The Effect of Sintering Time on Electronic Conductivity of LiFeGdPO$_4$/C as a Lithium-Ion Battery Cathode

Rahayu Iman*, Astutiningtyas Raissa Alaudina and Solihudin

Department of Chemistry, Faculty of Natural Sciences, Universitas Padjadjaran, Jl. Raya Bandung – Sumedang Km. 21 Jatinangor, INDONESIA

*iman.rahayu@unpad.ac.id

Abstract

Lithium iron phosphate (LiFePO$_4$) is an alternative cathode material choice in lithium-ion batteries because of its non-toxic nature, high voltage (3.45 V), the high theoretical capacity of LiFePO$_4$ (170 mAh/g), low cost, non-reactive and has good structural properties stability. However, LiFePO$_4$ has a low electronic conductivity ($10^{-10}$ S/cm) and a low diffusion coefficient of Li$^+$ ions ($10^{-12}$-$10^{-14}$ cm$^2$/s), so it affects electrochemical performance. There are several ways to increase the conductivity. These are namely carbon coating, metal ion doping and optimizing the sintering time. Optimal sintering time will increase crystallinity, thereby increasing the value of electronic conductivity. Then using the right sintering time will get a lot of the desired phase content.

This study aims to determine the effect of the sintering time variation 6 hours, 8 hours, 10 hours, 20 hours and 30 hours to increase the electronic conductivity of LiFeGdPO$_4$/C. The synthesis method used is the carbothermal reduction method with the precursors used are LiH$_2$PO$_4$, Fe$_2$O$_3$, Gd$_2$O$_3$ and carbon graphite. LCR meter and XRD are used to characterize samples. The results obtained indicate that the effect of sintering time can increase the value of the electronic conductivity of LiFeGdPO$_4$/C, with the highest conductivity value at a sintering time of 30 hours of 1.5296 x 10$^{-7}$ S/cm.

Keywords: Carbon coating, carbothermal reduction, electronic conductivity, LiFePO$_4$, sintering time.

Introduction

In this era of globalization, technological advances are very rapid, especially in recent years. Innovations are certainly very competitive in the world of technology, one of which is electrical energy storage in the form of batteries. Besides cost and safety, devices that use batteries, are usually rechargeable and have specific and volumetric density of stored energy. One of the batteries being developed today is the lithium-ion battery.

Lithium iron phosphate (LiFePO$_4$) is known to be the most promising alternative cathode material in lithium-ion batteries compared to lithium cobalt oxide (LiCoO$_2$), lithium spinel manganese (LiMn$_2$O$_4$), lithium nickel oxide (LiNiO$_2$), lithium vanadium oxide (LiV$_3$O$_8$) and olivine LiXPO$_4$ (X = Co, Mn, Ni). LiFePO$_4$ cathode exhibits high potential output, high theoretical capacity (170 mAh/g) and low cost. In addition, the LiFePO$_4$ has a high electrical voltage (3.45 V), good structural stability and is non-reactive. However, the drawbacks of LiFePO$_4$ are low electrical conductivity ($10^{-10}$ S/cm) and low diffusion coefficient of Li$^+$ ions ($10^{-12}$-$10^{-14}$ cm$^2$/s), thus causing low electrochemical performance.

To overcome these shortcomings, optimizing is possible through the size of the material, coating the surface with carbon and metal cation doping, as well as optimizing the precursor conditions, temperature and time during synthesis. Of these efforts, carbon plating is the most widely used method because of the many routes for electron transfer that cause a faster lithium-ion transfer to increase electronic conductivity. However, the carbon coating is not optimal enough to increase the value of the electronic conductivity of LiFePO$_4$. So, the effort that can be done is by doping metal cations, because it can change the distribution of electrons on the surface of LiFePO$_4$.

The element gadolinium has a particular electronic structure where the 4f electron shell is half-filled, because it has seven outer electrons. Gd$^{3+}$ metal cation doping can reduce particle size, can shorten Li$^+$ transport path, increase lattice disturbance in LiFePO$_4$/C and is expected to increase the electronic conductivity of LiFePO$_4$ proved by Rahayu et al that the conductivity value increased with Gd$^{3+}$ metal cation dopants which was 8.6901 x 10$^{-6}$ S/cm compared to without Gd$^{3+}$ metal cation dopants, which was 1.8952 x 10$^{-6}$ S/cm.

Optimal sintering time can affect the value of the electronic conductivity of LiFePO$_4$/C, because the sintering time is too short which will cause LiFePO$_4$/C not to react perfectly between the composite materials marked by their red color and causing low conductivity values. In addition, the sintering time that is too short, affects the crystals formed to be imperfect, so that it affects the electrochemical performance, where by prolonging the sintering time can increase the release capacity. Based on the research obtained by Sarwono et al, vary the sintering time of 4 hours, 6 hours, 8 hours and 10 hours. The crystal phase of LiFePO$_4$ was obtained at 10 hours of sintering.

Meanwhile, at the sintering time of 4 hours, 6 hours and 8 hours, other phases still formed such as Li$_3$Fe$_2$(PO$_4$)$_3$ and Fe$_3$O$_4$. It shows that as the sintering time increases, the content of the desired phase also increases. The sintering time of 30 hours in the study of Mi et al with variations in sintering time of 5 hours, 10 hours, 20 hours and 30 hours...
showed the best electrochemical performance as indicated by the high-capacity gain\(^4\).

This study aims to observe the effect of sintering time and to determine the optimum time for the synthesis of \(\text{LiFeGdPO}_4\)/C by carbothermal reduction method. The novelty of this research was carried out with variations in the sintering time of 6 hours, 8 hours, 10 hours, 20 hours and 30 hours as well as the optimum temperature referring to Rahayu et al\(^3\). The addition of Gd ion doping, carbon coating and optimizing the sintering time are expected to increase the electrical conductivity of \(\text{LiFeGdPO}_4\)/C, so that it can be applied to the cathode of lithium-ion batteries.

**Material and Methods**

**Materials:** Lithium dihydrogen phosphate (\(\text{LiH}_2\text{PO}_4\)) pa (Sigma Aldrich), iron (II) oxide (\(\text{Fe}_2\text{O}_3\)) pa (Sigma Aldrich), gadolinium oxide (\(\text{Gd}_2\text{O}_3\)) 99% pa (Merck), carbon graphite, acetone (\(\text{CH}_3\text{COCH}_3\)) pa Merck, ethanol (\(\text{C}_2\text{H}_5\text{OH}\)) pa Merck and argon gas.

**Preparation of \(\text{LiFeGdPO}_4\)/C:** The carbothermal reduction method was used to synthesize \(\text{LiFeGdPO}_4\)/C. At first, the precursors of \(\text{Fe}_2\text{O}_3\), \(\text{LiH}_2\text{PO}_4\) and \(\text{Gd}_2\text{O}_3\) were weighed with a mole ratio based on the formula \(\text{LiFe}_{0.93}\text{Gd}_{0.07}\text{PO}_4\). Then the three precursors were mixed, carbon graphite was added with a concentration of 6% (w/w) and a mixture of anhydrous ethanol:acetone (1:2). Then it was ground with a ball-mill (with a ratio of ball weight to powder (15:1) for 8 hours with a rotational speed of 280 rpm, so that \(\text{LiFeGdPO}_4\)/C powder was obtained. After that, the powder was molded in the form of pellets with a diameter of 2 cm with a thickness of ~1 mm and dried using an oven at 80°C for 2 hours\(^7\).

**Calcination:** After drying, the precursor mixture was calcined at 350°C for 6 hours in a furnace with argon gas flowing\(^7\).

**Carbothermal Reduction Process:** The powder was continued by sintering at a temperature of 850°C in a furnace with variations of sintering time for 6 hours, 8 hours, 10 hours, 20 hours and 30 hours\(^8,9\).

**Characterization:** The synthesis results were then characterized using an LCR meter to measure electrical conductivity and XRD to test the crystal structure\(^7\).

**Results and Discussion**

**Synthesis of \(\text{LiFe}_{0.93}\text{Gd}_{0.07}\text{PO}_4\)/C:** The synthesis of \(\text{LiFe}_{0.93}\text{Gd}_{0.07}\text{PO}_4\)/C cathode was done by using the carbothermal reduction method. The precursor was ground using a ball-mill for 8 hours and a red powder mixture of \(\text{Fe}_2\text{O}_3\) was obtained. The powder mixture sample is made into pellets to increase the effectiveness of the reaction between solids because the distance between the grains is getting closer. The precursor powder was molded into pellets with a diameter of 2 cm and a thickness of about 0.3 cm.

The pellets are heated in an oven to remove water and the acetone-ethanol mixture, then calcined to remove impurities in the form of oxide compounds through a carbon coating process. The calcination process on the pellets was carried out at a temperature of 350°C for 6 hours and the results of the sample were still red. According to Rahayu et al\(^7\), the release calcination oxide molecules such as \(\text{H}_2\text{O}\) at 100°C and a color palette that is still red, indicate an unreacted precursor\(^7\). The length of holding time for calcination affects the formed phase which becomes less and more crystalline, because the energy absorbed by the particles becomes more and more for diffusion so that there is a change in the crystal structure to become more crystalline.

\(\text{LiFe}_{0.93}\text{Gd}_{0.07}\text{PO}_4\)/C crystals formation process to achieve maximum results was sintered at a temperature of 850°C with variations in sintering time for 6 hours, 8 hours, 10 hours, 20 hours and 30 hours in a container in which there is already alumina crucible containing samples that are flowed with argon gas. The argon gas is flown during the calcination and processes sintering aimed at preventing oxidation of Fe, so that the reduction conditions are controlled by heating in the furnace\(^4\).

The sintering results are shown in figure 1. Each sample shows a cracked surface. This is due to the micro cavities formed due to the trapped gases in the composite which become stress concentration points and combine to form cracks which are affected by the high heating rate, causing fracture. The heating rate affects the density of a sample where the lower the sintering heating rate will increase the sample densification rate so as to increase the bond between the particles. Furthermore, the result of the synthesis of \(\text{LiFe}_{0.93}\text{Gd}_{0.07}\text{PO}_4\)/C was measured for its conductivity value to determine the effect of variations in sintering time.

**LCR meter analysis of \(\text{LiFe}_{0.93}\text{Gd}_{0.07}\text{PO}_4\)/C:** Figure 2 shows a graph of conductivity values with variations in sintering time measured by the LCR meter. The graph created is a correlation graph to determine the relationship between 6 hours, 8 hours, 10 hours, 20 hours and 30 hours of sintering time. This graph of 6 hours, 8 hours and 10 hours of sintering time variation shows a fairly sharp increase and the conductivity value from 10 hours to 30 hours shows a gentle graph. The measurement results are listed in the attachment and the highest electronic conductivity value is obtained at a sintering time of 30 hours at \(1.5296 \times 10^7\) S/cm.

The conductivity value in the 20 hour sintering time sample decreased in the conductivity value compared to 10 hours which was not shown on the curve of \(6.32877 \times 10^8\) S/cm. The surface of the sample looks different from the others, namely the surface that looks burnt. This is probably caused by a lot of carbon being burnt and reacting with oxygen obtained from the argon gas stream during the sintering process to form \(\text{CO}_2\), so that the carbothermal reduction process is hampered.
In addition, supported by a high heating rate causes the sample to be in a state of crack that is quite worse than the cracks of other samples, so that when the measurement of the conductivity value becomes uneven due to a bad surface, the conductivity value becomes low.

The results with the highest conductivity value at a sintering time of 30 hours showed a relatively low conductivity value. According to Mi et al.\(^4\), the particle size will experience a slight growth as the sintering time increases and if the sintering time is too long, it will obtain an abnormal particle size so that the morphology will appear to agglomerate and cause the conductivity value to decrease\(^4\).

**XRD analysis of LiFe\(_{0.93}\)Gd\(_{0.07}\)PO\(_4\)/C:** Analysis of LiFe\(_{0.93}\)Gd\(_{0.07}\)PO\(_4\)/C synthesized in 30 hours sintering time
was carried out using software Highscore Plus displayed in figure 3. The synthesis result was characterized by XRD with a wavelength of CuKα 1.541874 Å in the range between 10º-90º angle.

The results of XRD analysis show that the crystalline phase formed is the main phase LiFePO₄ (ICSD98-026-0571) and the secondary phase is Li₃Fe₂(PO₄)₃ (ICSD98-006-9345) seen in the diffraction peaks in figure 3. The phase of LiFePO₄ or called tryphylite shows an orthorhombic crystal system (space group Pnma), as well as quite sharp peaks at 20,789º, 25,643º, 29,731º and 35.615º while the secondary phase of Li₃Fe₂(PO₄)₃ shows a monoclinic crystal system with fairly sharp peaks of 20,726º, 20,852º and 29,397º. The secondary phase of Li₃Fe₂(PO₄)₃ is a transition phase that will react with Fe₂O₃ together with reducing carbon to reach the LiFePO₄ phase, while the O²⁻ anion will react with carbon to form CO₂. Gas CO₂ then evaporated and wasted following the Ar inert gas flow.

The transition phase formed indicates that the reaction has not reached the desired phase completely⁶. This is indicated by the percentage of LiFePO₄ phase formed at LiFe₀.₉₃Gd₀.₀₇PO₄/C of 11%. In addition, the impurities formed are in the form of the hematite phase Fe₂O₃. This is caused by several possibilities such as the O₂ gas carried by the gas flow or derived from O₂ trapped in bulk precursors causing oxidation.

The lattice parameters and cell volume are shown in table 1. The cell volume obtained almost reached the normal limit of 29.14 nm³. According to Lin et al⁵, generally crystalline LiFePO₄ has a poor crystallinity when the cell volume is greater than the normal value. This is due to the presence of defects such as the Gd position. The cell volume is influenced by the size of the doped ion radius. The larger is the ion radius than the doped ion radius, the larger the particle lattice volume will be. This is because the doping ion radius is larger to replace the lattice parameter position of the doped element. The volume of this cell can be decreased by compensating for thermal expansion or temperature.

The crystal size of LiFe₀.₉₃Gd₀.₀₇PO₄/C which was sintered for 30 hours was obtained at 1106 (110.6 nm) based on Scherrer calculations on the software Highscore Plus. These results indicate that the sintering time affects the crystal size. If the sintering time is larger, the crystal size also increases. The synthesized crystal size is large enough to affect the lithium ion intercalation/de-intercalation where the crystal size will narrow the surface area. This will reduce the contact between particles and the uneven distribution of particles, thereby reducing the conductivity value.

In addition, the length of sintering time also affects the crystallinity of LiFe₀.₉₃Gd₀.₀₇PO₄/C synthesized obtained 83.5%. If the sintering time is larger, the crystallinity also increases. This can be seen from the XRD diffraction pattern which shows the intensity of the peaks increasing and the peaks narrowing, where the height of the peaks and the thinness of the width of the peaks indicate that the crystallization level is quite high.

![Figure 3: Diffractogram synthesized result with a sintering time of 30 hours.](image)

<table>
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<th>LiFe₀.₉₃Gd₀.₀₇PO₄/C Lattice Parameters</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>V (nm³)</th>
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Table 1: LiFe₀.₉₃Gd₀.₀₇PO₄/C Lattice Parameters
Conclusion
The sintering time for 30 hours showed the highest increase in conductivity value of $1.5296 \times 10^{-7}$ S/cm with the sintering time variation as 6 hours, 8 hours, 10 hours, 20 hours and 30 hours in the synthesis of LiFe$_{0.93}$Gd$_{0.07}$PO$_4$/C. However, the conductivity value of LiFeGdPO$_4$/C is still relatively low due to the large crystal size of 110.6 nm.

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