Chapter 3

Synthesis and Characterization of LiFePO₄

3.1 Synthesis of LiFePO₄

Whittingham et al prepared Olivine LiFePO₄ by hydrothermal synthesis [1]. It has also been synthesized by hydrothermal synthesis [2–4], solid state synthesis [5, 6–14], sol-gel synthesis [15–19], microwave processing [20, 21], aqueous precipitation technique [22], organogel synthesis [23], emulsion drying synthesis [24] and ultrasonic spray pyrolysis [25]. In all the above methods, the precursor mixture is treated under Nitrogen, Argon or reducing atmosphere. Lithium iron phosphate has also been synthesized by Meng li et al [26] adopting the vacuum as environment for heating the starting materials.

Though LiFePO₄ has many advantages over the other lithium cathode materials from commercial point of view, one of the limitations is its low electronic conductivity, which directly influences the rate performance of the material [6]. The other two drawbacks in synthesis that limit high performance of LiFePO₄ are the formation of Fe³⁺ phase during the synthesis and the undesirable particle growth [14]. While the former destabilizes the olivine structure during charge – discharge cycle, the latter leads to slow electronic transport in the cathode caused by fairly low electronic conductivity of the active cathode material. In this context, synthesizing nanoparticles of LiFePO₄ assumes considerable importance, to help ensure short diffusion length for its reaction with lithium. One way to increase the intrinsic electronic conductivity is through cation doping [27]. The other is synthesizing an electronic conductive phase of carbon coated sub-micron particles of LiFePO₄ [14, 28–31].

In our laboratory, we have synthesized the nanoparticles of in-situ surface carbon coated LiFePO₄ using non-aqueous sol-gel route. The flowchart for the synthesis is given in figure 1. Initially Lithium acetate dihydrate (Loba chemicals), Ferrous oxalate dihydrate (Riedel-de Haén) and Ammonium dihydrogen phosphate (Merck) were taken in the stoichiometric ratio of Li:Fe:P = 1:1:1 and were thoroughly stirred in minimum amount of Ethylene Glycol (Ranbaxy, Mol.wt. = 62.07) to form a gel with the precursor materials mixed at the microscopic level. A certain amount (90mg) of the gel so obtained was transferred to an alumina crucible. Dynamic calcinations were carried out in the furnace of a thermo-gravimetric analysis (TG) device (NETZSCH STA 409 PC/PG). The precursor mixture was dynamically heated up to 1000°C with a heating rate of 10°C min⁻¹.
Figures 1 and 2 illustrate the synthesis and characterization process of LiFePO₄ nanoparticles. Figure 1 shows the flow chart of the sol-gel synthesis route adopted for nanoparticles of LiFePO₄. The synthesis process involves mixing the following chemicals in a 1:1:1 ratio: Lithium Acetate diHydrate, Ferrous Oxalate diHydrate, and Ammonium diHydrogen Phosphate. This mixture is then stirred for several hours to form a precursor gel. The gel is dried in a furnace at 700°C for 12 hours under nitrogen atmosphere. The resulting nanoparticles of LiFePO₄ are cooled to room temperature under nitrogen atmosphere and ground thoroughly in dry air.

Figure 2 shows the TG record on the precursor mixture of LiFePO₄ under N₂ atmosphere at a heating rate of 10°C/min. This record indicates that the precursor mixture should be heated around 700°C. To prevent oxidation, a continuous flow of nitrogen is maintained in the furnace during heating. The precursor gel is taken in an alumina crucible and kept in a furnace with dry nitrogen gas flushed for 2 hours, followed by heat treatment at 700°C for 12 hours. The sample is then cooled to room temperature under nitrogen atmosphere and ground thoroughly in dry air.
The selection of materials in our synthesis route differs from that of Jingsi Yang et al [18] due to the following reasons. Lithium acetate and ferrous oxalate were selected as starting materials (Fe$^{2+}$-oxalate in particular) as they belong to a select group of materials employed in solid-state chemistry for thermally induced synthesis of various nanocrystalline metal oxides [32–37]. The selection of ammonium dihydrogen phosphate also ensures the availability of sufficient amount of (PO$_4$)$^{3-}$ ions required for the reaction. Besides the decomposition of lithium oxalate and ferrous oxalate (in particular) in dynamic nitrogen atmosphere allows full participation-in the reaction(s)- of the gaseous intermediates (CO, CO$_2$), yielding only Fe$^{+2}$ ions at temperatures as high as above 535$^\circ$C, as reported by Martin et al [38]. Figure 2 represents the TG recorded on the precursor mixture in the temperature range from 30$^\circ$C to 1000$^\circ$C at 10$^\circ$C per minute. From this figure, it is clearly evident that ~ 700$^\circ$C, is the optimal temperature for the formation of monophasic LiFePO$_4$, The steps involved in this synthetic strategy are delineated in the mass losses suffered by the reactants. The mass lost at different stages due to heating the gel in the TG furnace could be ascribed to the following processes [38]:

1. Release of crystal water proceeding within the temperature range of 170 – 230$^\circ$C:
   \[
   \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{FeC}_2\text{O}_4 + 2\text{H}_2\text{O}
   \]
2. Thermal decomposition of ferrous oxalate to magnetite at temperature around 306$^\circ$C:
   \[
   3\text{FeC}_2\text{O}_4 \rightarrow \text{Fe}_3\text{O}_4 + 4\text{CO} + 2\text{CO}_2
   \]
3. Reduction of ferrous oxalate by CO to Fe$_3$C at temperatures above 360$^\circ$C:
   \[
   3\text{FeC}_2\text{O}_4 + 2\text{CO} \rightarrow \text{Fe}_3\text{C} + 7\text{CO}_2
   \]
4. Thermal conversion of Fe$_3$C at temperatures above 423$^\circ$C:
   \[
   \text{Fe}_3\text{C} \rightarrow 3\text{Fe} + \text{C}
   \]
5. Thermally induced reduction of magnetite to FeO by CO above 550$^\circ$C:
   \[
   \text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2
   \]

Upon heating the precursor mixture in a dynamic nitrogen atmosphere at elevated temperatures (above 600$^\circ$C), the decomposition of precursor mixture takes place releasing the Fe(+2) ions only. The continuous availability of the gaseous products (CO, CO$_2$) promotes the complete reductive decomposition of acetate and oxalate (iron oxalate in particular) and ensures the complete absence of Fe(+3) ions (or phases). It may be reasonably assumed that during the initial stage of heating, the decomposition of oxalates takes place slowly. At this stage of the synthesis, decomposed, undecomposed materials, and the gaseous products co-exist so that the release of Fe$^{++}$ ions is dynamically controlled. This controlled release of Fe$^{2+}$ ions would lead to their movement towards the already existing PO$_4$ tetrahedra to form FeO$_6$ octahedra and to enhance the formation of nucleation centers for the nanocrystalline growth. The Li$^+$ ions also released meanwhile go through the tunnels
formed by the interlocking of FeO₆ octahedra and PO₄ tetrahedra to form nanoparticles of phase pure LiFePO₄, as shown below.

\[ \text{Li}^+ + \text{Fe}^{2+} + (\text{PO}_4)^{-3} \rightarrow \text{LiFePO}_4 \]

3.2 Characterization

3.2.1 Crystal structure

The sample was characterized by X-ray diffraction (XRD) using PHILLIPS X-ray diffractometer with Cu-Kα radiation (λ=1.54056Å). The diffraction patterns were recorded in the angle range (2θ) range 15°-60° with a step size of 0.02°, as shown in figure 3.

![Figure 3. XRD pattern of the synthesized LiFePO₄ for 2θ values from 15°-60°, with identified hkl planes.](image)

A careful comparison of the as recorded X-ray pattern with the JCPDS cards of the possible lithium iron phosphate permitted the identification of tryphilite LiFePO₄ with orthorhombic phase and space group Pnma [39]. A detailed crystallite-size analysis of the X-ray diffracted pattern using Scherrer formula [40].

\[
t = \frac{0.94\lambda}{B\cos\theta_B}
\]

reveals that crystallites of LiFePO₄ with average sizes 45(5) nm are present. The calculated cell parameters obtained from method of least squares [40] for orthorhombic LiFePO₄ crystallites, a = 10.3427Å, b = 6.01814 Å, and c = 4.6972 Å, are in good agreement with previously reported values [39] thus validating our product.

3.2.2 Micro structure
3.2.3 Elemental Analysis

A pellet made of LiFePO₄ powder synthesized at 700°C is subjected to EDAX (Hitachi series environmental SEM at an accelerating voltage of 20 kV mode) for chemical compositions of the sample (except for Lithium) and to evaluate the in-situ surface carbon coated over LiFePO₄. The EDAX spectrum recorded on a pellet of LiFePO₄ is shown in figure 5, which shows that approximately 6.8% carbon is present in the sample.

3.2.4 Local structure

The local molecular structural features and different vibrational modes of carbon-coated LiFePO₄ have been extensively studied by infrared spectroscopy [41–44]. To understand the location of phosphate group, the 2–3 mg of the LiFePO₄ sample was made into a pellet after mixing with few
milligrams (3–5) of potassium bromide (KBr) and infrared (IR) spectrum was recorded using JASCO FT/IR-5300 in the wave number range ($\nu$) 2000 – 400 cm$^{-1}$ in the absorption mode with a resolution of 4 cm$^{-1}$. Figure 6 shows the as-recorded FTIR spectrum of C-LiFePO$_4$.

![Figure 6. Infrared absorption spectrum of the in-situ carbon coated nano particles of LiFePO$_4$.](image)

The vibrational motions in LiFePO$_4$ can be divided into two classes that originate from the intramolecular vibrations of the PO$_4^{3-}$ oxo-anion and the external optical modes of PO$_4$ [44]. While the earlier lie in the range of 1200-400 cm$^{-1}$, the latter is observed below 400cm$^{-1}$ (not shown in the figure). The FTIR spectrum of LiFePO$_4$ sample in the low-wave number region (400–700cm$^{-1}$) involves bending modes and in the high-wave number region (700–1300cm$^{-1}$) involves stretching vibrations. In LiFePO$_4$, the FeO$_6$ and PO$_4$ are part of a ‘train’ a molecular ions train providing a framework for the structure. While bending modes ($\nu_2$ & $\nu_4$) are more susceptible to small structural changes–being less localized than stretching modes ($\nu_1$ & $\nu_3$), the latter modes show order–disorder transition in the form of variations in the bond lengths of the phosphate ion. The bending and stretching modes of phosphate ion in LiFePO$_4$ observed have been tabulated in table1.

In the low-wave number region, the bands 428cm$^{-1}$, 468cm$^{-1}$, 498cm$^{-1}$, 549cm$^{-1}$, 577cm$^{-1}$, 635cm$^{-1}$ and 660cm$^{-1}$ are observed due to active symmetric and asymmetric ($\nu_2$–$\nu_4$) bending modes of P–O bonds. The first four modes are due to mixed bending vibrations of symmetric and anti symmetric bending modes ($\nu_2$+$\nu_4$), while the remaining two modes i.e., 635cm$^{-1}$ and 660cm$^{-1}$ are due to the anti symmetric bending modes ($\nu_4$). These low-frequency modes are thus particularly sensitive to the local environment and structure of the olivine lattice. In the high-wave number region, the band 957cm$^{-1}$ is due to symmetric stretching mode ($\nu_1$) and the bands observed at 1049cm$^{-1}$, 1064cm$^{-1}$, 1102cm$^{-1}$, and 1138cm$^{-1}$ are assigned to the antisymmetric stretching mode($\nu_3$). The factor group splitting of asymmetric stretching vibrations ($\nu_3$) for LiFePO$_4$ is $\Delta\nu_3 = 89$ cm$^{-1}$. The vibrations of the phosphate units are split into many components due to the correlation effect induced by the coupling
with of Fe–O units in the material. This rich spectrum thus gives the evidence that this sample is well crystallized.

Table 1: Observed FTIR bands in nanoparticles of C-LiFePO₄.

<table>
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<th>S. No.</th>
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<th>Assignment</th>
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</tr>
<tr>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>12</td>
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<td>ν₄+ν₂</td>
</tr>
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</table>

3.2.5 Phase Purity

It is a well known that any Fe³⁺ phase evolved during the synthesis of LiFePO₄ would destabilize the olivine structure during charge–discharge cycle [8]. Mössbauer spectroscopy was utilized to demonstrate this aspect of the material in discussion. The room temperature (RT) Mössbauer spectrum was recorded in transmission mode using ⁵⁷Co γ-ray source in a Rhodium matrix and multi-channel analyzer. The sample thickness was adjusted so that the Fe content was approximately 10 mg/cm². The calibrations for velocity and isomer shift were performed using iron (Fe) foil.
The $^{57}$Fe Mössbauer spectrum of the LiFePO$_4$ recorded at room temperature is shown in figure 7. The doublet is analysed by fitting to two Lorentzians. The spectrum reveals a symmetric doublet alone with isomer shift (IS) = 1.2468 mm/sec and quadrupole shift (QS) = 2.950(3) mm/sec. These values are typical for Fe$^{2+}$ in ferrous compounds as they exhibit lower electron density due to six 3d electrons on Fe$^{2+}$ as compared to Fe$^{3+}$ with five 3d electrons. These values are in agreement with those reported in the literature [45]. Significantly, Fe$^{3+}$ is conspicuous by its absence, which attests to the exclusively divalent nature of Fe in LiFePO$_4$. (Any incidence of Fe$^{3+}$ would result in a weak, easily detectable and distinguishable, and closely spaced doublet located in between the very strong Fe$^{2+}$ doublets, as was seen in the work of Prince et al [45]). At this stage it is pertinent to mention the very recent Mössbauer spectroscopic studies on orthorhombic K$_4$MgFe$_3$(PO$_4$)$_5$ with an intense closely spaced doublet - the unmistakable signature of Fe$^{3+}$ [46].

The very large QS (nearly five times greater than that of Fe$^{3+}$) value observed is due to high spin configuration of 3d electrons and the asymmetric local environment at the Fe in LiFePO$_4$ as explained by Yamada et al [13]. The IS and QS values are quite different from the IS = 0.435 mm/sec and QS = 0.68 mm/sec of Fe$^{3+}$ in FePO$_4$ [47]. The obtained IS and QS values are also substantially different from those of Fe$^{2+}$ in FeC$_2$O$_4$.2H$_2$O (one of the precursors), given as 1.20 mm/sec and 1.72 mm/sec respectively. This clearly reveals the drastic change in the microscopic environment at Fe$^{2+}$ in the synthesized LiFePO$_4$ relative to that of the iron oxalate precursor.

3.2.6 Conclusions
Sub-micron sized particles of LiFePO$_4$ with average crystallite size of 45(5) nm were prepared from oxalate precursors employing a non-aqueous sol-gel route. A uniform particle size distribution with grain size 100 – 150nm was observed using SEM with few irregular growths. The synthesis route that we have adopted has shown that the formation of Fe$^{3+}$ impurities has been scrupulously avoided. This was confirmed by the presence of only a well-separated symmetric doublet characteristic of Fe$^{2+}$ in the Mössbauer spectrum. The IS and QS values obtained from the symmetric doublet reveals the high spin configuration of 3d electrons and the asymmetric local environment at the Fe in phase-pure LiFePO$_4$. The observed FTIR spectrum was assigned to stretching and bending modes of the phosphate group.

References


