

STRONTIUM-DOPED LaCoO_3 PEROVSKITES IN SOLID OXIDE FUEL CELLS

V. V. Srdić*, L. Nikolić, V. Pejović^a

Department of Inorganic Technology and Materials Science, Faculty of Technology,
University of Novi Sad, Novi Sad, Yugoslavia

^aInstitute IRITEL, Belgrade, Yugoslavia

Cathode-electrolyte structures, for solid oxide fuel cells, are prepared by deposition of porous $(\text{La,Sr})\text{CoO}_3$ film on the surface of dense nanocrystalline 3 mol% Y_2O_3 stabilized zirconia electrolyte. The perovskite powder is prepared by a wet-chemical synthesis technique using metal-nitrates, mixed with a resin and organic solvents to form a paste that is deposited as a thick film by screen-printing technique. The characteristics of the synthesized powders, sintered samples and cathode-electrolyte structures are investigated.

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1. Introduction

A fuel cell is an energy conversion device that produces electricity by electrochemical combination of a fuel with an oxidant, and consists of two electrodes (the anode and cathode) separated by an electrolyte (Fig. 1) [1-3]. In solid oxide fuel cells (SOFCs) the electrolyte conducts oxygen ions produced at the cathode, by the reduction of gaseous oxygen, toward the anode.

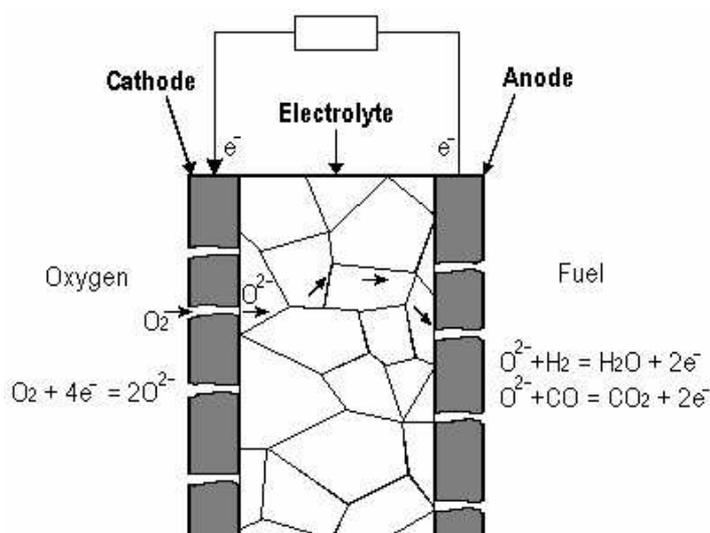


Fig. 1. Scheme of a solid oxide fuel cell.

* Corresponding author: srdicvv@uns.ns.ac.yu

The electrolyte material must be dense to prevent gas mixing, whereas the anode and cathode must be porous to allow gas transport to the electrochemical reaction zone [1]. Stabilized zirconia, especially yttria-stabilized zirconia, is the most common electrolyte in SOFCs because the material possesses an adequate level of oxygen-ion conductivity at the operating temperature (800-1000 °C), very low electronic conductivity and exhibits desirable stability in both oxidizing and reducing atmospheres [2,4]. The oxygen reduction reaction takes place on the SOFC cathode, usually deposited as a thick film on the electrolyte surfaces. Thus, for the application in SOFC-technology the cathode materials should have: a) good electronic conductivity, b) broad electrochemical reaction zone (the triple phase boundary between the electrode, electrolyte and gaseous oxygen), c) possibility for created oxide ions to be transported away from the reaction site into the bulk of the electrolyte, d) stability under working conditions (high temperature and oxidizing atmosphere) and e) a thermal expansion coefficient compatible with that of the solid electrolyte [3, 5]. All these requirements indicate that the properties of solid oxide fuel cell are strongly dependent on the electrode-electrolyte microstructure. Perovskite-type LaCoO_3 based structures are promising materials for the SOFC cathode [3,6]. Thus, substituting La on the A-site of LaCoO_3 with Sr^{2+} ion, the oxygen deficiency increases and hence the ionic conductivity is enhanced. This paper describes the preparation of $(\text{La,Sr})\text{CoO}_3$ perovskite thick film on yttria-stabilized zirconia electrolyte. Characteristics of the wet-chemically synthesized zirconia and perovskite powders as well as their sinterability are investigated, with the aim to find optimal processing conditions for preparation of cathode/electrolyte structure, which could be applied in SOFC technology.

2. Experimental

Perovskite $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ powders (where $x=0, 0.1, 0.2$ and 0.5) were prepared by a wet-chemical synthesis technique using the nitrate method. The corresponding quantities of La, Sr and Co nitrates were dissolved into distilled water and coprecipitated under the basic conditions in presence of NH_4OH and H_2O_2 . A coarse and dark perovskite powders were obtained after drying in air and calcination at different temperatures up to 900 °C. Sinterability of the perovskite powders was investigated by air sintering (at different temperatures up to 1300 °C) of uniaxially pressed pellet.

Zirconia doped with 3 mol% Y_2O_3 nanopowder (3Y-ZrO₂) was synthesized by the controlled hydrolysis of $\text{Zr}(\text{OC}_3\text{H}_7)_4$ (dissolved in anhydrous ethanol) with distilled water, from highly diluted ethanol solution of YCl_3 and H_2O , under acidic conditions. An aqueous sol was obtained by continuous evaporation and replacing the ethanol with distilled water without change the concentration and pH. The hydroxides were precipitated by slowly adding this aqueous sol to a well-stirred ammonium hydroxide solution. After washing several times in water and absolute ethanol the zirconia gel nanopowder was filtered, dried in air and calcined at 500 °C. The calcined 3Y-ZrO₂ powder was uniaxially pressed at 400 MPa in a hard metal die having a diameter of 10 mm. The dense electrolyte was formed by pressureless air sintering at 1070 °C of the zirconia pressed pellets.

The SOFC electrode was prepared by deposition of a paste (suspension of $(\text{La,Sr})\text{CoO}_3$ in organic mixture of a resin and solvents) as a thick film onto the sintered electrolyte 3Y-ZrO₂ pellet surfaces by screen-printing technique. The formed electrolyte-electrode samples were finally sintered in air.

The specific surface area was measured by nitrogen adsorption according to the BET method using a Micromeritics ASAP 2400 instrument, and used for calculation of the average particle size. The X-ray diffraction measurements were performed using a Siemens D5000 instrument with Ni-filtered Cu-K_α radiation, and the crystallite size was estimated using the Scherrer equation. The density of the pressed and sintered pellets was calculated from the geometry and the mass of the sample. Microstructure of the sintered electrolyte-electrode samples was investigated on fractured surfaces by high-resolution scanning electron microscope (HRSEM Philips XS 30).

3. Results and Discussion

Characteristics of the 3Y-ZrO₂ powder are presented in Table 1. The as-synthesized 3Y-ZrO₂ powder is amorphous and crystallizes after calcination in the tetragonal yttrium-doped zirconia solid solution [7]. The calcined 3Y-ZrO₂ powder has specific surface area of 122 m²/g, the corresponding average particle size of 8.2 nm (calculated from multipoint BET) and the average crystallite size of 7.8 nm determined by XRD (Table 1). On the other side, (La,Sr)CoO₃ powders calcined at 600 °C have very low specific surface area and corresponding particle size of about 60-90 nm (Table 1). XRD results [8] show that even the cobaltite powder calcined at 600 °C has high crystallinity, the almost pure perovskite phase can be obtained only at 900 °C. The cobaltite powders with lower strontium content (having $x \leq 0.2$) have rhombohedral structure, whereas only the La_{0.5}Sr_{0.5}CoO₃ powder has cubic perovskite phase (Fig. 2). This is the reason why the La_{0.5}Sr_{0.5}CoO₃ powder and calcination temperature of 900 °C were selected for preparation of the paste and formation of SOFC cathode film.

Table 1. Characteristics of the 3Y-ZrO₂ and La_{1-x}Sr_xCoO₃ powders.

	3Y-ZrO ₂ calcined at 500°C	LaCoO ₃ calcined at 600°C	La _{0.8} Sr _{0.2} CoO ₃ calcined at 600°C	La _{0.5} Sr _{0.5} CoO ₃ calcined at 600°C
Specific surface area [m ² /g]	122	11.4	14.2	10.8
Particle size from BET [nm]	8.2	72	61	87
Crystallite size [nm]	7.8	-	-	-
Mass loss (up to 1000°C) [%]	25.1	4.8	5.3	5.8
Green density [%TD]	39.5	44.6	43.8	48.7

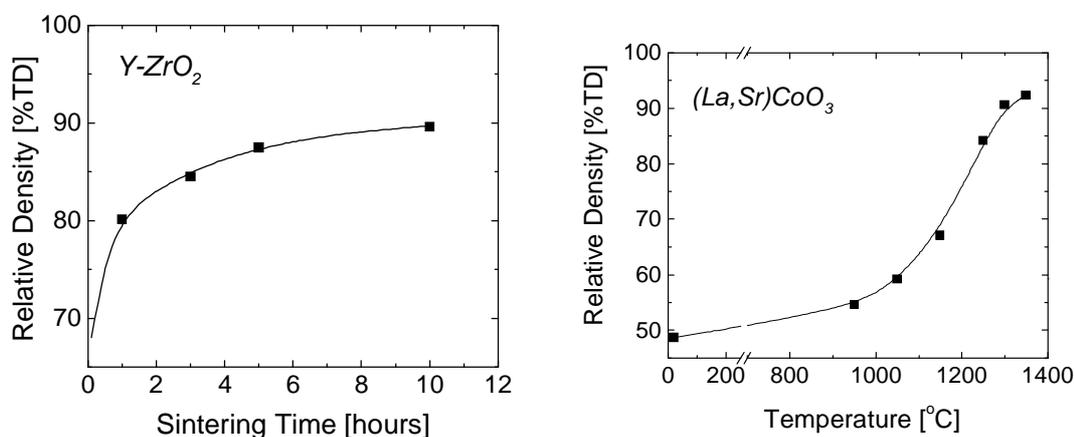


Fig. 2. XRD patterns of La_{1-x}Sr_xCoO₃ powders ($x = 0, 0.1, 0.2$ and 0.5) calcined at 900 °C.

The 3Y-TZP pellet uniaxially pressed at 500 MPa has a green density of 39.5 %TD (Table 1) and very fine microstructure with unimodal pore size distribution [7]. Density change with time during pressureless air sintering at 1070 °C is presented in Fig. 3a. Uniform microstructure with the average grain size less than 100 nm (Fig. 4a) and density of about 90 %TD (Fig. 3a) is obtained after air sintering at 1070 °C for 10 hours. Sintering behavior of the La_{0.5}Sr_{0.5}CoO₃ has been investigated too, because the porosity of the cathode film is one of the most important requirements for film application in SOFC-technology. The green density of the perovskite pellet, uniaxially pressed at 400 MPa, is 48.7 %TD (Table 1). Fig. 3b shows that densification starts at 900 °C and close porosity region is reached at temperature of ~1300 °C.

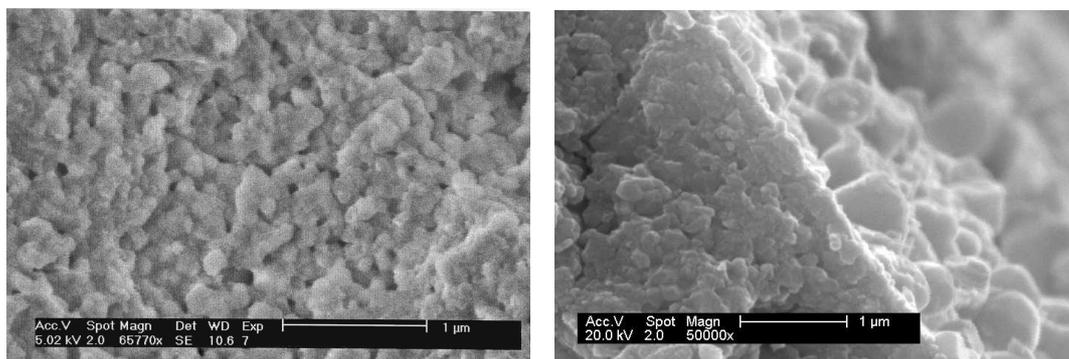


Fig. 3. Densification behavior of a) 3 mol% Y_2O_3 - ZrO_2 and b) $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$.

According to the sintering experiments the cathode-electrolyte samples for SOFC-application were prepared first by air sintering of the 3Y-ZrO₂ pellets at 1070 °C for 10 hours and finally by air sintering of the densified zirconia with deposited perovskite film, at 950 °C for 1 hour. The microstructure of the cathode-electrolyte contact area is presented in Fig. 4b. As can be seen, the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ film has relatively coarse grain structure, high fraction of porosity and uniform thickness less than 1 μm. In addition, the electrical conductivity, evaluated by complex impedance spectroscopy measurement [8], shows that the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ can be efficiently used as cathode material in the zirconia-based SOFCs.

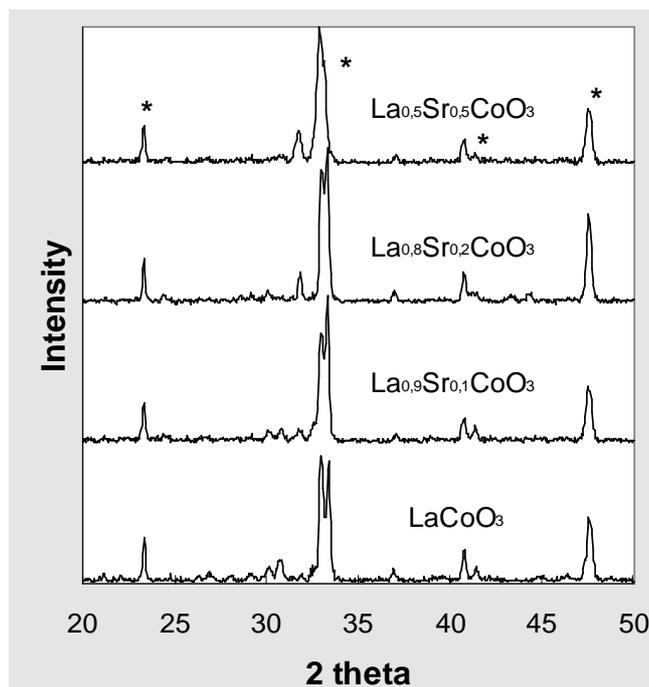


Fig. 4. High-resolution scanning electron micrographs of: a) 3Y-ZrO₂ air sintered at 1070 °C for 10 h and b) $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ film on dense 3Y-ZrO₂ substrate finally sintered in air at 950 °C.

4. Conclusion

Yttria stabilized zirconia nanopowder, synthesized by the controlled alkoxide hydrolysis, and perovskite $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ powder, obtained by a wet-chemical synthesis technique using the nitrate method, were used for preparation of the cathode-electrolyte samples for SOFC-application. The cathode-electrolyte structures were prepared first by air sintering of the 3Y-ZrO₂ pellets at 1070 °C for

10 hours, than by deposition of a paste (containing perovskite particles) as a thick film onto the sintered zirconia-electrolyte pellet surfaces by screen-printing technique and, finally, by air sintering of the prepared samples at 950 °C for 1 hour. The electrolyte zirconia phase has density of about 90 %TD and the average grain size less than 100 nm. It is also shown that the electrode La_{0.5}Sr_{0.5}CoO₃ film has relatively coarse grain structure, high fraction of porosity and uniform thickness, within 1 μm roughness, and can be used as the cathode material in zirconia based SOFC-s.

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