Journal of Power Sources 241 (2013) 70–79

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Crystal structure analysis and first principle investigation of F doping in $LiFePO_4$

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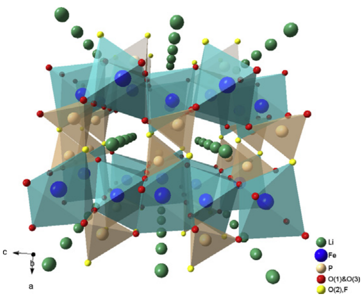
HIGHLIGHTS

- Nanostructured F-doped $LiFePO_4$/C composite is synthesized.
- Structure refinement shows that F ions are solely positioned at O(2) oxygen site.
- Theoretical modelings confirmed and support the experimental findings.
- Fluorine-doped olivine has finite density of states at the Fermi level.
- The powder delivered capacity of 164 mAh g^{-1}.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 February 2013
Received in revised form
1 April 2013
Accepted 21 April 2013
Available online 1 May 2013

Keywords:
Lithium iron phosphate ($LiFePO_4$)
Rietveld analysis
Fluorine doping
Cathode
Electronic band structure

ABSTRACT

This work presents the synthesis of F-doped $LiFePO_4$/C composite by the specific modification of the recently suggested synthesis procedure based on an aqueous precipitation of precursor material in molten stearic acid, followed by a high temperature treatment. Besides the lattice parameters and the primitive cell volume reductions, compared to the undoped sample synthesized under the same conditions, the Rietveld refinement also shows that fluorine ions preferably occupy specific oxygen sites. Particularly, the best refinement is accomplished when fluorine ions occupy O(2) sites exclusively. By means of up-to-date electronic structure and total energy calculations this experimental finding is theoretically confirmed. Such fluorine doping also produces closing of the gap in the electronic structure and consequently better conductivity properties of the doped compound. In addition, the morphological and electrochemical performances of the synthesized powder are fully characterized.

1. Introduction

In the on-going search for alternative cathode materials for Li-ion batteries, olivine-type lithium iron orthophosphate ($LiFePO_4$) is one of the most promising candidates due to its high energy density (with the theoretical capacity of 170 mAh g^{-1} and plateau voltage of 3.5 V vs. Li^+/Li), high safety, both electrochemical and thermal stability, environmental appropriateness and low raw materials cost. However, despite its numerous advantages this material suffers from poor rate performance due to its inherent conducting properties – low electronic conductivity coupled with slow diffusion rate of lithium ions [1]. This issue has become a huge obstacle for extensive applications of olivine-phosphate in high power rate devices such as hybrid electric vehicles and electric

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http://dx.doi.org/10.1016/j.jpowsour.2013.04.109

vehicles. Up until now, many efforts have been made to overcome such an obstacle. Generally, there are three different approaches to enhance electrochemical performance of $LiFePO_4$: (i) introduction of conductive additives, e.g., carbon coating of active material particles in $LiFePO_4$/C composite; (ii) particle size minimization and morphology control; and (iii) ion doping [2–6].

Various ions have been used as dopants in $LiFePO_4$ [7–15]. Depending on the type of the doping material one can have an anion or a cation doping. Cation doping at Li, or Fe sites, has been widely investigated and debated [7–9,12]. On the other hand, the anion doping of $LiFePO_4$ has been rarely investigated and has started only recently [10,11,13–15]. Earlier papers devoted to the layered structure cathode materials [16,17] inspired these works. The rate capability has been improved by the fluorine substitutions at oxygen sites, as well as capacity retention and cycle stability of $Li(M_{1x}M_{2y}M_{3z})O_2$ ($M_{1,2,3}$ = Co, Ni, Mn and $x + y + z = 1$) layered materials. It appears that anion doping has also improved the electrochemical performance of $LiFePO_4$. Namely, the doping of $LiFePO_4$ with F^-, Cl^- and S^{2-} gave very satisfactory results (cf., for instance, [13–15]).

Liao et al. [11] were among the first who investigated the effects of fluorine substitution on electrochemical behavior of $LiFePO_4$/C cathode. They concluded that F-substitution improved both the high rate capability and the cycling life at high temperatures, as compared with the pure material. Enhanced high rate performance and improved cycle stability of F-doped olivine-phosphate was also reported in the very recent studies [13,18,19]. However, there exists the uncertainty about the site in the crystal lattice, which the fluorine ion occupy. Two proposals were given: (i) the first one suggested that $3F^-$ ions replace PO_4^{3-} group as a whole [11,13], and (ii) the second one declared that F^- could only be replaced at the oxygen sites [18,19]. Considering the second proposition, there are three nonequivalent randomly occupied O sites (namely O(1), O(2) and O(3) site) in the crystalline elementary cell of $LiFePO_4$ [20]. The first principles computational results indicate that electronic properties, the lithium insertion voltage and general electrochemical behavior are very sensitive to the placement of fluorine ions in the structure of this compound [10]. Owing to that, it is very important to determine the most probable positions of the fluorine replacements in the lattice of $LiFePO_4$.

To the best of the author's knowledge there do not exist careful investigations of the most probable fluorine replacement sites in olivine compounds, as well as the exact stoichiometry of such fluorine doping. Earlier theoretical investigation of $Li_{0.5}FePO_{3.5}F_{0.5}$ (12.5% of oxygen is replaced by fluorine) [10], took improbably high content of fluorine, which is very non-trivial to obtain experimentally.

The structure of $LiFePO_4$ (Fig. 1) belongs to the orthorhombic space group *Pnma* (#62), consisting of a slightly distorted hexagonal close-packed (hcp) oxygen framework. The phosphorous atoms occupy 1/8 of tetrahedral sites, while lithium and iron atoms occupy 1/2 of octahedral sites (denoted as M(1) and M(2) sites, respectively). The edge-shared LiO_6 octahedra form linear chains running parallel to the *b*-axis; the FeO_6 form zigzag planes of corner-shared octahedra in the *b*–*c* planes. The PO_4 tetrahedra bridge between adjacent M(2) planes in the olivine structure.

In the present paper, F-doped $LiFePO_4$/C composite was synthesized by means of the newly suggested simple method, which was based on an aqueous co-precipitation of an Fe(II) precursor material in molten stearic acid followed by high temperature treatment. The effects of F-doping on the crystal structure were investigated in details and compared with the previously published results for the undoped $LiFePO_4$/C powder prepared under the same synthesis conditions [21]. In addition, morphological and electrochemical properties of the synthesized powder were investigated. Special attention has been paid to the refinement of the crystal structure of the synthesized powdered samples. The careful refinement of the X-ray diffraction data has indicated that fluorine ions prefer specific oxygen site in the crystal structure. In order to check our experimental findings concerning the most probable placement of fluorine into lithium iron orthophosphate, we investigated theoretically the electronic structure and crystal stability of both pure $LiFePO_4$ and fluorine doped compound, which we modeled by orthorhombic $LiFePO_{3.75}F_{0.25}$ compound. This has been done on the basis of density functional theory (DFT) with the generalized gradient approximation (GGA).

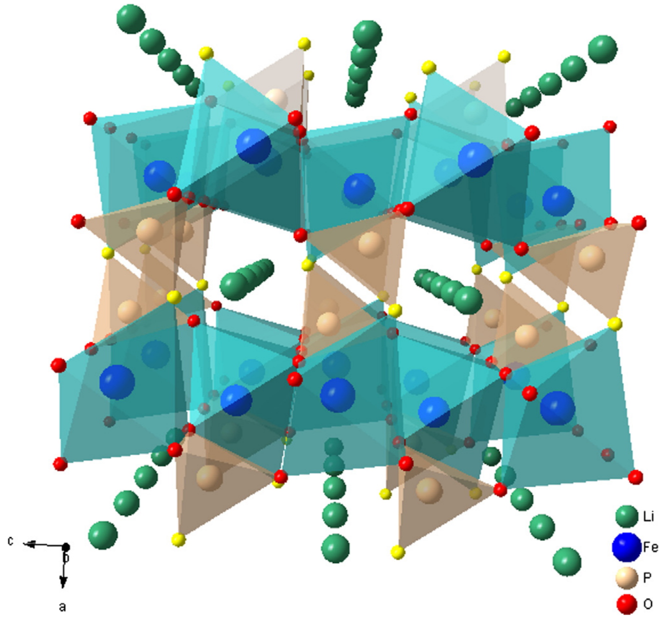

Fig. 1. Polyhedral representation of the structure of olivine type $LiFePO_4$ (space group *Pnma*) viewed along the *b*-axis. Note that oxygen's site O(2) is colored in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The rest of the paper is organized as follows. After summarizing the basics of the olivine type lithium iron orthophosphate as an alternative for cathode material of Li-ion type batteries and the earlier attempts to dope this material, the essential experimental conditions for the synthesis of $LiFePO_{3.98}F_{0.02}$/C and the experimental methods used for the characterization of the physical, chemical and electrochemical properties of this compound are given in Section 2, together with the thorough discussion of these results. The computational details used in our first principles simulations, jointly with the theoretical results relevant for comparisons with experiments, can be found in Section 3. Section 4 gives brief conclusion.

2. Experimental

2.1. Experimental details

F-Doped $LiFePO_4$/C composite powder was synthesized by aqueous precipitation in the presence of stearic acid and subsequent heat treatment. Synthesis procedure was the same as previously implemented for the synthesis of the undoped $LiFePO_4$/C composites [21], except for lithium source. The starting materials were $(NH_4)_2HPO_4$, $FeSO_4\cdot 7H_2O$, LiF, and stearic acid, mixed in equimolar quantities. This time LiF has served as both lithium and fluorine source. The obtained precursor powder was calcined at the temperature of 700 °C for 3 h in a flowing, slightly reductive