

# Activation Energy Calculation for $\text{Li}_2\text{TiO}_3$ Ceramics by Java Programming and Validation by Impedance Analyzer

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**Abstract:** In present work, problem of calculating activation energy of blanket material of the fusion energy reactor is successfully addressed. This kind of work needs a reactor which is not easily available for real experimental shot. A java computer programming was used to solve the problem. Activation energy calculation for fusion energy blanket material was done by a java programming and experimental validation was carried out by impedance analyser. Lithium titanate ( $\text{Li}_2\text{TiO}_3$ ) ceramics pebbles were prepared by a novel method of sol. gel followed by urea-acetone spherodization technique. Lithium titanate having monoclinic phase was obtained. DTA/TG analysis of green sample was carried out to know the thermal reactions. Calcination temperature was determined as  $600^0$  C. Activation energy was calculated as  $2.59 \times 10^{-18}$  ev/mole. Validation of this calculation was done by measuring impedance and by applying Arrhenius equation.

**Key Words:** Lithium titanate, sol. gel followed by urea-acetone technique, Java Programming, activation energy

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## I. INTRODUCTION

In present work, problem of calculating activation energy of blanket material of the fusion energy reactor is successfully addressed. This work needs a reactor which is not easily available for real experimental shot. A java computer programming was used to solve the problem. Lithium titanate ( $\text{Li}_2\text{TiO}_3$ ) ceramics have been reported as one of the promising tritium breeder material for fusion research reactor [1-3]. This material exhibits better tritium recovery, crush strength, thermal and physical properties in comparison of other breeder materials [1-8]. Reprocessing of  $\text{Li}_2\text{TiO}_3$  is also cost effective as it can be dissolved in low  $\text{HNO}_3$  concentration [6]. Low activation energy of the material for optimum tritium breeding is one of the essential requirements for suitability as breeder material.

It has been reported that low activation energy is helpful and essential for production and recovery of tritium [7]. Low activation energy for tritium release in blanket materials solves the problem of input high energy requirement in the reactor [6]. In present work activation energy of  $\text{Li}_2\text{TiO}_3$  was calculated by java programming. Data for programming were collected from published papers [7-11]. Activation energy was found as  $2.59 \times 10^{-18}$  ev/mole. Validation of this calculation was done by measuring impedance, conductivity etc and by applying Arrhenius equation.

## II. MATERIAL AND METHODS

### 2.1 Fabrication of lithium titanate pebbles

Titanium (IV) butoxide and lithium nitrate were taken as base material. Titanium (IV) butoxide was first dissolved in an appropriate amount of ethanol to make the solution

conc. Citric acid was diluted and made a citrate solution. Ammonia solution was added to the citrate solution to adjust the pH of the solution around 9.0. The lithium nitrate solution was mixed drop wise to the titanium sol by concurrently monitoring the pH of the solution. The detail process of fabrication is discussed in another paper of the corresponding author [17]. Flow diagram for preparation of lithium titanate pebbles is shown in Fig.1 Photographs of lithium titanate pebbles are displayed in Fig.2 & Fig.3 .

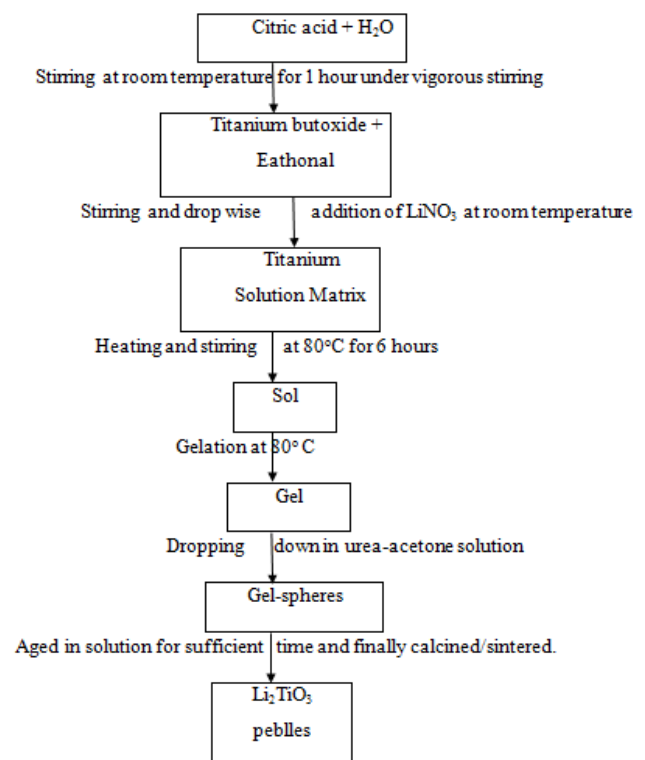


Fig.1 : Flow diagram chart for making  $\text{Li}_2\text{TiO}_3$  pebbles



Fig.2 – Photograph of lithium metatitanate pebbles prepared by sol gel route followed by spherodization

### Urea-acetone spherodization



Fig.3 Calcined Lithium titanate pebbles of dia 3 mm (approx)

DTA/TG analysis of green powder of lithium titanate was done to understand the complication of solid state reaction with variation of temperature. XRD analysis of calcined powder of lithium titanate was carried out to conform the proper phase. Calculation of activation energy by java programming and activation energy calculation of lithium titanate by using Arrhenus equation was also done. Detailed discussion is given in respective section of results and discussion.

## III. RESULT AND DISCUSSION

### 3.1 DTA/TG analysis

DTA/TG micrograph of green lithium titanate powder is displayed in Fig.4. Exothermic reactions were observed at 38.2<sup>o</sup> C, 106<sup>o</sup> C, 252<sup>o</sup> C and 535<sup>o</sup> C. While endothermic reactions were observed at temperature 63<sup>o</sup> C, 145<sup>o</sup> C, 265<sup>o</sup> C and 595<sup>o</sup> C. Peaks of endothermic reactions were due to

presence of volatile materials such as urea-acetone as well as water and acids used during fabrication of materials. Reaction was completed at 620<sup>o</sup> C as there was no weight loss after that temperature as per TG graph.

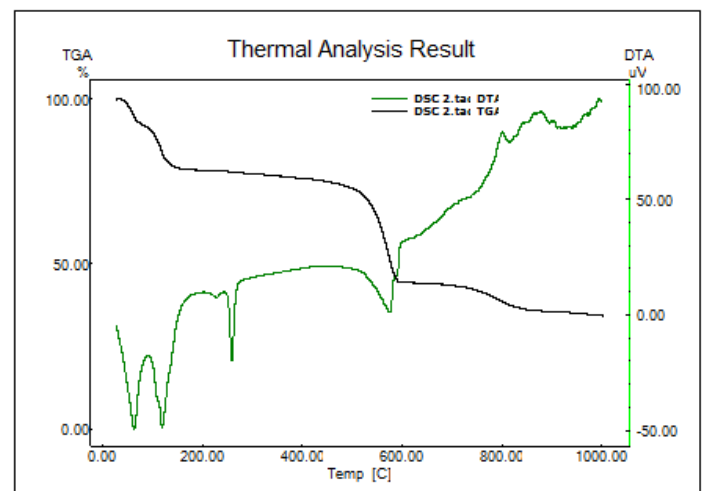


Fig. 4 DTA/TG micrograph of lithium titanate green powder

### 3.2 XRD Analysis

XRD micrograph of Li<sub>2</sub>TiO<sub>3</sub> is displayed in Fig.5 and data is given in Table-1. The XRD micrograph confirms the preparation of pure phase lithium titanate (Li<sub>2</sub>TiO<sub>3</sub>). The intensity peaks were found at various 2θ angles which match with the JCPDS data file and confirms the phase of monoclinic lithium titanate. Scherer formula was used to obtain the average crystallite size of the sample powder which was found to be around 35 nm. The observed peaks were matched with JCPDS file (PDF 33-0831) which confirmed the C2/c space group monoclinic structure.

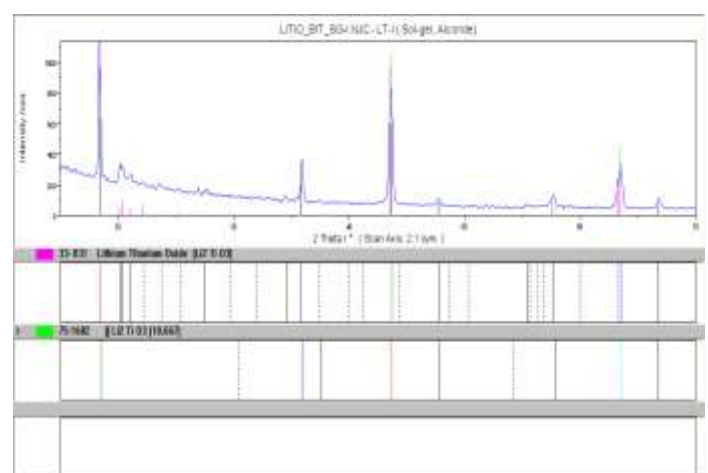


Fig. 5 - XRD Micrograph of calcined lithium metatitanate

### 3.3 Activation energy by computer programming

Computer programming to calculate activation energy was done by using Java. Data taken for two time interval i.e for 1 sec and 5 sec. Programming result is displayed in Fig. 6. Following data were taken ( all in SI unit) [7-11] – at T-1 sec. Grain radius- 0.00005, 0.0000322 at T-5 sec Grain radius- 0.00005, tritium volume generating rate- 0.0026, diffusivity- 0.0000502, effective desorption rate - 0.0000298. Activaton energy was calculated as  $2.59 \times 10^{-18}$  eV/mole.

```
The rate constant k : 0.004705710915816168
The value of gas constant R is 0.008314
Enter the value of temperature T :
298
Enter the value of Arrhenius constant A :
0.00000681
The value of activation energy E in j/mol : 16.198712641631932
The value of activation energy E in eV/mol : 2.59531977759192E-18
```

Fig.6 Activation energy by computer programming

### 3.4 Activation energy calculation by Impedance analyser

Impedance analysis of samples were done for calculation of activation energy . Fig. 7 represent the graph between  $\sigma$  and  $1/T$ . Electrical parameters measured by impedance analyzer is kept in Table-1. Measurement of L,C,R,Z and phase angle( $\theta$ ) values of sample were taken separately at different frequencies and at varying temperatures. After calculating  $Z\cos \theta(Z'')$  and  $-Z\sin \theta(Z'')$ ,a graph was plotted between  $Z''$  and  $Z'$  at a particular temperature. Curve was extended backward and imagined to touch the x-axis to give the leftmost x-intercept, which is the resistance of sample. Then the thickness and cross sectional area of samples were measured. From there resistivity and then conductivity of the sample were calculated at different temperatures. Natural logarithm of conductivities ( $\ln \sigma$ ) were obtained. As per Arrhenius equation,a graph was plotted between  $\ln \sigma$  and  $1/T$ . It's slope of graph equal to  $-Ea/K$ , where k is Boltzman constant. Finally acivation energy was calculated and was found as [13]-.

- Slope of the graph =  $-Ea/K$
- Calculated value of slope from the graph = - 12.053

Value of activation energy =  $2.35 \times 10^{-18}$  eV/mole

```
<terminated> ActiEn [Java Application] C:\Users\HIMANSHU\Document
Concentration for time t1 :-
Enter the grain radius :
0.00005
Enter the value of radial distance :
0.00005
Enter the value of tritium volume generating rate :
0.0038
Enter the value of diffusivity :
0.0000516
Enter the value of effective desorption rate :
0.0000322
Enter the time t1 :
1
The initial concentration is : 0.02027689770776391

Concentration for time t2 :-
Enter the grain radius :
0.00005
Enter the value of radial distance :
0.00005
Enter the value of tritium volume generating rate :
0.0026
Enter the value of diffusivity :
0.0000502
Enter the value of effective desorption rate :
0.0000298
Enter the time t2 :
5
The final concentration is : 0.0014540540444992357
The rate constant k : 0.004705710915816168
```

R(ohm)	$\rho$ ((mohm)(meter))	$\sigma=1/\rho$ (siemens/meter)	$\ln \sigma$	(1/temp) K <sup>-1</sup>
17.5691	864.625	1146.6	7.0445	3.1948
17.5544	865.538	1147.6	7.0454	3.0959
17.5399	866.3975	1148.5	7.0462	3.003
17.5208	867.2711	1149.8	7.0473	2.9154
17.5006	867.7824	1151.1	7.0484	2.8328
17.4824	868.6858	1152.3	7.0495	2.7548
17.4721	869.6885	1153	7.0501	2.6809
17.4545	870.6365	1154.2	7.0511	2.6109
17.4372	871.3563	1155.3	7.0521	2.5445
17.4188	872.086	1156.5	7.0531	2.4813

Table 1. Data for activation energy calculation for lithium titanate ceramics

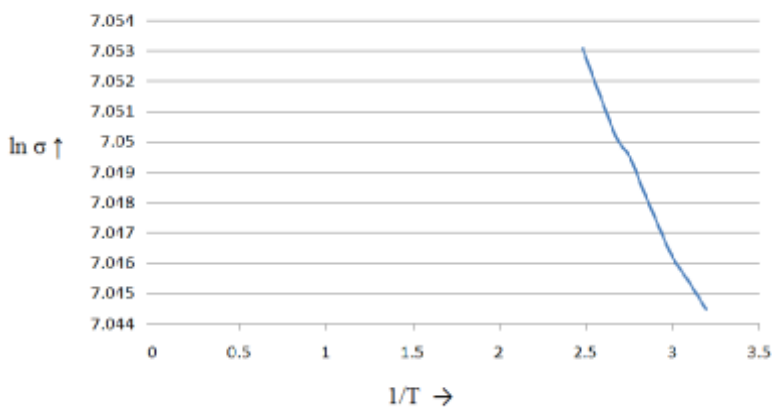


Fig.7 Graph between  $\ln \sigma$  ( siemens/meter) Vs  $1/T(K^{-1})$  for lithium titanate ceramics

### 3.4 SEM microscopy of Li<sub>2</sub>TiO<sub>3</sub> pebbles

SEM micrograph is shown in Fig. 8. Clear grains were

observed in micrograph. Average grain size was 3 to 5 micron [14-17].

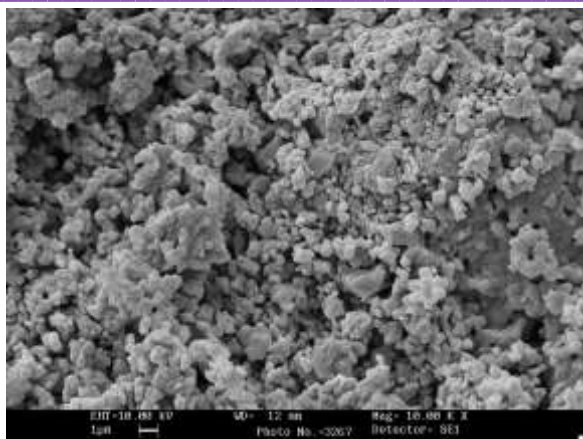


Fig. 8 SEM Image of Lithium Titanate Pebble

#### IV. CONCLUSIONS

Activation energy calculation for fusion energy blanket material was done by a java programming and experimental validation was carried out by impedance analyser. Lithium metatitanate pebbles having diameter 3 mm were successfully prepared by sol- gel followed by urea-acetone spheroidization. XRD test had confirmed the monoclinic structure of lithium metatitanate. Peaks of endothermic reactions were due to presence of volatile materials such as urea-acetone as well as water and acids used during fabrication of materials. Reaction was completed at 620<sup>o</sup> C as there was no weight loss after that temperature as per TG graph. Activation energy calculation was done by a computer programme and validation was successfully done by measuring electrical parameters and by applying Arrhenius equation. Activation energy was calculated as  $2.59 \times 10^{-18}$  ev/mole. Average grain size was found 3 to 5 micron.

#### V. ACKNOWLEDGEMENTS

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