

Microstructural effects on the electrical properties of grain boundary Fe-doped LSGM

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Abstract

Mixed conductors based on grain boundary Fe-doped $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ga}_{0.90}\text{Mg}_{0.10}\text{O}_{3-\delta}$ (LSGM) ceramics were obtained by selectively doping the grain boundaries with Fe. This was achieved using $\text{LaFeO}_{3-\delta}$ layers screen-printed onto LSGM, after annealing at high temperature in air for several hours to promote Fe diffusion into LSGM. The influence of the number of impregnation cycles, temperature of impregnation and microstructure of the host LSGM was evaluated by impedance spectroscopy and oxygen permeability. The impedance spectra consist of high and low frequency semicircles, ascribed to bulk and grain boundaries. The amplitude of both contributions decreases with increasing impregnation temperature and time, suggesting the onset of electronic conduction along grain boundaries. The effect is stronger for ceramics with larger grain size. The observed trends are fully consistent with estimates of p-type electronic conductivity obtained from oxygen permeability measurements using a simplified electrochemical cell.

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1. Introduction

High temperature electrochemical technologies such as solid oxide fuel cells or oxygen separation membranes require the development of functional materials that offer a significant level of both ionic and electronic conductivity [1]. Mixed conductors may be obtained simply by combining one ionic conducting phase with one electronic conductor in a two-phase mixture [2]. However, the most studied – and perhaps the most relevant – mixed conducting materials are single-phase materials based on the ABO_3 perovskite structure, where the A or B-site – or both – cations are partially substituted by different valence cations so that the concentration of charged defects (e.g., electron holes and/or oxygen vacancies) is increased. As an example, the well known solid electrolyte $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ is obtained by doping

LaGaO_3 with Sr and Mg, with the crystal net charge being compensated by formation of oxygen vacancies [3]. Further substitution of Ga by Fe increases the concentration of electronic defects [4]. Examples of the successful application of this strategy are well known and include, for example, $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ [5] or $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ [6].

A grain boundary engineering approach was recently suggested to induce electronic conduction in a solid electrolyte, by selectively doping the grain boundaries with a transition metal cation, as an alternative strategy to design mixed conductors [7,8]. The concept actually corresponds closely to a two-phase composite with a core-shell type microstructure, in which one component (core) is surrounded by the other (shell). This is not new to the field electroceramics, where commercially successful core-shell BaTiO_3 -based heterostructures are well known for their unique dielectric properties over a broad temperature range [9]. LSGM was selected as base solid electrolyte and Fe as dopant, to benefit both from the high ionic conductivity of LSGM [4] and the high diffusion coefficient of

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Fe along LSGM grain boundaries which is orders of magnitude higher than in the bulk [10]. This work complements previous impedance spectroscopy studies [7,8] with new results on the effect of the dopant level and LSGM microstructure on the p-type electronic conductivity of grain boundary Fe-doped LSGM, estimated from oxygen permeability measurements.

2. Experimental procedure

Two sets of $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ga}_{0.90}\text{Mg}_{0.10}\text{O}_{3-\delta}$ (LSGM) dense ceramic samples with different grain size were prepared. A brief description is given here since details are available elsewhere [11]. The first set, noted as LSGMcr, was obtained from powders prepared by conventional ceramic route. These powders were pressed into disk-shaped pellets and sintered at 1550 °C during 4 h. The resulting average grain size was in the range 5 to 10 μm . The second set of samples was also obtained via solid state reaction, but in this case from mechanically activated precursors, LSGMma. The precursors were dry grinded in a high energy planetary ball mill at ca. 380 rotations per minute and the activated powder was sintered at 1450 °C for 4 h. The average grain size was in the order of 250 nm. The density for both sets of samples was greater than 93% of the theoretical value. The ceramics were subsequently polished, covered with screen-printed $\text{LaFeO}_{3-\delta}$ layers on both sides and annealed in air at 1450 or 1550 °C during several cycles of 1 h each, to promote the diffusion of Fe through LSGM grain boundaries, as described in [7,8].

The effects of impregnation were evaluated by impedance spectroscopy in the frequency range 20–10⁶ Hz, with $V_{ac} = 100$ mV. The spectra were fitted to equivalent circuits using common software (EQUIVCRT and Z-View).

Oxygen permeability measurements were carried out using an electrochemical cell consisting of one YSZ disk, with 18 mm in diameter and 2 mm thick, with two sets of platinum electrodes applied on an engraved area of 10 mm in diameter and 1 mm depth. The electrodes were placed at 4 mm from each other, on each YSZ surface. The measured sample was sealed with an appropriate glass on top of the YSZ disk forming a closed chamber, as depicted in Fig. 1. The smaller electrodes are used to monitor the oxygen partial pressure inside the chamber (P_2), and the larger ones are connected to a dc source to work as an oxygen electrochemical pump. Under steady state, the pumping current (I_{pump}) is compensated by the permeation current through the sample ($I_o = I_{\text{pump}}$) and the minor p-type electronic conductivity at unit $p\text{O}_2$ (σ_p^0) may be estimated by

$$I_o FL/RTS = \sigma_p^0 (P_1^{1/4} - P_2^{1/4}) \quad (1)$$

where R , T and F have their usual meaning, L is the sample thickness and S the permeating area. The underlying relations and additional experimental details, including detection of leaks through glass seals, may be found in Refs. [4,12]. This cell is a simplified version of a previous set-up that offers the advantages of a single seal design and a smaller internal volume. However, operating sensor and pump in the same electrolyte may be a source of errors. For instance, under

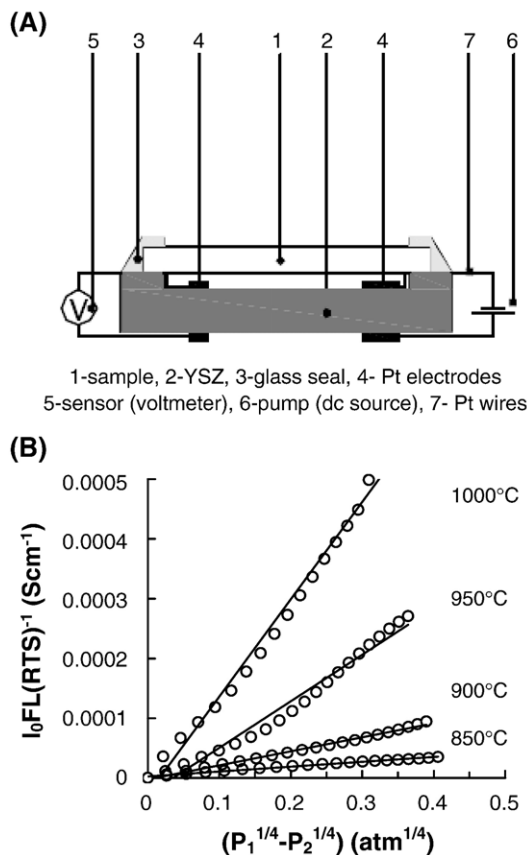


Fig. 1. Schematics of the electrochemical permeability cell (A); Oxygen permeability of LSGMcr impregnated three times at 1550 °C (B).

reducing conditions the pumping current may induce local ohmic drops that change the sensor reading [13]. This should hardly be a problem in the present study since it is restricted to oxidising conditions, well within the electrolytic domain of YSZ. Additional errors may result from changes in the reference potential due to the pumping current distribution within the solid electrolyte. This factor may be controlled by an accurate design of the electrode geometry ensuring symmetrical electrode arrangements and keeping them at a convenient distance. Based on finite elements simulations of the potential distribution [14], this distance was found to be of 3–4 mm for a 1 mm thick electrolyte. Finally, an oxygen concentration gradient may occur between the sample inner surface and the pumping electrodes leading to a non-equilibrium sensor reading. This is however unlikely given the extremely small chamber volume and the relatively moderate oxygen fluxes. Nevertheless, a comparison of results obtained with the two set-ups was carried out to validate the single seal cell and will be published in a separate study.

3. Results and discussion

Fig. 2 shows the impedance spectra collected in air, at 250 °C, for LSGMcr and LSGMma samples before and after impregnation with Fe. The non-impregnated samples spectra consist of the usual high and low frequency contributions, which may be attributed to the bulk and grain boundary

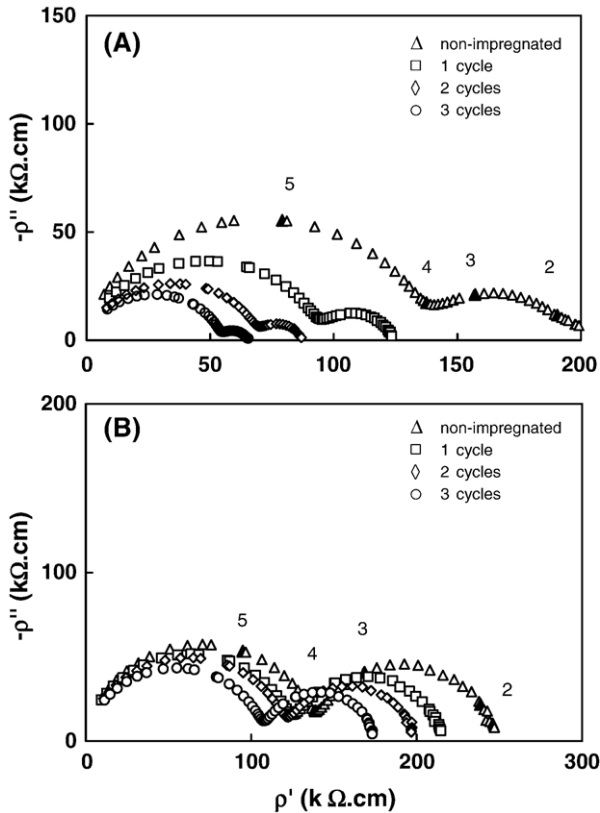


Fig. 2. Impedance spectra obtained in air at 250 °C for an increasing number of impregnation cycles at 1450 °C: LSGMcr (A) and LSGMma (B).

polarisations, respectively. It can be seen that the relative magnitude of the grain boundary semicircle is considerably larger for the LSGMma sample, in agreement with the considerably smaller grain size (thus higher grain boundary density). The effect of the impregnation with iron is apparent in the progressive decrease of the amplitude of both semicircles as the number of impregnation cycles increases. Moreover, the amplitude abatement is greater for the grain boundary contribution. This effect may be interpreted assuming an increasing level of electronic conduction along the grain boundaries, as previously suggested based on an equivalent circuit to model an ionic conductor grain bulk surrounded by mixed ionic/electronic conducting grain boundaries [7,8]. The spectra further suggest that the magnitude of the electronic conduction is smaller for the finer grained LSGMma ceramics. The impedance spectra, while providing information on the distinct behaviour of the interior and periphery of the grains, reveal a behaviour characteristic of fairly low temperatures that are of little technological interest. The ultimate confirmation of these assumptions can only be obtained at higher temperatures by a direct measurement of the electronic transport properties.

A typical set of oxygen permeability data collected in the 850–1000 °C temperature range is shown in Fig. 1(B) for a LSGMcr sample impregnated three times at 1550 °C to illustrate the application of the technique in order to estimate the p-type electronic conductivity (Fig. 3), according to Eq. (1). Firstly, it should be noticed that data obtained for the Fe-doped samples, contrary to the undoped material [4], deviate from the expected

linearity, especially at higher temperatures, where an apparent increase in σ_p^0 is observed. In fact, Eq. (1) is derived for homogeneous materials, assuming constant ionic conduction and a σ_p dependence on pO_2 of the type $\sigma_p = \sigma_p^0 \cdot pO_2^{1/4}$, whereas the impregnated samples are highly heterogeneous and little may be said about the defect chemistry of the doped regions. Nevertheless, any increase on the ambipolar current must be due to an increase in electronic conductivity. Therefore, as a first approximation, Eq. (1) was used to obtain σ_p^0 estimates for samples with different microstructures and levels of impregnation, as shown in Arrhenius coordinates in Fig. 3. These results reveal that the electronic conductivity increases with increasing number of impregnation cycles and with increasing impregnation temperature (LSGMcr series), following the expected increase in Fe content. Moreover, the lower σ_p^0 value found for LSGMma, when compared to the LSGMcr with the same impregnation treatment, is consistent with a lower Fe content in the former. These results are in excellent agreement with the impedance spectra collected at low temperature, thus representing an important qualitative validation of the previously proposed equivalent circuit model [7,8].

It should be noticed that the apparent low temperature increase in electronic conductivity observed for the doped samples by impedance spectroscopy is much higher than by oxygen permeability. Indeed, grain boundaries tend to become less resistive at higher temperatures and thus the bulk properties should play a major role on the oxygen permeability data. Therefore, the modest increase in σ_p^0 estimated at high temperature actually supports the preferred localisation of the dopant along the grain boundaries.

Considering this set of four samples, and irrespective of microstructure or impregnation history, the increase in σ_p^0 is paired to a significant increase in the activation energy from 1.74 to 2.47 eV, in contradiction with the behaviour observed for homogeneous Fe-doped LSGM [4]. One possible reason for such strong temperature dependence is related to the heterogeneous distribution of the Fe dopant, not only within the impregnated regions but also throughout the sample bulk, where the overall quantity is extremely small and concentrated in the cell outer layers. Such heterogeneous distribution may render the formation

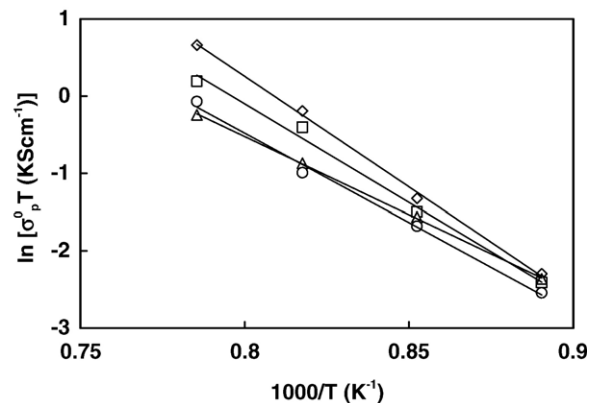


Fig. 3. p-type electronic conductivity at unit pO_2 for several LSGM ceramics: \diamond -LSGMcr, three cycles at 1550 °C; \square -LSGMcr, two cycles at 1550 °C; \circ -LSGMma, two cycles at 1450 °C; Δ -non-impregnated LSGMcr.

of small polarons associated to the $\text{Fe}^{3+}/\text{Fe}^{4+}$ couple energetically very demanding. Also, trapping of polarons by negatively charged defects is expected to result in a higher activation enthalpy for the ambipolar diffusion of such defect associates when compared to the diffusion of defects alone [15].

Finally, we note that the overall electronic conductivity of the best doped material is lower than found for homogeneously Fe-substituted LSGM [4]. This can be explained by an overall lower Fe content and a relatively poor distribution within the membrane thickness, as expected from the impregnation method. In thinner samples, however, the potential for enhancement of the observed effect is obvious.

4. Conclusions

An alternative design to obtain mixed conductors was demonstrated using a grain boundary engineering approach to induce electronic conduction in a LSGM solid electrolyte, by selectively doping the grain boundaries with Fe. A brief study of the effects of the Fe content and microstructure in the mixed conducting properties of grain boundary Fe-doped LSGM ceramics has shown that the p-type electronic conductivity consistently increases with a localised increase of the Fe content along the grain boundaries. The effect is favoured by host LSGM ceramics with larger grain size, probably due to shorter diffusion pathways of the Fe cations during the impregnation process.

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