

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/26717915>

Nature of Insulating-Phase Transition and Degradation of Structure and Electrochemical Reactivity in an Olivine-Structured Material, LiFePO_4

ARTICLE in INORGANIC CHEMISTRY · SEPTEMBER 2009

Impact Factor: 4.76 · DOI: 10.1021/ic9009114 · Source: PubMed

CITATIONS

15

READS

20

5 AUTHORS, INCLUDING:



Min-Sang Song

Samsung

32 PUBLICATIONS 1,245 CITATIONS

SEE PROFILE



Yong-Mook Kang

Dongguk University

111 PUBLICATIONS 2,707 CITATIONS

SEE PROFILE



Kyusung Park

University of Texas at Austin

59 PUBLICATIONS 1,975 CITATIONS

SEE PROFILE



Hyuk Sang Kwon

Korea Advanced Institute of Science and Tec...

203 PUBLICATIONS 3,165 CITATIONS

SEE PROFILE

Nature of Insulating-Phase Transition and Degradation of Structure and Electrochemical Reactivity in an Olivine-Structured Material, LiFePO_4

Min-Sang Song,^{†,||} Yong-Mook Kang,^{*,†} Yong-Il Kim,[§] Kyu-Sung Park,^{||} and Hyuk-Sang Kwon^{*,†}

[†]Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-Dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea, [‡]Division of Advanced Materials Engineering, Kongju National University, 275 Budae-dong, Cheonan, Chungnam, Republic of Korea,

[§]Korea Research Institute of Standards and Science, P.O. Box 102, Yuseong, Daejeon, Republic of Korea, and

^{||}Battery Group, Emerging Center, Samsung Advanced Institute of Technology, San 14-1 Nongseo-dong, Giheung-gu, Yongin-si, Gyeonggi-do, 446-712, Republic of Korea

Received May 11, 2009

Synthesis time using microwave irradiation was varied to elucidate the electrochemical degradation mechanism of LiFePO_4 related to the evolution of Fe_2P . When the amount of Fe_2P was above a critical level, LiFePO_4 tended to change into an insulating phase, $\text{Li}_4\text{P}_2\text{O}_7$. The correlation between structural analysis and electrochemical analysis attributed the initial degradation of LiFePO_4 to the low electronic conductivity of $\text{Li}_4\text{P}_2\text{O}_7$, whereas the deficiency of P and O evolved by $\text{Li}_4\text{P}_2\text{O}_7$ resulted in the cyclic degradation of LiFePO_4 . This kind of correlation between structure and electrochemical performance in intercalation materials will significantly contribute to an explanation of their degradation mechanism for their application.

Introduction

LiFePO_4 , with an olivine structure, has been spotlighted as a promising candidate cathode material due to its excellent thermal stability, the low cost of its precursors, the high reversibility of Li insertion/extraction, and a lack of toxicity.^{1–3} Although LiFePO_4 has an inherent poor kinetic property ($\sigma_e = 10^{-8} \text{ S cm}^{-1}$ (low electronic conductivity), $D_{\text{Li}^+} = 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ at room temperature (rt; low Li^+ diffusivity)),^{4,5} a marvelous improvement in its kinetic property was achieved during the past decade with the help of carbon coating

(LiFePO_4/C composite),^{6–11} particle size reduction,^{5,12,13} and supervalent cation doping.¹⁴ Actually, the electrochemical enhancement coming from these strategies made LiFePO_4 a feasible cathode material for commercialization.

In the early stage of LiFePO_4 research, Fe_2P , formed in a strong reductive atmosphere, was considered as a byproduct which should be prevented from forming during the synthesis of single-phase LiFePO_4 .¹² However, Subramanya Herle et al. demonstrated that metal phosphocarbides or Fe_2P (metallic compound, $\sigma: 10^{-1} \text{ S cm}^{-1}$ at rt) can contribute to improving the room-temperature conductivity of LiFePO_4/C drastically to $\sim 10^{-2} \text{ S cm}^{-1}$ thanks to its high electronic conductivity.¹⁵ Recently, Xu et al. verified the positive effect of Fe_2P on the electrochemical performance of LiFePO_4 by showing that LiFePO_4 including Fe_2P has the best rate capability in spite of having the largest particle size.¹⁶ However, our previous study demonstrated that the formation of Fe_2P can result in amphoteric effects on the electrochemical performance of LiFePO_4 depending on its quantity.¹⁷

*Corresponding author. Tel.: +82-16-257-9051 (Y.M.K.). Fax: +82-41-568-5776 (Y.M.K.). E-mail: dake1234@kongju.ac.kr (Y.M.K.), hskwon@kaist.ac.kr (H.S.K.).

(1) Giorgetti, M.; Berretoni, M.; Scaccia, S.; Passerini, S. *Inorg. Chem.* **2006**, *45*, 2750.

(2) Tarascon, J. M.; Armand, M. *Nature* **2001**, *414*, 359.

(3) Yamada, A.; Chung, S. C.; Hinokuma, K. *J. Electrochem. Soc.* **2001**, *148*, 224.

(4) Chung, S. Y.; Chiang, Y. M. *Electrochem. Solid-State Lett.* **2003**, *6*, 278.

(5) Prosini, P. P.; Carewska, M.; Scaccia, S.; Wisniewski, P.; Pasquali, M. *Electrochim. Acta* **2003**, *48*, 4205.

(6) Gabrisch, H.; Wilcox, J. D.; Doeff, M. M. *Electrochem. Solid-State Lett.* **2006**, *9*, 360.

(7) Ravet, N.; Chouinard, Y.; Magnan, J. F.; Besner, S.; Gauthier, M.; Armand, M. *J. Power Sources* **2001**, *97–98*, 503.

(8) Chung, H. T.; Jang, S. K.; Ryu, H. W.; Shim, K. B. *Solid State Commun.* **2004**, *131*, 549.

(9) Huang, H.; Yin, S. C.; Nazar, L. F. *Electrochem. Solid-State Lett.* **2001**, *4*, 170.

(10) Chen, Z.; Dahn, J. R. *J. Electrochem. Soc.* **2002**, *149*, 1184.

(11) Franger, S.; Bourbon, C.; Le Cras, F. *J. Electrochem. Soc.* **2004**, *151*, 1024.

(12) Arnold, G.; Garche, J.; Hemmer, R.; Ströbele, S.; Vogler, C.; Wohlfahrt-Mehrens, M. *J. Power Sources* **2003**, *119–121*, 247.

(13) Prosini, P. P.; Carewska, M.; Scaccia, S.; Wisniewski, P.; Passerini, S.; Pasquali, M. *J. Electrochem. Soc.* **2002**, *149*, 886.

(14) Chung, S. Y.; Bloking, J. T.; Chiang, Y. M. *Nat. Mater.* **2002**, *1*, 123.

(15) Subramanya Herle, P.; Ellis, B.; Coombs, N.; Nazar, L. F. *Nat. Mater.* **2004**, *3*, 147.

(16) Xu, Y.; Lu, Y.; Yan, L.; Yang, Z.; Yang, R. *J. Power Sources* **2006**, *160*, 570.

(17) Song, M. S.; Kim, D. Y.; Kang, Y. M.; Kim, Y. I.; Kwon, H. S.; Lee, J. Y. *J. Power Sources* **2008**, *108*(1), 546.

Generally, in previous reports, LiFePO_4 including Fe_2P below the critical amount displayed an enhanced electrochemical performance, whereas Fe_2P inclusion above the critical amount seriously deteriorated the electrochemical performance of LiFePO_4 . The positive effect of Fe_2P below the critical amount has been easily ascribed to Fe_2P -induced enhancement of electronic conductivity in LiFePO_4 because Fe_2P is electronically conductive. The reason why LiFePO_4 with Fe_2P above the critical amount has to undergo a significant degradation is assumed to be related to the Li^+ pathway being blocked by an excessive formation of Fe_2P in LiFePO_4 . Considering that the application (HEV, plug-in HEV, and EV) of LiFePO_4 requires high rate capability, the detailed change of the LiFePO_4 structure with the variation of the Fe_2P amount should be clarified in the first place for its commercialization.

So, in this paper, the effect of Fe_2P formation on the local structure of LiFePO_4 was correlated with the electrochemical performance of LiFePO_4 . For this, the local structure of LiFePO_4 was comprehensively analyzed with variation of the Fe_2P amount.

Experimental Section

Synthesis. LiFePO_4 (including carbon web) was synthesized by ball-milling and subsequent microwave heating. A stoichiometric amount (1:1, molar ratio) of Li_3PO_4 (Aldrich) and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Kojundo) was ball-milled at a ball-to-powder weight ratio of 8.10:1 with 5 wt % acetylene black for 30 min under an Ar atmosphere using a vibrant-type mill (SPEX-8000 mixer/mill), and then the ball-milled mixture was microwave irradiated (750 W) for several minutes in a microwave oven.

Cell Fabrication. LiFePO_4 cathodes were manufactured by casting, on an Al foil current collector, a *N*-methyl-2-pyrrolidene slurry composed of 72 wt % $\text{LiFePO}_4\text{-C}$, 20 wt % acetylene black, and 8 wt % polyvinylidene fluoride binder. A total of 2016 coin-type cells were assembled in an Ar-filled glovebox by stacking a microporous polypropylene separator (Celgard 2400) containing liquid electrolyte (1 M LiClO_4 in 1:1 EC/DMC) between the cathode and the lithium metal foil anode.

Structural and Electrochemical Analyses. Two- and three-phase Rietveld refinements for LiFePO_4 (including carbon web) were conducted using the General Structure Analysis System program.¹⁸ The X-ray diffraction (XRD) data for Rietveld refinement were measured from 15° to 120° at a step of 0.02° using $\text{Cu K}\alpha$ radiation with a graphite monochromator in the reflection geometry (Dmax2200 V, Rigaku). Si (NIST 640c) powder was used as an external standard to correct the zero-point shift for the measured diffraction data. The coordination number of atoms around the Fe atom in LiFePO_4 was evaluated by extended X-ray absorption fine structure (EXAFS, *R*-XAS) spectroscopy. Fe K-edge X-ray absorption spectra were recorded in the transmission mode at room temperature using the lab-scale EXAFS machine equipped with a 3 kW X-ray generator, Mo target, W filament, and Ge(220) crystal. The X-ray absorption spectra were Fourier-transformed using the IFEFFIT program based on FEFF8 ab initio theory. An ex situ XRD analysis (D/max-III C, Rigaku) of the LiFePO_4 (including carbon web) cathode after cycling was conducted from 15° to 45° at a scan rate of 1° min^{-1} using $\text{Cu K}\alpha$ radiation. Electrochemical impedance spectroscopy (EIS) analysis was conducted at room temperature using a HF frequency response

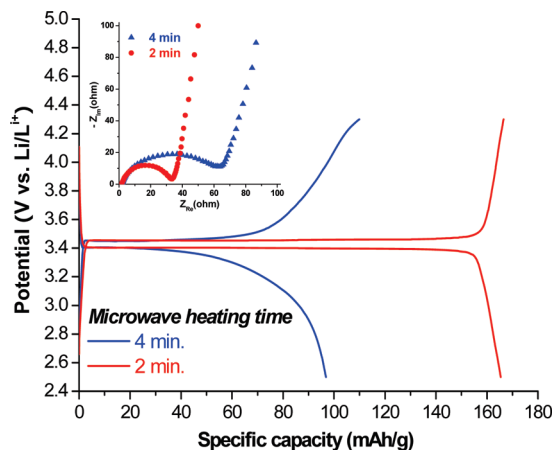


Figure 1. The initial charge/discharge curves of LiFePO_4 synthesized by microwave irradiation for 2 min (red-colored line) and 4 min (blue-colored line). Inset figure consists of Nyquist plots for 2-min-irradiated LiFePO_4 (red-colored sphere) and 4-min-irradiated LiFePO_4 (blue-colored triangle).

analyzer (SI1255, solartron instruments) connected to a potentiostat/galvanostat (273A, EG&G Princeton Applied Research). A small AC perturbation of 10 mV was applied with a frequency sweep from 0.1 Hz to 100 kHz during the measurements. The amount of iron dissolved from LiFePO_4 to the electrolyte in a cell was measured with an inductively coupled plasma mass spectrometer (ICP-MASS, Elan 6100, Perkin-Elmer).

Results and Discussion

The initial electrochemical reactivity of LiFePO_4 (including carbon web) synthesized from microwave irradiation is displayed in Figure 1. In the discharge curve for LiFePO_4 prepared by microwave heating for 2 min, a long, flat voltage plateau appears around 3.41 V, and then the voltage sharply drops to the cutoff value (2.5 V), leading to a high discharge capacity of 165 mAh g^{-1} (97.1% of the theoretical capacity of LiFePO_4). On the other hand, LiFePO_4 obtained by microwave heating for 4 min shows shorter voltage plateaus, followed by a low discharge capacity (97 mAh g^{-1}). An EIS analysis was carried out to investigate the change of charge-transfer resistance in LiFePO_4 with the variation of microwave heating time. As shown in the inset of Figure 1, the longer the microwave heating time for the synthesis of LiFePO_4 , the larger the charge-transfer resistance between the electrolyte and LiFePO_4 surface. Because the increase of microwave heating time was correlated with the evolution of Fe_2P , an extremely conductive phase (Figure S1, Supporting Information), a surge of charge-transfer resistance in the 4 min sample may imply that there is another phase transition explanatory of the electrochemical degradation of LiFePO_4 .

In order to clarify the reason why the 4 min sample encountered difficulty in the charge transfer leading to its electrochemical degradation, the local structure (lattice parameter, space of Li^+ diffusion path, occupation of Fe atoms in the Li site) of LiFePO_4 was probed using X-ray Rietveld refinement. Figure 2a shows the refinement results for LiFePO_4 irradiated for 2 min.¹⁷ Herein, two phases are observed, 0.56 wt % Fe_2P and 99.44 wt % LiFePO_4 , and the lattice parameters of LiFePO_4 from the refinement (Table S1, Supporting Information) are almost equal to those reported

(18) Larson, A. C.; Von Dreele, R. B. *Los Alamos National Laboratory Report LAUR*; Los Alamos National Laboratory: Los Alamos, NM, 1994; p 86.

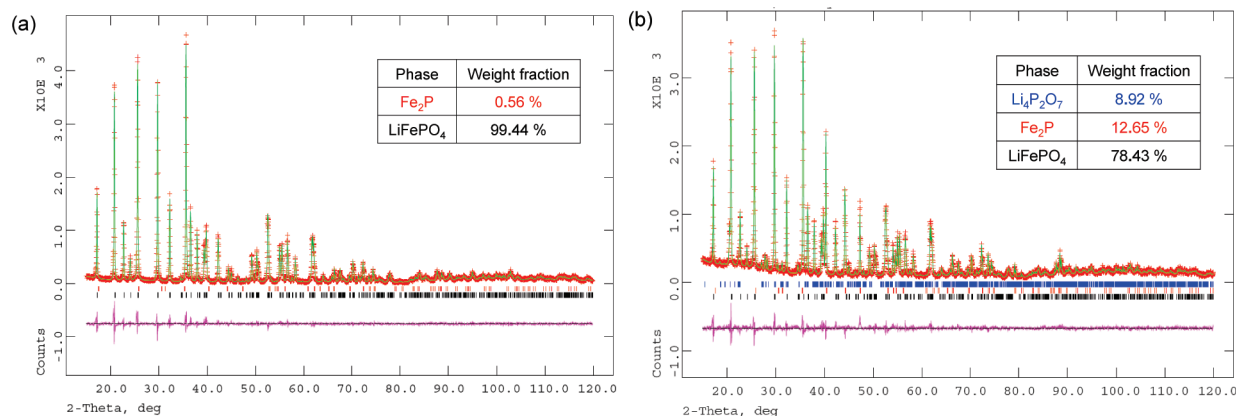
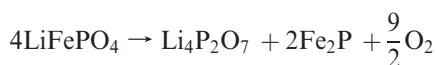


Figure 2. X-ray Rietveld refinement results for LiFePO₄ synthesized by microwave irradiation for (a) 2 min and (b) 4 min. Plus (+) marks represent the observed intensities, and the solid line illustrates calculated ones. A difference (obsd – calcd) plot is shown beneath. Tick marks above the difference data indicate the reflection position. In 2-min-irradiated LiFePO₄, the upper and lower tick marks above the difference data indicate the reflection position for Fe₂P and LiFePO₄ phases, respectively, and in 4-min-irradiated LiFePO₄, the upper, middle, and lower tick marks correspond to Li₄P₂O₇, Fe₂P, and LiFePO₄, respectively.

in the literature,^{19–22} implying that the structure of LiFePO₄ irradiated for 2 min is almost perfect. X-ray Rietveld refinement for LiFePO₄ irradiated for 4 min discloses a phase transition responsible for the electrochemical degradation observed in Figure 1. The refinement results for LiFePO₄ irradiated for 4 min are given in Figure 2b. Three phases were identified: 8.92 wt % Li₄P₂O₇, 12.65 wt % Fe₂P, and 78.43 wt % LiFePO₄. The drastic increment in the charge-transfer resistance of the 4 min sample can be explained by the formation of Li₄P₂O₇ because it has very low electronic conductivity ($\sim 10^{-20}$ S/cm at rt) and lithium-ion conductivity ($\sim 10^{-21}$ S/cm at rt) compared to those of LiFePO₄ itself.²³ Actually, it has been reported that the evolution of Li₄P₂O₇ deteriorates the lithium-ion conductivity of Li_{1+x}Ti_{2–x}Al_x(PO₄)₃ with a NASICON framework.²⁴ An abrupt formation of an insulating phase, Li₄P₂O₇, in LiFePO₄ irradiated for 4 min seems to be attributed to the excessive formation of Fe₂P. LiFePO₄ exposed to highly reductive atmosphere has to undergo the reduction of Fe below +2, inducing the formation of Fe₂P. Because Fe₂P is an electronically conductive phase, the formation of Fe₂P below a critical amount tends to help the electrochemical performance of LiFePO₄ become enhanced. However, an Fe₂P amount above the critical level is accompanied by a deficiency of Fe and P atoms constituting the framework of LiFePO₄. Naturally, LiFePO₄ should be changed into a mixture of several phases according to the following reaction:



Considering that the refinement simulation assuming three phases, Li₄P₂O₇, Fe₂P, and LiFePO₄, was appropriate for not the 2 min sample but the 4 min sample, we can know that the

phase transition to Li₄P₂O₇ is not mandatory when the amount of Fe₂P is below 1 wt % of LiFePO₄. The comparison between 4-min-irradiated LiFePO₄ and 2-min-irradiated LiFePO₄ under the refined lattice parameters made us believe that, irrespective of the formation of Li₄P₂O₇, the formation of Fe₂P hardly changes the one-dimensional structure of LiFePO₄ (Table S2, Supporting Information). The difference between the lattice parameters of two samples is within the error range. Furthermore, the unit cell volume of LiFePO₄ is almost in accordance with that (291.1 Å³) of LiFePO₄ with the perfect olivine structure regardless of the Fe₂P amount.²⁵ Even if the excessive Fe₂P accompanied by the formation of Li₄P₂O₇ deteriorates the charge-transfer resistance of our LiFePO₄, Fe atoms seemed to be perfectly ordered in the structure of LiFePO₄, and thus, Li⁺ motion through the one-dimensional (1D) path in LiFePO₄ looked like it was not disturbed, irrespective of the amount of Fe₂P formation. In order to examine the effect of Fe₂P formation on the 1D Li⁺ diffusion path composed of the linear chains of edge-shared LiO₆ octahedra, a change in the Li–O interatomic distance was also estimated. The distance between Li and O atoms in LiFePO₄ was also within the error range, proving that the excessive Fe₂P formation does not have a mal effect on Li⁺ diffusion path in LiFePO₄.

On the basis of the structural parameters obtained from X-ray Rietveld refinement, it seemed that the local structure of LiFePO₄ is not influenced by Fe₂P formation. However, considering that the peak intensity in XRD patterns of LiFePO₄ is dependent on the amount of Fe₂P, as shown in Figure 2, the local structure of LiFePO₄ needed to be probed in detail. Therefore, an Fe-edge EXAFS analysis was conducted to determine the coordination of atoms around the Fe atom. Figure 3 displays the Fe-edge EXAFS spectra, where the peak intensity is proportional to the coordination number of atoms around the Fe atom. From the previous report, it could be known that the first sphere, second sphere, and third sphere correspond to the Fe–O bond, Fe–P bond, and Fe–Fe bond, respectively. The EXAFS spectra for 2-min-irradiated LiFePO₄ are very similar to those of LiFePO₄ having the perfect olivine structure.²⁶ On the other hand, several

(19) Andersson, A. S.; Kalska, B.; Häggström, L.; Thomas, J. O. *Solid State Ionics* **2000**, *130*, 41.

(20) Cho, T. H.; Chung, H. T. *J. Power Sources* **2004**, *133*, 272.

(21) Prince, A. A. M.; Mylswamy, S.; Chan, T. S.; Liu, R. S.; Hannoyer, B.; Jean, M.; Shen, C. H.; Huang, S. M.; Lee, J. F.; Wang, G. X. *Solid State Commun.* **2004**, *132*, 455.

(22) Scarlet, N. V. Y.; Madsen, I. C.; Cranswick, L. M. D.; Lwin, T.; Groleau, E.; Stephenson, G.; Aylmore, M.; Agron-Olshina, N. *J. Appl. Crystallogr.* **2002**, *35*, 383.

(23) Burmakin, E. I.; Shekhtman, G. S.; Aparina, E. R.; Korovenkova, E. S. *Sov. Electrochem.* **1992**, *28*, 1014.

(24) Arbi, K.; Mandal, S.; Rojo, J. M.; Sanz, J. *Chem. Mater.* **2002**, *14*, 1091.

(25) Chen, J.; Whittingham, M. S. *Electrochem. Commun.* **2006**, *8*, 855.

(26) Deb, A.; Bergmann, U.; Cramer, S. P.; Cairns, E. J. *Electrochim. Acta* **2005**, *50*, 5200.

serious changes are shown in the atomic coordination numbers of 4-min-irradiated LiFePO_4 . This phenomenon is because the deficiencies of O, P, and Fe atoms are significant

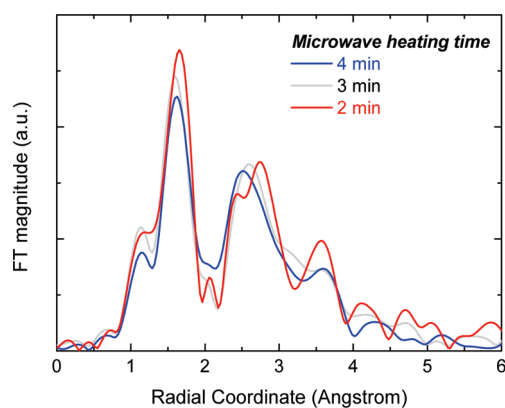


Figure 3. The radial distribution function obtained after Fourier transformation of $k^3\chi(k)$ in the k^3 -weighted Fe-edge EXAFS spectrum. First sphere (1.7–2.2 Å), second sphere (2.7–3.2 Å), and third sphere (3.7–4.2 Å) correspond to the Fe–O bond, Fe–P bond, and Fe–Fe bond, respectively.

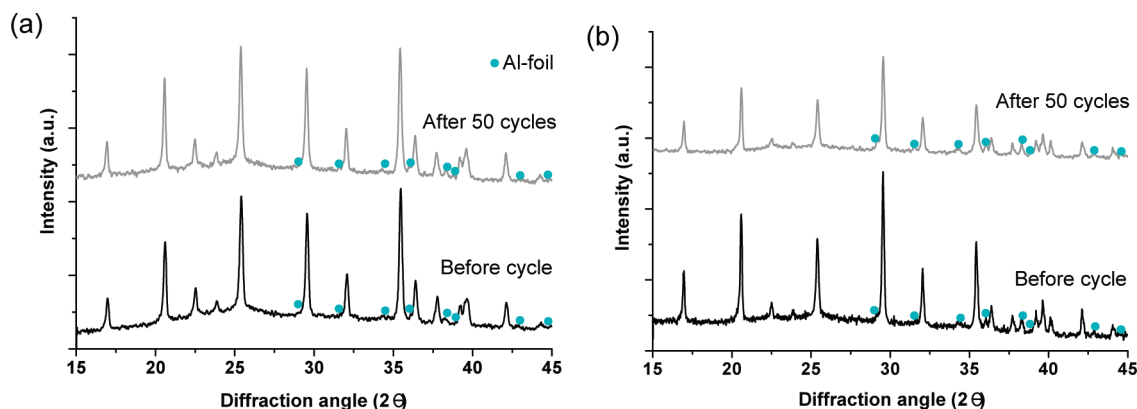


Figure 4. XRD patterns of LiFePO_4 before and after cycling: (a) 2 min microwave-irradiated sample, (b) 4 min microwave-irradiated sample.

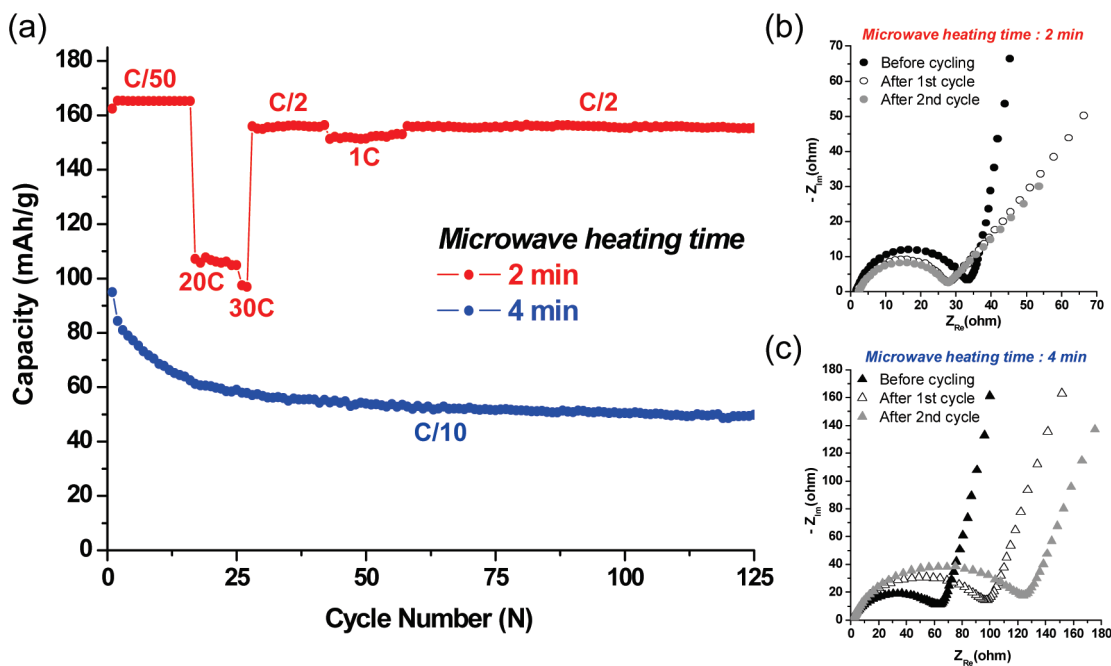


Figure 5. (a) The cyclic properties of LiFePO_4 synthesized by microwave irradiation for 2 min (red-colored line) and 4 min (blue-colored line). Nyquist plots for (b) 2-min-irradiated LiFePO_4 and (c) 4-min-irradiated LiFePO_4 before or after cycling.

in 4-min-irradiated LiFePO_4 , which has to undergo a phase transition to a mixture of Fe_2P and an insulating phase, $\text{Li}_4\text{P}_2\text{O}_7$. Because PO_4 tetrahedra are fundamental building blocks for the olivine structure of LiFePO_4 , a crucial structural instability can be induced by the deficiency of P and O atoms. With the absence of PO_4 tetrahedra, the structure of LiFePO_4 must collapse during the charge/discharge process. Figure 4 shows XRD patterns of LiFePO_4 before cycling and after 50 cycles. Even after 50 cycles, the initial structure of 2-min-irradiated LiFePO_4 was relatively well-maintained, whereas that of the 4-min-irradiated sample underwent a serious degradation. In accordance with EXAFS results, the structural instability of LiFePO_4 during cycling could be attributed to the phase transition to the mixture of Fe_2P and an insulating phase, $\text{Li}_4\text{P}_2\text{O}_7$. In Figure 5, it is shown how this structural instability is correlated with the electrochemical degradation of LiFePO_4 .

Figure 5a illustrates the electrochemical superiority of 2-min-irradiated LiFePO_4 compared to the 4 min sample. The 2 min sample featured a fabulous cyclic performance in spite of the variation of the charge/discharge rate, while the

4 min sample exhibited poor cyclic performance even at a very sluggish charge/discharge rate (C/10). This tendency in the cyclic performance was consistent with those in the charge/discharge capacity (Figure 1) and the rate capability (Figure S2, Supporting Information). As shown in Figure 5b and c, Nyquist plots obtained during the initial three cycles may correlate the electrochemical performance of LiFePO_4 with its local structure. The increase in the charge-transfer resistance of LiFePO_4 after cycling mainly comes from Fe dissolution into the electrolyte because the Fe ion dissolved from LiFePO_4 goes to an anode and then increases the interfacial impedance of the anode significantly by forming an insulating film on the surface of the anode, as reported by Amine et al.²⁷ From ICP-MASS analysis (Table S3, Supporting Information), the increment of Fe dissolution is perfectly in accordance with the above-mentioned structural instability coming from the increased Fe_2P formation followed by a phase-transition to $\text{Li}_4\text{P}_2\text{O}_7$. Herein, Fe_2P itself is not the fundamental reason for the increase in the charge-transfer resistance of LiFePO_4 during cycling, even if the amount of Fe ions present in the electrolyte is proportional to the amount of Fe_2P . Considering that the local structure change of LiFePO_4 depends on the evolution of Fe_2P , it seems to be more reasonable that the electrochemical degradation indicated by the increase of charge-transfer resistance is attributed to the deficiency of P and O evolved by the phase transition into a mixture of Fe_2P and $\text{Li}_4\text{P}_2\text{O}_7$.

(27) Amine, K.; Liu, J.; Belharouak, I. *Electrochem. Commun.* **2005**, *7*, 669.

Conclusion

In conclusion, the evolution of Fe_2P in LiFePO_4 above a critical concentration changed LiFePO_4 into an insulating phase, $\text{Li}_4\text{P}_2\text{O}_7$. The insulating nature of $\text{Li}_4\text{P}_2\text{O}_7$ leads to the initial degradation of LiFePO_4 in spite of the existence of a conducting phase, Fe_2P . The deficiency of P and O in the LiFePO_4 framework evolved by the phase transition to the mixture of Fe_2P and $\text{Li}_4\text{P}_2\text{O}_7$ resulted in the structural instability of LiFePO_4 , which deteriorated its cyclic performance. As a result, the phase transition into $\text{Li}_4\text{P}_2\text{O}_7$ induced by excessive Fe_2P formation brought out a dramatic degradation in the electrochemical properties of LiFePO_4 , and this degradation mechanism of LiFePO_4 suggests the criteria for the synthesis of high-performance LiFePO_4 in a reductive atmosphere.

Acknowledgment. The authors acknowledge the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean government (MEST) (R01-2008-000-11061-0). This research was also supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0072972) and a grant (2009K000186) from the Center for Nanoscale Mechatronics and Manufacturing, one of the 21st Century Frontier Research Programs, which are supported by the Ministry of Education, Science and Technology, Korea.

Supporting Information Available: Additional figures and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.