Spectroscopic Characterization of LiFePO₄ as Cathode Material for Li-ion Battery Prepared in the Pulse Thermo-acoustic Reactor

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Abstract:
Lithium iron phosphate (LiFePO₄) is a cathode material for the rechargeable-lithium batteries. In this paper is presented a novel method of fabrication carbon-coated LiFePO₄ in a pilot reactor built according to the principles of the thermo-acoustic burner of Helmholtz-type. Crystalline powder with a high percentage of LiFePO₄ was synthesized by incomplete combustion, i.e. in the reductive atmosphere, and calcined at 700 °C for 6 h. The obtained samples were characterized by X-ray diffraction, IR and Raman spectroscopy. The aim of this study was to demonstrate the production of the high-quality lithium-ion cathode material by the incomplete combustion. The synthesis of LiFePO₄ is completed during calcination and an ordered structure is attained. Fast synthesis in the reactor (less than 2 s) is achieved due to the reduction in the size of reactant's particles and a huge number of collisions owing to their strong turbulent flow associated with explosive combustion.

Keywords: LiFePO₄; Olivine structure; IR spectroscopy; Raman spectroscopy.

1. Introduction

Battery technology is a core technology for all future generation clean energy vehicles such as fuel cell vehicles, electric vehicles, and plug-in hybrid vehicles. Augmentation of this superior battery technology is essential for deployment of the same in different applications ranging from hybrid electric vehicles to consumer electronics. Improved battery performance depends on the development of materials for various battery components. Rechargeable lithium cell technology is promising for future applications. The lithium exists in its ionic state at the anode and hence the rechargeable lithium battery is called lithium-ion battery. Hu and coauthors has been used powder metallurgy route to
fabricate the solid state batteries (SSBs) [1]. SSBs that convert chemical energy into electrical energy have supported power for portable computers, sensors, and electric vehicles.

A large number of different synthetic methods for the preparation of Li-ion cathode materials have been introduced and evaluated. In the case of LiFePO₄ these methods can be divided into two groups and have been analyzed in many review articles [2-4]. All solid state or wet processes that have been reported so far for inorganic synthesis were used to make LiFePO₄, such as solid state reaction starting from all kinds of solid or liquid precursors [5-7] or wet chemistry processes including hydrothermal [8], solvo-thermal [9], ion-thermal [10], sol-gel [11], coprecipitation [12], or spray pyrolysis [13]. An interesting technique is also the solution combustion synthesis [14, 15].

The LiFePO₄ crystallizes in the orthorhombic system (No. 62) with Pnma space group. It consists of a distorted hexagonal-close-packed (hcp) oxygen network forming 16 octahedral and 32 tetrahedral sites. There are two distinct and different in size octahedral sites in this material: M1 is occupied by Li, and M2 is occupied by Fe. The M1 sites form linear chains of edge sharing octahedra along the b-axis, while the M2 sites form staggered lines of corner sharing octahedra along the b-axis. The metal atoms can be viewed as occupying bc-metal planes, where the planes are alternatively occupied by each type of metal, i.e., there is a Li-Fe-Li-Fe ordering along the a-axis. It makes possible the two-dimensional Li diffusion between the hcp-oxygen layers [16, 17], but b-axis is privileged.

Cations, Li (M1) and Fe (M2), are placed in half the octahedral sites and P ions in one-eighth of the tetrahedral sites [18]. The FeO₆ octahedra are distorted lowering their local cubic-octahedral O₆ to the Cs symmetry. Corner-shared FeO₆ octahedra are linked together in the bc-plane. The tetrahedral PO₄ groups bridge neighboring layers of FeO₆ octahedra by sharing a common edge with one FeO₆ octahedron and two edges with LiO₆ octahedra. The PO₄ bridges provide three-dimensionality to the lattice. Remarkably short O–O bonds at the shared PO₄ and FeO₆ edges screen the cation charges from each other. Structure of LiFePO₄ is illustrated in Fig. 1.

![Fig. 1. The structure of LiFePO₄. Gray is Li⁺, red O²⁻, brown Fe²⁺ and pink P⁵⁺. Reddish-brown coloured ones are FeO₆ octahedrons, and green ones PO₄ tetrahedrons.](image)

The LiFePO₄ structure consists of three non-equivalent O sites. Most of the atoms of the olivine structure occupy the 4c Wyckoff position except O(3) that lies in the general 8d position and Li⁺ ions occupying only the 4a Wyckoff position (M1 site on an inversion center). The Fe magnetic ions are in the divalent Fe²⁺ state of the FeO₆ units.
The aim of our work was to produce a high-quality LiFePO₄ by a pulse combustion reactor method. The obtained olivine LiFePO₄ was characterized using XRD, Raman and IR spectroscopy.

2. Materials and Experimental Procedures

The pulse combustion reactor that was used for the synthesis LiFePO₄ is presented in Ref. [19]. The material was synthesized on a reactor setup (Fig. 2), consisting of a Helmholtz-type pulse combustor [19].

Reactor is easy to scale, very energy-efficient, can combust stoichiometric fuel and air mixtures and is suitable for the production of powders in nanometric range because of acoustically driven droplet size reduction [20, 21]. Up to now, it has been used mainly in the synthesis of oxide materials [22, 23], therefore the synthesis of a material which demands a reducing environment is a special challenge. In the LiFePO₄ synthesis, iron has to take the oxidation state of Fe²⁺, wherein the iron in the precursor is in the Fe³⁺ state and must be reduced. Reduction is possible in the presence of carbon monoxide at temperatures near 800°C. This means that we need incomplete combustion, which generates monoxide and high enough temperatures for the synthesis. Resulting LiFePO₄ particles for cathode material must also have a coating carbon layer. Two sources of carbon for the formation of the coating are available. The first source is a precursor addition in the form of hydrocarbons, which can’t be completely combusted (sugar) and which form a carbonaceous material, increasing the porosity of the particles. Another source is soot generated by the incomplete combustion of acetylene (C₂H₂). The carbon coating enables the electrical current to reach each particle. Carbon should therefore be in the form of graphite, which has a higher conductivity than amorphous carbon.

![Fig. 2. The pulse combustion reactor.](image)

Air is supplied to the combustor by way of a blower through an aerodynamic valve. The flow of air is measured using a thermal mass flow meter. Fuel gas (propane) is supplied to the combustor at a constant flow and pressure using a thermal mass flow meter and controller. The amount of air needed to completely combust the supplied amount of fuel is calculated. According to this calculation a ratio between fuel and air can be set by varying the motor rotating speed of the blower or changing the fuel mass flow. Additionally, propane can be diluted with nitrogen to control the frequency and amplitude of pressure oscillations in the reactor.
In the neck of the Helmholtz combustor there is a secondary gas inlet. This gas inlet is for maintaining or enhancing the reductive atmosphere by injecting acetylene or hydrogen into the stream of flue gases from the chamber of the combustor. The flow of acetylene or hydrogen is controlled with a thermal mass flow meter and controller. The neck of the combustor is coupled to the reactor pipe with a T-section that makes it possible to spray the precursors into the hot zone of the reactor. The positions of thermocouples are presented in Fig. 3.

![Fig. 3. The reactor pipe.](image)

The precursor is sprayed with a two fluid nozzle, the spraying gas being 99.9 % nitrogen with a pressure of 1.5 bar and a flow of 45 NL min⁻¹, measured using a thermal mass flow-meter. The precursor composition is 41.3 g of LiNO₃, 230.5 g of Fe(NO₃)₃.9H₂O, 69.0 g of NH₄H₂PO₄, 137.1 g of urea, 78.2 g of sucrose and 46.4 g of NH₄NO₃, dissolved in 700 g of deionized water. The reactor is operating under different conditions with the main difference being the frequency and amplitude of pressure oscillations. The sample was synthesized in reductive reactor conditions with low pressure amplitude (10 mbar). XRD analysis show that as prepared material is 71.5 % LiFePO₄, 19.8 % Li₃Fe₂(PO₄)₃ and 8.7 % α-Fe₂O₃. Obtained material was annealed in the inert atmosphere. Annealing is taking place in an electrical oven under a constant argon flow and in presence of carbon at 700 °C for 6 h. High temperature and inert environment allow a reduction of Fe³⁺ from α-Fe₂O₃ and formation of additional LiFePO₄ according to: 4 Li₃Fe₂(PO₄)₃ + 2 Fe₂O₃ + 3C → 12 LiFePO₄ + 3CO₂.

Characterization of the sample was carried out by several methods:

- X-ray diffraction analysis was performed on X-ray diffractometer (Rigaku Corporation, Japan) at room temperature. CuKα radiation (λ = 0.15418 nm) with a step size of 0.01° in the range of 2θ = 10-60° was used for all samples. The peaks were identified using the Powder Diffraction File (PDF) database created by International Centre for Diffraction Data (ICDD).
- The infrared (IR) reflectivity measurements were carried out with a BOMMEM DA-8 Fourier transform (FTIR) spectrometer at ambient temperature. A DTGS pyroelectric detector was used to cover the wave number range from 50 cm⁻¹ to 700 cm⁻¹.
- The micro-Raman spectra were taken in the backscattering configuration by Jobin Yvon T64000 spectrometer, equipped with nitrogen cooled charged coupled device detector. As an
excitation source we used the 532 nm line of Ti: Sapphire laser, with laser power 50 mW. The measurements were performed in the spectrum range 200 cm⁻¹ to 1100 cm⁻¹.

3. Results and Discussion

The result of X-ray diffraction measurement is shown in Fig. 4. The diffraction pattern clearly shows that in the tested sample is present only single phase olivine LiFePO₄. Obtained diffractogram is compared with the data from the Powder Diffraction Files: PDF-2 83-2092 for lithium iron phosphate. LiFePO₄ is crystallized in a structural type of olivine (triphylite) in the space group Pnma. In this structural type ions of lithium occupy a special crystallographic positions 4a ((0, 0, 0)) with a local symmetry Ī, ions of iron and phosphorus are in special crystallographic positions 4c ((x, ¼, z)) with the local symmetry m, oxygen ions O(1) and O(2) occupy crystallographic positions 4c, also and O(3) general crystallographic position 8d with the local symmetry Ī. The iron and lithium ions are located in an octahedral, and phosphorus ions are in tetrahedral environment of oxygen ions which is illustrated in Fig. 1.

Using the Le Bail profiled refinement and FullProf program lattice parameters for the mono-phase LiFePO₄ are determined and the obtained results are shown in Table I. By the Koalariet computing program [24], using the fundamental parameter approach to the direct determination of microstructural parameters, the size of the crystallites and the microstrain are determined (Table I).

| Tab. I Lattice parameters, crystallite size and microstrain. |
|------------------------------------------------------------|
| a [Å] | b [Å] | c [Å] | Crystallite size [nm] | Microstrain [%] |
| Sample | 10.3190(5) | 6.0040(3) | 4.6925(3) | 142(1) | 0.193(5) |

Fig. 4. XRD spectrum of LiFePO₄, as prepared in incomplete combustion method and calcined at 700 °C for 6 h.
Vibrational modes of phosphate-based materials can be divided into internal and external modes. Internal modes originate from modes of free $PO_4^{3-}$ groups split by the presence of other surrounding ions. The free $PO_4$ group representations decompose into the irreducible representations of the point group $Td$ with its site group $S_C$, i.e. symmetry group $A_1 + E + F_1 + 3F_2$. The corresponding internal vibrations are:

- $A_1 (\nu_1)$ - symmetric $P–O$ stretching,
- $E (\nu_2)$ - symmetric $O–P–O$ bond bending,
- $F_1 (\nu_3)$ - antisymmetric $P–O$ stretching and
- $F_2 (\nu_4)$ - antisymmetric $O–P–O$ bond bending.

In an olivine structure, $FeO_6$ octahedra are linked with $PO_4^3−$ tetrahedron; therefore, the four fundamental modes of $PO_4^3−$ will split into many components due to the correlation effect induced by $Fe–O$ units.

External vibrations are composed primarily of translatory motions of the cations as well as whole - body translations and librations (pseudo-rotations) of the anions. A factor group gives

- acoustic modes: $\Gamma_{total} = B_{1u} + B_{2u} + B_{3u}$ and
- optical modes: $\Gamma_{total} = 11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g} + 10A_u + 13B_{1u} + 9B_{2u} + 13B_{3u} + 10A_d$ are inactive.

In olivine $LiFePO_4$ there are 35 infra-red active modes from the centre of Brillouin zone $13B_{1u} + 9B_{2u} + 13B_{3u}$. Among them, 29 theoretically predicted modes [25] are in the range of our measurements (50-700 cm$^{-1}$).

Far-infrared reflectivity spectrum of the investigated sample (open circles), measured at room temperature, is presented in Fig. 5. The solid line in Fig. 5 is the calculated spectrum obtained by the fitting procedure based on 4-parameters, coupled-phonon model for the dielectric function $\varepsilon(\omega)$ [26-28]:

$$\varepsilon(\omega) = \varepsilon_\infty \prod_{i} \frac{\omega_{LO}^2 - \omega^2 + j\omega\gamma_{LO}}{\omega_{TO}^2 - \omega^2 + j\omega\gamma_{TO}}$$  

(1)

Our sample is a dielectric and the complex dielectric function has only the lattice vibration contribution $\omega_{LO}/\omega_{TO}$ are longitudinal (transverse) frequencies and $\gamma_{LO}/\gamma_{TO}$ their dampings, and $\varepsilon_\infty$ is the high frequency dielectric constant. 18 modes are clearly observed in Fig. 5. Kramers-Krönig (KK) analysis of reflectivity spectra shows $\varepsilon_2(\omega)$ and loss function, $\sigma(\omega) = -\text{Im}(1/\varepsilon(\omega))$. Maximums of $\varepsilon_2(\omega)$ correspond to the values of $\omega_{TO}$, and maximums of $\sigma(\omega)$ to $\omega_{LO}$. Values obtained by fitting procedure are in satisfactory accordance with values obtained by KK analysis (except modes at the range edges, where the signal-to-noise ratio is bad). In Table II are given the best fit parameters together with values of $\omega_{LO}/\omega_{TO}$ obtained by KK analysis for reflectivity spectrum of the sample $LiFePO_4$.

Infrared reflectivity spectra of our carbon-coated $LiFePO_4$ sample, clearly exhibited fundamental modes of $PO_4$ at 461-495 $(\nu_2)$ and 572-635 cm$^{-1} (\nu_3)$, indicating that the $LiFePO_4$ was properly crystallized [28]. Below 400 cm$^{-1}$ are external modes - primarily translation and libration of the $PO_4^{3-}$ ions and translation motions of the $Fe^{2+}$ ions. Far-infrared peak at about 225 cm$^{-1}$ is characteristic of an asymmetric stretching vibration of $Li - O$ bonds. Also, $\nu_2$ modes are a mixture of $Li$ translations and $PO_4$ bending motions of the same symmetry. Burba and Frech [29] suggest that 506 and 470 cm$^{-1}$ bands in $LiFePO_4$ are predominantly $Li$-ion “cage modes”, i.e. $Li$-translation.
Tab. II Oscillator fit parameters of reflectivity spectra of LiFePO₄, as prepared in incomplete combustion and resonance mode of reactor and calcined at 700 °C for 6 h.

| \(\omega_{\text{TO}}\) [\text{cm}^{-1}] | \(\gamma_{\text{TO}}\) [\text{cm}^{-1}] | \(\omega_{\text{LO}}\) [\text{cm}^{-1}] | \(\gamma_{\text{LO}}\) [\text{cm}^{-1}] |
|-----------------|-----------------|-----------------|-----------------|
| 71 (68.6)       | 45              | 79 (72.8)       | 50              |
| 138 (137.5)     | 60              | 144 (140.1)     | 50              |
| 172.5 (172.8)   | 27              | 175 (173.1)     | 22              |
| 191 (189.6)     | 18              | 201 (200.4)     | 18              |
| 226.5 (226)     | 25              | 235 (234.4)     | 18              |
| 247 (246.3)     | 20              | 260.5 (260.5)   | 20              |
| 283 (284)       | 45              | 303.5 (305)     | 45              |
| 311 (310.4)     | 25              | 314.5 (315)     | 25              |
| 345.5 (344.8)   | 27              | 358.5 (357.4)   | 27              |
| 379 (378.2)     | 25              | 391 (391.5)     | 25              |
| 399 (399.1)     | 22              | 403 (403.2)     | 29              |
| 438 (438)       | 35              | 442.5 (441)     | 33              |
| 467.5 (466.2)   | 35              | 482 (483.3)     | 35              |
| 500 (499.4)     | 40              | 514 (510.6)     | 45              |
| 549 (548.7)     | 20              | 556 (555.6)     | 20              |
| 577.5 (576.6)   | 20              | 583 (581)       | 20              |
| 615 (614.8)     | 20              | 616 (616.7)     | 20              |
| 639.5 (636.8)   | 30              | 650 (647.6)     | 30              |

\(\varepsilon_{\infty} = 2.25\)

Fig. 5. IR spectrum at room temperature of LiFePO₄, as prepared in incomplete combustion method and calcined at 700 °C for 6 h.
To explore the surface properties of the LiFePO₄ particles, Raman spectra have been measured; the penetration depth for carbon with Raman spectroscopy is approximately 30 nm [30]. This is one order of magnitude larger than the thickness of the carbon coat deposited at the surface of the LiFePO₄ particles in case of a uniform carbon distribution. Therefore, any screening effect of carbon on the LiFePO₄ spectra is not expected. The penetration depth inside LiFePO₄ is unknown, but it should be small, so that the detector in the Raman experiments collects the signal within the light penetration depth, which basically represents the total amount of carbon and a few per cent of the amount of LiFePO₄.

Raman spectrum of the investigated sample measured at room temperature in the range of 200-1100 cm⁻¹ is presented in Fig. 6. Strong narrow peaks in the spectrum, especially characteristic peak at about 950 cm⁻¹, confirm that combustion synthesized nanomaterial is well-crystallized. According to XRD analysis, sample is of pure LiFePO₄ without any trace of impurities (i.e. starting or intermediate compounds). Positions of obtained Raman modes are in agreement with other experimental data [31-33].

There are 36 Raman active modes $11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g}$ in olivine LiFePO₄ structure. Fourteen modes are registered in our Raman spectrum, Fig. 6, and assigned according to theoretical calculation of Shi at al. [33].

![Fig. 6. Raman spectrum at room temperature of LiFePO₄, as prepared in incomplete combustion method and calcined at 700 °C for 6 h.](image)

4. Conclusion

We have successfully prepared nanosized lithium iron phosphate as Li-ion cathode materials using a pulse combustion reactor method. The new method is fast, environmentally friendly and easy to scale. X-ray powder diffraction (XRD) shows that LiFePO₄ olivine structure is dominant in the form of fine crystallites with average size 142 nm. In the room temperature Raman spectra are observed 12 first-order Raman active modes. An IR reflectivity spectrum is fitted by 18 modes.
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Садржај: Литијум гвожђе фосфат (LiFePO₄) је катодни материјал за пуњиве литијум-јонске батерије. У овом раду приказано је добијање LiFePO₄ новом методом у пилот реакцију изграђену на принципу пулсног горионика Хелмхотеловог типа. Кристални прах са високим процентом LiFePO₄ је синтетисан при непотпуном сагоревању, тј. у редуцијној атмосфери и потом калцинисан на 700 °C током 6 h. Добијени узорци су карактерисани методом рендгенске дифракције, инфрацрвеној спектроскопији и Рамановом спектроскопијом. Циљ овог рада је био да прикаже добијање квалитетног литијум-јон катодног материјала при непотпуном сагоревању. Током калцинације комплетира се синтеза LiFePO₄ и постиже уређена структура. Брза синтеза у реактору (мање од 2 секунде) постиже се смањењем честица реактаната и огромним бројем њихових судара због јаког турбулентног струјања повезаног са експлозивним сагоревањем.

Кључне речи: LiFeO₄, olivin struktura, инфрацрвена спектроскопија, Раман спектроскопија.

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