

$(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Mn}_{1-y}\text{Fe}_y)\text{O}_{3\pm\delta}$ oxides for ITSOFC cathode materials? Electrical and ionic transport properties

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Available online 1 April 2005

Abstract

The oxygen transport properties in $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Mn}_{1-y}\text{Fe}_y)\text{O}_{3\pm\delta}$ (LSMF) with various iron contents $y=0, 0.2, 0.5, 0.8$ and 1 were determined by the IEDP technique. Both oxygen diffusion and surface exchange coefficients were found to be greater for $y=0.8$ and 1 than those of LSM ($y=0$). Moreover, for $y \leq 0.5$, grain boundary diffusion was the rate limiting step especially at lower temperatures. Thus, in the LSMF perovskite materials, the oxygen diffusion via oxygen vacancies is enhanced by Fe. The LSMF electrical performances were measured by impedance spectroscopy. Compared to LSM and LSF ($y=1$), porous LSMF cathodes with $y=0.2-0.8$ exhibit poor electronic conductivity: Fe, by reducing the number of couples $\text{Mn}^{3+}/\text{Mn}^{4+}$, decreases the amount of available hopping sites, limiting the electrical conduction. For LSF, the charge disproportionation $\text{Fe}^{3+}/\text{Fe}^{5+}$ improves the electrical properties. In conclusion, only the LSMF compounds with $y \sim 1$ or 0 can be considered as good cathode materials for SOFC applications.

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Keywords: Electrical properties; Ionic conductivity; Perovskites; Fuel cells

1. Introduction

In order to improve the properties of solid oxide fuel cells (SOFCs) at 700°C , it is needed to better understand the factors limiting the cathodic performances and to optimize the cathode materials. One solution consists in using a mixed ionic electronic conductor to lower the cathode polarization. In this view, the electrical and ionic conductivities of the $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Mn}_{1-y}\text{Fe}_y)\text{O}_{3\pm\delta}$ perovskites (denoted LSMF) were investigated.¹ It can be expected that the substitution of Fe for Mn leads to the formation of high valence B-cation in the perovskite structure ABO_3 , i.e. Mn^{4+} and Fe^{4+} , and induces important modifications in its magnetic, transport and electrocatalytic properties. It is well known that various bulk and surface properties like metal–insulator transition, colossal magneto-resistance or catalytic activity of both Mn- and Co-based perovskites are due to the formation of

B^{4+} cation.² For instance, the presence of $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$ units gives rise to semiconductor–metal transition related to the double-exchange mechanism³. The present work aims at evaluating the prevailing role of Mn and Fe cations in the transport properties of LSMF by isotopic exchange depth profile (IEDP) technique and impedance spectroscopy.

2. Preparation and preliminary characterization of the LSMF compounds

The LSMF samples were synthesized by the glycine-nitrate process. Part of the samples was dry pressed and sintered at 1400°C for 4 h and finally polished. LSMF films of few hundred nanometers thick were deposited onto polycrystalline zirconia (YSZ) by dip-coating associated with sol–gel process. The Mössbauer spectroscopy revealed that, for $y=1$ (LSF), the complete substitution of Fe for Mn induces the formation of Fe^{5+} . The $\text{Fe}^{3+}/\text{Fe}^{5+}$ charge

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Table 1

Chemical formula and oxygen non-stoichiometry δ of $(\text{La}_{0.8}\text{Sr}_{0.2})\text{-(Mn}_{1-y}\text{Fe}_y)\text{O}_{3\pm\delta}$ determined by Mössbauer spectroscopy, ICP-AES analysis and chemical titration at low temperature (150 K or RT)

LSMF	Chemical formula	δ
22	$\text{La}_{0.800}^{3+}\text{Sr}_{0.182}^{2+}\text{Mn}_{0.518}^{3+}\text{Mn}_{0.305}^{4+}\text{Fe}_{0.195}^{3+}\text{O}_{3.084}$	+0.084
25	$\text{La}_{0.802}^{3+}\text{Sr}_{0.190}^{2+}\text{Mn}_{0.364}^{3+}\text{Mn}_{0.141}^{4+}\text{Fe}_{0.503}^{3+}\text{O}_{3.04}$	+0.04
28	$\text{La}_{0.797}^{3+}\text{Sr}_{0.189}^{2+}\text{Mn}_{0.161}^{3+}\text{Mn}_{0.045}^{4+}\text{Fe}_{0.808}^{3+}\text{O}_{2.992}$	-0.008
210	$\text{La}_{0.796}^{3+}\text{Sr}_{0.187}^{2+}\text{Fe}_{0.936}^{3+}\text{Fe}_{0.081}^{5+}\text{O}_{2.94}$	-0.06

The powders were treated at 800 °C under air during 60 h. The S.D. of cationic composition is $\pm 1\%$.

disproportionation is about 8%, as already reported.^{4,5} However, for LSMF with $y=0.2\text{--}0.8$, no tetravalent iron cation was identified in air involving that only the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couples were electronically active in the bulk.⁵ This study, supplemented by ICP-AES analysis and chemical titration, showed the existence of vacancies, cationic for the iron-poor compounds or anionic for the iron-rich ones (Table 1).

3. Impedance spectroscopy measurements

Complex impedance measurements were carried out in air between 400 and 1100 K. Symmetrical cells composed of porous LSMF electrodes deposited on both surfaces of a dense YSZ pellet were tested. These films had high surface area and complex microstructure, features close to those of the cathode material in the operating SOFC conditions. The samples were pressed between two platinum grids and the impedance diagrams were analyzed using the Z view software. Fig. 1 shows a typical impedance diagram recorded for LSMF with $y=0.5$. The low-frequency contribution was attributed to the cathode phenomena.⁶ The chord of the low-frequency circle, namely R_{LF} , characterizes the polarization resistance under zero dc current conditions.

Fig. 2 shows the Arrhenius plot of the normalized polarization resistance $R_{\text{pol}} = R_{\text{LF}}S/2$, where S is the electrode surface area. It can be observed that R_{pol} increases with iron content up to $y=0.8$ and then decreases.

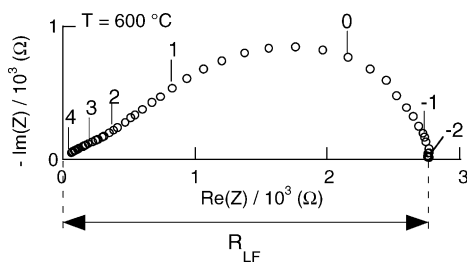


Fig. 1. Impedance diagram recorded on porous LSMF ($y=0.5$) at 600 °C in air. Numbers indicate the logarithm of the ac measuring frequency. The YSZ resistance has been subtracted.

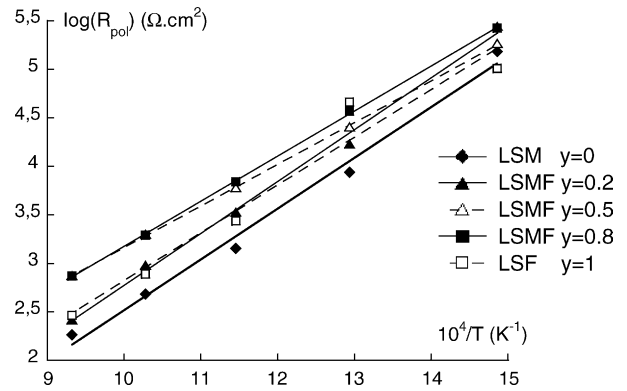


Fig. 2. Arrhenius plots of the polarization resistance of LSMF in air.

4. Oxygen diffusion and surface exchange processes

The oxygen diffusion coefficients were determined by SIMS depth profiling of the ^{18}O tracer after isotopic exchange. Densified and polished pellets, preannealed in ^{16}O were treated in ^{18}O (98%) between 973 and 1173 K. Two kinds of analyses were carried out according to the penetration depth of ^{18}O in LSMF: profilometry mode from the surface to the heart of the sample for penetration smaller than 5 μm or mapping of $^{16}\text{O}^-$ and $^{18}\text{O}^-$ ions over the cross section of the sample. Tracer diffusivities were determined by using the Crank equation:

$$C'(x, t) = \frac{C(x, t) - C_0}{C_S - C_0} = \text{erfc} \left(\frac{x\sqrt{D^*t}}{2} \right) - \exp \left(\frac{k}{D^*}x + \frac{k^2}{D^*}t \right) \text{erfc} \left(\frac{x\sqrt{D^*t}}{2} + \frac{k}{D^*}\sqrt{D^*t} \right) + A_{\text{gb}} \exp \left(-Z_{\text{gb}}x^{6/5} \right)$$

where $C'(x, t)$ is the ^{18}O isotopic concentration at the depth x , t is the exchange time (s), C_S is the ^{18}O concentration at the surface (98%), C_0 is the natural isotopic background level of ^{18}O (0.2%), D^* is the bulk ^{18}O diffusion coefficient, k is the ^{18}O surface exchange coefficient. A_{gb} and Z_{gb} are specific constants characterizing the grain boundary diffusion.

In Fig. 3a are represented the variations of D^* for the perovskite compound LSMF (this study), LSM [7] and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3\pm\delta}$ [8]. From these Arrhenius plots, it can be observed that the Fe substitution for Mn improves the oxygen diffusion coefficients, D^* . The D^* values recorded for LSF are similar to those determined for $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$, a well known mixed conductor⁸ (Fig. 3a). Moreover, the surface exchange coefficient of LSF is at least 150 times higher than for low iron contents (Fig. 4). The activation enthalpy for oxygen bulk diffusion as a function of the iron content (Fig. 3b) is related to the defect chemistry in the LSMF compounds. For $y=1$, the low value of ΔH_{D^*} reveals the facility of both formation of oxygen vacancies and incorporation of oxygen in this material.

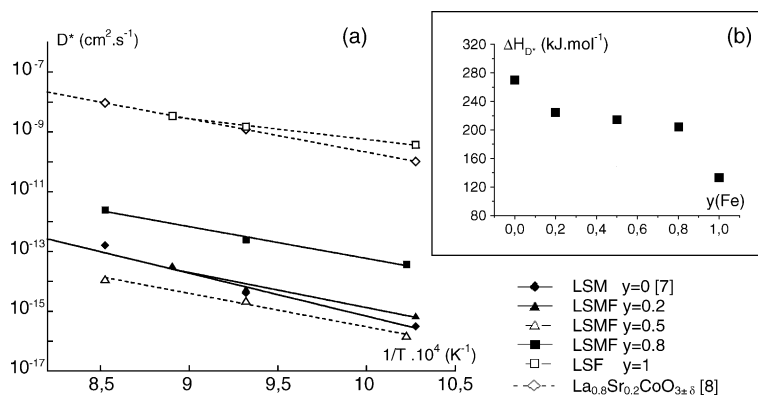


Fig. 3. (a) Arrhenius diagram of the bulk oxygen tracer diffusion for LSMF and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3\pm\delta}$. The experimental error is lower than 10% (estimated from several profiles obtained on the same sample). (b) Activation enthalpy for oxygen tracer diffusion in the bulk as a function of iron content.

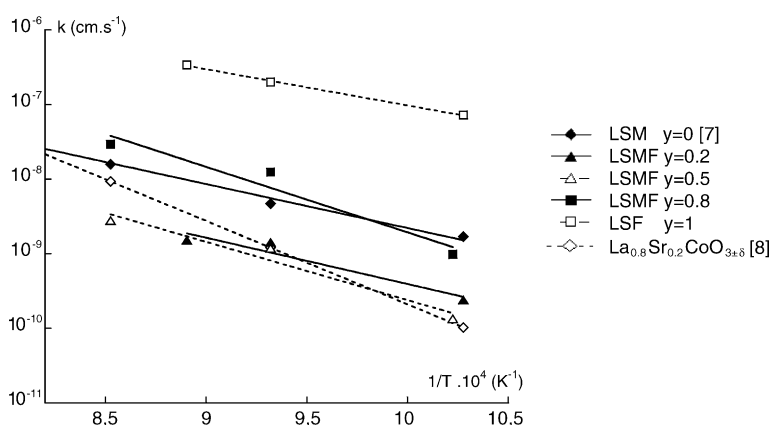


Fig. 4. Arrhenius diagram of the surface exchange coefficients for LSMF and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3\pm\delta}$.

From the extended tails of the oxygen depth profiles and using the Le Claire's equation,^{9,10} the role of the grain boundary diffusion can be characterized. The D_{gb}^* coefficients of LSMF with $y=0.2$ and 0.5 are reported in Fig. 5 in comparison with D^* , showing that, for iron-poor compositions, the

grain boundary diffusion coefficient is three orders of magnitude higher than the bulk diffusion one.

5. Conclusion

Doping with Fe decreases the $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$ units, and therefore the available hopping sites. The double exchange is reduced, limiting metallic conduction. Thus, when the bulk properties are considered, the LSMF compounds with $y \neq 1$ do not seem to be good materials as SOFC electrodes. For $y=1$, the charge disproportionation $\text{Fe}^{3+}/\text{Fe}^{5+}$ improves the electrical properties. Furthermore, comparison with ionic transport properties, shows that iron plays a key role in both oxygen diffusion and surface exchange processes. With iron content increasing ($y=0.8-1$), the concentration in oxygen vacancies increases, facilitating the oxygen diffusion via anionic vacancies. Thus, compared to (ferro)manganite perovskites, LSF ($y=1$) electrodes exhibit promising electrocatalytic properties in agreement with the values of the surface exchange coefficient, k . Consequently, a comparative study in working conditions of ITSOFCs after optimization of

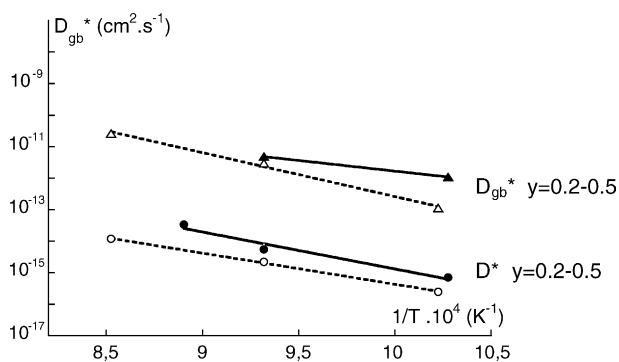


Fig. 5. Arrhenius diagram of oxygen diffusion coefficient in bulk (D^*) and grain boundaries (D_{gb}^*) for LSMF with $y=0.2$ (full markers) and 0.5 (empty markers).

the cathode microstructure for the compositions $y=1$ (LSF) and 0 (LSM) is in progress in order to test both electrical properties and reactivity with YSZ commonly used as solid electrolyte.

Acknowledgments

The authors gratefully acknowledge the contribution of CIRIMAT-LCMIE-Toulouse, Paul Sabatier University, France, for the thin films preparation. They also wish to thank, for their financial support, ADEME and EDF (Contract 0074023) and French CNRS and Regional Council of Burgundy [Grant number 1002972 to one of us (M.P.)].

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