EXAFS Study on LiFePO₄ Powders Produced From Two Sol-Gel Routes

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Abstract. The local structure of LiFePO₄ powders has been investigated using Fe K-edge Extended X-Ray Absorption Fine Structure (EXAFS) Spectroscopy data. The synthesis of LFP powders was carried out using two different sol-gel methods. The raw materials for Fe source were ironstone and commercial precursor of FeCl₂·4H₂O. Synthesis using natural materials produced two phases, namely LiFePO₄ olivine and Li₄Fe₄(PO₄)₂ nasicon, whereas that using a commercial product produced a single phase of LiFePO₄ olivine. The EXAFS data for both samples were collected at Synchrotron Light Research Institute (SLRI), Thailand. Fitting of the model on the experimental curve provided parameters that can be interpreted as the distance between Fe as the absorber and the nearest atoms on the LFP materials. The EXAFS data analysis has shown that synthesis of LFPs using different Fe sources gives slightly different nearest-neighbor distances, namely Fe-O of 0.21% - 0.23%, Fe-P of 0.14% - 0.16%, Fe-Fe of 0.12% for both samples, respectively.

1. Introduction

Lithium batteries have the required criteria as energy storage media for portable electronic devices since they exhibit large capacity and energy density, high electrochemical potential, durable and rechargeable [1], [2]. The lithium battery components are cathode, anode, electrolyte, and separator. The common cathode materials include LiMn₂O₄ [3], LiCoO₂ [4] and LiFePO₄ [5]. Among these cathode materials, LiFePO₄ is very promising because it has a theoretical capacity of about 170 mAh/g, a specific energy of 0.59 Wh/g, the density of 3.60 g/cm³, the potential of 3.5 V, non-toxic and environmental friendly [1], [6]. However, it has a low electrical conductivity of approximately 10⁻⁹–10⁻¹⁰ S/cm and slow diffusion rate about 10⁻¹²–10⁻¹⁴ cm²/s [7]. These characteristics are attributed to the general structural nature of the material.

The local structure is the distribution of atoms around the absorbing atom. The local structure examines the distance between the absorber atom and the nearest neighbor atoms, while the crystal structure studies about the distance between the diffraction planes in a crystal building. The local structure can be determined through Extended X-ray Absorption Fine Structure (EXAFS) data analysis. The EXAFS spectrum is affected by photoelectron scattering in the absorption range from ~30 to ~1000 eV above absorption edge and provides information about the local structure, the number of coordination, interatomic distance, Debye-Waller disorder parameter [8], [9].
Methods that can be used in LiFePO₄ synthesis included solid-state reaction, sol-gel, and hydrothermal. The sol-gel method, however, has advantages on controlling the morphology and particle size of the product, resulting in homogeneous particles and high phase purity. In this research, the basic materials used are a natural material, namely ironstone, and commercial product, i.e. FeCl₂·4H₂O. The effect of the Fe source on the local structure of LFP was investigated using EXAFS. Differences in local structure may affect the physical properties, such as the electrical conductivity. The distance between the absorber atom and the nearest neighbor atoms should be larger than the ionic radius of Li⁺ as the charge carrier, in order to make the ionic Li⁺ move around the neighboring atoms.

In this study, we compare the results of LFP characterization produced by two different sol-gel methods. The studied issues are the formed phases and the local structure of LFP.

2. Experimental Section

2.1 Synthesis using natural materials

The ironstone as the Fe source was dissolved in HCl 37% at 100 °C. Then filtering was done to separate the solution with the nonmetallic elements. Li₃CO₃ (lithium carbonate, Merck) and NH₄H₂PO₄ (ammonium dihydrogen phosphate, Merck) were dissolved in HCl 37% and deionized water. Each solution was mixed dropwise with continuous stirring at temperature 100 °C for 1 hour. After that NH₄OH (ammonium hydroxide) was added to the solution until pH 4 was achieved while stirring was continued until a gel has formed. The gel was dried at temperature 300 °C. The precursors were milled for 6 hours using planetary ball milling and alcohol as mixing medium. The resultant was dried and calcined at 600 °C for 10 hours under a flow N₂ atmosphere at a heating rate of 5 °C min⁻¹. The product was a powder and denoted as sample A.

2.2 Synthesis using commercial materials

From resulting of stoichiometry, FeCl₂·4H₂O and NH₄H₂PO₄ were dissolved in deionized water, and Li₃CO₃ was dissolved in HCl 37%. The solutions were mixed dropwise with continuous stirring. The next steps are similar to those in the use of natural stone except that (1) the pH was 7, (2) gel formation temperature of 80 °C, (3) drying at 120 °C and (4) calcination at 700 °C for 10 hours under a flow Ar atmosphere with the heating rate of the furnace was 5 °C min⁻¹. The powder product was designated as sample B.

2.3 Analysis of EXAFS data

EXAFS measurement was carried out at beamline 8 at the Synchrotron Light Research Institute (SLRI), Thailand. Analysis of EXAFS data was processed using Athena and Artemis program using FEFF8 program-based theoretical standard calculation [10]. The files that can be fed on FEFF8 are "feff.inp" using the Atom program. For crystalline materials, the Stand Alone Atom program can also directly translate crystallographic data (cif) into the form of "feff.inp"[11]. The sequence of EXAFS data processing is first, normalized then interpolated to k-space. Information which can be obtained from an EXAFS data analysis includes the distance between atoms, the number of coordination and Debye-Waller factors (σ²) [11].

The identification phase was verified by X-ray diffraction (XRD) using Match!2 program. The morphology of sample was observed by Scanning Electron Microscope (SEM). The local structure was obtained from Extended X-ray Absorption Fine Structure (EXAFS) measurement.

3. Result and Discussion

3.1 Identification phase of LiFePO₄

Figure 1 shows the X-ray diffraction pattern of Samples A and B. Sample A contains two phases, i.e. olivine LiFePO₄ (PDF 083-2092) and nasicon Li₁Fe₂(PO₄)₃ (PDF 078-1465), whereas Sample B contains only olivine. The presence of two phases in Sample A is due to the ironstone used as the Fe source has two Fe ions, i.e., Fe²⁺ and Fe³⁺. LFP olivine has a Fe²⁺ oxidation state and LFP nasicon has a Fe³⁺ oxidation state [12]. Meanwhile, synthesis using FeCl₂·4H₂O as the Fe source gives
single phase olivine. The reason is that the base material has only one type of Fe ion in the formation of LFP, that is Fe$^{2+}$.

![X-ray diffraction pattern of LFP synthesized using natural material (A) and commercial material (B).](image)

**Figure 1.** X-ray diffraction patterns of LFP synthesized using natural material (A) and commercial material (B). (Θ = LiFePO$_4$; □ = Li$_3$Fe$_2$(PO$_4$)$_3$)

### 3.2 Local structure of LiFePO$_4$

The normalized background-subtract k$^3$-weighted [$k^3\chi(k)$] Fe EXAFS pattern for LFP which the synthesis from Samples A and B are shown in Figure 2. It can be seen that in principle they have a similar peak shape.

Data $\chi(k)$ describes the oscillation of backscattering waves in the area around ~10Å, which provides information around the central atom (Fe absorber) [13]. The k-weight spectrum in k-space defines the area of the spectrum to be analyzed and depends on the element used. The $\chi(k)$-k$^3$ patterns in k-space oscillate periodically indicating that $\chi(k)$ as a wave function derives from regularly arranged atoms. This ordered arrangement is then extracted in the form of atomic positions using Fourier transforms by changing EXAFS oscillations $\chi$ from k-space to r-space.

![Normalized background-subtract k$^3$-weighted [k$^3\chi(k)$] Fe EXAFS for LFP for samples A and B.](image)

**Figure 2.** Normalized background-subtract k$^3$-weighted [$k^3\chi(k)$] Fe EXAFS for LFP for samples A and B.

The results of the Fourier transform of the background-subtract k$^3$-weighted ($k^3\chi(k)$) was used to determine the radial structure function of EXAFS Fe K-edge of LFP - see Figure 3. The function of the radial structure of the result of a match between the experimental results and the model obtained from the Fourier transform of the EXAFS Fe K-edge spectrum. The first high peak can be associated with the scattered electron that is released at the nearest atom of the oxygen-containing absorber. The
second and third peaks appear as the effect of the scattered electron that is respectively released by phosphor and iron. Both samples have the same shape and intensity of Fe-O, Fe-P and Fe-Fe peaks that imply similar local structures [13].

The fitting of the Fe-edge EXAFS patterns provides an output of parameters that interprets the distance between Fe absorbing atom to the nearest atoms in the LFP materials as summarized in Table 1. The distance between atoms and coordination numbers for LFP samples A and B are not much different which indicates that their local structures are similar [13]. The natural LFP (A) has a slightly shorter interatomic distance as compared to the commercial LFP (B). The difference between interatomic distances for both samples is 0.12% for Fe-Fe, 0.14% - 0.16% for Fe-P and 0.21% - 0.23% for Fe-O. The difference in the distance between the atoms for each sample or the shift of atoms from its equilibrium position can be due to a charge difference of the structure that can generate an internal electric field. This internal electric field may affect the movement of charged particles in the structure. Charged particles with free movement would result in a greater electrical conductivity so that it affects the electrical properties of the LFP. It is interesting to note that Li\(^+\) ion has an ionic radius of 0.9 Å [16], while the distance between Fe-O atoms is about 1.93140 Å and 1.93576 Å for LFP A and B respectively. Thus Li\(^+\) ions in both LFP samples may perform intercalation equally well.

| Sample | Sphere | Zr-Zs | CN | r(Å) | σ²(Å²) | R-factor (%) |
|--------|--------|-------|-----|------|--------|--------------|
| A      | Fe-O   | 1     | 2   | 1.93140 | 0.02677 |              |
| A      | Fe-O   | 1     | 1   | 1.97600 | 0.05139 |              |
| A      | Fe-O   | 1     | 1   | 2.07410 | 0.16056 |              |
| A      | Fe-P   | 2     | 1   | 2.70140 | 0.00156 | 1.88         |
| A      | Fe-P   | 2     | 1   | 3.07830 | 0.51775 |              |
| A      | Fe-P   | 2     | 3   | 3.11730 | 0.05089 |              |
| A      | Fe-Fe  | 3     | 4   | 3.71310 | 0.27080 |              |
| B      | Fe-O   | 1     | 2   | 1.93576 | 0.02740 |              |
| B      | Fe-O   | 1     | 1   | 1.98036 | 0.06359 |              |
| B      | Fe-O   | 1     | 1   | 2.07846 | 0.13774 |              |
| B      | Fe-P   | 2     | 1   | 2.70576 | 0.00209 | 1.85         |
| B      | Fe-P   | 2     | 1   | 3.08266 | 0.58178 |              |
| B      | Fe-P   | 2     | 3   | 3.12166 | 0.09857 |              |
| B      | Fe-Fe  | 3     | 4   | 3.71746 | 0.16697 |              |

\(a\) Central absorber and scattering atom correlation
\(b\) Coordination number
\(c\) Interatomic distance
\(d\) Debye-Waller factor

Figure 3. The result of fitting experimental data and EXAFS Fe K-edge model data for LFP
samples A and B.

4. Conclusions

The result of LFP synthesis using natural materials has two phases namely LiFePO$_4$ olivine and Li$_3$Fe$_2$(PO$_4$)$_3$ nasonicon and for LFP synthesis using commercial materials have a single phase that is LiFePO$_4$ olivine. Analysis of their local structures using EXAFS data resulted in acceptable fittings with an R-factor value of less than 0.02. Both materials have almost the same peak shape and intensity which implies that their local structures are similar.

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