



## Thermogravimetric study of the kinetics of lithium titanate reduction by hydrogen

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### HIGHLIGHTS

- $\text{Li}_2\text{TiO}_3$  powder is synthesized by the gel combustion route.
- Activation energy of reduction of  $\text{Li}_2\text{TiO}_3$  by  $\text{H}_2$  found out to be 27.45 kJ/mol  $\text{H}_2$ .
- Non-stoichiometric phase of  $\text{Li}_2\text{TiO}_3$  is formed in hydrogen atmosphere.
- One-dimensional diffusion appears to be the most probable mechanism of reduction.

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### ABSTRACT

The lithium titanate powder was synthesized by gel-combustion route. The mechanism and the kinetics of hydrogen interaction with lithium titanate powder were studied using non-isothermal thermogravimetric technique. Lithium titanate underwent reduction in hydrogen atmosphere which led to the formation of oxygen deficient non-stoichiometric compound in lithium titanate. One-dimensional diffusion appeared to be the most probable reaction mechanism. The activation energy for reduction of lithium titanate under hydrogen atmosphere was found to be 27.4 kJ/mol/K. Structural changes after hydrogen reduction in lithium titanate were observed in X-ray diffraction analysis.

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### 1. Introduction

Lithium based ceramics such as  $\text{LiAlO}_2$ ,  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_2\text{ZrO}_3$ ,  $\text{Li}_2\text{TiO}_3$  in the form of ceramic pebbles are the candidate tritium breeding materials in upcoming International Thermonuclear Experimental Reactor (ITER) [1–4]. Among various tritium breeding materials, lithium titanate in the form of ceramic pebbles is the most promising candidate material because of its high thermal conductivity, low moisture absorption, resistance to high neutron flux and better tritium release properties [5]. The tritium will be generated in the test blanket module during the reactor operation by ( $n, \alpha$ ) reaction with lithium [6]. The tritium thus released is likely to interact with the lithium titanate and cause structural, compositional and functional changes [7]. Therefore tritium interaction with lithium titanate is an important aspect to be investigated.

Tritium being the isotope of hydrogen behaves more or less similar to that of hydrogen and hence the studies on the mechanism of hydrogen interaction with solid  $\text{Li}_2\text{TiO}_3$  are equally valid for tritium as well. It has been reported earlier that in case of  $\text{Li}_2\text{TiO}_3$  pebbles exposed to hydrogen atmosphere, multiple micro cracks were generated on the surface. The reduction in the theoretical density was also observed [7–9]. The structural changes have been explained on the basis of reduction  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  which led to the formation of oxygen deficient phase:  $\text{Li}_2\text{TiO}_{3-x}$  [10]. However, the knowledge on the mechanism and kinetics of hydrogen reduction of  $\text{Li}_2\text{TiO}_3$  is very limited. Evaluation of kinetic parameters and identification of reaction mechanism will help to understand long term effects of hydrogen on lithium titanate pebbles.

In the present study, the mechanism and kinetics of hydrogen interaction with  $\text{Li}_2\text{TiO}_3$  powder has been investigated. The lithium titanate powder used in the present investigation was synthesized by gel-combustion technique. The kinetics of the reaction of synthesized lithium titanate with hydrogen is studied by non-isothermal thermo-gravimetric technique at different heating

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rates. Various models are applied to evaluate kinetic parameters and to determine the possible reaction mechanisms. Structural changes taking place in lithium titanate upon hydrogen reduction were observed in X-ray diffraction analysis.

## 2. Experimental

### 2.1. Powder synthesis and characterization

Lithium titanate powder was synthesized by combustion technique. Lithium carbonate (Sojuzchimexpor, 1297) and tetrabutyl orthotitanate (Fluka analytical, 86910) were used as the starting materials for the synthesis of lithium titanate. Lithium carbonate was dissolved in required molarity of nitric acid to form lithium nitrate. Tetrabutyl orthotitanate (TBOT) was slowly added to the ethanol and the mixture was vigorously stirred for 15 min by glass rod. De-ionized water was then slowly added to the solution till the white precipitates of titanium hydroxide were formed. Precipitated titanium hydroxide was filtered and dissolved in required amount of nitric acid to form titanyl nitrate. Stoichiometric amount of lithium nitrate and titanyl nitrate were mixed with citric acid in a beaker. The solution was then heated on a hot plate till a thick white gel was formed. On continued heating, spontaneous combustion reaction took place and a white powder of lithium titanate was formed. The powder thus obtained was calcined at 700 °C in air to remove carbonaceous residues.

### 2.2. Powder characterization

X-ray diffraction pattern of synthesized powder was obtained using X-ray diffractometer (GBC EMMA) in standard theta–theta geometry with a scan rate of 0.5 min<sup>-1</sup>. Standard Cu K $\alpha$  radiation source, curved graphite monochromator and sealed proportional counter were used in the machine for the study. The diffraction profile was obtained at a nominal power of 1 kW with the tube voltage and tube current being 35.0 kV and 28.4 mA respectively. Mean powder particle size ( $d_{50}$ ) was determined by light scattering technique using Malvern Mastersizer (2000 S). The powder morphology was observed by scanning electron microscope (SEC SNE-3000).

### 2.3. Thermogravimetry

Hydrogen interaction study of the Li<sub>2</sub>TiO<sub>3</sub> powder has been carried out using a CI-Make thermogravimetric unit in the temperature range of 473–1000 K in flowing hydrogen gas at the common flow rate of 200 ml/min. The hydrogen pressure inside the reaction chamber has been maintained at one atmosphere. The furnace was operated in the manual mode up to 473 K and thereafter subjected to various heating rates (2, 5, 10 and 15 C/min). The obtained data was used to study the reaction kinetics and the mechanism of hydrogen interaction of lithium titanate.

## 3. Kinetic analysis

### 3.1. Theory

The rate of a chemical reaction is commonly expressed by equation:

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

where  $d\alpha/dt$  is the reaction rate and  $\alpha$  is the degree of conversion expressed as

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (2)$$

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.  $k$  in Eq. (1) is the rate constant given by the Arrhenius equation.

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

where  $A$  is the pre exponential factor in min<sup>-1</sup>,  $E$  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

$$\beta = \frac{dT}{dt} \quad (4)$$

Eq. (1) can be rewritten as

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

Using Eq. (3) and Eq. (5)

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

and

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

### 3.2. Determination of activation energy

Flynn–Wall–Ozawa (FWO) [11,12] is an isoconversional method which allows determination of activation energy without any knowledge of reaction mechanism.

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

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

FWO formula is derived from Eq. (9) using Doyle's approximation [13]

$$\ln(\beta) = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.052 \frac{E}{RT} \quad (9)$$

Using Eq. (10), the activation energy can be determined from the slope of  $\ln(\beta)$  versus  $(1000/T)$  for a given value of  $\alpha$ .

### 3.3. Determination of reaction mechanism

The Coats–Redfern equation [14] is widely applied to determine the kinetic parameters using with non-isothermal thermogravimetric data. The kinetic parameters are evaluated from following equation

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (10)$$

The  $g(\alpha)$  is the algebraic expression for various reaction models listed in Table 1. Accordingly  $\ln(g(\alpha)/T^2)$  is calculated and plotted against  $1/T$  for all possible reaction mechanisms listed in Table 1. The best fitting line with correlation coefficient ( $R^2$ ) more than 0.98 gives the valid mechanism of reaction.

## 4. Results and discussion

### 4.1. Powder synthesis and characterization

The XRD pattern of the synthesized Li<sub>2</sub>TiO<sub>3</sub> powder is shown in Fig. 1. Before XRD analysis, the powder was calcined in air at 700 °C to remove residual carbonaceous products generated during synthesis. The X-ray diffraction pattern of as synthesized powder

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