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Synthesis and characterization of $La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ oxide as cathode for Intermediate Temperature Solid Oxide Fuel Cells

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ABSTRACT

Nanocrystalline $La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (LSFCu) material was synthetized by combustion method using EDTA as fuel/chelating agent and NH_4NO_3 as combustion promoter. Structural characterization using thermodiffraction data allowed to determine a reversible phase transition at 425 °C from a low temperature *R-3c* phase to a high temperature *Pm-3m* phase and to calculate the thermal expansion coefficient (TEC) of both phases. Important characteristics for cathode application as electronic conductivity and chemical compatibility with $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO) electrolyte were evaluated. LSFCu presented a p-type conductor behavior with maximum conductivity of 135 S cm^{-1} at 275 °C and showed a good stability with CGO electrolyte at high temperatures. This work confirmed that as prepared LSFCu has excellent microstructural characteristics and an electrical conductivity between 100 and 60 S cm^{-1} in the 500–700 °C range which is sufficiently high to work as intermediate temperature Solid Oxide Fuel Cells (IT-SOFCs) cathode. However a change in the thermal expansion coefficient consistent with a small oxygen loss process may affect the electrode-electrolyte interface during fabrication and operation of a SOFC.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are electrochemical devices considered as one of the most promising candidates for power generation from large stationary plants to small and portable distributed generation applications with superior benefits than other fuel cells [1]. Nowadays there is a great interest on developing Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs) working in the 500–700 °C temperature range [2]. One of the main research topics is the development of highly active and long term stable cathodes for IT-SOFCs. Moreover lowering the operating temperature reduces electrode kinetics and increases the interfacial polarization resistances, particularly on the cathode side of the cell. As a consequence, a major effort is being made to enhance the cathode performance using different synthesis routes and compositions to obtain porous materials, with small particle sizes and high purity [3–5].

The best cathode materials that have been described so far are based on the simple perovskite structure $ABO_{3-\delta}$, with cation disorder in the *A* and *B* sites and a significant proportion of disordered oxygen vacancies. In most cases where B cations are multivalent, these materials are mixed ionic-electronic conductors (MIECs) favouring the reduction of the cathode area specific resistance (ASR) [6]. Some of the reported cathode materials with highest electrochemical activities for the oxygen reduction reaction (ORR) are compounds such as $(Ba,Sr)(Co,Fe)O_{3-\delta}$ (BSCF) [7–9], $(La,Sr)(Co,Fe)O_{3-\delta}$ (LSFC) [10] and $LnBaCo_2O_{5+\delta}$ [11]. The presence of the Co^{+3}/Co^{+4} pair in these perovskites enhance the ORR kinetics leading to a very low polarization loss. Nevertheless these cathode compositions with high cobalt content show large thermal expansion coefficients (TEC), larger than the ceria-based electrolytes (CGO: $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ and CSO: $Ce_{0.9}Sm_{0.1}O_{2-\delta}$) and interconnector materials (ferritic stainless steel) available for IT-SOFCs applications limiting the cell life.

Recently, the preparation of cobalt-free cathodes [12,13] has taken much relevance and iron-based perovskite as $Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$ and $La_{1-x}Sr_xFeO_{3-\delta}$ have attracted much attention due to its lower TEC and superior structural stability than cobalt-based materials [14,15]. Unfortunately, these materials present a lower activity due to the low

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electrical conductivity and oxygen permeation compared to cobalt-based perovskite [16]. Novel cathodes using copper as substituent have proven to be an interesting alternative since the presence of Cu^{+2}/Cu^{+3} in the structure instead of Fe^{+3}/Fe^{+4} increases the electronic conductivity, reduces the polarization resistance and increases the oxygen vacancies, which enables their use in IT-SOFC applications [17–20]. Additionally Cu-substituted Fe perovskites can be prepared at lower temperatures than pure Fe ones, allowing for a better control of the microstructure. $La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ was reported as a novel cathode material by Zhou et al. [19] as substituent and demonstrate to be a promising material for IT-SOFC with high electrical conductivity, low polarization resistance for oxygen reduction reaction (ORR) and thermal expansion coefficient (TEC) similar to ceria-based electrolytes.

Here we describe a modified gel combustion route using EDTA as fuel/complexation agent and assisted with NH_4NO_3 which has proven to be a good method for preparing nanocrystalline oxides [20]. This synthesis method was used successfully to prepare nanocrystalline $La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (LSFCu) powders. A detailed microstructural characterization was performed by Transmission Electron Microscopy (TEM) and the structure and thermal expansion coefficients were studied using synchrotron X-ray diffraction data at different temperatures. Additionally, important parameters for SOFC-cathode application, such as electrical conductivity and chemical compatibility with $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ electrolyte are presented.

2. Materials and methods

2.1. Synthesis of $La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ powder

$La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (LSFCu) powder was prepared by a modified gel combustion route, using ethylenediaminetetraacetic acid (EDTA) as fuel and complexation agent. In gel combustion routes the most used fuels are glycine, citric acid and urea, due to their ability to form stable complexes with metal ions and because they prevent the precipitation of metal ions during the water evaporation process [21]. Additionally these compounds self-ignite at high temperature providing the needed start of the combustion process.

We use EDTA in basic medium (pH = 10) that is a stronger titration agent than glycine and urea, but does not ignite upon heating below 350 °C, so it is necessary to employ NH_4NO_3 as combustion promoter to enhance the auto-ignition and self-sustained combustion.

The synthesis of 5 g of LSFCu was performed using $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Fe(C_5H_7O_2)_2$ and $Cu(NO_3)_2 \cdot 3H_2O$ (all > 99.9%, from Sigma-Aldrich) as metal sources. The reagents were dissolved in stoichiometric amounts in 100 ml distilled water in a 800 ml beaker and EDTA was added as complexation agent. The EDTA/metal ion ratio was 1:1.1 (10% of EDTA in excess) to ensure the complete complexation of the cations HNO_3 (70%) and NH_4OH (28–30%) were added to form NH_4NO_3 in-situ and promote the combustion of EDTA. The solution with pH = 10 was heated over a hot plate with constant stirring at 150 °C until the gel was formed. The stirring bar was then removed from the dark-red gel that was posteriorly heated at 350 °C until self-ignition. The optimized quantities of HNO_3 and NH_4OH for this synthesis were 1.2 ml HNO_3/g EDTA and 3.5 ml NH_4OH/g EDTA. This proportion was found high enough to promote the full combustion of the gel but low enough to prevent an explosive combustion, due to the highly exothermic decomposition of NH_4NO_3. As final step the obtained ashes were pressed in 13 mm pellets at 25 MPa and fired at 900 °C for 5 h with a heating rate of 5 °C min^{-1} to obtain fine nanocrystalline LSFCu powders.

2.2. Transmission electron microscopy characterization

Morphological characterization and electron diffraction of cathode powder was performed by transmission electron microscopy (TEM) using a Philips CM 200 UT instrument with a LaB_6 filament operated at 200 kV. Some mg of the powdered samples were suspended in isopropyl alcohol and ultrasonicated for 5 min, a drop of the liquid was transferred into a Ultrathin/Holey Carbon film coated gold TEM grid of 300 Mesh (Ted Pella INC.) and allowed to dry in air.

2.3. Synchrotron X-ray thermodiffraction

The LSFCu sample was characterized by thermodiffraction from RT to 900 °C in air atmosphere using the ARARA furnace at D10B-XPD beamline of the Brazilian Synchrotron Light Laboratory (LNLS). The beamline is equipped with a θ–2θ reflection-geometry diffractometer with a Mythen 1000 linear position sensitive detector (PSD).

X-rays with energies of 10 keV and 7.13 keV ($\lambda_{10\ keV} = 1.24058$ Å and $\lambda_{7.13\ keV} = 1.74016$ Å) were used to illuminate the sample mounted in a spinning flat holder during data collection in the $2\theta = 10$–$120°$ range in steps of 0.5°. The detector, spanning 3°, collected data six times at each 2θ value. Data reduction and averaging was carried out to obtain a powder pattern with a 2θ step = 0.005°. Rietveld refinement was used to characterize the structure of the observed phases and extract structural parameters for thermal expansion coefficient (TEC) determination. The pattern was fitted using the FullProf Suite including anomalous scattering (f' and f'') corrections for all atomic species for 10 keV and 7.13 keV incident radiation [22].

2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to determine the oxygen loss of the LSFCu sample between RT and 850 °C in air atmosphere on a Shimadzu TGA-50 analyser. The sample was mounted in a platinum crucible and heated at 5 °C/min in a synthetic air flow of 50 ml/min.

2.5. Electrical conductivity

The electrical conductivity of LSFCu was studied using the standard DC four-probe technique with an Agilent Digital multimeter (model 34401A) from RT to 850 °C. LSFCu was prepared pressing the powder in disks of 13 mm at 25 MPa and then annealed at 1000 °C for 12 h to obtain dense pellets. The data collection was performed on quasi static conditions with a heating rate of 1 °C/min without airflow.

2.6. Chemical compatibility

X-ray diffraction (XRD) patterns were recorded to study the cathode-electrolyte chemical compatibility using a conventional powder diffractometer (Rigaku Ultima IV, operating at 40 kV and 30 mA using Cu$K\alpha$ radiation) operating in θ–θ Bragg–Brentano geometry. Powdered mixtures of LSFCu with CGO in the ratio 70/30 (wt%) were ground in agate mortar, pressed in to pellets and fired at 900 °C for 24, 48 and 120 h. The scans were performed in the 2θ range of 20–70° with a 0.04° step and a time collection step of 2 s.

3. Results and discussion

The material $La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ has a perovskite-type structure with La and Sr sharing the *A*-site and Fe and Cu the