

Short communication

Effect of synthesis conditions on the properties of LiFePO_4 for secondary lithium batteries

Do-Kyun Kim^{a,b}, Hyun-Min Park^b, Su-Jin Jung^b,
Yeon Uk Jeong^a, Joon-Hyung Lee^a, Jeong-Joo Kim^{a,*}

^a Department of Inorganic Materials Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea

^b New Materials Evaluation Center, Korea Research Institute of Standard and Science, Taejeon 305-600, Republic of Korea

Available online 8 June 2006

Abstract

LiFePO_4 is one of the promising materials for cathode of secondary lithium batteries due to its high energy density, low cost, environmental friendliness and safety. However, LiFePO_4 has very poor electronic conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$) and Li-ion diffusion coefficient ($\sim 1.8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$) at room temperature. In an attempt to improve electrochemical properties, Li_xFePO_4 with various amounts of Li contents were investigated in this study. Li_xFePO_4 ($X = 0.7\text{--}1.1$) samples were synthesized by solid-state reaction. High resolution X-ray diffraction, Rietveld analysis, BET, scanning electron microscopy, and hall effect measurement system were used to characterize these samples. Electronic conductivities of the samples with Li-deficient and Li-excess in Li_xFePO_4 were 10^{-3} to $10^{-1} \text{ S cm}^{-1}$. Discharge capacities and rate capabilities of the samples with Li-deficient and Li-excess in Li_xFePO_4 were higher than those of stoichiometric LiFePO_4 sample. $\text{Li}_{0.9}\text{FePO}_4$ samples fired at 700°C had discharge capacity of 156 and 140 mAh g^{-1} at 0.1 C- and 2 C-rate, respectively.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Li-ion batteries; LiFePO_4 ; Surface area; Electronic conductivity

1. Introduction

Secondary lithium batteries are attractive power sources for portable electronic devices as well as electrical vehicle. Lithium batteries have high energy and power density and good cycle life compared to those of nickel metal hydride and nickel cadmium batteries [1]. Recently, attention has been focused on LiFePO_4 as an alternative cathode material, which was proposed by Dr. Goodenough and co-workers [2]. In spite of poor electronic conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$) and density, low cost and environmental friendliness have drawn attentions for the future market. One of the challenging objectives for LiFePO_4 is to improve electronic conductivity and various approaches have been made. Huang et al. reported LiFePO_4 containing carbon-gel gives 100% of theoretical capacity at 80°C at 0.1 C discharge rate [3]. Masquelier found high capacities at elevated temperatures using extensive milling of the material with carbon [4]. Chiang et al. proposed doped LiFePO_4 , $\text{Li}_{1-x}\text{M}_x\text{FePO}_4$ ($M = \text{Nb, Mg, Ti and Zr}$), has excellent electrochemical behavior,

which increased electronic conductivity of LiFePO_4 by a factor of $\sim 10^8$ [5]. But, this result is very debatable, Nazar et al. suggest that the high electronic conductivity is related to formation of Fe_2P , which is very conductive and is formed by carbothermal reaction at high temperature [6]. It is supposed that the differences in synthesis conditions may result in the properties of final products. This paper describes the substantial effort to clarify the effects of various synthesis conditions on the electrical and electrochemical properties of LiFePO_4 .

2. Experimental

Li_xFePO_4 ($X = 0.7\text{--}1.1$) samples were synthesized by solid-state reaction. Li_2CO_3 (Aldrich), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich), $\text{NH}_4\text{H}_2\text{PO}_4$ (Aldrich) as starting materials were milled with zirconia ball in acetone for 24 h. After acetone was removed, the mixture was then decomposed at 350°C for 10 h in flowing N_2 gas to avoid oxidation of Fe^{2+} . The powder was ground again using mortar and pestle, then it was pelletized and formed by CIP (2000 atm). Finally the samples were heated at 700°C for 24 h in flowing N_2 gas. To analyze crystal structure of the products, X-ray powder diffraction patterns were obtained by

* Corresponding author. Tel.: +82 53 950 5635; fax: +82 53 950 5645.
E-mail address: jjkim@knu.ac.kr (J.-J. Kim).

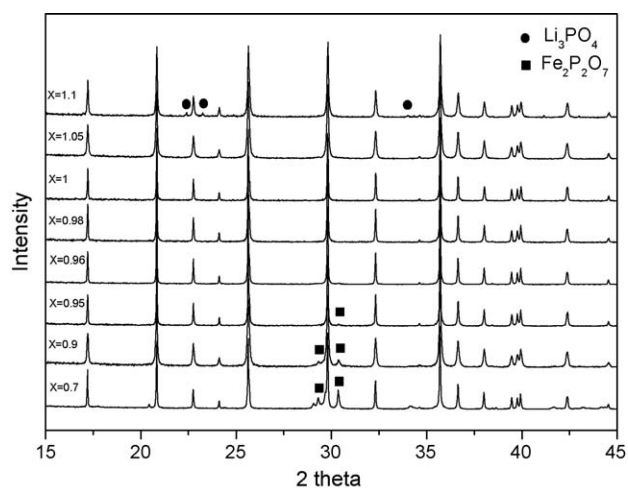


Fig. 1. High resolution XRD patterns of Li_xFePO_4 with various Li contents.

using an high resolution X-ray diffractometer (8C2 beam line, Pohang Accelerator Lab, Korea) and Rietveld analysis was performed. Scanning electron microscope (DS-130C, Akashi) was used to observe morphology of each sample. BET (nova 2000 & autosorb-1-c) was used to measure surface area of samples. In order to measure electronic conductivity, hall effect measurement system (HEM-2000, Sang-Rok, Korea) was used. The electrochemical performance of the Li_xFePO_4 as cathode was evaluated by using a coin-type cell (size 2016). Composite cathode films were prepared by mixing of 75 wt% active material, 15 wt% acetylene black as a conductive additive and 10 wt% polyvinylidene fluoride (PVDF) as a binder, and *N*-methyl pyrrolidone (NMP) as a solvent. Lithium metal was used as anode. For electrolytes, 1.15 M LiPF_6 was dissolved in the solution of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) with ratio of 3:6:1. The galvanostatic charge/discharge test was performed between 2 and 4 V with different current densities (0.1, 0.2, 0.5, 1 and 2 C), and 1 C rate was 120 mAh g^{-1} .

3. Results and discussions

In order to investigate the effect of synthesis conditions on the structure and properties, Li_xFePO_4 ($X=0.7$ – 1.1) samples were synthesized by solid-state reaction. High resolution XRD patterns of these samples were shown in Fig. 1. While $\text{Fe}_2\text{P}_2\text{O}_7$ impurity was found in Li_xFePO_4 ($X=0.7$ – 0.95) samples, Li_3PO_4 impurity was found in Li_xFePO_4 ($X=1.1$) sample

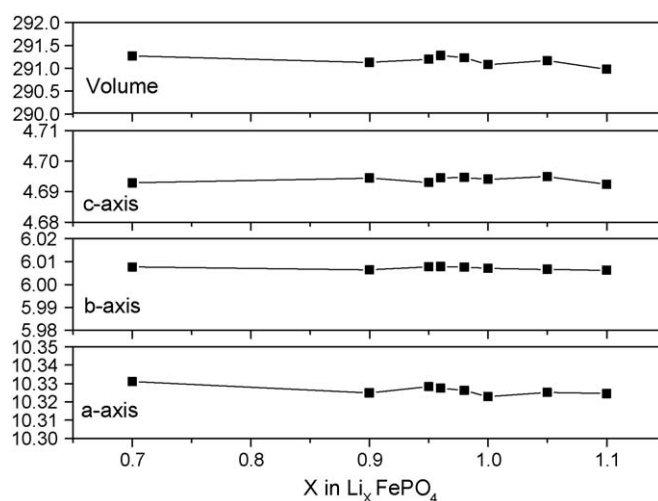


Fig. 2. Lattice parameters of Li_xFePO_4 with various Li contents.

Table 1

Results of Rietveld refinement of Li_xFePO_4 in accordance with various Li contents

	R_p	R_{wp}	R_{exp}	X^2
$\text{Li}_{0.9}\text{FePO}_4$	7.26	10.2	6.83	2.23
$\text{Li}_{0.95}\text{FePO}_4$	7.78	11.8	6.81	3
LiFePO_4	6.22	8.88	6.76	1.72
$\text{Li}_{1.05}\text{FePO}_4$	6.72	9.71	6.82	2.02
$\text{Li}_{1.1}\text{FePO}_4$	8.15	12.4	6.81	3.31

$$R_{wp} = \left(\frac{\sum w_i (y_i(\text{obs}) - y_i(\text{calc}))^2}{\sum w_i (y_i(\text{obs}))^2} \right)^{1/2}, R_p = \left(\frac{\sum |y_i(\text{obs}) - y_i(\text{calc})|}{\sum y_i(\text{obs})} \right), X^2 = (R_{wp}/R_{exp})^2$$

and single phases were found in Li_xFePO_4 ($X=0.96$ – 1.05) samples. Fig. 2 shows that lattice constants of these samples are approximately similar values. Table 1 give the results of Rietveld refinement (Rietveld refinement profiles are not shown). In Li_xFePO_4 ($X=1$) sample, we could gain very reasonable R_p and X^2 value (6.22 and 1.72, respectively). but, the value of the other samples are comparatively high. These high R_p and X^2 values might be due to second phase. Therefore, variation of Li content in the samples had no effect on the change of the crystal structures and lattice constants. SEM images of samples with various Li contents were shown in Fig. 3 and Electronic conductivities and surface area of samples were shown in Fig. 4. While Li_xFePO_4 ($X=1$) gives relatively larger particles and small surface area of $10 \text{ m}^2 \text{ g}^{-1}$, Li deficient or excess composition samples have much larger surface areas. These

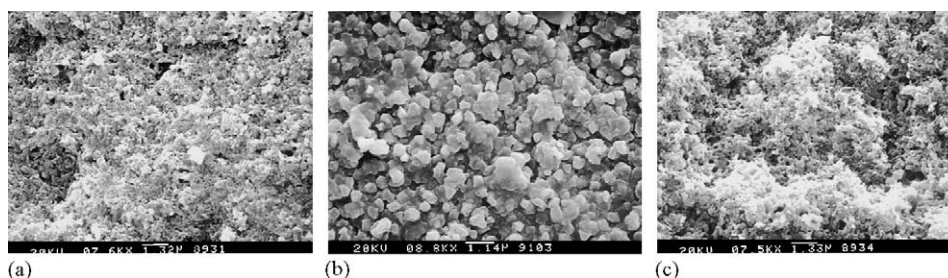


Fig. 3. S.E.M. images of Li_xFePO_4 with various Li contents. (a) $\text{Li}_{0.9}\text{FePO}_4$, (b) LiFePO_4 and (c) $\text{Li}_{1.1}\text{FePO}_4$.

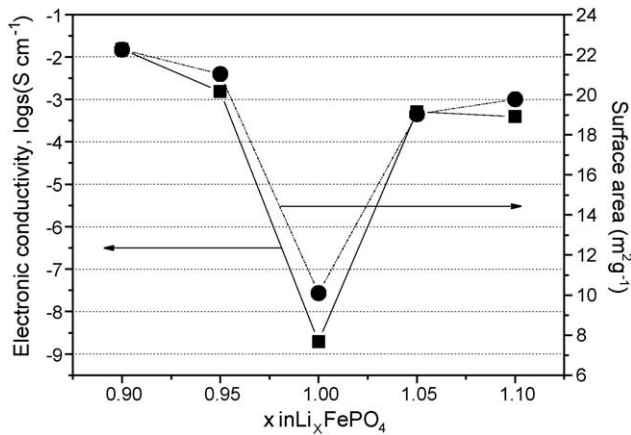


Fig. 4. Electronic conductivity and surface areas of Li_xFePO_4 with various Li contents.

might be due to the retardation of particle growth by impurity. While Li deficient or excess composition samples give 10^{-3} to $10^{-2} \text{ S cm}^{-1}$, LiFePO_4 has a very low electronic conductivities of $10^{-9} \text{ S cm}^{-1}$. These might be due to the effect of impurities that mentioned before as well as different amounts of remaining carbon in the samples. The effect of remaining carbon for various synthesis conditions was previously reported by Armand et al. [7].

Fig. 5 shows the results of charge and discharge test for Li_xFePO_4 ($X=0.9, 1$ and 1.1) samples. In the case of LiFePO_4 sample, discharge capacities were 112 and 56 mAh g^{-1} at 0.1

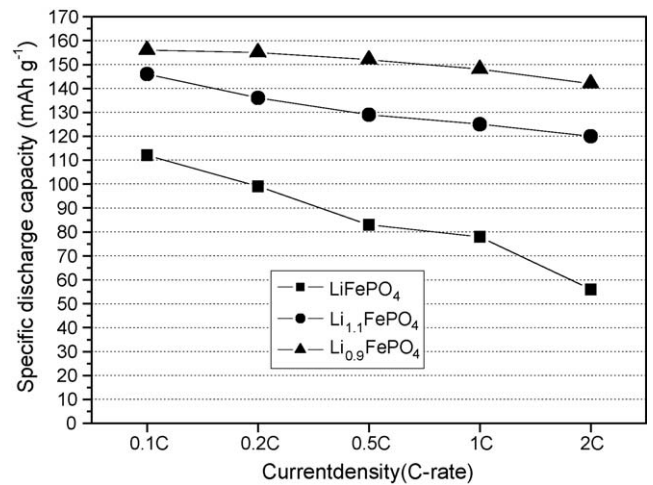


Fig. 6. Comparison of discharge capacities of Li_xFePO_4 with various current densities.

and 2 C, respectively. $\text{Li}_{0.9}\text{FePO}_4$ and $\text{Li}_{1.1}\text{FePO}_4$ samples give 0.1 C-rate capacities of 156 and 146 mAh g^{-1} , and 2 C-rate capacities of 142 and 120 mAh g^{-1} , respectively. Comparison of discharge capacities of samples with various current densities is shown in Fig. 6. $\text{Li}_{0.9}\text{FePO}_4$ sample was found to have more capacity and better rate capability. This result suggested that particle size and ionic conductivity determined the electrochemical properties of mixed ionic conductor in our experiments. In addition to that, the effect of impurities might play a role in this result.

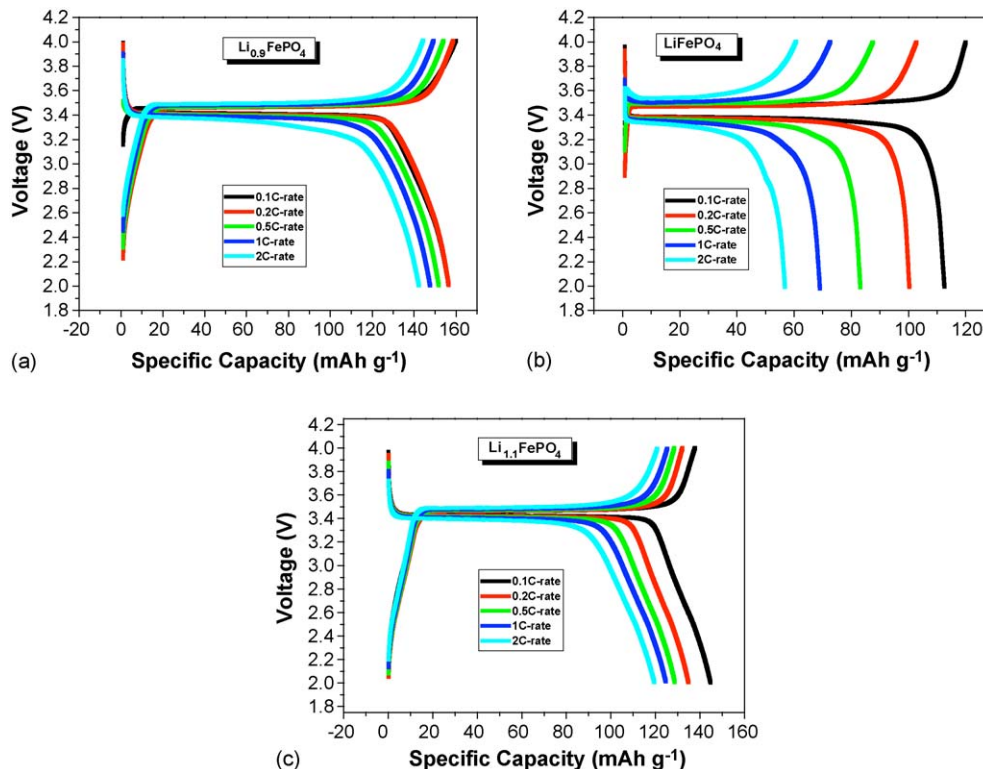


Fig. 5. Charge/discharge profile of Li_xFePO_4 with various Li contents (a) $\text{Li}_{0.9}\text{FePO}_4$, (b) LiFePO_4 and (c) $\text{Li}_{1.1}\text{FePO}_4$.

4. Conclusions

Li_XFePO_4 ($X=0.7\text{--}1.1$) samples were synthesized by solid-state reaction. Li deficient and excess samples included $\text{Fe}_2\text{P}_2\text{O}_7$ and Li_3PO_4 as impurities, respectively. Results of high resolution XRD and Rietveld refinement confirmed that significant changes were not found in crystal structure and lattice constant. Li deficient and excess samples had smaller particle size and higher electronic conductivities than those of LiFePO_4 sample. These might be due to the effect of various impurities in the samples. $\text{Li}_{0.9}\text{FePO}_4$ sample was found to have higher capacity and better rate capability. Higher surface area and Li ion diffusion resulted in better electrochemical properties of cathode material for Li ion batteries. Controls of synthesis conditions and microstructure are thought to be significant factors of development of promising candidate for Li ion batteries.

Acknowledgements

This work was supported by the National Research Laboratory grant from the Ministry of Science and Technology (MOST) and Korea Science and Engineering Foundation (KOSEF).

References

- [1] M. Armand, *Solid State Ionics* 69 (1994) 309.
- [2] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [3] H. Huang, S.C. Yin, L.F. Nazar, *Electrochem. Solid-State Lett.* 4 (2001) A170.
- [4] C. Masquelier, C. Wurm, M. Morcrette, J. Gaubicher, *International Meeting on Solid State Ionics*, Cairns, Australia, July 9–13, 2001, International Society of Solid State Ionics, A-IN-06, 2001.
- [5] S.Y. Chung, J.T. Bloking, Y.M. Chiang, *Nature Mater.* 1 (2002) 123.
- [6] P.S. Herle, B. Ellis, N. Coombs, L.F. Nazar, *Nature Mater.* 3 (2004) 147.
- [7] N. Ravet, A. Abouimrane, M. Armand, *Nature Mater.* 2 (2003) 702.