Mixed conductivity, stability and electrochemical behavior of perovskite-type
$(\text{Sr}_{0.7}\text{Ce}_{0.3})_1-x\text{Mn}_1-y\text{Cr}_y\text{O}_3-\delta$

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A B S T R A C T

The total conductivity, Seebeck coefficient, thermal and chemical expansions, and steady-state oxygen permeability of $\text{Sr}_x\text{Ce}_{0.3}\text{Mn}_1-y\text{Cr}_y\text{O}_3-\delta$ with tetragonal perovskite structure were analyzed in the oxygen partial pressure range $10^{-4}$ to 0.3 atm at 600–1270 K. The oxygen permeation fluxes, governed by surface exchange kinetics and bulk ionic transport, were assessed and compared to $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. While the perovskite lattice of $(\text{Sr}_x\text{Ce}_{0.3})_{1-x}\text{Mn}_1-y\text{Cr}_y\text{O}_3-\delta$ is almost intolerant with respect to A-site cation deficiency, the stability limits of $(\text{Sr}_x\text{Ce}_{0.3})_{1-x}\text{Mn}_1-y\text{Cr}_y\text{O}_3-\delta$ in reducing atmospheres are essentially unaffected by Cr doping and correspond to oxygen partial pressures of $(0.4-1.5)\times10^{-12}$ atm at 1223 K. The substitution of chromium for manganese decreases $p$-type electronic conduction predominant in the whole phase stability domain, suppresses chemical expansion on reducing $p(O_2)$ due to lowering oxygen stoichiometry variations, but leads also to moderately higher thermal expansion. The electrical properties indicate strong hole trapping by chromium cations and progressive charge-carrier localization. The steady-state polarization studies of porous $\text{Sr}_x\text{Ce}_{0.3}\text{Mn}_1-y\text{Cr}_y\text{O}_3-\delta$ electrodes in contact with two apatite-type silicate electrolytes, $\text{La}_{10}\text{Si}_5\text{Al}_0\text{O}_{26.5}$ and $\text{La}_{6.83}\text{Pr}_3\text{Si}_{4.5}\text{Fe}_{1.5}\text{O}_{26}$ + 0.4, show a relatively poor electrochemical performance, which may be partly associated with microstructural degradation and cation interdiffusion between the cell components.

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1. Introduction

Solid oxide fuel cells (SOFCs) attract a significant attention as alternative power generation systems due to high energy-conversion efficiency, low emission of pollutants, fuel flexibility and low noise [1–4]. Numerous efforts are focused on reducing SOFC operation temperatures down to 800–1070 K, which makes it possible to suppress chemical interaction between the cell components, to enhance microstructural stability of porous electrodes, and to use cheaper materials for the interconnects and stack components [2–4]. This is accompanied, however, with increasing role of electrode polarization as the performance-determining factor. In particular, conventional cathodes based on perovskite-type $\text{La}_1-x\text{Sr}_x\text{MnO}_3$ ($\text{LSM}$) have a poor oxygen-ionic conductivity and insufficient electrocatalytic activity at these temperatures [4].

Recently, a new group of perovskite-related manganites, $\text{Sr}_1-x\text{Ce}_x\text{MnO}_3$, was suggested for SOFC cathodes [5,6]. The parent compound, $\text{SrMnO}_3$, is hexagonal at temperatures below 1730 K and atmospheric oxygen pressure, and transforms into the perovskite polymorph on heating [78]. The hexagonal phase is essentially oxygen-stoichiometric in air below 1310 K, with $\delta \rightarrow 0$ and predominant tetravalent state of manganese cations [8]; as a result, the total conductivity is quite low, $0.5 \text{ S} \times \text{cm}^{-1}$ at 1273 K [5]. The partial substitution of cerium for strontium stabilizes the perovskite-type structure down to room temperature. The perovskite solid solution range in $\text{Sr}_1-x\text{Ce}_x\text{MnO}_3$ system corresponds to $0.1 \leq x \leq 0.35$ [5,9,10]. Cerium doping induces a shift in the manganese oxidation state from $4^+$ to $3^+$, which increases electronic transport. The highest total conductivity, $>300 \text{ S} \times \text{cm}^{-1}$ at 870–1070 K, was reported for $\text{Sr}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ [5]. In addition, $\text{Sr}_1-x\text{Ce}_x\text{MnO}_3$ exhibits a higher oxygen permeability with respect to $\text{La}_1-x\text{Sr}_x\text{MnO}_3$ [11]. The thermal expansion coefficients (TECs) of $\text{Sr}_1-x\text{Ce}_x\text{MnO}_3$, varying in the range $(10.1-12.4) \times 10^{-6}$ K$^{-1}$ [5,6,11], are compatible with those of commonly used solid electrolytes based on zirconia and ceria.

A promising combination of transport and physicochemical properties is also known for another attractive group of the SOFC electrode materials, $(\text{La},\text{Sr})(\text{Mn,Cr})_2\text{O}_3$ perovskites [12–16]. These are characterized with a high thermodynamic and dimensional stability under both cathodic and anodic conditions, provided by the presence of chromium cations with relatively stable oxidation state. Other advantages include a substantial electrocatalytic activity in oxidizing and reducing atmospheres, moderate TECs, and chemical compatibility with various solid electrolytes [12–16]. The performance of $(\text{La},\text{Sr})(\text{Mn,Cr})_2\text{O}_3$ electrodes is, however, strongly affected by the electronic transport-related processes associated with insufficient level of the total conductivity [16].
The present work was centered on the studies of electronic conduction, oxygen permeability, thermal and chemical expansion, phase stability and electrochemical activity of perovskite-type $\text{Sr}_{10-2x} \text{Ce}_x \text{Mn}_1-y \text{Cr}_y \text{O}_{3+x}$ ($y = 0 - 0.5$). As creation of A-site cation vacancies in LSM leads often to improved electrode performance [17], emphasis was also given to cation-deficient ($\text{Sr}_{10-2x} \text{Ce}_x$)$_3$$_{1-y}$$\text{Mn}_1-y$$\text{Cr}_y$$\text{O}_{3+x}$ ($x = 0 - 0.05$). The cathodic behavior of porous $\text{Sr}_{0.7} \text{Ce}_{0.3} \text{Mn}_0.5 \text{Cr}_0.5 \text{O}_3$ was evaluated in contact with two silicate-based solid electrolytes with apatite structure, namely $\text{La}_{10-3x} \text{Si}_x \text{Al}_{20-5x} \text{O}_{33+x}$ [18] and $\text{La}_{9.2} \text{Pr}_0.8 \text{Si}_{4.5} \text{Fe}_{1.2} \text{O}_{33+x}$ [19]. The electrolytes based on apatite-type $\text{La}_{10-3x}(\text{SiO}_4)_{6+x}$ may provide serious advantages for practical applications due to relatively low costs [20]; information on their performance in high-temperature electrochemical cells is, however, very scarce.

2. Experimental

The powders of ($\text{Sr}_{0.7} \text{Ce}_{0.3}$)$_{1-y}$$\text{Mn}_{1-y}$$\text{Cr}_y$$\text{O}_{3+x}$ ($x = 0 - 0.05$, $y = 0 - 0.5$) were synthesized by the glycine-nitrate process (GNP), a self-combustion technique using metal nitrates as oxidant and glycine as a fuel and chelating agent [21]. In the course of GNP, aqueous glycine-nitrate solutions containing metal cations in the stoichiometric proportions were heated until auto-ignition. The foam-like products were ground and annealed in air at 1173 K for 2 h in order to remove organic residues. Dense ceramic samples were pressed uniaxially at 350–400 MPa and sintered in air for 5 h; the sintering temperatures are listed in Table 1. Gas-tightness of the ceramic samples was verified by testing under the total pressure gradient of 2–3 atm at room temperature. After sintering and polishing, all materials were annealed at 1273 K for 2 h and slowly (2 K/min) cooled in order to achieve equilibrium with air at low temperatures.

X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-8 diffractometer ($\text{CuK}_{\alpha}$, $2\theta = 5–105^\circ$, step 0.02°) at room temperature. Rietveld analysis of the diffraction data was performed using Fullprof software [22]. A Hitachi S-4100 scanning electron microscope (SEM) with a Rontec UHV Detection system for energy dispersive spectroscopy (EDS) was used for microstructural studies. Thermogravimetric analysis (TGA, Setaram SetSys 16/18, sensitivity 0.4 µg, sample weight of 0.7–1.0 g) was performed on heating and cooling in a flow of dried air at 2 K/min. The dilatometric studies were carried out using a vertical Linseis L75 instrument in air and in flowing Ar–O$_2$ and CO–O$_2$ gas mixtures where the oxygen partial pressure, $p$(O$_2$), was controlled by an electrochemical oxygen pump and a sensor; description of the experimental set-up and technique was published earlier [23]. The measurements of total conductivity ($\sigma$, 4-probe DC) and Seebeck coefficient ($\alpha$) as function of temperature and oxygen partial pressure were performed at 573–1223 K in the $p$(O$_2$) range $10^{-2}$ to 0.3 atm, as described elsewhere [24]. The criteria for equilibration after a change in either oxygen pressure or temperature included the relaxation rates of the conductivity and Seebeck coefficient less than 0.01%/min and 0.001 V/(K×min), respectively. The steady-state oxygen permeation fluxes ($j$) through dense ceramic membranes were measured at 1123–1248 K as reported in Ref. [25]. For all data presented in this work, the oxygen partial pressure at the membrane feed side ($p$(O$_2$)) was equal to 0.21 atm; the membrane thickness ($d$) varied from 0.60 to 1.00 mm.

Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_{\text{anneal}}$, K</th>
<th>Relative density, %</th>
<th>Average thermal expansion coefficients ($\Delta T_{0.03}$)</th>
<th>Activation energy for the total conductivity ($\Delta T_{0.03}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sr}<em>{0.7} \text{Ce}</em>{0.3} \text{Mn}_0.9 \text{Cr}_0.1 \text{O}_3$</td>
<td>1713</td>
<td>93.5</td>
<td>8.92</td>
<td>12.04</td>
</tr>
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<td>$\text{Sr}<em>{0.7} \text{Ce}</em>{0.3} \text{Mn}_0.8 \text{Cr}_0.2 \text{O}_3$</td>
<td>1733</td>
<td>94.0</td>
<td>9.33</td>
<td>12.16</td>
</tr>
<tr>
<td>$\text{Sr}<em>{0.7} \text{Ce}</em>{0.3} \text{Mn}_0.9 \text{Cr}_0.1 \text{O}_3$</td>
<td>1753</td>
<td>97.2</td>
<td>9.60</td>
<td>12.25</td>
</tr>
<tr>
<td>$\text{Sr}<em>{0.7} \text{Ce}</em>{0.3} \text{Mn}_0.8 \text{Cr}_0.2 \text{O}_3$</td>
<td>1773</td>
<td>96.2</td>
<td>9.72</td>
<td>12.31</td>
</tr>
<tr>
<td>$\text{Sr}<em>{0.7} \text{Ce}</em>{0.3} \text{Mn}_0.9 \text{Cr}_0.1 \text{O}_3$</td>
<td>1793</td>
<td>93.8</td>
<td>9.99</td>
<td>12.80</td>
</tr>
</tbody>
</table>

Fig. 1. Room-temperature XRD patterns of as-prepared $\text{Sr}_{0.7} \text{Ce}_{0.3} \text{Mn}_0.9 \text{Cr}_0.1 \text{O}_3$ (A) and $\text{Sr}_{0.7} \text{Ce}_{0.3} \text{Mn}_0.8 \text{Cr}_0.2 \text{O}_3$ (B), and reduced $\text{Sr}_{0.7} \text{Ce}_{0.3} \text{Mn}_0.9 \text{Cr}_0.1 \text{O}_3$ quenched after annealing at 1223 K and oxygen partial pressures of $2 \times 10^{-2}$ atm (C) and $2 \times 10^{-5}$ atm (D) during 24 h.
The steady-state electrode polarization was studied by the 3-electrode technique in cells with symmetrical working and counter electrodes (WE and CE), as reported elsewhere [16,26]; the cell configuration was selected according to Ref. [27]. The porous WEs (sheet density 13±1 mg/cm²) were made of as-prepared Sr₀.₇Ce₀.₃−
Mn₀.₉Cr₀.₁O₃−δ powder annealed in air at 1373–1473 K for 10 h, deposited onto dense La₁₀Si₅AlO₂₆.₅ and La₆.₈₃Pr₃Si₄.₅Fe₁.₅O₂₆+δ substrates, and then sintered at 1503 K for 2 h. The counter and reference electrodes, both made of porous Pt, were sintered at 1273 K for 0.5 h. The measurements were performed in the galvanostatic mode using an AUTOLAB PGSTAT302 instrument at 973–1073 K in atmospheric air. The values of ohmic and polarization resistances (R_{bulk} and R_η) were determined from the impedance spectra collected in the frequency range 10 mHz to 1 MHz. The relaxation times after a change in the working electrode potential were 30–70 min. The phase composition and microstructure of the electrode layers before and after electrochemical measurements were examined by XRD and SEM/EDS.

3. Results and discussion

3.1. General characterization

As expected, XRD analysis confirmed perovskite-type solid solution formation in the pseudobinary Sr₀.₇Ce₀.₃Mn₁−yCr⁺₉O₃−δ system at y=0–0.5. Two typical XRD patterns of as-prepared ceramic materials are shown in Fig. 1(A and B). The structure was identified as tetragonal (space group I₄/mcm), in agreement with literature data on the parent composition [5,6,10]. In the case of (Sr₀.₇Ce₀.₃)₁−xMn₁−yCr⁺₉O₃−δ (x=0.03–

![Fig. 2. SEM micrographs of polished (Sr₀.₇Ce₀.₃)₁−xMn₁−yCr⁺₉O₃−δ ceramics.](image-url)
segregation of significant amounts of Mn$_3$O$_4$ was observed. Also, the unit cell parameters of the A-site deficient compositions were found similar to parent Sr$_0.7$Ce$_0.3$MnO$_3$$_{−\delta}$ [10]. This indicates that, in contrast to LSM, the perovskite lattice of Sr$_0.7$Ce$_0.3$MnO$_3$$_{−\delta}$ is almost intolerant with respect to creation of A-site cation vacancies, justifying the limited attention dedicated to the electrical characterization of these materials.

The density of all ceramic materials was higher than 93% of their theoretical density calculated from XRD data (Table 1). SEM/EDS inspections confirmed the low porosity and homogeneous microstructure (Fig. 2). No traces of liquid phase formation at the grain boundaries were observed. The average grain size varied from 1–4 µm for (Sr$_0.7$Ce$_0.3$)$_{1−x}$Mn$_{1−y}$Cr$_y$O$_3$$_{−\delta}$ and Sr$_0.7$Ce$_0.3$Mn$_{0.9}$Cr$_{0.1}$O$_3$$_{−\delta}$ to 7–14 µm for Sr$_0.7$Ce$_0.3$Mn$_{0.5}$Cr$_{0.5}$O$_3$$_{−\delta}$ increasing with temperature necessary to sinter gas-tight ceramics.

The dilatometric curves of (Sr$_0.7$Ce$_0.3$)$_{1−x}$Mn$_{1−y}$Cr$_y$O$_3$$_{−\delta}$ ceramics in air exhibit a non-linear behavior at 300–1370 K (Fig. 3A); the TEC values increase with temperature (Table 1). While the average TECs of (Sr$_0.7$Ce$_0.3$)$_{1−x}$MnO$_3$$_{−\delta}$ are close to that of the parent material ($\alpha$=11.8×10$^{-6}$ K$^{−1}$ at 460–1100 K [28]), doping with chromium leads to a higher thermal expansion. At the same time, for all studied materials the variations of oxygen nonstoichiometry ($\delta$) on heating in air are lower than 0.003 atoms per formula unit in the temperature range 573–1273 K and tend to decrease with chromium additions (Fig. 3B). The non-linear expansion cannot be, hence, ascribed to oxygen losses from the perovskite lattice. This type of behavior may be associated with progressive disproportionation of trivalent manganese cations and shifting equilibrium between the Mn$^{3+}$/4+ and Cr$^{3+}$/4+ redox couples on heating, as for (La$_{0.75}$Sr$_{0.25}$)$_{0.95}$Mn$_{0.5}$Cr$_{0.5}$O$_3$$_{−\delta}$ [16].

Another important factor relates to the phase transition characteristic of Sr$_0.7$Ce$_0.3$MnO$_3$$_{−\delta}$ [6], where the perovskite structure transforms from tetragonal into cubic at approximately 873 K [6]. Whatever the mechanisms, the TECs of Sr$_0.7$Ce$_0.3$Mn$_{1−y}$Cr$_y$O$_3$$_{−\delta}$ in the intermediate-temperature range are compatible with those of apatite-type solid electrolytes [18,19].

The chemically-induced expansion of Sr$_0.7$Ce$_0.3$Mn$_{1−y}$Cr$_y$O$_3$$_{−\delta}$ on reducing $p$(O$_2$) down to $6×10^{-4}$ atm is almost negligible, less than 0.07% at $y$=0.1 and 1223 K (Table 2). This suggests that moderate cathodic polarization under oxidizing conditions may not induce
considerable stresses in the electrode layer due to changing oxygen chemical potential. The chemical expansion decreases on cooling as the oxygen stoichiometry variations become smaller. In reducing atmospheres, however, increasing \( \delta \) and the corresponding changes in the variable-valence cation radii result in a larger expansion, 0.45–0.69% with respect to atmospheric oxygen pressure at 1023–1223 K. These values are substantially higher compared to \( \text{LaMnO}_3 \)- and \( \text{LaCrO}_3 \)-based materials under similar conditions [16,29,30]. Although Cr doping suppresses chemical expansion, this effect seems rather insufficient. Any exposure of \( \text{Sr}_{0.7}\text{Ce}_{0.3}\text{MnO}_3 \)-based electrodes to reducing atmospheres may lead, therefore, to significant mechanical stresses and cracking.

### 3.2. Electronic transport

The total conductivity of \( \text{Sr}_{0.7}\text{Ce}_{0.3}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3 \), Fig. 4, is predominantly electronic. For all studied materials, the ionic contribution estimated from the oxygen permeation data is lower than 0.003% at 1298 K and atmospheric oxygen pressure, and further decreases on cooling. The conductivity of A-site cation-deficient compositions \( x=0.03–0.05 \) is very similar to that of the parent material, as expected. The substitution of chromium for manganese results in a gradual decrease of the electronic transport and in higher activation energy \( (E_a, \text{Table 1}) \). Again, analogous behavior is known for \( \{\text{La,Sr}\}(\text{Mn,Cr})\text{O}_3 \) [31]. All Cr-containing phases display a semiconducting behavior in the studied temperature range (Fig. 4); for the materials with \( y \geq 0.2 \), an increase in the \( E_a \) values is observed above approximately 820 K. As for thermal expansion, this phenomenon may originate from shifting redox equilibrium between the manganese and chromium cations at elevated temperatures [16].

When analyzing the electrical properties vs. oxygen partial pressure, one should note that the conductivity of \( \text{Sr}_{0.7}\text{Ce}_{0.3}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3-(x=0.1-0.2) \) decreases with reducing \( p(\text{O}_2) \) at 1123–1223 K, but the corresponding changes are modest (Fig. 5). The values of \( \sigma \) become essentially \( p(\text{O}_2) \)-independent at lower temperatures and at higher chromium concentrations. The Seebeck coefficient is almost constant under oxidizing conditions, decreasing weakly when temperature increases; Cr doping raises the thermopower from negative to minor positive values (Figs. 6 and 7A).

These trends are primarily associated with the very low deviations from oxygen stoichiometry at the oxygen partial pressures close to atmospheric (Fig. 3B). As a result, the concentration of electronic charge carriers governed by the Mn:Cr ratio and temperature, is

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**Fig. 5.** Oxygen partial pressure dependencies of the total conductivity of \( \text{Sr}_{0.7}\text{Ce}_{0.3}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3 \)-under oxidizing conditions.

**Fig. 6.** Oxygen partial pressure dependencies of the Seebeck coefficient of \( \text{Sr}_{0.7}\text{Ce}_{0.3}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3 \)-under oxidizing conditions.
almost independent of the oxygen chemical potential. In the case of parent $\text{Sr}_0.7\text{Ce}_0.3\text{MnO}_3-\delta$, the electronic conduction is presumably $p$-type and occurs via a broadband mechanism, whilst the relative hole concentration ($p$) is higher than a half of the number of states ($N$), leading to negative thermopower [28]. Consequently, the doping-induced changes in the conductivity and Seebeck coefficient of $\text{Sr}_0.7\text{Ce}_0.3\text{Mn}_{1-y}\text{Cr}_y\text{O}_3-\delta$ may be interpreted in terms of strong trapping of electron-holes by chromium cations, which appear essentially excluded from the electronic transport processes; this causes progressive localization of $p$-type electronic charge carriers and decreases their concentration. For instance, Fig. 7(B) presents the $(p/N)$ ratio estimated from the Seebeck coefficient by the Heikes formula [32], neglecting transported heat of the electronic charge carriers and spin-degeneracy effects. This quantity tends to increase with temperature, which reflects the growing tendencies to disproportionation and shifting redox equilibrium between the variable-valence cations as mentioned above. Increasing chromium concentration results in a drastic decrease of the estimated $(p/N)$ ratio. Taking into account the crystal electroneutrality condition and very low oxygen nonstoichiometry under oxidizing conditions [Fig. 3(B)], the latter trend clearly indicates that Cr cations have a higher average valency with respect to Mn, but may only act as hole traps without any significant contribution to the electronic conduction. These hypotheses were further validated by the estimations of hole mobility ($\mu_p$, Fig. 7(C)) calculated assuming that the transport is only governed by manganese cations. In the case of $\text{Sr}_0.7\text{Ce}_0.3\text{Mn}_{0.9}\text{Cr}_{0.1}\text{O}_3-\delta$, the $\mu_p$ values are almost temperature-independent and are higher than 0.1 $\text{cm}^2\text{s}^{-1}\text{V}^{-1}$, the characteristic threshold considered to separate small-polaron and broadband conduction. When chromium content increases up to 50%, the mobility decreases and becomes thermally-activated, thus confirming transition to an essentially localized state of the $p$-type electronic charge carriers.

Fig. 7. Temperature dependence of the Seebeck coefficient (A), $p/N$ ratio (B) and mobility of $p$-type electronic charge carriers (C) in $\text{Sr}_0.7\text{Ce}_0.3\text{Mn}_{1-y}\text{Cr}_y\text{O}_3-\delta$ at $p(\text{O}_2)=10^{-2}$ atm.

Fig. 8. Oxygen partial pressure dependence of the total conductivity (A) and Seebeck coefficient (B) of $\text{Sr}_0.7\text{Ce}_0.3\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3-\delta$ in a wide $p(\text{O}_2)$ range.

Fig. 9. Oxygen permeation fluxes and specific oxygen permeability of $\text{Sr}_0.7\text{Ce}_0.3\text{Mn}_{0.7}\text{Cr}_{0.3}\text{O}_3-\delta$ membranes with different thickness vs. oxygen partial pressure gradient at 1248 K. The inset shows ambipolar conductivity estimated by Eq. (2).
The variations of electrical properties in moderately reducing atmospheres, illustrated by Fig. 8, are qualitatively similar to those in (La,Sr)MnO$_{3-\delta}$ and (La,Sr)CrO$_{3-\delta}$ systems [17,33]. In particular, these data show a predominant role of $p$-type electronic conduction in the whole $p$(O$_2$) range where the perovskite-type phases exist. The low-$p$(O$_2$) stability limits of Sr$_{0.7}$Ce$_{0.3}$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ are briefly discussed below.

3.3. Oxygen permeability

The oxygen transport through dense Sr$_{0.7}$Ce$_{0.3}$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ membranes was found limited by both bulk ionic conduction and surface exchange kinetics, as for undoped Sr$_{0.7}$Ce$_{0.3}$MnO$_{3-\delta}$ [11]. For example, Fig. 9 presents the data on oxygen permeation fluxes and specific permeability, $J$(O$_2$) (mol×s$^{-1}$×cm$^{-2}$), for two Sr$_{0.7}$Ce$_{0.3}$Mn$_{0.7}$Cr$_{0.3}$O$_{3-\delta}$ membranes with different thickness. The permeability was calculated as [25]:

$$J(O_2) = j \times d \left( \ln \frac{p_2}{p_1} \right)^{-1}$$

(1)

where $p_1$ is the permeate-side oxygen partial pressure. Increasing membrane thickness leads to lower oxygen fluxes, whereas the specific permeability proportional to $j \times d$ increases due to a decreasing role of the surface exchange processes. In these conditions, the bulk ionic conductivity ($\sigma_O$) can be estimated calculating the average ambipolar conductivity ($\sigma_{amb}$) by the approximate relationship [28]

$$\ln \left( \frac{p_2}{p_1} \right) = \frac{16F^2}{RT \sigma_{amb}} d + \left( \frac{k_{ex}^f}{k_{ex}^p} - 1 \right)$$

(2)

where the permeation data for at least two membranes with different thickness are required, $k_{ex}$ is the exchange coefficient, and the superscripts $f$ and $p$ denote the feed and permeate sides, respectively. This simplified model makes it possible to calculate two parameters, $\sigma_{amb}$ and $\left( \frac{k_{ex}^f}{k_{ex}^p} - 1 \right)$, from the oxygen fluxes through two membranes with different thicknesses under a given oxygen pressure gradient. The basic assumptions used to derive Eq. (2) are that the surface exchange coefficients depend primarily on the oxygen chemical potential in the gas phase, whilst the average ambipolar conductivity values in the membranes placed under the same $p$(O$_2$) gradient are similar.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J \times 10^{10}$, mol×s$^{-1}$×cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($d=1.00$ mm, $p_2=0.21$ atm, $p_1=0.021$ atm)</td>
</tr>
<tr>
<td>Membrane 1</td>
<td>12.2</td>
</tr>
<tr>
<td>Membrane 2</td>
<td>13.9</td>
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Fig. 10. Temperature dependence of the oxygen permeation fluxes through (Sr$_{0.7}$Ce$_{0.3}$)$_{1-x}$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ membranes under fixed oxygen pressure gradient. The data on other electrode materials, including Sr$_{0.7}$Ce$_{0.3}$MnO$_{3-\delta}$ [11], La$_{0.75}$Sr$_{0.25}$MnO$_{3-\delta}$ [34], (La$_{0.75}$Sr$_{0.25}$)$_{1.5}$Mn$_{1.5}$Cr$_{0.5}$O$_{3-\delta}$ [16] and La$_{0.75}$Sr$_{0.25}$Fe$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ [34], are shown for comparison.

Fig. 11. Example illustrating determination of the low-$p$(O$_2$) phase stability boundary from the data on electrical properties, for Sr$_{0.7}$Ce$_{0.3}$Mn$_{0.7}$Cr$_{0.3}$O$_{3-\delta}$ at 1223 K.

Fig. 12. Low-$p$(O$_2$) phase stability limits of Sr$_{0.7}$Ce$_{0.3}$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$. The phase boundaries of Mn$_2$O$_3$ [38] and LaMnO$_{3-\delta}$ [39], and two iso-composition lines for CeO$_{2-\delta}$ [40] are shown for comparison.
gradient are essentially similar [28]. Such simplifications lead to a serious uncertainty when the transport properties are strongly dependent of the oxygen nonstoichiometry, but enable to assess critical parameters determining oxygen transport. Typical results of these estimations are presented in the inset of Fig. 9. As the ambipolar conductivity is more than $10^4$ times lower than the total conductivity (Fig. 5), $\sigma_{\text{amb}} \approx \sigma_O$. The ionic transport increases with increasing oxygen partial pressure gradient, showing that oxygen diffusion in the membrane bulk is limited by the low vacancy concentration.

Fig. 10 displays the temperature dependence of oxygen permeation fluxes through $\text{Sr}_{0.7}\text{Ce}_{0.3}\text{Mn}_{1-y}\text{Cr}_y\text{O}_3-\delta$ ceramics under fixed oxygen chemical potential gradient. All studied materials are characterized with an essentially similar level of the specific oxygen permeability, $(3\text{–}9) \times 10^{-10}$ mol s$^{-1}$ cm$^{-2}$ at 1223 K. This level is lower compared to (La,Sr)(Fe,Co)O$_3$–$\delta$ perovskites, but is considerably higher with respect to most manganite- and chromite-based systems, such as (La,Sr)MnO$_3$–$\delta$ and (La,Sr)(Mn,Cr)O$_3$–$\delta$ [16,34–37]. The latter feature may provide significant advantages for the electrode applications. Minor doping with chromium has no considerable effects on the oxygen permeability. When chromium content in the B-sublattice of $\text{Sr}_{0.7}\text{Ce}_{0.3}\text{Mn}_{1-y}\text{Cr}_y\text{O}_3-\delta$ increases up to 30%, a slight decrease in the permeation fluxes is observed. Such behavior results from decreasing oxygen deficiency (Fig. 3B) and increasing metal-oxygen bonding energy; in particular, the oxygen-vacancy diffusion coefficients in perovskite chromites are typically low if compared to manganite analogues [35]. An anomalous increase
in the oxygen transport was found, however, on further doping (Fig. 10). Note that the permeation fluxes through Sr$_0.7$Ce$_0.3$Mn$_0.9$Cr$_{0.1}$O$_{3-\delta}$ exhibit a relatively good reproducibility within the limits of experimental uncertainty (Table 3). Additional studies are necessary to identify exact mechanisms responsible for increasing oxygen permeability. As a hypothesis, one may suggest that this phenomenon is associated with a greater contribution of grain-boundary diffusion characteristic of LaCrO$_3$-based ceramics under oxidizing conditions (e.g. [36,37] and references cited).

3.4. Decomposition in reducing atmospheres

The phase stability limits of Sr$_0.7$Ce$_0.3$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ ceramics at reduced oxygen chemical potentials were evaluated from the p(O$_2$)-dependencies of electrical properties as illustrated by Fig. 11. The oxygen partial pressure, at which the perovskite decomposition processes begin and the total conductivity and Seebeck coefficient start to deviate from plateau-like behavior, was considered as phase boundary at a given temperature; further reduction leads to a sharp irreversible drop of the conductivity and to rising thermopower. These limits were validated by XRD analysis. While the tetragonal perovskite structure is preserved after annealing at the oxygen chemical potentials slightly higher than the stability boundary (Fig. 1C), formation of multiphase mixtures containing Sr$_2$MnO$_4$ and CeCrO$_3$ and MnO was observed after reduction at lower p(O$_2$), Fig. 1(D).

Fig. 12 compares the approximate phase stability boundaries of Sr$_0.7$Ce$_0.3$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ with literature data on Mn$_3$O$_4$ [38] and LaMnO$_3$ [39]; two iso-compositional lines of CeO$_2$ [40] are also given for comparison. The results show that the stability of perovskite-type Sr$_x$Ce$_y$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ in reducing atmospheres is essentially independent of the dopant content. In fact, the decomposition of Sr$_0.7$Ce$_0.3$Mn$_2$O$_{3-y}$CeCrO$_3$ occurs even at slightly higher oxygen chemical potentials with respect to the materials with y=0.1–0.2. Comparison of these data and CeO$_2$ iso-nonstoichiometry lines suggests that any possible changes in cerium oxidation state within the stability domain of Sr$_2$CeO$_3$(Mn,Cr)O$_{3-\delta}$ should be minor. The decomposition of Sr$_2$CeO$_3$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ is therefore related to changing manganese oxidation state on reduction, as for LaMnO$_{3-\delta}$. The formation of substantial amounts of Mn$^{2+}$ and oxygen vacancies leads to excessive stresses in the perovskite lattice and, then, in structural collapse. This situation and, most likely, phase decomposition mechanism differ from those in (La,Sr)(Mn,Cr)O$_3$ structural collapse. This situation and, most likely, phase decomposition with the oxygen permeability and ionic conductivity. For instance, the cathodic overpotentials of Sr$_0.7$Ce$_0.3$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ half-cells at 1073 K are 4–6 times higher than those of porous La$_{0.6}$Ni$_{0.3}$Ce$_{0.1}$O$_{3-\delta}$ electrodes in contact with the same solid electrolyte [26]. In the case of La$_{0.6}$Pr$_{0.4}$Si$_{1.5}$Fe$_{1.5}$O$_{3-\delta}$, electrolyte, the polarization was even higher. The latter difference can be partly related to the worse transport properties of La$_{0.6}$Pr$_{0.4}$Si$_{1.5}$Fe$_{1.5}$O$_{3-\delta}$ compared to La$_{0.6}$Si$_{1.5}$AlO$_{2.5}$ [18,19], as a general rule, the electrode polarization resistance increases with increasing electrolyte resistivity [41]. This effect may be further promoted by cathodic reduction of iron and praseodymium cations in La$_{0.6}$Pr$_{0.4}$Si$_{1.5}$Fe$_{1.5}$O$_{3-\delta}$, leading to a lower concentration of mobile oxygen interstitials in the apatite lattice and, thus, to lower ionic conduction [19].

At the same time, no tendencies to limiting currents are observed in the studied current density range (Fig. 14). Inspection of the impedance spectra (Fig. 15) reveals the presence of at least two contributions. Taking into account the surface-limited oxygen transport in Sr$_0.7$Ce$_0.3$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ and numerous literature data (e.g. [42] and references cited), the low-frequency process should be ascribed to the oxygen exchange reaction at the electrode surface, whilst the high-frequency electrode contribution can be assigned to impeded ion transfer at the electrode/electrolyte interface.

SEM analysis of the electrochemical cells after polarization measurements during 150–200 h demonstrated strong agglomeration of the electrode grains (Fig. 13C and D). This degradation may be associated with silica diffusion as indicated by EDS/TEM for La$_{0.6}$Ni$_{0.3}$Ce$_{0.1}$O$_{3-\delta}$ electrodes [26]. In the case of Sr$_0.7$Ce$_0.3$Mn$_0.9$Cr$_{0.1}$O$_{3-\delta}$, however, detection of SiO$_2$ traces on the surface of porous electrode was impossible due to overlapping of the Si and Sr peaks in EDS spectra. Nevertheless, the EDS studies unambiguously showed an important role of the cation interdiffusion between Sr$_0.7$Ce$_0.3$Mn$_{0.9}$Cr$_{0.1}$O$_{3-\delta}$ electrodes and apatite-type solid electrolytes. Fig. 16 presents one typical example of the EDS spectra, where substantial penetration of manganese and strontium into the surface layer of Sr$_0.7$Ce$_0.3$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ layers applied onto La$_{0.6}$Si$_{1.5}$AlO$_{2.5}$ and La$_{0.6}$Pr$_{0.4}$Si$_{1.5}$Fe$_{1.5}$O$_{3-\delta}$ solid electrolytes (A), and comparison of the cathodic and anodic polarization curves of Sr$_0.7$Ce$_0.3$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ electrode in contact with La$_{0.6}$Si$_{1.5}$AlO$_{2.5}$.

Fig. 14. Cathodic overpotentials of porous Sr$_0.7$Ce$_0.3$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ layers applied onto La$_{0.6}$Si$_{1.5}$AlO$_{2.5}$ and La$_{0.6}$Pr$_{0.4}$Si$_{1.5}$Fe$_{1.5}$O$_{3-\delta}$ solid electrolytes (A), and comparison of the cathodic and anodic polarization curves of Sr$_0.7$Ce$_0.3$Mn$_{1-y}$Cr$_y$O$_{3-\delta}$ electrode in contact with La$_{0.6}$Si$_{1.5}$AlO$_{2.5}$. 


2189
La$_{10}$Si$_5$AlO$_{26.5}$ and aluminum into Sr$_{0.7}$Ce$_{0.3}$Mn$_{0.9}$Cr$_{0.1}$O$_{3-\delta}$ is clearly visible. The introduction of Sr$^{2+}$ in the lanthanum sites of La$_{10}$Si$_5$AlO$_{26.5}$ decreases ionic conductivity due to lowering oxygen content [20]; an analogous negative effect on the electrode electronic conductivity may result from the Al$^{3+}$ incorporation [28]. Moreover, significant changes in the electrode composition near the solid-electrolyte surface (Fig. 16A) should induce partial decomposition of the perovskite phase and formation of blocking interlayers. The cation deficiency of La$_{6.83}$Pr$_3$Si$_4.5$Fe$_{1.5}$O$_{26+\delta}$apatite is expected to promote phase interaction. Irrespectively of the microscopic mechanisms relevant to microstructural degradation, the results indicate that the relatively high polarization resistance of Sr$_{0.7}$Ce$_{0.3}$Mn$_{0.9}$Cr$_{0.1}$O$_{3-\delta}$ cathodes in contact with the silicate-based electrolytes is contributed by cation interdiffusion between the cell components. As for LSM [1,2], this makes it necessary to decrease the cell fabrication and operation temperatures down to possible minimum, and/or to deposit protective interlayers.

The incorporation of transition metal cations into the electrolyte surface may cause significant differences in the anodic and cathodic performance of oxide electrodes [26]. Anodic polarization increases the oxygen chemical potentials both in the electrode and in the interfacial electrolyte layers, where a local increase of the oxygen-ion concentration is expected due to oxidation of the variable-valence cations. For the oxygen-hyperstoichiometric silicates where ionic transport is dominated by interstitial anions, the interfacial processes related to oxygen transfer and diffusion should hence be facilitated under anodic polarization and hampered due to cathodic reduction. Indeed, the anodic performance of Sr$_{0.7}$Ce$_{0.3}$Mn$_{0.9}$Cr$_{0.1}$O$_{3-\delta}$ is significantly better compared to cathodic (Fig. 14B).

On the other hand, increasing anodic current density is accompanied with irreversible degradation of the electrochemical cells due to formation of microcracks, reflected by rising ohmic resistance (Fig. 17); in cathodic conditions the ohmic losses were found essentially independent of current and time. The subsequent microstructural inspections revealed crack propagation and even local exfoliation of the electrolyte surface layer (Fig. 13E). Most likely, these effects originate from the volume contraction in Mn-enriched interlayer under anodic oxidation, when the average oxidation state of manganese cations increases and their radius becomes smaller. Sintering at elevated temperatures results in differential strain across the electrochemical cells since the TECs of apatite-type solid electrolytes [18,19] are moderately lower than those of Sr$_{0.7}$Ce$_{0.3}$Mn$_{0.9}$Cr$_{0.1}$O$_{3-\delta}$ (Table 1); further polarization-induced electrolyte contraction increases mechanical stresses leading to cracking.

4. Conclusions

The total conductivity, Seebeck coefficient, thermal and chemical expansions, and steady-state oxygen permeability of Sr$_{0.7}$Ce$_{0.3}$Mn$_{1-\gamma}$Cr$_{\gamma}$O$_{3-\delta}$ ($\gamma$=0–0.5) were studied in the oxygen partial pressure range 10$^{-16}$ to 0.3 atm at 600–1270 K. The conductivity of Sr$_{0.7}$Ce$_{0.3}$Mn$_{1-\gamma}$Cr$_{\gamma}$O$_{3-\delta}$, predominantly $p$-type electronic within the whole stability
domain of the tetragonal perovskite-type phases, decreases on doping due to strong hole trapping by chromium cations and progressive charge-carrier localization. The low-p(O$_2$) stability limits are essentially independent of the dopant content. The substitution of chromium for manganese decreases oxygen stoichiometry variations and suppresses chemical expansion on reducing p(O$_2$), but leads also to moderately higher TECs varying in the range (12.0–12.8)×10$^{-6}$ K$^{-1}$ at 550–950 K and (15.0–15.8)×10$^{-6}$ K$^{-1}$ at 950–1370 K. The oxygen permeability of dense Sr$_0.7$Ce$_0.3$Mn$_{1−x}$Cr$_x$O$_3$–δ membranes, determined by both exchange kinetics and bulk ionic diffusion limited by the low oxygen-vacancy concentration, is 10–30 times higher compared to (La,Sr)MnO$_3$. Porous Sr$_0.7$Ce$_0.3$Mn$_{0.9}$Cr$_{0.1}$O$_3$–δ electrodes in contact with apatite-type silicate electrolytes showed, however, a relatively poor performance, which may be partly associated with microstructural degradation and cation interdiffusion between the cell components. Contrary to (La,Sr)MnO$_3$, the perovskite lattice of Sr$_{0.7}$Ce$_{0.3}$Mn$_{1−x}$O$_3$–δ is almost intolerant with respect to A-site cation deficiency.

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