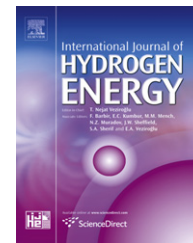


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La_{2-x}Sr_xCoO_{4-δ} (x = 0.9, 1.0, 1.1) Ruddlesden-Popper-type layered cobaltites as cathode materials for IT-SOFC application

Y. Hu^a, Y. Bouffanais^a, L. Almar^b, A. Morata^b, A. Tarancon^b, G. Dezanneau^{a,*}

^aLaboratoire Structures, Propriétés et Modélisation des Solides, École Centrale Paris, Grande Voie des Vignes, 92295 Châtenay-Malabry, France

^bAdvanced Materials for Energy, Catalonia Institute for Energy Research (IREC), Jardins de les dones de negre1, Planta2, 08930 Sant Adrià Besòs (Barcelona), Spain

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ABSTRACT

La_{2-x}Sr_xCoO_{4-δ} (x = 0.9, 1.0, 1.1) compounds with Ruddlesden-Popper K₂NiF₄-type structure have been investigated as potential cathode materials for IT-SOFC application. Materials have been prepared by citrate-nitrate combustion method. Structural evolution analysed by XRD shows a shortened Co–O–Co bond length within the perovskite layer as Sr substitution increases, while the interlayer distance at the same time increases. An oxygen stoichiometry close to 4 has been found for all compositions at room temperature. Thermal expansion coefficients have been obtained from temperature-dependent XRD analysis and show large values (>20 × 10⁻⁶ K⁻¹) compared to the currently utilized electrolyte materials. Electrochemical characterisation has been performed by means of impedance spectroscopy on symmetric cells with CGO electrolyte. Pure electrodes have a high Area Specific Resistance, probably due to limited oxygen ion diffusion. By using composite electrode (50 wt.% CGO), an Area Specific Resistance of 0.25 Ω cm² is obtained at approximately 700 °C for all the three compounds suggesting promising electrochemical properties for IT-SOFCs.

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1. Introduction

During last years, considerable efforts have been carried out to reduce the operating temperature of solid oxide fuel cells to an intermediate range (IT-SOFC), ideally 500–700 °C [1], looking for lower costs, materials compatibility and long-term durability. However, a great challenge for IT-SOFC development lies in the strong decrease of electrolytes conductivity and increased electrode overpotentials at lower temperature,

resulting in a great reduction of fuel cell voltage and output power in working conditions. One known strategy is to explore new electrolyte and electrode materials with high performances in the temperature range of interest. Special efforts have been dedicated to investigate new cathode materials due to the fact that the oxygen reduction is the more difficult reaction to activate at reduced temperatures, making cathodes the major source of cell voltage losses for the whole system [2,3].

* Corresponding author.

E-mail address: guilhem.dezanneau@ecp.fr (G. Dezanneau).

The so-called Ruddlesden-Popper (RP) layered perovskite oxides ($A_{n+1}B_nO_{3n+1}$), particularly the Ln_2MO_4 oxides with K_2NiF_4 -type structure, have been investigated as promising candidates for IT-SOFC cathode materials due to their mixed ionic-electronic conductivity (MIEC), appropriate electronic and electrochemical properties, and suitable chemical and mechanical compatibilities with other SOFC components. The K_2NiF_4 -type structure can be described as succession of ABO_3 perovskite layers alternating with (or sandwiched between) AO rock-salt layers. This structure enables to accommodate large amount of interstitial oxygen anions into the rock-salt layers favouring the bulk ionic transport to occur via diffusion of interstitial ions in the rock-salt layers, giving rise to fast oxygen diffusivity [4–6]. Among this series of materials, rare-earth nickelates altered by A and/or B sites substitutions have been the most intensively investigated because they exhibit very attractive electrochemical performance [7–13]. As one of the most important features of MIEC cathode materials, remarkable oxygen ion diffusion and exchange coefficients were found in these materials by various experimental techniques [4,9,14]. Moreover, low thermal expansion coefficients (TEC) were measured for $Ln_2NiO_{4+\delta}$ based compounds, $\sim 11\text{--}14 \times 10^{-6} \text{ K}^{-1}$ [7,15,16], being well compatible with the most commonly used electrolytes such as $Zr_{1-x}Y_xO_{2-\delta}$, $Ce_{1-x}Gd_xO_{2-\delta}$ and $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$.

Nevertheless, so far, not much attention has been paid to the RPs cobaltites as cathode materials, despite previous investigations of oxygen transport on $La_2CoO_{4+\delta}$ [17] and $La_2Ni_{1-x}Co_xO_{4+\delta}$ [18,19] which demonstrated competitive oxygen diffusivity and raised surface exchanges. Besides, electrical properties in A-site substituted cobaltites $La_{2-x}Sr_xCoO_4$ could be adjusted by A-site Sr substitution to obtain an appropriate electrical conductivity [16,20,21], considering the poor electrical conductivity in RP phases compared to other perovskite cathode materials [22–26]. Finally, good catalytic properties were also demonstrated in $La_{2-x}Sr_xCoO_4$ materials [27,28].

In this study, we synthesized $La_{2-x}Sr_xCoO_{4-\delta}$ ($x = 0.9, 1.0, 1.1$) compounds and investigated their physical–chemical properties as well as electrochemical performance using pure and composite electrodes in order to determine their potential as IT-SOFC cathode materials.

2. Experimental

$La_{2-x}Sr_xCoO_{4-\delta}$ with $x = 0.9, 1.0$ and 1.1 were synthesized via a microwave-assisted citrate-nitrate combustion route. La_2O_3 (99.9%-Gd, STREM) was dissolved with HNO_3 (53%, MERCK) in de-ionized water and successively added with $Sr(NO_3)_2$ (99%, SETREM), $Co(NO_3)_2 \cdot 6H_2O$ (99%, STREM) in a stoichiometric ratio. Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, 99.5–100%, MERCK) was added as chelating agent in the proportion $n(\text{citric acid}) : n(\text{total positive charges of metallic cations in solution}) = 1:1$. The aqueous solution was then continuously stirred and heated at 80°C during roughly 1 h until a complete homogenization and a viscous gel were obtained. A domestic microwave oven was then used to dehydrate the obtained solution and

generate the combustion process induced by the microwave radiation of 600 W during 20–30 min. The residual product was heat-treated at 500°C for 1.5 h, followed by grinding and a final thermal treatment at 950°C for 4 h in air.

The as-synthesized powders were characterized by X-ray powder diffraction (XRD, Rigaku D/max-2550/pc, Cu $K\alpha$ radiation, $\lambda_{K\alpha 1} = 1.5405 \text{ \AA}$). Structural information were extracted through LeBail refinement of XRD data using the Fullprof suite program. Oxygen stoichiometry was determined by iodometric titration [29], for which the investigated powders were intensely grinded in an agate mortar then followed by a 3-h isothermal heating period at 700°C and a slow cooling to room temperature at a rate of 100°C/h in air, in order to ensure thermodynamic equilibrium. An average value of oxygen non-stoichiometry was taken from three titration experiments for each composition.

Temperature-dependent XRD experiments (ambient– 700°C) were carried out in air on powder samples, on a laboratory diffractometer (Rigaku Rotaflex RA-HF18) using Cu $K\alpha$ radiation. The evolution of cell parameters as a function of temperature was obtained from the same profile matching approach used for room temperature data analysis. TECs were deduced from XRD data analysis.

Electrochemical properties were characterised by electrochemical impedance spectroscopy (EIS) on symmetrical cells, using $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) as electrolyte. The CGO substrates were prepared from a commercial nano-scale powder (CGO 90/10 SY UHSA, ANAN) by cold isostatic pressing at 750 MPa and sintering at 1450°C for 12 h, achieving high density (96–97% of theoretical density). Electrodes were deposited symmetrically on the two surfaces of CGO electrolyte substrates by airbrush spraying. In this work, two kinds of configuration were studied: 1) pure $LaSrCoO_{4-\delta}$ electrode and 2) composite 50 wt.% $La_{2-x}Sr_xCoO_{4-\delta}$ – 50 wt.% CGO electrodes for $x = 0.9, 1.0$ and 1.1 . The first configuration served as a first attempt to evaluate the influence of processing parameters on electrochemical properties. The ink for airbrush was prepared through the mixing of electrode powders (with or without 50 wt.% CGO) in ethanol with an organic dispersant (Tween20, Sigma-ALDRICH), followed by a stirring of several days to obtain well dispersed suspension ink. Diverse sintering temperatures were tested for the pure $LaSrCoO_{4-\delta}$ electrode, whilst all composite electrodes were sintered at 1100°C for 3 h. In order to obtain good current collection, a gold paste (METALORM, GOLD PASTE M-0034) was coated onto the electrodes to form an Au layer serving as current collector. Impedance spectroscopy was performed at open circuit voltage (OCV) using a Solartron 1260 Frequency Response Analyser, with an excitation voltage of 50 mV over the frequency range from 0.01 Hz to 10 MHz. The temperature-dependent measurements were conducted over $300\text{--}800^\circ\text{C}$ in a 5 L/h air flow. Zview 2 electrochemical impedance software (Scribner Associates Inc.) was used for data analysis. The microstructure of the cells with composite electrodes were examined in cross section after measurements by using Scanning Electron Microscopy (SEM) in conjunction with EDS to verify the absence of minor secondary phases.

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