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Li_{3x}La_{2/3-x}TiO₃ nanoparticles with different morphologies and self-organization, obtained from simple solution precipitation methods

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ABSTRACT

We present a novel synthesis strategy of Li_{3x}La_{2/3-x}TiO₃ (LLTO) softly agglomerated nanoparticles by simple precipitation from solution and based on controlling the fractal self-organization. In this way we avoid the use of bulky organic ligands frequently used to avoid the irreversible aggregation of nanoparticles but that also often degrade the LLTO functional properties. We show that the pH of precipitation of titanium and lanthanum hydroxides (LLTO precursors) strongly affects the so-called “filtration coefficient” and the hierarchic structure of LLTO precursors (mass or surface fractal self-organization). For mass-fractal aggregation of the precursors, a high filtration coefficient was obtained with soft and readily friable aggregates of the hydroxide precipitates. Moreover, the fractal self-organization of the synthesized precursors strongly modifies the final LLTO nanoparticles morphology and the material connectivity. The LLTO nanoparticles synthesized from mass-fractal agglomerated precursors obtained from the so-called sequential precipitation of hydroxides (SPH, prepared at pH_{Ti(OH)₄} = 3.5 and pH_{La(OH)₃} = 8.5) had a much lower agglomeration ability than the surface-fractal agglomerated precursors obtained from the so-called co-precipitation of hydroxides (CPH, at pH_{Ti(OH)₄} = pH_{La(OH)₃} = 8.5).

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1. Introduction

The search of new materials to improve electrochemical systems, particularly for the transformation and the conservation of electric energy and for chemical sensors, is a strong catalyst for research. The electrolyte is one of the important parts of these electrochemical systems and the improvement of the conductivity of solid electrolytes remains, at the time, a great challenge in research. Inorganic Li ion-conducting solid conductors always attract great interest since they may present several advantages, i.e. high electrochemical stability window, high thermal stability, high mechanical resistance and the possibility of miniaturization by preparing thin or thick films. In such a context, Li-conducting ceramics based on Li_{3x}La_{2/3-x}TiO₃ (named hereafter LLTO) hold an important place among them because of their high ionic conductivity at room temperature, i.e. $\sigma = 10^{-3}$ S cm⁻¹ for $x = 0.10$ [1,2]. However, besides this high bulk conductivity, the grain-boundary resistance of these ceramics remains high and limits considerably the applications of these polycrystalline ceramics. The

electrical properties of the grain boundaries differ essentially from the bulk because of the presence of strained or missing bonds in the interface region that may lead to a change of the mobile species mobility. Structural or space charge effects in this interfacial region have been suggested to explain these variations [3–5]. Further, based on the grain-boundary core-space-charge layer model, it has been shown that grain boundary resistance can change depending on the grain size. These suggestions were experimentally confirmed on stabilized zirconium oxide nanomaterials, where it has been shown that specific grain boundary conductivity can be increased by obtaining nanodimensional grains [6,7]. In such a context, the attempt to synthesize nanosized LLTO ceramics appeared to be of great interest.

For obtaining nanosized ceramics of oxides, it is necessary not only to prepare nanoparticles of precursors but also to control the process of their aggregation during the synthesis. In order to avoid the irreversible agglomeration of inorganic nanoparticles, bulky organic surfactants can be used. By this way, it is also often possible to control their size and shape. However, drawbacks resulting from surface adsorbed surfactants are the unpredictable influence on the toxicity of nanoparticles, and the diminished accessibility to the particle surface [8,9]. The latter can be serious issue regarding grain boundary ionic transport even after high-temperature heat-treatment.

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Another way to control the formation of nanoparticles and their agglomeration is to grow self-organized fractal structures forming during the synthesis. Thus, it has been shown that nanoparticles have the ability to self-organize in networks, with formation of fractal structures. By changing the synthesis conditions, control of the type of fractal self-organization is possible, resulting in the formation of either soft or hard agglomerated nanoparticles. Thus, in recent papers, Belous et al. [10,11] have shown that, by using precipitation from solution as synthesis method, by controlling the pH of the solution and by changing the sequence of hydroxides precipitation, it was possible to obtain different types of fractal self-organization of nanoparticles of zirconium and yttrium hydroxides (bulk and surface). This fractal self-organization of the precursor powder affects the morphology of the final oxide powder and the properties of the ceramics (sintering temperature, size of grains).

In this work, we investigated and compared self-organization of the precursor and final LLTO nanoparticles synthesized by two routes: the sequential precipitation (SPH) and the coprecipitation (CPH) synthesis. The LLTO precursors used are a mixture of titanium and lanthanum hydroxides to which a lithium hydroxide solution is added after hydroxide precipitation in an adequate quantity.

The aim of this paper is to investigate the self-organization of the LLTO precursor nanoparticles obtained and its influence on final morphology. We first investigated separately, the precipitation conditions of titanium and lanthanum hydroxides (pH and concentration of reduction agent). As is known, these factors can efficiently affect the dispersion (or self-organization) of the precipitates and their agglomeration. Afterwards, we investigated the influence of the sequence of precipitation of the two hydroxides (sequential or co-precipitation) on the fractal structure and on the microstructure of the precursor and final LLTO nanoparticles.

2. Experimental procedure

Synthesis and characterization of $\text{La}(\text{OH})_3$ and $\text{Ti}(\text{OH})_4$ hydroxides: $\text{La}(\text{OH})_3$ was precipitated from an aqueous solution of $\text{La}(\text{NO}_3)_3$ by aqueous solution of NH_4OH to adjust the pH from 8 to 11. $\text{Ti}(\text{OH})_4$ was precipitated from an isopropanol solution of TiCl_4 by aqueous solution of NH_4OH to adjust the pH from 2 to 8.5. The concentration of NH_4OH used for adjusting the pH was varied (1 mol%, 5% or 25% NH_3) since it can influence the morphology of the precipitates. The so-obtained precipitates of La and Ti hydroxides were filtered and washed from the mother solution with distilled water until Cl^- and NO_3^- ions disappear from the washing solutions. Afterwards, hydroxide precipitates were washed additionally with 500 ml of distilled water in order to determine filtration coefficient K_f . Filtration coefficient, K_f , of each fresh precipitate was calculated using Darsi formula [12]:

$$Q = K_f \times S \times \frac{H}{L} \times t \quad (1)$$

where Q —filtrate volume, cm^3 ; K_f —filtration coefficient, cm s^{-1} ; S —precipitate surface on the filter, cm^2 ; H —pressure under filter, cm of Hg ; L —thickness of precipitate layer, cm ; t —time of filtration, s . Precipitates were then dried at 80°C .

The compactness of the hydroxide pellets (g cm^{-3}) was determined from the mass, diameter and height of pellets after sintering. Pellets were obtained by uniaxial compression at 16 MPa (kg cm^{-2}) of hydroxide powders, followed by a heat treatment at 600°C .

Infra Red (IR) spectroscopy and thermal analyses (DTA, TGA) were used to characterize the La and Ti hydroxides. IR spectra were recorded on a Specord-M80 spectrometer in the 250–4000 cm^{-1} frequency range. Samples consisted of pellets prepared by pressing

the hydroxide with dehydrated KBr (1 wt%). DTA and TGA experiments were carried out with a Setaram TGDTA92 equipment, at a heating rate of 5°C min^{-1} , in air using Pt crucible.

Preparation of the precursors of LLTO: The synthesis of the precursors of LLTO has been carried out either by sequential precipitation of the hydroxides (SPH) or by their coprecipitation (CPH). The mixture of titanium and lanthanum hydroxides obtained by SPH was carried out in the following way: the titanium hydroxide was first precipitated at $\text{pH}=3.5$ and afterwards lanthanum hydroxide was precipitated at $\text{pH}=8.5$. In the case of CPH method, lanthanum and titanium hydroxides were precipitated simultaneously at $\text{pH}=8.5$. After obtaining the mixture of these two hydroxides, the precipitates were kept for 2 h in solution to control the loss of metal cations during washing procedure. Then, hydroxide mixtures washed with distilled water and an appropriated amount of an aqueous solution of LiOH was added in order to obtain the chemical composition $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$. The obtained suspension was dried afterwards in an oven at 80°C .

The microstructure of these precursors was studied by small angle X-ray scattering (SAXS). Measurements were performed in transmission mode through vacuum with sample pellets of known density and thicknesses obtained by uniaxial pressure. The instrument source is a high flux RigakuTM copper rotating anode and the beam is set by three pinholes after an OsmicTM confocal mirror that delivered a monochromatic ($\lambda \sim 1.54 \text{ \AA}$) and cylindrical X-ray beam of 2×10^7 photons s^{-1} over $350 \mu\text{m}$ in diameter with an angular divergence below 0.5 mrad . To obtain a wide range of wave vectors (0.015 \AA^{-1} to 2 \AA^{-1}) we combined a 2D gas detector and a “flat image plate” for larger angles, with a broad overlap from 0.1 to 0.3 \AA^{-1} . The absolute q -range was calibrated from the known diffraction lines of Ag-Behenate powder and intensities were given in absolute scale units calculated from the water scattering level (intensities in cm^{-1} , i.e. cm^2 per cm^3 of sample material).

Morphological observations were performed using Transmission Electronic Microscopy (TEM). Thin specimens were obtained by ultrasonically dispersing particles in ethanol and depositing one droplet of the resulting suspension on a Cu grid covered with a holey carbon film. After drying, the grid was fixed in a side-entry 30° double-tilt specimen holder and was introduced in a JEOL-2010 electron microscope operating at 200 kV.

Synthesis of LLTO powder: LLTO has been synthesized from these precursors by heat treatment at 900°C in air for 2 h. Powder X-ray diffraction (XRD) patterns have been recorded at room temperature with a Philips X'Pert PRO diffractometer (Cu $K\alpha$ radiation), equipped with a linear X'Cellerator detector, in the 2θ range from 5 to 70° with an interpolated step of 0.08° . TEM has also been carried out to determine the microstructure of the final oxide.

The lithium content in the LLTO powders was determined using chemical analysis. $\text{K}_2\text{S}_2\text{O}_7$ was added in excess to LLTO powders and alloyed during 24 h on a sand bath. The alloy was then dissolved in acidified water. The analysis of the solutions was carried out with an atomic absorption spectrometer (SP-9 PueU-nicom) showing a lithium content below 2%. To overcome this substantial loss of lithium after the heat treatment of LLTO precursor, we thus used an excess of LiOH for the LLTO synthesis.

3. Results and discussion

Characterization of individual precipitates of $\text{La}(\text{OH})_3$ and $\text{Ti}(\text{OH})_4$: Previous investigations performed during the precipitation of zirconium and yttrium oxides have shown that the pH of the solution affects efficiently the filtration coefficient, K_f , of the precipitates. This coefficient is correlated to the fractal structure of the precipitates and to the strength of the bounds formed between the particles during precipitation. The higher the filtration

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