X-ray Diffraction (XRD) and X-ray Absorption Near Edge Spectroscopy (XANES) Analyses of LiFe$_{1-x}$Cu$_x$PO$_4$ Powders

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Abstract. Data analyses of XRD and XANES using Fe as absorber have been conducted which were aimed for phase identification, Fe oxidation state determination, absorption edge value ($E_0$) calculation, and valence electron determination of LiFe$_{1-x}$Cu$_x$PO$_4$ ($x = 3\%$, $4\%$, and $5\%$) powders. The powders were prepared by a dissolution method with the source of Fe was local ironstone from South Kalimantan, Indonesia. Analyses of the x-ray diffraction data of the powders were done using the Rietveld method. The XANES data were acquired using Fe K-edge spectral techniques at Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. Results showed that olivine was the only identified phase in the LiFe$_{1-x}$Cu$_x$PO$_4$ powders. Further analyses gave the crystallite size of 188, 193, and 205 nm and cell volume of 278.96, 279.12, and 280.52 Å$^3$, for the $x = 3$, 4, and 5% samples, respectively. Qualitative analysis of the XANES data acquired for all samples showed the oxidation state of Fe$^{2+}$, and the absorption edge values ($E_0$) were 7121.56, 7121.71, and 7121.75 eV for the samples.

Keywords: LiFe$_{1-x}$Cu$_x$PO$_4$, XANES, Rietveld method, crystallite size, absorption edge.

1. Introduction

The increasing world electricity needs and tight community activities require a breakthrough in energy storage that is easy to carry, namely batteries. One of the excellent batteries regarding energy storage is the lithium battery [1]. There are several types of lithium battery compilers, namely lithium cobalt oxide (LCO), nickel cobalt aluminum (NCA), nickel manganese cobalt (NMC), lithium manganese oxide (LMO), lithium iron phosphate (LFP). LFP has good characteristics, which has a long lifecycle, high gravimetric energy density, [2], thermal stability, and high power capability [3]. However, the LiFePO$_4$-type battery has disadvantages, i.e., relatively low electrical conductivity [3] and low ion diffusion [4]. Therefore, modifications are needed so that the lacking characteristics are overcome. One of them is using Cu doping which aims to increase electrical conductivity.

Previously, Cu-doped LiFePO$_4$ (LFCP) was synthesised by polyol method using FeSO$_4$.7H$_2$O precursor [5], sol-gel method using FeCl$_2$.4H$_2$O precursor [6], mechanical ball milling method using Fe$_2$(C$_2$O$_4$)$_3$.6H$_2$O precursor [7], and hydrothermal method using Fe$_3$O$_4$ precursor [8]. The literature shows that commercial Fe precursor was used for synthesising LFCP. In this study, we use a natural
resource namely ironstone as the Fe precursor for synthesizing LFCP. The LiFe$_{1-x}$Cu$_x$PO$_4$ powder is explored on their crystal and local structures. There are 2 types of lithium ferro phosphate namely olivine and nasicon. The olivine structure has an oxidation state of 2+ [9] while the nasicon structure has an oxidation state 3+ [10]. In this study, we focus on the olivine phase which has relatively enhanced properties. The oxidation state can be studied using XANES [11].

2. Methods
The Fe precursor used for the synthesis of the LFP is ironstone from South Kalimantan, Indonesia. The ironstone was ground and then dissolved with HCl at 100°C for 1 hour. The solution was filtered to separate the impurities in the solution. From the treatment, we obtained a FeCl$_2$+FeCl$_3$ solution. Then, the solution was added with a solution of CuCl$_2$ (considering dopant percentage of 3, 4, and 5 at.%), called solution A. An amount of lithium carbonate was dissolved in HCl solution at 100°C. This solution was called solution B. NH$_4$H$_2$PO$_4$ powder was dissolved in water at room temperature and called solution C. Then, solutions A and B were thoroughly stirred, and then the solution C was added to the mixed solution. The treatment gave solution D, which was titrated with NH$_4$OH until pH 4 was obtained. This solution was heated at 100°C for an hour to form a gel and then was further heated at 350°C for drying. After that, the powder was calcinated at 700°C for 10 hours in a nitrogen atmosphere. The calcined powders were characterized using XRD to identify the phase and crystal structure of the material, and XANES for oxidation state analysis. The XANES measurement was performed by using Fe K-edge spectral techniques at Beam-line 8 of the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. The XANES data were analyzed using ATHENA presented by IFEFFIT [12].

3. Results and Discussion
Figure 1 displays the XRD patterns of all samples. The diffraction pattern confirms the olivine phase LiFePO$_4$ according to PDF number 083-2092. The diffraction pattern shows no other phase, but there is one unidentified peak of impurity which is not the peak of Cu. This indicates that Cu ions have successfully substituted some of the Fe ions in the olivine phase, to form LiFe$_{1-x}$Cu$_x$PO$_4$ (LFCP). The success of doping can be proven by Rietveld analysis using Rietica. The results of Rietveld analysis using Rietica and MAUD are shown in Table 1. The lattice parameter values of the samples are similar to the literature [13]. The greater the percentage of dopants, the greater the lattice and cell volume parameters. This is caused by the ionic size of the dopant (Cu$^{2+}$) is larger than that of iron, which is in accordance with the literature [14].

A relatively broadened peaks in the diffraction pattern (Figure 1) indicates that the samples have subnanometric crystal sizes [15]. This is approved by the Rietveld analysis using MAUD (COD database 1101111), the results of which are shown in Table 1. The values of the goodness of fit were around 1.7% (Sig) implying that the Rietveld refinement was accepted. The crystallite size value for the samples is about ±190 nm. It is worth noting that the greater the percentage of dopants, the greater the crystallite size.

The XANES data of all samples are presented in Figure 2. The pre-edge peak is informative to describe the oxidation state and coordination number of Fe. The peak of the pre-edge denotes a transition from 1s-states to 3d-states. In our case, the peak also indicates that there is mixing of the transition between the d-states of the Fe atom and the p-states of oxygen atoms surrounding the Fe atom [16]. The pre-edge and $E_0$ values are shown in Table 2. The pre-edge values of all samples are ~7112 eV which are in a good agreement with the theoretical and previous experimental values [9]. Figure 2 also shows that Fe atoms are octahedrally coordinated by oxygen atoms. The weak intensity is an indication for octahedral coordination of Fe (the 3d orbital) and O (the 4p orbital), whereas a strong intensity shows tetrahedral coordination [16].
Figure 1. XRD pattern of LiFe$_{1-x}$Cu$_x$PO$_4$ samples

Table 1. Rietveld analysis results using Rietica and MAUD software.

| Sample (% Cu) | Rietica | MAUD |
|--------------|---------|------|
|              | $a$ (Å) | $b$ (Å) | $c$ (Å) | Cell volume ($\text{Å}^3$) | $G_0$ | Size (nm) | Sig (%) |
| 3            | 10.1826 | 5.9196 | 4.6279 | 278.96 | 1.651 | 188 | 1.79 |
| 4            | 10.1865 | 5.9231 | 4.6260 | 279.12 | 1.335 | 193 | 1.62 |
| 5            | 10.2026 | 5.9303 | 4.6363 | 280.52 | 1.566 | 205 | 1.79 |

In Figure 3, Fe K-edge (pre-edge) XANES spectra of LFCP samples are compared with those of standard iron oxides (FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$). The comparison is presented with the aim to clarifying the oxidation state of Fe in the LFCP. Lower oxidation corresponds with lower absorption energy. The figure shows that the pre-edge position of LFCP is in general similar to that of FeO standard (~7112 eV). It means that the oxidation state of LFCP is 2+ which is comparable to the literature [9]. It is known that the pre-edge peak of Fe$^{3+}$ is ~7114 eV while Fe$^{2+}$ is ~7112 eV [9]. In addition, the “edge” ($E_0$) is described as the first derivative peak in an XAS spectrum [17]. The $E_0$ values of all samples are presented in Table 2. They are ~7121 eV which again corresponds to the literature [18]. In this study, the addition of dopant did not affect the oxidation state of the samples.
Figure 2. XANES spectra of LiFe$_{1-x}$Cu$_x$PO$_4$ samples at the Fe K-edge

Figure 3. Fe K-edge (pre-edge) XANES spectra comparison of LFCP and standard iron oxides.

Table 2. $E_0$ values of all samples

| Sample (% Cu) | Pre-edge (eV) | $E_0$ (eV) |
|---------------|--------------|------------|
| 3             | 7112.34      | 7121.56    |
| 4             | 7112.54      | 7121.71    |
| 5             | 7112.97      | 7121.75    |

4. Conclusion

Solid solution of LiFe$_{1-x}$Cu$_x$PO$_4$ (x = 3, 4, and 5 at.%) powders have been successfully synthesized by a hydrothermal method with Fe source was ironstone from South Kalimantan, Indonesia. XRD data analysis showed that the crystallite size and cell volume were 188, 193, and 205 nm and were 278.96, 279.12, and 280.52 Å, for the x = 3, 4, and 5% samples, respectively. Furthermore, the Fe K-edge XANES data showed that the LiFe$_{1-x}$Cu$_x$PO$_4$ powders exhibited 2+ oxidation number with absorption edge values of 712.56, 712.71 and 712.75 eV for the same series.

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