



# Isothermal kinetic analysis of the effects of high-energy ball milling on solid-state reaction of $\text{Li}_4\text{Ti}_5\text{O}_{12}$



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## ABSTRACT

The effects of high-energy ball milling on the solid-state reaction were determined by X-ray diffractometry, scanning electron microscopy, and activation energy calculation, respectively. Isothermal kinetic analysis of solid-state reaction of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was studied using an isothermal thermogravimetric tests. The results indicate that the anatase to rutile transformation of  $\text{TiO}_2$  and formation of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  occur at a lower temperature, because the particle size of raw materials reduced by high-energy ball milling. In contrast to Jader equation, the model based on Johnson–Mehl–Avrami equation shows better linear fitting within temperature interval from 450 to 550 °C. The value of the kinetic parameter  $m$  is approximate to 0.4, indicating that the formation of products could be a diffusion controlled mechanism. Meanwhile, the activation energy of solid-state reaction decreases from 119.4 to 95.2 kJ/mol after high-energy ball milling. Electrochemical tests show that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  samples synthesized by high-energy ball milling exhibit better rate capacity and cycle performance.

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## 1. Introduction

Compared with graphite and carbon-based anode materials,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) has attracted considerable attention as a potential alternative anode material, because of its high safety, excellent cycle stability and high power density [1,2]. Therefore,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is expected as anode materials in high power density and long cycle life applications, such as hybrid electric vehicles and sustainable energy storage. Lithium titanate can be synthesized by solid-state [3,4], hydrothermal [5,6], sol–gel [7], combustion [8], and spray-pyrolysis [9] methods. For large-scale application, a conventional solid-state reaction using  $\text{TiO}_2$  and  $\text{Li}_2\text{CO}_3$  as raw materials is used to synthesize  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , because of its scale-up ability, low cost, and non-requirement of sophisticated apparatus [10].

Solid-state reaction is complex process which has several stages, such as decomposition of reactants, diffusion of ions or atoms, nucleation of a new solid phase, growth of nuclei, and equilibrium of structure. The solid-state formation mechanism of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  has been reported by many researchers. Shen et al. [11] and Abe et al. [12]

are in agreement with that  $\text{TiO}_2$  and  $\text{Li}_2\text{CO}_3$  initially react to form monoclinic  $\text{Li}_2\text{TiO}_3$ , followed at higher temperature by a reaction with the remaining  $\text{TiO}_2$  to yield  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . However, the solid-state reaction mechanism at different stages is not clear. It is necessary to elucidate the reaction model in the formation of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , which provides a better understanding of reaction mechanism and an easier way to obtain pure powders.

According to previous works [13,14], the most common kinetic functions in solid-state reaction have been classified into three groups: the diffusion, the chemical reaction, and the nucleation model. These kinetic functions are used to simulate the experimental curves in kinetic methodology. Generally, two major calorimetric methods are applied to study the reaction kinetic, such as isothermal and non-isothermal method. Non-isothermal method has its practical advantages, which does not require time to reach the experiment temperature. Hu et al. [15] have studied the kinetic of one-step solid-state reaction of  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  with a non-isothermal method. The calculated activation energy shows a significant difference at different conversion fractions. However, this model fitting method attempts to determine all three components of the triplet simultaneously, which increases the error in determining reaction model and Arrhenius parameters [16,17]. Benoit et al. [17] have reported that solid state decomposition reactions are not readily accommodated by non-isothermal computational methods. Ghaffari et al. [18] have pointed out that fundamental kinetic studies are by preference performed on isothermal rather than non-isothermal reaction conditions, because the relative reaction rates change frequently at different temperatures. Meanwhile, the isothermal method is fitting

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**Table 1**  
The most common mechanism functions  $f(\alpha)$  and  $g(\alpha)$  in solid-state reaction.

Mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Three-dimensional diffusion (Jander equation)	$D_3$	$3(1-\alpha)^{2/3}/2[(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstling equation)	$D_4$	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2/3\alpha)-(1-\alpha)^{2/3}$
Phase boundary controlled reaction (tridimensional shape)	$R_3$	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$
Random nucleation and growth of nuclei (Johnson–Mehl–Avrami equation)	$A_m$	$m(1-\alpha)[- \ln(1-\alpha)]^{1-1/m}$	$[- \ln(1-\alpha)]^{1/m}$

experimental data to different reaction models. When the reaction model is fixed, the activation energy and the pre-exponential factor are obtained.

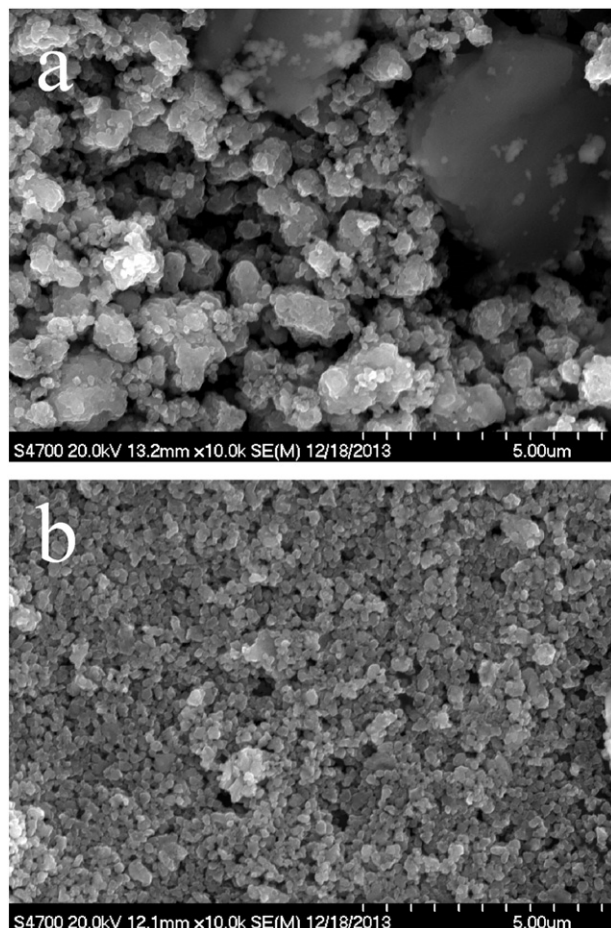
Mechanochemical activation by high-energy ball milling of  $\text{Li}_2\text{CO}_3$  and  $\text{TiO}_2$  is an effective way to decrease the reaction temperature and particle size as well as increase the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  content in obtained powders [19–21]. In our previous work [22], we have also reported the evolutions of Raman spectra and XRD patterns of anatase  $\text{TiO}_2$  after high-energy ball milling. However, the quantitative description of the decrease of reaction activation energy is still lacking in these works. Thus, isothermal thermogravimetric analysis was firstly used to study the solid-state reaction of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and the obtained reaction kinetic. Meanwhile, the effects of high-energy ball milling were also studied.

## 2. Experimental

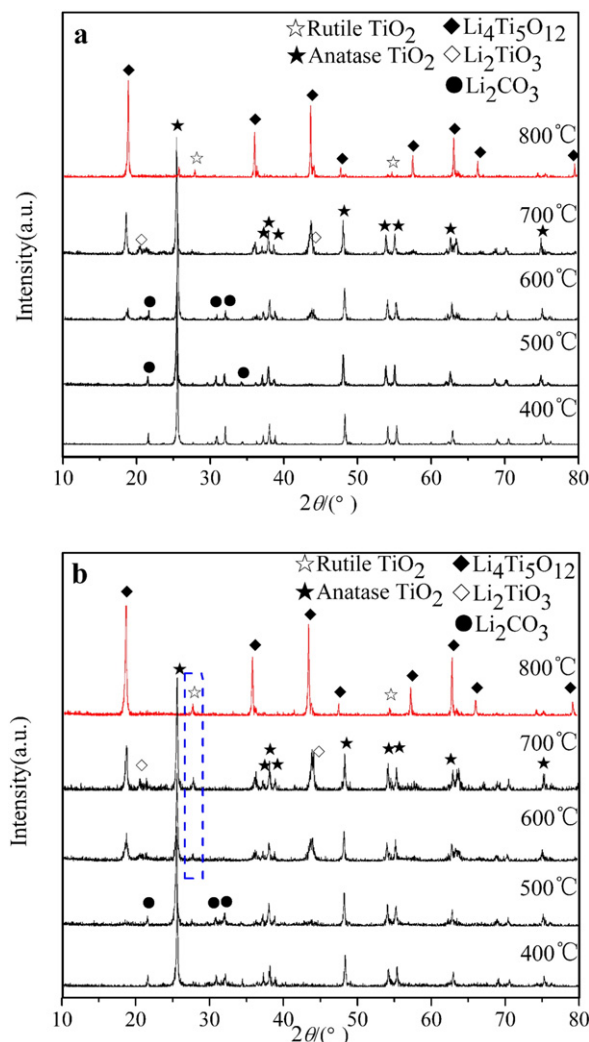
The commercial  $\text{Li}_2\text{CO}_3$  ( $\geq 99.9\%$ , Sichuan Tianqi Lithium Industries Inc., China) and anatase-type  $\text{TiO}_2$  ( $\geq 99.5\%$ , Shanghai Pengbo Titanium Oxide Co. Ltd., China) were used as raw materials.  $\text{Li}_2\text{CO}_3$  and  $\text{TiO}_2$  with a Li/Ti stoichiometric ratio of 0.84 were dispersed in de-ionized water and ground by a high-energy ball milling machine (SNM05,

Shanghai Sunller Machinery and Equipment Co. Ltd., China) for 60 min at a speed of 2500 r/min using 0.4 mm  $\text{ZrO}_2$  beads as grinding media. The sample before and after high-energy ball milling were denoted as pristine and HEBM, respectively. After drying, grinding and sieving, the mixed powders were heated to different temperatures in air at a heating rate of 2 °C/min.

The morphology of samples was observed by scanning electron microscope (S4700, Hitachi). The particle size distribution of samples was measured by laser particle analyzer (Mastersizer 2000, Malvern). The crystal structure was characterized by X-ray diffractometry (D/max-2200PCX, Rigaku) with  $\text{Cu-K}\alpha$  radiation. Thermogravimetric analysis of mixtures from ambient temperature to 800 °C was performed on a thermal analyzer (STA449F3, NETZSCH) at a heating rate of 10 °C/min to obtain the main weight loss temperature. For isothermal experiment, about 25 mg of powders placed in alumina crucible was heated to desired temperature (450, 500, 550 °C) at 10 °C/min under flow of argon with a rate of 40 mL/min on the thermal analyzer. Then the isothermal



**Fig. 1.** SEM images of raw materials before (a) and after (b) high energy ball milling.



**Fig. 2.** X-ray diffraction at different temperatures: (a) pristine and (b) HEBM.

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