



PHYSICAL CHEMISTRY 2012

¹¹th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Under the auspices of the
University of Belgrade

Proceedings

The Conference is dedicated to
Professor Ivan Draganić

September 24-28, 2012
Belgrade, Serbia

ISBN 978-86-82475-27-9 <i>Volume 1</i> ISBN 978-86-82475-28-6 <i>Volume II</i>

Title: PHYSICAL CHEMISTRY 2012 (Proceedings)

Editors: S. Anić and Ž. Čupić

Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia

Publisher: Society of Physical Chemists of Serbia

For Publisher: S. Anić, President of Society of Physical Chemists of Serbia

Printed by: “Jovan” Printing and Publishing Company; 200 Copies;

Number of pages: 6+ 497; **Format:** B5; Printing finished in September 2012.

Text and Layout: “Jovan”

200- Copy printing

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SYNTHESIS AND STRUCTURAL PROPERTIES OF F-DOPED LiFePO₄/C COMPOSITE

M. Milović¹, D. Jugović¹, M. Mitrić², B. Jokić³, D. Uskoković¹

¹*Institute of Technical Sciences of SASA, Belgrade, Serbia*

²*Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia*

³*Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia*

Introduction

Olivine type LiFePO₄ is used as a cathode material for Li-ion batteries because of its high energy density (with capacity of 170 mAh/g and plateau voltage of 3.5 V vs. Li⁺/Li), stability, safety, environmental friendliness and low cost. However, the low intrinsic electronic and ionic conductivity limits its application.

Effects of cation doping on improving electrochemical performance of LiFePO₄ has been widely studied and debated [1]. On the other hand, anion doping has not been sufficiently investigated. It is generally accepted that doping of LiFePO₄ with fluorine would enhance its electrochemical performance. Several papers are dealing with the influence of small quantities of fluorine dopant on the properties of LiFePO₄ [2, 3]. In this paper, we report on the impact of F doping on the crystal structure of LiFePO₄/C composite obtained through the co-precipitation in molten stearic acid, a new method established by our group [4].

Experimental

F-doped LiFePO₄/C was synthesized by co-precipitation in molten stearic acid [4]. In the molten stearic acid, stoichiometric amounts of aqueous solutions of (NH₄)₂HPO₄ and FeSO₄·7H₂O were added sequentially when precipitation occurred. Dry melt was reground and mixed with solid LiF, which served as both lithium and fluorine source. Thus obtained powder was calcined at temperature of 700°C for 3 hours in a slightly reductive atmosphere (Ar + 5%H₂), then washed in distilled water and dried under vacuum. The properties of thus obtained powder were compared with the previously published data of the undoped one obtained under the same synthesis conditions, except for lithium salt [4].

X-ray diffraction data were collected on a Philips PW 1050 diffractometer with Cu-Kα_{1,2} radiation (Ni filter) at the room temperature. Measurements were done in 2θ range of 10-110° with scanning step width of 0.02° and 14 s times per step. Crystal structure refinement was based on the Rietveld full profile method [5] using the Koalariet computing program [6]. Chemical composition of the final compound was Li:Fe:P = 0.99:1.00:1.00 determined by inductively coupled plasma (ICP) analysis. The fluorine in the sample was detected with SA720 ion selective electrode (ISE).

Results and Discussion

X-ray powder diffraction pattern (Fig. 1) was used for phase identification and structural analysis. Olivine type LiFePO_4 was obtained as a major phase with FeS as an impurity phase. There is no evidence of a crystalline carbon, so internal carbon could be treated as a contribution to the background. The structure of F-doped LiFePO_4 has been refined in the space group $Pnma$ (D_{2h}^{16}) in olivine type with following crystallographic positions: Li^+ ions in special crystallographic position $4a$ [0,0,0] with local symmetry $\bar{1}$; Fe^{2+} and P^{5+} ions occupy two different crystallographic $4c$ positions $[x,0.25,z]$ with local symmetry m ; O^{2-} ions occupy three different crystallographic positions: additional two $4c$ positions and one general $8d$ position $[x,y,z]$ with local symmetry 1 .

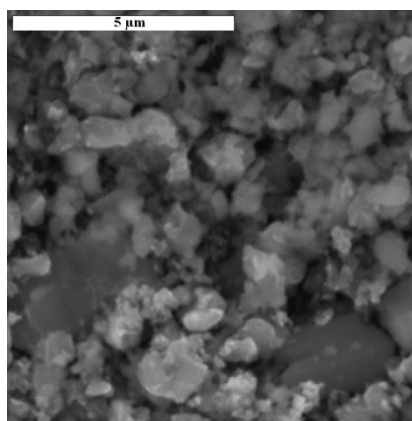
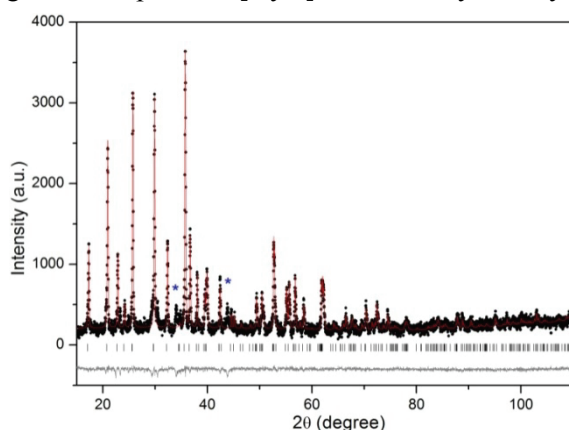


Fig. 1. The observed (\bullet), calculated ($-$), and difference (bottom) X-ray diffraction data of F-doped LiFePO_4/C taken at room temperature; vertical markers below the diffraction pattern indicate positions of possible Bragg reflections; the

Fig. 2. Scanning electron microscopy image of F-doped LiFePO_4/C prepared via co-precipitation method.

The Rietveld refinement results (Table 1 and 2) indicate decreased lattice parameters and primitive cell volume compared with the undoped sample synthesized under the same conditions [4]. This finding is an evidence that F^- ions are successfully incorporated in the lattice, since F^- ions are smaller than O^{2-} ions ($r^{\text{VI}}(\text{F}^-) = 1.33 \text{ \AA}$, $r^{\text{VI}}(\text{O}^{2-}) = 1.40 \text{ \AA}$). There are three kinds of O sites (namely O1, O2, and O3) in the lattice that may be occupied by fluorine separately or randomly. The best refinement was accomplished when O2 site was allowed to be occupied by fluorine ions. The calculated value of dopant concentration matches well with the chemical composition of the powder. Furthermore, doping with fluorine resulted in increased crystallite size. The Rietveld refinement also showed additional electron density on the lithium sites indicating so-called "anti-site" defect in which Li ion (on the M1 site) and Fe ion (on the M2 site) are interchanged.

Table 1. The final results of the structural refinement for undoped [4] and F-doped LiFePO₄.

	Lattice parameters [Å]	Primitive cell volume [Å ³]	Mean crystallite size [nm]	Li site occ. by Fe	O2 site occ. by F	R factor [%]
LiFePO ₄	a = 10.3279(3) b = 6.0096(2) c = 4.6994(1)	V = 291.68(9)	75(10)	0.020(5)	-	Rwp = 4.49
F-doped LiFePO ₄	a = 10.3340(2) b = 6.0086(1) c = 4.6943(3)	V = 291.49(8)	150(9)	0.027(3)	0.04(1)	Rwp = 2.07

Table 2. Fixed and refined atomic coordinates.

Fractional coordinates	LiFePO ₄			F-doped LiFePO ₄		
	x	y	z	x	y	z
Li (4a)	0	0	0	0	0	0
Fe (4c)	0.2820(3)	0.25	0.9749(4)	0.2820(2)	0.25	0.9724(8)
P (4c)	0.0924(4)	0.25	0.4140(6)	0.0939(6)	0.25	0.4155(6)
O(1) (4c)	0.1039(6)	0.25	0.7343(7)	0.1076(9)	0.25	0.7331(2)
O(2) (4c)	0.4563(6)	0.25	0.2100(7)	0.4650(9)	0.25	0.2126(6)
O(3) (8d)	0.1682(1)	0.0426(7)	0.2828(6)	0.1691(9)	0.0365(9)	0.2804(5)

The typical SEM image of as-prepared F-doped LiFePO₄/C composite is presented in Fig. 2. It shows wide particle size distribution, with increased particle size compared to the undoped powder. Apparently, F substitution catalyzes the growth of the primary particles. By comparing mean particle size estimated from SEM image (Fig. 2.) with mean crystallite size (Table 1) it can be concluded that particles are polycrystalline composed of a number of crystallites.

Conclusion

F-doped lithium iron phosphate powder was successfully synthesized by facile co-precipitation in molten stearic acid followed by thermal treatment. Crystal structure refinement showed that doping with fluorine ions preserves olivine structure. According to the Rietveld refinement fluorine ions occupy separately O2 oxygen site. Scanning electron microscopy showed that F substitution catalyzes the growth of the primary particles.

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CIP Volume I

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

544(082)
621.35(082)
66.017/.018(082)

MEĐUNARODNA konferencija iz fundamentalne i
primenjene fizičke hemije (11 ; 2012 ;
Beograd)

Physical Chemistry 2012 : proceedings.
#Vol. #1 / 11th International Conference on
Fundamental and Applied Aspects of Physical
Chemistry, September 24-28, 2012, Belgrade ;
[editors S.[Slobodan] Anić and Ž.[Željko]
Čupić ; organized by Society of Physical
Chemists of Serbia ... et al.]. - Belgrade :
Society of Physical Chemists of Serbia, 2012
(Belgrade : Jovan). - VI, 498 str. : ilustr.
; 24 cm

"The Conference is dedicated to Professor
Ivan Draganić" --> nasl. str. - Tiraž 200. -
Bibliografija uz svaki rad.

ISBN 978-86-82475-27-9
1. Društvo fizikohemičara Srbije (Beograd)
a) Физичка хемија - Зборници b)
Електрохемијско инжењерство - Зборници c)
Наука о материјалима - Зборници
COBISS.SR-ID 193432332