



A bottom-up building process of nanostructured $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ electrodes for symmetrical-solid oxide fuel cell: Synthesis, characterization and electrocatalytic testing

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HIGHLIGHTS

- Pure-phase LSCM nanopowder has been successfully synthesized by combustion method.
- A detailed morphological, textural and structural characterization is presented.
- A bottom-up building process of LSCM nanoelectrodes onto LSGMg electrolyte was performed.
- Electrocatalytic responses of the cells, under oxidizing and reducing atmospheres, are discussed.
- The ASR trends obtained were correlated with the electrode microstructure.

ARTICLE INFO

Article history:

Received 11 April 2013

Received in revised form

19 June 2013

Accepted 22 June 2013

Available online 4 July 2013

Keywords:

Perovskite oxide
Combustion method
Nanocrystallites
Nanoelectrodes
Symmetrical cells
Solid oxide fuel cells

ABSTRACT

Pure-phase $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) nanocrystallites have been successfully synthesized by the combustion method, employing glycine as fuel and complexing agent, and ammonium nitrate as combustion trigger. A detailed morphological and structural characterization is performed, by using of X-ray diffraction, N_2 physisorption and electron microscopy. The LSCM material consists in interconnected nanocrystallites (~ 30 nm) forming a sponge-like structure with meso and macropores, being its specific surface area around $10 \text{ m}^2 \text{ g}^{-1}$. Crystalline structural analyses show that the LSCM nanopowder has trigonal/rhombohedral symmetry in the $R\bar{3}c$ space group. By employing the spin coating technique and quick-stuck thermal treatments of the ink-electrolyte, electrodes with different crystallite size (95, 160 and 325 nm) are built onto both sides of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ -disk electrolyte. To test the influence of the electrode crystallite size on the electrocatalytic behavior of the symmetrical cells, electrochemical impedance spectroscopy measurements at 800°C were performed. When the electrode crystallite size becomes smaller, the area specific resistance decreases from 3.6 to $1.31 \Omega \text{ cm}^2$ under 0.2O_2 – 0.8Ar atmosphere, possibly due to the enlarging of the triple-phase boundary, while this value increases from 7.04 to $13.78 \Omega \text{ cm}^2$ under 0.17H_2 – $0.03\text{H}_2\text{O}$ – 0.8Ar atmosphere, probably due to thermodynamic instability of the LSCM nanocrystallites.

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1. Introduction

Solid oxide fuel cells (SOFCs) have attracted a great attention due to its high efficiency and the more clean electrical power

generation [1]. A SOFC device mainly consists of three components: a porous cathode, a porous anode and a dense electrolyte. The traditional materials used in SOFC operating between 800 and 1000°C are yttria-stabilized zirconia (YSZ) as electrolyte, Ni/YSZ cermet as anode and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ as cathode [2]. Strontium-substituted manganites have been chosen due to their excellent electronic conductivities and good catalytic behavior toward oxygen reduction [2]. Ni/YSZ offers excellent catalytic properties, electronic/ionic conductivity and good current collection. However, such cermets present some disadvantages

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related to the low tolerance to sulfur and carbon built up when using hydrocarbon fuels [3–5].

Symmetrical-solid oxide fuel cells (S-SOFC), as an alternative approach to this configuration, adopt the same material both as anode and cathode, simultaneously. It has several advantages compared to the conventional SOFCs. The reduced number of cell components could facilitate the assembly of a fuel cell in a single thermal treatment and minimize compatibility requirements (thermal and chemical). Besides, this configuration could overcome two main drawbacks associated with SOFC technology when it directly operates with hydrocarbon fuels, i.e., the reversible sulfur poisoning and carbon deposition due to the possibility to revert the gas flow which will oxidize any sulfur species or carbon deposit [6,7]. The requirements for candidate symmetrical electrode materials are rather stringent, as they should include all the conditions applicable to an anode and cathode simultaneously: (1) good catalytic activity toward oxygen reduction and fuel oxidation; (2) chemical stability under both reducing and oxidizing atmospheres; (3) compatible thermal expansion with the other fuel cell components; and (4) acceptable electron and oxygen ion conductivity in both reducing and oxidizing atmospheres. Therefore, it is a challenging task to find materials that meet all requirements simultaneously. Thus, the typical performances obtained for S-SOFCs are somewhat lower as compared to traditional Fuel Cells due to the extreme difficulty to find a perfect material that fulfills all the requirements [8].

Up to now, only a very limited number of materials has been successfully demonstrated as electrodes of symmetrical-SOFCs [8–11]. A promising combination of properties, including phase and dimensional stability, high electrochemical activity in both reducing and oxidizing atmospheres, and chemical compatibility with various solid electrolytes, was recently reported for $(\text{La,Sr})(\text{Cr,Mn})\text{O}_{3-\delta}$ perovskites [12–19]. $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) represents one of the most attractive materials [7,10,12,16,20,21]. The LSCM composition arises from the need to combine the properties of $\text{La}_{1-x}\text{A}_x\text{CrO}_{3\pm\delta}$ and $\text{La}_{1-x}\text{A}_x\text{MnO}_{3\pm\delta}$ materials. Chromite-based materials have been generally employed as interconnecting materials for SOFCs due to their relatively good stability in both reducing and oxidizing atmospheres at high temperatures [12,22]. The reported polarization resistance using these materials is too high for efficient SOFC operation, although significant improvements have been achieved by using doping in the B-site [12]. Manganite-based materials, as mentioned above, are the standard choice as cathode but they are unstable in anode conditions [7,23]. The main limitation to the LSCM material is its lower ionic conduction compared with the known mixed-conducting electrode materials and solid electrolytes [24].

The electrocatalytic performances of the anode and the cathode in SOFCs are critically dependent on the microstructures of the electrode layer, in particular, the total length of the triple-phase boundary (i.e. interface between electrolyte disk, electrode material and gas phase) and its porosity and tortuosity. These properties, in turn, are strongly dependent on the features of the starting oxide powder and its synthesis process [20]. In the literature, solid state reaction is the main synthesis process reported for type-perovskite LSCM oxides [6,12,17,18,25–30]. This synthesis route produces materials with large particle sizes ($>5\text{ }\mu\text{m}$) and low porosity, mainly due to the high synthesis temperature employed ($>1300\text{ }^\circ\text{C}$). Therefore, the preparation of fine and pure-phase LSCM powders with less agglomeration is desirable to improve the electrode performance.

In this context, the so-called combustion method has been considered as an attractive way to synthesize a wide variety of ultrafine particles of metallic oxides including perovskites [31,32]. This is a simple method with the advantage of using inexpensive

precursors and producing highly reactive nano-sized powders. The resulting powders are crystalline, homogeneous, softly agglomerated, and vary in size between 1 and 100 nm depending upon composition and synthesis parameters. This process is simple, rapid, low cost, and environmentally compatible [33]. However, the mechanism of the combustion reaction is quite complex because many parameters influence the reaction such as the chemical nature of the fuel molecule, the fuel to oxidizer ratio, the use of excess oxidizer, the use of combustion aid, the ignition temperature and the water content of the precursor mixture. In a previous work we reported the synthesis and characterization of pure-phase LSCM fine-crystallites showing a size distribution around 200 nm, which were prepared by the combustion method evaluating the influence of the glycine-to-nitrates molar ratio and the subsequent thermal treatment [34].

In the present study, the former aim is the optimization of the combustion synthesis conditions to obtain a pure-phase $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ nanopowder. The addition of ammonium nitrate in the combustion precursor gel, as oxidizer agent and to trigger the combustion, was evaluated. A detailed morphological, structural and textural characterization of the nanostructured LSCM materials was performed. The next aim is the bottom-up building process of LSCM nanoelectrodes in symmetrical-SOFC. The attention is focused to keep as much as possible the nanostructured nature of the starting LSCM powders in the final morphology of the electrodes in the symmetrical (LSCM/LSCMg/LSCM) cells. Finally, preliminary electrocatalytic testing of the symmetrical cells in both oxidizing and reducing symmetric atmospheres for electrodes with different crystallite size are presented and discussed.

2. Experimental section

2.1. Synthesis of electrode material

Nanostructured powders of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ composition were prepared by combustion synthesis employing glycine as fuel and complexing agent, and ammonium nitrate as trigger to promote the combustion process. Glycine is known to act as a complexing agent for a number of metal ions, as it has a carboxylic acid group at one end and an amino group at the other end [31]. This zwitterionic characteristic of the glycine molecule enables the effective formation of complexes with metal ions of varying ionic sizes. These complexes help to maintain compositional homogeneity among the constituents by preventing their selective precipitation. On the other hand, glycine also serves as a fuel in the combustion reaction, as it is oxidized by nitrate ions. Glycine acts as a fuel during the combustion reaction, being oxidized by the nitrate ions. Oxygen from air does not play an important role during this combustion process [35]. On the other hand, ammonium nitrate is often chosen as a combustion aid in combustion synthesis because of its low cost and highly exothermic decomposition. Also, generates gaseous products only, without altering the proportion of other elements that are produced [32].

In a typical procedure, stoichiometric amounts of La_2O_3 (Alfa Aesar, 99.99%), SrCO_3 (Alfa Aesar, 99%), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Aesar, 98.5%) and metallic Mn (Alfa Aesar, 99.99%) were dissolved in a HNO_3 (Cicarelli, 65%) diluted solution. In order to obtain the nitrates mixture, the metal ions solution was heated at $T \sim 80\text{ }^\circ\text{C}$ during 24 h. Then, distilled water, $\text{NH}_2\text{CH}_2\text{COOH}$ (Aldrich, 98%) and NH_4NO_3 (Mallinckrodt, 99.99%) were added to the dried metal-nitrates mixture. The glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) content was adjusted to an elemental stoichiometric coefficient (φ) equal to 1.8, according to the results reported elsewhere [34]. The φ coefficient is defined as the ratio between the total valences of the fuel

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