High-temperature transport properties, thermal expansion and cathodic performance of Ni-substituted LaSr$_2$Mn$_2$O$_{7-\delta}$

A.A. Yaremchenko$^a$, D.O. Bannikov$^{a,b}$, A.V. Kovalevsky$^{a,c}$, V.A. Cherepanov$^b$, V.V. Kharton$^{a,*}$

$^a$ Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
$^b$ Department of Chemistry, Ural State University, Lenin av. 51, Ekaterinburg 620083, Russia
$^c$ Materials Department, Flemish Institute for Technological Research (VITO), 2400 Mol, Belgium

A R T I C L E  I N F O

Article history:
Received 22 May 2008
Received in revised form
18 July 2008
Accepted 24 July 2008
Available online 9 August 2008

Keywords:
Ruddlesden–popper manganite
Mixed conductor
Oxygen permeability
Solid oxide fuel cell cathode
Seebeck coefficient
Thermal expansion

A B S T R A C T

The substitution of manganese with nickel in LaSr$_2$Mn$_2$O$_{7-\delta}$ where the solubility limit corresponds to approximately 25% Mn sites, enhances the Ruddlesden–Popper phase stability at elevated temperatures and atmospheric oxygen pressure. The total conductivity of LaSr$_2$Mn$_{2-y}$Ni$_y$O$_{7-\delta}$ ($y = 0–0.4$) decreases with nickel additions, whilst the average thermal expansion coefficients calculated from dilatometric data in the temperature range 300–1370 K increase from $(11.4–13.7) \times 10^{-5}$ K$^{-1}$ at $y = 0$ up to $(12.5–14.4) \times 10^{-5}$ K$^{-1}$ at $y = 0.4$. The conductivity and Seebeck coefficient of LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$, analyzed in the oxygen partial pressure range $10^{-18}$–0.3 atm at 600–1270 K, display that the electronic transport is n-type and occurs via a small polaron mechanism. Reductive decomposition is observed at the oxygen pressures close to Ni/NiO boundary, namely $2.3 \times 10^{-11}$ atm at 1223 K. Within the phase stability domain, the electronic transport properties are essentially $p$(O$_2$)-independent. The steady-state oxygen permeability of dense LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ membranes is higher than that of $(\text{La,Sr})\text{MnO}_3$ but lower if compared to perovskite-like $(\text{Sr,Ce})\text{MnO}_3$. Porous LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ cathodes in contact withapatite-type La$_{10}$Si$_5$Al$_6$O$_{26.5}$ solid electrolyte exhibit, however, a relatively poor electrochemical performance, partly associated with strong cation interdiffusion between the materials.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

Manganese-based Ruddlesden–Popper (RP) phases possess an attractive combination of structural, magnetic and electrical properties, including the colossal magnetoresistance (CMR) effect [1–15]. One potential application of these materials relates also to porous cathodes of solid oxide fuel cells (SOFCs), the alternative power generation systems enabling to increase energy conversion efficiency. Several RP manganites and nickelates were evaluated recently for possible use in the intermediate-temperature SOFCs operating at 870–1070 K [5,16]; the higher-order RP phases, with general formula $\mathrm{AnB}_{n+1}O_{3n+1}$, where $n = 2$ or 3, were suggested as promising cathode materials [16].

This work is focused on synthesis and characterization of LaSr$_2$Mn$_{2-x}$Ni$_x$O$_{7-\delta}$ system at elevated temperatures necessary for the fuel cell fabrication and operation. The parent compound, LaSr$_2$Mn$_2$O$_7$, has a layered $n = 2$ RP structure which can be described as a succession of perovskite bilayers alternating with rock-salt (LaSr)O sheets along the crystallographic c-axis. Since the first observations of CMR in bilayered manganites in 1990s [1], the crystal chemistry, electrical and magnetic properties of LaSr$_2$Mn$_2$O$_7$ and related oxide systems, La$_{2-x}$Sr$_{1+x}$Mn$_{2-y}$B$_y$O$_{7-\delta}$ (B—transition metal cation), were extensively studied at temperatures below 350 K (e.g. [6–15] and references cited). Information on the high-temperature properties of these materials is, however, almost absent. LaSr$_2$Mn$_2$O$_7$ was reported to be nearly oxygen-stoichiometric in air [10]. Due to equal concentrations of Mn$^{2+}$ and Mn$^{4+}$ cations, a highest conductivity level in the La$_{2-x}$Sr$_{1+x}$Mn$_{2-y}$B$_y$O$_{7-\delta}$ family can be expected for this compound. As the solubility of strontium and manganese cations in the corresponding sublattices of La$_3$Ni$_2$O$_7$ is very low [17,18], the present study was centered on the Mn-rich part of LaSr$_2$Mn$_{2-x}$Ni$_x$O$_{7-\delta}$ system. Taking into account the superior electrode behavior of numerous RP nickelates (e.g. [5]), doping of LaSr$_2$Mn$_2$O$_7$ with nickel might be expected to enhance the oxygen-ionic transport and electrochemical activity. Attention was also focused on other properties relevant for potential applications in SOFC cathodes, including the electronic conductivity, thermal expansion and phase stability. The cathodic performance of porous electrodes was evaluated in contact with La$_{10}$Si$_5$Al$_6$O$_{26.5}$ solid electrolyte [19]. The ionic conductors based onapatite-type La$_{10-x}$SiO$_x$O$_{26.5}$ may provide serious advantages for the intermediate-temperature SOFCs owing to a substantially high oxygen diffusivity and relatively low costs [20]; however, data on their behavior in high-temperature electrochemical cells are still scarce.
2. Experimental

Submicron powders of La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$ (y = 0–0.6) were prepared 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 dried and heated until auto-ignition. The foam-like products were ground, annealed in air at 1173 K for 2 h in order to remove organic residues, and then ball-milled. Ceramic samples were pressed uniaxially at 350–400 MPa and sintered in air at 1673–1823 K for 10–40 h. After sintering and polishing, all materials were annealed at 1273 K for 2 h and slowly (1–2 K/min) cooled down to room temperature in order to achieve equilibrium with atmospheric oxygen. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-B diffractometer (Cu Kα, 2θ = 10–100°, step 0.02°). A Hitachi S-4100 scanning electron microscope (SEM) with a Rontec UHV detection system for the energy dispersive spectroscopy (EDS) was used for microstructural studies. Thermogravimetric analysis (TGA, Setaram SetSys 16/18) was performed in a flow of dried air in continuous heating/cooling regime (2 K/min). The dilatometric studies were carried out using a vertical Linseis L75 instrument (accuracy ±2 μm, sample length of 10–12 mm) in air. General characterization of the ceramic materials included also determination of steady-state oxygen permeation fluxes (j) as function of temperature and oxygen partial pressure gradient, and measurements of the total conductivity (σ, 4-probe DC) and Seebeck coefficient (α). The equipment and experimental procedures used for materials characterization were described elsewhere ([119,22,23] and references therein). The electrical properties were studied at 600–1270 K in the oxygen partial pressure range 10$^{-15}$–0.3 atm; 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 0.05%/min and 0.001 μV/K/min, respectively. The investigations of steady-state electrode polarization were carried out by the 3-electrode technique in cells with symmetrical working and counter electrodes (WE and CE); the cell geometry was selected according to Ref. [24]. The porous WE (sheet density of 18.4 mg/cm²) were made of single-phase La$_{1+y}$Sr$_2$Mn$_{1+x}$Ni$_y$O$_{7-δ}$ powder annealed in air at 1423–1593 K for 40 h with several intermediate milling steps; the powder was suspended in ethanol and deposited onto dense La$_2$O$_3$Al$_2$O$_3$ substrates, followed by the final annealing step 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 processing conditions of La$_2$O$_3$Al$_2$O$_3$ electrolyte ceramics were described elsewhere [19]. The polarization experiments were carried out in the galvanostatic mode using an AUTOLAB PGSTAT302 instrument at 873–1073 K in atmospheric air. The values of the ohmic and polarization resistances were determined from the impedance spectra collected in the frequency range from 10 mHz to 1 MHz; the relaxation times after a change in the WE 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

XRD analysis of La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$ (y = 0–0.4) ceramics sintered at 1773 K in air, showed the formation of tetragonal Sr$_2$TiO$_4$-type structure (Figs. 1A, D and 2A). However, whilst La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$ is single-phase, XRD patterns of La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$ (y = 0–0.2) indicate the presence of secondary perovskite-type component. Longer sintering time at this temperature resulted only in a larger fraction of the perovskite phase impurity, as illustrated by Fig. 1B. Single-phase La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$ ceramics were only obtained after sintering at lower temperatures, such as 1723 K (Figs. 1C and E), insufficient to achieve density higher than 90% (Table 1). Attempts to prepare single-phase La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$ failed. The samples of this composition comprise a major perovskite phase after sintering at 1823 K (Fig. 2C), and melt at 1873 K. In addition to the Sr$_2$TiO$_4$-type solid solution, La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$ ceramics sintered at 1673–1773 K comprise also a KxNiF$_4$-type phase impurity (Figs. 2D–F); increasing the duration of thermal treatment has rather a negligible effect on the intensity of secondary phase reflections. Therefore, the solubility limit of nickel cations in La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$ at atmospheric oxygen pressure corresponds to approximately 25% manganite phases.

The crystal structure of La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$ (y = 0–0.4) was refined in I4/mmm space group. The substitution of manganite with nickel leads to a lattice contraction along the ab planes and to an expansion along the c-axis (Table 1). As a result, the unit cell volume decreases on doping. Due to an enhanced thermodynamic stability of the n = 2 RP phase containing 20% Ni at elevated temperatures which makes it possible to sinter gas-tight ceramic materials with density higher than 95% in air (Table 1), the maximum attention in this work was focused on La$_{1+y}$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-δ}$.
The dilatometric curves of LaSr$_2$Mn$_{2-y}$Ni$_y$O$_7$ ceramics in air are almost linear, but exhibit a tendency to increasing thermal expansion coefficients (TECs, $\bar{a}$) when temperature increases (Fig. 3). The average TECs vary from $(11.4\text{--}12.5) \times 10^{-6} \text{K}^{-1}$ at 300--900 K up to $(13.7\text{--}14.4) \times 10^{-6} \text{K}^{-1}$ at 900--1370 K (Table 2). Doping with nickel also leads to moderately higher thermal expansion which remains, however, still compatible with that of solid oxide electrolytes [20]. As there was no evidence of structural changes in the studied temperature range, the modest non-linearity of the RP lattice expansion might be associated with so-called chemical contribution originating from progressive oxygen losses on heating and the corresponding reduction of the transition metal cations, increasing their radii. At the same time, the variations of the oxygen content in LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_7$ at 570--1370 K are less than 0.015 atoms per formula unit at atmospheric oxygen pressure (Fig. 4). This suggests that the increase in TECs should be contributed by parallel inter-related processes in the manganese sublattice, such as thermally induced Mn$^{3+}$ disproportionation and shifting the equilibrium between Mn$^{3+}$/Mn$^{4+}$ and Ni$^{2+}$/Ni$^{3+}$ redox couples on heating, and/or by increasing anharmonicity of the atomic vibrations on doping. The low variations of Seebeck coefficient with temperature and the conductivity behavior, discussed below, may argue in favor

![Fig. 2. XRD patterns of as-prepared LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_7$-$\delta$ (A) and LaSr$_2$Mn$_{1.4}$Ni$_{0.6}$O$_7$-$\delta$ (C–F) ceramics sintered under different conditions, and LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_7$-$\delta$ ceramics after the measurements of electrical properties in reducing atmospheres and subsequent re-oxidation (B).]

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sintering conditions</th>
<th>$\rho_{\text{exp}}$ (g cm$^{-3}$)</th>
<th>$\rho_{\text{exp}}/\rho_{\text{theor}}$ (%)</th>
<th>Unit cell parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$a$ (Å)</td>
</tr>
<tr>
<td>LaSr$<em>2$Mn$</em>{2-y}$Ni$_y$O$_7$-$\delta$</td>
<td>1723 K/20 h</td>
<td>3.92</td>
<td>66.3</td>
<td>3.878(1)</td>
</tr>
<tr>
<td>LaSr$<em>2$Mn$</em>{1.8}$Ni$_{0.2}$O$_7$-$\delta$</td>
<td>1723 K/20 h</td>
<td>4.95</td>
<td>83.1</td>
<td>3.864(1)</td>
</tr>
<tr>
<td>LaSr$<em>2$Mn$</em>{1.6}$Ni$_{0.4}$O$_7$-$\delta$</td>
<td>1773 K/10 h</td>
<td>5.70</td>
<td>95.1</td>
<td>3.850(2)</td>
</tr>
</tbody>
</table>

Note: $\rho_{\text{exp}}$ and $\rho_{\text{theor}}$ are the experimental density and theoretical density calculated from the XRD data, respectively.
La0.6Sr1.4MnO4 that of perovskite-type La0.5Sr0.5MnO3 than \( \frac{2}{C2} \). The conductivity values of all single-phase La2Sr2Mn2O7 at 650–1000 K [5].

It should also be mentioned that the electrical resistivity in other La2Sr2Mn2O7 series at 300–1073 K [5]). Hence, in contrast to the nickelate- and ferrite-based RP families [26], the activation energies are, however, similar for all title materials with pressures as low as 10\(^{-2} \) atm. Subsequent re-oxidation is accompanied with a large increase of the conductivity and to an increase of the average TECs of La2Sr2Mn2O7 ceramics in air. Literature data on La2Sr1.8Mn1.6Ni0.4O7 with \( \approx 54\% \) density [16] are shown for comparison.

The total conductivity of La2Sr2Mn2O7 ceramics is almost constant at fixed \( p(O_2) \) (Fig. 6). Also, the Seebeck coefficient is almost constant at \( p(O_2) \) (Fig. 7A). These trends reflect very minor changes of the oxygen nonstoichiometry at \( p(O_2) \) values close to atmospheric conditions, in agreement with thermogravimetric data (Fig. 4). The negative sign of thermopower indicates that the electronic transport is n-type. Neglecting the transported heat of electrons and spin degeneracy phenomena, the Seebeck coefficient can be expressed by Heikes formula [29]:

\[
a = -k_e \ln \left( \frac{N - n}{n} \right)
\]

where \( n \) and \( N \) are the concentration of electrons and the number of states, respectively. The \( n/N \) ratio estimated from the Seebeck coefficient data is 0.28–0.29 under oxidizing conditions (Fig. 7A). This value confirms that the conduction involves Mn\(^{3+}/Mn^{4+}\) pairs where Mn\(^{3+}\) can be considered as the electronic charge carriers localized on manganese cations, whereas Ni\(^{2+}/Ni^{3+}\) ions are essentially excluded from the transport processes; analysis of the relevant mechanisms can be found in literature (e.g., see [11–15] and references cited). The electron mobility (\( \mu_e \)) calculated assuming that the electronic conductivity is governed exclusively by manganese cations, exhibits a temperature-activated character with values typical for small polaron conductors, 0.040–0.055 cm\(^2\)/Vs at 973–1223 K (Fig. 7B).

The electrical properties of La2Sr2Mn1.6Ni0.4O7–\( \delta \) in moderately reducing conditions remain almost unchanged down to oxygen pressures as low as \( 10^{-10} \) atm at 1223 K (Fig. 8). Further reduction leads to a slow decrease of the conductivity and to an increase of thermopower, followed by abrupt conductivity drop below \( 10^{-12} \) atm. Subsequent re-oxidation is accompanied with a large

Fig. 4. Relative variations of the oxygen nonstoichiometry of La2Sr2Mn1.6Ni0.4O7–\( \delta \) in air, calculated from the thermogravimetric data.

Fig. 5. Total conductivity of La2Sr2Mn1.6Ni0.4O7–\( \delta \) ceramics in air. Literature data on La2Sr1.8Mn1.6Ni0.4O7–\( \delta \) is essentially \( p(O_2) \)-independent at 973–1223 K under oxidizing conditions, when the oxygen partial pressure is above \( 10^{-5} \) atm (Fig. 6). Also, the Seebeck coefficient is almost constant at fixed \( p(O_2) \) (Fig. 7A). These trends reflect very minor changes of the oxygen nonstoichiometry at \( p(O_2) \) values close to atmospheric conditions, in agreement with thermogravimetric data (Fig. 4). The negative sign of thermopower indicates that the electronic transport is n-type. Neglecting the transported heat of electrons and spin degeneracy phenomena, the Seebeck coefficient can be expressed by Heikes formula [29]:
hysteresis with two transitions visible in the $\sigma$ vs. $p(O_2)$ and $z$ vs. $p(O_2)$ curves; the initial values of conductivity and Seebeck coefficient cannot be reproduced after re-oxidation during 30–50 h. XRD inspection showed the appearance of small impurity peaks assigned to K$_2$NiF$_4$-type phase (Fig. 2B). The drastic decrease in the total conductivity results, hence, from phase decomposition occurring via separation of the $n = 1$ RP compound, as for La$_4$Ni$_2$O$_7$ [30]. The oxygen partial pressure, at which the electrical properties start to deviate from the plateau-like behavior, was considered as an approximate stability limit at the given temperature. The phase stability boundary of La$_2$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ corresponds to higher oxygen chemical potentials if compared to (La,Sr)MnO$_{3-\delta}$, and is similar to that of NiO (Table 3). At the same time, the reduction of Mn$_3$O$_4$ into MnO occurs at still higher $p(O_2)$ values. The decomposition of La$_2$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ is hence related to changing manganese and nickel oxidation state at the initial stage; increasing oxygen deficiency and formation of substantial amounts of Mn$^{2+}$ and Ni$^{2+}$ result in excessive stress in the lattice and collapse of the $n = 2$ RP structure, followed by nickel reduction into metal.

Selected results on the oxygen permeability of dense La$_2$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ membranes are presented in Figs. 9 and 10.

The dependencies of oxygen permeation flux on $p(O_2)$ gradient (Fig. 9) deviate from the Wagner-type behavior [34] described by the classical equation:

$$j = \frac{RT}{16F^2d} \frac{\sigma_n}{\sigma_e + \sigma_0} \ln \frac{p(O_2)}{p_1}$$

where so-called ambipolar conductivity, $\sigma_{amb}$, is determined by the partial ionic ($\sigma_0$) and electronic ($\sigma_e$) conductivities. Nonetheless, even the rough estimations of ion transference numbers by Eq. (2) unambiguously demonstrated that electronic contribution to the total conductivity of La$_2$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ is more than $10^4$ times higher than oxygen-ionic, thus showing that $\sigma_{amb} \approx \sigma_0$. The ionic transport in La$_2$Sr$_2$(Mn,Ni)$_2$O$_{7-\delta}$ ceramic bulk is expected to occur via the oxygen-vacancy diffusion in (MnO$_2$)$_2$ planes, and should increase with reducing $p(O_2)$ due to rising oxygen deficiency. The deviation from linear permeation flux dependencies on the oxygen chemical potential gradient may be attributed, therefore, to limiting effect of the oxygen surface exchange kinetics which typically increases on reducing $p(O_2)$ [34]. Whatever the microscopic mechanisms, the oxygen permeability of La$_2$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ (Fig. 10) is higher than that of (La,Sr)MnO$_{3-\delta}$ and (La,Sr)(Mn,Cr)O$_{3-\delta}$ perovskites [35,36] widely used for SOFC electrodes, but is lower compared to other cathode materials, such as (Sr,Sc)MnO$_{3-\delta}$ [37] or (La,Sr)(Fe,Co)O$_{3-\delta}$ (e.g. [35]). These relationships are primarily associated with higher oxygen-vacancy concentration in the latter perovskite compounds.

Fig. 11 illustrates typical microstructure of as-prepared porous La$_2$Sr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ layers applied onto La$_{10}$Sr$_5$AlO$_{26.5}$ electrolyte. The electrode morphology was quite uniform, with grain sizes in the range 0.4–1.8 μm. The cathodic polarization curves at atmospheric oxygen pressure are presented in Fig. 12A. No tendencies to limiting currents are observed in the studied overpotential range. Inspection of the impedance spectra (Fig. 13) reveals the presence of at least two contributions. Taking into account the trends displayed by the oxygen permeation fluxes through...
LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ and numerous literature data (e.g. [38–40] and references cited), the low-frequency process should be ascribed to rate-determining oxygen exchange reaction at the electrode surface, while the high-frequency electrode contribution can be assigned to impeded ion transfer at the electrode/electrolyte interface. Generally, the electrochemical activity of LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ is substantially lower compared to nickelate-based electrode materials, such as La$_2$Ni$_{0.8}$Cu$_{0.2}$O$_4^{+\delta}$ [39], in correlation with oxygen permeability (Table 4). For instance, the cathodic overpotential of LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$/La$_{10}$Si$_5$AlO$_{26.5}$ half-cell at 1073 K and current density of $-40$ mA/cm$^2$ (Fig. 12A) is about eight times larger than that of porous La$_2$Ni$_{0.8}$Cu$_{0.2}$O$_{4^{\delta}}$ applied onto the same electrolyte [39].

---

**Table 3**

Comparison of the low-$p$(O$_2$) stability limits of manganite- and nickelate-based phases

<table>
<thead>
<tr>
<th>Composition</th>
<th>T (K)</th>
<th>$p$(O$_2$) (atm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaSr$<em>2$Mn$</em>{1.6}$Ni$_{0.4}$O$_7$</td>
<td>1223</td>
<td>$2.3 \times 10^{-11}$</td>
<td>This work</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>1273</td>
<td>$1.2 \times 10^{-15}$</td>
<td>[31]</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_3$</td>
<td>1173</td>
<td>$4.2 \times 10^{-18}$</td>
<td>[31]</td>
</tr>
<tr>
<td>Mn$_3$O$_4$</td>
<td>1223</td>
<td>$6.6 \times 10^{-15}$</td>
<td>[32]</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$NiO$_4$</td>
<td>1223</td>
<td>$4.1 \times 10^{-8}$</td>
<td>[32]</td>
</tr>
<tr>
<td>La$_2$Ni$_3$O$_4$</td>
<td>1223</td>
<td>$8.0 \times 10^{-12}$</td>
<td>[32]</td>
</tr>
<tr>
<td>La$_2$MnO$_4$</td>
<td>1223</td>
<td>$6.3 \times 10^{-14}$</td>
<td>[33]</td>
</tr>
</tbody>
</table>

---

**Fig. 8.** Oxygen partial pressure dependence of the total conductivity (A) and Seebeck coefficient (B) of LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$, measured in a wide $p$(O$_2$) range on reduction and subsequent re-oxidation, at 1223 K. The arrows indicate the direction of oxygen pressure changes. The dotted line indicates approximate phase stability limit.

**Fig. 9.** Dependence of the oxygen permeation flux through a dense LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ membrane on the oxygen partial pressure gradient at 1248 and 1123 K.

**Fig. 10.** Temperature dependence of the oxygen permeation fluxes through LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ under fixed $p$(O$_2$) gradient. The data on other electrode materials, including La$_{0.5}$Sr$_{0.5}$MnO$_3$ [35], (La$_{0.75}$Sr$_{0.25}$)$_{0.95}$Mn$_0.5$Cr$_{0.5}$O$_3$ [36], Sr$_0.7$Ce$_{0.3}$MnO$_3$ [37] and La$_{0.5}$Sr$_{0.5}$Fe$_{0.5}$Co$_{0.5}$O$_3$ [35], are shown for comparison.
Another important factor, which may be responsible for the relatively poor performance of LaSr$_{2}$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$/C electrodes, relates to partial blocking of the electrochemical reaction zone by silica due to surface diffusion, as indicated by EDS/TEM for La$_2$Ni$_{0.8}$Cu$_{0.2}$O$_4$ electrodes [39]. In the case of LaSr$_{2}$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$/C electrodes, however, detection of SiO$_2$ traces on the surface was impossible due to overlapping of the Sr and Si peaks in EDS spectra. Nevertheless, EDS analysis of the electrolyte/electrode interfaces confirmed a critical role of cation interdiffusion between LaSr$_{2}$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$/C and La$_{10}$Si$_5$AlO$_{26.5}$ electrolyte. Fig. 14 presents one example of the EDS spectra, clearly showing a substantial penetration of strontium into the surface layers of La$_{10}$Si$_5$AlO$_{26.5}$ and Mn/Ni depletion in LaSr$_{2}$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$/C electrode near the interface. Notice that the introduction of Sr$^{2+}$ in the La$^{3+}$ sites of apatite-type La$_{10}$Si$_5$AlO$_{26.5}$ lattice decreases ionic conduction due to lowering the concentration of mobile interstitial oxygen anions [20]; as a general rule, the electrode polarization resistance increases with increasing electrolyte resistivity [38]. Moreover, significant changes in the electrode composition near the electrode/electrolyte interface (Fig. 14 A) should induce partial decomposition of the $n$ = 2 RP phase and formation of thin interlayers with low ionic conductivity. Irrespective of the nature of ion transfer-blocking phenomena, the results indicate that relatively high polarization resistance of LaSr$_{2}$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$/C cathodes in contact with lanthanum silicate-based electrolyte is contributed by fast cation interdiffusion between the electrochemical cell components. As for (La,Sr) MnO$_{2.3}$-based cathodes, this makes it necessary to decrease the cell fabrication and operation temperatures down to possible minimum and/or to deposit protective interlayers.

**Table 4**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$R_Z$ (Ohm cm$^2$)</th>
<th>$j^*$ (mol/s cm$^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaSr$<em>{2}$Mn$</em>{1.6}$Ni$<em>{0.4}$O$</em>{7-\delta}$/C</td>
<td>24</td>
<td>54</td>
<td>6.6 x 10$^{-11}$</td>
</tr>
<tr>
<td>La$<em>2$Ni$</em>{0.8}$Cu$_{0.2}$O$_4$</td>
<td>1.5</td>
<td>3.2</td>
<td>11.1</td>
</tr>
</tbody>
</table>

$^*$ $d$ = 1.00 mm, $p_2$ = 0.21 atm, $p_1$ = 0.021 atm.

The anodic performance of LaSr$_{2}$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$/C at atmospheric oxygen pressure is considerably better compared to cathodic performance (Figs. 12A and B). Such behavior seems to be in agreement with the interstitial oxygen diffusion mechanism in La$_{10}$Si$_5$AlO$_{26.5}$ [19,20], where the incorporation of transition metal cations from the manganite-based electrodes should promote...
the electron-transfer-related processes. The decomposition of LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ in reducing conditions is observed at the oxygen partial pressures close to Ni/NiO boundary, for example $\sim 2.3 \times 10^{-15}$ atm at 1223 K. The steady-state oxygen permeability of dense LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ membranes lies in the range typical for manganite-based electrode materials, such as perovskite-type ($\text{La}_2\text{Sr}_2\text{Mn}_3\text{O}_{7-\delta}$), ($\text{La}_2\text{Sr}_2\text{Mn}_2\text{Cr}_2\text{O}_{7-\delta}$) and ($\text{Sr}_2\text{Ce}_2\text{Mn}_3\text{O}_{7-\delta}$). Irrespective of considerably high electronic conductivity and significant oxygen permeability, porous LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ cathodes exhibit a relatively poor electrochemical performance in contact with apatite-type La$_{10}$Si$_5$AlO$_{26.5}$ Solid electrolyte, which may be partly associated with strong cation interdiffusion between the cell components.

4. Conclusions

The solubility of nickel cations in the $n = 2$ RP series LaSr$_2$Mn$_{2-y}$Ni$_y$O$_{7-\delta}$ corresponds to $y \approx 0.5$. Doping with nickel decreases the tetragonal unit cell volume and total conductivity, and moderately increases thermal expansion. The average TECs vary in the range $(11.4-12.5) \times 10^{-6}$ K$^{-1}$ at 300–900 K and $(13.7-14.4) \times 10^{-6}$ K$^{-1}$ at 900–1370 K in air. The total conductivity, Seebeck coefficient and oxygen permeability of LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ ceramics were studied in the oxygen partial pressure range $10^{-4}$–0.3 atm at 600–1270 K. The electrical properties are essentially $P$(O$_2$)-independent within the RP phase stability domain, reflecting almost negligible variations of the oxygen nonstoichiometry. The conductivity is predominantly n-type electronic, with oxygen-ionic contribution lower than 0.002% at 1248 K in air. The relatively low, temperature-activated mobility of electronic charge carriers suggests a small polaron conduction mechanism where nickel cations are substantially excluded from the electrode bulk and near the electrode/electrolyte interface (A), and La$_{10}$Si$_5$AlO$_{26.5}$ in the electrolyte bulk and near interface (B).

Fig. 14. Comparison of the EDS spectra of LaSr$_2$Mn$_{1.6}$Ni$_{0.4}$O$_{7-\delta}$ grains in the porous electrode bulk and near the electrode/electrolyte interface (A), and La$_{10}$Si$_5$AlO$_{26.5}$ in the electrolyte bulk and near interface (B).

Acknowledgments

This work was supported by the FCT, Portugal (Project PTDC/CTM/64357/2006), and by the Belgian Federal Science Policy foundation.

References