
Indonesian Physical Review

Volume 4 Issue 3, September 2021

P-ISSN: 2615-1278, E-ISSN: 2614-7904

Effect of Calcination Temperature on F-Doped LiFePO₄ Cathode Material on Formation of Olivine Phase

Ahmad Ilham Ramadhani^{1*}, Lukman Noerochim², Diah Susanti², Eli Novita Sari³

^{1*} Department of Fisheries Mechanical, Politeknik Kelautan dan Perikanan Bitung, Indonesia.

E-mail: ahmadilhamramadhani2@gmail.com

² Department of Materials Engineering, Faculty of Industry Technology, Institut Teknologi Sepuluh Nopember, Indonesia. E-mail: lukman@mat-eng.its.ac.id

³ Department of Mechanical Engineering, Faculty of Engineering, Universitas Billfath, Indonesia.

E-mail: elinovitasari5@billfath.ac.id

ARTICLE INFO

Article info:

Received: 29-04-2021

Revised: 06-06-2021

Accepted: 13-07-2021

Keywords:

Olivine Single Phase;
Lithium-Ion Battery
Cathode; Solid State
Reaction; Calcination
Temperature; TGA-DSC
Method

How To Cite:

Ramadhani, A.I.,
Noerochim, L., Susanti, D.,
Sari, E.N. (2021). Effect of
Calcination Temperature
on F-Doped LiFePO₄
Cathode Material on
Formation of Olivine
Phase. Indonesian Physical
Review 4(3) pp 116-121

DOI:

[https://doi.org/10.29303/i
pr.v4i3.99](https://doi.org/10.29303/i
pr.v4i3.99)

ABSTRACT

Olivine single phase of LiFePO₄ was successfully synthesized by solid-state reaction (SSR) method through the formation of Fe₂P₂O₇ from precursors of Li₂CO₃, F₂O₃, NH₄H₂PO₄, and LiF as materials doping. Variations at temperatures of calcination 670 °C, 700 °C and 750 °C with doped 0.1F. TGA-DSC test results show that the LFP sample undergoes decomposition in the temperature range 0-600 °C. The olivine phase formed at temperatures of more than 650 °C and the oxidation process on the LiFePO₄/C sample was completed and the sample mass was constant. The olivine phase formed was determined by comparing the 2θ value obtained through characterization with the ICDD LFP (01-081-1173), and accordingly with experiment. The increase of the temperature results from a dominant LFP phase with a larger grain size. The effect of increasing the calcination temperature at 0.1F has resulted in an enlargement of the particle size.

Copyright © 2021 Authors. All rights reserved.

Introduction

Lithium iron phosphate (LiFePO₄ or LFP) has attracted considerable attention as a promising replacement for LiCoO₂. If LFP compared with commercial cathode materials Lithium-Ion battery, LFP materials have dominant characteristics like small cost and a little toxicity, and

also good capacity discharge around ~ 170 mAh/g [1,2]. There are two main problems with the electrochemical performance of LFP: (1) small electronic conductivity of around 10^{-10} S/cm and (2) low Lithium-Ion conductivity of around 10^{-17} - 10^{-14} S/cm. Several LFP problems can be overcome by carrying out several methods, namely: (a) reducing the particle size (b) carbon-coating and adding a carbon conductor/carbon source, (c) cation/anion doping is done by adding cations and anions to the LFP, and (d) the calcination temperature used to obtain single-phase active olivine LFP [3,4].

In general, there are two types of phases in LFP, namely olivine and nasicon. Both phases are influenced by the calcination temperature during the synthesis process of the active LFP material. The nasicon phase has a theoretical capacity (128.2 mAhg $^{-1}$) lower than the Olivine (theoretical capacity of 170 mAhg $^{-1}$) [5]. In the nasicon phase, the Li-Ion charge is difficult to escape and move from its main bond. Whereas in the olivine phase, the Li-Ion charge tends to move freely in the process of delivering an electric current to the outer circuit.

This causes the nasicon phase that is in the LFP to be increased to the olivine phase in the presence of an increase in the calcination temperature. Calcination temperature also has an important role in the formation of single phase, particle size, and morphology of LFP. A previous study [6], it identified the effect of temperature 600 °C, 650 °C, and 700 °C on the synthesis of nano-LiFePO $_4$ /C. It was obtained that the degree of crystallinity of LFP/C increased with increasing calcination temperature. Based on three differences in synthesis treatment temperatures, the three of them showed single phase olivine with different levels of crystallinity. So that a further study is needed to get single phase olivine on the dominant LFP / C. formed at calcination temperatures above 650 °C to ~ 750 °C. Therefore, in this work analysis the effect of various calcination temperatures synthesized by ball milling method to obtain olivine single phase LFP doped LiF.

Experimental Method

Precursor LFP was synthesized through a solid reaction method with prepared by formation Fe $_2$ P $_2$ O $_7$ previously. The precursor Fe $_2$ P $_2$ O $_7$ was prepared by mixing Fe $_2$ O $_3$, NH $_4$ H $_2$ PO $_4$, C $_6$ H $_8$ O $_7$.H $_2$ O as carbon additive, and ethanol for 4 hours according to stoichiometric proportions. After dry, precursor powder Fe $_2$ P $_2$ O $_7$ is calcined subsequently at 700 °C for 6 hours. Then, material active mixed again with Li $_2$ CO $_3$ in ethanol for 4 h and calcined with various temperature 670 °C, 700 °C, and 750 °C. An amount 0.1F as source dopant was doped LFP with ratio mole LFP:F 1:0.1 respectively. The precursor LFP/F mixtures were mixed at mortar pestle for 1 hour and calcined with various temperature 670 °C, 700 °C, and 750 °C for 1 hour. Characterization process of material active LFP/F was carried out using TGA-DSC with free air conditions, without any additional argon and use temperature 0 until 900 °C. Identification of formation LFP/F was observed during combustion in the temperature range 0- 900 °C. In each 100 °C range, changes in mass and decomposition of LFP/F were observed. The phase formed is characterized by X-ray diffraction (XRD). The peaks formed in LFP were identified using PANalytical with Cu K α radiation ($\lambda=15.4178$ nm) in a range from 10° to 90° at room temperature. The olivine phase formed was determined by comparing the 2θ value obtained through characterization with reference database ICDD LFP (01-081-1173).

Result and Discussion

Thermogravimetric Analysis (TGA) aims to determine changes in the mass of a compound associated with temperature changes. Figure 1 shows a decrease in the peak on the TGA graph. TGA test was only carried out on LFP/C 750 °C with doping 0.1F, because the amount of carbon source added to each variation of the sample samples was constant.

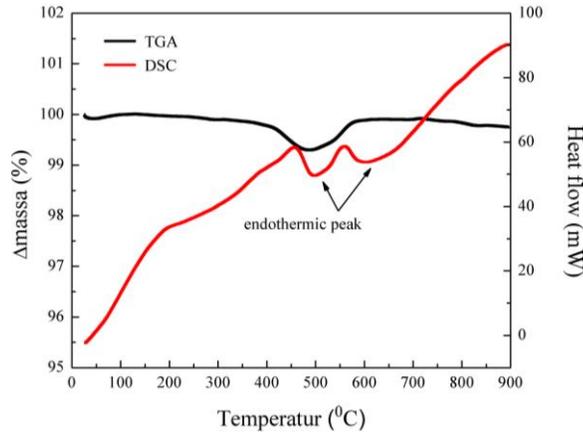


Figure 1. Graph of TGA-DSC test on sample LFP / C 750 °C with 0.1F doping

TGA is an analytical technique used to determine material thermal stability and it's the fraction of volatile components changes by monitoring the weight change that occurs as a sample is heated. Furthermore, Differential Scanning Calorimetry (DSC) is a thermal analysis apparatus measuring how the physical properties of a sample change, along with temperature against time. Result TGA/DSC graph obtained shows several temperature points that indicate a compound decomposition process. The Temperature range at 0-120 °C has occurred dehydrate decomposition of H₂O and other elements of precursor powder. Increasing the temperature, causing the contained volatile decomposition. In the temperature range 400-500 °C, the carbon element (C₆H₈O₇.H₂O) decomposes according to a decrease in the TGA graph and the formation of an endothermic peak in the DSC graph. A mass decrease of 0.43% in the temperature range 400-500 °C, indicating the amount of carbon contained.

At the temperature range of 500-600 °C, the LFP sample undergoes oxidation with the formation of Fe₂O₃ compounds and the mass compaction process occurs along with the mass increase in the TGA increase curve. The oxidation process occurs because the Argon gas sample is not streamed, but instead uses O₂ or free air in the combustion process. The oxidation phenomenon that occurs in the LFP sample causes the formation of a Li₃Fe₂(PO)₃ and Fe₂O₃. Oxidation results obtained has a similar result in the results of the research [7] and [8] described at a temperature of 350 °C, LiFePO₄/C is oxidized to Li₃Fe₂(PO)₃ and Fe₂O₃ with marked masses sample that starts to grow. The Temperature range at 600-650 °C, the oxidation process in LiFePO₄/C samples has been completed and the sample mass is

constant. This shows that no volatile phase has been wasted and at a temperature of 650 °C. Start from temperature 650 °C, the olivine phase begins to form and the higher the temperature, the more olivine phase is formed.

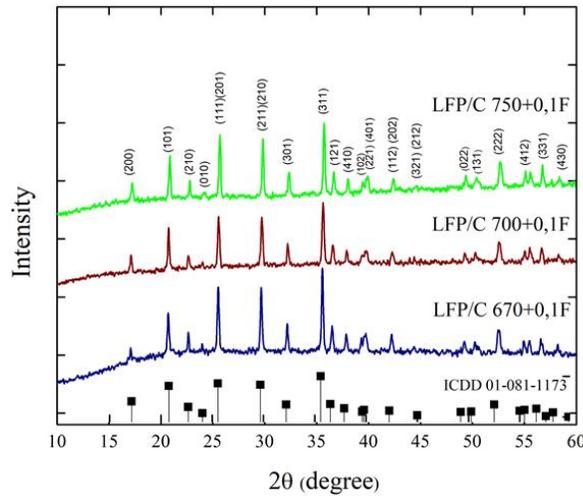


Figure 2. XRD result on sample LFP/C various temperature

The crystal structure of the LFP/C sample with temperature variations of 670 °C, 700 °C, and 750 °C at 0.1F was tested using an XRD (PANalytical). The diffraction peak results of the sample temperature variation are shown in Figure 2.

The diffraction peak in the identification of the crystal structure has formed a diffraction peak at an angle of 2θ about 17.14°; 20.74°; 22.63°; 24,00°; 25.55°; 29.68°; 32.16°; 35.58°; 36.58°; 37.88°; 39.83°; 42.27°; 44.41°; 49.24°; 50.27°; and 52.52°. The olivine single phase formed was determined by comparing 2θ values with the ICDD LFP data (01-081-1173). As the calcination temperature increases, the impurity phase decreases and tends not to exist. This proves that the olivine crystal structure has been formed in the *Pnma* space group that is present in each sample of temperature variations. (Figure 2).

Table 1. Lattice parameters and volume cell at temperatures 670 °C, 700 °C, and 750 °C doped 0.1F.

Sampel	Lattice Parameters			Volume cell (Å ³)
	a (Å)	b (Å)	c (Å)	
LFP reference (ICDD 01-081-1173)	10,33200	6,01000	4,69200	291,3500
LFP 670 °C+0,1F	10,32110	6,00442	4,69127	290,7288
LFP 700 °C+0,1F	10,32402	6,00333	4,69211	290,8099
LFP 750 °C+0,1F	10,33032	6,00797	4,69204	291,2083

In addition to the formation of the increasingly dominant single-phase olivine, the temperature variation at 0.1F causes a greater change in the unit cell volume as shown in Table 1. The volume of cells is getting bigger at temperature variations 670 °C, 700 °C, and

750 °C, due to the decrease in the amount of carbon in the sample. So that no element inhibits the growth of particles. The larger cell volume corresponds to the SEM results obtained.

Morphological identification of LFP, using SEM (FEI Inspect S50) with tungsten as the electron source. The magnitude of the acceleration voltage is 20 kV and the magnification given is 15,000 times. The results of the synthesis of battery cells that have shown the dominant olivine LFP phase in each sample, then carried out SEM testing. SEM-EDX testing aims to determine the surface morphology of the LFP and determine the grain size range obtained.

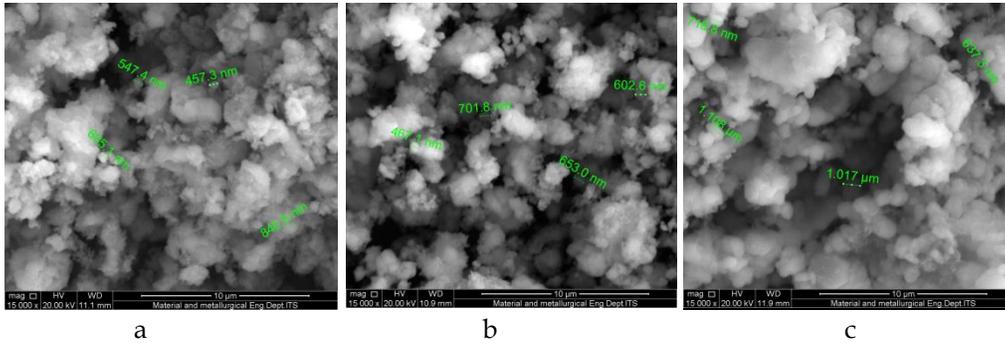


Figure 3. SEM results on LFP/C samples (a) 670 °C, (b) 700 °C and (c) 750 °C + 0.1F with a magnification of 15,000x.

Magnification of 15,000x can be seen in the morphology of the grain. It is known that the particle size range at calcination temperature is 670 °C (457.3 nm-605.1 nm), 700 °C (467.1 nm-701.8 nm), and 750 °C (637.3 nm-1,108 µm). Based on SEM images at the same magnification, it can be seen that the higher the calcination temperature used, the better the crystal structure. In addition, along with the increase in the calcination temperature at 750 °C, the larger the particle size obtained. This is because the element of carbon that plays a role in preventing grain growth has been reduced. This causes some grains to grow and the grain size to get bigger. That is, when the grain size gets bigger and fused, the particle size will also get bigger. This of course inhibits the discharge process from the cell. The same thing was also found in research [9] which explained that a higher synthesis temperature of 750 °C would result in large particles.

Conclusion

The olivine phase formed at temperatures of more than 650 °C and the oxidation process on the LiFePO₄/C sample was completed and the sample mass was constant. LFP/C material as promotional material for Lithium-Ion Batteries. With temperature variations of 670 °C, 700 °C, and 750 °C at 0.1 F formed the dominant olivine phase with the Pnma space group and has been appropriate with the LFP standard data (ICDD 01-081-1173). The effect of increasing the calcination temperature at 0.1F has resulted in an enlargement of the particle size.

Acknowledgment

The authors wish to thank for the support from the Laboratory of Corrosion and Failure Research Department of Materials and Metallurgical Engineering, ITS and other departments who provided insight and service for material development and testing.

References

- [1] C. Julien. A. Mauger. A. Vijn. K. Zaghbi (2016). Lithium Batteries, Science and Technology. Library of Congress. Springer International Publishing. New York.
- [2] Pier P Prosini (2011). Iron Phosphate Materials as Cathodes for Lithium Batteries. Library of Congress. Springer International Publishing. New York.
- [3] Yongan Huang. Yunlong Xu. Xu Yang. (2013). Enhanced electrochemical performances of LiFePO₄/C by co-doping with magnesium and fluorine. *Electrochimica Acta*, 113, 156-163.
- [4] Z. C. Huertas (2017). Alternative approaches for the fabrication of electrodes based on LiFePO₄ as cathodes in LIBs. Dissertation. Chemistry Departement. Faculty of Science. Univ: Autonoma de Barcelona.
- [5] Hassan Karami & Foroozandeh Taala (2016). Synthesis, characterization and application of Li₃Fe₂(PO₄)₃ nanoparticles as cathode of lithium-ion rechargeable batteries. *Journal of Power Source*, 196, 6400-6411.
- [6] Ahmat Örneç, Emrah Bulut, and Mahmut Özacar (2011). Effect of Temperature on Synthesis of Nano LiFePO₄/C Cathode Active Material for Lithium-Ion Batteries. *Advanced Science, Engineering, and Machine*, 3, 104-104.
- [7] C. Miao. P. Bai. Q. Jiang S. Sun. X. Wang (2014). A novel synthesis and characterization of LiFePO₄ and LiFePO₄/C as a cathode material for lithium-ion battery. *Journal of Power Source*, 246, 232-238.
- [8] Rakesh Saroha & Amrish K Panwar (2017). Effect of in situ pyrolysis of acetylene (C₂H₂) gas as a carbon source on the electrochemical performance of LiFePO₄ for rechargeable lithium-ion batteries. *Journal of Physics D: Applied Physics*, 50, 1-12.
- [9] Wang. L. Liang. G.C. Ou. X.Q. Zhi. X.K. Zhang. J.P. Cui. J.Y (2009). Effect of Synthesis Temperature on The Properties of LiFePO₄/C Composites Prepared by Carbothermal Reduction. *Journal of Power Sources* 189, pp 423-428.