High-Entropy Perovskites Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_3$–δ ($x = 0$–0.5): Synthesis and Oxygen Permeation Properties

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Abstract: High-entropy perovskite oxides have already been studied in various fields owing to their high-entropy-induced properties. Partial substitution of an element by a lower valence element usually improves the oxygen permeability of perovskite oxides, but high substitution amounts may lead to structural instability. In this work, pure high-entropy perovskites Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_3$–δ with high amounts Sr up to $x = 0.5$ were synthesized via a sol–gel method. Several characterization methods prove that the solubility of Sr increases with higher temperatures of the heating treatment. The ceramic with $x = 0.5$ shows a transition from semi-conductive to metallic behavior when the temperature reaches 873 K. Its oxygen flux is comparable to the low-entropy counterpart La$_{0.6}$Sr$_{0.4}$Co$_{0.5}$Fe$_{0.5}$O$_3$–δ. A stable run of ca. 46.2 h was documented for oxygen permeation under an air/CO$_2$ gradient.

Keywords: high-entropy oxide; perovskite; mixed ionic–electronic conducting membrane; oxygen separation; sol–gel synthesis

1. Introduction

Since the discovery of single-phase alloys with five equiatomic components in 2004 [1], high-entropy materials have been attracting increasing research interest due to their high-entropy-induced properties, e.g., the tendency to form single phases and great tolerance to lattice distortion [2–5]. The extension of high-entropy materials is, therefore, continuously expanded. To date, many new systems have been developed, such as high-entropy oxides [6–9], high-entropy carbides [10,11], and high-entropy metal–organic frameworks [12]. As for perovskites with the general formula ABO$_3$, both the M$_{IIA}$(TM)O$_3$ family and the RE(TM)O$_3$ family can be crystallized to single phase [2,8,9,13–16], where M$_{IIA}$ and RE are metals of group IIA and rare earth metals on the A-site, and TM stands for transition metals on the B-site.

The effects of high entropy on the performance of perovskites can be summarized in three points. First, due to the probable stabilization effect of high-entropy, perovskites can have enhanced temperature and chemical stability. As an electrode material for solid oxide fuel cells, (La,Nd,Sm,Ca,Sr)MnO$_3$ is stable at 1473 K for at least 100 h and has a higher chemical compatibility with the electrolyte 8YSZ (8 mol% Y$_2$O$_3$ stabilized ZrO$_2$) compared to the low-entropy relatives La$_{1-x}$Sr$_x$MnO$_3$–δ [13]. Second, chemical disorder and lattice distortion can be induced by high entropy, resulting in extra phonon disorder and thus leading to low thermal conductivity and better thermoelectric performance [14,17]. Third, more elements can be packed into pure perovskites, rendering the synergetic effect of cations and improving the catalytic activities of La$_{0.6}$Sr$_{0.4}$(Co,Fe,Mn,Ni,Mg)O$_3$ in oxygen evolution reactions [15], Pb(Ni,W,Mn,Nb,Zr,Ti)O$_3$ in oxygen reduction reactions [18], and La(Co,Fe,Mn,Ni,Mg)O$_3$ in CO oxidation reactions [19].

Although high-entropy perovskites have already been studied in various fields such as proton conducting materials [16,20], electrode materials in solid oxide fuel cells [13,21],...
The partial substitution of A-site element by group IIA metals (e.g., Sr) is a commonly used strategy to boost the oxygen permeability in the field of oxygen-transporting materials, since it introduces additional ionic charge carriers (i.e., mobile oxygen vacancies) upon high substitution amount [21,26,27]. In addition, the electrical conductivity can also be enhanced by partial substitution due to the 3d$_{TM}$-2p$_O$ orbital overlapping and the change of oxidation state of the TM elements on B-site [21,26–28]. However, introducing those elements usually escalates the lattice distortion and leads to structural instability. Dąbrowa et al. [21,29] have found that the solubility of strontium is limited in RE(Cr,Mn,Fe,Co,Ni)O$_3$-δ, being 0.3 for RE = La and 0.1 for RE = Pr. Secondary phases, e.g., Sr(CO$_3$)$_2$ or SrCrO$_4$, are found when the limit is exceeded. As a comparison, common Sr-doped perovskite oxides, e.g., Pr$_{1-x}$Sr$_x$(Co$_{0.5}$Fe$_{0.5}$)O$_3$-δ, can remain single phase even if $x = 0.4$ [26,30–34]. This is somehow inconsistent with the high-entropy stabilization effect, which is believed that high mixed entropy $\Delta S_{\text{mix}}$ leads to a negative Gibbs free energy $\Delta G_{\text{mix}}$ when $T\Delta S_{\text{mix}} > \Delta H_{\text{mix}}$ as indicated by the following equations (in ideal solid solutions) [4,9]:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$  \hspace{1cm} (1)

$$\Delta S_{\text{mix}} = -R \left[ \sum_{\alpha=1}^{n} x \ln x \right]_{\text{A-site}} + \left[ \sum_{\beta=1}^{n} y \ln y \right]_{\text{B-site}} + 3 \sum_{\gamma=1}^{n} z \ln z \right]_{\text{O-site}}$$  \hspace{1cm} (2)

where $R$ is the gas constant, and $x$, $y$, and $z$ are the mole fraction of elements on A-, B-, and O-sites, respectively. According to Equation (2), Pr$_{0.6}$Sr$_{0.4}$(Co$_{0.5}$Fe$_{0.5}$)O$_3$-δ has a lower mixed entropy of 1.37R compared to Pr$_{0.8}$Sr$_{0.2}$(Cr,Mn,Fe,Co,Ni)O$_3$-δ and Pr$_{0.5}$Sr$_{0.5}$(Cr,Mn,Fe,Co,Ni)O$_3$-δ, where the values are 1.93R and 2.30R, respectively.

In this work, as an example of doped RE(TM)O$_3$ family, a group of single-phase high-entropy perovskites Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_3$-δ ($x = 0$–0.5) is synthesized via a sol–gel method with subsequent heating treatments. The influence of Sr content on the electrical conductivity and the oxygen permeability is presented.

2. Materials and Methods

2.1. Material Synthesis

The chemical formulae of high-entropy perovskite oxides reported in this work are written as Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_3$-δ ($x = 0$–0.5) as recommended by the International Union of Pure and Applied Chemistry [35]. The nominal amounts of B-site elements are equal, i.e., all have a stoichiometric number of 0.2. The powders were synthesized by adapting a previously reported sol–gel method [36] using stoichiometric amounts of metal nitrates, ethylene-diamine-tetraacetic acid, and citric acid in a molar ratio of 1:1:2. Reactants were purchased from Alfa Aesar and used without further purification. Except for powders studied in phase analysis (Section 3.1), all powders were calcined at 1423 K for 10 h, followed by tabletting at 300 MPa for 0.25 h and sintering at 1673 K for 10 h (with natural cooling, see Figure A2).

2.2. Structural Characterization

The phase purity and crystal structure of products were investigated by X-ray diffraction (XRD) using a diffractometer (D8 Advance, Bruker AXS GmbH) with Cu-Kα radiation (40 kV and 40 mA, $\lambda = 0.154$ nm) and a step size of 0.01° in the 2θ range from 10° to 85°.
Rietveld refinements of XRD patterns were performed on the software TOPAS (Version 6, Bruker AXS GmbH). PrCrO$_3$ (Pnma, ICSD 251098) and SrCrO$_4$ (P2$_1$/n, ICSD 40922) were used as starting structures. The elemental composition and microstructure of membranes were examined by two field-emission scanning electron microscopes (FE-SEM): JEOL JSM-6700F equipped with an energy-dispersive X-ray spectrometer (EDXS, Oxford Instruments INCA-300) and JEOL JSM-7610FPlus with twin EDXS (Bruker XFlash 6/60). Before measurements, the cross-sections of membranes were vibratory-polished by VibroMet (Buehler). The backscattered electron channeling contrast images were captured at an acceleration voltage of 15 kV.

2.3. Electrical Conductivity Measurements

The sintered membranes were cut into bars with a conductive area of 2 mm$^2$ and a length of 10 mm. The sample was fixed between two platinum plates, which were connected to a sweep/function generator (1 Hz square waveform, Wavetek Model 180) and digital multimeters (KEITHLEY 2100, Keithly Instruments) by platinum wires. The measurement cell was heated to 1223 K in a horizontal tube furnace (Carbolite Gero EVZ 12/450N) and the data were recorded by using the software LabVIEW 2015 (Version 15.0.0) at equilibrium conditions during the cooling process.

2.4. Oxygen Permeation Measurements

The oxygen permeabilities of sintered membranes were characterized from 1023 K to 1223 K by a home-made high-temperature permeation cell, which is described in detail elsewhere [32]. Before mounting the samples, membranes were polished to 1 mm thick by using 1200-grit sandpaper and washed with ethanol. The sample was then sealed on an alumina tube with a commercial ceramic sealant (Huitian 2767). Synthetic air (20 vol.% O$_2$ and 80 vol.% N$_2$) was used at a rate of 150 mL/min on the feed side of the sample, while on the sweep side, 1 mL/min of Ne and 29 mL/min of He were used. The flow rates were regulated by mass flow controllers (EL-Flow® , Bronkhorst, AK Ruurlo, The Netherlands) in normal conditions (273.15 K, 101 325 Pa). The concentration of the effluent was analyzed by an on-line gas chromatograph (Agilent 7890A) equipped with a Carboxen® 1000 column (Merck, Darmstadt, Germany) and a thermal conductivity detector. Due to imperfect sealing, a small amount of N$_2$ was also detected in the effluent and the leakage of oxygen was subtracted in the calculation of the oxygen permeation flux [37].

3. Results and Discussion

3.1. Phase Analysis of Powders

The XRD patterns of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-δ}$ ($x = 0–0.5$) powders calcined at 1223 K and 1673 K are shown in Figure 1a,b. Details of Rietveld refinement are listed in Table A3. After calcinating at 1223 K, all powders have an orthorhombic perovskite structure (Pnma). The reflections of SrCrO$_4$ become noticeable along with an increasing $x$. For the powder with $x = 0.1$, the solely visible reflection of SrCrO$_4$ overlaps with the 111 reflection of the perovskite. Nevertheless, as shown in Figure 1c, a comparison between one-phase Rietveld refinement (PrCrO$_3$ as starting structure) and two-phase Rietveld refinement (PrCrO$_3$ and SrCrO$_4$ as starting structures) leads to the conclusion that the powder with $x = 0.1$ also has SrCrO$_4$ as a secondary phase. This finding, although in good agreement with the work of Dąbrowa et al. [29], seems to be somehow contrary to the commonly understood high-entropy effect, namely that a single-phase solid solution tends to be formed when $ΔS_{mix}$ higher than 1.5R [2,4,38]. Note that $ΔS_{mix}$ increases as the $x$ value increases from 0 to 0.5 (see Table A2).

In view of the Goldschmidt tolerance factor $t$, mixed entropy $ΔS_{mix}$, size difference of A-site cations $Δ(R_A)$, and size difference of B-site cations $Δ(R_B)$, the powders with $x$ from 0 to 0.5 should be pure phase, as shown in Table A2:

- All the $t$ factors are greater than 0.75 and become closer to 1 when $x$ approaches 0.5, suggesting that a stable perovskite structure can be obtained [39].
The $\Delta S_{\text{mix}}$ increases from 1.61R for $x = 0$ to 2.30R for $x = 0.5$ as calculated by using Equation (2). Larger mixed entropy should indicate a more stable structure and thus pure phase upon substitution [2,4,38]. The $\Delta(R_A)$ and $\Delta(R_B)$ are smaller than 6.5%, which means it is possible to form single-phase high-entropy perovskite [8,13,40].

Note that although $\Delta(R_A)$ is smaller than 6.5%, it does increase along with the greater $x$ due to the different ionic radii of Pr$^{3+}$ and Sr$^{2+}$ (see Table A1). The formation of the secondary phase may be correlated to the relatively large $\Delta(R_A)$.

![Figure 1. Room-temperature XRD patterns of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_3$ [8,13,40] powders calcined at (a) 1223 K and (b) 1673 K. Reflections of the main phase were indexed according to the results of Rietveld refinement using PrCrO$_3$ (ICSD 251098) as the starting structure. The diamond symbols denote Bragg positions of SrCrO$_3$ (ICSD 251098) as the starting structure. The solid lines present the Rwp factors of refinements using PrCrO$_3$ (Pnma, ICSD 251098) as the starting structure, while the dashed lines draw the Rwp factors of refinements using PrCrO$_3$ (Pnma, ICSD 251098) and SrCrO$_4$ (P2$_1$/n, ICSD 40922) as the starting structures.

However, when a higher calcination temperature of 1673 K is used, the powders are still pure phase even with a large amount of Sr (i.e., $x = 0.5$), as proven by the XRD patterns in Figure 1b and the corresponding Rietveld refinements in Figures 1d and 1e. As shown in Table A3, the powders are considered as pure phase when treated after 1223 K for $x = 0$, 1423 K for $x \in [0, 0.1]$, and 1673 K for $x \in [0, 0.5]$. For the calcination temperature of 1223 K, only the sample with $x = 0$ has Rwp and GOF factors from one-phase refinements that are smaller than those from two-phase refinements. For the calcination temperature of 1423 K and $x \in [0, 0.1]$, the Rwp and GOF factors from one-phase refinements are smaller than those from two-phase refinements. For the calcination temperature of 1673 K, all the Rwp and GOF factors from one-phase refinements are smaller than those from two-phase refinements. It seems that a high temperature is beneficial to maintain the perovskite structure and thus increase the strontium solubility. A higher temperature results in greater $T\Delta S_{\text{mix}}$, and thus a more negative $\Delta G_{\text{mix}}$ according to Equation (1), which can compensate the effect of large $\Delta(R_A)$ and ensure the formation of the pure phase.
Since all the powders are pure phase and have an orthorhombic \( Pnma \) structure, the quasi-cubic lattice parameter \( a_0 \), which is calculated assuming the unit cell of the orthorhombic system is four times larger than the corresponding cubic system (i.e., \( a \times b \times c = \sqrt{2}a_0 \times 2a_0 \times \sqrt{2}a_0 \)), is used to probe the influence of Sr content. The lattice parameters of the orthorhombic system can be found in Table A3. A sharp decrease in \( a_0 \) can be clearly seen from \( x = 0 \) to \( x = 0.3 \) (Figure 2), while this trend slows down for \( x = 0.4 \) and \( x = 0.5 \). The shrinkage of \( a_0 \) along with increasing Sr content, i.e., partial substitution of \( \text{Pr}^{3+} \) by \( \text{Sr}^{2+} \), indicates that charge compensation mechanism contributes more upon substitution, rather than the formation of oxygen vacancy [21]. Additionally, with more Sr in the composition, i.e., \( x \in [0.4, 0.5] \), the impact of oxygen vacancy growths and thus endows the unit cell the ability to expand, so that the decreasing trend of the lattice parameters becomes slower. The relationship between \( a_0 \) and \( x \) gives a hint that Sr enters the unit cell of \( \text{Pr}_{1-x}\text{Sr}_x(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} \), rather than evaporating during heating treatment. A more precise analysis is presented in Section 3.2. The influence of Sr content on the electrical conductivity and oxygen permeability will be discussed in Sections 3.3 and 3.4.

![Figure 2. Quasi-cubic lattice parameter of \( \text{Pr}_{1-x}\text{Sr}_x(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} \) (\( x = 0-0.5 \)) powders after heating at 1673 K.](image)

To further investigate the influence of heating temperatures on the Sr solubility, uncalcined \( \text{Pr}_{0.5}\text{Sr}_{0.5}(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} \) were divided into five portions and treated at temperatures from 1223 K to 1673 K followed by natural cooling. The results are visualized in Figure 3 and the cooling rate can be found in Figure A2. After cooling down to room temperature from 1223 K, reflections from \( \text{SrCrO}_4 \) and an unknown phase are present between the 101 and 200 reflections of the perovskite phase (Figure 3a). The reflections of \( \text{SrCrO}_4 \) and the unknown phase disappear after heating at 1623 K. The \( Rwp \) values of the Rietveld refinements in Figure 3b also indicate that after heating at 1673 K, one-phase refinement (\( Pnma \)) fits better than two-phase refinement (\( Pnma + P2_1/n \)). The content of \( \text{SrCrO}_4 \) in powders decreases from 10.5% to 0% (under the detection limit of XRD) as the heating temperature varies from 1223 K to 1673 K.

Interestingly, increasing the treatment temperature to 1673 K did not bring about a pure phase for the Sr amount of \( x = 0.7 \), as shown by the XRD pattern in Figure A3. Moreover, the surface and cross-section of the \( x = 0.7 \) membranes were porous after sintering (Figure A6), which is not qualified as oxygen separation membranes. According to Equation (2), the mixed entropy \( \Delta S_{\text{mix}} \) increases with \( x \) from 0 to 0.5 and decreases with \( x \) from 0.5 to 1. Since \( \text{Sr}^{2+} \) has the largest ionic radius among \( \text{Pr}_{1-x}\text{Sr}_x(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} \) and it reacts readily with Cr [21], we speculate that during the sintering process (1673 K for 10 h), \( \text{Pr}_{0.3}\text{Sr}_{0.7}(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} \) is not stable and tends to release Sr to maximize \( \Delta S_{\text{mix}} \). In other words, when the doping ratio of Sr exceeds 0.5, the system has a tendency
to decrease the amount of Sr, letting the amount of Sr equals the amount of Pr; the released Sr may react with Cr, forming SrCrO₄.

![Figure 3](image-url) (a) Room-temperature XRD patterns of Pr₀.₅Sr₀.₅(Cr,Mn,Fe,Co,Ni)O₃₋δ powders treated at temperatures in the range of 1223 K to 1673 K followed by natural cooling. The cooling rates are shown in Figure A2. Reflections of the main phase were indexed according to the Rietveld refinement using PrCrO₃ (Pnma, ICSD 251098) as the starting structure. The diamond symbols denote Bragg positions of SrCrO₄ (P2₁/n, ICSD 40922). (b) The influence of heating temperatures on the SrCrO₄ content and the corresponding Rwp factors obtained by Rietveld refinements.

3.2. Characterization of Membranes

In Section 3.1, we have proved that the pure phase of PrₓSrₓ(Cr,Mn,Fe,Co,Ni)O₃₋δ with x ranging from 0 to 0.5 can be obtained after heating at 1673 K. The powders were then tableted and sintered at 1673 K for 10 h to prepare membranes. The vibratory-polished cross-sections of membranes were investigated by EDXS and SEM to gain insights into the content and distribution of elements in addition to the microstructure of membranes. The average compositions of the membranes are listed in Tables A4 and A5, while the stoichiometry of the cations is illustrated in Figure 4. It is quite interesting that for both measurement areas of 200,000 µm² and 336 µm² the calculated stoichiometry matches well with the desired chemical formulae. The sum of Pr and Sr is about 1 and the other cations are all circling around 0.2. This finding suggests that during the calcination and sintering processes, there is no loss of elements, at least not of a single element.

![Figure 4](image-url) Cation stoichiometry of PrₓSrₓ(Cr,Mn,Fe,Co,Ni)O₃₋δ (x = 0–0.5) calculated from results of EDXS (Tables A4 and A5) under the assumption that the sum of A-site cations and B-site cations is two. The solid lines present data obtained on an effective area of 200,000 µm² by a lithium-drifted silicon detector while the dashed lines are data on an effective area of 336 µm² by silicon drift detectors. The cross-sections of samples were vibratory-polished and sputtered with a carbon layer before measurement.
The SEM investigation in the backscattered electron channeling contrast mode produced similar images of membranes with \( x = 0 \) and \( x = 0.5 \) (Figure 5a,b), indicating that no intergrowths are formed after introducing Sr into \( \text{Pr} \) into \( \text{Pr}_{0.5}\text{Sr}_{0.5}(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} \). The electron channeling contrast comes from the change of the angle between the crystal lattice orientation and the incident electron beam. The following images further visualize the uniform distribution of each element in both samples without enrichment of Sr or Cr, which is found in \( \text{Ln}_{1-x}\text{Sr}_x(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} \) (\( \text{Ln} = \text{La, Pr, Nd, Sm, Gd} \)), as reported in reference [21,29].

Figure 5 also demonstrates that the Sr content affects grain size of \( \text{Pr}_{1-x}\text{Sr}_x(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} \) membranes. The average grain size increases with increasing strontium content, and is 4.6 µm for \( x = 0 \) and 14.7 µm for \( x = 0.5 \) (Figure A4). The Sr effect on grain size is explicitly shown by the SEM images of the membrane surface in Figure A5. A similar effect has been found in its low-entropy counterparts, e.g., \( \text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 \) [27,41,42]. Possible reasons could be the formation of a transient liquid phase or defects that facilitate mass transport during the sintering process [27]. Although this phenomenon is interesting and should be further investigated, it is beyond the scope of this work.

![Figure 5. Electron channeling contrast images of vibratory-polished cross-sections of membranes (a) Pr(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} and (b) Pr_{0.5}\text{Sr}_{0.5}(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})\text{O}_{3-\delta} and corresponding elemental distributions derived from silicon drift detectors.](image)

### 3.3. Electrical Conductivity

The temperature dependence of the electrical conductivity of sintered samples was recorded in ambient air. Since the ionic conductivity is much smaller than the electronic conductivity in perovskite [25,26], the electrical conductivity can be regarded as the electronic conductivity. The conductivity increases with higher temperatures, reaches a maximum at a certain temperature, and then starts to decrease in the case of \( x > 0.3 \), as depicted in Figure 6a, showing a transition from a semi-conductive to metallic behavior.
Figure 6. (a) Temperature-dependent electrical conductivity of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ ($x = 0$–0.5) membranes and (b) its Arrhenius plot.

The semi-conducting behavior is related to a p-type small polaron hopping mechanism, i.e., the mobility of localized electronic carriers is thermally activated, while the decrease in conductivity after $T_{\text{max}}$ (1073 K for $x = 0.4$, 873 K for $x = 0.5$) could be attributed to the loss of oxygen from the lattice [26,33]. With the loss of oxygen, the concentration of charge carriers is reduced as described by Equation (3) [26]:

$$2B^*_B + O^*_O \leftrightarrow 2B^*_B + V^*_{O} + \frac{1}{2}O_2 \quad (3)$$

where $B^*_B$ and $V^*_{O}$ are tetravalent cations (electron holes) on the B-site and oxygen vacancy, respectively. Moreover, the overlap between the 3d-orbitals of the B-site cations and the 2p-orbitals of oxygen is decreased with the loss of oxygen, and consequently causing a decline in conductivity since the overlap is responsible for the electron transportation [43].

Table 1 lists the maximum conductivity, the corresponding temperature, as well as the activation energy determined from the linear part of the Arrhenius plot (Figure 6b). While the activation energies of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ ($x = 0$–0.5) are close to La$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ ($x = 0$–0.3), as reported by Dąbrowa et al. [21], the clear difference lies in the maximum values of electronic conductivity. We attribute the difference of higher electronic conductivity to the close contact among the grains as shown by the cross-sectional images in Figure 5a,b and the top-view images in Figure A5. High electronic conductivity is beneficial to applications involving solid oxide fuel cells or mixed ionic–electronic conductors [44]. It is obvious that adding Sr to the A-site significantly enhances the electronic conductivity and reduces the activation energy, which is 578% in $\sigma_{\text{max}}$ and 34% in $E_a$ when comparing $x = 0.5$ to $x = 0$. Similar effects of Sr doping are also found in Sr-doped La, Pr, and Nd perovskites [26,33,34,45,46].

Table 1. Activation energies $E_a$ of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ ($x = 0$–0.5) membranes determined from the linear range of the Arrhenius plots shown in Figure 6b. $\sigma_{\text{max}}$ and $T_{\text{max}}$ are the maximum values of electrical conductivity and corresponding temperature among the measured data points.

| $x$ | $E_a$ (eV) | Temperature Range (K) | $\sigma_{\text{max}}$ (S cm$^{-1}$) | $T_{\text{max}}$ (K) |
|-----|-----------|------------------------|-----------------------------------|----------------------|
| 0   | 0.29      | 303–1223               | 28.39                             | >1223                |
| 0.1 | 0.23      | 303–1223               | 49.37                             | >1223                |
| 0.2 | 0.20      | 303–1223               | 77.69                             | >1223                |
| 0.3 | 0.13      | 303–1153               | 81.82                             | >1153                |
| 0.4 | 0.11      | 303–1073               | 121.89                            | 1073                 |
| 0.5 | 0.10      | 303–873                | 163.99                            | 873                  |
3.4. Oxygen Permeation

The permeation performance was evaluated on \( \text{Pr}_{1-x}\text{Sr}_x(\text{Cr,Mn,Fe,Co,Ni})\text{O}_{3-\delta} \) (\( x = 0-0.5 \)) membranes by using helium as sweep gas between the temperature of 1023 K to 1223 K. The oxygen fluxes of samples with \( x \in [0, 0.2] \) are below the detection limit of gas chromatography and thus not shown here. Data of samples with \( x \in [0.3, 0.5] \) are presented in Figure 7a. The influence of temperature and Sr content is evident: oxygen fluxes increase with elevated temperature and higher Sr content. Meanwhile, the magnitude of the increase in oxygen flux is also larger when \( x \) changes from 0.4 to 0.5 than when \( x \) changes from 0.3 to 0.4. Taking the changes in quasi-cubic lattice parameter (Figure 2) and electrical conductivity (Figure 6) into account, we can conclude that when increasing \( x \) from 0.4 to 0.5, more oxygen vacancies are introduced than increasing \( x \) from 0.3 to 0.4. The oxygen vacancy leads to expansion in cell volume, thus compensating for the effect of the tetravalent B-site cations and slowing down the decreasing trend of lattice parameter at high \( x \) values (Figure 2). Since the creation of one oxygen vacancy annihilates two electron holes (see Equation (3)), the \( T_{\text{max}} \) lowers with an increased \( x \), and the decrease in electronic conductivity after \( T_{\text{max}} \) becomes steeper (Figure 6a).

![Figure 7. Oxygen flux of \( \text{Pr}_{1-x}\text{Sr}_x(\text{Cr,Mn,Fe,Co,Ni})\text{O}_{3-\delta} \) (\( x = 0-0.5 \)) membranes as functions of (a) temperature and (b) duration. Test conditions: 150 mL min\(^{-1}\) synthetic air as the feed gas, 29 mL min\(^{-1}\) He or CO\(_2\) as the sweep gas, and 1 mL min\(^{-1}\) Ne as the internal standard gas. Membrane thickness: 1.0 mm. Data for the \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta} \) (LSCF) membrane were taken from our previous study [47].](image-url)
Figure 8. XRD patterns of the spent Pr$_{0.5}$Sr$_{0.5}$(Cr,Mn,Fe,Ni)O$_{3-\delta}$ membrane after the experiment displayed in Figure 7 (CO$_2$ + Ne sweep at 1223 K for 46.2 h and He + Ne sweep for 2 h). Reflections were indexed according to the results of Rietveld refinement using PrCrO$_3$ (ICSD 251098) as the starting structure. Arrows: Bragg positions of CaCO$_3$ (ICSD 52151) from XRD sample holders.

4. Conclusions

Sr-doped high-entropy perovskites Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Ni)O$_{3-\delta}$ ($x = 0$–0.5) were successfully synthesized via a sol–gel method. Examination of phase purity by XRD, SEM, and EDXS demonstrated that raising the temperature of heating treatment can be used to increase the content of Sr in the pure phase. According to the results of Rietveld refinements, the quasi-cubic lattice parameter had a declined tendency towards higher Sr content and the tendency slowed down when $x > 0.3$. Starting from this composition ($x > 0.3$), a transition of semi-conductive to metallic behavior was observed in the electrical conductivity measurement within 1223 K. Furthermore, oxygen flux could be detected from 1023 K to 1223 K, and it was greatly enhanced by increasing the Sr content. The membrane Pr$_{0.5}$Sr$_{0.5}$(Cr,Mn,Fe,Ni)O$_{3-\delta}$ exhibited a permeation behavior similar to La$_{0.6}$Sr$_{0.4}$Co$_0.5$Fe$_{0.5}$O$_{3-\delta}$, in view of the magnitude of oxygen flux and the chemical stability against CO$_2$ in the range of tested temperatures.

Author Contributions: Conceptualization, A.F. and Z.Z.; Methodology, Z.Z. and L.R.; Validation, Z.Z. and L.R.; Formal Analysis, Z.Z. and L.R.; Investigation, Z.Z., L.R. and F.S.; Data Curation, Z.Z. and L.R.; Writing—Original Draft Preparation, Z.Z.; Writing—Review and Editing, Z.Z., L.R., F.S. and A.F.; Visualization, Z.Z.; Supervision, A.F.; Project Administration, A.F.; Funding Acquisition, A.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—project number 435833397.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank R. Hinterding and K. Kruppa for their assistance during the electrical conductivity measurements, O. Stölting for his preparation of some samples, R. Almeev for access to the JSM-7610FPPlus scanning electron microscope, and A. Sarkar from the Karlsruhe Institute of Technology for helpful scientific exchange.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

- MIEC mixed ionic–electronic conductor
- BSCF Ba$_{0.5}$Sr$_{0.5}$Co$_0.8$Fe$_{0.2}$O$_{3-\delta}$
- XRD X-ray diffraction
- FE-SEM field-emission scanning electron microscope
- EDXS energy-dispersive X-ray spectrometer
- LSCF La$_{0.6}$Sr$_{0.4}$Co$_0.5$Fe$_{0.5}$O$_{3-\delta}$
Appendix A

Figure A1. Rietveld refinements of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ ($x = 0$–$0.5$) powders treated at 1673 K. PrCrO$_3$ (Pnma, ICSD 251098) was used as starting structure since the powders are pure phase after heating at 1673 K, as discussed in Section 3.1 in the main text.
Figure A2. Temperature profile of the Carbolite HTF 1700 oven during natural cooling. The cooling rate is derived from the first-order derivative of the temperature curve. Ambient temperature: 297 ± 1 K. The cooling process was conducted three times. Error bars are inside the hollow squares.

Figure A3. XRD pattern of Pr$_{0.3}$Sr$_{0.7}$(Cr,Mn,Fe,Co,Ni)$_3$O$_{3-\delta}$ powder treated after 1673 K for 10 h. Reflections were indexed according to the results of Rietveld refinement using PrCrO$_3$ (ICSD 251098) as the starting structure.
Figure A4. Grain size distribution of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ membranes ($x = 0,0.5$) fitted with a log-normal density function. The dashed lines show the distribution of grains from the membrane surface, whereas the solid lines demonstrate the distribution of grains from the membrane cross-section. The grain diameter $d$ is calculated according to $d = \sqrt{4A/\pi}$, where $A$ is the measured area of grains. In each case, 100 grains were evaluated.

Figure A5. SEM images of the Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ ($x = 0–0.5$) membrane surface. (a) $x = 0$; (b) $x = 0.1$; (c) $x = 0.2$; (d) $x = 0.3$; (e) $x = 0.4$; (f) $x = 0.5$. The close contact among the grains is responsible for enhanced electrical conductivity compared to La$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni) O$_{3-\delta}$ ($x = 0 – 0.3$), as reported by Dąbrowa et al. [21].
**Figure A6.** SEM images of Pr$_{0.3}$Sr$_{0.7}$(Cr,Mn,Fe,Co,Ni)O$_3$–$\delta$ membrane: (a) surface; (b) cross-section.

**Figure A7.** SEM images of the spent Pr$_{0.5}$Sr$_{0.5}$(Cr,Mn,Fe,Co,Ni)O$_3$–$\delta$ membrane and corresponding elemental distributions: (a) feed side and (b) sweep side. The surfaces were polished prior to the oxygen permeation measurement, and, therefore, no grain boundary is visible.
Table A1. Ionic radii of elements in Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ ($x = 0$–$0.5$) [50,51]. LS and HS stand for low spin and high spin, respectively.

| Ion           | Coordination Number | Ionic Radius (pm) |
|---------------|---------------------|-------------------|
| Pr$^{3+}$     | XII                 | 132               |
| Sr$^{2+}$     | XII                 | 144               |
| Cr$^{3+}$     | VI                  | 61.5              |
| Mn$^{3+}$     | VI                  | 59$^{LS}$, 64.5$^{HS}$ |
| Fe$^{3+}$     | VI                  | 55$^{LS}$, 64.5$^{HS}$ |
| Co$^{3+}$     | VI                  | 54.5$^{LS}$, 61$^{HS}$ |
| Ni$^{3+}$     | VI                  | 56$^{LS}$, 60$^{HS}$ |
| Cr$^{4+}$     | VI                  | 55               |
| Mn$^{4+}$     | VI                  | 53               |
| Fe$^{4+}$     | VI                  | 58.5             |
| Co$^{4+}$     | VI                  | 53               |
| Ni$^{4+}$     | VI                  | 48               |
| O$^{2-}$      | VI                  | 140              |

Table A2. Goldschmidt tolerance factor $t$, size difference of A-site cations $\Delta(R_A)$, size difference of B-site cations $\Delta(R_B)$, and mixed entropy $\Delta S_{mix}$ of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ ($x = 0$–$0.5$). LS and HS stand for low spin and high spin, respectively.

| Sample | $t$ (B$^{3+}$) | $t$ (B$^{4+}$) | $\Delta(R_A)$ | $\Delta(R_B)$ | $\Delta S_{mix}$ |
|--------|---------------|---------------|---------------|---------------|-----------------|
| $x = 0$ | 0.98$^{LS}$, 0.95$^{HS}$ | 0.99 | 0.00% | 4.47$^{LS}$, 2.99$^{HS}$ | 6.37% | 1.29  |
| $x = 0.1$ | 0.98$^{LS}$, 0.95$^{HS}$ | 1.00 | 2.70% | 4.47$^{LS}$, 2.99$^{HS}$ | 6.37% | 1.93  |
| $x = 0.2$ | 0.98$^{LS}$, 0.96$^{HS}$ | 1.00 | 3.57% | 4.47$^{LS}$, 2.99$^{HS}$ | 6.37% | 2.11  |
| $x = 0.3$ | 0.99$^{LS}$, 0.96$^{HS}$ | 1.01 | 4.06% | 4.47$^{LS}$, 2.99$^{HS}$ | 6.37% | 2.22  |
| $x = 0.4$ | 0.99$^{LS}$, 0.97$^{HS}$ | 1.01 | 4.30% | 4.47$^{LS}$, 2.99$^{HS}$ | 6.37% | 2.28  |
| $x = 0.5$ | 1.00$^{LS}$, 0.97$^{HS}$ | 1.02 | 4.35% | 4.47$^{LS}$, 2.99$^{HS}$ | 6.37% | 2.30  |

* Assuming that the elements on B-site all have a valence of +4, which implies the absence of oxygen vacancies;
** The size difference is calculated as in Equation (A1).

$$
\Delta(R_A) = \sqrt[\sum_i c_i}{\left(1 - R_{A_i}\right) / \left(\sum_i c_i R_{A_i}\right)}
$$

(A1)

where $R_{A_i}$ is ionic radius of $i^{th}$ cation on the A-site and $c_i$ is the mole fraction of $i^{th}$ cation.

Table A3. Results of Rietveld refinements of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ ($x = 0$–$0.5$) after different heating treatments. As an initial point of the refinement, the PrCrO$_3$ (Pnma, ICSD 251098) and SrCrO$_4$ (P2$_1$/n, ICSD 40922) structures were used. The bold numbers highlight the smallest $x$ value, from which the samples are not considered as pure phase (Pnma) any more, as reflected by their corresponding Rwp values. It is clear that with higher heating temperatures, the maximum $x$ value in the pure phase of Pr$_{1-x}$Sr$_x$(Cr,Mn,Fe,Co,Ni)O$_{3-\delta}$ is increased.

| $x$ | $a$ (Å) | $b$ (Å) | $c$ (Å) | Rwp (%) | GOF | $P2_1/n$ (wt%) | $a$ (Å) | $b$ (Å) | $c$ (Å) | Rwp (%) | GOF |
|-----|---------|---------|---------|---------|-----|----------------|---------|---------|---------|---------|-----|
| 0   | 5.4698(2) | 7.6982(3) | 5.4407(2) | 2.67 | 1.29 | -- | -- | -- | -- | -- | -- |
| 0.1 | 5.4576(4) | 7.7007(5) | 5.4491(4) | 2.53 | 1.23 | 1.8(2) | 5.4577(4) | 7.7008(5) | 5.4491(4) | 2.47 | 1.2 |
| 0.2 | 5.4459(8) | 7.6939(1) | 5.4537(8) | 3.17 | 1.5 | 7.7(2) | 5.4461(6) | 7.6939(8) | 5.4536(6) | 2.28 | 1.09 |
| 0.3 | 5.4505(1) | 7.6853(2) | 5.4309(1) | 4.48 | 2.3 | 11.3(2) | 5.4501(7) | 7.6862(1) | 5.4305(7) | 2.64 | 1.36 |
| 0.4 | 5.423(2)  | 7.668(3)  | 5.453(2)  | 3.96 | 2.03 | 10.1(2) | 5.4228(2) | 7.668(2)  | 5.4531(2) | 2.87 | 1.47 |
| 0.5 | 5.434(6)  | 7.663(8)  | 5.470(6)  | 5.62 | 2.99 | 10.5(5) | 5.433(5)  | 7.659(6)  | 5.466(5)  | 4.69 | 2.5  |
### Table A3. Cont.

| x   | a (Å)       | b (Å)       | c (Å)       | Rwp (%) | GOF | P2/n (wt%) | a (Å)       | b (Å)       | c (Å)       | Rwp (%) | GOF |
|-----|-------------|-------------|-------------|---------|-----|------------|-------------|-------------|-------------|---------|-----|
| 0   | 5.470(1)    | 7.697(2)    | 5.440(3)    | 3.71    | 1.71| –          | –           | –           | –           | –       | –   |
| 0.1 | 5.452(1)    | 7.699(2)    | 5.4526(1)   | 3.52    | 1.57| 0.0(5)     | 5.4520(2)   | 7.699(2)    | 5.4528(1)   | 3.52    | 1.57|
| 0.2 | 5.4379(4)   | 7.6940(6)   | 5.4552(4)   | 3.48    | 1.54| 0.1(4)     | 5.4380(4)   | 7.6940(6)   | 5.4552(4)   | 3.47    | 1.54|
| 0.3 | 5.4578(4)   | 7.6842(5)   | 5.4584(3)   | 3.98    | 1.91| 2.7(3)     | 5.4578(4)   | 7.6842(5)   | 5.4585(4)   | 3.93    | 1.89|
| 0.4 | 5.4204(4)   | 7.6700(7)   | 5.4568(5)   | 3.47    | 1.54| 0.1(4)     | 5.4204(4)   | 7.6700(6)   | 5.4569(4)   | 3.43    | 1.61|
| 0.5 | 5.4166(7)   | 7.6589(1)   | 5.4597(7)   | 4.68    | 2.29| 7.5(4)     | 5.4166(7)   | 7.6588(1)   | 5.4597(7)   | 4.68    | 2.29|

### Table A4.

Average composition of $\text{Pr}_{1-x}\text{Sr}_x\text{(Cr,Mn,Fe,Co,Ni)}\text{O}_{3-δ}$ ($x = 0–0.5$) obtained on an effective area of 200,000 µm$^2$ by a lithium-drifted silicon detector.

| Average Composition (at.%) Ratio of Cations |
|--------------------------------------------|
| $x$  | Pr  | Sr | Cr | Mn | Fe | Co | Ni | O   | Pr | Sr | Cr | Mn | Fe | Co | Ni |
|-----|-----|----|----|----|----|----|----|-----|----|----|----|----|----|----|----|
| 0   | 19.04 | 0.00 | 4.57 | 3.14 | 4.39 | 3.75 | 3.46 | 62.50 | 1.02 | 0.00 | 0.24 | 0.17 | 0.19 | 0.20 | 0.18 |
| 0.1 | 17.05 | 2.00 | 4.22 | 3.25 | 3.52 | 3.62 | 3.55 | 62.78 | 0.92 | 0.11 | 0.23 | 0.17 | 0.19 | 0.19 | 0.19 |
| 0.2 | 15.97 | 4.31 | 4.46 | 3.38 | 3.66 | 3.68 | 3.66 | 60.89 | 0.82 | 0.22 | 0.23 | 0.17 | 0.19 | 0.19 | 0.19 |
| 0.3 | 13.30 | 6.45 | 4.20 | 3.54 | 3.58 | 3.74 | 3.94 | 60.70 | 0.52 | 0.52 | 0.21 | 0.18 | 0.18 | 0.19 | 0.20 |
| 0.4 | 11.71 | 8.49 | 4.20 | 3.78 | 3.64 | 3.69 | 3.71 | 60.78 | 0.60 | 0.43 | 0.21 | 0.19 | 0.19 | 0.19 | 0.19 |
| 0.5 | 10.49 | 10.49 | 4.20 | 3.54 | 3.58 | 3.74 | 3.94 | 60.70 | 0.52 | 0.52 | 0.21 | 0.18 | 0.18 | 0.19 | 0.20 |

### Table A5.

Average composition of $\text{Pr}_{1-x}\text{Sr}_x\text{(Cr,Mn,Fe,Co,Ni)}\text{O}_{3-δ}$ ($x = 0–0.5$) obtained on an effective area of 336 µm$^2$ by silicon drift detectors.

| Average Composition (at.%) Ratio of Cations |
|--------------------------------------------|
| $x$  | Pr  | Sr | Cr | Mn | Fe | Co | Ni | O   | Pr | Sr | Cr | Mn | Fe | Co | Ni |
|-----|-----|----|----|----|----|----|----|-----|----|----|----|----|----|----|----|
| 0   | 27.30 | 0.00 | 5.75 | 5.54 | 5.97 | 6.05 | 5.56 | 43.82 | 0.97 | 0.00 | 0.20 | 0.19 | 0.20 | 0.19 | 0.20 |
| 0.1 | 23.57 | 3.10 | 5.51 | 5.35 | 5.77 | 5.80 | 5.41 | 45.49 | 0.86 | 0.11 | 0.20 | 0.20 | 0.21 | 0.22 | 0.20 |
| 0.2 | 21.57 | 6.57 | 5.47 | 5.32 | 5.75 | 5.81 | 5.66 | 43.84 | 0.77 | 0.23 | 0.19 | 0.19 | 0.20 | 0.20 | 0.20 |
| 0.3 | 18.29 | 8.97 | 5.51 | 5.38 | 5.76 | 5.74 | 5.56 | 44.78 | 0.66 | 0.33 | 0.20 | 0.19 | 0.21 | 0.21 | 0.20 |
| 0.4 | 15.76 | 11.94 | 5.51 | 5.48 | 5.79 | 5.81 | 5.86 | 43.85 | 0.56 | 0.43 | 0.20 | 0.20 | 0.21 | 0.21 | 0.21 |
| 0.5 | 13.12 | 14.73 | 5.40 | 5.48 | 5.58 | 5.67 | 5.81 | 43.99 | 0.47 | 0.53 | 0.19 | 0.20 | 0.21 | 0.20 | 0.21 |

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