

Electrochemical activity of co-precipitated $\text{LnBaCo}_2\text{O}_{5+x}$ ($\text{Ln} = \text{La}, \text{Y}$)

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Introduction

Layered perovskite oxide compounds of the series $\text{LnBaCo}_2\text{O}_{5+x}$ ($\text{Ln} = \text{Lanthanide ion}$) have been identified as promising cathodes for Intermediate Temperature SOFC [1]. Their structure arises from the ordering of Ln and Ba cations in a double perovskite structure ($\text{LnCoO}_{3-x} - \text{BaCoO}_{3-x}$), wherein Ln and Ba occupy alternate layers of the perovskite structure, instead of being randomly distributed on the A site. This ordering occurs if Ln and Ba have sufficiently large difference of ionic size. As a result of this ordering, and due to the different bond strength between Ln-O and Ba-O, oxygen vacancies are usually located in the Ln-O layer. The most relevant properties are: a high electronic conductivity at intermediate to high temperatures; a high oxygen vacancy concentration; good ion transport capability and high oxygen surface exchange coefficients compared to disordered perovskites. In the present work, a simple and cost-effective coprecipitation synthesis in aqueous medium was applied to prepare $\text{LaBaCo}_2\text{O}_{5+x}$ (LBC) and $\text{YBaCo}_2\text{O}_{5+x}$ (YBC) compounds and their electrochemical and chemical properties were characterized by application of different techniques.

Materials and Methods

LBC and YBC cathode precursor powders were prepared via coprecipitation route, by dissolution of stoichiometric amounts of metal nitrates in H_2O at 60°C ($\sim 1\text{M}$ total metal ion concentration) and addition to a solution of the precipitating agent [2]. The powders were then calcined at 1150°C to form the desired active phase. X-Ray Diffraction (XRD) was applied to check phase purity and structural parameters. The electrical conductivity and the polarization resistance of the cathodic materials were measured as a function of temperature with a potentiostat/galvanostat (Amel 7050) equipped with a FRA (510 V10, Materials & Mates). The electrical conductivity was measured via a four-electrode DC method on sintered bars of the cathodic powders, between 25 to 850°C , in flowing air. Electrochemical Impedance Spectroscopy (EIS) tests were performed using a symmetric cell configuration with LSGM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-x}$) as the electrolyte. Pellets ($1\text{ cm } \varnothing$) were fabricated from commercial LSGM powders (Fuel Cell Materials) calcined at 1450°C for 5 h in air. A slurry of the cathodic material was applied on each side of the electrolyte pellet, dried at 110°C for 12 h in air, and then calcined to reach adhesion (at 1050°C for YBC, and 900°C for LBC). The EIS tests were performed in flowing air between 450 and 800°C , in the frequency range $0.1\text{ Hz} - 1\text{ kHz}$ with 10 mV signal amplitude. Ag meshes and ink were applied to form the electrodes. TPO tests ($2\% \text{ O}_2$ in He flow, 20 Ncc/min , $25 - 850^\circ\text{C}$, 2°C/min ramp rate) were also performed to characterize the oxygen exchange properties of the materials.

Results and Discussion

The coprecipitation synthesis and the preparation procedure allowed to obtain an almost pure YBC phase, as revealed by XRD characterization and Rietveld analysis. The phase was indexed with a tetragonal primitive cell (space group P4/mmm) corresponding to that of

$\text{YBaCo}_2\text{O}_{5+x}$. The YBC material behaved as expected with respect to the electrical conductivity (Fig. 1a), which increased from 10 S/cm at room temperature to a maximum of 40 S/cm at $\sim 300^\circ\text{C}$ and further decreased when heating to 850°C , coherently with the expected transition from a semiconductor- to metal-type conductivity. Noteworthy, the EIS tests on the symmetric YBC/LSGM/YBC cell between 500 and 800°C showed that the Area Specific Resistance (Fig. 1b, $E_{\text{act}} = 0.96\text{ eV}$) was lower than those found in the literature for the same material prepared via different routes (typically, solid state reaction [3]). EIS spectra always revealed a single arch (Fig. 1c): ageing tests (up to 400 h) indicate that both the polarization and the ohmic resistance increase with time on stream. Post-mortem XRD analyses confirmed the growth of secondary phases, due to the intrinsic instability of YBC and to YBC/LSGM interactions.

The LBC cathode showed better performances in terms of activity and stability. XRD spectra indicate that the LBC powder was constituted of a perovskite-phase of general formula $(\text{La}_{1-x}\text{Ba}_x)\text{CoO}_3$ that well agrees with the cubic pattern of PDF File #00-032-0480, with no traces of side phases. Also in this case, the electrical conductivity showed a semiconductor- to metal-type transition, set to higher values compared to YBC (a maximum of 100 S/cm was observed at $\sim 300^\circ\text{C}$). EIS investigation and ASR estimation ($E_{\text{act}} = 1.1\text{ eV}$) revealed resistances fully in line with the literature, significantly lower than those of YBC. EIS spectra with more than one arch were found at all the investigated temperatures, likely due to the superposition of chemical and diffusive effects. Good stability was observed in the ageing tests, with limited increase of the polarization resistance. Post-mortem XRD analysis confirmed the absence of interactions between LSGM and LBC, with modest growth of secondary phases.

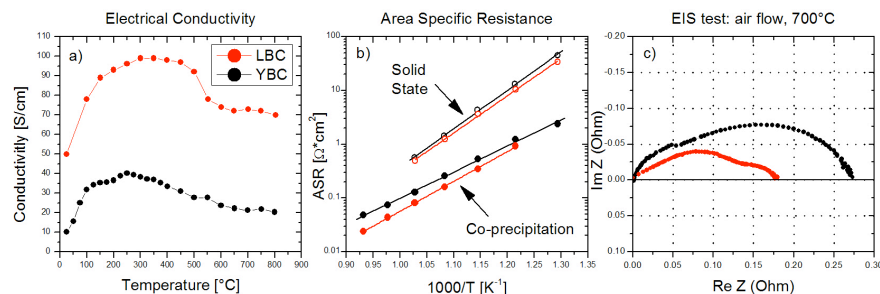


Fig. 1. LBC (●) and YBC (●) characterization. Panel a: electrical conductivity. Panel b: Area Specific Resistance. Empty symbols are taken from Ref. [3]. Panel c: EIS spectra at 700°C .

Significance

Coprecipitation synthesis is a promising route for preparing cathodic materials for IT-SOFC. The characterization of the electrochemical activity of YBC and LBC cathodes indicates that very active materials can be obtained, with performances well comparable to those reported in the literature for material obtained via different preparation routes.

References

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