Thermogravimetric analysis and kinetic study of formation of lithium titanate by solid state route

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ABSTRACT

The kinetics of formation of lithium titanate from the solid state reaction of lithium carbonate and titanium oxide was studied using non-isothermal thermogravimetric technique. Thermogravimetric data for the reaction of lithium carbonate and titanium oxide was obtained at various heating rates. The methods such as Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose were used to estimate the kinetic parameters from the obtained thermogravimetric data. The average activation energy for the formation of lithium titanate by solid state route was found to be 243 kJ/mol K. The reaction mechanism was determined by the method given by Malek. It was found that the three dimensional diffusion model best describes the reaction kinetics. A kinetic equation describing the reaction is proposed and reaction mechanism is discussed.

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1. Introduction

Lithium based ceramics such as $LiAlO_2$, Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3 in the form of ceramic pebbles are candidate tritium breeding materials in upcoming International Thermonuclear Experimental Reactor (ITER) [1–3]. Among various tritium breeding materials, lithium titanate in the form of ceramic pebbles is a promising candidate material because of its high thermal conductivity, low moisture absorption, high irradiation resistance and better tritium release properties [4,5]. The tritium will be generated in the test blanket module during the reactor operation by (n, α) reaction with lithium [6].

Various routes to prepare lithium titanate have been reported. Lithium titanate powders have been synthesized by sol–gel, combustion synthesis and hydrothermal route [7–11]. Among all these methods, the conventional route to prepare lithium titanate by solid state reaction of lithium carbonate with titanium oxide is widely reported [12,13]. In this route, the reaction between Li_2CO_3 and TiO_2 is carried out at 1173–1273 K for the duration of 10 h to several days [13]. This method offers control over the final stoichiometry of the product making it useful for synthesizing excess lithium containing non-stoichiometric Li_2TiO_3 [14].

Although many reports are available on preparation of lithium titanate by various routes, they lack the information on the kinetics of reaction. No kinetic model is reported for the synthesis of lithium titanate. The knowledge of reaction kinetics will help in understanding and optimizing the process. The objective of this paper is to study the kinetics of formation of lithium titanate by solid state reaction between lithium carbonate and titanium oxide. The thermogravimetric data for the reaction of lithium carbonate and titanium oxide is obtained at various heating rates. This data is used to investigate kinetics by non-isothermal thermogravimetric technique. The models such as Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose are used to estimate the kinetic parameters for the reaction. The method given by Malek is used to determine the most probable reaction mechanism. Obtained data is evaluated and a kinetic equation describing the reaction is proposed.

2. Experimental

Lithium carbonate (Sojuzchimexpor, 1297) and titanium oxide (Merck Specialties Pvt. Ltd., India) were the raw materials used for the synthesis of lithium titanate. A homogenous mixture of lithium carbonate and titanium oxide was prepared by wet milling in alcohol medium. The wet milled powder mixture was then dried in vacuum oven. The samples for thermogravimetric analysis (TGA) were prepared from this mixture. The thermogravimetric analysis was carried out on these samples in air atmosphere in the temperature range from ambient temperature to 1273 K at four different heating rates: 2, 5, 10, 15 K/min. SETARAM labsys model was used for carrying out the above experiments. The obtained thermogravimetric data was used to evaluate kinetic parameters as per the recommendations given by the ICTAC kinetics committee. The Phase

analysis of the mixture before and after thermogravimetric analysis was carried out using XRD (GBC EMMA).

3. Kinetic analysis

The rate of a chemical reaction is commonly expressed by equation

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{1}$$

where $\frac{d\alpha}{dt}$ is the reaction rate and α is the degree of conversion expressed as

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \tag{2}$$

where m_i, m_t and m_f are the initial mass, mass at any arbitrary time t and final mass of the sample. $f(\alpha)$ is the function dependent on reaction mechanism. The algebraic expressions for various reaction mechanisms are given in Table 1 [15]. k in Eq. (1) is the rate constant given by the Arrhenius equation.

$$k = A \cdot \exp\left(\frac{-E}{RT}\right) \tag{3}$$

where A is the pre exponential factor in min^{-1}, E is the activation energy (kJ/mol K), R is the universal gas constant (J/mol K) and T is the temperature in kelvin.

The heating rate is expressed as

$$\beta = \frac{dT}{dt} \tag{4}$$

Eq. (1) can be rewritten as

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \cdot \frac{dT}{dt} = k \cdot f(\alpha) \tag{5}$$

Using Eqs. 3–5, following two equations can be derived.

$$\frac{d\alpha}{dT} \cdot \beta = A \cdot \exp\left(\frac{-E}{RT}\right) \cdot f(\alpha) \tag{6}$$

Table 1
Algebraic expressions for various reaction mechanisms.

Reaction mechanism	$f(\alpha)$	$g(\alpha)$
Avarami–Erofe'ev Eq. (1) (A2)	$2 \cdot (1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avarami–Erofe'ev Eq. (2) (A3)	$3 \cdot (1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avarami–Erofe'ev Eq. (3) (A4)	$4 \cdot (1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Contracting area (R2)	$2 \cdot (1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
Contracting volume (R3)	$3 \cdot (1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
1D diffusion (D1)	$1/2 \cdot \alpha$	α^2
2D diffusion (D2)	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha) + \alpha$
3D diffusion-Jander Eq. (D3)	$3/2 \cdot (1-\alpha)^{\frac{2}{3}}/[1-(1-\alpha)^{2/3}]$	$[1-(1-\alpha)^{1/3}]^2$
Ginstling–Brounshtein (D4)	$3/2 \cdot [(1-\alpha)^{-1/3} - 1]$	$(1-2\alpha/3) - (1-\alpha)^{2/3}$
Chemical reaction first order (F1)	$(1-\alpha)$	$-\ln(1-\alpha)$
Chemical reaction first order (F2)	$(1-\alpha)^2$	$(1-\alpha)^{-1} - 1$
Chemical reaction first order (F3)	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2} - 1]$
Chemical reaction first order (F3/2)	$(1-\alpha)^{3/2}$	$2[(1-\alpha)^{-1/2} - 1]$
Power law (P1)	$4 \cdot \alpha^{3/4}$	$\alpha^{1/4}$
Power law (P2)	$3 \cdot \alpha^{2/3}$	$\alpha^{1/3}$
Power law (P3)	$2 \cdot \alpha^{1/2}$	$\alpha^{1/2}$
Power law (P4)	$2/3 \cdot \alpha^{-1/2}$	$\alpha^{3/2}$

and

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \cdot \exp\left(\frac{-E}{RT}\right) \cdot dT \tag{7}$$

Eq. (7) can be expressed in the form of its integral, $g(\alpha)$ as

$$g(\alpha) = \int_0^\alpha \frac{d(\alpha)}{f(\alpha)} = \int_0^T \frac{A}{\beta} \cdot \exp\left(\frac{-E}{RT}\right) \cdot dT \tag{8}$$

However $g(\alpha)$ does not have any analytical solution. A new variable $x = E/RT$ is introduced and substituted into Eq. (8).

$$g(\alpha) = \frac{AE}{\beta R} \int_x^{-\infty} \frac{\exp(-x)}{x^2} \cdot dx \tag{9}$$

Eq. (9) can be re-written as

$$g(\alpha) = \frac{AE}{\beta R} p(x) \tag{10}$$

where

$$p(x) = \int_x^{-\infty} \frac{\exp(-x)}{x^2} \cdot dx \tag{11}$$

Doyle [16] gives approximation for the term $p(x)$ as

$$\ln p(x) = -5.331 - 1.052x \tag{12}$$

Substituting value of $\ln p(x)$ in Eq. (12), the following equation can be derived

$$\ln(\beta) = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E}{RT} \tag{13}$$

Using Eq. (13), the activation energy can be determined from the slope of $\ln(\beta)$ versus $(1000/T)$ for a given value of α. This method to determine activation energy by Eq. (13) is known as Flynn–Wall–Ozawa method (FWO) [17,18]. FWO is an isoconversional method which allows determination of activation energy without any knowledge of reaction mechanism. The activation energy is determined from the slope of $\ln(\beta)$ versus $(1000/T)$ for different values of α.

Using Eq. (10) and Coats–Redfern approximation, the Kissinger–Akahira–Sunose method arrives at the following equation [19–21]:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT} + \ln\left(\frac{df(\alpha)}{d\alpha}\right) \tag{14}$$

The activation energy is determined from the slope of the plot of $\ln(\beta/T^2)$ versus $1000/T$ for a constant degree of conversion (α). Both FWO and KAS methods are model free methods and hence do not require knowledge of reaction mechanism to evaluate activation energy.

Once the activation energy is determined, the method given by Malek can be used to determine a suitable model for the reaction [22]. In the method given by Malek, two new functions $y(\alpha)$ and $z(\alpha)$ are introduced which are expressed as follows:

$$y(\alpha) = \frac{d\alpha}{dt} \cdot \exp\left(\frac{E}{RT}\right) \tag{15}$$

$$z(\alpha) = \frac{d\alpha}{dt} \cdot \exp\left(\frac{E}{RT}\right).\pi(x) \tag{16}$$

where $\pi(x)$ is an approximation of the temperature integral which can be expressed as follows [23]:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 240x + 120} \tag{17}$$

where $x = E/RT$. The $y(\alpha)$ function is proportional to $f(\alpha)$ function and hence the shape of $y(\alpha)$ model can be used to identify the right kinetic model. The $y(\alpha)$ and $z(\alpha)$ functions are plotted against α