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Electrical characterization of co-precipitated $LaBaCo_2O_{5+\delta}$ and $YBaCo_2O_{5+\delta}$ oxides

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Abstract

RE$BaCo_2O_{5+\delta}$ layered perovskite oxides (*RE* = Rare Earth) are promising cathodes for IT-SOFCs. In this work, a simple co-precipitation synthesis in aqueous medium was applied to prepare $LaBaCo_2O_{5+\delta}$ (LBC) and $YBaCo_2O_{5+\delta}$ (YBC) cathodes. The chemical and electrochemical properties of both materials were characterized via XRD, SEM, TPO, TG–DTA, 4-probe conductivity measurement, and EIS tests on symmetric cells. The coprecipitation synthesis revealed a promising preparation route: the measured ASR values of both materials were well comparable with the literature ones. A kinetic investigation of the O_2 reduction process was performed on LBC (600–800 °C, 5–100% O_2, v/v), whose results were analyzed with equivalent circuits. The main steps were identified (oxygen diffusion and charge transfer at high frequency, O_2 chemisorption at medium frequency), and their activation energy and reaction order were quantified. Aging tests (500 h time on stream, 500–800 °C) revealed quick deactivation for YBC and good stability for LBC.

Keywords: Co-precipitation; LBC; YBC; IT-SOFC; EIS

1. Introduction

A-site ordered perovskite oxides with general formula *RE*$BaCo_2O_{5+\delta}$ (*RE* = Rare Earths) have been traditionally investigated for their low-temperature electrical and magnetic properties,[1,2] and more recently they raised considerable interest in the Solid Oxide Fuel Cell (SOFC) community as promising low temperature cathodes; several studies were therefore devoted to investigate their high temperature properties, especially the crystal structure, the electrical conductivity and the electrochemical performance.[3–10] The most important characteristic of these compounds is the ordering of the A-site cations in alternating layers, *RE*-O, Co-O, Ba-O, Co-O along the *c*-axis of the perovskite lattice. The properties that make these materials promising as low temperature cathodes are the high electronic conductivity at intermediate temperatures, the high oxygen vacancy concentration, the good ion transport activity and the very high oxygen surface exchange coefficients, if compared to A-site disordered perovskites.[7,11,12] This class of compounds can accept a wide range of oxygen stoichiometries ($0 \leq \delta \leq 1$), driven by the mean Co oxidation state; the oxygen content in the final material depends on the size of the *RE* cation, but it can also be governed by the annealing conditions. As the size of the *RE* cation decreases, the oxygen content at room temperature decreases from nearly 6 for La (either in ordered or disordered structure), ~5.7 for Pr and Nd, ~5.5 for Y, ~5.4 for Sm, Eu, Gd and Tb, down to ~5.3 for Dy and Ho. These values typically vary depending on the treatment atmosphere and the preparation procedure. Moreover, the oxygen content decreases upon increasing the temperature. Interestingly, a linear relationship has been reported between the oxygen content and A-site ionic radii difference $[r_{(RE)} - r_{(Ba^{2+})}]$.[12]

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Also, the relative ionic radii of the two A-site cations drives structural transitions in these compounds.[5] When the size difference between *RE* and Ba is small, the disordered structure is preferentially obtained; nonetheless, the ordered structure can be achieved by carefully tailoring the annealing temperatures and the preparation atmospheres, as in the case of $RE = \mathrm{La}$.[13] Overall, the defect chemistry of both ordered and disordered perovskite structures appears to have a great influence on the electrochemical properties of these materials.

Our group has recently applied a simple carbonate co-precipitation technique to synthesize mixed oxides with perovskite structure for application in Solid Oxide Fuel Cells. Reasonably good materials were obtained, both for the electrolyte[14,15] and the electrodes,[16] with fair conduction properties and stability, despite some deviations from the ideal stoichiometries. Several reasons make the coprecipitation a valuable preparation technique. The coprecipitation synthesis allows to achieve a very intimate mixing of the perovskite precursors, in the present case in form of carbonates and hydroxides. A homogenous precipitate is obtained, with fine grain size distribution. The achievement of small grain sizes depends on the operating conditions of the synthesis, namely temperature, pH, nature and concentration of the precursors, parameters that can be tailored and controlled during the preparation. The perovskite phase is obtained via one-step calcination, at the same temperature generally required by other techniques: the final material retains the original homogeneity and a fine grain size, compatibly with some expected sinterization. Compared to the solid state preparation route (the most widespread synthesis method for SOFC materials), considerable amount of energy is saved by mixing liquid solutions instead of solid powders, thus avoiding expensive and time-consuming milling steps. In the present work, the carbonate co-precipitation method is proposed for the preparation of $RE\mathrm{BaCo_2O_{5+\delta}}$ with $RE = \mathrm{La}$ and Y (hereafter referred to as LBC and YBC respectively). Disordered structure of $\mathrm{LaBaCo_2O_6}$ and ordered $\mathrm{YBaCo_2O_{5+\delta}}$ perovskites were adopted as model compounds to assess the suitability of the preparation route. The evaluation of the co-precipitation method on $RE\mathrm{BaCo_2O_{5+\delta}}$ layered perovskites faces the challenge of finding the proper conditions for the quantitative precipitation of all the desired cations, which in turn influence the obtainment of the target stoichiometry. In particular, two conflicting challenges must be overcome: the hydroxides of alkaline earth metals (Ba in the present case) show a slight, non-negligible, solubility in water, therefore some losses might be expected during the preparation. The second challenge concerns the stability of $\mathrm{Co{-}NH_3}$ complexes in basic environments, which prevents the precipitation of Co as carbonate or hydroxide. To deal with these drawbacks, in this work, equilibria calculations were performed with the Medusa software[17] and the experimental conditions of the preparation were maintained as close as possible to the optimal thermodynamic indications. For each material prepared, the powders were characterized via X-ray diffraction, SEM–EDS, TG–DTA and TPO analyses. The electrochemical properties were also evaluated by measuring the total electrical conductivity, via 4-probe method on sintered bars, and the polarization behavior, via electrochemical impedance spectroscopy (EIS), on symmetric cell configuration. In the case of LBC, good results were achieved and a quantitative electro-kinetic study on the impedance spectra was proposed. In the case of YBC, even though it has been recently revealed that the structure is unstable at high temperature in air,[18] the electrochemical performances of the as-synthesized material allowed to draw positive conclusions about the goodness of the preparation route (also in view of structure-stabilization via substitution of Ba with Sr[18]).

2. Materials and methods

2.1. Synthetic procedure

$\mathrm{La(NO_3)_3{\cdot}6H_2O}$ (99.99%, Sigma–Aldrich), $\mathrm{Y(NO_3)_3{\cdot}4H_2O}$ (99.99%, Sigma–Aldrich), $\mathrm{Ba(NO_3)_2}$ (99%, Sigma–Aldrich), $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$ (99%, Sigma–Aldrich) salts were used as precursors in the co-precipitation synthesis; the precipitating agent was $\mathrm{(NH_4)_2CO_3}$ and the solvent was distilled water. The synthetic procedure is reported in details elsewhere.[16] Briefly, the procedure simply involves the addition of a solution of the nitrates of the constituents to a solution of the precipitating agent with the proper concentrations, followed by a 3 h aging period and a filtration step to separate the precipitates from the solution. The evaluation of the optimal precipitation conditions was performed by calculating the theoretical precipitation equilibria, using the Hydra thermodynamic database and the Medusa software.[17] In the calculations, different simulations were performed by changing the concentration and amount of the precipitating agent, while keeping constant the concentrations of the metal salts. The solution volume was also kept constant and equal to the sum of the volumes of the metal salt solution and of the precipitating agent solution. Plots of the calculated fraction of species at equilibrium vs. pH were used to estimate the optimal precipitating agent concentration and pH range.

After the filtration process, the powders were desiccated at 110 °C and then crushed in a mortar and fired at temperatures up to 1000 °C in air, with heating and cooling rates of 2 °C/min and dwell time of 10 h. After the filtration process, the solutions were collected and analyzed via Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Thermo X series II instrument) to search for any metal ion left.

2.2. Powders characterization

The powders of the two materials were characterized by X-ray diffraction (XRD) with a Bruker D8 instrument, using graphite monochromated Cu K_α radiation; the diffraction patterns were collected in the range 10–80° 2θ with a step of 0.02° 2θ and a counting time of 12 s per step. The XRD spectra of the samples fired at 1000 °C were refined with the Rietveld method[19] using the GSAS software[20] for the determination of the structural parameters. XRD analyses were carried out also on mechanical mixtures (50/50 wt%) of YBC and LSGM, as well as of LBC and LSGM. The mixtures were fired at different temperatures to evaluate the occurrence of any chemical interaction between the electrolyte and the cathode, 1100 °C in the case of YBC and 900 °C in the case of LBC. These two temperatures are those