

Characterization of $(1 - x) \text{La}_{0.83}\text{Sr}_{0.17}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.83} - x\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ ($0 \leq x \leq 1$) composite cathodes

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Abstract

Composites prepared by mixing $\text{La}_{0.83}\text{Sr}_{0.17}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.83}$ (LSGM) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) powders $(1 - x)\text{LSGM} - x\text{LSM}$ ($x = 0, 0.01, 0.05, 0.25, 0.50, 0.75$ and 1), have been studied. Composites have been sintered at 1300°C in air for 2 h, and their relative densities vary in the range 89–85%. Characterization includes phase analysis based on X-ray powder diffraction data taken at room temperature after thermal treatments at temperatures suitable for IT-SOFCs, scanning electron microscopy for detecting the grain size, the porosity and the homogeneity of the samples, and complex impedance spectroscopy measurements of the electrical conduction properties in the temperature range $300\text{--}800^\circ\text{C}$. The total conductivity was about $2 \times 10^{-2} \text{ S cm}^{-1}$ at 800°C for samples with 1% and 5% LSM; such low conductivity is consistent with the values found in the literature for pure LSGM sintered at 1400°C and may account for the low relative densities and the small grain size of the samples. Present results have been compared with those obtained by electrical measurements and EDX analysis on LSGM thick films sandwiched between LSM electrodes. In both experiments there was no evidence of the formation of new phases.

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1. Introduction

In recent years intermediate-temperature solid oxide fuel cells (IT-SOFCs), i.e. working below 800°C , have attracted the interest of researchers for their potential applications in stationary power generation plants with reduced manufacturing costs with respect to conventional SOFCs, operating at about 1000°C . Sr- and Mg-doped LaGaO_3 ^{1,2} (LSGM) is an attractive electrolyte material for application in IT-SOFCs, due to its high oxygen ion conductivity at intermediate temperatures ($600\text{--}800^\circ\text{C}$). However, real advancements in IT-SOFCs technology will strictly depend on the availability of suitable electrode materials.

The properties required for good cathode materials used in IT-SOFC are mainly: high electronic conductivity ($>100 \text{ S cm}^{-1}$) and good anionic conductivity (0.1 S cm^{-1}), high catalytic activity for oxygen molecule dissociation and oxygen reduction, chemical stability in oxidising environment and with respect to electrolytes and interconnects and matching the TEC of other cell components.³ Sr-doped LaMnO_3 (LSM) mixed (ionic + electronic) conductor is successfully applied as cathode material in YSZ-based fuel cells, while it shows higher overpotentials if coupled with LSGM electrolyte.⁴ A research route to solve this problem attains development of composite cathodes, in which an electronic conductor and an ionic conductor are physically mixed, as for LSM/LSGM⁵ and LSM/YSZ⁶ electrodes showing better performances than LSM alone. Nevertheless, several authors have reported the occurrence of cations interdiffusion between LSM and LSGM during both the sin-

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tering step at elevated temperatures and at working temperatures suitable for IT-SOFC.^{6–9} Disagreements remain on the extension of the diffusion layer and about the effects of diffusion on the cathodic properties. In this work the microstructural features and the electrical behaviour of mixtures of $\text{La}_{0.83}\text{Sr}_{0.17}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.83}$ – $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ fired at 1300 °C were investigated and the results were compared with those obtained on the interface of two screen-printed thick films of both materials.

2. Experimental

$\text{La}_{0.83}\text{Sr}_{0.17}\text{Ga}_{0.83}\text{Mg}_{0.17}$ was synthesised via a sol–gel route. The appropriate amounts of the salts $\text{La}(\text{OCOCH}_3)_3$ (Sigma Aldrich, 99.9%), $\text{Sr}(\text{OCOCH}_3)_2$ (Sigma Aldrich, 99.995%), $\text{Ga}(\text{NO}_3)_3$ (Sigma Aldrich, 99.9%), $\text{Mg}(\text{OCOCH}_3)_2$ (Sigma Aldrich, 99.999%) were dissolved in water. The solution was heated to 60 °C and NH_4OH was slowly added until the pH reached the value of 9 and precipitation occurred; the suspension was then cured for several hours under continuous stirring. The solvent was evaporated on a thermal plate. The remaining water was removed by heating at 130 °C for 12 h. The powders were calcined at 1200 °C for 6 h and finally sintered at 1480 °C for 12 h, in air. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) was produced by the common solid state route; La_2O_3 , SrCO_3 and MnCO_3 (Sigma Aldrich, 99.9%) were mixed and heated in air at 600 °C for 3 h and at 1350 °C for 6 h in air, with intermediate regrinding.

Sintered LSGM, LSM powders and 2 wt% of organic binder (polyethyleneglycol—PEG 8000) were mixed in an agate mortar in the ratios listed in Table 1 and then pressed in a die ($\varnothing = 13$ mm) at 460 MPa for 30 s. The pellets were sintered at 1300 °C for 2 h with a 5 °C/min ramp and later the densities were measured using the Archimedeian method. Cell parameters estimated from X-ray powder patterns were used for the calculation of the theoretical densities and the mixture rule was applied for the calculation of relative densities of composites. Electrical characterisation was performed by the impedance spectroscopy (IS) measurements carried out over the temperature range 300–800 °C, in air. The current collectors were made by painting the opposite pellet faces with platinum paste and heating at 850 °C for 1.5 h. Morphology

and microstructure of the composites were investigated by scanning electron microscopy (SEM) on polished sections of the samples.

3. Results and discussion

3.1. Phase composition

The XRD patterns of the M05 and M75 samples are reported together with the diffraction patterns of the starting LSGM and LSM powders in Fig. 1; LSM powders were found to be fully single phase, while the pattern of LSGM powders contains the reflections of the melilite-type compound $\text{LaSrGa}_3\text{O}_7$ (JPCDS PDF #45-0637, see peak at $2\theta = 29.911^\circ$), in addition to those of the perovskite phase. The occurrence of $\text{LaSrGa}_3\text{O}_7$ on sintering at 1480 °C is indeed possible since the stoichiometry of $\text{La}_{0.83}\text{Sr}_{0.17}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.83}$ is at the border line of the single-phase region.

The LSGM cell parameters, refined in the space group *Imma* using the software Topas P,¹⁰ are $a = 5.5283(3)$ Å, $b = 7.8197(5)$ Å, $c = 5.5510(8)$ Å, cell volume = 240 Å³ and density = 6.648 g/cm³. LSM cell parameters, refined in the space group *R-3c*, were $a = b = 5.5144(2)$ Å, $c = 13.3630(7)$ Å, $\gamma = 120^\circ$, cell volume = 352 Å³ and density = 6.557 g/cm³. The formation of reaction products was not observed in the XRD patterns of the composites,

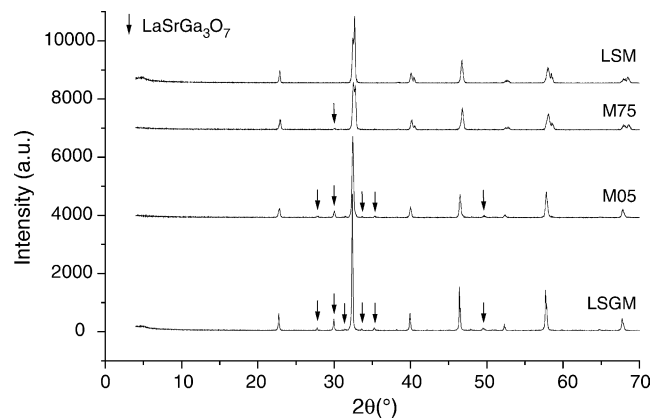


Fig. 1. X-Ray powder diffraction patterns of LSGM (bottom), M05, M75, LSM (top).

Table 1

Sample	T (°C)	LSGM (wt%)	LSM (wt%)	Relative density	σ at 800 °C (S cm ⁻¹)
M00	1500	100	–	92	1.49×10^{-1}
M01	1300	99	1	89	2.18×10^{-2}
M05	1300	95	5	86	2.10×10^{-2}
M25	1300	75	25	87	1.26×10^{-2}
M50	1300	50	50	X	2.50×10^{-1}
M75	1300	25	75	85	8.48×10^{-1}
M100	1300	–	100	X	X

while in M75 there was evidence of a slight peak shifting of LSGM toward higher 2θ . These results are compatible with the formation of a solid solution of formula $\text{La}_{0.83}\text{Sr}_{0.17}\text{Ga}_{1-x-y}\text{Mn}_x\text{Mg}_y\text{O}_{3-\delta}$. However, the small

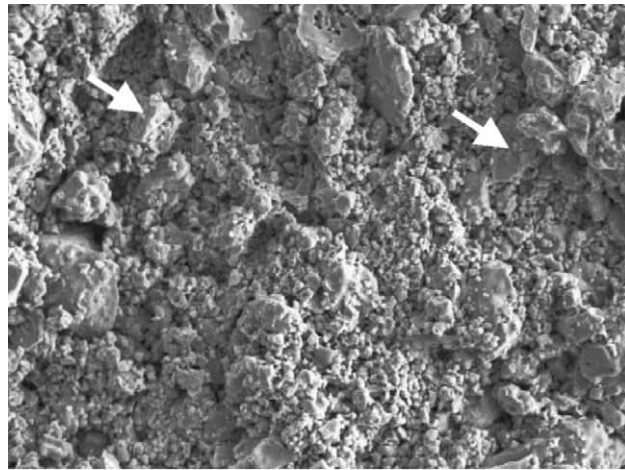
decrement of the cell volume from M01 to M75 does not allow us to evaluate with certainty the possible cations diffusion between LSGM and LSM.

3.2. Relative densities

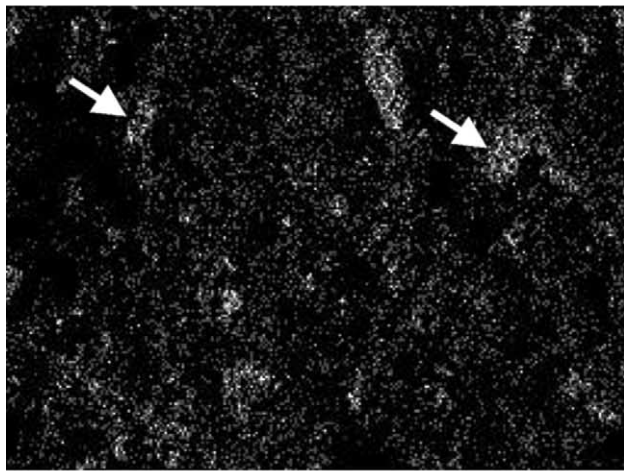
Since doped LaGaO_3 is known to sinter completely at temperatures above 1400°C , it is easily expected that the relative densities of the samples would not reach the theoretical values. $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ sintered at 1300°C is known to produce samples with relative densities of around 85%,¹¹ which agrees with the values obtained in this work, summarised in Table 1.

3.3. Microstructure

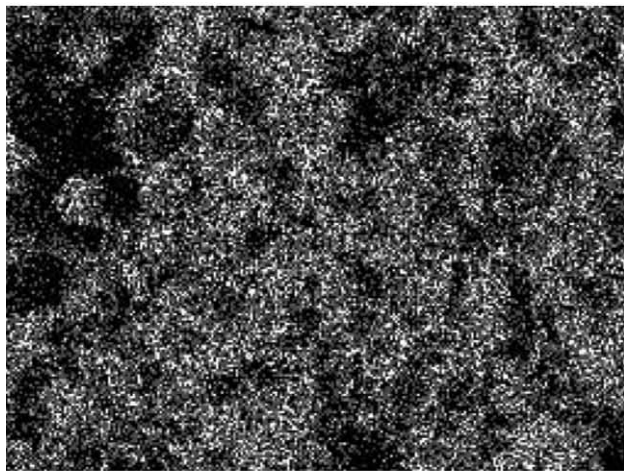
In Fig. 2a SEM Micrograph of the 75% LSM sample is reported. Fig. 2b and c report the composition map for gallium and manganese, respectively; arrows were added for easier recognition of some LSGM particles. As one can observe small aggregates of LSGM particles are well dispersed into the LSM matrix; pores are also visible, as black areas. The grain size dimension lies in the range $1\text{--}5\ \mu\text{m}$, much smaller than in sample M00 sintered at 1500°C . Similar grain size and porosity were found in the



80 μm (a)



80 μm (b)



80 μm (c)

Fig. 2. (a) SEM micrograph of M75 composite; (b) Ga map; (c) Mn map.

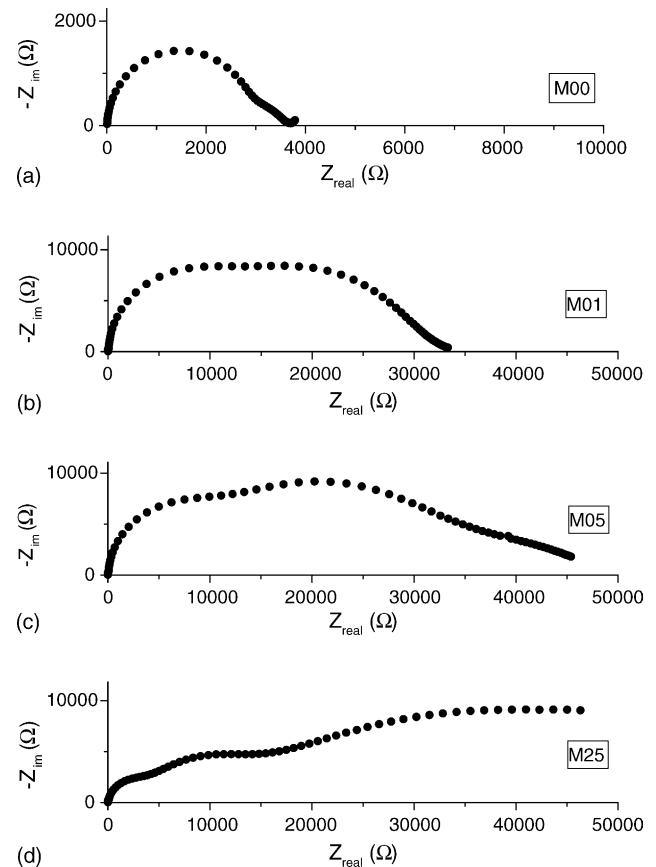


Fig. 3. Impedance Spectra measured at 325°C for (a) pure LSGM, (b) M01, (c) M05 and (d) M25 composites.

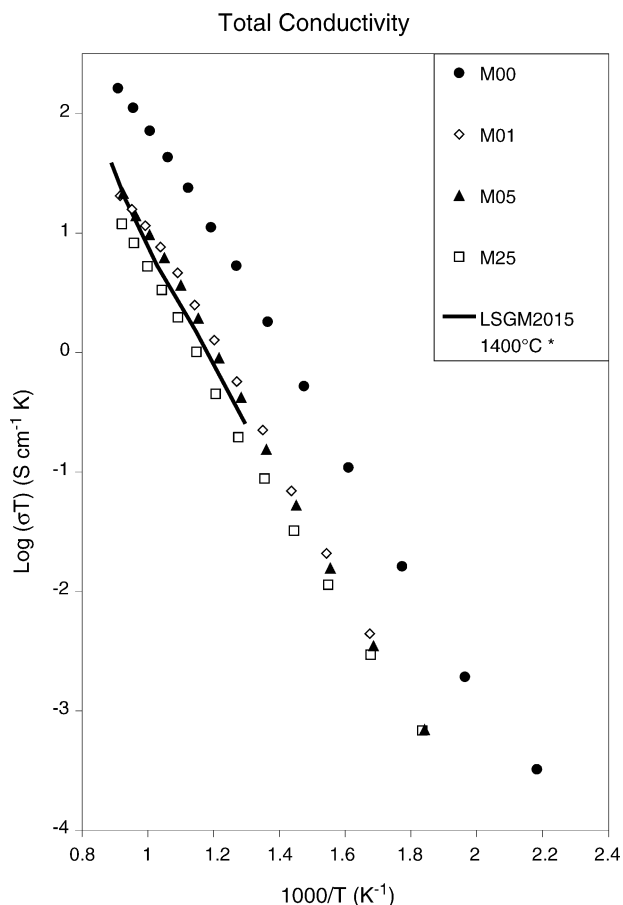


Fig. 4. Arrhenius plot of the total electrical conductivity of sample M00 sintered at 1500 °C, composites M01, M05, M25, sintered at 1300 °C, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ sintered at 1400 °C. (*) Data taken from literature.¹³

other samples of the series, despite the different component ratios.

3.4. Impedance spectroscopy

The impedance spectra measured at 325 °C are reported in Figs. 3 and 4. Nyquist diagrams of M00 compound showed two RC arcs due to bulk and grain boundary contributes to total conductivity (Fig. 3a). The spectra of M01, M05 and M25 composites were more difficult to justify because of the presence, at lower frequencies, of an additional arc (Fig. 3b–d); the diagrams of M50 and M75 showed a single point laying along Zreal axis over a wide range of frequencies and thus are not shown. In any case it was possible to define the total conductivity of each sample.

The Arrhenius plots of M00, M01, M05 and M25 composites together with pure LSGM sintered at 1400 °C are given in Fig. 3 and compared. All these samples exhibit thermally activated conducting mechanism. The conductivities of M01 and M05, similar to that reported for 1400 °C sintered sample, are one order of magnitude smaller than that of M00. The significant smaller values could arise from

the relative density of the composites (89–85%) due to the lower preparation temperature (1300 °C). The presence of high LSM concentration in the case of M50 and M75 composites led to the quasi-metallic behaviour due to electron percolation.

The effect on the conductivity ascribed to the migration of Mn cations from LSM electrode material into LSGM electrolyte, previously reported at LSGM/LSM interface, appears to be not significant in the investigated composites.¹²

4. Conclusions

Mixtures of LSGM electrolyte and LSM were prepared and sintered at 1300 °C; porous samples with 89–85% relative densities were obtained. The formation of reaction products was not observed in the XRD patterns of the composites, the small decrement of the cell volume from M01 to M75 does not allow us to evaluate with certainty the possible cations diffusion between LSGM and LSM. The grain size dimensions were in the range 1–5 μm, much smaller than for sample M00 sintered at 1500 °C. The 1% and 5% of LSM into the electrolyte matrix showed no measurable harmful effects on the electrical conductivity, which is consistent with the values found in literature on pure LSGM samples, sintered at 1400 °C. The presence of large quantity of LSM induces high electronic conductivity, probably due to percolation effect, and these composites could be suitable as electrode cathodic material in IT-SOFC.

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