | 0.5(3)   | 6.7(6) | 0.5(1)|
| O2            | 2g   | 0.97(2)   | 0.0 | 0.0 | 0.762(5) | 5.6(5)   | 5.6(5) | 1.3(1)|
| O3            | 2e   | 0.77(2)   | 0.5 | 0.0 | 0.5   | 5.2(4)   | 9.5(9) | 2.0(2)|

SrCoₐNₐ Nb₁₋₉ Snₐ₂O₂₋₉ (SCNT3), space group: P₄/mmm, a = 3.8803 (1) Å, c = 7.7796 (3) Å, R_p = 6.38%, R_wp = 8.28%, R_exp = 4.20%, R_Bragg = 8.15%, \( \chi^2 = 3.89 \). Bond distances: Co1/Nb1/Sn1-O1 (×4) = 1.9402(1) Å, Co1/Nb1/Sn1-O2 (×2) = 1.848(5) Å, Co2/Nb2/Sn2-O2 (×2) = 2.041(5) Å, Co2/Nb2/Sn2-O3 (×4) = 1.9402(1) Å

Table 2. Structural parameters and bond distances from Rietveld refinements of neutron powder diffraction data at 25°C for SCNT5.

| Atom          | Site | Occupancy | x   | y   | z     | U(100Å²) | U₁₁  | U₂₂  | U₃₃  |
|---------------|------|-----------|-----|-----|-------|----------|------|------|------|
| Sr1           | 2h   | 1         | 0.5 | 0.5 | 0.2530(7) | 3.2(2)   | 3.2(2) | 0.6(1)|
| Co1/Nb1/Sn1   | 1a   | 1         | 0.0 | 0.0 | 0.0   | 2.6(7)   | 2.6(7) | 0.6(1)|
| Co2/Nb2/Sn2   | 1b   | 1         | 0.0 | 0.0 | 0.5   | 2.8(6)   | 2.8(6) | 0.6(1)|
| O1            | 2f   | 1.00(2)   | 0.5 | 0.0 | 0.0   | 1.4(4)   | 7.2(7) | 1.0(1)|
| O2            | 2g   | 0.86(2)   | 0.0 | 0.0 | 0.7660(9) | 4.7(7)   | 4.7(7) | 0.6(1)|
| O3            | 2e   | 0.90(2)   | 0.5 | 0.0 | 0.5   | 7.0(6)   | 9.4(9) | 0.5(1)|

SrCo₀.₈₇Nb₀.₁₂Sn₀.₀₁O₂₋₉ (SCNT5), space group: P₄/mmm, a = 3.8875 (1) Å, c = 7.7966 (3) Å, R_p = 5.79%, R_wp = 7.55%, R_exp = 4.61%, R_Bragg = 6.54%, \( \chi^2 = 2.68 \). Bond distances: Co1/Nb1/Sn1-O1 (×4) = 1.9438(1) Å, Co1/Nb1/Sn1-O2 (×2) = 1.820(5) Å, Co2/Nb2/Sn2-O2 (×2) = 2.069(5) Å, Co2/Nb2/Sn2-O3 (×4) = 1.9438(1) Å
The oxygen stoichiometry was found to increase with increasing Sn concentration due to the higher oxidation state of Sn relative to Co. The change in the oxygen stoichiometry was determined by thermogravimetric analysis as a function of temperature in air, as shown in Figure 4. The graph shows that the oxygen stoichiometry decreases from approximately 250°C, reaching values of 2.59, 2.66, and 2.70 at 900°C for SCN, SCNT3, and SCNT5, respectively. This decrease is attributed to the release of lattice oxygen at high temperatures.

The surface structure and chemical nature of SCN, SCNT3, and SCNT5 were examined using XPS. Detailed analysis was conducted by the curve fitting of Co 2p\textsubscript{3/2} and O 1 s peaks, as shown in Figure 5. The Co 2p\textsubscript{3/2} peak was deconvoluted into three components. The first peak, with a binding energy of 778.5–779.1 eV, is attributed to Co\textsuperscript{3+}, while the peaks with binding energies of 779.8–780.6 eV and 781.9–782.5 eV are attributed to Co\textsuperscript{2+} and Co\textsuperscript{4+}, respectively. These values are in good agreement with the literature [45]. The peak positions of all deconvoluted Co 2p\textsubscript{3/2} peaks were shifted to higher energy values for SCNT3 and SCNT5 in comparison with SCN, suggesting that the bond strength of Co-O increases upon Sn substitution. Deconvolution of the O 1 s peak resulted in two components. The first peak, with a binding energy of 529.7–530.1 eV, is assigned to the lattice oxygen, whereas the second peak, with a binding energy of 530.6–532 eV, is attributed to the surface oxygen. Both peak positions, for the lattice- and surface oxygen, shifted to higher values, thus indicating that the average (Co, Nb, Sn)-O bond strength increases with increasing Sn concentration. The impact of the change in surface structure will be discussed in the next section.

SEM micrographs of the sintered SCN, SCNT3, and SCNT5 membranes, shown in Figure 6, exhibit dense microstructure with well-grown grains. The average grain sizes are comparable for all samples and are in the range of 8–13 μm. All sintered membranes had a relative density higher than 95%, which enables oxygen permeation measurements.

Figure 7 shows the oxygen permeation flux through dense SCN, SCNT3, and SCNT5 membranes with 1 mm thickness as a function of temperature in the range of 700°C – 850°C. From the graph, the oxygen permeation fluxes of SCNT3 and SCNT5 are slightly lower than that of SCN. This observation could be associated with the decrease in the oxygen nonstoichiometry upon Sn substitution, which agrees with the findings from the neutron diffraction, redox titration, and thermogravimetric studies. The activation energy for the permeation flux was calculated from the slope of the graph. An activation energy value of 56 ± 2 kJ\textper mol\textsuperscript{$-1$} was found for SCN, while the values for SCNT3 (70 ± 3 kJ\textper mol\textsuperscript{$-1$}) and SCNT5 (71 ± 7 kJ\textper mol\textsuperscript{$-1$}) were higher. Since it
has been reported that the oxygen surface exchange reaction exhibits a higher activation energy value than oxygen ion diffusion [2,14,46], the small amount of Sn could play an important role for the oxygen transport characteristics for SCNT3 and SCNT5 membranes.

In order to further investigate the oxygen transport properties of SCN, SCNT3, and SCNT5 membranes, the oxygen permeation flux measurements were performed as a function of membrane thickness (1.0 mm, 1.2 mm, and 1.4 mm) (Figure 8). When the oxygen ion diffusion is the sole limiting parameter, the oxygen permeation flux is proportional to the reciprocal membrane thickness, exhibiting linear behavior. This can be seen for SCN in Figure 8(a), because the critical thickness (above which oxygen transport is governed by the oxygen ion diffusion) of SCN is 110–542 μm in the temperature range of 600–800° C [30].

Contrastingly, the permeation flux of SCNT3 and SCNT5 showed nearly independent behavior as

Figure 5. Deconvoluted XPS spectra of Co 2p<sub>3/2</sub> (left) and O 1 s (right) for SCN (a, b), SCNT3 (c, d), and SCNT5 (e, f).

Figure 6. Surface scanning electron micrographs of dense (a) SCN, (b) SCNT3, and (c) SCNT5 membranes.
a function of the reciprocal membrane thickness. This suggests that the oxygen permeation of SCNT3 and SCNT5 is entirely limited by the oxygen surface exchange process. This could be explained by the surface structure of SCNT3 and SCNT5, since the XPS study confirms that the bond strength of (Co, Nb)-O increases with Sn-doping, resulting in a sluggish oxygen surface exchange reaction for SCNT3 and SCNT5. Although it has been reported that the bulk diffusion and surface exchange coefficients of SrCo$_{0.6}$Fe$_{0.35}$Sn$_{0.05}$O$_{3-\delta}$ are approximately 50% higher than those of SrCo$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ [37], the oxygen permeation flux of SCNT3 and SCNT5 cannot be further enhanced owing to the limited surface exchange reaction upon Sn substitution with SCN. Therefore, both the oxygen ion diffusion and the oxygen surface exchange reaction should be considered for the development of novel mixed ionic-electronic conducting materials with high oxygen permeability.

4. Conclusions

We have systematically investigated the structure and oxygen permeability of Nb and Sn co-doped SrCoO$_{3-\delta}$. Combined X-ray and neutron diffraction studies confirmed that SrCo$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$ exhibits a tetragonal perovskite structure while the crystal structures of SrCo$_{0.87}$Nb$_{0.1}$Sn$_{0.03}$O$_{3-\delta}$ and SrCo$_{0.85}$Nb$_{0.1}$Sn$_{0.05}$O$_{3-\delta}$ are closer to the ideal cubic structure. XPS showed that the average bond energy of (Co, Nb, Sn)-O increased upon Sn-doping, whereas the oxygen permeation flux decreased with increasing Sn concentration for SrCo$_{0.9-x}$Nb$_{0.1}$Sn$_{x}$O$_{3-\delta}$ due to the annihilation of oxygen vacancies. This agrees with thermogravimetry and neutron powder diffraction results. The dependence of the oxygen permeation flux on membrane thickness for SrCo$_{0.9-x}$Nb$_{0.1}$Sn$_{x}$O$_{3-\delta}$ proved that the oxygen ion diffusion is the limiting process for SrCo$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$, while the oxygen surface exchange reaction

Figure 7. Temperature dependence of the oxygen permeation flux of SCN, SCNT3, and SCNT5 membranes with 1 mm thickness.

Figure 8. The oxygen permeation flux of SCN, SCNT3, and SCNT5 membranes as a function of thickness and temperature at 700–850 °C.
limits the oxygen permeability of SrCo$_{0.9-x}$Nb$_{0.1}$Sn$_x$O$_{3-δ}$ membranes. We believe that Nb and Sn co-doping strategies could be applied universally to perovskite oxides to stabilize cubic bulk crystal structures; however, for such applications it is essential to understand surface and transport properties.

**Disclosure statement**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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