Synthesis and Characterization of Lithium Iron Phosphate Carbon Composite (LFP/C) using Magnetite Sand Fe₃O₄

Zuffa Anisa,¹ Mochammad Zainuri²

¹Chemistry Department, Faculty of Science and Engineering, University of Bojonegoro
²Physics Department, Faculty of Mathematics and Sciences, Institute Technology of Sepuluh Nopember

*Corresponding email: zuffa.anisa@gmail.com

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ABSTRACT

Lithium Ferro Phosphate Carbon Composite (LFP/C) had been synthesized using solid-state reaction method. Magnetite sand Fe₃O₄ was used as Fe-source in LFP/C synthesized. Calcination temperature of the sample performed at 400, 500, and 600°C. The phase and composition of samples determined by Rietveld analysis of X-ray diffraction (XRD) pattern. The dominant identified phase at 400°C was diphosphate LiFeP₂O₇, and the others phases were nasicon Li₃Fe₂(PO₄)₃ and hematite Fe₂O₃. As the temperature getting higher the diphosphate phase LiFeP₂O₇ transform to nasicon Li₃Fe₂(PO₄)₃. The chemical bonds, lattice vibration and other structural features of the sample were investigated using FTIR spectroscopy in range of 1400 – 400 cm⁻¹. Specific vibration modes in LFP-1 to LFP-3 for each bonding were shown by the high intense in certain wavenumber.

Key word: LFP/C, Magnetite, Nasicon, Diphosphate, Phase

INTRODUCTION

The demand for rechargeable batteries, lithium-ion batteries has increased significantly. Unfortunately several lithium batteries such as LiCoO₂, LiNiO2 are toxic and not environmentally benign [1]. Another efforts has paid attention by using Fe-based material as an alternative replacement for the active materials of Lithium Ferro Phosphate (LFP) in lithium ions batteries. Recently, the LFP has also attracted manufacturer interest because it has a lot of advantages like charging capacity and many others. The theoretical charging capacity of LFP is 170 mAh/g [2]. And also, it has a high value of capacity than the other cathode materials such as LiMn₂O₄ with 117 mAh/g charging capacity. Moreover, the LFP is environmentally more benign material than the other cathode materials. For example LiCoO₂, indicates toxicity issue and also costly in preparation. Conversely, the LFP based materials also has a good cycle stability, and excellent thermal stability. These advantages, coupled with abundantly source of iron for the LFP synthesis become a promising and reasonable concern for production. However, the LFP based material has a low electrical conductivity. This paper applies citric acid as a carbon source was to be added to make a Lithium Iron Phosphate Carbon composite (LFP/C) for overcoming of the drawback [3].

Research using natural iron sand composed of Fe₂O₄ can be used as iron sources to form LFP/C precursor are still a wide apart. Some divalent and trivalent Fe-sources such as FeC₆H₅O₆,2H₂O, Fe(CH₃COO)₂, FeSO₄, and Fe(NO₃)₃ had been practiced as well [4]. However, these materials are still very expensive and even some of them are toxics.
Based on the preliminary study indicated that the natural iron sand from Tanah Laut Kalimantan, Indonesia, contained 98% of Fe. It was analyzed using x-ray fluorescent (XRF) spectrometer. Further analysis using x-ray diffraction (XRD) spectrometer showed the natural iron sand phase was identified as magnetite Fe₃O₄. The Fe₃O₄ is composed of FeO·Fe₂O₃ which have trivalent Fe³⁺ in Fe₂O₃ and divalent Fe²⁺ ion in FeO. This paper reports the work result of applying of this natural iron sand from this specific location for LFP/C precursor. Several papers have reported similar concerns, due to the electrochemical performance of Fe₃O₄ and also the low-cost production potency. However no work have been reported in manufacturing using of the local Indonesian resources. Many methods have been used to make LFP/C such as coprecipitation, solvothermal, hydrothermal, solid-liquid, and freeze granulation [5], but some of them are rather complicated. In this study, LFP/C was synthesized by a simple methodology, and implementing of the solid state synthesis strategy using high energy ball milling process [6,7].

EXPERIMENT

Chemicals and Instrumentation

Materials used for this research were lithium carbonate Li₂CO₃ (Sigma-Aldrich), di-ammonium hydrogen phosphate (NH₄)₂HPO₄ (Sigma-Aldrich) with purity >98%, citric acid C₆H₈O₇·H₂O, and natural iron sand with 98% Fe element content.

The instruments used for this study are oven, furnace, differential scanning calorimetry-thermal gravimetric analysis (DSC-TGA) (Mettler Toledo Star SW 10.0, thermal analysis from room temperature to 1400 °C and sample weight 15.2 mg), x-ray diffraction (XRD) spectrometer (Siemens D-501, Ni filter and graphite monochromator, x-ray source from Cu Ka radiation lambda 1.5406 A, with scanning angel from 15° to 65°) to identify the phase of LFP/C, and the FTIR spectrophotometer (recorded in Shimadzu 8400S).

Synthesis of Precursor

LFP/C compounds were prepared by high energy ball milling method [8]. The materials being used are Li₂CO₃, (NH₄)₂HPO₄, and Fe₃O₄ with 3:6:2 of mole ratio. A 5.0% weight citric acid as carbon sources was added to these materials to enhance the electron conductivity and to avoid oxidation of Fe ion. Then, 5.0 mL of alcohol was poured into a milling jar and milled together in 300 rpm rotation speed, for 3 hours. The resulted precursor was dried at 100°C (LFP-0) in oven. Then, similar procedure was applied and calcination was undergone in different temperature, i.e. 400°C (LFP-1), 500°C (LFP-2), and 600°C (LFP-3).

Characterization

The thermal properties of the sample was investigated using DSC-TGA for determine the variation temperature will be given to the sample. The calcination temperatures were varied in the range of (400-700 °C) to observe the formed phases of Lithium Ferro Phosphate Carbon composite (LFP/C) [9]. The sample before getting heat treatment named LFP-0, while the samples had been calcinated in 400, 500, and 600 °C named LFP-1, LFP-2, and LFP-3 respectively. XRD was adopted to identify crystalline phases on the samples. Chemical bonds, structural properties, and lattice dynamics was examined by Fourier Transformed Infrared Spectroscopy (FTIR). The crystalline phases and its composition in the XRD pattern were analyzed using Search Match software qualitatively and Rietica quantitatively.
RESULT AND DISCUSSION
DSC-TGA Analysis

The thermal properties of LFP/C were analyzed using DSC-TGA at room temperature until 1300°C. A large negative gradient at 100 to 300°C range temperature indicates a significant mass reduction in sample weight. The heat flow diagram in figure 1 shows that there is a thermal phenomenon at 400°C until 700°C. This indicates, that within this temperatures, a phases transformation undergoes. It is showed by thermal uprising decline the mass of sample. At temperature 200-300 °C, a weight-mass loss is sharply observed. However, in temperature above 300°C, there is no significant mass reduction observed. Within this temperature range, the implemented heat can not reduce the the mass sample farther. However, it is predicted that, the heat radiated the sample is absorbed for a phase transformation. In this temperature, the phase of Lithium Ferro Phosphate LFP is formed. Phases transformation from the initial composition for Li2CO3, (NH4)2HPO4, and magnetite Fe3O4, to other phases, such as diphosphate LiFeP2O7, nasicon Li3Fe2(PO4)3 and hematite.

Figure 1. The result from DSC-TGA analysis of the sample
The detailed of mass loss of LFP/C from DTA-TGA analysis indicate the physical properties of this material. The stepwise loss occur in peak of 149.81 °C and 196.83 °C, and 276.69 °C. The mass loss recorded is 2.99, 2.96, and 0.70 mg/°C, respectively. It is predicted the decomposed of volatile compounds, such as water, alcoholic matter and ammonia. Furthermore, the rest of the temperature shows a steady line and is predicted that the compounds with a stable composition is formed.

XRD Analysis

Figure 2 is showed the XRD diffractogram of the samples lithium iron phosphate/carbon composite (LFP/C) before and after calcination process. Calcination at 100 °C (LFP-0), 400 °C (LFP-1), 500 °C (LFP-2), and 600 °C (LFP-3). In overall, similar diffraction pattern is observed for LFP-1, LFP-2, and LFP-3. These similarity can also indicate similar composition and crystallinity of the LFP/C composite synthesized.

![Figure 2. The XRD diffractogram of lithium iron phosphate/carbon (LFP/C) composite](image)

Phase compositions of LFP-0 are 75.4: 16.9: 7.7 % weight comparison for (NH₄)₂HPO₄: Fe₃O₄: Li₂CO₃ respectively. The formed phases at 400, 500, 600°C temperature are trigonal Fe₂O₃, monoclinic LiFeP₂O₇ and Li₃Fe₂(PO₄)₃ [10], with the composition are summarized in Table 1. Calcination process at higher temperature give different LFP/C composite phase. The magnetite Fe₃O₄ is transformed become hematite Fe₂O₃. The major phase was formed at 400°C (LFP-1) calcination is diphosphate LiFeP₂O₇. Meanwhile, at higher temperature calcination, 500°C, the diphosphate phase of LiFeP₂O₇ is converted gradually, and turn it into nasicon Li₃Fe₂(PO₄)₃. Lastly, at the highest temperature
Calcination, 600°C (LFP-3), the dominant phases formed are nasicon $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ in 85.72%, in the absence of diphosphate LiFeP$_2$O$_7$ is abeerved.

Furthermore, it is also observed that increasing calcincation temperature indicate crystal agglomeration undergone. The diphosphate form, LiFeP$_2$O$_7$ is predicted become triphosphate, LiFe(PO$_4$)$_3$ form. And also, the hematite Fe$_2$O$_3$ composition is gradually decreased and turn in trace. Previously, the presence of this kind impurity deteriorated the battery performance, such as cyclability, charge-discharge capacity, and conductivity [11]. Calcination at 600°C give the highest content of LFP and a very low of impurities.

**Table 1. %-Weight phase composition of LFP/C after calcination**

| Sample  | Diphosphate (LiFeP$_2$O$_7$) (%) | Nasicon (Li$_3$Fe$_2$(PO$_4$)$_3$) (%) | Hematite (Fe$_2$O$_3$) (%) |
|---------|---------------------------------|--------------------------------------|--------------------------|
| LFP-1   | 58.28                           | 12.06                                | 29.66                    |
| LFP-2   | 32.57                           | 47.89                                | 19.54                    |
| LFP-3   | -                               | 85.72                                | 14.28                    |

**FTIR Analysis**

Lattice dynamics of lithium iron phosphate-based materials composite in carbon (LFP-1, LFP-2, and LFP-3) are studied by using FTIR spectrophotometric. The presence of functional group of these materials in the surface are recorded as the vibrational of each group due to irradiated by photon in infra red wavelength. Absorbance values (in absorption unit) is correlated to the energy absorbed by the specific functional group composed in LFP/C composite.

![Figure 3. The FTIR spectra of LFP/C sample](image-url)
The nasicon Li$_3$Fe$_2$(PO$_4$)$_3$ is built from anion framework of Fe$_2$(PO$_4$)$_3$, in which lithiums situated in the interstitial void in this framework [12]. The basic crystallography unit in diphosphate LiFeP$_2$O$_7$ is P$_2$O$_7$ anion with 2 main PO$_4$ tetrahedral bridging $\theta_{\text{POP}}$ angle. Modes in diphosphate consist of PO$_3$ and POP, and double bond PO [13]. The mode vibration located at 1227 cm$^{-1}$ assigned to the terminal P$_2$O$_7^{4-}$ ions stretching mode [10] as presented in Figure 3. The spectra band appears at 764 cm$^{-1}$ which is attributed to stretching modes of P-O-P bridges. The width and intense modes observed in 949 cm$^{-1}$ are due to the normal vibration of the bridging oxygen atom with alkali ion [14]. Moreover, the asymmetric stretching vibration of PO$_3$ appears in 1126 cm$^{-1}$, with the highest intensity detected in LFP-1 and also found in LFP-2. The nasicon framework, Fe$_2$(PO$_4$)$_3$, consists of the octahedral of FeO$_6$ and tetrahedral of PO$_4$ ion. Meanwhile, the vibration octahedral of FeO$_6$ occurs below 450 cm$^{-1}$, and vibration of the valence bond from the PO$_4^{3-}$ group is observed in between 400 and 700 cm$^{-1}$. The splitting of band peak at 1026, 1038, and 1072 cm$^{-1}$ are attributed to the coupling vibration of PO$_4$ in the nasicon compound, and that is not observed in LFP-1. Conversely, these band peak are clearly observed in LFP-3 which is dominated by nasicon phase.

The more broadening bands observed in LFP-1 and LFP-2 show more variation of vibration occurring, and because of more phases is formed. In LFP-3 there is two phase, so the peak intensity can be differ clearly, even in the XRD pattern of LFP-3 show less peak with the high crystallinity.

CONCLUSION

In short, lithium iron phosphate/carbon composite-based material cane synthesized in three different temperature of calcination. Their phase and composition are also able to be determined. The diphosphate phase LiFeP$_2$O$_7$ at is obtained at 400°C (LFP-1). The higher calcination temperature to at 600°C (LFP-3), decreased it gradually and transformed into nasicon Li$_3$Fe$_2$(PO$_4$)$_3$. The FTIR analysis also confirms the presence of their functional groups vibration modes. The highest composition of nasicon is produced in 85.72% after calcination at 600 °C (LFP-3). It is also provide a low amount of impurity and give a stable LFP phase.

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