Journal of Power Sources 195 (2010) 4779–4784

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Synthesis, structural analysis and electrochemical performances of BLSITCF*x* as new cathode materials for solid oxide fuel cells (SOFC) based on BIT07 electrolyte

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ARTICLE INFO

*Article history:*
Received 23 July 2009
Received in revised form 15 February 2010
Accepted 21 February 2010
Available online 26 February 2010

*Keywords:*
SOFC
Oxides
Complex impedance spectroscopy
Cathode
BIT07

ABSTRACT

$BaIn_{0.3}Ti_{0.7}O_{2.85}$ (BIT07) is a suitable electrolyte for Solid Oxide Fuel Cell (SOFC) but half cells based on $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) as a cathode material show a degradation of the Area Specific Resistance (ASR) at 700 °C with time. This study deals with the characterization of alternative cathode materials showing a better compatibility with BIT07 than LSCF. A new solid solution, $Ba_xLa_{0.58(1-x)}Sr_{0.4(1-x)}In_{0.3x}Ti_{0.7x}Co_{0.2(1-x)}Fe_{0.8(1-x)}O_{3-\delta}$, with $0 \leq x \leq 1$, also called BLSITCF*x*, with in this case *x* expressed in molar %, derived from BIT07 and LSCF, has been synthesized at 1350 °C in air using BIT07 and LSCF powders. Two compositions, BLSITCF12 and BLSITCF25, have been selected due to their thermal expansion and conductivity properties. Symmetrical half cells based on these two new materials deposited on BIT07 electrolyte have been studied by complex impedance spectroscopy in air versus temperature and time. Their behaviour is comparable to LSCF's, with ASR values never exceeding 0.2 $\Omega cm^2$ at 700 °C, and moreover their less important Thermal Expansion Coefficient (TEC) mismatch with BIT07 lead to a better mechanical compatibility with time. These new compounds are therefore better candidates than LSCF as cathode materials for SOFC based on BIT07 electrolyte.



## 1. Introduction

Solid oxide fuel cells (SOFC) are all-solid devices converting the chemical energy of gaseous fuels into electricity via electrochemical processes with high energy conversion efficiency and low greenhouse gas emission [1]. To develop the SOFC technology, its operating temperature has to be lowered, since at high temperatures (800–1000 °C), the fuel cell materials degradation is accelerated [2]. However, intermediate temperature SOFCs (ITSOFC) working at ≈700 °C exhibit quite low performances in terms of energy density, ionic conductivity of the electrolyte and ohmic drop at the cathode–electrolyte interface. To develop the ITSOFC technology, it is essential to reduce both the polarization and resistance losses of the cell. These contributions can be reduced significantly by using materials in the form of thin films, resulting in a decrease of the overall cell resistance [3,4]. Low polarization losses can also be achieved by employing electrode materials with high activity for the electrochemical reactions and by optimizing the microstructure in the electrode/electrolyte interface region.

$BaIn_{0.3}Ti_{0.7}O_{2.85}$ (BIT07) is an alternative electrolyte material for ITSOFC [5], because, below 700 °C, its ion conductivity level is comparable to that of YSZ, the usual electrolyte material. Moreover BIT07, which is a cubic perovskite type oxide, is expected to present an excellent structural compatibility with perovskite cathode substrates (e.g. LSM, LSCF...). In order to validate its use in SOFC, this material has to fulfill several criteria. First BIT07 has to be chemically compatible with usual cathode materials, second the assembly BIT07/cathode has to exhibit similar electrochemical performances to the actual very performing YSZ/cathode and thirdly it has to show long-term cycle life. In a previous study [6], it has been shown that BIT07 is compatible with the well-known cathode materials LSCF ($La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) [7–12] and can be used with this material without requiring the use of intermediate layers [13,14], which is time and cost-effective, as the design and the firing step of the intermediate layer is avoided. However, an ageing problem has been noticed, probably associated to the TEC mismatch between BIT07 and LSCF. In the same study, it has been shown that, at 1000 °C, a reaction between BIT07 and LSCF occurred, leading to the formation of a new single-phase compound with a perovskite type structure. This phase which appears at the electrolyte/cathode interface could show interesting characteristics such as ionic or electronic conductivity leading to an improvement of its mechanical properties without lowering the electrochemical performances of the assembly. In contrary, this phase could be an insulating layer at the cathode/electrolyte interface [15].

In order to go further, new compositions have been synthesized at high temperatures starting from different mixtures of BIT07 and

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doi:10.1016/j.jpowsour.2010.02.052

LSCF. In this paper we present these new compounds which have been characterized and tested from electrochemical and mechanical points of view. Anode materials compatible with BIT07 have been prepared by the authors [16] and their optimization with these new materials will be published elsewhere.

## 2. Experimental

### 2.1. Sample preparation

BIT07 is synthesized as detailed in [5]: its constituents, high purity barium carbonate (Alfa Aesar, Germany), indium oxide (Alfa Aesar, Germany) and titanium dioxide (Rhône Poulenc) were weighed as per the stoichiometric ratio and mixed in mortar and pestle using alcohol. The mixture was first calcined at 1200 °C for 24 h, then ground and compacted into a pellet of 40 mm diameter. This compact was then heated at 1350 °C for 24 h, ground and passed through mesh 100.

$Ba_xLa_{0.58(1-x)}Sr_{0.4(1-x)}In_{0.3x}Ti_{0.7x}Co_{0.2(1-x)}Fe_{0.8(1-x)}O_{3-\delta}$ ($0 \le x \le 1$) oxide materials have been synthesized by solid state reaction at 1350 °C for 4 h from a mixture of $x$ mol of BIT07 and $(1-x)$ mol of LSCF powders, provided by Marion Technologie. It has been checked by Energy Dispersive X-ray Spectrosocopy (EDX) that neither Ba, In nor Co have been volatilized during the synthesis processes.

To simplify the formula, these compounds have been called BLSITCF$x$ where $x$ express the molar ratio (in %) of BIT07 in the initial mixture. Table 1 gathered the initial compositions according to the expected formula. X-ray powder diffraction (XRPD) patterns of these materials were recorded at RT, in Bragg–Brentano reflection geometry using a Brüker "D8 Advance" powder diffractometer with a Cu-anode as X-ray source and equipped with the Vαrio1, a Johansson type Germanium (1 1 1) monochromator that provides pure $K\alpha_1$ radiation ($\alpha$ = 1.54056 Å, $20^\circ < 2\theta < 80^\circ$, step = 0.02°) and a 1-D position-sensitive detector (Vantec). Refinements of cell parameters were carried out using the program FULLPROF [17] in the full pattern matching mode, and its interface: the program WinPLOTR [18].

A few selected samples of BLSITCF$x$ were uniaxially pressed under 60 bars in the form of pellets for conductivity and electrochemical characterization, and sintered for 24 h at 1350 °C. Powders were previously ball milled, in 12 ml silicon nitride pot with 6 silicon nitride balls in ethanol, during 4 h at 500 rpm using FRITSCH P7 planetary micro-mill. XRPD analysis confirms that no contamination occurs during the milling step. Samples with ca 95% apparent density (using both the weight to volume ratio and the theoretical density) were obtained by this process. For DC conductivity measurement, samples were in the form of rectangular bars (5 mm × 0.9 mm × 0.9 mm) which have been cut out from the dense pellet using a diamond saw. Symmetrical half cells have been prepared by screen-printing LSCF, BLSITCF12 or BLSITCF25 on BIT07 using a DEK245 apparatus. Slurries based on a terpineol – ethyl cellulose vehicle, were screen printed on the two faces of BIT07 dense pellets (surface 0.6 $cm^2$ and thickness 0.6 cm) and then heated at 1150 °C for 12 h. One cell was also prepared using a treatment at 1050 °C for 6 h.

### 2.2. Electrochemical characterization

DC conductivities of LSCF, BLSITCF12, BLSITCF25 and BLSITCF50 were measured in air between 400 °C and 850 °C, after a stabilisation time of 1 h using a DC four points method.

Half cells cathode/electrolyte were characterized by impedance spectroscopy as a function of temperature. The impedance spectra were obtained from a frequency response analyser Solartron 1260 between 450 °C and 700 °C, by steps of 50 °C, with an isotherm of 1 h at each step. Each spectrum has been recorded at open-circuit voltage (OCV), under an ac perturbation of 100 mV and with 84 points scattered in a frequency range from 2 MHz to 0.01 Hz. It has been previously checked that the amplitude of the perturbation signal is small enough to meet the linearity requirement of the transfer function [19].

The evolution of the electrochemical performances versus time was studied using symmetrical half cells maintained at 700 °C for 320 h. Impedance spectra were recorded every 4 h.

### 2.3. Mechanical properties

Thermal Expansion Coefficients (TECs) have been determined from XRD data as a function of temperature, using a Brüker "D8 Advance" powder diffractometer equipped with an Anton Paar 1200 N high temperature attachment. Data were collected in Bragg–Brentano geometry with a Cu-anode X-ray source ($\lambda_{CuK\alpha1}$ = 1.540598 Å and $\lambda_{CuK\alpha2}$ = 1.544410 Å, $20^\circ < 2\theta < 80^\circ$, step = 0.02°). Data were recorded every 100 °C from room temperature to 1000 °C. The relation between cell parameters evolution and TEC is:

$$\mathrm{TEC} = \frac{1}{3} \times \frac{\left(\delta\left(\frac{\Delta a}{a_0}\right) + \delta\left(\frac{\Delta b}{b_0}\right) + \delta\left(\frac{\Delta c}{c_0}\right)\right)}{\delta T} \quad (1)$$

where $a$, $b$ and $c$ are the cell parameters at the considered temperature and $a_0$, $b_0$ and $c_0$, the cell parameters at room temperature. Refinements of cell parameters were carried out using the program FULLPROF [17] in the full pattern matching mode, and its interface: the program WinPLOTR [18].

The microstructure of the interface cathode/BIT07 has been analysed by Scanning Electron Microscopy (SEM) equipped with an X-ray dispersive spectrometer (JEOL 6400).

## 3. Results and discussion

### 3.1. Structural characterization

Fig. 1 shows the X-ray powder diffraction (XRPD) diagrams of the mixture of BIT07 and LSCF in the molar ratio 25/75 before (a) and after 24 h at 1350 °C (b). After the sintering process at 1350 °C, LSCF and BIT07 mixture leads to the formation of a single-phase product which is not a composite. Fig. 1(b) shows, for example, the

**Table 1**
Molar and weight ratios of BIT07 and LSCF in the initial mixtures, formula and names of the new phases.

| Molar % of BIT07 | Molar % of LSCF | Weight % of BIT07 | Weight % of LSCF | Formula | Material |
|---|---|---|---|---|---|
| 0 | 100 | 0 | 100 | $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ | LSCF |
| 12 | 88 | 13.56 | 86.44 | $Ba_{0.12}La_{0.51}Sr_{0.35}In_{0.04}Ti_{0.08}Co_{0.18}Fe_{0.7}O_{3-\delta}$ | BLSITCF12 |
| 25 | 75 | 27.72 | 72.28 | $Ba_{0.25}La_{0.44}Sr_{0.3}In_{0.08}Ti_{0.18}Co_{0.15}Fe_{0.6}O_{3-\delta}$ | BLSITCF25 |
| 38 | 62 | 41.36 | 58.64 | $Ba_{0.38}La_{0.36}Sr_{0.25}In_{0.11}Ti_{0.27}Co_{0.12}Fe_{0.5}O_{3-\delta}$ | BLSITCF38 |
| 47 | 53 | 50.51 | 49.49 | $Ba_{0.47}La_{0.31}Sr_{0.21}In_{0.14}Ti_{0.33}Co_{0.11}Fe_{0.42}O_{3-\delta}$ | BLSITCF47 |
| 50 | 50 | 53.51 | 46.49 | $Ba_{0.5}La_{0.29}Sr_{0.2}In_{0.15}Ti_{0.35}Co_{0.1}Fe_{0.4}O_{3-\delta}$ | BLSITCF50 |
| 75 | 25 | 77.54 | 22.46 | $Ba_{0.75}La_{0.15}Sr_{0.1}In_{0.23}Ti_{0.53}Co_{0.05}\ Fe_{0.2}O_{3-\delta}$ | BLSITCF75 |
| 100 | 0 | 0 | 100 | $BaIn_{0.3}Ti_{0.7}O_{2.85}$ | BIT07 |