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Pure and Mn-doped $La_4SrTi_5O_{17}$ layered perovskite as potential solid oxide fuel cell material: Structure and anodic performance

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HIGHLIGHTS

- Pure and Mn-doped layered La/Sr titanates were studied as SOFC anode materials.
- Structural studies confirm their monoclinic symmetry in air or diluted hydrogen.
- The pure compound presents a better catalytic behaviour for methane steam reforming.
- Optimized LST/YSZ electrode preparation gives a Rp of 1.17 Ω cm^2 at 900 °C in wet H_2.

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ABSTRACT

Pure and 5% Mn doped layered perovskites $La_4SrTi_5O_{17}$, members of the $La_4Sr_{n-4}(Ti,Mn)_nO_{3n+2}$ series with $n = 5$, have been synthesized and investigated as anode materials for Solid Oxide Fuel Cells. The use of XRD, neutron and electron diffraction techniques allows clarifying some divergences concerning the structural characterization within the family, not only in air but also in anodic-like $N_2/H_2(97/3)$ atmosphere. The electrical conductivity of both compounds is very low in air but those values increase by two orders of magnitude in diluted hydrogen. The study of catalytic properties for methane steam reforming as well as in-depth analysis of the SOFC anodic behaviour of both materials are described, for which a microstructure optimization of the electrode allows to demonstrate the potential interest of the lamellar materials upon the classical three-dimensional cubic-like LSTs.

1. Introduction

Solid Oxide Fuel Cells major issues are related to the degradation of electrode materials, as well as the electrode-electrolyte and electrode-interconnect interfaces during long term operation or transient phases. It makes heating or cooling procedures sometimes heavy and complex. The most widely used SOFC anode is a cermet (ceramic-metal composite) of nickel and yttria-stabilized zirconia (YSZ); Ni/YSZ cermet is commonly chosen due to low cost and high chemical stability in the reducing atmosphere of the anode; furthermore, its thermal expansion coefficients are compatible with YSZ electrolyte [1–3]. Nickel in the cermet anode acts as an electrocatalyst in the electrochemical oxidation of hydrogen and provides high electronic conductivity. YSZ phase adds the ionic conductivity component to the anode that helps increasing the number of triple-phase boundaries (TPB) where the reaction can take place. At the same time, the YSZ network maintains the dispersion of nickel particles and acts as a growth inhibitor of metal grains during elaboration and operation of the cell. Unfortunately, the activity of the classical cermets and the cell performance can be affected due to kinetically favoured reactions such as carbon deposition when directly using hydrocarbon fuels at

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the anode, especially at low current density or in transient conditions. Carbon formation on the nickel surface can block the TPB [4,5], leading to a decrease in the power efficiency of the cell. Most research aiming at overcoming the limitations of nickel-based anodes has focused on the development of alternative materials that are catalytically active for the oxidation of hydrocarbons (directly or indirectly) and inactive for cracking reactions that lead to carbon deposition. Other problems of Ni-YSZ cermets are the irreversible losses of activity stemming from sulphur poisoning in the case of realistic fuels as well as coarsening of Ni-particles in operation and redox cycling, the two latter being true even in H_2/H_2O or H_2/CO atmospheres [2,6–12].

Due to their high resistance toward reducing and sulphur-containing atmospheres, perovskite compounds (of general formula ABO_3) have in during the last decade attracted great interest in replacement of Ni-cermets [11–13]. Most of doped-$SrTiO_3$ that have been considered as anode materials are of classical tridimensional perovskite structure, with principally La^{3+} (LST) or Y^{3+} (YST) doping at the A-site [14–17]. To improve the electrochemical performance of those materials, still too low to be used as a single phase anode, cation doping at the B-site of the perovskite has been considered; among them, Mn^{3+} doping [18,19] and Ga^{3+}/Mn^{n+} co-doping [20] are worth mentioning, but with limited success [21]. Actually, for the anode side, no real attention has been played to new structure types, especially layered materials that have revealed interesting performance as a cathode component (*e.g.* oxygen vacancy ordered $REBaCo_2O_{5+\delta}$ [22] or Ruddlesden–Popper type $RE_2NiO_{4+\delta}$ [23,24]. In the case of La-substituted strontium titanates, literature agrees with the presence of lamellar compounds of discrete $La_4Sr_{n-4}Ti_nO_{3n+2}$ compositions (with $n = 4$, 4.5, 5 and 6), that correspond to the La-rich part of the $SrTiO_3–La_2Ti_2O_7$ phase diagram. Layered perovskites corresponding to the homologous series $A_nB_nO_{3n+2}$ have been first studied by Carpy et al. [25–15], then, by other authors like Nanot et al. [26–30]. More recently, an exhaustive study and review on the $A_nB_nO_{3n+2}$ family was done by Lichtenberg et al., not only on completely oxidized compounds but also for reduced materials, what is of great interest in the case of SOFC anodes [31,32].

In a general manner, these compounds are related to the perovskite structure as built of [110] perovskite slabs separated by oxygen over stoichiometric crystallographic shear planes, each slab offsetting from one another by $1/2[001]_p$ and containing n octahedra layers per block (see Figs. 2–4 in Ref. [30]). We recently evidenced that the layered compound corresponding to $n = 5$ (hereafter referred to as LST2D) was more resistive to reduction than cubic perovskite-like $La_xSr_{1-x}TiO_{3+\delta}$ homologues (LST3D), with randomly distributed overstoichiometric oxygen atoms in the form of local defects, even at high temperature. Nevertheless, although LST2D exhibits in N_2/H_2(3%) electrical conductivity values that are two orders of magnitude lower than LST3D ($x = 0.33$) ($2.3.10^{-2}$ S cm^{-1} vs. 8.0 S cm^{-1} at 800 °C, respectively), a better catalytic activity for steam reforming was shown for the lamellar compounds, making those materials of interest for SOFC anodes operating on Natural Gas [33,34].

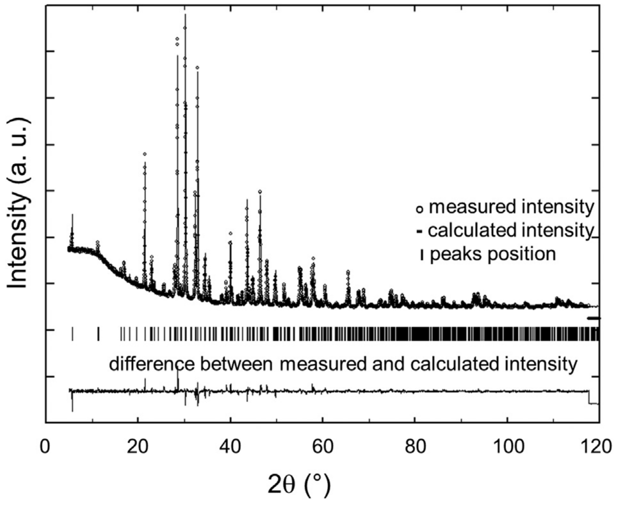

Fig. 1. Rietveld refinement of LST415 using powder XRD data and performed in the *Pmnn* space group.

In this paper, we systematically combined X-Ray, Neutron and Electron Diffraction techniques to unambiguously reveal the actual structure of $La_4SrTi_5O_{17}$ (LST415) and 5% Mn-doped $La_4Sr(Ti_{0.95}Mn_{0.05})_5O_{17}$ (LSTM415) after synthesis in air and reduction in diluted hydrogen. With the aim to develop those layered compounds as SOFC anode material, their electrical and catalytic properties were compared and the microstructure and composition of an LST2D containing anode was optimised in regards to its electrochemical behaviour.

2. Experimental

$La_4Sr(Ti,Mn)_5O_{17}$ powders were prepared using the standard Pechini route [35]. A Ti^{4+} aqueous solution was formed from titanium (IV) isopropoxide (Alfa Aesar, 99.995%) mixed with ethylene glycol and citric acid in a 1:20:5 M ratio. About 0.5 mL of deionised water per gram of citric acid was added in order to help citric acid dissolution. La_2O_3 (Rhodia, 99.99%), $SrCO_3$ (Alfa Aesar, 99.9%) and $MnCO_3$ (Alfa Aesar, 99.985%) were weighed in stoichiometric quantities. Nitric acid was regularly poured until complete dissolution of the precursors, without further pH adjustment. The solutions were evaporated on a magnetic stirring plate until the formation of perfect gels that were subsequently dried and pyrolyzed overnight at approximately 250 °C. After grinding, the resulting powders were heat treated in air at 700 °C for 5 h in order to remove the excess of nitrates and organic residues, then pressed into pellets before being treated in air several times at 1400 °C or 1500 °C for 24 h with intermediate grindings to obtain single phase samples of LST415 and LSTM415, respectively.

Powder X-Ray diffraction (XRD) data were collected at room temperature (RT) using a Bruker AXS D8 Advance diffractometer working in Bragg-Brentano geometry with Cu $K\alpha_{1,2}$ radiations and an energy dispersive detector (Sol-X). Structural refinements using the Rietveld method were performed with the Fullprof Suite program [36]. A Pseudo-Voigt function was applied for the peak profiles and the atomic positions as well as the isotropic atomic displacements of all atoms were refined. Since no superstructure peaks were observed, when several atoms shared the same atomic site, a statistic occupation was always considered.

Neutron Diffraction experiments (ND) were carried out at room temperature on the high resolution D2B beam line of ILL (Grenoble); the neutron wavelength $\lambda = 1.59525(3)$ Å was obtained from Rietveld refinement of ND data fixing the cell parameters obtained after preliminary refinement using XRD data. The ND pattern was recorded in the angular range $2\theta = 0.3–160°$ with a 0.05° step, using approximately 8 g of powder introduced in a vanadium tubular sample holder.

Selected Area Electron Diffraction (SAED) patterns and high resolution images were obtained by Transmission Electron Microscopy on a Philips CM30 and a Jeol 4000EX, respectively. For such purposes, the material was finely ground and dispersed on a holey carbon film deposited on a Cu grid.