Solid State Ionics 308 (2017) 46–53

Contents lists available at ScienceDirect

Solid State Ionics

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

# Formation of cubic $Li_2TiO_3$ by mechanical activation and its transformation to monoclinic phase: Stability in helium and hydrogen flows

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## ARTICLE INFO

*Keywords:*
Lithium titanium oxides
Mechanochemical synthesis
Physicochemical stability
Nuclear fusion
Batteries

## ABSTRACT

Lithium metatitanate ($Li_2TiO_3$) is one of the most attractive candidates as a solid breeder in the blanket of D–T fusion reactors and ionic conductors in lithium-ion batteries. In this work, a new synthesis route, avoiding the use of solvents, high temperatures and dangerous sub-products, is used to obtain cubic and monoclinic $Li_2TiO_3$ nanopowders. This method consists of ball milling of LiCl, $TiO_2$ and NaOH in air atmosphere at room temperature and posterior calcination. Structural, microstructural and textural characteristics of the $Li_2TiO_3$ powders as well as of the pellets before and after annealing were determined. Remarkable contraction of the material and high mechanical stability was observed after treatment at 800 °C for 5 h. Finally, the behaviour in reductive and inert atmospheres of the sintered and green pellets was studied, characterizing the extension and impact of the reactions on the physicochemical and structural stability of the material. It can be concluded that the sintered pellets became mechanically stable due to the thermal treatment, showing no physicochemical modifications after analysis in different atmospheres up to 800 °C.

## 1. Introduction

Lithium metatitanate ($Li_2TiO_3$) is a lithium-based ceramic with a wide range of industrial applications. Among them, it is one of the most attractive candidates as a solid breeder in the blanket of the D–T fusion reactors [1–3] due to its properties (potentially high tritium generation, excellent tritium release at low temperature, reasonable lithium atom density, good compatibility with other materials at high temperatures, low chemical reactivity and high thermal stability). Also, $Li_2TiO_3$ is a promising component in microwave devices for the wireless and mobile communication industry, due to its good microwave dielectric properties (high quality factor, appropriate permittivity and near zero temperature coefficient of resonator frequency) [4]. Between other applications, $Li_2TiO_3$ is used as electrode material in lithium-ion batteries because its capacity of stabilize the high capacity cathode conducting agents and allow the occurrence of lithium diffusion [5].

$Li_2TiO_3$ possesses three structural modifications: α, β and γ [6,7]. The cubic α-$Li_2TiO_3$ (space group $Fm\bar{3}m$) is metastable and transforms irreversibly to the monoclinic β-$Li_2TiO_3$ (space group $C2/c$) above 300 °C [7]. The β-$Li_2TiO_3$ remains stable up to 1155 °C [6]. Above this temperature, it transforms reversibly to the cubic γ-$Li_2TiO_3$ (space group $Fm\bar{3}m$). The β-$Li_2TiO_3$ phase has a stoichiometric range from 47 to 51.5 mol% $TiO_2$ including at low temperature (from 600 to 1100 °C). Considering that the stoichiometry of the material has a strong influence in different properties such as thermal conductivity, thermal expansion, dielectric constant and ion mobility, it is an important factor to be modulated for industrial applications.

In previous investigations, β-$Li_2TiO_3$ has been usually synthesized by solid-state reaction using titanium dioxide ($TiO_2$) and lithium carbonate ($Li_2CO_3$) as starting materials [8–11] at temperatures above 800 °C. Although this method has the advantage of avoiding using solvents, it requires high temperatures and produces a material with poor diffusivity properties and large grain size. On the other hand, β-$Li_2TiO_3$ could also be obtained through some soft-chemical methods, such as sol–gel synthesis [12], hydrothermal [13,14], in-situ hydrolysis method [15], and solution combustion synthesis [16–18]. However, some of these synthesis procedures do not only generate large amounts of waste, but are also energy-intensive and expensive. In the case of α-$Li_2TiO_3$, it has been synthesized by a hydrothermal method with $TiO_2$ and LiOH as precursors and water as solvent [14]. However, this phase was not observed using others synthesis procedures [8–12].In this context, mechanochemical processing emerges as an alternative route to produce nanocrystalline solid materials, avoiding the use of solvents, expensive precursors and waste generation [19,20]. In this process

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http://dx.doi.org/10.1016/j.ssi.2017.05.017
Received 26 March 2017; Received in revised form 19 May 2017; Accepted 26 May 2017

(during either ball milling or the subsequent low temperature heat treatment), precursors undergo a reaction to produce the required material which allows recovering an ultrafine powder. Although some previous studies produce $Li_2TiO_3$ or $Li_4Ti_5O_{12}$ by milling, $Li_2CO_3$ [21,22] and/or LiOH were used as precursors [23,24]. To the authors knowledge there are not any previous investigations on the synthesis of nanostructured $Li_2TiO_3$ by mechanochemistry processing of the LiCl and $TiO_2$ precursors with NaOH.

Structural, microstructural and textural characteristics of $Li_2TiO_3$ (like specific surface area, phase composition and crystallite size) are determined by the different synthesis routes and precursors used, which influence the properties and stability of the final material in operating conditions for different applications. In the case of breeder material in a fusion reactor this is worth considering since tritium release is favoured by low crystallite size and by adding $H_2$ into inert sweep gas [25,26]. In addition, in reducing atmospheres, titanium in $Li_2TiO_3$ can be reduced and lithium vaporisation can be increased [3,27], producing mass decrease and change in $Li_2TiO_3$ properties. Consequently, investigating the influence of the synthesis route on the microstructure and its relation with reduction behaviour of the synthesized $Li_2TiO_3$ becomes of great importance.

In the present work a new synthesis route to produce $Li_2TiO_3$ by mechanochemical reaction of LiCl and $TiO_2$ precursors with NaOH is developed. In order to evaluate the potentiality of the synthesized $Li_2TiO_3$ powders as breeder material, pellets of $Li_2TiO_3$ were heated under different atmospheres (helium, air and hydrogen) to analyse their physicochemical stability and their changes on the structure, microstructure and texture.

## 2. Experimental procedures

The starting materials used were anhydrous LiCl (Aldrich, 99%), $TiO_2$ (Aldrich, purity 99 wt%, anatase ≈ 75 wt% and rutile ≈ 25 wt%) and NaOH (Biopack, purity 98 wt%). The milling was carried out in a planetary ball mill (Fritsch Pulverisette P6), using both vial and balls of stainless steel. A ball to powder weight ratio of 53:1 was employed. Mixtures of 2.2 LiCl-1.0 $TiO_2$-2.2 NaOH powders were ball milled in air using 400 rpm for different periods of time. After milling, the samples were calcined in alumina crucible at 600 °C for 5 h and washed with water in order to eliminate NaCl produced as a sub-product of the reaction. The sample was dried at 120 °C overnight and it was calcined again at 600 °C for 24 h. The yield of the synthesis procedure was determined by calculation of the ratio between the experimental mass of $Li_2TiO_3$ obtained and the theoretical mass of $Li_2TiO_3$ expected according reaction (1).

Synthesized powders of $Li_2TiO_3$ were pressed by uniaxial compression (800 MPa) to produce green pellets (no binders added). Thermal treatment (800 °C for 5 h) was conducted on the green pellets in order to make them denser.

Structural and microstructural changes were studied by X-ray Powder Diffraction (XRPD), using PANaytical Empyrean equipment with graphite monochromator, CuKα radiation at 40 kV and 30 mA. X-ray diffractograms were collected using a step size of 0.013° and scan speed (°/s) of 0.0248. Textural characteristics of the samples were studied using a Micromeritics ASAP 2020 analyser. $N_2$ adsorption isotherms were collected at − 196 °C on 0.2 g of sample, after evacuation at 350 °C overnight. Surface area and pore distribution were obtained applying the BET and BJH methods, respectively. Solid phase IR spectra were obtained with an FTIR Perkin Elmer Spectrum 400 spectrometer in the range of 500–4000 $cm^{-1}$. The selected samples were grounded with dry KBr, pressed to pellets and put in a specially designed cell closed in an argon-filled glove box with moisture and oxygen content lower than 10 ppm. Morphological analyses of the samples were performed by Scanning Electron Microscopy (SEM Nova Nano 230, FEI Company) equipped with Energy Dispersive X-ray Spectroscopy (EDS) microanalysis. Transmission Electron Microscopy (TEM) studies were performed using either a Philips CM200 or a FEI Tecnai F20 G2 microscope operating at 200 kV. Samples for TEM were prepared by dispersing a small amount of powder in hexane and depositing a drop of the resulting suspension on a commercial holey-carbon coated copper grid. TEM cross sectional lamella was prepared with a Focused Ion Beam (FIB)/SEM dual beam system (FEI Helios Nanolab 650).

The thermal behaviour of the samples was studied under helium and hydrogen atmosphere by thermogravimetry (TG, TA Instruments HP50) using a heating rate of 10 °C $min^{-1}$ and gas flow rate of 50 ml $min^{-1}$. The sample (about 80 mg) was maintained at room temperature for 30 min, in order to stabilize the baseline and remove physisorbed species. Then, it was heated to 800 °C, kept for 30 min and returned to its initial temperature. This cycle was repeated in order to obtain the baseline.

## 3. Results and discussion

### 3.1. Synthesis and characterization of cubic and monoclinic $Li_2TiO_3$ powders

The mechanochemical synthesis of $Li_2TiO_3$ powders from Li and Ti precursors in the presence of NaOH is a novel method, which is analogue to the synthesis procedure for oxide solid solutions developed by our group [28]. The expected reaction is thermodynamically favourable and can be expressed at room temperature as:

$$2LiCl(s) + TiO_2(s) + 2\,NaOH(s) \rightarrow Li_2TiO_3(s) + 2\,NaCl(s) + H_2O(l) \tag{1}$$

$\Delta G^\circ$ (293 K) = − 168.3 kJ/mol [29]

In order to get the best milling conditions to produce reaction 1, preliminary tests were performed. In stoichiometric mixtures (2 LiCl-1 $TiO_2$-2 NaOH), the formation of monoclinic $Li_2TiO_3$ and cubic $Li_{4/3}Ti_{5/3}O_4$ was observed after combination of calcination, washing and calcination (see supplementary Fig. 1 of Appendix A). This indicates lithium loss and, as previous works have highlighted that an excess of lithium benefits the stability of the material [30], ball milling was implemented upon mixtures with 10 at.% Li excess (2.2 LiCl-1.0 $TiO_2$-2.2 NaOH).

Fig. 1 shows X-ray diffractograms for mixtures milled during different periods of time (15 min, 1 h, 2 h, 3 h and 5 h) and the assignations of reflections to the identified phases. In mixtures milled for 2 h to 5 h (Fig. 1c–e), the progressive advance of reaction 1 is observed, yielding $Li_2TiO_3$ as the metastable cubic phase. For shorter milling times (15 min, 1 h), NaCl is formed close to an intermediate phase, i.e. LiOH·$H_2O$. This indicates that LiCl first reacts with NaOH to produce LiOH and NaCl, being this reaction thermodynamically favoured (reaction 2) [29]. However, no appreciable quantity of $TiO_2$ reacts with LiOH during this step (reaction 3). For 5 h of milling, the formation of α-$Li_2TiO_3$ is practically complete; while a minor amount of $TiO_2$

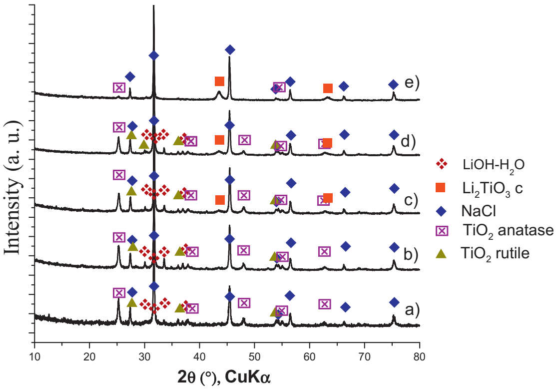

**Fig. 1.** XRPD patterns obtained after different milling times: a) 15 min, d) 1 h, c) 2 h, d) 3 h, and e) 5 h.