

Институт техничких наука САНУ
Кнез Михаилова 35/IV
Београд

Предмет: Захтев за покретање поступка за избор Милоша Миловића, истраживача
приправника у звање истраживач сарадник

НАУЧНОМ ВЕЋУ ИНСТИТУТА ТЕХНИЧКИХ НАУКА САНУ

Молим Вас да, у складу са Правилником о поступку и начину вредновања, и квантитативном исказивању научноистраживачких резултата истраживача (Сл. Гласник РС, бр. 38/08), и Правилником о стицању звања истраживач сарадник, Научно веће Института техничких наука САНУ покрене поступак за мој избор у звање истраживач сарадник.

За чланове комисије за припрему извештаја Научном већу предлажем:

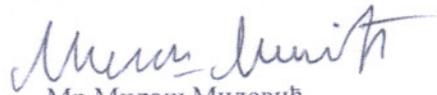
- др Драгану Југовић, научног сарадника Института техничких наука САНУ
- др Смиљу Марковић, вишег научног сарадника Института техничких наука САНУ
- др Магдалену Стевановић, вишег научног сарадника Института техничких наука САНУ

У прилогу достављам:

1. Биографију,
2. Доказ о укупној просечној оцени на основним и мастер студијама,
3. Доказ о уписаним докторским студијама,
4. Библиографију са копијом рада.

У Београду,
8.5.2013.

Подносилац захтева



Мр Милош Миловић,

Истраживач приправник ИТН САНУ

Биографија

Милош Д. Миловић рођен је 1987. године у Приштини. Гимназију је завршио у Рашкој. Године 2006. уписује Факултет за физичку хемију Универзитета у Београду. Мастер рад „Креирање неуронске мреже у циљу процене садржаја гвожђа у мозгу оболелих од амиотрофичне латералне склерозе“ одбранио је 2011. године. За изузетан успех током студирања награђен је Повељом Универзитета у Београду као најбољи студент генерације Факултета за физичку хемију који је дипломирао у школској 2010/11. Докторске студије уписује 2011. на свом матичном факултету.

У Институту техничких наука САНУ запослен је од децембра 2011. као истраживач приправник на пројекту интегралних и интердисциплинарних истраживања ИИИ 45004, „Молекуларно дизајнирање наночестица контролисаних морфолошких и физичкохемијских карактеристика и функционалних материјала на њиховој основи“.

У област научног интересовања спадају: катодни материјали, хемијски извори струје, литијумске батерије, кристалографија.

Библиографија

M21 Рад у врхунском међународном часопису:

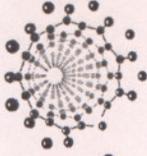
1. Miloš Milović, Dragana Jugović, Nikola Cvjetičanin, Dragan Uskoković, Aleksandar S. Milošević, Zoran S. Popović, Filip R. Vukajlović, Crystal structure analysis and first principle investigation of F doping in LiFePO₄, Journal of Power Sources (2013), DOI: <http://dx.doi.org/10.1016/j.jpowsour.2013.04.109>

M33 Саопштење са међународног скупа штампано у целини:

1. M. Milović, D. Jugović, M. Mitrić, B. Jokić, D. Uskoković, Synthesis and structural properties of F-doped LiFePO₄/C Composite, 11th International Conference on Fundamental and Applied Aspects of Physical Chemistry-Physical Chemistry 2012, Proceedings Volume I, p. 441-443, Belgrade, Serbia, 2012

M34 Саопштење са међународног скупа штампано у изводу:

1. M. Milović, M. Mojović, A. Ignjatović, Applicability of neural networks in the estimation of brain iron content in the diagnosis of amyotrophic lateral sclerosis, The Tenth Young Researchers' Conference Materials Science and Engineering, Program and the Book of Abstracts, p. 10, Belgrade, Serbia, 2011
2. D. Jugović, M. Mitrić, M. Milović, B. Jokić, D. Uskoković, Synthesis and characterization of LiFePO₄/C composite obtained by cellulose template, Fourteenth Annual Conference-Yucomat 2012, Program and the Book of Abstracts, p. 76, Herceg Novi, Montenegro, 2012
3. M. Milović, D. Jugović, M. Mitrić, B. Jokić, D. Uskoković, Synthesis and characterization of Li₂FeSiO₄/C composite, Fourteenth Annual Conference-Yucomat 2012, Program and the Book of Abstracts, p. 77, Herceg Novi, Montenegro, 2012
4. M. Milović, D. Jugović, M. Mitrić, B. Jokić, M. Vukomanović, D. Uskoković, New facile synthesis route for obtaining phase pure LiFePO₄/C composite, The Eleventh Young Researchers' Conference Materials Science and Engineering, Program and the Book of Abstracts, p. 102, Belgrade, Serbia, 2012



Универзитет у Београду
**ФАКУЛТЕТ ЗА
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Студентски трг 12-16, п. пр. 47, 11158 Београд 118, ПАК 105305 // тел +381 11 2635-545, тел/факс +381 11 2187-133, ffh@ffh.bg.ac.rs

Број : 662011
Београд, 29 .09. 2011. године

На основу члана 161. Закона о општем управном поступку (СГ СРЈ 33/97 и 31/2001), а у вези са чланом 25. и члана 95. Закона о високом образовању, дозволе за рад број 612-00-00564/2009-04 од 11.06.2009. године које је издало Министарство просвете Републике Србије и службене евиденције Факултета, а по захтеву Милош Миловића издаје се следеће

У В Е Р Е Њ Е

Да је **МИЛОШ МИЛОВИЋ**, отац Драгош, рођен 23.11.1987. место Приштина, општина Приштина, Република Србија, уписан школске 2010/11. године, а дана **28. септембра 2011.** године завршио мастер академске студије другог степена на студијском програму мастер академских студија физичке хемије обима 60 (шездесет) бодова ЕСПБ са просечном оценом 9,60 (девет и 60/100).

Комисија у саставу: Др Љиљана Колар-Анић, редован проф., Факултет за физичку хемију, Др Јелена Радић-Перић, редован проф., Факултет за физичку хемију, Др Љиљана Дамјановић, ванредан проф. Факултет за физичку хемију, донела одлуку да је кандидат Милош Миловић одбранио завршни мастер рад са оценом 10 (десет) под насловом:

“ Креирање неуронске мреже у циљу процене садржаја гвожђа у мозгу оболелих од амиотрофичне латералне склерозе.“

На основу тога издаје је се ово уверење о стеченом академском називу

МАСТЕР ФИЗИКОХЕМИЧАР

Уверење се издаје на лични захтев и важи до издавања дипломе.

Декан
Факултета за физичку хемију

Миљанић
/ Др Шћепан Миљанић, проф./





Република Србија
Универзитет у Београду
Факултет за физичку хемију
Број индекса: 2006/0028
Датум: 23.05.2011.

На основу члана 161 Закона о општем управном поступку и службене евиденције издаје се

УВЕРЕЊЕ О ПОЛОЖЕНИМ ИСПИТИМА

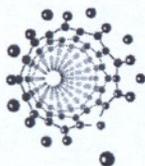
Милош Миловић, име једног родитеља Драгош, ЈМБГ 2311987910022, рођен 23.11.1987. године, Приштина, Република Србија, уписан школске 2006/07. године, дана 08.10.2010. године завршио је основне академске студије на студијском програму Основне академске студије физичке хемије, у трајању од четири године, обима 240 (две стотине четрдесет) ЕСПБ бодова, и стекао стручни назив дипломирани физикохемичар. Током студија положио је испите из следећих предмета:

Р.бр.	Шифра	Назив предмета	Оцена	ЕСПБ	Фонд часова**	Датум
1.	06УСМ	Увод у структуру материје	10(десет)	4	I:(30+30+0)	30.01.2007.
2.	06ПМФХ	Практикум из математике за физикохемичаре	9(девет)	2	I:(15+30+0)	12.02.2007.
3.	06М1	Математика 1	10(десет)	12	I:(60+60+0)	12.02.2007.
4.	06УЛР	Увод у лабораторијски рад	10(десет)	4	I:(15+0+90)	20.01.2007.
5.	06ОКФХ1	Општи курс физичке хемије 1	9(девет)	8	I:(60+0+60)	23.02.2007.
6.	06НХ	Неорганска хемија	10(десет)	6	II:(60+0+0)	11.06.2007.
7.	06ХТД	Хемијска термодинамика	10(десет)	7	II:(60+0+60)	18.06.2007.
8.	06УФХЖС	Увод у физичку хемију животне средине	10(десет)	2	II:(15+0+30)	12.07.2007.
9.	06ОКФХ2	Општи курс физичке хемије 2	10(десет)	7	II:(60+0+60)	06.07.2007.
10.	06Ф1	Физика 1	10(десет)	8	II:(45+30+30)	14.09.2007.
11.	06Ф2	Физика 2	10(десет)	7	III:(45+30+30)	11.04.2008.
12.	06ХСМ	Хроматографија и сепарационе методе	10(десет)	4	III:(15+0+30)	22.02.2008.
13.	06Е1	Енглески језик 1	10(десет)	2	III:(30+30+0)	28.02.2008.
14.	06М2	Математика 2	10(десет)	10	III:(60+60+0)	23.02.2008.
15.	06КАХ	Класична аналитичка хемија	10(десет)	7	III:(30+0+90)	12.09.2008.
16.	06КОЛ	Колоиди	10(десет)	4	IV:(15+0+30)	24.06.2008.
17.	06Ф3	Физика 3	10(десет)	6	IV:(45+15+30)	16.07.2008.
18.	06АТ	Атомистика	10(десет)	10,5	IV:(60+15+60)	03.07.2008.
19.	06Е2	Енглески језик 2	10(десет)	1,5	IV:(30+30+0)	11.07.2008.
20.	06ОХ	Органска хемија	10(десет)	8	IV:(60+0+60)	28.06.2008.
21.	06РНХ	Радиохемија и нуклеарна хемија	10(десет)	7	V:(60+0+60)	18.02.2009.
22.	06АСХ	Атомска спектрохемија	10(десет)	7	V:(60+0+60)	13.03.2009.
23.	06БХ	Биолошка хемија	10(десет)	4	V:(30+0+30)	28.09.2009.
24.	06СТД	Статистичка термодинамика	10(десет)	7	V:(60+30+0)	06.02.2009.
25.	06ПРФХ	Примена рачунара у физичкој хемији	10(десет)	6	VI:(60+30+0)	09.07.2009.
26.	06ХК	Хемијска кинетика	8(осам)	8	VI:(60+0+60)	15.07.2009.
27.	06МСХ	Молекулска спектрохемија	9(девет)	8	VI:(60+0+60)	09.09.2009.
28.	06ЕХ	Електрохемија	10(десет)	8	VI:(60+0+60)	27.06.2009.
29.	06ФХП	Физичка хемија плазме	10(десет)	5	VI:(30+0+30)	21.07.2009.



Овлашћено лице факултета

Milovan



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Универзитет у Београду
Факултет за физичку хемију
Број индекса: 2006/0028
Датум: 23.05.2011.

Р.бр.	Шифра	Назив предмета	Оцена	ЕСПБ	Фонд часова**	Датум
30.	06КХ	Квантна хемија	10(десет)	7	VII:(60+60+0)	16.02.2010.
31.	06БФХ1	Биофизичка хемија 1	10(десет)	7	VII:(60+0+60)	20.04.2010.
32.	06ИА	Инструментална анализа	10(десет)	5,5	VII:(30+0+30)	08.02.2010.
33.	06ММФХ	Математичке методе у физичкој хемији	10(десет)	5	VII:(60+30+0)	10.02.2010.
34.	06ФХА	Физичкохемијска анализа	9(девет)	7	VIII:(60+0+60)	25.06.2010.
35.	06ФХС	Физичка хемија чврстог стања	10(десет)	7	VIII:(60+0+60)	02.07.2010.
36.	06ФОРФХ	Форензичка физичка хемија	10(десет)	5,5	VIII:(30+0+30)	15.09.2010.

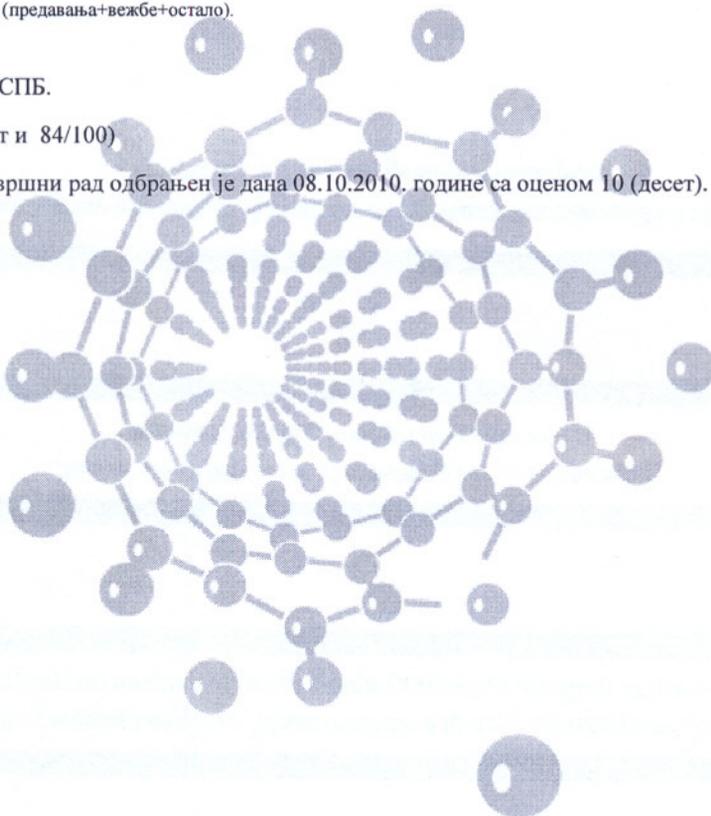
* - еквивалентираан/признат испит.

** - Фонд часова је у формату (предавања+вежбе+остало).

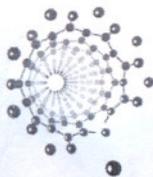
Укупно остварено 240 ЕСПБ.

Општи успех: 9,84 (девет и 84/100)

Завршни рад обрађен је дана 08.10.2010. године са оценом 10 (десет).



Овлашћено лице факултета



Република Србија
Универзитет у Београду
Факултет за физичку хемију
Број индекса: 2011/0308
Датум: 11.01.2013.

На основу члана 161 Закона о општем управном поступку и службене евиденције издаје се

УВЕРЕЊЕ О ПОЛОЖЕНИМ ИСПИТИМА

Милош Миловић, име једног родитеља Драгош, рођен 23.11.1987.године, Приштина, Република Србија, уписан школске 2011/2012. године на докторске академске студије, школске 2012/2013. године уписан на статус финансирање из буџета, студијски програм Физичка хемија, током студија положио је испите из следећих предмета:

Р.бр.	Шифра	Назив предмета	Оцена	ЕСПБ	Фонд часова**	Датум
1.	Д07ИФХН	Физичка хемија наноматеријала	10(десет)	15		20.10.2012.
2.	Д07НФМ	Нове физичкохемијске методе	10(десет)	15		19.04.2012.

* - еквивалентран/признат испит.

** - Фонд часова је у формату (предавања+вежбе+остало).

Општи успех: 10,00 (десет и 00/100)



Овлашћено лице факултета

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Република Србија
Универзитет у Београду
Факултет за физичку хемију
Д.Бр.2011/0308
Датум: 11.01.2013. године

На основу члана 161 Закона о општем управном поступку и службене евиденције издаје се

УВЕРЕЊЕ

Миловић (Драгош) Милош, бр. индекса 2011/0308, рођен 23.11.1987. године, Приштина, Република Србија, уписан школске 2012/2013. године, у статусу: финансирање из буџета; тип студија: докторске академске студије; студијски програм: Физичка хемија.

Према Статуту факултета студије трају (број година): три године.
Рок за завршетак студија: у двоструком трајању студија.

Ово се уверење може употребити за регулисање војне обавезе, издавање визе, права на дечији додатак, породичне пензије, инвалидског додатка, добијања здравствене књижице, легитимације за повлашћену возњу и стипендије.

Овлашћено лице факултета



Accepted Manuscript

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

Miloj Milović, Dragana Jugović, Nikola Cvjetičanin, Dragan Uskoković, Aleksandar S. Milojević, Zoran S. Popović, Filip R. Vukajlović



PII: S0378-7753(13)00717-9

DOI: [10.1016/j.jpowsour.2013.04.109](https://doi.org/10.1016/j.jpowsour.2013.04.109)

Reference: POWER 17275

To appear in: *Journal of Power Sources*

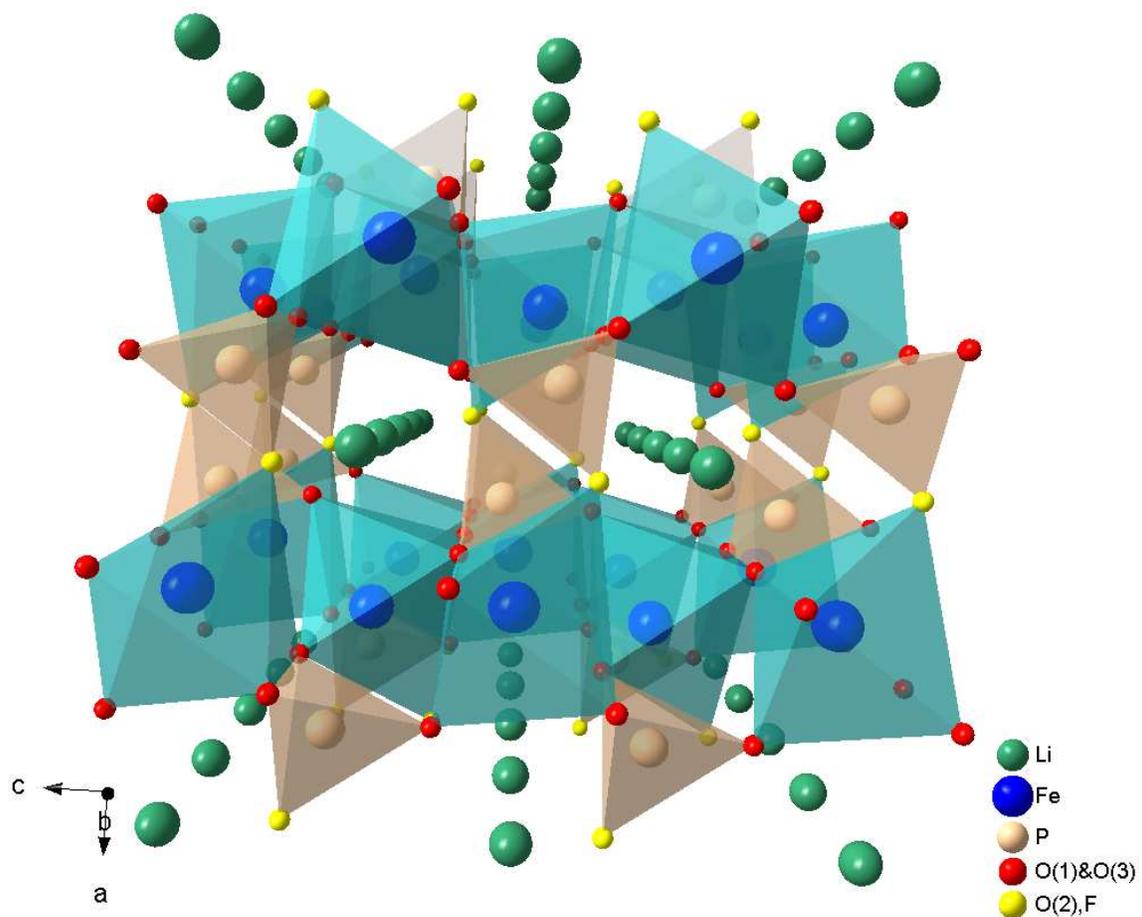
Received Date: 21 February 2013

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This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



ACCEPTED

**Crystal structure analysis and first principle investigation of F doping in
LiFePO₄**

Miloš Milović ^a, Dragana Jugović ^{a*}, Nikola Cvjetičanin ^b, Dragan Uskoković ^a, Aleksandar S. Milošević ^c, Zoran S. Popović ^c, Filip R. Vukajlović ^d

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^b Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, P.O. Box 137, Belgrade, Serbia

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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.

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

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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 mAhg^{-1} and plateau voltage of $3.5 \text{ V vs. Li}^+/\text{Li}$), 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 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 $\text{Li}(\text{M}_{1x}\text{M}_{2y}\text{M}_{3z})\text{O}_2$ ($\text{M}_{1,2,3} = \text{Co, Ni, Mn}$ 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 $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ (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 $\text{LiFePO}_{3.75}\text{F}_{0.25}$ compound. This has been done on the basis of density functional theory (DFT) with the generalized gradient approximation (GGA).

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 $\text{LiFePO}_{3.98}\text{F}_{0.02}/\text{C}$ and the experimental methods used for the characterization of the physical, chemical and electrochemical properties of this compound are given in Sec. 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 Sec. 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 $(\text{NH}_4)_2\text{HPO}_4$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 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 $700\text{ }^\circ\text{C}$ for 3 hours in a flowing, slightly reductive atmosphere ($\text{Ar} + 5\%\text{H}_2$), then washed in distilled water and dried under vacuum.

X-ray diffraction data were collected on the Philips PW 1050 diffractometer with $\text{Cu-K}\alpha_{1,2}$ radiation (Ni filter) at the room temperature. Measurements were done in 2θ range of $15\text{--}110^\circ$ with step size of 0.02° and counting time of 14 s per step. Crystal structure refinement was based on the Rietveld full profile method [22] using Koalariet software [23].

The morphology of the synthesized powder was analyzed by field emission scanning electron microscopy (FESEM, Supra 35 VP, Carl Zeiss). More detailed analysis of particle microstructure was accomplished using transmission electron microscopy (JEOL JEM 2000 FX) with acceleration voltage of 200 keV.

The particle size analyzer (PSA) Mastersizer 2000 (Malvern Instruments Ltd., UK) has been used for the determination of the particle size distributions.

Chemical composition of the final powder was determined by the ICP-AES measurements combined with SA720 ion selective electrode (ISE) analysis. The ICP-AES measurements were performed by simultaneous ICP-AES using a Thermo Scientific iCAP-6500 DUO ICP (Thermo Fisher Scientific, UK) spectrometer.

Electrochemical measurements were carried out in a closed, argon filled two-electrode cell, with metallic lithium as a counter electrode. 1M solution of LiClO_4 (p.a., Chemmetall GmbH) in PC (p.a., Honeywell) was used as electrolyte. Working electrodes were made from synthesized material, carbon black and polyvinylidene fluoride (PVdF, Aldrich) mixed in 75:15:10 weight percent ratio and deposited on platinum foils from slurry prepared in N-methyl-2-pyrrolidone. Galvanostatic charge/discharge tests were performed between 2.3 and 4.1 V at different current rates by using Arbin BT 2042 battery test system.

2.2 Experimental Results and Discussion

The morphology of the powder, revealed by scanning electron microscopy, is shown in Fig. 2. The particles are irregular in shape, highly agglomerated with nodular structures, quite similar to the morphology of the undoped powder [21]. Particle bonding and neck formation, denoting inter-particle sintering, can be observed as well. Apparently, the morphology of the powder was not affected by fluorine doping. The particle size distribution (PSD) curve of the powder (Fig. 3) has a lognormal shape with a high degree of uniformity, showing span value of 1.2 and mean particle size of 330 nm.

X-ray powder diffraction pattern (Fig. 4) was used for both phase identification and structural analysis. Olivine structured LiFePO_4 is obtained as a major phase, with small amount (roughly 2 wt.%) of $\gamma\text{-Li}_3\text{PO}_4$ and $\text{Fe}_2\text{P}_2\text{O}_7$ phases. These unwanted products are almost certainly caused by slightly exceeded gas reductivity as a consequence of the thermal treatment.

During pyrolytic degradation, stearic acid decomposes to carbon, creating at the same time more reductive atmosphere that prevents the iron oxidation and the formation of Fe^{3+} sites [24]. Chemical analysis of the powder gave Li:Fe:P:F molar ratio of 0.98:1:1:0.02, respectively. There is no evidence of a crystalline carbon, so internal carbon could be treated as a contribution to the background. The amount of an in situ formed carbon (5 wt.%) was determined by heating the powder in air considering that only Fe^{2+} ions oxidize and contribute to the weight gain [25].

Rietveld refinement was performed using Koalariet computing program based on a fundamental parameters convolution approach to generate line profiles [23]. The structure of fluorine doped LiFePO_4 powder has been refined in the space group $Pnma$ (D_{2h}^{16}) in olivine type with the following crystallographic positions: Li^+ ions in the crystallographic position $4a$ [0,0,0] with the local symmetry $\bar{1}$; Fe^{2+} and P^{5+} ions occupy two nonequivalent $4c$ crystallographic positions $[x,0.25,z]$ with local symmetry m . Oxygen O^{2-} ions occupy three different crystallographic positions: additional two $4c$ positions and one general $8d$ position $[x,y,z]$ with local symmetry 1.

The Rietveld refinement results (Tables 1) indicate lattice parameters and primitive cell volume reduction compared to the undoped sample synthesized under the same conditions [21]. This is the indication that F^- ions are incorporated in the lattice, since F^- ionic radius is smaller than O^{2-} one ($r^{\text{VI}}(\text{F}^-) = 1.33 \text{ \AA}$, $r^{\text{VI}}(\text{O}^{2-}) = 1.40 \text{ \AA}$ [26]). Furthermore, doping with fluorine resulted in increased crystallite size in comparison with the undoped compound. Comparing the mean particle size estimated from PSD (Fig. 3), with the mean crystallite size from Table 1, one can conclude that these particles are of polycrystalline type made up of many crystallites.

Concerning fluorine ion, it is natural to presume that it substitutes one of the oxygen ions, rather than the whole $(\text{PO}_4)^{3-}$ group, as it has been stated in [11, 13]. Additionally, positively charged $\text{V}_{\text{PO}_4}^{3+}$ defect has very high formation energy [27], and therefore it is quite unlikely to

expect such a substitution. There are three nonequivalent O sites (usually denoted as O(1), O(2), and O(3)) in the olivine lattice that may be occupied by fluorine ions. During the refinement procedure fluorine ions were free to occupy any of the three allowed O sites. The best refinement was accomplished when fluorine ions occupied O(2) sites exclusively, while the total site occupancy of that position for oxygen and fluorine ions was constrained to unity. The refined value of dopant concentration matches well, within the experimental error, with the fluorine concentration obtained by chemical analysis (two mole percents: $\text{LiFePO}_{3.98}\text{F}_{0.02}$). At the beginning we had much more fluorine in the precursor. However, fluorine ions usually sublime in open systems, with a gas flowing during the formation of olivine phase, so its actual concentration in the synthesized compound is much smaller than the nominal concentration in the precursor powder.

The Rietveld refinement has also shown additional electron density on the lithium sites indicating the formation of the so-called "antisite" defect. This is the defect in which the Li ion (on the M(1) site) and the Fe ion (on the M(2) site) are interchanged, thus creating $\text{Fe}_{\text{Li}}^+ - \text{Li}_{\text{Fe}}^-$ antisite pair. This antisite disorder (ca. 1-2 mol %) is believed to be intrinsic property of olivine LiFePO_4 [28]. It seems that fluorine doping leads to a slight reduction in the concentration of Li-Fe antisite defects (cf. Table 1). However, from the Rietveld refinement of the X-ray diffraction data, we cannot discriminate between the formation of antisite defects and the usual lithium deficiency, due to the well-known small X-ray atomic scattering factor of lithium ions.

Both refined and fixed fractional atomic coordinates (Table 2) were used for the calculation of all relevant bond distances and bond angles that enabled us to determine the coordination polyhedra. Relevant bond distances for undoped and doped powders are provided in Table 3. The calculated P-O(2) distance is significantly shorter, implying the presence of fluorine ion at the specific O(2) site, while the Fe-O(2) distance is consequently longer due to the Fe-O-P

inductive effect. The PO_4 tetrahedron is distorted because of the presence of one short and one stretched P–O bond equal to 1.5044 Å and 1.6130 Å, respectively. The average P–O distance of 1.569 Å is consistent with the value of 1.55 Å estimated from the effective ionic radii of the four-coordinated P^{5+} and O^{2-} [26]. In the introductory part we mentioned that PO_4 tetrahedra bridge between adjacent M(2) planes in the olivine structure. More specifically, three of four oxygen ions of PO_4 tetrahedron (namely O(1), and two O(3)) lie in the same zigzag M(2) layer, while the fourth oxygen (that is O(2)) belongs to the adjacent M(2) layer (cf. Fig. 1). As a consequence, these PO_4 tetrahedrons practically define the free volume for the Li-ions movement. It is interesting to observe that the closest atomic site to the lithium ‘channel’ is the O(2) oxygen site.

In order to perform detailed analysis of the microstructure of the synthesized powder we used images obtained on the basis of transmission electron microscopy (TEM), which are given in Figs. 5 and 6. The significant particle agglomeration is evident from the image depicted in Fig. 5. Therein, the grain boundaries are not quite clear and because of that the size of the individual primary particles is hard to estimate from this figure. Magnifying the specific part of the thin particle edge of our sample, by means of high resolution TEM (HRTEM), we were able to reveal the amorphous carbon film there. This carbon film is 3 nm thick and it is deposited on the (121) crystal plane of orthorhombic LiFePO_4 (Fig. 6). Accordingly, we can conclude that carbon nicely coats the synthesized olivine particles during the pyrolytic degradation of stearic acid producing, as a consequence, well-known improvement of the electrical conductivity of the synthesized powders.

The electrochemical performance of our sample, used as a cathode in a two-electrode cell, was examined by the charge-discharge tests. The galvanostatic cyclings were done with the same current rate, for both charging and discharging processes. The voltage vs. capacity discharge curves for different discharge rates are depicted in Fig. 7. The discharge rates are given in C/n,

where C is the nominal capacity equal to 170 mAhg^{-1} , and n is the discharge time given in hours needed for the complete discharge. Flat plateaus widths in the region around 3.4 V , observed during the discharge, are decreasing with increasing the current rate. Almost theoretical value of 164 mAhg^{-1} has been reached when $0.1C$ current was used for the discharging. It is also evident from Fig. 7 that reversible capacity at variable discharge rates shows excellent rate capability, during the cycling process.

3. Theoretical method

3.1 Computational Details

The spin unrestricted density functional theory (DFT) calculations for antiferromagnetic (AF) ordering were carried out firstly for the experimental lattice parameters of LiFePO_4 [21] using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2K code (Blaha et al. Ref. 29). The unit cell is partitioned into non-overlapping muffin-tin spheres around the atomic sites and interstitial region. For these two regions different basis sets were used and the Kohn-Sham equations were solved self-consistently on an $2 \times 4 \times 6$ \mathbf{k} -mesh in the first Brillouin zone (BZ) resulting in 48 \mathbf{k} -points. The exchange correlation potential was treated using: (a) the generalized gradient approximation (GGA) as parametrized by Perdew et al. [30] (we will refer to this calculation as PBE) and (b) the Tran-Blaha recipe [31] applied on a modified version of the Becke and Johnson exchange potential [32] for a more appropriate calculation of the band gap (we will refer to this calculation as TB-mBJ). The muffin-tin radii (R_{MT}) were 1.84 bohrs for Li, 1.89 bohrs for Fe, and 1.32 bohrs for P and O. Same radii were also used for determining the weighting of the partial densities of states for each atomic type and for

integrating the net electron spin within each muffin-tin sphere. The parameter $R_{KMAX} = R_{MT} * K_{MAX}$ determines convergence, where R_{MT} is the smallest muffin-tin sphere radius and K_{MAX} is the plane wave cut-off. We take this parameter to be $R_{KMAX} = 7$ while the reciprocal space truncation was controlled by parameter G_{MAX} for which we used 12 Bohr^{-1} . For the self-consistency cycle we used two convergence criteria: $\Delta E_{tot} < 10^{-4} \text{ Ry}$ and $\Delta q < 10^{-4} e$ (where e is the elementary charge). All graphs obtained on the basis of the FP-LAPW were produced with the Gaussian broadening of 0.04 eV . The scissors operator, which shifts the conduction band bottom, was not applied.

The spin polarized AF calculations were also performed with the GPAW computer code [33], based on real space grid implementation of the projector augmented wave (PAW) method with the grid spacing of 0.15 \AA [34, 35]. This method has been used for the extensive relaxation investigations because it is much faster than FP-LAPW method. The electronic exchange and correlation effects were described again using the PBE functional [30]. The calculations reported in this work were performed both for the experimental crystal structure of olivine-type lithium iron orthophosphate [20, 21], as well as for the properly relaxed pure LiFePO_4 and doped $\text{LiFePO}_{3.75}\text{F}_{0.25}$ (with one oxygen ion, out of sixteen, replaced with fluorine at three different possible oxygen positions: O(1), O(2) or O(3)). Atomic positions of all atoms are relaxed until force components on atoms were smaller than 0.05 eV/\AA . The structure optimization was carried out utilizing the BFGS (Broyden–Fletcher–Goldfarb–Shanno) algorithm [36]. The calculations for pure LiFePO_4 started by employing an orthorhombic unit cell with 28 atoms in four formula units (space group $Pnma$ (#62)), whose experimental lattice parameters are given in Table 1. The sampling of the corresponding Brillouin zone was done with 8 ($2 \times 2 \times 2$) Monkhorst-Pack special \mathbf{k} -points and the Fermi temperature broadening of 0.1 eV [37]. Additional convergence tests were also done with 32 ($2 \times 4 \times 4$) \mathbf{k} -points and the Fermi temperature of 0.03 eV . In the current work we

have chosen the AF ordering which preserves the inversion symmetry, present in the paramagnetic state. Bearing in mind that our main goal here is to investigate the most favourable place for fluorine to substitute oxygen in the olivine-type lithium iron orthophosphate, this will not be a serious limitation. Especially, if one takes into account earlier very small differences between the relaxed parameters and total energies obtained for various possible AF orderings in pure LiFePO_4 [38].

In order to estimate the influence of pronounced electronic correlations, characteristic for this compound, we also did additional test calculations for both pure and doped olivine with the effective Hubbard $U_{\text{eff}} = 4.3$ eV correlation correction included at Fe sites in the framework of so-called DFT + U approach, as implemented by Anisimov et al. [39, 40]. We will refer to these calculations as PBE+ U calculations (many workers refer to such calculations also as GGA+ U calculations).

3.2 Theoretical Results and Discussion

The antiferromagnetic calculations, with the same spins on sites related by inversion symmetry within crystalline unit cell, were performed on the basis of two different methods: FP-LAPW and PAW.

Firstly, we did FP-LAPW calculations (PBE, PBE+ U and TB-mBJ) with *experimental* values for lattice parameters and atomic positions (cf. Table 1, and Refs. 20 and 21). The one-electron spectra in terms of total and partial densities of states (DOS) can give us a qualitative picture of various contributions to the self-consistent results and of the bonding characteristics of the pure and fluorine doped olivine compounds. Figures 8 and 9 show total and the atom-resolved partial density of states for pure LiFePO_4 and doped $\text{LiFePO}_{3.75}\text{F}_{0.25}$ with one oxygen atom (out of

sixteen) at the O(2) position changed with fluorine. While phosphorous and lithium atoms are just giving their valence electrons without much hybridization with other atoms, oxygen p and iron d states hybridization produces certain order of covalence of Fe-O bonds. The dominant electronic character near the Fermi level is due to Fe $3d$ states, and a noticeable mixing with O $2p$ states is apparent approximately between -4 eV and -2 eV. Minority Fe $3d$ states are located in the narrow region around the band gap with practically no mixing with O or other cations in pure LiFePO_4 . The same is true for one fluorine atom substitution of oxygen O(2) atom, except for the Fermi level shift in the region of finite density of minority Fe d states with the consequent improvement in the electronic conductivity of doped $\text{LiFePO}_{3.75}\text{F}_{0.25}$. While the pure compound is an insulator with a tiny band gap within PBE, and more appropriate gap values with additional exchange-correlation corrections included in the framework of PBE+ U and TB-mBJ, the fluorine-doped olivine has finite density of states (DOS) at the Fermi level for both PBE and PBE+ U exchange-correlation functionals used. As a consequence, in the doped compound the band gap disappears, although the DOS is not too high in that region. Table 4 lists the gap values and the magnetic moments at all atomic sites obtained by means of the three upper mentioned exchange-correlation functionals for pure LiFePO_4 . Table 5 lists the magnetic moments at atomic sites obtained by the use of PBE and PBE+ U exchange-correlation functionals in $\text{LiFePO}_{3.75}\text{F}_{0.25}$. Let us note here that the half-metallic solution has been obtained for PBE exchange-correlation functional (cf. Fig. 9 which shows a gap in the down spin channel only). In order to show how the doping influence the character of electronic states around the gap, we have given the band structure results for antiferromagnetic LiFePO_4 and the doped $\text{LiFePO}_{3.75}\text{F}_{0.25}$ obtained by FP-LAPW with PBE, as well as the total density of states for $\text{LiFePO}_{3.75}\text{F}_{0.25}$, in the region $[-2, 2]$ eV around the Fermi level (Fig. 10). Half-metallic solution is evident for the doped compound.

Secondly, we performed full structural optimization for the pure LiFePO_4 compound, by means of GPAW. That is, for pure compound we have relaxed both lattice parameters and atomic positions. The relaxation changes of lattice parameters for the doped $\text{LiFePO}_{3.75}\text{F}_{0.25}$, when one of the oxygen atoms in the unit cell is replaced by fluorine, have been insignificant. Therefore, the appropriately relaxed lattice parameters of the pure LiFePO_4 were used for olivine doped with fluorine and later on we only performed relaxation of the atomic positions. The relaxed volume of the crystal unit cell is 2% larger than the experimental unit cell volume (the relaxed lattice parameters are: $a=10.404 \text{ \AA}$, $b= 6.049 \text{ \AA}$ and $c= 4.726 \text{ \AA}$).

The total energy of LiFePO_4 after fluorine doping at the O(2) site is 140 meV and 129 meV lower than if that substitution is made at the O(1) site O(3) site, respectively. This result is in accordance with our best Rietveld refinement achievement when fluorine ion was substituted at the O(2) site. The Fe-F bond length is longer than the previous Fe-O bond. The quite significant distortion of the original FeO_6 octahedron is shown in Fig. 11. The crystal structure of olivine has three different types of oxygen atoms, which form octahedrons around Fe and Li atoms and tetrahedrons around P atoms. This compound has zigzag planes of corner-shared FeO_6 octahedra in the b-c planes. The PO_4 tetrahedron share common O(3)-O(3) edge with FeO_6 octahedron and common corner at O(1) position with another FeO_6 octahedron from the same Fe layer, therefore stabilizing the crystal structure in that iron layer. The O(2) atom is common corner of PO_4 tetrahedron and FeO_6 octahedron from adjacent zigzag Fe layer. These O(2) atoms are making connections between the different Fe layers and thus taking their part in backing up the crystal structure (Fig. 1). There are no direct superexchange paths between the Fe atoms in these planes and long-range interactions, such as Fe-O-P-O-Fe triple exchange, were suggested [20]. Longer exchange paths along this direction are probable reason for the small 52 K value of the Neel's AF transition temperature [20]. The O(2) atoms are the type of oxygen closest to the

Li atomic channel. As such, they are probably prone to being replaced by fluorine at their positions because the extra free electrons, which appear in the system after doping, have come from lithium atoms and they are naturally striving to take the place of the closest oxygen. We are aware that this is just one extremely qualitative explanation of the reason why F substitution takes place at the O(2) sites.

Fig. 12 shows total AF density of states calculated for the relaxed atomic positions of doped $\text{LiFePO}_{3.75}\text{F}_{0.25}$ by using the GPAW method. Instead of insulating state characteristic for pure LiFePO_4 compound, we are getting a metallic solution with finite density of states at the Fermi energy. This metallic type solution endures even if we include Hubbard type $U_{\text{eff}} = 4.3$ eV correlation correction at the Fe sites. The extra electron, which appeared in the system after the substitution of one oxygen atom in the unit cell with fluorine, is striving to the iron atoms with their unfilled d electronic states. We also present the partial density of states of Fe, O(2) and F in pure and doped olivine (Fig. 13). Note a quite insignificant overlapping between the fluorine and iron states. The change of the character of the states at the Fermi energy and increased mobility of electrons for fluorine-doped olivine will clearly enhance the chemical diffusion of Li ions in the doped compound.

One possibility to illustrate graphically the extra electron distribution through the elementary cell of the doped compound is to present the isosurface plots of the total charge density difference between fluorine-doped olivine $\text{LiFePO}_{3.75}\text{F}_{0.25}$ and pure LiFePO_4 ($\Delta\rho = \rho_{\text{doped}} - \rho_{\text{pure}}$). Fig. 14 depicts this density difference calculated using GPAW with PBE exchange-correlation functional. Note that the electron density of LiFePO_4 was calculated for the oxygen O(2) placed at the relaxed position of fluorine in doped $\text{LiFePO}_{3.75}\text{F}_{0.25}$. It is clearly seen from this figure that extra electron is leaving the atomic sphere around the fluorine atom (yellow contour) and is transferred mostly to the iron atoms (gray contours).

In order to represent our results in more quantitative terms, we offer in Table 6 the exact extra electron distribution between the atoms in the unit cell. Note that this extra electron is obtained by integration of total charge density between -0.4 eV and E_f , at the bottom of the conduction band.

4. Conclusions

F-doped lithium iron phosphate powder was successfully synthesized by facile precipitation in molten stearic acid, followed by thermal treatment. Crystal structure refinement showed that doping with fluorine ions preserves olivine structure, and that fluorine ions are solely positioned at O(2) oxygen site. The obtained powder showed excellent electrochemical performances with high rate capability.

Theoretical modelings confirmed and support these experimental findings. The fluorine substitution of O(2) oxygen is energetically most stable solution. The obtained metallic solution (no matter how poor that metallic state could be) with the expected increase in mobility of electrons for fluorine-doped olivine will, without a doubt, enhance the chemical diffusion of Li ions and positively influence electrochemical performance of the doped compound. Since a substitution of one oxygen with one fluorine atom in the crystal unit cell breaks the inversion symmetry of a doped compound, we also got noticeable ferrimagnetic moment per unit cell on the order of $\sim 0.25\mu_B$, where μ_B is the Bohr magneton. This effect could be measured by SQUID magnetometer on the carefully synthesized samples (samples without magnetic impurities).

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Table 1. The final results of the Rietveld structural refinement.

	LiFePO ₄ [21]	F-doped LiFePO ₄
Lattice parameters (Å)	a = 10.3279(3)	a = 10.3288(5)
	b = 6.0096(2)	b = 6.0065(3)
	c = 4.6994(1)	c = 4.6934(3)
Primitive cell volume (Å ³)	V = 291.68(9)	V = 291.18(2)
Mean crystallite size (nm)	75(4)	85(9)
Li site occ. by Fe	0.019(5)	0.017(7)
O2 site occ. by F	-	0.03(1)
R factor (%)	Rwp = 3.76	Rwp = 1.74

Table 2. Fixed and refined atomic coordinates and isotropic displacement parameters.

Fractional coordinates	F-doped LiFePO ₄			B (Å ²)
	x	y	z	
Li (4a)	0	0	0	2.7
Fe (4c)	0.2820(2)	0.25	0.9774(8)	1.4
P (4c)	0.0941(5)	0.25	0.4138(9)	0.4
O(1) (4c)	0.1059(10)	0.25	0.7423(11)	2.1
O(2) (4c)	0.4596(11)	0.25	0.2096(11)	2.1
O(3) (8d)	0.1690(9)	0.0380(10)	0.2822(10)	2.1

Table 3. Selected bond lengths (in Å).

M – O bond	LiFePO ₄	F-doped LiFePO ₄
Fe – O(1)	2.1593	2.1277
Fe – O(2)	2.1126	2.1341
Fe – O(3) x 2	2.2425	2.2424
Fe – O(3)' x 2	2.0425	2.0220
(Fe – O) _{ave}	2.1403	2.1318
Li – O(1) x 2	2.2288	2.2166
Li – O(2) x 2	2.0780	2.0704
Li – O(3) x 2	2.2018	2.2034
(Li – O) _{ave}	2.1695	2.1635
P – O(1)	1.5099	1.5466
P – O(2)	1.5218	1.5044
P – O(3) x 2	1.5954	1.6130
(P – O) _{ave}	1.5556	1.5692

Table 4. Calculated gap values and magnetic moments in Bohr magnetons (μ_B) at all atomic sites by use of FP-LAPW with *experimental* lattice parameters and PBE, PBE+ U and mBJ exchange-correlation functionals for pure antiferromagnetic LiFePO₄.

	$\mu[\mu_B]$ PBE	$\mu[\mu_B]$ mBJ	$\mu[\mu_B]$ PBE+ U
int.	0.00000	0.00000	0.00000
Li	-0.00059	-0.00022	-0.00046
Li	0.00059	0.00022	0.00046
Fe	3.38049	3.60538	3.53302
Fe	-3.38049	-3.60538	-3.53302
P	-0.00359	-0.00292	-0.00290
P	0.00359	0.00292	0.00290
O(1)	0.02814	0.02126	0.01982
O(1)	-0.02814	-0.02126	-0.01982
O(2)	0.02224	0.01745	0.01585
O(2)	-0.02224	-0.01745	-0.01585
O(3)	-0.02047	-0.001476	-0.01107
O(3)	0.02047	0.01476	0.01107
tot.	0.00000	0.00000	0.00000
E _g [eV]	0.508	2.782	2.845

Table 5. Calculated magnetic moments in Bohr magnetons (μ_B) at atomic sites by use of FP-LAPW with experimental lattice parameters and PBE, PBE+ U and mBJ exchange-correlation functionals for doped olivine $\text{LiFePO}_{3.75}\text{F}_{0.25}$.

	μ [μ_B] PBE	μ [μ_B] PBE+ U
int.	-0.01912	-0.05536
Li	-0.00054	-0.00057
Li	-0.00054	-0.00057
Li	0.00053	-0.00017
Li	0.00053	-0.00017
Fe1	3.10307	3.35806
Fe2	3.19215	3.45083
Fe3	-3.20630	-3.47467
Fe4	-3.28679	-3.51067
P	-0.00311	-0.00256
P	-0.00295	-0.00257
P	0.00004	-0.00120
P	0.00291	0.00257
O(1)	0.02809	0.01860
O(1)	0.02467	0.01915
O(1)	-0.01548	0.01995
O(1)	-0.02275	-0.01945
F	0.00899	0.00543
O(2)	0.01613	0.01430
O(2)	-0.02075	-0.01568
O(2)	-0.02121	-0.01609
O(3)	-0.02058	-0.01530
O(3)	-0.01678	-0.01297
O(3)	-0.01677	-0.01297
O(3)	-0.02058	-0.01530
O(3)	0.01082	0.00603
O(3)	0.01120	0.00727
O(3)	0.01120	0.00727
O(3)	0.01081	0.00602

cell -0.25309 -0.28068

Table. 6 The extra electron distribution between the atoms and the interstitial (Int.) region of the unit cell for doped olivine $\text{LiFePO}_{3.75}\text{F}_{0.25}$ obtained by an integration of the total charge density between -0.4 eV and E_f (cf. Fig. 9)^{*)}.

	Fe1	Fe2	Fe3	Fe4	F	Int.	sum	cell
PBE	↑	0	0	0	0	0	0	0
	↓	0.3526	0.4295	0.0025	0.0030	0.0038	0.1693	0.9607
PBE+ U	↑	0.0045	0.0028	0.0736	0.0124	0.0107	0.1567	0.2607
	↓	0.2427	0.0198	0.0049	0.0029	0.0182	0.2594	0.5479

^{*)} The next to last column (sum) gives the sum of up and down spin contributions in previous columns, while the last column gives the result of the integration of total charge density between -0.4 eV and E_f , at the bottom of the conduction band. Let us note here quite different distribution of extra electron between the atoms, obtained by PBE and PBE+ U approaches, although the net ferrimagnetic moment per unit cell is approximately the same for both exchange-correlation functionals used (on the order of $\sim 0.25\mu_B$, cf. previous table).

> 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 mAhg^{-1} .

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Figure captions

Fig. 1. (Color online) 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.

Fig. 2. The image of the F-doped LiFePO_4/C obtained by FESEM.

Fig. 3. The size distribution of the particles in synthesized powder of the F-doped LiFePO_4/C .

Fig. 4. (Color online) The observed (\bullet), calculated (-), and difference (bottom) X-ray diffraction data of the F-doped LiFePO_4/C taken at room temperature. Vertical markers bellow the diffraction patterns indicate positions of possible Bragg reflections.

Fig. 5. TEM image of the F-doped LiFePO_4/C powder.

Fig. 6. HRTEM image of the F-doped LiFePO_4/C powder. Amorphous carbon film, with a thickness of 3 nm, is deposited on the (121) crystal plane of the orthorhombic LiFePO_4 .

Fig. 7. Charge-discharge curves of the F-doped LiFePO_4/C powder at different current rates and its rate performance (inset).

Fig. 8. (Color online) The antiferromagnetic total and partial DOS for LiFePO_4 calculated using the DFT with generalized gradient corrections (PBE), DFT with Coulomb correlations at Fe sites included (PBE+ U , $U_{\text{eff}}=4.3$ eV), and TB-mBJ approach [31]. Zero energy is taken at the Fermi level. Red, green and blue curves designate the s , p and d states in respective atomic spheres, while gray curves stand for the interstitial region contributions.

Fig. 9. (Color online) The AF total and partial DOS for doped $\text{LiFePO}_{3.75}\text{F}_{0.25}$ calculated using the PBE and PBE+ U , $U_{\text{eff}}=4.3$ eV. Red, green, blue, and gray curves designate the s , p , d and interstitial contributions.

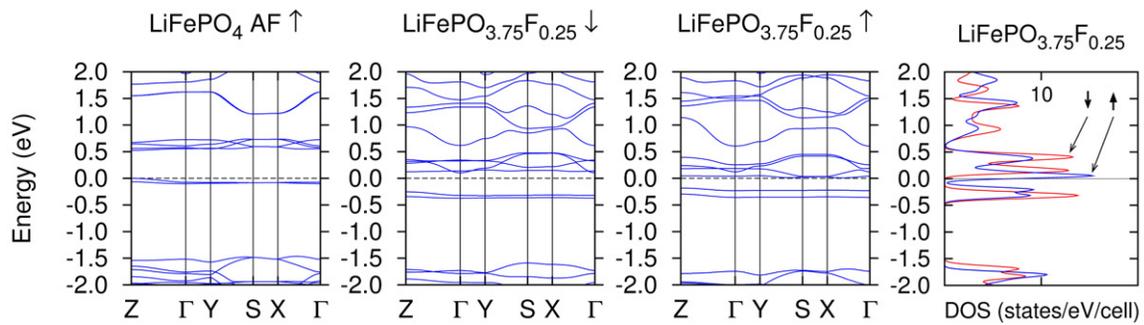
Fig. 10. (Color online) Band structure of LiFePO_4 (left), $\text{LiFePO}_{3.75}\text{F}_{0.25}$ (middle), and DOS for doped compound (extreme right) in narrow region around the Fermi level (energy range $E_f - 2$ eV to $E_f + 2$ eV)..

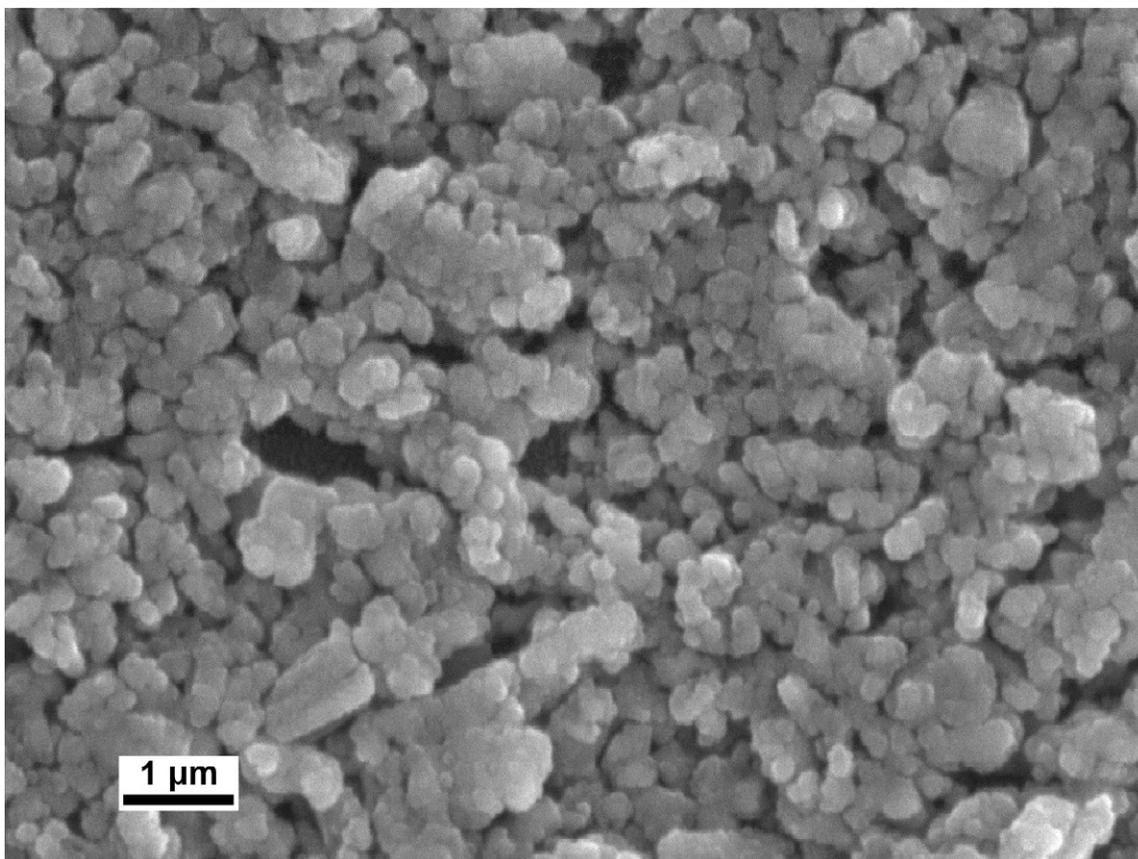
Fig. 11. (color online) The deformation of the FeO_6 octahedron caused by fluorine doping of LiFePO_4 , Up : the distorted octahedron when O(2) oxygen is replaced by F (note that F doping affects the other Fe-O bond lengths), and $Down$: FeO_6 octahedron.

Fig. 12. (color online) The AF total DOS for $\text{LiFePO}_{3.75}\text{F}_{0.25}$ calculated using the GPAW: a real-space implementation of the projector augmented-wave method [33] with GGA corrections included [30]. DOS has been calculated with the Gaussian width of 0.2 eV or 0.05 eV (inset).

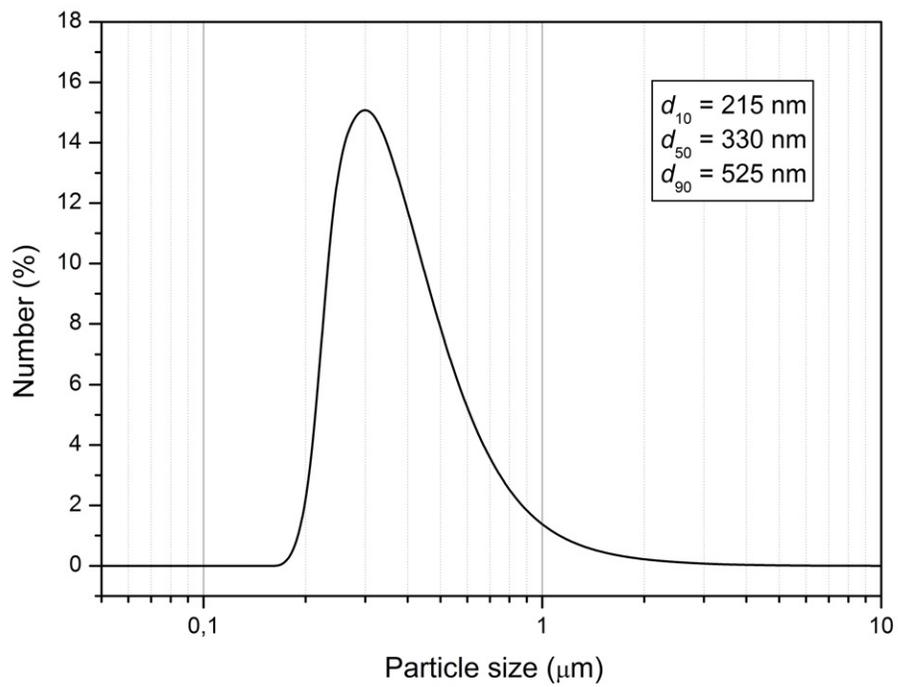
Fig. 13. (color online) The AF partial DOS calculated both for LiFePO_4 (iron and oxygen): (a) and (b), and for $\text{LiFePO}_{3.75}\text{F}_{0.25}$ (iron and fluorine): (c) and (d) by use of the GPAW with PBE corrections. Partial DOS has been calculated with the (Gaussian) width of 0.2 eV or 0.05 eV (insets). Oxygen's partial density of states changed insignificantly for the doped compound to deserve additional graphical presentation.

Fig. 14. (color online) Two isosurfaces of $\Delta\rho$ (see the text for the definition). Yellow contours stand for the electron density depletion (charge density difference for one negative value in arbitrary units), while the gray ones depict the electron density enhancement (positive density difference of the same absolute value in the same arbitrary units) within the unit cell. The volumes enclosed by gray and yellow contours, around the respective atoms, could be used as the approximate measure of accumulation/depletion of the electron density (entirety of one extra electron) at these places in the unit cell.

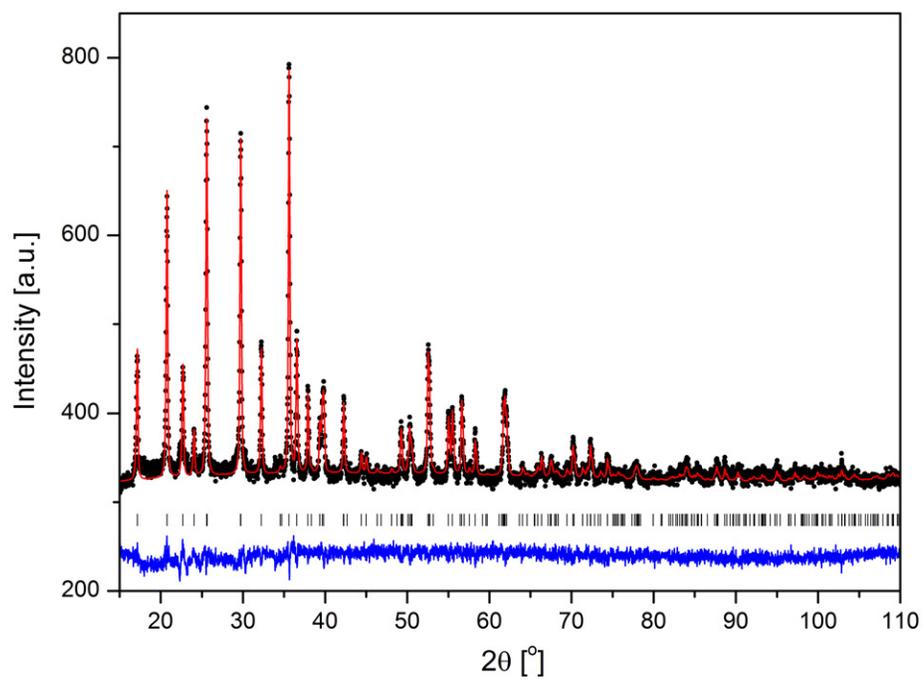


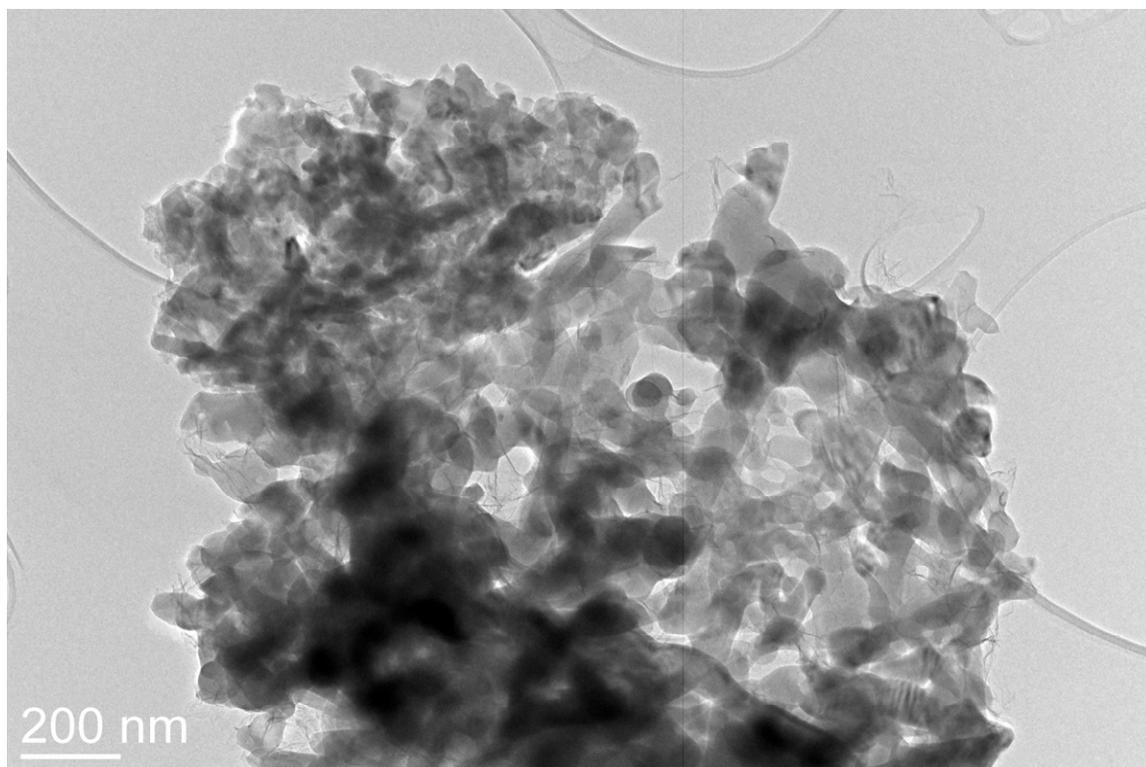


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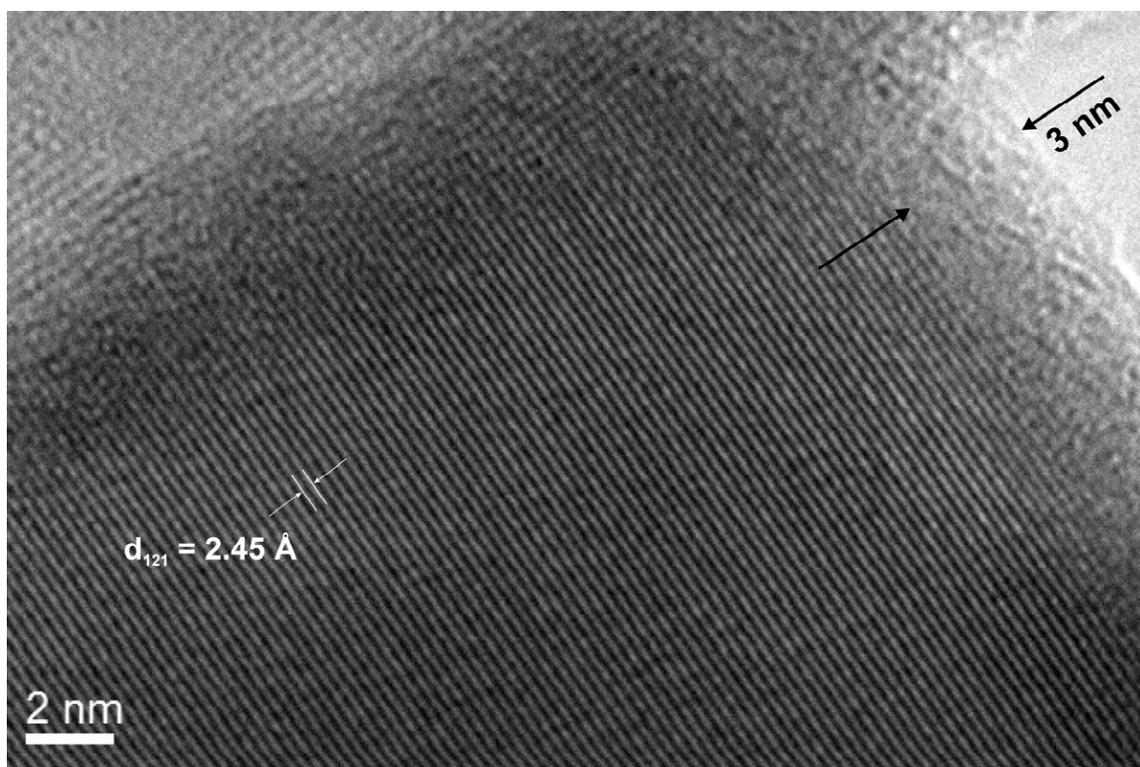


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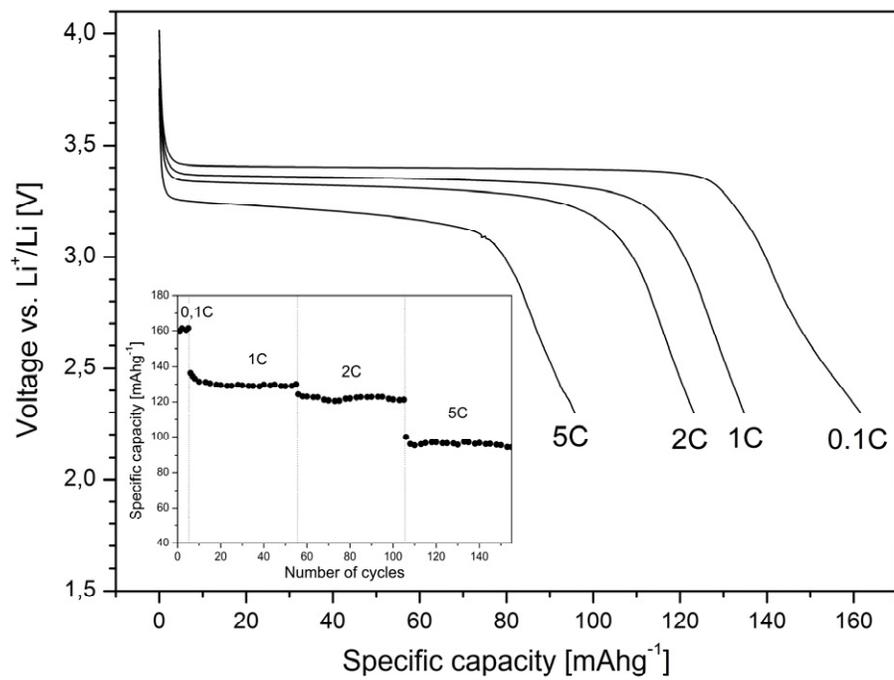


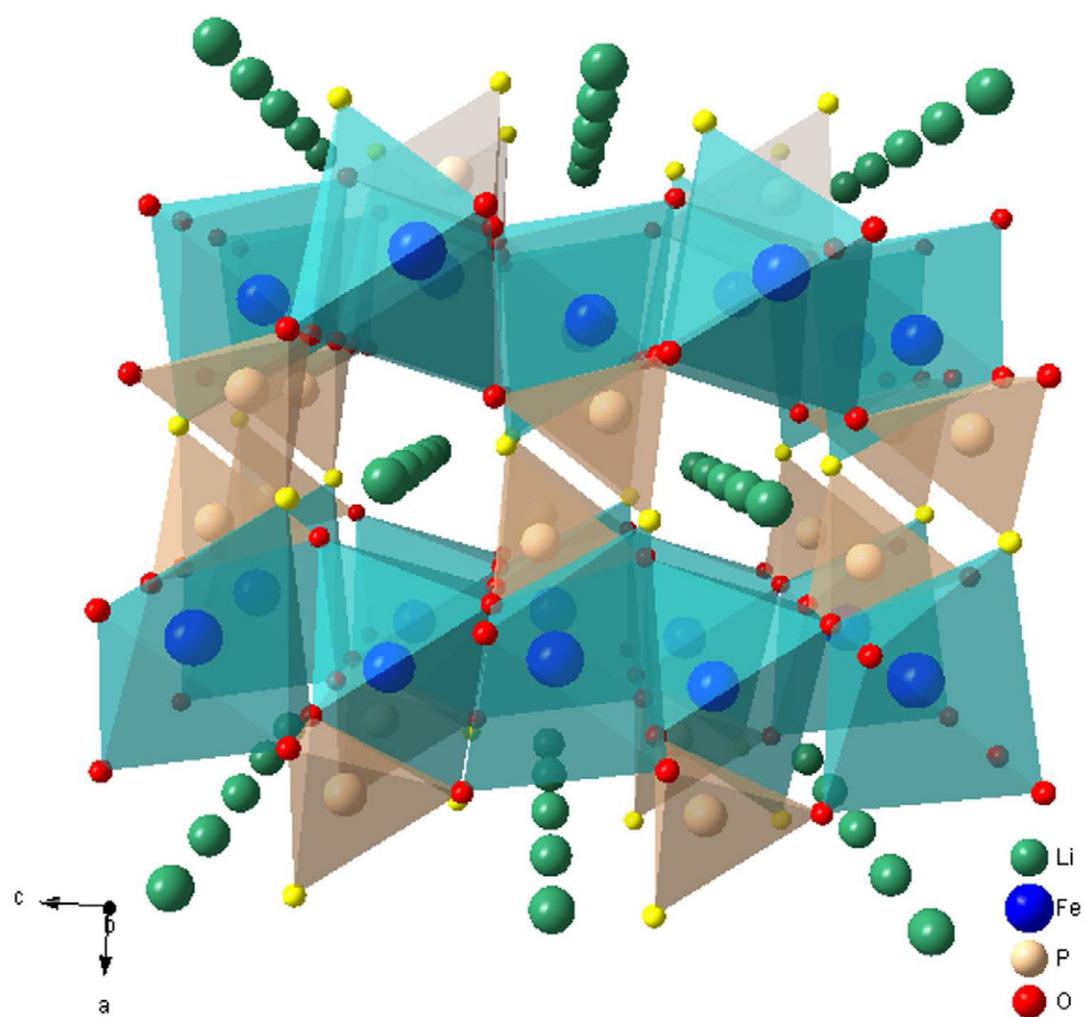


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