

# **(La<sub>0.8</sub>Sr<sub>0.2</sub>)(Mn<sub>1-y</sub>Fe<sub>y</sub>)O<sub>3±δ</sub> Oxides for ITSOFC Cathode Materials ?**

## **Electrical and Ionic Transport Properties**

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### **Abstract**

The oxygen transport properties in (La<sub>0.8</sub>Sr<sub>0.2</sub>)(Mn<sub>1-y</sub>Fe<sub>y</sub>)O<sub>3±δ</sub> (LSMF) were determined by the IEDP technique. Both oxygen diffusion and surface exchange are improved for LSMF with y=0.8 and 1 compared with LSM (y=0). For y≤0.5, grain boundary diffusion is preponderant. Thus, in the LSMF perovskite materials, the oxygen diffusion *via* the 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 Mn<sup>3+</sup>/Mn<sup>4+</sup>, decreases the amount of available hopping sites, limiting the electrical conduction. For LSF, the charge disproportionation Fe<sup>3+</sup>/Fe<sup>5+</sup> improves the electrical properties. In conclusion, only the LSMF compounds with y~1 or 0 can be considered as good cathode materials for SOFC applications.

**Keywords** : Electrical properties, Ionic conductivity, Spectroscopy, Perovskites, Fuel cells.

### **1. Introduction**

In order to improve the properties of solid oxide fuel cells (SOFCs) at 700 °C, it is needful to better understand the factors limiting the cathode 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  $\text{ABO}_3$ , *i.e.*  $\text{Mn}^{4+}$  and  $\text{Fe}^{4+}$ , and induce 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  $\text{B}^{4+}$  cation [2]. For instance, the presence of  $\text{Mn}^{3+}$ -O- $\text{Mn}^{4+}$  units gives rise to semiconductor-metal transition related to the double-exchange mechanism [3]. The present work aims at evaluating the prevailing role of the 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 hours 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  $\text{Fe}^{5+}$ . However, for LSMF with  $y=0.2$ - $0.8$ , no  $\text{Fe}^{4+}$  exists in air and only the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  couples are electronically active [4]. 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.

## **3. Impedance spectroscopy measurements**

Complex impedance measurements were carried out under 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. The low-frequency contribution was attributed to the cathode phenomena [5]. The chord of the low-frequency circle, namely  $R_{LF}$ , characterizes the polarization resistance under zero dc current conditions.

Fig. 1 shows the Arrhenius plot of the polarization resistance  $R_{pol}$  obtained in these conditions.  $R_{pol}$  is normalized using the following relation :  $R_{pol}=R_{LF}S/2$ , where  $S/2$  is the half surface area as usually for symmetrical cells. It can be observed that  $R_{pol}$  increases with iron content increasing in a large temperature range except for  $y=1$ , pointing out that the electrical conductivity and electrochemical activity of LSM ( $y=0$ ) and LSF ( $y=1$ ) are promising.

#### 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  $\mu m$  or mapping of  $^{16}O^-$  and  $^{18}O^-$  ions over the cross section of the sample. Tracer diffusivities were determined by using the Crank equation :

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

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  $Z_{gb}$  characterize the grain boundary diffusion.

From the Arrhenius plots, it can be observed the Fe substitution for Mn improves the oxygen diffusion coefficients,  $D^*$ , and the surface exchange coefficients,  $k$ . Moreover, the iron-rich LSMF compounds exhibit good performances at 700 °C when compared with other mixed conductors  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  [6] (Fig. 2a). The same is true for  $k$ . The activation enthalpy for oxygen bulk diffusion as a function of the iron content (Fig. 2b) is related to the defect chemistry in the LSMF compounds. For  $y=1$ , the low value of  $\Delta H_{D^*}$  reveals the facility of both formation of oxygen vacancies and incorporation of oxygen in this material.

From the extended tails of the oxygen depth profiles and using the Le Claire's equation [8, 9], the role of the grain boundary diffusion can be characterized. The  $D_{\text{gb}}^*$  coefficients of LSMF with  $y \leq 0.5$  are reported in Fig. 3 in comparison with  $D^*$ , showing that, for iron-poor compositions, the grain boundaries oxygen diffusion is three orders of magnitude higher than the bulk diffusion.

## Conclusion

Doping with Fe decreases the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  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 the oxygen diffusion and surface reduction. With iron content increasing ( $y=0.8-1$ ), the concentration in oxygen vacancies increases, facilitating the oxygen diffusion *via* the 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, the compositions  $y=1$  (LSF) and 0 (LSM) were tested in working conditions of ITSOFCs after optimization of the cathode microstructure.

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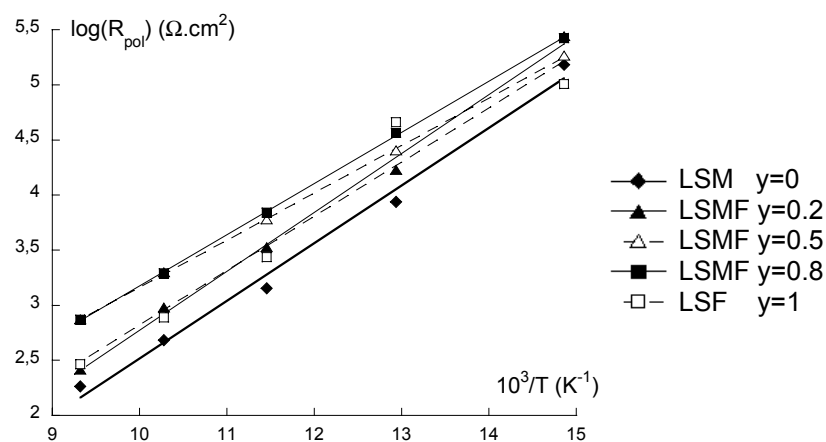


Fig. 1. Arrhenius plots of the polarization resistances of LSMF2Y obtained with symmetrical cells with porous cathodes under air.

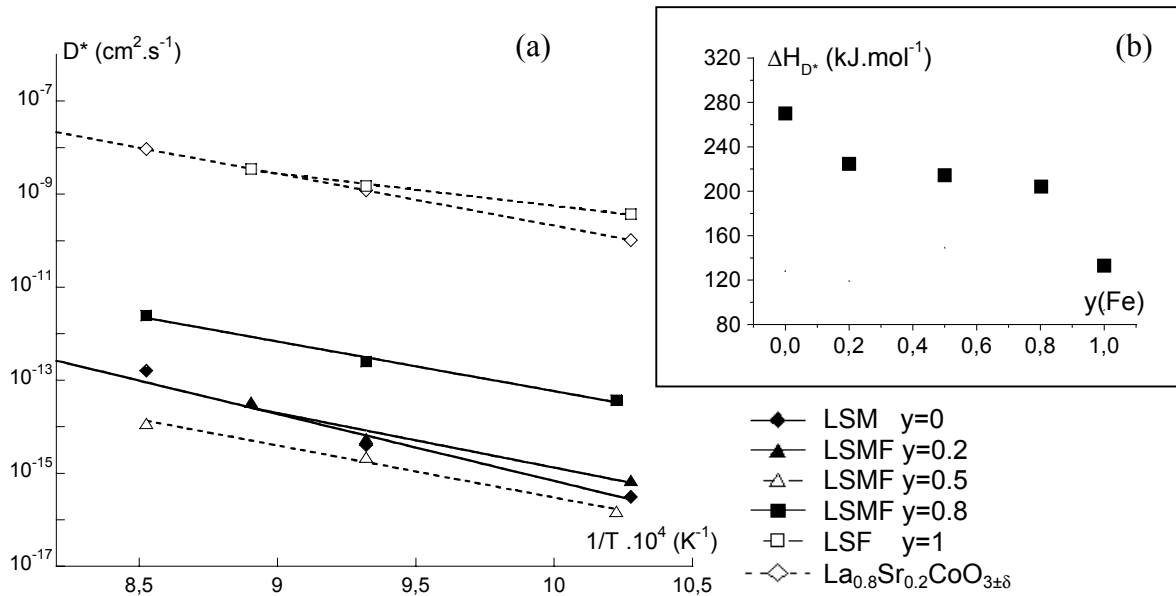


Fig. 2. (a) Bulk oxygen tracer diffusion obtained for LSMF, LSMC25 and LSF48 ceramics as a function of inverse temperature. (b) Activation enthalpy for oxygen tracer diffusion in the bulk as a function of iron content. The data for LSM20 result from ref. 7.

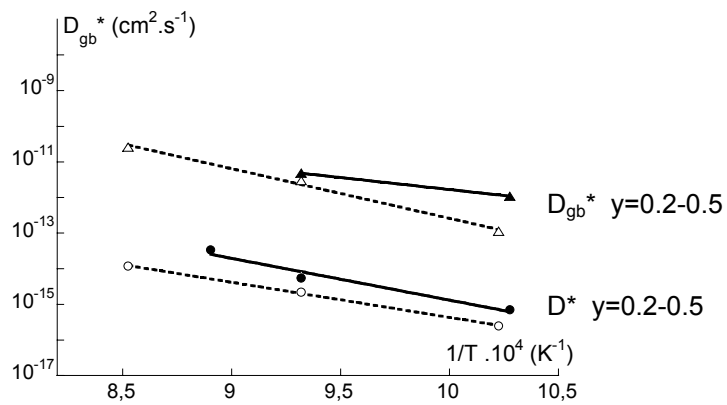


Fig. 3. Bulk and grain boundary oxygen tracer diffusion obtained for LSMF  $y=0.2-0.5$ .