Mechano-thermally Activated Solid-state Synthesis of $Li_4Ti_5O_{12}$ Spinel from Li_2CO_3-TiO_2 Mixtures

Vittorio Berbenni, Chiara Milanese, Giovanna Bruni, and Amedeo Marini

CSGI – Unità Operativa di Pavia – Dipartimento di Chimica Fisica della Università di Pavia,
Via Taramelli 16, 27100 Pavia, Italy

Reprint requests to Dr. Vittorio Berbenni. Fax: +39-0382-987575.
E-mail: vittorio.berbenni@unipv.it

Z. Naturforsch. **2010**, *65b,* 23 – 26; received September 10, 2009

Simultaneous TG/DSC measurements performed on mixtures $2Li_2CO_3$-$5TiO_2$ (anatase) subjected to high-energy milling showed that both the temperature and the enthalpy of Li_2CO_3 decomposition are much lower than in the case of TG/DSC runs performed on a sample of a physical mixture. On the basis of the thermoanalytical evidence a solid-state synthesis of the spinel compound $Li_4Ti_5O_{12}$ has been proposed that combines mechanical (by high-energy milling) and thermal activation (8 h annealing at 973 K): the obtained compound shows a lattice constant in very good agreement with that expected for the pure phase $Li_{1+x}Ti_{2-x}O_4$ ($x = 0.333$). The molar heat capacity of $Li_4Ti_5O_{12}$ has been determined in the temperature range 323 – 633 K by quasi-isothermal Modulated Differential Scanning Calorimetry (MDSC). The specific surface area of $Li_4Ti_5O_{12}$ has been determined by gas adsorption.

Key words: $Li_4Ti_5O_{12}$, Solid-state Synthesis, High-energy Milling, Molar Heat Capacity

Introduction

The spinel $Li_4Ti_5O_{12}$ has been demonstrated to be a valid anodic material to be used in lithium batteries due to its zero volume change during charge/discharge cycles [1, 2]. $Li_4Ti_5O_{12}$ has been prepared by solid-state reaction in mixtures of precursors such as $LiOH{\cdot}H_2O$ and anatase [1], or Li_2CO_3 and rutile [3, 4]. In this approach, the mixtures had to be thermally treated at temperatures between 1073 and 1173 K for periods of 12 – 24 h. Recently [5] the solid-state synthesis of $Li_4Ti_5O_8$ has been performed by microwave heating of a stoichiometric mixture of Li_2CO_3 and TiO_2: 15 min of microwave irradiation at 700 W were needed to reach a temperature high enough to obtain $Li_4Ti_5O_{12}$.

The synthesis of $Li_4Ti_5O_{12}$ has also been performed by alternative methods such as the sol-gel route [6, 7]. In this case the gel precursors were calcined for 24 h at 1073 K to get phase-pure $Li_4Ti_5O_{12}$. Other synthetic routes have been attempted to synthesize $Li_4Ti_5O_{12}$ such as the emulsion-gel synthesis [8] where a thermal treatment of 10 h at 1073 K had to be performed, or the hydrolysis of a mixture of lithium acetate dihydrate and tetra-*n*-butyl titanate followed by a calcination stage of 12 h at 1073 K [9]. $Li_4Ti_5O_{12}$ has also been prepared by a cellulose-assisted combustion synthesis [10]: after cellulose was repeatedly impregnated with the reagents and dried, again a final step of calcination (5 h at 1023 K) was necessary to obtain phase-pure $Li_4Ti_5O_{12}$. Obviously in all previous non-solid-state syntheses a final step of calcination at temperatures of at least 1023 K had to be included. In order to lower the temperature at which the synthesis can be performed, the combination of mechanical and thermal energy was applied to obtain $Li_4Ti_5O_{12}$ [11]. A mixture of lithium acetate dihydrate and anatase was maintained for 1 h at 773 K yielding a mixture of Li_2TiO_3 and unreacted anatase. Afterwards, an amino acid (such as glycine or alanine) was added to the mixture which was then milled for 3 h. A final stage of 1 h at 973 K led to a product that is constituted mainly of $Li_4Ti_5O_{12}$ (97 % phase-pure).

The present work reports a solid-state synthesis process for $Li_4Ti_5O_{12}$ starting from mixtures of Li_2CO_3 and TiO_2 (anatase) subjected to a combination of mechanical (high energy milling for 4, 8, 16 and 30 h) and thermal energy (annealing for 8 h at 973 K in an electric furnace). Such a combined treatment leads to the desired 100 % phase-pure product at a relatively low temperature without use of other reagents and in

0932–0776 / 10 / 0100–0023 $ 06.00

only two stages compared to the method previously applied [11]. The molar heat capacity of $Li_4Ti_5O_{12}$ has been determined in the temperature range 323 – 633 K by quasi-isothermal Modulated Differential Scanning Calorimetry (MDSC). Furthermore the specific surface area of $Li_4Ti_5O_{12}$ has been determined by gas adsorption.

Experimental Section

The starting chemicals [TiO_2 (anatase, purity 99.7 %) and Li_2CO_3 (purity 99.9 %)] were purchased from Aldrich Chimica (Italy). Physical mixtures of a molar ratio Li/Ti = 0.8 were prepared by weighing the appropriate amounts of precursors and by stirring the powders in an acetone suspension for 3 h. Finally the solvent was allowed to evaporate in an oven at 333 K overnight. The mechanically activated mixtures were prepared by dry milling lots of 1 g of the physical mixtures: the powders were put into zirconia jars (12.5 mL) of a planetary mill (Pulverisette 7 by Fritsch, Germany) with 4 zirconia balls (12 mm diameter; the mass ratio between the milling balls and the sample powder was 9 : 1). The mill was operated at 400 rpm (rotation speed) for different times (4, 8, 16 and 30 h).

TG/DSC measurements were performed with a TG-DSC Q600 simultaneous TG/DSC analyzer (TA Instruments Inc. USA). Samples of ≈ 50 mg of the mixtures were placed into alumina cups and heated (10 K min^{-1}, air flow 100 mL min^{-1}) from 298 K up to 1123 K. X-Ray powder diffraction patterns were recorded in step scan mode (step 0.015°, 3 s per step, 40 kV, 40 mA, 2ϑ = 15 – 115°, CuK_α with an X-ray powder diffractometer (Bruker D5005).

The molar heat capacity of $Li_4Ti_5O_{12}$ was determined by MDSC (Q2000 DSC, T_{zero} technology, TA Instruments Inc. USA, nitrogen flow of 50 mL min^{-1}). The samples (≈ 20 mg) were placed in a closed aluminum pan and heated in a quasi-isothermal mode: the sample was heated at temperatures between 323 and 633 K in steps of 10 K (10 min per step) while the temperature was oscillating (amplitude: ± 0.5 K; period: 70 s). In this way the true reversing heat capacity could be measured. Before the measurements, the instrument was calibrated under the same experimental conditions with a sapphire disk according to the manufacturer's instructions: a calibration constant of $[C_{P,sapphire,tab} / C_{P,sapphire,meas}] = 1.103 \pm 0.006$ was obtained.

The specific surface area of $Li_4Ti_5O_{12}$ was determined by N_2 adsorption (BET method). The nitrogen adsorption curve was recorded by a Sorptomatic 1990 instrument (Thermo Electron Corporation) operating according to the static volumetric principle. The correction for the volume of the sample was introduced by measuring the N_2 adsorption with the empty buret.

Table 1. DSC data of the physical mixture and of the milled samples.

Mixture	ΔH ($J\,g^{-1}$)	ΔM (%)	ΔH (kJ mol^{-1} Li_2CO_3)
Physical	379 ± 30	-15.6 ± 0.2	107 ± 8
Milled 4 h	162 ± 13	-11.9 ± 0.5	60 ± 5
Milled 8 h	153 ± 5	-11.88 ± 0.25	56.8 ± 1.9
Milled 16 h	132.7 ± 4.6	-10.27 ± 0.08	56.9 ± 2.2
Milled 30 h	135 ± 10	-9.4 ± 0.2	63.0 ± 4.6

Results and Discussion

Fig. 1 shows the TG/DTG curves of the physical and of the milled mixtures. It can be seen that the mass loss process in the physical mixture attains the maximum rate at ≈ 973 K and is over at ≈ 1023 K. As regards the milled mixtures, the maximum rate of mass loss is attained at 673 – 700 K, and the process is over at ≈ 873 K.

The DSC data, the mean enthalpy values of the broad endothermic peak due to the decomposition of lithium carbonate, are reported in Table 1. Also reported in Table 1 are the relevant mass losses recorded under the DSC peaks, and the mean enthalpy values calculated in units of kJ mol^{-1} of Li_2CO_3.

It can be seen that the decomposition enthalpy in the case of the milled mixtures is nearly 60 % of that recorded for samples of the physical mixture.

Hence the TG part of the experiment brings into evidence that the Li_2CO_3 decomposition in the milled mixture occurs at much lower temperatures (≈ 720 K) than in the physical mixture where it sets in at its spon-

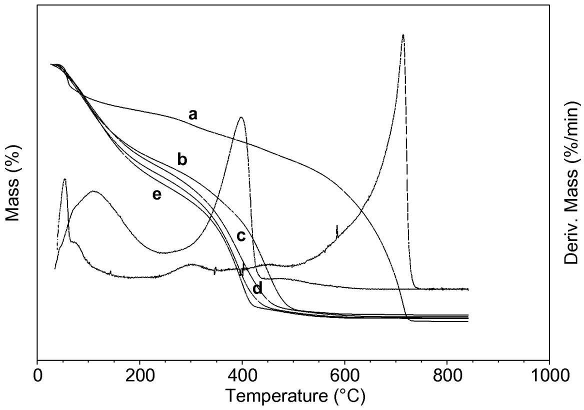

Fig. 1. TG/DTG curves obtained for samples of a physical mixture (a) and samples of mixtures milled for 4 h (b), 8 h (c), 16 h (d), and 30 h (e). For reasons of clarity the DTG curves are reported only for the physical mixture (curve with maximum at ≈ 973 K) and for that milled for 30 h (curve with maximum at ≈ 673 K).

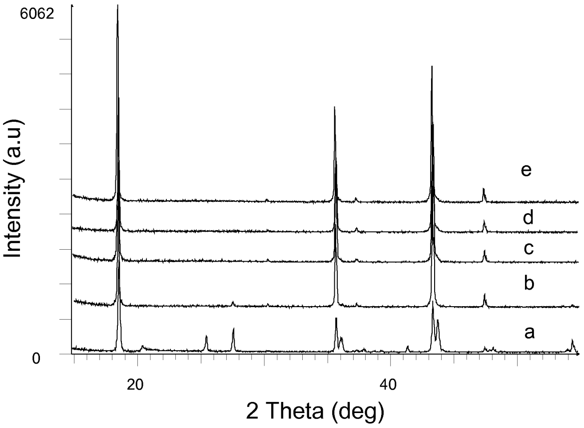

Fig. 2. XRPD patterns of the residuals recovered from the TG/DSC runs performed up to 850 °C. (a) Physical mixture; mixture milled for 4 h (b), 8 h (c), 16 h (d), and 30 h (e).

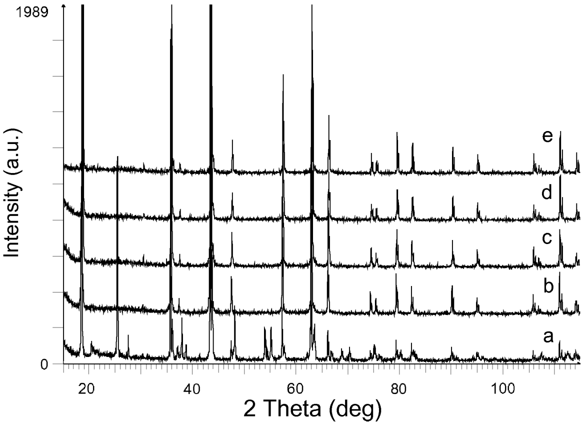

Fig. 3. XRPD patterns of samples of mixtures thermally treated for 8 h at 700 °C. (a) Physical mixture; mixture milled for 4 h (b), 8 h (c), 16 h (d), and 30 h (e).

taneous temperature ($T \approx 810$ K). This means that, in the milled mixtures, Li_2CO_3 decomposition is driven by the reaction with titanium dioxide. Furthermore the fact that the decomposition enthalpy is lower in the milled mixtures (≈ 60 kJ mol^{-1} of Li_2CO_3) than in the physical mixture (≈ 107 kJ mol^{-1} Li_2CO_3) means that an enthalpic release (mean value -48 ± 3 kJ mol^{-1} of Li_2CO_3) occurs corresponding to the endothermic peak of the milled mixtures. The residuals recovered at the end of the thermal runs were examined by X-ray diffractometry, and the relevant powder patterns are shown in Fig. 2.

The following considerations apply:

i) The only peaks present in the patterns of the residuals of the mixtures milled for 8, 16 and 30 h (traces c, d and e) are those characteristic of the compound $Li_4Ti_5O_{12}$. In the patterns of the residual of the 4 h-milled mixture (trace b) the 100 % intensity peak of the rutile phase is present ($2\vartheta \approx 27°$) besides those of $Li_4Ti_5O_{12}$.

ii) The patterns of the residual of the physical mixture (trace a) show the presence of unreacted TiO_2 [in form of both anatase ($2\vartheta \approx 25°$) and rutile ($2\vartheta \approx 27°$)]. Clearly, a considerable amount of Li_2TiO_3 appears to be present but this cannot be put into evidence by XRPD since nearly all the peaks characteristic of Li_2TiO_3 are expected at angular positions very close those of $Li_4Ti_5O_{12}$.

The XRPD evidence combined with the DSC results allows to conclude that the enthalpy release corresponding to the endothermic peak of the milled mixtures (-48 ± 3 kJ mol^{-1} of Li_2CO_3) is due to the reaction between nascent Li_2O and TiO_2 and Li_2O and Li_2TiO_3.

Therefore, on the basis of the TG/DSC experiments, it has been decided to attempt the synthesis of phase-pure $Li_4Ti_5O_{12}$ by thermal treatment of the mechanically activated mixtures. Thermal treatments at 923 K of variable duration were performed on samples of milled mixture, and it could be demonstrated that all the peaks present are those characteristic of $Li_4Ti_5O_{12}$ (with no unreacted anatase/rutile) only for very long annealing times (> 300 h) since the thermal treatment at such a temperature also causes phase transition of TiO_2 from anatase to rutile which is less reactive towards Li_2O.

A thermal treatment of 8 h at 973 K was performed on all the mixture samples, and Fig. 3 shows the relevant XRPD patterns. For sake of comparison, also the XRPD pattern of a sample of a physical mixture subjected to the same thermal treatment is presented.

It can be seen that the patterns of the physical mixture (trace a) show the peaks of unreacted anatase and rutile while the patterns of the milled mixtures only show the peaks of $Li_4Ti_5O_{12}$ (traces b, c, d, e). Therefore it can be concluded that a short thermal treatment at 973 K of the milled mixtures yields 100 % phase-pure $Li_4Ti_5O_{12}$.

From the XRPD patterns of the samples of the milled and annealed mixtures the values of the lattice constant of $Li_4Ti_5O_{12}$ have been calculated (Table 2).

The lattice constant values of the samples obtained from mixtures milled for periods ≥ 8 h are in very

Table 2. Lattice constant of $Li_4Ti_5O_{12}$ obtained from mixtures milled for different times and annealed for 8 h at 700 °C.

Milling time (h)	a (Å)	x in $Li_{1+x}Ti_{2-x}O_4$
4	8.37 ± 0.01	–
8	8.357 ± 0.001	0.333
16	8.3584 ± 0.0007	0.325
30	8.358 ± 0.003	0.330

Table 3. C_P data of $Li_4Ti_5O_{12}$ obtained from mixtures milled for different times and subsequently annealed for 8 h at 700 °C. A, B and C represent the coefficients of the second order polynomial fitting the experimental data as a function of temperature ($C_P = A + B\,T + C\,T^2$).

Milling time (h)	A	B	C
4	386 ± 8	0.65 ± 0.02	$-(9.6 \pm 0.5) \cdot 10^{-4}$
8	385.52 ± 4.42	0.6324 ± 0.0217	$-(9.0 \pm 0.6) \cdot 10^{-4}$
16	384.97 ± 3.82	0.6315 ± 0.0256	$-(9.0 \pm 0.6) \cdot 10^{-4}$
30	382.62 ± 9.77	0.6254 ± 0.0146	$-(9.2 \pm 0.7) \cdot 10^{-4}$

close agreement with the value (a = 8.35882 Å) reported in literature [12] and with the value calculated (a = 8.35733 Å) according to the relationship $a = 0.8405 - 0.0143\,x$ where x (= 0.333) indicates the excess lithium in $Li_{1+x}Ti_{2-x}O_4$ [13].

The reversing molar heat capacity of $Li_4Ti_5O_{12}$ obtained from the mixtures milled and thermally treated for 8 h at 973 K has been determined by quasi-isothermal Modulated Differential Scanning Calorimetry (MDSC) in the temperature range from 323 to 623 K. The experimental data are shown in Fig. 4.

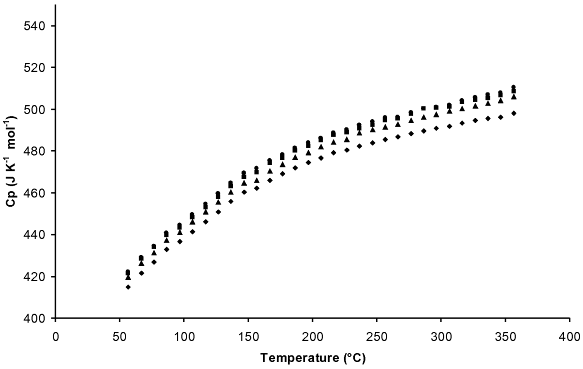

Fig. 4. C_P data obtained on samples of $Li_4Ti_5O_{12}$ prepared from mixtures $2Li_2CO_3$-$5TiO_2$ milled for 4 h (triangles), for 8 h (crosses), for 16 h (lozenges), or for 30 h (squares), and subsequently annealed for 8 h at 700 °C.

They can be fitted by 2nd order polynomials ($C_P = A + B\,T + C\,T^2$), and Table 3 reports the relevant coefficients (A, B, C).

It can be seen that all the coefficients of the polynomials are in good agreement taking into account the relevant standard deviations.

Finally, the specific surface area of $Li_4Ti_5O_{12}$ obtained from the milled mixtures thermally treated for 8 h at 973 K have been determined, and the mean value $A = 5.3 \pm 0.1$ m^2 g^{-1} has been found. It corresponds to a grain size $d \approx 320$ nm according to the relationship $d = 6/(A\,\rho)$ where ρ is the density (3.25 g cm^{-3}).

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