



## Kinetics Study of $\text{LiFePO}_4$ Synthesis Reaction with Solid State Method

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**ABSTRACT:** Lithium Ferro Phosphate ( $\text{LiFePO}_4$ ) is a cathode that has the advantage of abundant raw material, inexpensive and easily upgraded compared to other cathode. The method commonly used for  $\text{LiFePO}_4$  synthesis is solid state. It is important to study kinetics in this process for product optimization. There are two methods in determining the kinetics of product formation including Thermogravimetric Differential Thermal Analysis (TG-DTA) and X-ray Diffraction (XRD). Meanwhile, Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). Meanwhile, CV and EIS were used to determine electrochemical kinetics.

Keywords:  $\text{LiFePO}_4$ , solid state, kinetic.

### 1. Introduction

Energy has a very important role in today's modern life. This is evidenced by the development of one of the energy consumption of electronic equipment that is difficult to separate from human life. Increased energy demand will also increase the need for reliable tools for energy storage. Battery is one of the energy storage devices that is commonly used in everyday life. Lithium ion batteries are currently used as a source of energy for portable electronic devices and are more promising than other batteries as they have high potential, high energy density and good cycling stability.

Compared to other lithium battery cathode materials, lithium ferro phosphate ( $\text{LiFePO}_4$ ) was a promising material due to its non-toxicity, availability and high energy density [1].

Methods have been used to obtain  $\text{LiFePO}_4$  particles as a battery cathode such as flame assisted spray pyrolysis [2], hydrothermal [3], carbo thermal [4] and solid state reaction [5][6]. Solid state reactions are the conventional and commonly used route, usually involving intimate friction and sintering of the stoichiometric sum of the starting material mixture. They have been used to prepare

LiFePO<sub>4</sub> for Li-ion batteries because they are economical, powerful and can be easily upgraded.

It was important to study the kinetic formation because it was closely related to the mechanism of the reaction. In this paper, present about the kinetic study of LiFePO<sub>4</sub> synthesis using the solid-state.

## 2. Method of Determining LiFePO<sub>4</sub> Formation Kinetics

### 2.1 Thermogravimetric Differential Thermal Analysis (TG-DTA)

TG-DTA was a simple method of determining kinetic parameters, such as pre-exponential factor and energy activation. Two methods are available to determine kinetic parameters using isothermal and non-isothermal system TG-DTA. Although isothermal methods are more efficient, non-isothermal more applicable to all kinetic determination [7].

The reaction of LiFePO<sub>4</sub> to the formation of LiOH, FeSO<sub>4</sub>.7H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> precursor decomposition with Li: Fe: P = 1: 1: 1 mol ratio was investigated. The experiment was conducted using a method of thermogravimetric differential thermal analysis (TG-DTA) using a constant heating rate nitrogen as an atmosphere to obtain kinetic constant parameters. Many heating levels have been selected, viz. 5, 7, 10, 15, 17.5, min<sup>-1</sup> at 22.5 and 25°C. The TG-DTA analysis was performed to determine the temperature effect for each precursor. Halim et al. [8] was concluded from the TG-DTA analysis that the mechanism for the formation of LiFePO<sub>4</sub> began with the release H<sub>2</sub>O molecules of FeSO<sub>4</sub>.7H<sub>2</sub>O into FeSO<sub>4</sub>.6H<sub>2</sub>O. In addition, FeSO<sub>4</sub>.6H<sub>2</sub>O releases H<sub>2</sub>O to form FeSO<sub>4</sub> slowly at the same time as releases of NH<sub>3</sub> from (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> to form NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. FeSO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> melted and coated LiOH at 425°C. LiFePO<sub>4</sub> was developed at 550°C from Li<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and FeO. It can be concluded from this

mechanism that LiFePO<sub>4</sub>'s formation reaction has been gradual. At the heating rate 10°C min<sup>-1</sup>, the decomposition reaction was started at 119°C.

General reaction rate for solid state are:

$$\frac{dx}{dt} = f(x) k(T) \quad (1)$$

Where f(x) is a function of the volume or mass fraction of the reacted precursor, k(T) is the Arrhenius equation measured dependence temperature:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

Temperature of the decomposition reaction to form a LiFePO<sub>4</sub> has been affected by the heating rate. Energy activation and constant reaction order could be obtained on the basis of a decomposition reaction that was analyzed at several constant heating rates. The pre-exponential factor, activation energy and reaction order were taken using the Kissinger method and obtained 56.086 kJ/mol, either 6.95 min<sup>-1</sup>, and 1,058 respectively. The formation reaction equation of LiFePO<sub>4</sub> using non-isothermal TG-DTA analysis has the result:

$$\frac{dx}{dt} = 6,95 \times 10^9 \exp\left(-\frac{56.086 \times 10^3}{T}\right) \left[(1 - x)^{-1/3} - 1\right]^{-1} \quad (3)$$

Another study using non-isothermal methods was conducted by Setiawan et al [9] about the kinetic formation reaction of hydroxyapatite from inorganic precursors. Non-isothermal analysis was conducted using methods Kissinger.

Via Ozawa-Flynn-Wall and Kissinger methods, the kinetic parameters frequency factor, A, and apparent activation energy, E, were determined. In order to obtain a reliable and accurate value, the option of reaction mechanism was avoided for these two methods [10]. These two methods provide the benefit of requiring no experience working of the reaction process

to assess the activation energy in contrast with other approaches, and researchers usually use the activation energy collected using these two methods to test their models of their system of thermal degradation [11].

Yuan et al [12] applied the Kissinger method to obtain Co<sub>43</sub>Fe<sub>20</sub>Ta<sub>5.5</sub>B<sub>31.5</sub> kinetic glass crystallization. Various conversions and heating rates have significantly impacted the activation energy. Several models with Surinach curve fitting procedure were used to consider the conversion effect. The result showed that in low conversions the reaction rate equation started with the model-like kinetic Johnson-Mehl-Avrami and in high conversions the reaction rate equation started with the model-like kinetic Normal Grain Growth.

As research conducted by Yang et al [13], the use of Li, P, and Fe sources affects the temperature of the formation of LiFePO<sub>4</sub> single phase olivine, reaction mechanism, and activation energy needed for each reaction. The kinetic analysis method was Coats Redern and Doyle method to determine the average value of activation energy that affects the reaction to the formation of single phase olivine LiFePO<sub>4</sub>. The equations of the two methods are compared using the integral function of conversion

$$F(\alpha) = \frac{A}{\beta} \int_{T_0}^{T_p} \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

(Integral function of Conversion)

$$\ln \frac{F(\alpha)}{T^2} = \ln \frac{AR}{\beta \cdot E_a} \left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{RT} \quad (5)$$

(Coats Redern Eq.)

$$\ln F(\alpha) = \ln \frac{AE_a}{\beta \cdot R} - 5.3305 - 1.052 \cdot \frac{E_a}{R} \cdot \frac{1}{T} \quad (6)$$

(Doyle Eq.)

$$\alpha = (w - w_0)/(w - w_c) \quad (7)$$

T<sub>0</sub> is the initial temperature and T<sub>p</sub> is the value at α = α<sub>p</sub>, w<sub>0</sub> is the weight of the initial sample, w is the actual weight, w<sub>c</sub> is the final weight of the sample, and α is the degree of decomposition. The value of F (α) varies for each reaction mechanism. The reaction kinetics are determined from the reaction mechanism that produces the best linear value from the Coats Redern and Doyle method compared to the decrease in the integral function of conversion. Based on these studies, it can be seen that the Coats Redern method has an activation energy that is close to the decrease in the integral function of conversion.

## 2.2 X-ray Diffraction (XRD)

The kinetics of LiFePO<sub>4</sub> formation through solid state was done by the non-isothermal method. Data analysis used XRD as a function of temperature. The kinetics data were interpreted from the XRD pattern with a peak (011) of the olivine compound. The reaction is considered complete if the conversion fraction (F) of LiFePO<sub>4</sub> is 1.0 at set temperature (T\*) (powder into a single phase) and peak intensity varies with increasing temperature (T). Conversion fraction can be formulated from the intensity ratio as follows [14]:

$$F(T) = \frac{I(T)}{I(T^*)} \quad (8)$$

Several kinetic equations were evaluated to describe solid state reactions. These equations included the mechanism of nuclei growth limit reaction, diffusion, interfacial reaction, exponential law and power-law. Among these equations, power law has appropriate criteria for non-isothermal reactions. The result is a kinetic equation:

$$\frac{1}{0,7} \frac{F^{0,7}}{(1-F)^{0,7}} = 2,23 \times 10^{11} \exp\left(-\frac{24,1}{T}\right) t \quad (9)$$

Fractional conversions can be predicted with the above kinetic equation. The formation of olivine compound is expected to occur at low temperatures and rapid reactions [14].

### 3. Method of Determining LiFePO<sub>4</sub>

#### Electrochemical Kinetics

LiFePO<sub>4</sub> carbon composite was synthesized using solid state reaction which was prepared using Li<sub>2</sub>CO<sub>3</sub>, FeC<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, and acetylene black as precursors for carbon sources. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses were performed on cathode materials that have been fabricated on coin-cells. CV and EIS are carried out to determine the diffusion coefficient on LiFePO<sub>4</sub> which has been composited by carbon. CV was operated in the voltage range 2.1 – 4.5 V and EIS at frequencies from 10 mHz to 100 kHz with vibration of 10 mV [15].

One of the challenges in using LiFePO<sub>4</sub> as a material of lithium ion batteries is the low rate capability which can result in a decrease the kinetics of lithium ion diffusion coefficient (10<sup>-14</sup> to 10<sup>-16</sup> cm<sup>2</sup> s<sup>-1</sup>) dan electrical conductivity (<10<sup>-9</sup> cm<sup>-1</sup>) [16,17]. The low electrical conductivity causes a low kinetics charge and discharge.

In a solid state reaction, carbon was usually mixed with the raw material of LiFePO<sub>4</sub>. After reactions occur at high temperatures, LiFePO<sub>4</sub> formed with carbon coating the surface of the particles that improves electrochemical performance. The increasing of electrochemical performance is due to the carbon layer covering the surface of the particle thereby increasing the kinetics and reversibility of the lithium insertion/de-insertion cycle [18].

CV is used to evaluate the electrochemical performance of LiFePO<sub>4</sub> material carbon composite. The CV profile exhibit that un-compossable LiFePO<sub>4</sub> has a

cathode/anode peak value at 4.08 V/2.88 V at a scan rate of 0.1 mV s<sup>-1</sup>, so the difference in redox peak (ΔV) 1.2 V. On material that is composited using carbon, the value of ΔV for each composition was different where the highest carbon composition has the smallest value of ΔV. So from this analysis it can be shown that the electrochemical behaviour is controlled by diffusion step and the improvement of electrochemical performance is obtained by arrange material with carbon [15].

The EIS is used to evaluate the diffusion coefficient on lithium ions and is used to analyse the effect of carbon on lithium ion transfer on LiFePO<sub>4</sub>. The analysis shows the charge transfer resistance (R<sub>ct</sub>) which is described as a semicircle shape in the Nyquist plot. The greater the diameter of the semicircle the greater the value of R<sub>ct</sub>. The addition of carbon to the material shows a decrease in diameter in the semicircle so that it can be concluded that the higher the carbon composition in the material the lower the R<sub>ct</sub> value thereby increasing battery performance [19].

To determine how much the lithium ion diffusion coefficient value from the EIS analysis can be calculated using the equation:

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 s^2} \quad (10)$$

D = diffusion coefficient of lithium ion; R = gas constant; T = absolute temperature; A = surface area of the cathode; F = Faraday constant; C = concentration of lithium ion; n = number of electrons per molecule through oxidation; s = specific area of porous electrode. The value of D will increase as the amount of carbon increases. The results of this analysis are supported by CV and EIS analysis which shows that the addition of carbon can improve electrochemical performance. Thus, the increase in lithium ion kinetics can be influenced by the addition of carbon [15].

Zhu et al [20], also used EIS to determine the chemical diffusion coefficient of inserted ions in solid electrodes with different storage temperatures. The rate of diffusion of Li<sup>+</sup> in electrolyte solutions is much better than in active solid state materials. Thus, the charging transfer resistance can be determined by the rate-determining step during charge and discharge of the Li<sup>+</sup> diffusion process. Warburg solution impedance response and diffusion coefficient ( $D_{Li}$ ) greatly affect the determination of the characteristics of lithium ion diffusion which can be calculated by equations (11) and (12).

$$Z_{re} = R_{ct} + R_s + \sigma\omega^{-1/2} \quad (11)$$

$$D_{Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (12)$$

where  $Z_{re}$  is an electrolyte resistance,  $R_s$  is ohmic resistance,  $R_{ct}$ ,  $R$ ,  $T$ ,  $A$ ,  $n$ ,  $F$ , and  $C$  are the same as equation (9) whereas  $\sigma$  is Warburg factor. The result is that the diffusion coefficient of lithium ion increases with increasing storage temperature which causes Fe<sup>2+</sup> present in the electrolyte during storage of LiFePO<sub>4</sub> cells at high temperatures.

#### 4. Conclusions

Reaction kinetics of LiFePO<sub>4</sub> material synthesis using solid state method can be determined through TG-DTA and XRD analysis. Meanwhile, to determine the electrochemical kinetics using CV and EIS. TG-DTA was a simple method of determining kinetic parameters, such as pre-exponential factor and energy activation. Kissinger, Ozawa-Flynn-Wall, Coats Redern and Doyle method was used to analyze the kinetics of LiFePO<sub>4</sub> synthesis. XRD peaks can be used to interpret the formation kinetics of the material using the non-isothermal method. Power law is the most suitable equation for solid state formation kinetics of LiFePO<sub>4</sub>. By using CV and EIS, the electrochemical performance can be seen by looking at the step in the

diffusion coefficient. In each diffusion step the effect of carbon on the transfer of lithium ions to the LFP will be known. The electrochemical performance gets better with the addition of carbon because the lithium ion increases.

#### References

- [1] S.Y. Chew, T.J. Patey, O. Waser, S.H. Ng, R. Büchel, A. Tricoli, F. Krumeich, J. Wang, H.K. Liu, S.E. Pratsinis, P. Novák, Thin nanostructured LiMn<sub>2</sub>O<sub>4</sub> films by flame spray deposition and in situ annealing method, *J. Power Sources*. 189 (2009) 449–453. <https://doi.org/10.1016/j.jpowsour.2008.12.085>.
- [2] O. Waser, R. Büchel, A. Hintennach, P. Novák, E. Sotiris, Europe PMC Funders Group Continuous flame aerosol synthesis of carbon – coated nano – LiFePO<sub>4</sub> for Li – ion batteries, *J. Aerosol Sci.* 42 (2011) 657–667. <https://doi.org/10.1016/j.jaerosci.2011.06.003>.Continuous.
- [3] F. Brochu, A. Guerfi, J. Trottier, M. Kopeć, A. Mauger, H. Groult, C.M. Julien, K. Zaghbi, Structure and electrochemistry of scaling nano C-LiFePO<sub>4</sub> synthesized by hydrothermal route: Complexing agent effect, *J. Power Sources*. 214 (2012) 1–6. <https://doi.org/10.1016/j.jpowsour.2012.03.092>.
- [4] L. Wang, G.C. Liang, X.Q. Ou, X.K. Zhi, J.P. Zhang, J.Y. Cui, Effect of synthesis temperature on the properties of LiFePO<sub>4</sub>/C composites prepared by carbothermal reduction, *J. Power Sources*. 189 (2009) 423–428. <https://doi.org/10.1016/j.jpowsour.2008.07.032>.
- [5] A. Liu, Y. Liu, Z. Hu, G. Gao, Y. Xu, L. Lei, Electrochemical performance of LiFePO<sub>4</sub>/C synthesized by solid state reaction using different lithium and iron sources, *J. Phys. Chem. Solids*. 72 (2011) 831–835. <https://doi.org/10.1016/j.jpcs.2011.04.009>.
- [6] J.F. Martin, A. Yamada, G. Kobayashi, S.I. Nishimura, R. Kanno, D. Guyomard, N.

- Dupř, Air exposure effect on LiFePO<sub>4</sub>, *Electrochem. Solid-State Lett.* 11 (2008) 12–16.  
<https://doi.org/10.1149/1.2801016>.
- [7] D. Blečić, Ž. D. Živković, M. Martinović, A new method for the determination of reaction kinetics from DTA and TG curves. Part I. Definition of the method, *Thermochim. Acta.* 60 (1983) 61–68.  
[https://doi.org/10.1016/0040-6031\(93\)85006-U](https://doi.org/10.1016/0040-6031(93)85006-U).
- [8] A. Halim, W. Widiyastuti, H. Setyawan, S. Winardi, Kinetic of lifepo<sub>4</sub> formation using non-isothermal thermogravimetric analysis, *Bull. Chem. React. Eng. Catal.* 9 (2014) 60–65.  
<https://doi.org/10.9767/bcrec.9.1.5508.60-65>.
- [9] A. Setiawan, Kinetika Reaksi Hydroxyapatite Berdasarkan Analisis Thermogravimetri dan Differensial Thermal, in: *Proceeding Semin. Nas. Fundam. Dan Apl. Tek. Kim., Surabaya*, 2011.
- [10] L. He, X. Liu, Z. Zhao, Non-isothermal kinetics study on synthesis of LiFePO<sub>4</sub> via carbothermal reduction method, *Thermochim. Acta.* 566 (2013) 298–304.  
<https://doi.org/10.1016/j.tca.2013.06.014>.
- [11] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, *Thermochim. Acta.* 520 (2011) 1–19.  
<https://doi.org/10.1016/j.tca.2011.03.034>.
- [12] Z.Z. Yuan, X.D. Chen, B.X. Wang, Y.J. Wang, Kinetics study on non-isothermal crystallization of the metallic Co<sub>43</sub>Fe<sub>20</sub>Ta<sub>5.5</sub>B<sub>31.5</sub> glass, *J. Alloys Compd.* 407 (2006) 163–169.  
<https://doi.org/10.1016/j.jallcom.2005.06.022>.
- [13] X. Yang, D. Liu, X. Xu, X. He, J. Xie, Mechanism and Kinetic Studies on the Synthesis of LiFePO<sub>4</sub> via Solid-State Reactions, *CrystEngComm.* 15 (2013) 10648–10656.  
<https://doi.org/10.1039/C3CE41063C>.
- [14] H.H. Chang, C.C. Chang, H.C. Wu, Z.Z. Guo, M.H. Yang, Y.P. Chiang, H.S. Sheu, N.L. Wu, Kinetic study on low-temperature synthesis of LiFePO<sub>4</sub> via solid-state reaction, *J. Power Sources.* 158 (2006) 550–556.  
<https://doi.org/10.1016/j.jpowsour.2005.09.005>.
- [15] H. Liu, C. Li, H.P. Zhang, L.J. Fu, Y.P. Wu, H.Q. Wu, Kinetic study on LiFePO<sub>4</sub>/C nanocomposites synthesized by solid state technique, *J. Power Sources.* 159 (2006) 717–720.  
<https://doi.org/10.1016/j.jpowsour.2005.10.098>.
- [16] R. Amin, P. Balaya, J. Maier, Anisotropy of electronic and ionic transport in LiFePO<sub>4</sub> single crystals, *Electrochem. Solid-State Lett.* 10 (2007) 12–16.  
<https://doi.org/10.1149/1.2388240>.
- [17] P.P. Prosini, M. Lisi, D. Zane, M. Pasquali, Determination of the chemical diffusion coefficient of lithium in LiFePO<sub>4</sub>, *Solid State Ionics.* 148 (2002) 45–51.  
[https://doi.org/10.1016/S0167-2738\(02\)00134-0](https://doi.org/10.1016/S0167-2738(02)00134-0).
- [18] J. Wang, X. Sun, Understanding and recent development of carbon coating on LiFePO<sub>4</sub> cathode materials for lithium-ion batteries, *Energy Environ. Sci.* 5 (2012) 5163–5185.  
<https://doi.org/10.1039/c1ee01263k>.
- [19] D. Zane, M. Carewska, S. Scaccia, F. Cardellini, P.P. Prosini, Factor affecting rate performance of undoped LiFePO<sub>4</sub>, *Electrochim. Acta.* 49 (2004) 4259–4271.  
<https://doi.org/10.1016/j.electacta.2004.04.022>.
- [20] Y.R. Zhu, Y. Xie, R.S. Zhu, J. Shu, L.J. Jiang, H. Bin Qiao, T.F. Yi, Kinetic study on LiFePO<sub>4</sub>-positive electrode material of lithium-ion battery, *Ionics (Kiel).* 17 (2011) 437–441.  
<https://doi.org/10.1007/s11581-011-0523-9>.