The Structural Transition and Magnetic Properties of Lithium Deintercalation in LiFePO$_4$

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Lithium deintercalation of $(1-x)$ LiFePO$_4$/$x$ FePO$_4$ ($0 \leq x < 1$) have been studied with X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectrometer (ICP-AES), and Mössbauer spectroscopy. Lithium deintercalation to obtain $(1-x)$ LiFePO$_4$/$x$ FePO$_4$ was done by chemical oxidation process using NO$_2$BF$_4$. The crystal structure was found to be an orthorhombic with space group $Pnma$ for each sample. There exists a mixture of LiFePO$_4$ and FePO$_4$ phase between $x = 0$ and 1. The Mössbauer spectra have been taken at various temperatures ranging from 4.2 K to room temperature. The magnetic Néel temperature ($T_N$) was determined to be 51 and 114 K for LiFePO$_4$ and FePO$_4$. Also, the iron ions were ferric and ferrous for LiFePO$_4$ and FePO$_4$, both occupying the octahedral sites at various temperatures. We confirmed that the change of Mössbauer spectrum shape as the evidence of two-valence state of iron ions coexists on lithium deintercalation in LiFePO$_4$ from 4.2 K to room temperature.

Index Terms—Li-ion battery, Mössbauer spectroscopy, olivine.

I. INTRODUCTION

OLIVINE lithium iron phosphate is the most promising material for rechargeable Li-ion batteries with enhanced energy storage capacity that can be used in fuel cell. LiFePO$_4$ is an orthorhombic olivine structure, space group $Pnma$, combined with PO$_4$ tetrahedra, corner-sharing FeO$_6$ octahedra, and edge-sharing LiO$_6$ octahedra. Since Goodenough et al. 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. The theoretical modeling of lithium deintercalation in olivine structure suggest that the lithium ions can be migrated along the $b$-axis [2], [3]. Yonemura et al. provided the experimental evidence for FePO$_4$LiFePO$_4$ two-phase electrochemical reaction in Li$_x$FePO$_4$ during lithium intercalation (deintercalation) [4]. Recently, Delmas et al. explained the lithium deintercalation via “domino-cascade model” [5]. This model described localized Fe$^{2+}$/Fe$^{3+}$ polarons have very fast reaction. Also, Yamada et al. presented that the visualization of lithium distribution along the $[010]$ direction when lithium is deintercalated from LiFePO$_4$ [6]. The detailed analysis on the mol rate of LiFePO$_4$/FePO$_4$ and hyperfine interaction of pure LiFePO$_4$ at low temperature were done with Mössbauer spectroscopy [7], [8].

In this paper, we report on the structural transition and magnetic properties of lithium deintercalation in LiFePO$_4$. Also, first reports on the magnetic hyperfine interaction of Fe$^{2+}$/Fe$^{3+}$ in LiFePO$_4$/FePO$_4$ at low temperature have been studied by Mössbauer spectroscopy.

II. EXPERIMENT PROCEDURES

The pure LiFePO$_4$ powder was synthesized using lithium carbonate (Li$_2$CO$_3$), iron(II) oxalate dehydrate (Fe$_2$C$_2$O$_4$.H$_2$O), and ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) as the starting materials of the compound. They were ground and 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 $(1-x)$ LiFePO$_4$/$x$ FePO$_4$ was done by chemical oxidation process. Pure LiFePO$_4$ powder with nitronium tetrafluoroborate (NO$_2$BF$_4$) in acetonitrile solution was stirred at room temperature for 10 h under air. The proportion of LiFePO$_4$/FePO$_4$ was controlled by the concentration of NO$_2$BF$_4$ in acetonitrile solution from the following reaction:

$$\text{LiFePO}_4 + x\text{NO}_2\text{BF}_4 \rightarrow x(\text{FePO}_4 + \text{LiBF}_4 + \text{NO}_2) + (1-x)\text{LiFePO}_4.$$  \hspace{1cm} (1)

The obtained mixtures were centrifuged and washed several times with acetonitrile, and then dried under vacuum.

The phase purity and crystal structure of all samples were examined using an X-ray diffractometer (XRD) with Cu-K$_\alpha$ radiation ($\lambda = 1.5406$ A) and analyzed by Rietveld refinement. Chemical analysis for each of the $(1-x)$ LiFePO$_4$/$x$ FePO$_4$ two-phase mixture was performed by inductively coupled plasma-atomic emission spectrometer (ICP-AES). Mössbauer spectra were recorded from 4.2 K up to room temperature with a $^{57}$Co source in Rh matrix. The spectrometer was calibrated by collecting the Mössbauer spectra of a standard Fe$^{3+}$-Fe foil at room temperature. To produce a uniform thickness over the area of the Mössbauer absorber, each sample was clamped between two beryllium discs 0.005 in thick and 1 in in diameter. The low-temperature spectra were obtained using a model SHI-850 closed-cycle refrigerator system (Janis Research Company) with a RDK-205D cold head (Sumitomo Heavy Industries, Ltd.), and the temperature controller was a model 332 manufactured by Lake Shore Cryotronics, Inc. The Mössbauer parameters were obtained by least squares fitting program assuming Lorentzian line shapes.

III. RESULTS AND DISCUSSION

The crystal structure of $(1-x)$ LiFePO$_4$ + $x$ FePO$_4$ powders was orthorhombic structure with space group $Pnma$. Fig. 1...