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Research Article

Kinetic of $LiFePO_4$ Formation Using Non-isothermal Thermogravimetric Analysis

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Abstract

The formation reaction of $LiFePO_4$ from decomposition of precursors LiOH, $FeSO_4.7H_2O$ and $(NH_4)_2HPO_4$ with mole ratio of Li:Fe:P=1:1:1 was investigated. The experiment was carried out by thermogravimetric differential thermal analysis (TG-DTA) method using nitrogen as atmosphere at a constant heating rate to obtain kinetic constant parameters. Several heating rates were selected, viz. 5, 7, 10, 15, 17.5, 22.5 and 25 °C min^{-1}. Activation energy, pre-exponential factor and reaction order were taken using Kissinger method and obtained 56.086 kJ/mol, 6.95×108 min^{-1}, and 1.058, respectively. Based on fitting result between reaction model and experiment were obtained that reaction obeyed the three dimension diffusion model.

Keywords: $LiFePO_4$; Thermogravimetric Differential Thermal Analysis; Kinetics Reaction

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1. Introduction

Energy has a very significant role in modern life today. Increasing energy demand, will also increase the need for efficient energy storage devices. One of the energy storage devices widely used in daily life is the battery. Currently, lithium ion batteries are widely used as an energy source for portable electronic devices and more promising than other batteries because it has a high potential, high energy density and good cycling stability. Chew *et al*. [1] compared with other materials for lithium batteries cathode, $LiFePO_4$ was a promising material because it was not toxic, the availability and had a great energy density.

There were several methods to produce $LiFePO_4$ particles as a battery cathode like flame spray pyrolysis [2], hydrothermal [3], carbothermal [4] and solid state reaction [5]. The kinetic formation was important to be studied because it was closely related to reaction mechanism.

Chang [6] analyzed the kinetic formation of $LiFePO_4$ in solid state phase from $Li(CH_3COO)$ and $FePO_4$ as precursor. Non-isothermal approach was carried out using hot gases as heating medium in XRD device. The crystallinity of precursor was used to analyze the conversion rate. Reaction mechanism was not known in detail. Furthermore, previous researches were more dominant to investigate the operating conditions effect to battery performance. Therefore, the formation kinetic of $LiFePO_4$ was not well

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known in detail.

TG-DTA was simple method to determine kinetic parameters like activation energy and pre-exponential factor. There are two methods to determine kinetic parameters using TG-DTA that is isothermal and non-isothermal method. Although isothermal methods are more efficient but non-isothermal methods are more applicable to be used for all kinetic determination [7]. Significant error in isothermal methods was often occurred when the reaction having proceeded before the temperature achieved or stabilized at the selected temperature. In non-isothermal methods, this error may be hindered [6]. Several methods to derive the formation kinetic using non-isothermal methods have been reported by numerous authors. Zivkovic and Dobovisec [8] proposed the method using single constant heating rate based on a relation for the first order reaction rate and Arrhenius's equation. The energy activation and pre-exponential factor were determined by graphical method. Altorfer [9] proposed new method to determine kinetic parameters by solved the reaction rate equation numerically. Experimental were carried out to evaluate this method using $CaCO_3$ decomposition. Blecic *et al*. [6] solved numerically more detailed with considering concentration effect, . Many models have used to evaluate kinetic parameters of calcite and magnesite decomposition experimentally [10]. Kissinger [11] used the several constant heating rates to determine kinetic parameters like activation energy and pre-exponential factor. Then, the reaction order was obtained by solving the non-linear equation.

Several researches have applied the non-isothermal methods to derive kinetic parameters. Murugan *et al*. [12] used themogravimetric analysis to determine combustion and pyrolysis reaction of Forterton oil. Non-isothermal and isothermal experiments have been carried out using nitrogen and air atmosphere to determine the pyrolysis and combustion reaction, respectively. The result revealed that the reaction order for non-isothermal and isothermal investigations were from 0.8-1. This indicated that the order reaction approach unity. Arrhenius model showed suitable fit between experimental and prediction data.

Beside the kinetic parameters as activation energy and pre-exponential factor, the reactant conversions have significant influence in reaction rate equation. Many conversion effect models have been recognized by authors. These models were listed in Table 1.

Yuan *et al*. [13] used the Kissinger method to obtain glass crystallization kinetic of $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$. The activation energy was affected significantly by various conversions and heating rates. The conversion effect was considered by using several models with Surinach curve fitting procedure. The result revealed that in low conversions, the reaction rate equation began with Johnson-Mehl-Avrami model-like kinetic and in high conversions, the reaction rate equation began with Normal Grain Growth model-like kinetic. Setiawan *et al*. [14] has studied the formation reaction kinetic of hydroxyapatite from inorganic precursor using TG-DTA. Non-isothermal analysis was carried out using Kissinger methods.

Here, the formation reaction kinetic of $LiFePO_4$ using $FeSO_4.7H_2O$, LiOH and $(NH_4)_2HPO_4$ as precursor was studied by Kissinger method. The conversion effect in reaction rate equation has been implemented with several models using Surinach curve fitting procedure.

2. Materials and Methods

Experiments were performed using thermogravimetric differential thermal analysis (TG-

Table 1. Theoretical Kinetic Model Equations

Model	$f(\alpha)$	Ref
• Johnson-Mehl-Avrami	$n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$	[13]
• Normal grain growth	$(1-\alpha)^{n+1}$	[13]
• One dimensional diffusion	$\frac{1}{2}\alpha$	[6]
• Two dimensional diffusion	$-\frac{1}{\ln(1-\alpha)}$	[6]
• Three dimensional diffusion	$\frac{1}{(1-\alpha)^{1/3}-1}$	[13]
• Avrami I equation	$[-\ln(1-\alpha)]^{1/2}$	[6]
• Avrami II equation	$[-\ln(1-\alpha)]^{1/3}$	[6]
• Phase boundary reaction: Cylindrical symmetry.	$2\left[1-(1-\alpha)^{1/2}\right]$	[6]

DTA) apparatus (DTA-60/60H, Shimadzu) with alumina as sample pan. The apparatus is shown in Figure 1. The operating temperature range was from room temperature to 1000 °C with a heating rate of 5, 7, 10, 15, 17.5, 22.5 and 25 °C min^{-1}.

Nitrogen was used as a purge gas with constant flow rate at 50 ml/min. LiOH (98% by weight, Merck KGaA, Germany), $FeSO_4.7H_2O$ (99% by weight, Merck KGaA, Germany) and $(NH_4)_2HPO_4$ (99% by weight, Merck KGaA, Germany) were used as precursors. Precursor was made by mixing several grams of LiOH powder, $FeSO_4.7H_2O$ powder and $(NH_3)_2HPO_4$ with mole ratio of Li:Fe:P=1:1:1. About 10 mg of precursors was placed on a cleaned alumina sample pan. Nitrogen then was flushed through the TG-DTA tube furnace and the temperature was ramped. After the final temperature was reached, still under nitrogen atmosphere, the TG-DTA furnace was cooled back to room temperature. The weight loss, energy that absorbed or released, temperature and time datum were detected and saved for further analysis.

3. Result and Discussion

3.1. TGDTA analysis of precursors

The TGDTA analysis has been carried out to know the temperature influence at constant heating rate for each precursor. Figure 2 is TG-DTA graph of $FeSO_4.7H_2O$ at 10 °C/min. This graph showed that at the temperature of about 50 °C, $FeSO_4.7H_2O$ began to decrease about 4 % by weight. At this temperature, water molecules released according to following reaction:

$$FeSO_4.7H_2O \rightarrow FeSO_4.6H_2O + H_2O \qquad (1)$$

At a temperature of about 100 °C weight loss of about 40 % was occurred. At this temperature, the water molecules are still present in the solid evaporates by the reaction:

$$FeSO_4.6H_2O \rightarrow FeSO_4 + 6H_2O \qquad (2)$$

Both reactions were also accompanied by endothermic peak. Furthermore, at a temperature of about 550 °C, $FeSO_4$ decomposed and released SO_2 and O_2 molecule with a weight of about 28 % based on the reaction:

$$2FeSO_4 \rightarrow 2FeO + 2SO_2 + O_2 \qquad (3)$$

From the TGDTA graph of LiOH (Figure 3) at temperatures around 100 °C occurred the heat absorption and decrease of weight about 14 %. Heat absorption was caused by the release of the H_2O molecules reserved by LiOH. Solid anhydrous LiOH can absorb H_2O being $LiOH.H_2O$. At the temperature of about 400 °C heat absorption occurred in the absence of weight loss, that was the melting point of LiOH approximately 425 °C. At a temperature of about 475 °C occurred the heat absorption and decrease of weight about 32 %. In these conditions, the OH group attached to the LiOH molecule decomposed to form H_2O molecules by the reaction:

$$2LiOH \rightarrow Li_2O + H_2O \qquad (4)$$

Figure 4 reveals that the $(NH_4)_2HPO_4$ decrease of weight began at 150 °C followed by heat absorption. In this condition, $(NH_4)_2HPO_4$ released step by step the NH_3 by the reaction:

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3 \qquad (5)$$

Furthermore, $NH_4H_2PO_4$ released NH_3 and H_2O and formed a phosphate oxide based on the reaction:

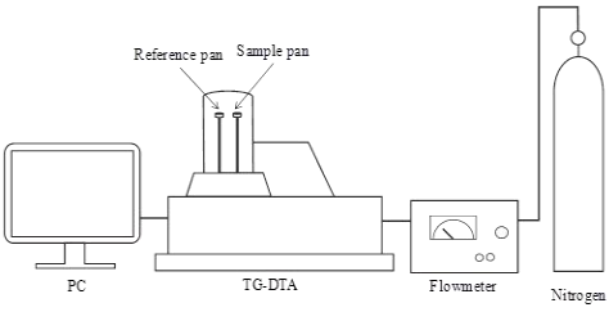

Figure 1. Experimental set-up apparatus

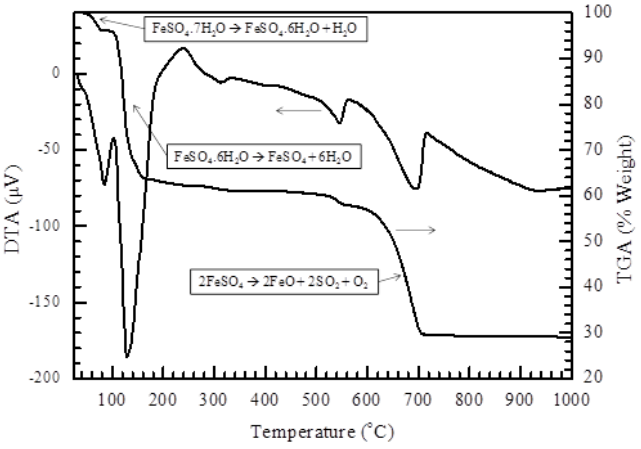

Figure 2. TGDTA graph of $FeSO_4.7H_2O$

$2NH_4H_2PO_4 \rightarrow 4NH_3 + 3H_2O + P_2O_5$ (6)

with the final weight was 54 % of initial weight at a temperature of about 550 °C. Decreased of P_2O_5 weight up to 85 % due to P_2O_5 having a low melting point (340 °C) and easily sublimed at a temperature of 360 °C.

To analyze the reaction mechanism, about 10 mg mixture precursor consist of $FeSO_4.7H_2O$, LiOH and $(NH_4)_2HPO_4$ with atomic ratio of Li:Fe:P were 1:1:1. Nitrogen gas was used as flue gas to maintain the atmospheric in inert condition. The heating rate was fixed at 10 °C min^{-1} from room temperature to 1000 °C.

Figure 5 shows the result of TGDTA analysis. The graph showed that TGDTA of mixture precursor was a combination of each precursor. From the TGDTA analysis was concluded that the mechanism of $LiFePO_4$ formation from $FeSO_4.7H_2O$, LiOH and $(NH_4)_2HPO_4$ was starting with the release of H_2O molecules of $FeSO_4.7H_2O$ (1) to form $FeSO_4.6H_2O$. Furthermore, $FeSO_4.6H_2O$ release H_2O to form $FeSO_4$ (2) gradually simultaneous with the release of NH_3 from $(NH_4)_2HPO_4$ to form $NH_4H_2PO_4$ (3). At 425 °C LiOH melted and coated $FeSO_4$ and $NH_4H_2PO_4$ (4). At 550 °C Li_2O, P_2O_5 and FeO was fuse to form $LiFePO_4$ (5). From this mechanism, can be conclude that the formation reaction of $LiFePO_4$ from $FeSO_4$, LiOH and $(NH_4)_2HPO_4$ was gradual manner. At heating rate 10 °C/min, the decomposition reaction was started at 119 °C.

General reaction rate for solid state was:

$$\frac{dx}{dt} = f(x)k(T) \quad (7)$$

where $f(x)$ is a function of volume or mass fraction of reacted precursor, $k(T)$ is account of dependence temperature which is calculated by Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (8)$$

The decomposition reaction temperature to form a $LiFePO_4$ was affected by heating rate. Based on decomposition reaction that analysed at several constant heating rate could be obtained energy activation and constant reaction order and further used to get the reaction equation. This method has been proposed by Kissinger [11,15]. By the following Kissinger equation [15], the kinetic parameter could be calculated:

$$\ln\frac{\phi}{T_m^2} = -\frac{E}{RT_m} + \ln\frac{AR}{E} \quad (9)$$

where ϕ was constant heating rate, T_m was decomposition temperature, E was activation energy, R was ideal gas constant (8134 J/kmol °C) and A was pre-exponential factor. By plotting $\ln(\phi/T_m^2)$ and $1000/T_m$ that shown in Figure 6, obtained the activation energy and pre-exponential factor were 56.086 kJ/mol and 6.95×10^8 min^{-1}, respectively.

The reaction order could be got by solving the following non linier equation [11]:

$$S = \frac{(3-\alpha)[\beta-(3-\alpha)]}{(3+\alpha)[\beta-(3+\alpha)]} \quad (10)$$

$$\alpha = \sqrt{9 - 4\left(2 - \frac{1}{n}\right)\left(1 - \frac{2RT}{E}\right)} \quad (11)$$

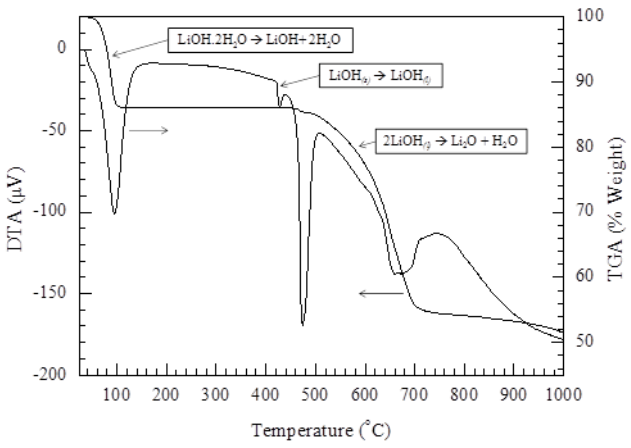

Figure 3. TGDTA graph of LiOH

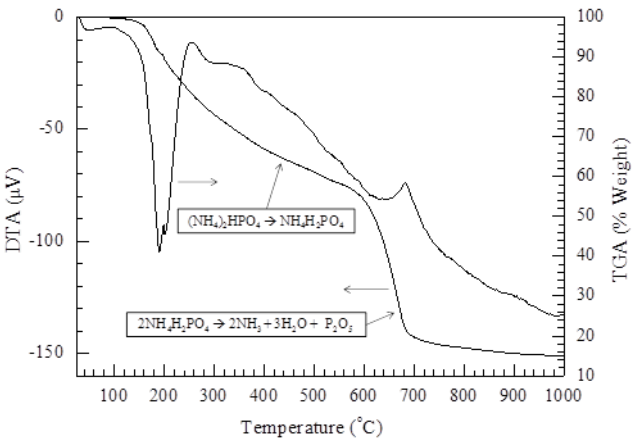

Figure 4. TGDTA graph of $(NH_4)_2HPO_4$

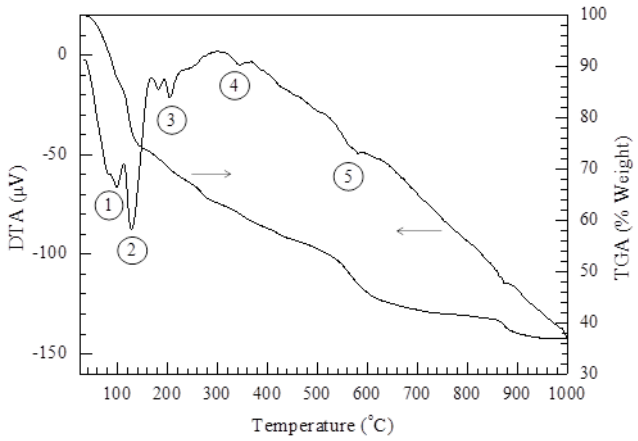

Figure 5. TGDTA graph of precursors

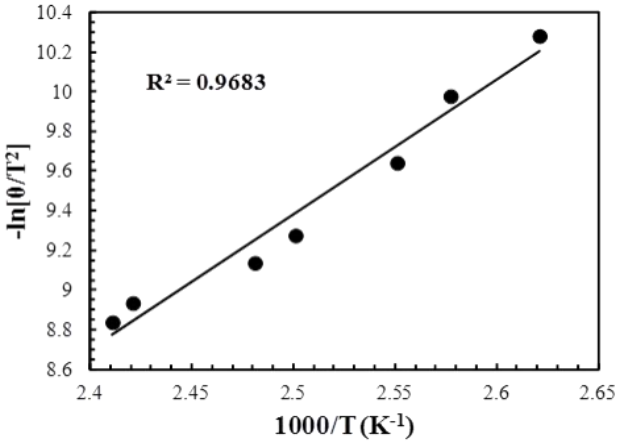

Figure 6. Graph of Kissinger equation

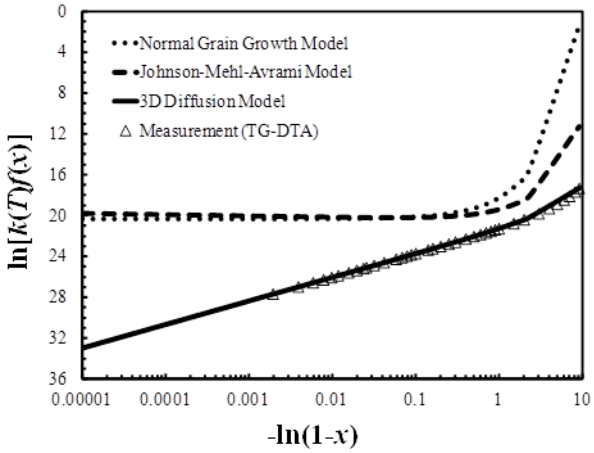

Figure 7. Model kinetic compared with experiment

$$\beta = 2\left(2 - \frac{1}{n}\right) \quad (12)$$

$$n = 1.265^{1/2} \quad (13)$$

and obtained n = 1.058.

$f(x)$ was evaluated with agreement of experiment to correlation in Table 1. Comparing the plot of $\ln(K(T).f(x))$ versus $-\ln(1-x)$ from experimental data with the theoretical model functions. The result was shown in Figure 7.

It can be seen that the 3 dimensional diffusion model has a good agreement between experiment and correlation. Therefore, the formation reaction equation for $LiFePO_4$ was:

$$\frac{dx}{dt} = 6{,}95 \times 10^{8} \exp\left(\frac{56{,}086 \times 10^{3}}{T}\right)\left[(1-x)^{-1/3} - 1\right]^{-1} \quad (14)$$

4. Conclusions

TGDTA method can be used to get the reaction equation of formation $LiFePO_4$ from LiOH, $FeSO_4.7H_2O$ and $(NH_4)_2HPO_4$ as precursor. The activation energy, pre-exponential factor and reaction order were 56.086 kJ/mol, 6.95×10^8 min^{-1} and 1.058, respectively. The formation reaction equation was good agreement with 3 dimensional diffusion model.

Acknowledgments

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