



Kinetic analysis of the thermal decomposition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ pellets

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Abstract

A single dynamic kinetic analysis, describing the surface decomposition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ pellets, has been performed. Samples were analyzed by X-ray diffraction and scanning electron microscopy. The analyses were performed between 1000 and 1100°C and different times, perceiving the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decomposition to $\text{Li}_2\text{Ti}_3\text{O}_7$, with a loss of lithium. As expected, more rapid decomposition behaviour was found at higher temperatures. Finally, the activation energy for this decomposition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to $\text{Li}_2\text{Ti}_3\text{O}_7$ was estimated to be equal to 383 kJ/mol.

Keywords: kinetics; $\text{Li}_4\text{Ti}_5\text{O}_{12}$, thermal properties, X-ray diffraction

I. Introduction

In the last two decades, interest in lithium ceramics has been increased because of their technological applications.

For example, in recent years reports have been made on research about their application as electronic devices, batteries, low thermal expansion glass-ceramics used in ceramic hobs, as CO_2 captors and as breeder materials for nuclear fusion reactors [1–10]. In most of these fields, even though different properties determine the possible application of a specific ceramic, the ceramics must be very stable under mechanical, thermal and chemical conditions, because of the extreme conditions present in some of these applications [11,12]. Consequently, the study of different thermodynamic properties is very important.

Even though lithium titanates have been widely studied for some of the already mentioned applications, [13–19], the thermal stability of these ceramics has not been thoroughly analyzed, only the sintering process of Li_2TiO_3 has been reported [20]. Hence, the aim of this work was to study in more detail the thermal stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The changes in the structure and composition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, due to thermal treatments, were analyzed

in order to obtain kinetic information about its thermal decomposition process.

II. Experimental

Stoichiometric amounts of lithium carbonate (Li_2CO_3 , Aldrich) and titanium oxide (TiO_2 , J.T. Baker), both of reagent-grade purity, were mixed for a few hours with water. The powders were then dried, pulverized and calcined at 800°C for 14 hours to synthesise $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Later, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was cold pressed into 10 mm-diameter pellets under a pressure of 5 tons. These pellets were typically 1 mm thick. Finally, the pellets were heat treated again at different temperatures for varying amount of time. Each sample was placed in the furnace directly after the appropriate heat treatment temperature had been reached. After heat treatment, the samples were removed from the furnace and air-cooled to room temperature.

The samples were characterized by two different techniques; powder X-ray diffraction (XRD), and scanning electron microscopy (SEM). The XRD patterns were obtained with a Bruker AXS Advance D8 diffractometer coupled to a Cu anode X-ray tube. The $\text{K}\alpha_1$ wavelength was selected with a diffracted beam monochromator, and compounds were identified conventionally using the JCPDS database: Li_2TiO_3 (33-0831), $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (49-0207), $\text{Li}_2\text{Ti}_3\text{O}_7$ (40-0303), and TiO_2 rutile

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(96-9084). The percentages of the various compounds were estimated from the total area under the most intense peak for each identified phase, having an estimated experimental error of around $\pm 3\%$. On the other hand, a scanning electron microscope (Stereoscan 440, Cam-

bridge) was used to determine the particle size and morphology of the surface pellets, where all these features were observed in secondary electron image. In order to avoid the lack of conductivity of the samples, they were previously covered with gold.

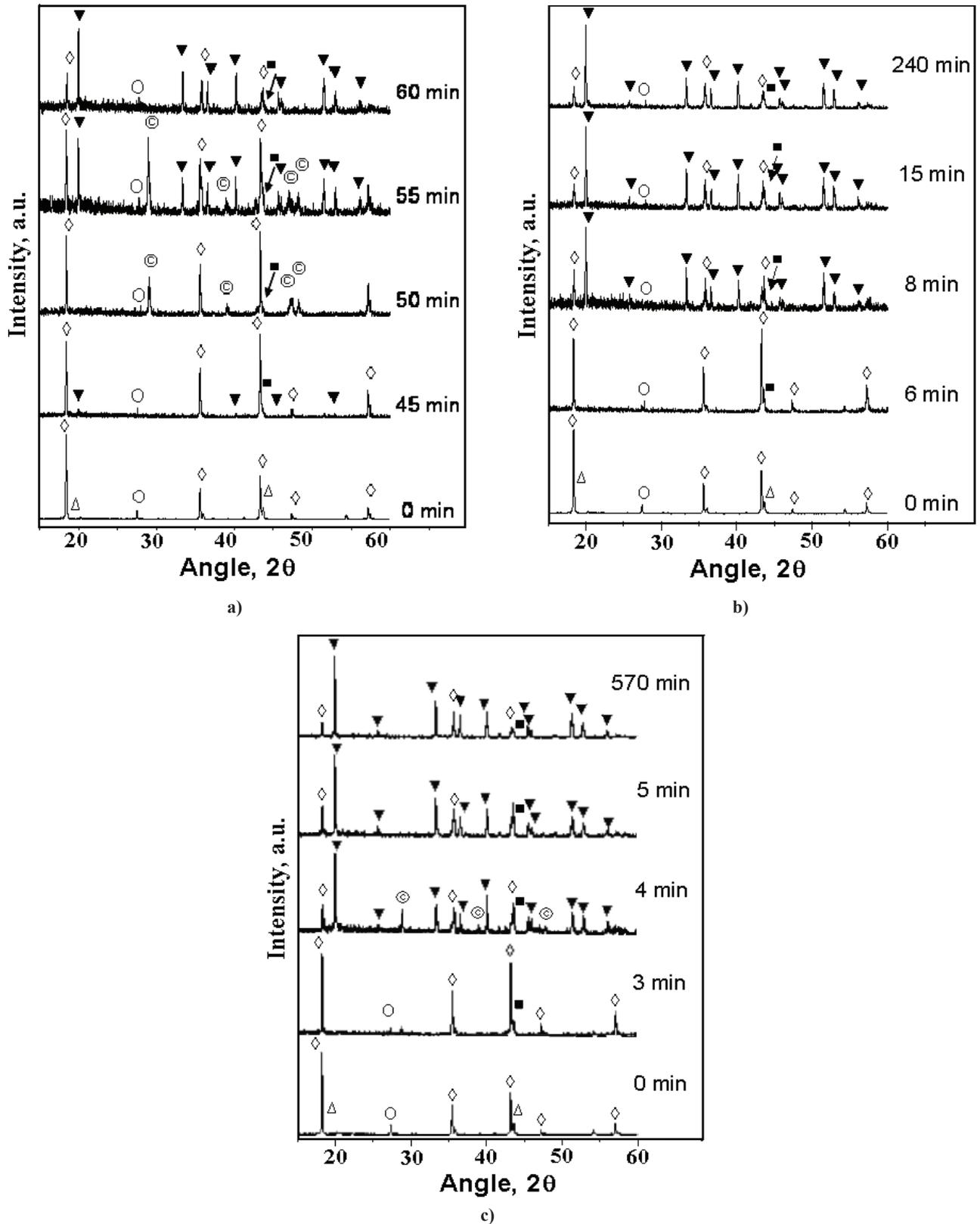


Figure 1. XRD patterns of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ pellets heat treat at: a) 1000°C , b) 1050°C and c) 1100°C for different times (the labels correspond as follows: \diamond $\text{Li}_4\text{Ti}_5\text{O}_{12}$; \circ TiO_2 ; \blacktriangledown $\text{Li}_2\text{Ti}_3\text{O}_7$; \blacksquare $c\text{-Li}_2\text{TiO}_3$ and \triangle $m\text{-Li}_2\text{TiO}_3$, \odot unknown phase)

III. Results and discussion

The final composition of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders used for the production of the pellets was $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (89%), monoclinic lithium metatitanate ($\text{m-Li}_2\text{TiO}_3$, 8%) and TiO_2 (3%), data not shown.

According to the TiO_2 - Li_2O phase diagram [21], the eutectic temperature of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is 930°C . Therefore, the temperatures chosen for the kinetic decomposition analysis were 1000°C , 1050°C and 1100°C . Figure 1b shows the XRD patterns of the pellets heat treated at 1050°C for different times. The only change observed, in the pellets heat treated for up to 6 minutes, is the presence of the lithium metatitanate with a cubic phase ($\text{c-Li}_2\text{TiO}_3$) with the corresponding disappearance of the $\text{m-Li}_2\text{TiO}_3$. However, when the pellet was heat treated for 8 minutes a dramatic change was observed. As could be expected, $\text{Li}_2\text{Ti}_3\text{O}_7$ appeared. Finally, it should be mentioned that the amount of the $\text{c-Li}_2\text{TiO}_3$ was almost constant, $9 \pm 4\%$, during all sintering experiments, which is in disagreement to the TiO_2 - Li_2O phase diagram. Also, TiO_2 did not vary their compositions at any time. This indicates that these compounds did not interfere with the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decomposition process. Therefore, the following reaction explains the process that occurred (reaction 1):



Similar results were obtained when the analyses were performed at other temperatures. At 1000°C , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ transforms into $\text{Li}_2\text{Ti}_3\text{O}_7$ once again, but at this temperature, the conversion occurred after 55 minutes. Finally, the conversion time at 1100°C occurred in only four minutes. Furthermore, at those temperatures, the rest of the composition underwent the same changes, $\text{m-Li}_2\text{TiO}_3$ transformed to $\text{c-Li}_2\text{TiO}_3$ and the TiO_2 concentration remained unchanged.

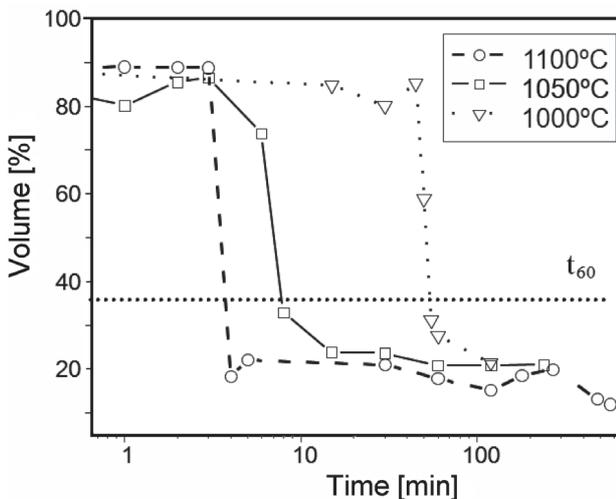


Figure 2. Plots of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ conversion ratio as a function of time, during the isothermal treatment at different temperatures

The estimated percentages of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ found on the surface of the pellets heat treated at different temperatures as a function of time are summarized in Fig. 2. At all temperatures the final quantity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is almost the same, $\approx 20\%$. In other words, the reaction 1 was not completed. This may be associated to diffusion problems. As the decomposition takes place at the surface of the pellets, at the beginning lithium is able to sublime without any problem. However, as soon as a surface shell of $\text{Li}_2\text{Ti}_3\text{O}_7$ is formed, lithium has to diffuse through it in order to reach the surface and sublimate.

Taking equation 1 into consideration, the decomposition kinetics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ could be described as:

$$-\frac{d[\text{Li}_4\text{Ti}_5\text{O}_{12}]}{dt} = k[\text{Li}_4\text{Ti}_5\text{O}_{12}]^n \quad (2)$$

$$\frac{1}{[\text{Li}_4\text{Ti}_5\text{O}_{12}]^n} d[\text{Li}_4\text{Ti}_5\text{O}_{12}] = -k dt \quad (3)$$

$$\frac{1}{(n-1)[\text{Li}_4\text{Ti}_5\text{O}_{12}]^{n-1}} = -kt + C \quad (4)$$

where k is the reaction constant, t is time, n is the reaction order, $[\text{Li}_4\text{Ti}_5\text{O}_{12}]$ is the concentration of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and C is a constant. Evaluating the last equation at 60% of the total $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decomposition, the expression becomes:

$$\frac{1}{(n-1)[\text{Li}_4\text{Ti}_5\text{O}_{12}]_{60}^{n-1}} = -kt_{60} + C \quad (5)$$

where $[\text{Li}_4\text{Ti}_5\text{O}_{12}]_{60}$ is the concentration of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at 60% of its total decomposition and t_{60} is the time required to reach this condition. As previously mentioned, the t_{60} values are 55, 8 and 4 minutes at 1000°C , 1050°C and 1100°C , respectively. As $[\text{Li}_4\text{Ti}_5\text{O}_{12}]_{60}$ is a constant value the equation 5 can be rewritten simply as $A = -k \cdot t_{60}$. Therefore, if this process is linearly correlated to temperature, the Arrhenius kinetic theory (equation 6) must be fulfilled, and the activation energy for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decomposition process could be calculated.

$$k = k_0 \cdot \exp(-Ea/RT) \quad (6)$$

Therefore, equation 6 can be rewritten as:

$$B \exp(-Ea/RT) = t_{60} \quad (7)$$

where B is a constant that depends on the initial concentration of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and k_0 . Figure 3 shows a plot of the $\ln t_{60}$ versus $1/T$, which strongly suggest a straight line, which agrees with the assumption of the Arrhenius kinetic theory. Therefore, from this plot, the activation energy for the decomposition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to $\text{Li}_2\text{Ti}_3\text{O}_7$ can be estimated to be 383 kJ/mol.

There is little data published in the literature about the thermal decomposition of similar pellet ceramics. Nevertheless, this energy value could be consid-

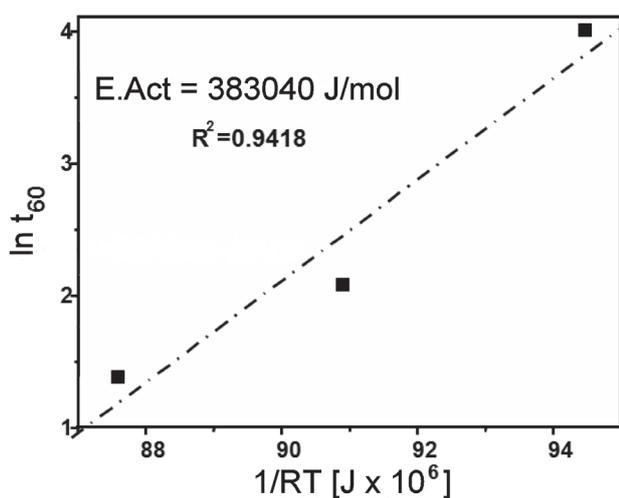


Figure 3. Plot of $\ln t_{60}$ versus $1/T$ for the thermal decomposition process of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

ered as a high energy value in comparison to, for example, Li_2ZrO_3 and LiNiO_2 decomposition energies of 210 and 76 kJ/mol, respectively [2,10]. Nevertheless, most of these works strongly suggest that diffusion of lithium ions to the surface of the pellets is the rate determining step in the decomposition of these ceramics. This theory agrees very well with the present study, as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a highly packed structure, which inhibits lithium diffusion.

Additionally, lithium diffusion over the surface of the pellets is significantly inhibited by the sintering effect observed by SEM (Fig. 4). These images clearly show that the particle size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ increased from 0.6 μm to 3 μm , in average, due to the sintering process. At the same time, this effect reduced macro-porosity of the pellet considerably, which must be directly related to the sublimation of lithium.

IV. Conclusions

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared by solid state reaction using TiO_2 and Li_2CO_3 as reactants. Then, it was pressed

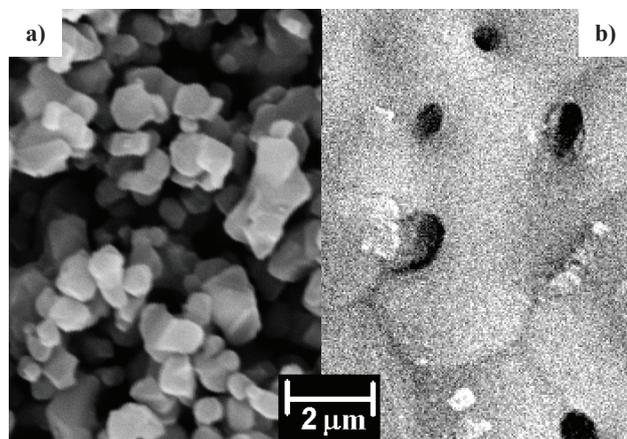


Figure 4. SEM images of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ pellets heat treated at 1000°C (a) and 1100°C (b)

into pellets and thermally treated at different temperatures and times. Temperature was found to be an important factor in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ surface decomposition to $\text{Li}_2\text{Ti}_3\text{O}_7$. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decomposed when it was heat treated for longer times than 55 minutes at 1000°C. The same behaviour was observed for 1050°C and 1100°C, but the conversion time was shorter at these higher temperatures. The activation energy for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decomposition process was estimated to be 383 kJ/mol.

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