The use of the same material as anode and cathode in symmetrical solid oxide fuel cells (SFCs) promises notable benefits as easier fabrication, hence lower cost production and resistance to carbon formation upon fuel cracking. Although chromites and chromo-manganites have been proposed as candidate electrode materials for this novel SOFC configuration, demonstrating promising performances, further work is required to develop compositions exhibiting higher efficiencies. In the present work we evaluate the structural evolution from cubic to orthorhombic unit cells with increasing the Fe content and the performance of La$_4$Sr$_8$Ti$_{12-x}$Fe$_x$O$_{38-\delta}$ (LSTF) phases and compare their response with other symmetrical electrodes. The electrochemical performance is 20% higher when using graded LSTF electrodes than in other perovskite-based systems.

**Keywords:** Solid Oxide Fuel Cells, Symmetrical solid oxide fuel cells, electrodes, perovskites, composites.

1. INTRODUCTION

Fuel cells are at the forefront of the emerging clean technologies that promise efficient power generation to substitute traditional methods based on the combustion of fossil fuels. Among them, solid oxide fuel cells promise high efficiencies and tolerance to fuels as a consequence of their relatively high operating temperatures (600-1000°C) required for adequate levels of oxide ion mobility in the solid electrolyte. ZrO$_2$ substituted with 3-12% of Y$_2$O$_3$ (YSZ) is the most commonly used electrolyte material, whereas a ceramic-metal composite Ni-YSZ is usually chosen as anode and Sr-substituted LaMnO$_3$ as cathode. Over the last decade, several strategies have been adopted in the search for efficient devices that may operate under hydrocarbon feed in the intermediate temperature range (below 800°C), some of them related to the development of novel anode materials for direct hydrocarbon operation and/or the use of ceria-based or perovskite-based electrolytes. Indeed, some of the alternatives to Ni-YSZ cermets such as Cu-based cermets and perovskite-based phases (1-4) exhibit rather competitive performances, especially the former materials.

Nevertheless further progress may also be achieved via the use of well-known materials considering approaches such as the optimisation of the microstructure using various routes, i.e. pore formers, infiltration techniques, organic templates, etc (1,5-6). In this context, a novel concept of SOFC has been recently proposed: the symmetrical fuel cell (SFC), which consists of the use of the same material as anode and cathode. The reduction in the number of different cell components would imply certain benefits related to easier fabrication processes and management. It should be noted that coke formation could be avoided by reversing the gas flows, i.e. periodically the starting anode becomes the cathode and receives oxygen that would remove any carbonaceous deposit formed on the electrode surface. Although the requirements of the candidate materials are rather restrictive, Irvine and co-workers (7) and several other research groups (8-9) have...
proved the validity of this concept in the high temperature range. The first reports were focused on lanthanum-strontium chromo-manganites (LSCM) based composites, exhibiting power densities of approximately 0.5 and 0.3 Wcm⁻² under humidified H₂ and CH₄ atmospheres respectively at 950 °C (8). Chromites commonly used as interconnects have also been evaluated in symmetric configuration, although the performances were more modest (10), possibly due to the poor catalytic activity of these phases towards fuel oxidation (11).

Perovskite-based titanates have been usually considered as potential anode materials or anode support (current collector) as they exhibit high conductivity, stability under reducing conditions, S-tolerance and do not react with the state of the art electrolytes (12-15). On the other hand, ferrrites substituted with Ti in the B-site have been extensively studied as mixed conducting oxide membranes and/or SOFC cathode materials (16-18) due to their high mixed (ionic-electronic) conductivity and chemical compatibility with YSZ electrolytes. In a previous work, the Ti-rich part of the La₆Sr₃Ti₁₂Fe O₃₋₈ solid solution was explored in the search for symmetric electrode materials (19). Although the performances were rather modest, the relatively high OCVs when operating under methane suggested that these phases could find application in SFCs upon further optimisation. Herein, we present some further information regarding phases with 0.0 ≤ x ≤ 6.0 and compare them with other symmetrical electrode candidate materials.

2. EXPERIMENTAL SECTION

La₁₆Sr₆Sr₃₂₃₅₂₅ₓFe O₃₋₈ (LSTF), La₆Sr₆Sr₃₂₃₅₂₅ₓCrO₃₋₈ (LSCM) and La₆Ca₆CrO₃₋₈ (LCC) phases were prepared via the traditional solid state reaction. Pre-dried stoichiometric amounts of the corresponding oxides and carbonates (>99%, Aldrich) were milled in zirconia ballmills using acetone as solvent for 30 minutes and then fired at 1100-1200°C for 3-12 hours. The resulting powders were milled again for 30 minutes and pressed uniaxially into pellets at 1 metric ton. The pellets were then fired at 1300-1500 °C for 48 hours, showing relative densities >90% after sintering.

The structure of LSTF was investigated by combining X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD experiments were performed on a PANalytical dифрактометр equipped with a X'Celerator detector with monochromatic CuKα₁ radiation (λ = 1.54056 Å) in the 2θ range 10°-110°, scan step size of 0.01 for 1.5s. Rietveld refinements of the data were performed using the Fullprof program (20). The backgrounds were fitted using a linear interpolation and peak shapes were modelled by a Thompson Cox Hasting function. Compatibility studies of the electrode materials with the YSZ electrolytes used in the present study were carried out by firing an intimate mixture of 1:1 YSZ/LSTF powders up to 1350°C in air for several hours.

TEM studies were carried out on a Jeol 2011 electron microscope operating at 200 kV and equipped with a ±20° double-tilt sample holder and an Oxford Link EDS detector. Samples were prepared by dispersing finely ground ceramic powder in acetone and depositing a drop of the resulting dispersion on a perforated C-coated Cu grid.

Polarisation studies were performed using 2 mm thick fully-dense YSZ electrolytes prepared as described elsewhere [8,19] coated with 1:1 LSTF-YSZ, LSCM-YSZ and LCC-YSZ electrodes and a thin layer of Pt on top under 3%H₂O/4%H₂/96%Ar, 3%H₂O/97%H₂ and 3%H₂O/97%CH₄. These studies were carried out on a 1260 Solartron frequency response analyser in the 0.1 Hz-1 MHz range applying a 50 mV signal.

LSTF, LCC and LSCM electrodes for fuel cell testing were prepared by applying a thin layer (typically 50µm) of 1:1 LSTF-YSZ composites mixed with binder (Decoflux WB41, Zschimmer and Schwartz) on both sides of the YSZ electrolyte and fired at 1200 °C for 2 hours to ensure good adhesion. In the case of LSTF electrodes a fine layer of Au and Pt was used at the anode and the cathode respectively to act as a current collector to avoid any possible catalytic activity, as Pt favours the electrochemical oxidation of methane. It could be argued that Pt also favours oxygen reduction, though the effect on a high-temperature fuel cell is less marked and Pt is commonly used as current collector at the cathode in laboratory tests [1]. Pt was also used as current collector in LSCM and LCC-based electrodes.

The fuel cell tests were performed on a two electrode setup (8,19) using humidified 5% H₂/Ar, H₂ and CH₄ as fuels and O₂ as oxidant at the cathode (flow rates 150-200 ml/min). The polarisation measurements were carried out using an IM6e Zahner unit at open circuit voltage conditions in the 0.1-3x10⁻² Hz frequency range using a 50 mV perturbation in the 950-800°C temperature range. Cyclic-voltammetries at 4-12mVs⁻¹ were also performed using the same equipment.

The microstructure of the cells measured (top view and cross sections) was monitored by SEM on a JSM-6300 Jeol electron microscope operating at 5-30 kV.

3. RESULTS AND DISCUSSION

3.1. Structural characterisation.

The n=12 member (La₆Sr₆Ti₁₂O₃₋₈) of the La₆Sr₆Ti₁₂O₃₋₈ series has been previously described as a XRD cubic phase (13,21). The introduction of Fe in the B-sites does not result in the formation of La₆TiO₃-like layered domains in the crystals as can be observed in figure 1. This is a critical parameter as the formation of layers causes a dramatic decrease of the electronic conductivity, preventing potential applications as fuel cell electrodes (3). On the other hand, oxygen-vacancy ordering has been extensively described in perovskite-based ferrites (22), giving rise to intermediate structures between the primitive perovskite and brownmillerite as a result of ordered layers along the b-axis. In the present case, there was no evidence of long-range ordering along a particular crystallographic direction, although there are regions where an incipient microdomain texture is evident (figure 1b). Consequently, the presence of Grenier-like phases (22 and references therein) has not been considered during refinement.

The substitution of Ti by Fe in the perovskite B-sites causes a gradual distortion of the cubic perovskite unit cell, s.g. Pm-3m (x=0). i.e. diffraction maxima split as the Fe content increases and some weak superlattice peaks also appear due to reverse octaehdra tilting in consecutive layers. Although the peak splitting of the originally cubic reflections is subtle, structural transitions from Pm-3m to I4/mcm to Imma and finally to Pnma with increasing x in the La₆Sr₆Ti₁₂Fe O₃₋₈ solid solution occur. It is worth noting that not all the superlattice reflections can be detected by XRD as they depend on weak anion scattering.
to Imma in a first order transition, which is discontinuous as the structure changes from having tilts around the tetrad axis \((a^0a/c)\) to tilts around a diad axis of the oxygen octahedra \((a'b'b)\). At higher Fe contents \((x>3.0)\), there is a Imma to Pnma transition, without symmetry discontinuity as involves gain/loss of the in-phase tilting. This phase transition sequence is rather habitual in perovskites with both increasing \(x\) in the solid solution (23) and/or temperature (24) and similar results have been reported for related ferrite-titanate systems (16-17). Figure 2 shows a segment from the observed and calculated diffraction patterns for Fe contents \(x=0, 0.5, 2.5\) and 3.0. In figure 2a neither distortions nor superlattice reflections are apparent in the non-substituted phase in agreement with previous reports (21). However and as mentioned above, the introduction of Fe results in the presence of superlattice reflections due to octahedra tilting (marked with an arrow) and splitting of the main cubic reflections (figures 2b-c). It is interesting to note that there is a reversal of the intensities in the 200 cubic reflection pair (figures 2b-c), which implies a transition from \(I_4/mcm\) to the Imma pseudo-tetragonal space group (25). Figure 2d shows the pseudo-orthorhombic distortion from the 200 cubic reflection that splits to the combination of the 220 and 004 reflections corresponding to the Pnma space group.

Regarding XRD pattern refinement, the perovskite A-sites were fully occupied at random by 2 Sr and 1 La, whilst Ti and Fe were placed in the B sites. In this structural model, such a situation was treated by assigning to the different atoms the same \(x,y,z\) site and the same displacement parameters \(U_{ij}\). As there was a strong correlation between the site occupancy and the displacement factor, it was preferable to refine them in alternating cycles until convergence. Assuming that there existed a certain number of oxygen vacancies, the corresponding oxygen site occupancy was varied freely until the final value was reached (26). Table 1 gives the refined cell parameters as well as the fit agreement factors obtained for several compositions.
The compatibility studies performed after firing intimate mixtures of LSTF powders with YSZ and CeO$_2$ revealed that no significant chemical interaction occurs as the diffraction peaks remain nearly unchanged up to fabrication temperature (figure 3), which is consistent with previous reports on similar compositions and other titanate-based electrodes (16-17). A similar trend and therefore the Fe-rich compositions (x=5.0, 5.5 and 6.0) were considered as the most adequate electrode candidates for symmetric fuel cells. Figure 4 corresponds to the polarisation resistance of the x=5.0 composition compared with LSCM and LCC-based electrodes in air and 5% H$_2$/Ar. In all cases the responses in oxidising conditions are much lower, which implies that the systems studied (including Pt and Au pastes) are more electrocatalytically active towards oxygen reduction than hydrogen oxidation, i.e. they perform better as cathodes rather than anodes. Arguably the presence of Pt at the cathode may play an important role in the responses observed, although Pt itself is considered as a poor electrocatalyst. Table 1 shows the refined cell parameters and the fit agreement factors obtained using Rietveld refinement corresponding to the La$_4$Sr$_8$Ti$_{12-x}$Fe$_x$O$_{38-x}$ series for compositions 0≤x≤5.5.

### Table 1. Refined Cell Parameters and the Fit Agreement Factors Obtained Using Rietveld Refinement Corresponding to the La$_4$Sr$_8$Ti$_{12-x}$Fe$_x$O$_{38-x}$ Series for Compositions 0≤x≤5.5.

<table>
<thead>
<tr>
<th>S.G.</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V(Å$^3$)</th>
<th>R$_p$ (%)</th>
<th>R$_wp$ (%)</th>
<th>R$_B$ (%)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pm-3m</td>
<td>3.9061(1)</td>
<td>5.5384(1)</td>
<td>5.5376(1)</td>
<td>5.5439(1)</td>
<td>5.5406(1)</td>
<td>5.5553(1)</td>
<td>5.5617(1)</td>
<td>5.5413(1)</td>
</tr>
<tr>
<td>I4/mcm</td>
<td>3.9061(1)</td>
<td>5.5384(1)</td>
<td>5.5376(1)</td>
<td>7.8190(1)</td>
<td>7.8194(1)</td>
<td>7.8267(1)</td>
<td>7.8278(1)</td>
<td>7.8085(1)</td>
</tr>
<tr>
<td>Imma</td>
<td>3.9061(1)</td>
<td>7.8433(1)</td>
<td>7.8424(1)</td>
<td>5.5323(1)</td>
<td>5.5321(1)</td>
<td>5.5389(1)</td>
<td>5.5415(1)</td>
<td>5.5233(1)</td>
</tr>
<tr>
<td>Pnma</td>
<td>59.599(2)</td>
<td>240.582(5)</td>
<td>240.486(5)</td>
<td>239.816(5)</td>
<td>239.676(6)</td>
<td>240.827(6)</td>
<td>241.250(4)</td>
<td>238.986(6)</td>
</tr>
</tbody>
</table>

3.2. Electrochemical characterisation

It has been previously reported that the overall conductivity of the La$_4$Sr$_8$Ti$_{12-x}$Fe$_x$O$_{38-x}$ (0≤x≤6.0) system increases with increasing the Fe content under both oxidising and reducing conditions (19). The electrocatalytic properties followed a similar trend and therefore the Fe-rich compositions (x=5.0, 5.5 and 6.0) were considered as the most adequate electrode candidates for symmetric fuel cells. Figure 4 corresponds to the polarisation resistance of the x=5.0 composition compared with LSCM and LCC-based electrodes in air and 5% H$_2$/Ar. In all cases the responses in oxidising conditions are much lower, which implies that the systems studied (including Pt and Au pastes) are more electrocatalytically active towards oxygen reduction than hydrogen oxidation, i.e. they perform better as cathodes rather than anodes. Arguably the presence of Pt at the cathode may play an important role in the responses observed, although Pt itself is considered as a poor electrocatalyst.
SOFC cathode. The responses of LSTF were better than those reported in (19) possibly due to differences in the microstructure. Obviously, these polarisation values are rather high compared to the state of the art SOFC electrode materials (typically 0.1 Ωcm²), though further optimisation via the use of graded compositions, optimisation of the microstructure or the addition of phases with catalytic activity may reduce the gap.

Regarding cell performance, at 950°C the overall cell polarisation values are 3.4, 2.4 and 9.8 Ωcm² under 3%H₂O/4%H₂/93%Ar, 3%H₂O/97%H₂ and 3%H₂O/97%CH₄ respectively (figure 4c). It is very important to note that contrary to the previous results, the values in the present work have been obtained using Au as current collector at the anode rather than Pt. The use of Pt as current collector at the anode is rather controversial as this noble metal exhibits catalytic properties towards hydrocarbon oxidation, hence potentially masking the real response coming from the ceramic material. Although, Au nanoparticles are also well-known for their catalytic activity in redox processes (27), the temperature range considered in the present work is very close to the melting point, which implies that Au agglomerates and thereby acts mostly as current collector. Moreover, metal coarsening may have a negative impact as large Au clusters can certainly block the electrode pores, hence preventing the access of gases to the active sites.

Nevertheless, it should be pointed out that LSTF-based electrodes render power and current densities under pure hydrogen similar to those LSCM and LCC-based electrodes, i.e. 100 mWcm⁻² at 950°C (figure 5). The performance under methane is rather modest in terms of maximum power densities, although it is important to note that an optimisation of the electrode composition, i.e. use of graded compositions and the use of CeO₂ to enhance the catalytic properties, may result in enhanced open circuit voltages (OCVs). For instance, the use of a two layered electrode, i.e. 1:1 LSTF:CeO₂ layer on top of a 1:1 LSTF:YSZ layer, renders OCVs in excess of 1 V, which is 15-20% more than the results reported for other perovskite-based SFC electrodes, including simple LSTF electrodes. In other words, an adequate optimisation of LSTF-based electrodes could yield in theory higher current and power densities. Although further research work is required to determine exactly such enhanced voltage values, it is likely that these electrodes present certain activity towards methane oxidation.

4. CONCLUSIONS

In the present work, La₅Sr₃Ti₁₂₋ₓFeₓO₇₋δ phases have been investigated for their potential application as electrodes for high temperature symmetric fuel cells. The structural characterisation revealed that the introduction of Fe in the n=12 member of the La₅Sr₃Ti₁₂₋ₓO₇₋δ series does not give rise to the formation of La₅Ti₁₂O₃-like oxygen-rich layers that usually result in drastic drops of the electronic conductivity. However the introduction of Fe in the perovskite B-sites causes a distortion of the parent XRD cubic unit cell through to orthorhombic symmetries. This is accompanied by a gradual increase of the overall conductivity and also in the electrochemical activity of these materials for both oxygen reduction and hydrogen oxidation as previously observed (19).

Compared with other symmetric electrode candidate materials recently reported in the literature, Fe-substituted LSTF based-electrodes offer rather promising performances in fuel cells fed with hydrogen, although further research work is highly demanded to optimise both the microstructure and graded compositions. Indeed, preliminary results on two-layered electrodes, i.e. a 1:1 LSTF:YSZ plus a 1:1 LSTF:CeO₂ exhibit enhanced performances compared to the simpler 1:1 LSTF:YSZ electrodes and other perovskite-based composites (LSCM or LCC). This is especially relevant when using methane as fuel, as the use of graded electrodes results in OCVs in excess of 1.0 V, i.e. 15-20% larger than in the case of habitual symmetric electrodes, including LSTF simpler electrodes, which in theory implies higher power and current densities.

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