Physicochemical stability under inert and reductive atmospheres of Li_2TiO_3 produced from Li_2CO_3 obtained from Argentinean brines
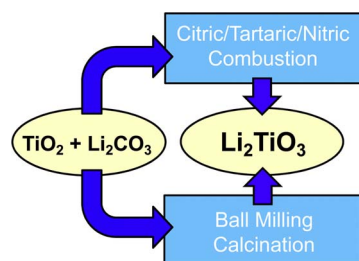
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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Lithium metatitanate (Li_2TiO_3) is one of the most promising candidates as tritium breeder material in a fusion reactor due to its physical and chemical properties. In this paper, the syntheses of Li_2TiO_3 by combustion in solution (SCS) and solid-solid (SSS) were developed using as raw material Li_2CO_3 produced from Argentinean brines and TiO_2. In SCS, aqueous solution of Li_2CO_3 and TiO_2 as metal precursors, citric/tartaric acids as complexing agent/fuel and HNO_3 as oxidant was formed, heated to dryness and then self-combusted. The solid obtained was calcined at 550 °C for 12 h to obtain nanometric Li_2TiO_3 (monoclinic phase, 90%), with particle sizes < 0.5 μm and meso/macropores. In SSS, Li_2CO_3-TiO_2 mixture was ball milled in air at room temperature and subsequently annealed. The effect of milling time and calcined temperature in the formation of Li_2TiO_3 was studied. High yields of Li_2TiO_3 (> 90% and 99%) were obtained even at low heating temperatures (400 and 600 °C for 24 h, respectively). The synthesized powders show mean grain sizes in the nanometric range, particle sizes < 0.7 μm and macropores. Changes that occur during heat treatment in inert and slightly reductive atmospheres (5% H_2/Ar) were identified.

The SSS and SCS methods developed using easy to handle and low-priced precursors constitute cost-attractive processes for large scale production of Li_2TiO_3 nanopowders.

1. Introduction

The breeding blanket is a key component of fusion reactors because it directly involves the tritium breeding and energy extraction, both critical aspects to the development of fusion energy processes. In current designs, the solid breeding blanket is formed by the breeder (lithium compound), a coolant for heat removal and a structural material containing and supporting the breeder [1]. The breeder is responsible to

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produce tritium by reaction with neutrons and release it to maintain the fuel cycle within the reactor, according to the following reaction:

$$^6Li + n \rightarrow He + T + 4.86 \, MeV \tag{1}$$

Lithium ceramic such as Li_2TiO_3, Li_4SiO_4, Li_2ZrO_3 are considered potential candidates [1,2]. In particular, monoclinic lithium metatitanate (β-Li_2TiO_3) is one of the most promising as tritium breeding materials in the D-T fusion reactors owing to its high lithium atom density, good compatibility with structural materials and its good tritium release property. Several physicochemical properties are demanded on these materials and they are depending of the microstructure and final composition achieved during the synthesis procedure [2,3]. Considering that a fusion power plant of 1 GW could require approximately 30 Tn per year of Li_2TiO_3 containing natural lithium [4], it is evident the importance to develop synthesis procedure for industrial purposes.

Numerous methods have been developed to produce Li_2TiO_3 powders such as solid-state (thermal treatment, mechanical milling, urea assisted solid state) [5–10] and wet-chemistry methods (sol-gel [11,12], combustion [13–16], hydrothermal [17–19], in-situ hydrolysis method [20]). Further performance of the ceramic in operating conditions (reductive atmosphere, high temperature, irradiation effects) is strongly dependent of the synthesis procedure, the presence of impurities and the final microstructure obtained. Among the possible methods, the solution combustion synthesis (SCS) is an effective procedure for the production of nanoscale materials and offer well-known advantages of liquid phase reactions with respect to solid phase reactions [21–23]. The metal precursors in an aqueous solution are mixed with the fuel (glycine, urea, sucrose) and oxidizers (nitrates, sulfates). The dispersion of reactants takes place optimally producing a homogeneous mixture and increasing the reactivity of precursors. After preheating to the ignition temperature, the reaction begins and provides the heat for reaction sustainability, producing valuable products. SCS has the advantage of rapidly producing fine and homogeneous powders. In addition, it is a simple and efficient method for the scalable synthesis of mixed oxide powders, saving time and energy.

One major drawback in some wet-chemistry methods is the high volume of liquid or gaseous waste generated. As alternative, solid-state synthesis (SSS) emerges as potential option for the preparation of stoichiometric single-phase material but this procedure usually requires high-temperature of thermal treatment to favor the diffusion of the components.

To overcome this drawback, the use of high energy mechanical milling in combination with post annealing allows the production of amorphous and/or nanocrystalline metal/non-metal composite materials at lower temperatures [24–26]. In the ball milling step, plastic deformation, cold-welding and fracture are predominant factors, which leads to the refinement of the microstructure (particle and grain sizes reduction) and surface/bulk defects generation [24]. These modifications improve the posterior reactivity of the components and the final product could be obtained at lower temperature in comparison with the traditional solid-state reaction.

In this work, Li_2TiO_3 powders were prepared by two different synthesis procedures: combustion reaction in solution (SCS) and solid-solid synthesis (SSS). These procedures were designed to use as raw material, Li_2CO_3 obtained from Argentinean brines and commercial TiO_2. According to the literature [10–17,19], the usual lithium precursors for the wet chemical synthesis of Li_2TiO_3 are lithium hydroxide and lithium nitrate. High purity Li_2CO_3 is available in the North of Argentina. It is obtained by vaporization, precipitation and refinement of natural brines containing lithium in addition to other ions and is the main source in the manufacture of lithium battery electrodes, an increasingly important device in the accumulation and transport of energy. The stability, availability and low comparative price of this local precursor makes it attractive for the syntheses proposed in this paper, seeking to expand the possible applications of the resource in the

generation of energy through DT fusion reactors. On the other hand, the use of cheaper and easy to handle TiO_2 in comparison with other conventional titanium sources ($TiCl_4$ [11], $TiO(NO_3)_2$ [13,15], Tetrabutyltitanate [10,16]) provides an economical benefit.

Microstructural, chemical, structural and textural characteristics of the powders produced by SCS and SSS were studied. In addition, thermal behavior of the Li_2TiO_3 in both He and $H_2(5\%)$/He flows were evaluated to identify possible mass loss mechanisms. This work was developed as part of the activities in the subprogram of controlled nuclear fusion at CNEA (National Commission of Atomic Energy, Argentina).

2. Experimental

The starting material were Li_2CO_3 (98%) produced in Argentina from natural brines and TiO_2 (Aldrich, 99%) powders. Other chemical reagents were of analytical purity and were used without additional purification.

For SCS an aqueous solution was prepared using stoichiometric Li_2CO_3 and TiO_2 as lithium and titanium precursors, respectively. The chelating-fuel and oxidant agents selected were citric/tartaric acids and HNO_3. The molar ratio citric acid, tartaric acid to total nitrate was 1.8:1:0.3. The mixed solution was heated at 70 °C with continuously stirring for several hours till the solution became yellowish sol. After that, the sol changed into a dry-gel and it was auto-ignited by a self-propagating combustion yielding a solid product. This material was milled in a mortar and heated at 550 °C for 12 h to produce a white powder.

For SSS, the Li_2CO_3-TiO_2 mixture (1:1 mol ratio) was milled under air at room temperature for different times (10 min, 0.5 h, 1 h, 5 h) using a planetary ball mill (Fritsch Pulverisette P6). The milling chamber and the balls were of stainless steel. The experimental milling conditions were ball to powder weight ratio of 53:1 and operation at 400 rpm. The as-milled powders were annealed at 400 °C, 600 °C and 800 °C for different times. The yield of the synthesis procedure was determined by calculation of the ratio between the mass of desired product (Li_2TiO_3) and the total mass.

Crystal structure of the powders was studied by X-ray Powder Diffraction (XRPD, PANaytical Empyrean, con CuKα and graphite monochromator). The estimations of mean grain size (D) and microstrains (ε) were performed by Williamson-Hall method ($\Gamma_{instrumental} = 0.065°$) [27]. Microstructure was observed by Scanning Electron Microscopy (SEM Nova Nano 230, FEI Company) equipped with EDS (Energy Dispersive Spectroscopy) for chemical microanalysis. Textural characteristics of the powders were studied using a Micromeritics ASAP 2020 analyzer. 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.

Physicochemical stability of the samples as a function of the temperature and the atmosphere was evaluated using thermogravimetry (TG, TA Instruments HP50) and temperature programmed reduction (TPR, Micromeritics AutoChem 2910). For TPR runs, the mixture 5% H_2/Ar (100 cm^3/min) was introduced into the reactor containing 0.25 g of sample and 30 min were waited up to flow stabilization. Then, the temperature was increased from room temperature up to 800 °C using 10 °C/min ramp. Hydrogen consumption was monitored using TCD detector. When CO_2 is generated due to Li_2CO_3 decomposition, an internal calibration was performed to quantify CO_2. For TG measurements, ~0,12 g were heated under gas flow (He or H_2 (5%)/Ar). The sample, previously heated at 200 °C for 1 h under dry inert gas, was heated from room temperature to 800 °C using a 10 °C/min ramp and 50 cm^3/min flow. Solid phase IR spectra were obtained with an FTIR Perkin Elmer Spectrum 400 spectrometer in the range of 800–4000 cm^{-1}. The selected samples were grounded with dry KBr, pressed to pellets and put in specially designed cell in air.
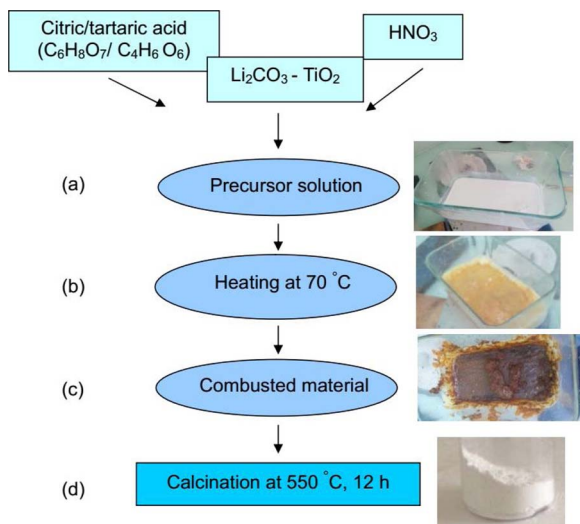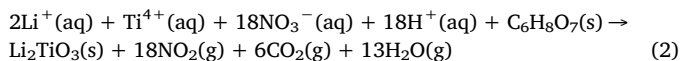
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Fig. 1. Scheme of the solution combustion synthesis route to produce Li_2TiO_3.

3. Results and discussion

3.1. Synthesis of Li_2TiO_3 by different synthesis procedures

A scheme of the SCS route and the representative photographs of materials at different stage of the Li_2TiO_3 synthesis are shown in Fig. 1. Lithium and titanium precursors and HNO_3 were stirred to obtain a white dispersion (Fig. 1a). Tartaric and citric acids were added and then the solution was heated up to 80 °C on a hot plate under continuous stirring until all liquid evaporated. The starting mixture changes from white to yellow color (Fig. 1b). There was evolution of fumes towards the end of the reaction leaving a fluffy mass in the recipient. The reaction is completed by self-combustion giving a brown product (Fig. 1c). At this point, the powder was milled and calcined at 550 °C for 12 h to obtain a white powder (Fig. 1d). The global reaction of the SCS route can be represented as:

$$2Li^+(aq) + Ti^{4+}(aq) + 18NO_3^-(aq) + 18H^+(aq) + C_6H_8O_7(s) \rightarrow Li_2TiO_3(s) + 18NO_2(g) + 6CO_2(g) + 13H_2O(g) \quad (2)$$

After annealing, the final phases were analyzed by XRPD (Fig. S1) and the composition of mixture was monoclinic-Li_2TiO_3 (90 wt%), TiO_2 as rutile (2 wt%) and Li_2CO_3 (8 wt%). The yield of the synthesis procedure was 90%.

The SSS route is depicted in Fig. 2. The XRPD patterns obtained after 10 min, 1 h and 5 h of milling show the presence of both starting materials. No evidence of reaction induced by mechanical processing was detected between Li_2CO_3 and TiO_2 from XRPD patterns. As an example, Fig. 3 displays the X-ray diffractogram of the Li_2CO_3-TiO_2 mixture after 1 h of milling. It can be seen the most intense peaks of the
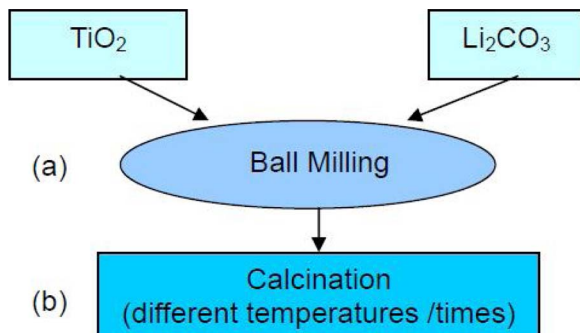

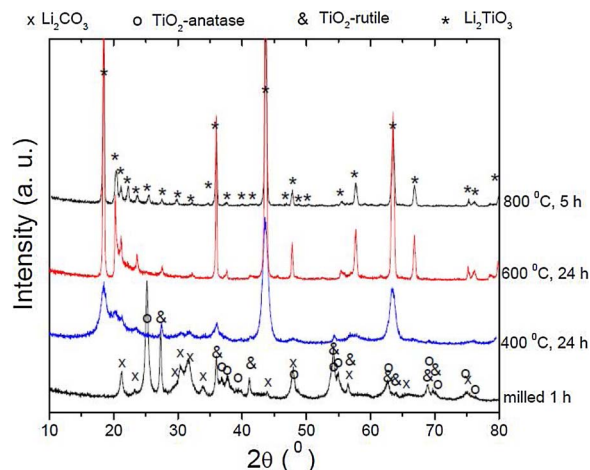Fig. 2. Scheme of the solid-state synthesis route to produce Li_2TiO_3.

Fig. 3. XRPD patterns of the Li_2CO_3-TiO_2 mixture after 1 h of milling, annealed at 400 °C (24 h), 600 °C (24 h) and 800 °C (5 h).

Li_2CO_3 and TiO_2 (anatase and rutile phases). Then, the mechanical milling favors the physical mixture between the reactants without promotion of the reaction between them. On the other hand, it is known that mechanical milling induces microstructural modifications in the starting materials, such as reduction in the grain size and or introduction of microstrains, which could favor further reaction between reactants with temperature raising [24,26].

The Li_2CO_3-TiO_2 mixture after 1 h of milling was annealed at different temperatures and times. Fig. 3 shows the evolution of the Li_2TiO_3 formation with the temperature. After heating at 400 °C for 24 h the most intense diffraction peaks of Li_2TiO_3 are identified as well as those corresponding with Li_2CO_3 and TiO_2 (rutile). Similar thermal treatment at 600 °C (24 h) and 800 °C (5 h) leads to the complete formation of Li_2TiO_3, without evidence of remnant starting materials. The solid state reaction can be expressed as:

$$Li_2CO_3(s) + TiO_2(s) \rightarrow Li_2TiO_3(s) + CO_2(g) \quad (3)$$
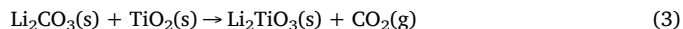
The brittle nature of the starting materials avoid the adherence between the powders and the milling chamber, which possibilities their posterior recovery for the thermal treatment. The SSS procedure has a yield > 99%.

To clarify the influence of the milling time on the Li_2TiO_3 formation during thermal treatment, samples milled for different times were annealed at 600 °C for 24 h. The XRPD patterns are shown in Fig. 4. For
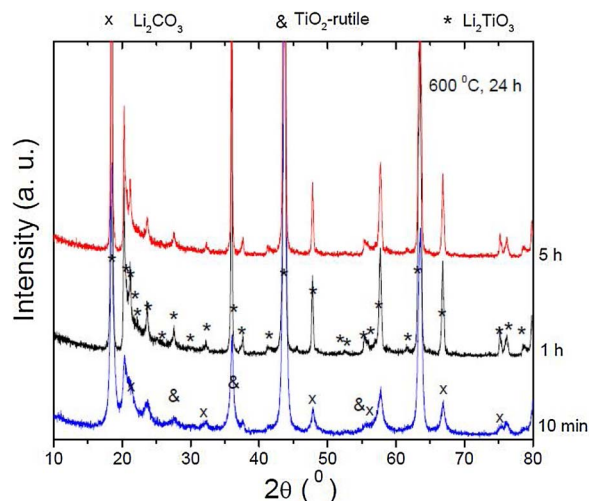

Fig. 4. XRPD patterns of the Li_2CO_3-TiO_2 mixture milled 10 min, 1 h and 5 h and afterwards annealed at 600 °C (24 h).

mixture milled for 10 min and annealed, besides Li_2TiO_3 presence also the starting materials are identified, which indicates the incomplete Li_2TiO_3 formation. On the contrary, the combination of 1 h of milling (or 5 h) and equal thermal treatment (24 h, 600 °C) induces the complete formation of Li_2TiO_3 and the complete Li_2CO_3 consumption. By comparison of the results shown in Figs. 3 and 4, for a thermal treatment of 600 °C during 24 h, milling for 1 h is enough to produce the desired material. For the next studies it was selected Li_2TiO_3 produced under moderate conditions because the short milling time (1 h) minimizes possible contamination with the material of the milling chamber and balls, and the intermediate temperature (600 °C) of annealing reduces the energetic consumption.

Therefore, SCS and SSS allow the production of Li_2TiO_3 with high yield, using as starting materials precursors of low cost and good chemical stability: Li_2CO_3 obtained from Argentinean natural resources and TiO_2. These synthesis procedures constitute valuable production methods on the industrial scale. In the case of SSS, the combination of mechanical milling and thermal treatment reduces the Li_2TiO_3 formation temperature and the overall energetic requirements in comparison with the conventional ceramic synthesis. Production of Li_2TiO_3 by SCS requires low temperature, short time and simple equipment, resulting in an energy-efficient method.

3.2. Characterization of Li_2TiO_3 powders produced by SCS and SSS routes

Samples of Li_2TiO_3 produced by SCS and SSS were studied to characterize their morphology, microstructure, structure, chemical composition and texture. Fig. 5 show the micrographs of SEM for both samples (magnifications 50000× and 100000×). The powder obtained by SSS displays a compact and homogeneous morphology, with particle sizes lower than 0.7 μm (Fig. 5A) which are linked and/or sintered (Fig. 5C). Due to the neck grain growth, the shape of the particles is not clear but the presence of pores is even visible. In opposition, the powders produced by SCS show an open microstructure, with pores clearly identified between the particles (Fig. 5B). The existence of connected pores is expected to provide large internal surface for tritium and helium release during irradiation [28,29]. The particles have rounded and defined edges with a wide distribution of sizes from 0.1 μm to 0.5 μm (Fig. 5D). For the samples produced by SCS and SSS routes, several EDS analyses were performed on wide areas (200 μm × 200 μm) to identify possible contaminations. Minor amounts of Si (Si/Ti ratio lower than 2 at.%) were detected in the sample produced by SCS method. No Fe contamination was noticed in the Li_2TiO_3 powders produced by SSS.

From XRPD patterns of Figs. S1 and Figure 4, it can be estimated the cell parameters of the samples produced by SCS and SSS which are, within the experimental error, similar than the reported values (ICDD-PDF card #33-831). The mean grain size calculated for the Li_2TiO_3 powders produced by SCS method is about 70 nm (microstrain, $\varepsilon = 0.6\%$). For the sample milled 1 h and annealed at 600 °C for 24 h the mean grain size is 130 nm ($\varepsilon = 0,1\%$). This information indicates that each particle identified by SEM is an agglomeration of single-crystal domains.

Textural characterization of the Li_2TiO_3 powders obtained by both methods was performed by nitrogen physisorption (Fig. 6). The isotherm for Li_2TiO_3 produced by SCS is Type II (according IUPAC classification) and presents a slight hysteresis, which indicates the presence of macropores (> 50 nm) and some mesopores. The specific surface
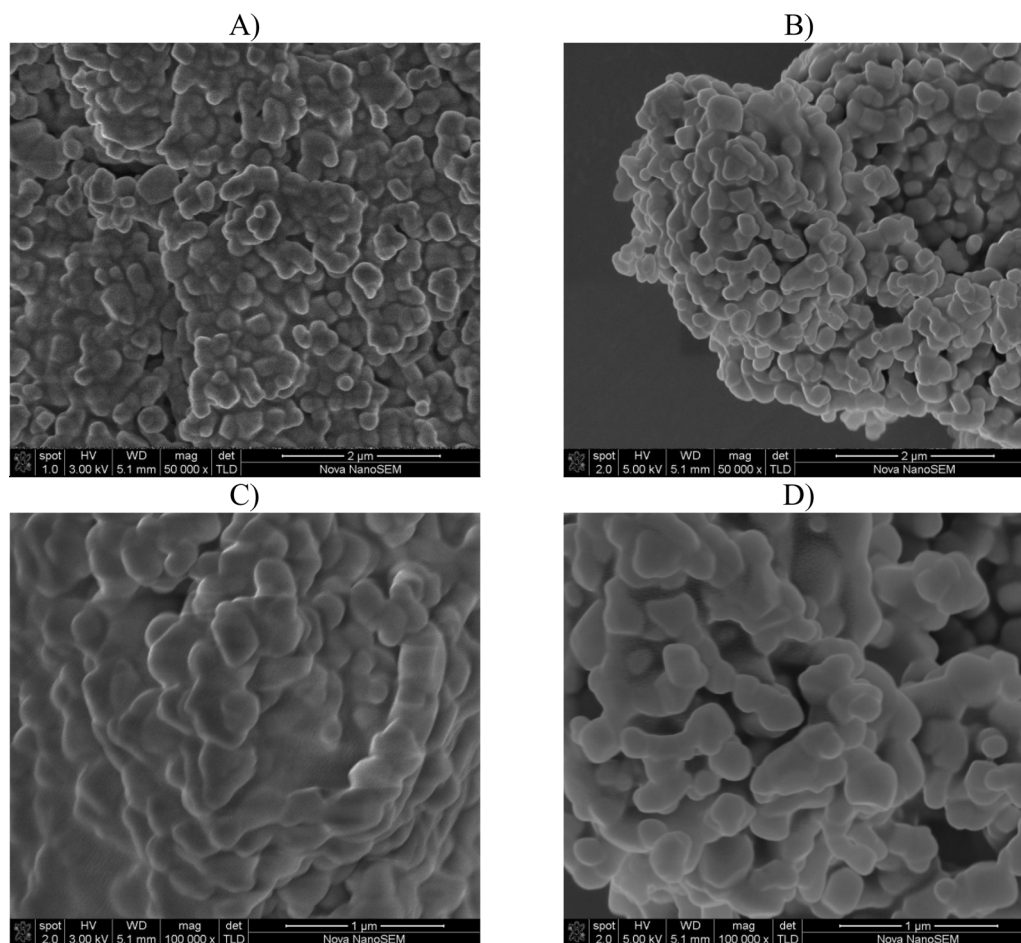

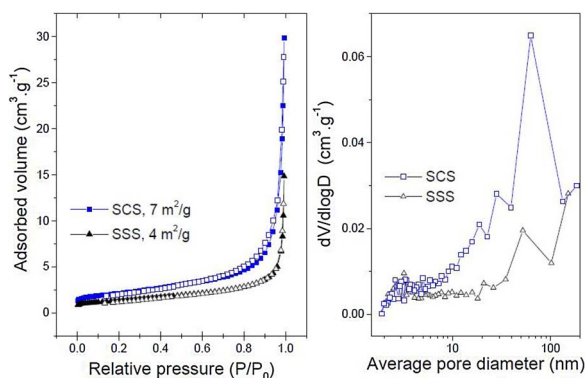**Fig. 5.** SEM micrographs of the powders obtained by SSS (A, C) and SCS (B, D).

Fig. 6. Adsorption/desorption isotherm of nitrogen for as-synthesized Li_2TiO_3 powders produced by SCS and SSS.

area is $7\,m^2/g$. In the case of SSS, it was observed an isotherm type II, without hysteresis, with a surface specific area of $4\,m^2/g$ and macropores presence. Then, the material obtained by SCS has higher area than those produced by SSS, with a porous microstructure (meso and macropores), smaller grain size and particles with smaller size (associated with several crystallographic domains). The small grain size obtained for Li_2TiO_3 using both synthesis procedure is promising, considering that the final grain size affect the tritium release ability and thermal conductivity, being optimum values less than $5\,\mu m$ [30].

It is important to remark that in SCS the microstructure of the products can be controlled by fuel type, fuel-to-oxidizer ratio and combustion mode [23]. In particular, citric acid can act as a fuel and also as complexant for metal ions avoiding precipitation. A recent work studied the effect of the fuel-to-oxidizer ratio on both the combustion mode and the microstructure of the Li_2TiO_3 powders [16]. A crystallite size of Li_2TiO_3 between 18 and 36 nm and density more than 90% of theoretical density (TD) were obtained by sintering at low temperature (800 °C), which avoids grain size increasing and sintering. These results evidence the potentiality of SCS as an effective method for the production of nanoscale Li_2TiO_3, with controlled microstructure and sinterability by an adequate control of the synthesis parameters.

3.3. Physicochemical stability of the Li_2TiO_3 powders produced by SCS and SSS routes under different atmospheres

It is known that lithium ceramics such as Li_2TiO_3 absorb moisture and carbon dioxide from the air to produce $LiOH(H_2O)$ and/or Li_2CO_3 compounds. Thermal treatments of these ceramics under dry conditions induces both $LiOH(H_2O)$ and Li_2CO_3 decomposition into Li_2O and gaseous species such as H_2O and CO_2 [31]. On the other hand, in the blanket of DT fusion reactors it is expected that the tritium generated by the lithium ceramics has to be swept by He gas or $H_2(100\,Pa)/He$ mixed gas to obtain a high tritium recovery efficiency, assuming that physisorbed species were removed before operation [32]. In fact, the tritium produced by the breeder could interact physically and/or chemically with the breeding material itself, both with species in the surface and/or with the bulk. Hence, it is important to investigate the aging behavior of Li_2TiO_3 in inert and reductive flows existing during sweep gas conditions. To analyze the physicochemical stability of the material during the thermal treatment under inert atmosphere (He), the mass loss of the Li_2TiO_3 powders as a function of temperature was measured using a heating ramp of 10 °C/min (Fig. 7). The as-synthesized Li_2TiO_3 powders show different behavior, depending of the synthesis procedure. The SSS sample has a small mass loss (about 1–1.5%, curve a). Considering that the sample was handled under atmospheric conditions, the mass loss can be related from FTIR measurements with the presence of moisture (broad band at $3420\,cm^{-1}$) and carbonate species (1430 and $1506\,cm^{-1}$) onto the powders surface (see Fig. S2-A). The band at $1635\,cm^{-1}$ is related with H_2O vibration of atmospheric water

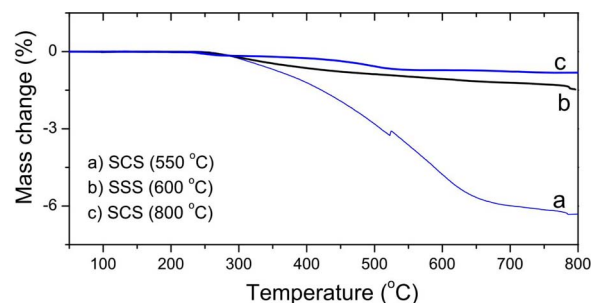**Fig. 7.** TG curves under helium flow for SSS and SCS samples: a) as-synthesized SCS; b) as-synthesized SSS; c) SCS calcined at 800 °C for 5 h.

vapor. In the case of SCS sample, the presence of un-reacted Li_2CO_3 (8 wt%, determined by XRPD) is the responsible of about 4.5% of the mass loss measured due to CO_2 releasing (Fig. 7, curve b). In addition, an extra mass loss of about 1.5% is possible by similar species than in the case of SSS sample (see Fig. S2-A), i.e. moisture and CO_3^{2-} anions due to the surface absorption of CO_2 [33]. As important point, no bands corresponding to organic residual compounds were detected in the FTIR spectrum of SCS sample.

To corroborate these interpretations, the SCS sample was ex-situ annealed in air at 800 °C (Fig. 7, curve c) to complete Li_2CO_3 decomposition. FTIR performed on this sample after short atmospheric exposition confirms the elimination of moisture and a reduction of surface carbonates species (Fig. S2-B). After this, the mass change of this sample was evaluated as a function of temperature in He flow. The mass loss observed in He for SCS sample treated at 800 °C was the smallest (< 1%). At the end of the TG measurements, the samples were analyzed by XRPD. The only phase detected was monoclinic Li_2TiO_3 and no evidence of the presence of other species was found.

To evaluate the behavior of the samples under reductive atmosphere, programmed temperature reduction measurements were performed using $H_2(5\%)/Ar$ flow up to 800 °C. The TCD signal as a function of temperature is shown in Fig. 8. The as-synthesized SCS and SSS samples show different behavior, with a peak centered at 680 and 650 °C, respectively, being the signal three times higher for the SCS sample. The SSS sample consumed a low amount of hydrogen ($83\,\mu mol\,g^{-1}$), which was detected due to the high sensibility of the TCD detector. In the case of SCS sample, the presence of unreacted Li_2CO_3 (confirmed in TG measurement, Fig. 7a) leads to the superposition of the signals of CO_2 release and hydrogen consumption. Using an internal calibration for CO_2 and assuming 8 wt% of Li_2CO_3, the amount of hydrogen consumed in the SCS sample was $62\,\mu mol\,g^{-1}$. Then, both samples display the same order of magnitude of the
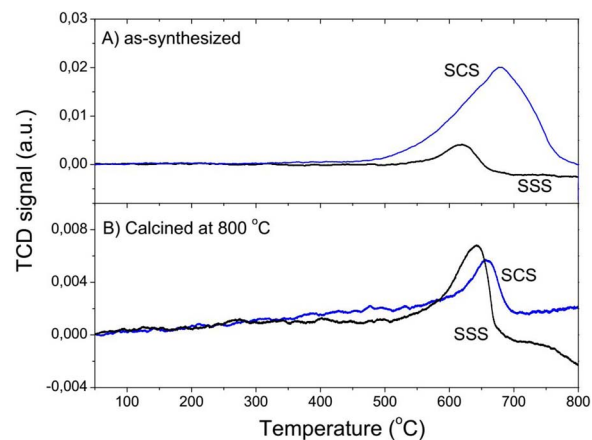

Fig. 8. TPR curves of SCS and SSS samples. A) as-synthesized; B) calcined at 800 °C. Heating ramp: 10 °C/min, $H_2(5\%)/Ar$, flow: $100\,cm^3/min$.
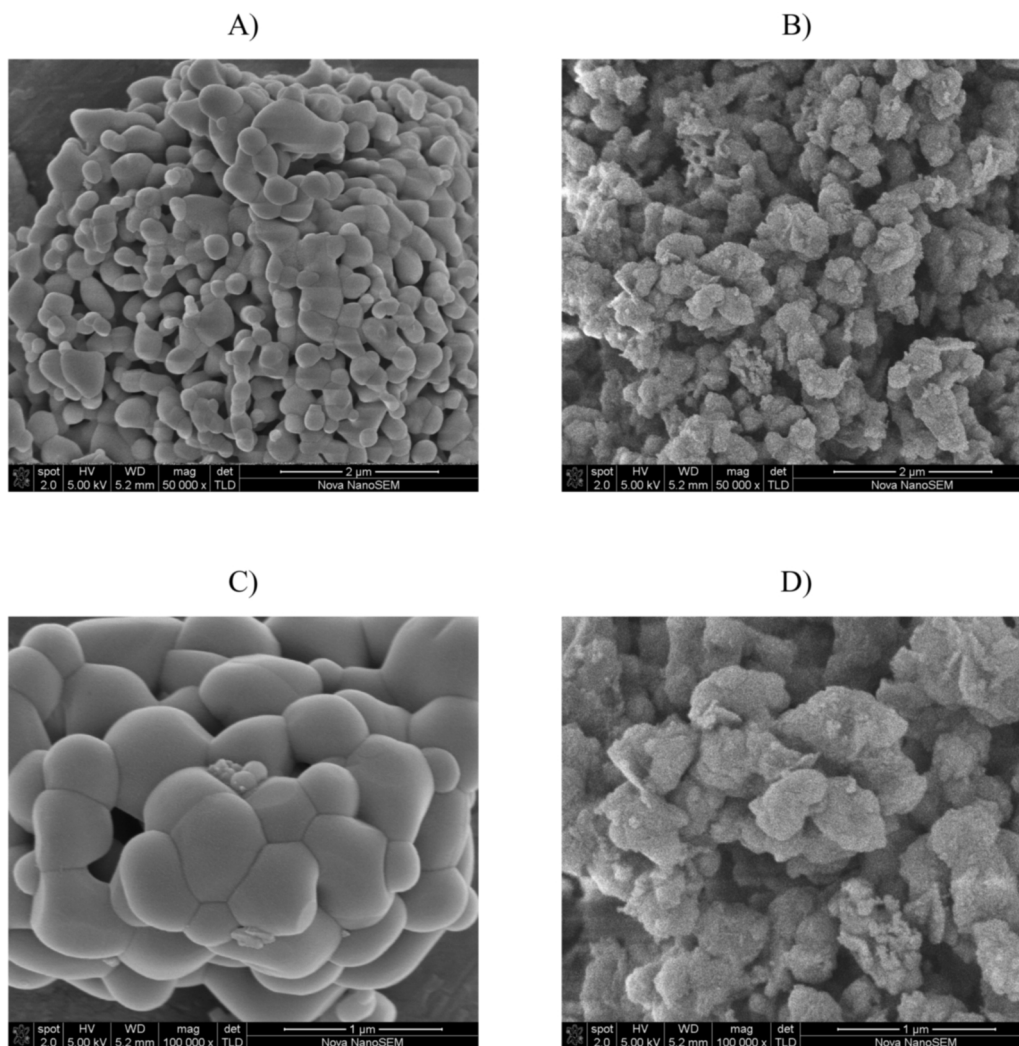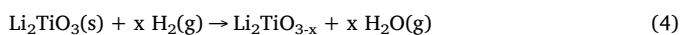
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Fig. 9. SEM micrographs of the powders obtained by SSS (A, C) and SCS (B, D) after reduction under H_2(5%)/Ar flow.

reduction, according the reaction

$$Li_2TiO_3(s) + x\ H_2(g) \rightarrow Li_2TiO_{3-x} + x\ H_2O(g) \qquad (4)$$

with x values is between 0.0068 and 0.0091.

Extra TPR curves of SCS and SSS samples after calcination at 800 °C show similar shape and amount of hydrogen consumed (between 60 and 90 μmol g^{-1}). In addition, for SSS sample, the TPR curve after calcination at 800 °C is similar than that obtained as-synthesized. The powders show a change in the color from white to blue, which could be associated with some defects formation due to reduction. The white color could be recovered by heating of the powder under air.

The microstructure of the as-synthesized samples after the reduction was studied using SEM. The photographs are shown in Fig. 9(A–D) (magnification 50000× y 100000×). It can be seen that SSS sample has particles with size (0.5–0.7 μm) similar those observed before reduction (Fig. 5). Some elimination of porosity and the formation of defined grain structure were observed due to a minor degree of sintering. As a difference, the SCS sample shows disaggregated particles, with edge and shape undefined probably due to the CO_2 releasing.

XRPD patterns obtained with the samples at the end of the TPR curves reveal the presence of Li_2TiO_3, without evidence of other detectable changes in the structure. These results suggest that Li_2TiO_3 powders are relatively stable under hydrogen flow and only a small reduction is detected, even when the hydrogen content (5%H_2/He) is higher than that used in the sweep gas. All results constitute evidence of the comparatively high thermal stability of Li_2TiO_3 obtained by SSS

method.

Finally, SSS and SCS methods allow the production of Li_2TiO_3 powders with particle sizes lower than 0.7 μm and minimum grain growth, even after thermal treatment at 800 °C under inert or reductive atmospheres. Special attention is devoted to SCS method due to the possibility to modify different parameters that influence the microstructure. The Li_2TiO_3 powders produced using citric acid/fuel ratio 6:1 show the presence of interconnected pores and crystallite sizes lower than those obtained by SSS, all factors considered beneficial for the tritium and helium release during irradiation [28–30]. Although a 90% of TD required for fusion application [34,35] could be obtained from Li_2TiO_3 powders produced by SCS [16], it is known that lithium density decreases during operation conditions due to burn-up. For this reason, advanced breeder materials such as a mixture of Li_2TiO_3 (0.44 g/cm^3) with Li_4SiO_4 (0.54 g/cm^3) [36,37] among others [35] are being studied to improve the lithium density in Li_2TiO_3. Consequently, it is necessary to advance in the development of improved breeder materials as well as in their experimental evaluation under irradiation conditions.

4. Conclusions

Powders of Li_2TiO_3 were successfully synthesized, using same starting materials, by combustion solution technique and ball milling followed by thermal treatment. Both Li_2CO_3 and TiO_2 were selected as precursors due to their availability, simple handling and low cost in comparison with the usual lithium and titanium precursors selected in

wet chemical methods. SCS allows producing monoclinic Li_2TiO_3, with crystallite size of 70 nm, a specific area of 7 m^2/g, macropores (> 50 nm) and some mesopores. SSS exhibits higher yield, given nanopowders of mean grain size of 130 nm, specific area of 4 m^2/g and macropores.

The as-synthesized Li_2TiO_3 powders by SCS and SSS show the presence of moisture and carbonate species on the surface after handling under atmospheric conditions. These species were eliminated by heating at 800 °C under He flow. This thermal treatment improves sample stability for posterior exposition to air. Independently of the synthesis procedure, the samples display a limited reducibility under H_2(5%)/He, even if the material was annealed at 600 °C (24 h) or 800 °C (5 h).

The microstructure of the synthesized materials and their thermal stability after surface cleaning both in inert and reduced atmospheres is promising as breeder material for DT fusion reactors. The synthesis methods developed can be scaled-up and cost-effective for the industrial production of Li_2TiO_3.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.fusengdes.2018.03.022.

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