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The structural transition and magnetic properties of lithium deintercalation in LiFePO_4

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Introduction

Lithium iron phosphate is the most promising material for rechargeable lithium batteries with enhanced energy storage capacity that can be used in fuel cell. Since Goodenough and co-workers investigated the fascinating electrochemical property of LiFePO_4 [1], studies have been attempted to understand the mechanism of lithium intercalation/deintercalation and there have been reports on improved electrochemical property. Yonemura, *et al.* provided the experimental evidence for $\text{LiFePO}_4/\text{FePO}_4$ two-phase electrochemical reaction in Li_xFePO_4 during lithium intercalation (deintercalation) [2]. Recently, Delmas *et al.* explained the lithium deintercalation via ‘domino-cascade model’ [3]. This model described localized $\text{Fe}^{2+}/\text{Fe}^{3+}$ polarons have very fast reaction. The detailed analysis on the mol-rate of $\text{LiFePO}_4/\text{FePO}_4$ was done with Mössbauer spectroscopy [4].

In this paper, we report on the structural transition and magnetic properties of lithium deintercalation in LiFePO_4 . Also we study the magnetic hyperfine interaction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in $\text{LiFePO}_4/\text{FePO}_4$ using by Mössbauer spectroscopy.

Experiments

The pure LiFePO_4 powder was synthesized using lithium carbonate (Li_2CO_3), iron(II) oxalate dehydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) as the starting materials of the compound. They were grounded, followed by calcination at 300°C . Then, the powder was pressed into a pellet and sealed in an evacuated quartz tube. This quartz tube was annealed at 700°C for 10 h. Lithium deintercalation to obtain $\text{LiFePO}_4/\text{FePO}_4$ was done by chemical oxidation process. Pure LiFePO_4 powder with nitronium tetrafluoroborate (NO_2BF_4) in acetonitrile solution was stirred at room temperature for 10 h in air. The proportion of $\text{LiFePO}_4/\text{FePO}_4$ powder was controlled by the concentration of NO_2BF_4 in acetonitrile solution.

The crystal structure of the each samples were examined using an X-ray diffractometer (XRD) with $\text{Cu-K}\alpha$ radiation and analyzed by Rietveld refinement. Mössbauer spectra were recorded from 4.2 K up to room temperature with a ^{57}Co source in Rh matrix.

Results and discussion

The crystal structure of $\text{LiFePO}_4/\text{FePO}_4$ powders were orthorhombic structure with space group $Pnma$. Fig.1 shows that there exists a mixture of LiFePO_4 and FePO_4 phase accord with Delmas *et al.* [4] As the concentration of NO_2BF_4 in acetonitrile solution increases, the intensity of LiFePO_4 phase decreases. At the same time, FePO_4 phase increases with the concentration of NO_2BF_4 . This result confirms that the localized two crystallographic structure co-exist in mixed powders.

Fig.2 shows Mössbauer spectra of $\text{LiFePO}_4/\text{FePO}_4$ at room temperature. The spectrum of LiFePO_4 (a) and FePO_4 (f) were fitted with single doublet which describes Fe^{2+} and Fe^{3+} iron state according to the measured value of $\delta_{\text{a}} = 1.1 \text{ mm/s}$ and $\delta_{\text{f}} = 0.31 \text{ mm/s}$. The electric quadrupole splitting of LiFePO_4 is larger than that of FePO_4 for $\text{LiFePO}_4 \Delta E_Q$ is 2.97 mm/s and for $\text{FePO}_4 \Delta E_Q$ is 1.53 mm/s . However, for (b), (c), (d) and (e) samples with varying NO_2BF_4 concentration shows the spectra become asymmetric. Therefore, these spectra were fitted with the 2-doublet having mixed iron states of $\text{Fe}^{2+}/\text{Fe}^{3+}$. As the sample approaches to FePO_4 (f), LiFePO_4 (a) absorption decreases with agrees with the XRD patterns of samples.

[2] Yonemura, M., Yamada, A., Takei, Y., Sonoyama, N. & Kanno, R. *J. Electrochem. Soc.* **151**, A1352–A1356 (2004).

[3] C. Delmas, M. Maccario, L. Croguennec, F. Le Cras and F. Weill. *Nature Mater.* **7**, 665–671 (2008).

[4] D. X. Gouveia, V. Lemos, J. A. C. de Paiva, A. G. Souza Filho, and J. Mendes Filho. M. Lala, L. A. Montoro, and J. M. Rosolen. *Phys. Rev. B.* **72**, 024105 (2005).

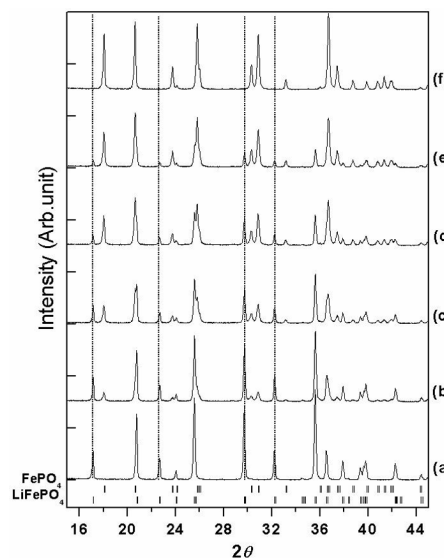


Fig.1 XRD patterns of $\text{LiFePO}_4/\text{FePO}_4$ samples at room temperature. (a) LiFePO_4 , the concentration of NO_2BF_4 for each samples ($\text{LiFePO}_4 : \text{NO}_2\text{BF}_4$) (b) 1 : 0.1, (c) 1 : 0.2, (d) 1 : 0.3, (e) 1 : 0.4 and (f) 1 : 2.0 for FePO_4 .

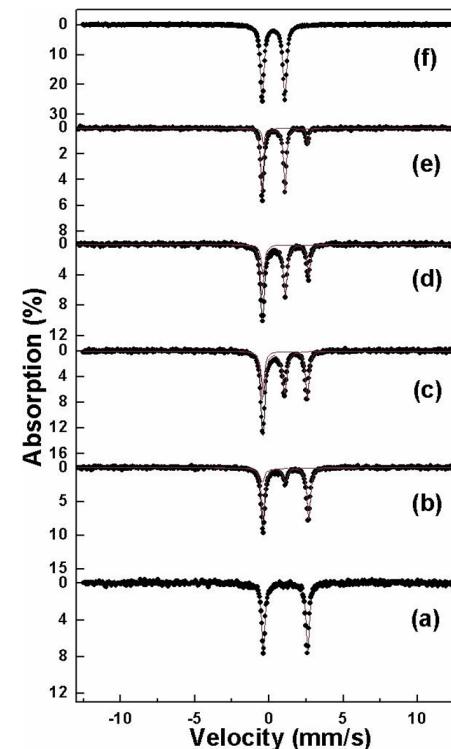


Fig.2 Mössbauer spectra of $\text{LiFePO}_4/\text{FePO}_4$ samples at room temperature.

[1] Padhi, A. K., Nanjundaswamy, K. S. & Goodenough, J. B. *J. Electrochem. Soc.* **144**, 1188–1194 (1997).