

リチウムイオン二次電池オリビン正極材料の
XAFS法による状態分析

X-ray absorption spectroscopic study of the olivine-type
cathode materials for rechargeable lithium-ion batteries

工藤 喜弘

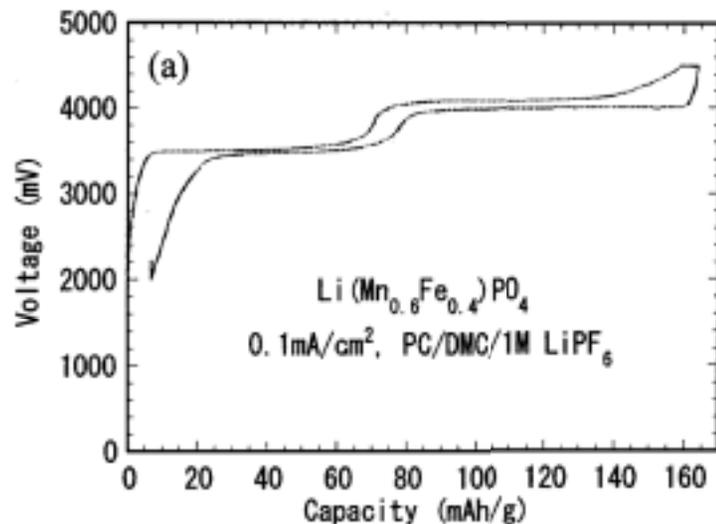
Yoshihiro Kudo

ソニーEMCS(株) 解析技術センター

Materials Analysis Center, Sony EMCS Corporation

Outline

The charge/discharge curve of the lithium-ion rechargeable battery using the olivine-type $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ as a cathode active material shows two plateau stages, 3.5V and 4.1V, suggesting two processes of charge/discharge. X-ray absorption spectroscopic study was performed to reveal the mechanism of charge/discharge process for $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$.

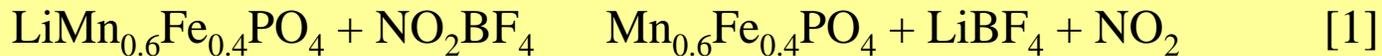


Charge-discharge curves.

Sample preparation

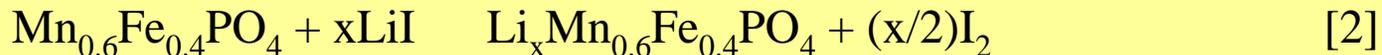
The $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ compound was prepared by solid-state reaction of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, MnCO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and Li_2CO_3 .

Chemical oxidation to obtain $\text{Mn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ was performed by reacting $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ with nitronium tetrafluoroborate (NO_2BF_4) in acetonitrile. The reaction is written as

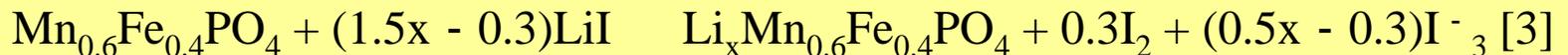


Lithiated samples of $\text{Li}_x\text{Mn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ ($0 < x < 1$) were prepared by reacting $\text{Mn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ with various amounts of LiI in acetonitrile.

In the present case for the 4.1V region of $\text{Li}_x\text{Mn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ ($0 < x < 0.6$), all of the Li^+ in acetonitrile supplied by LiI is incorporated into $\text{Mn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$



For the 3.5V region of $\text{Li}_x\text{Mn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ ($0.6 < x < 1$), only Reaction 1 is induced and the excess LiI was added to produce the desirable composition assuming the following Reaction 3



All the products were analyzed using inductively coupled plasma spectroscopy-atomic emission spectroscopy (ICP-AES) to determine their exact compositions.

Experimental conditions

X-ray absorption measurements were performed at the Industrial Consortium Beamline BL16B2. A white x-ray beam was monochromatized by Si-111 double-crystal monochromator. The half cylindrical Rh-coated total-reflection mirror was used to eliminate the harmonics with the energy higher than about 13 keV.

X-ray absorption spectra were taken in the transmission mode near the Mn and Fe K-edges. The intensities of incident and transmitted x-ray beams were measured by ionization chambers filled with 100% nitrogen gas and nitrogen gas mixed with Ar gas by 15%, respectively.

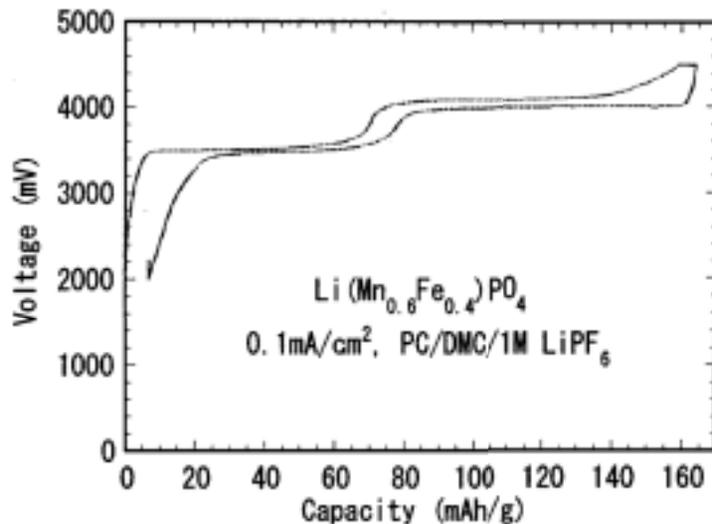
$\text{Li}_x\text{Mn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ powders were mixed with boron nitride by weight ratio 1/1 to achieve the appropriate jump at the absorption edges. The density of the mixed powders for the measurements was 0.45 mg/mm².

Performance of the $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ cathodes

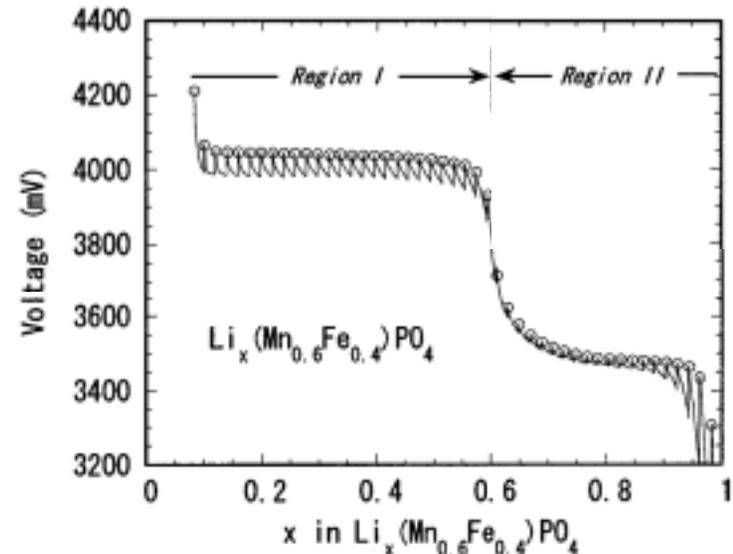
The performance of the $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ cathodes was evaluated using a coin-type cell (size 2025) with a lithium metal anode. The cathode was a highly homogeneous mixture of $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ /carbon black/polyvinylidene fluoride (PVDF) with weight ratio 90/8/2, and the electrolyte was 1 M LiPF_6 -propylene carbonate/dimethyl carbonate (PC/DMC) solution.

The galvanostatic charge/discharge experiment with 0.12 mA/cm^2 was performed between 2.0 and 4.5 V at 23°C . At the end of the charge process, the cell voltage was kept constant at 4.5 V until the current density decreased to $<0.012 \text{ mA/cm}^2$.

For OCV measurements, an intermittent discharge mode was used with alternating 20 min intervals of continuous discharge at 0.3 mA/cm^2 and 240 min rest intervals until the voltage dropped below 2.0 V, which gave an acceptable equilibrium condition.

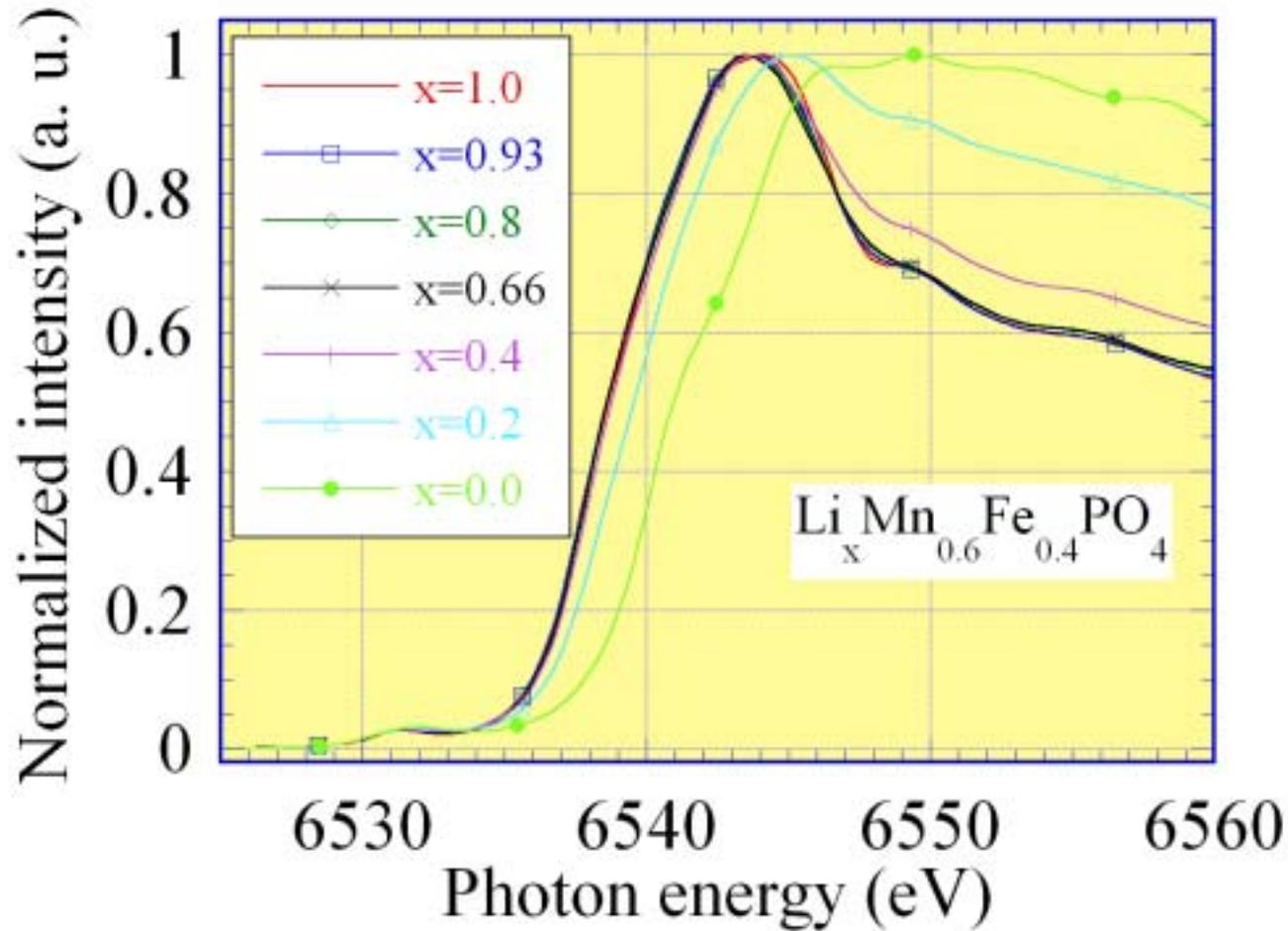


Galvanostatic charge/discharge curves.



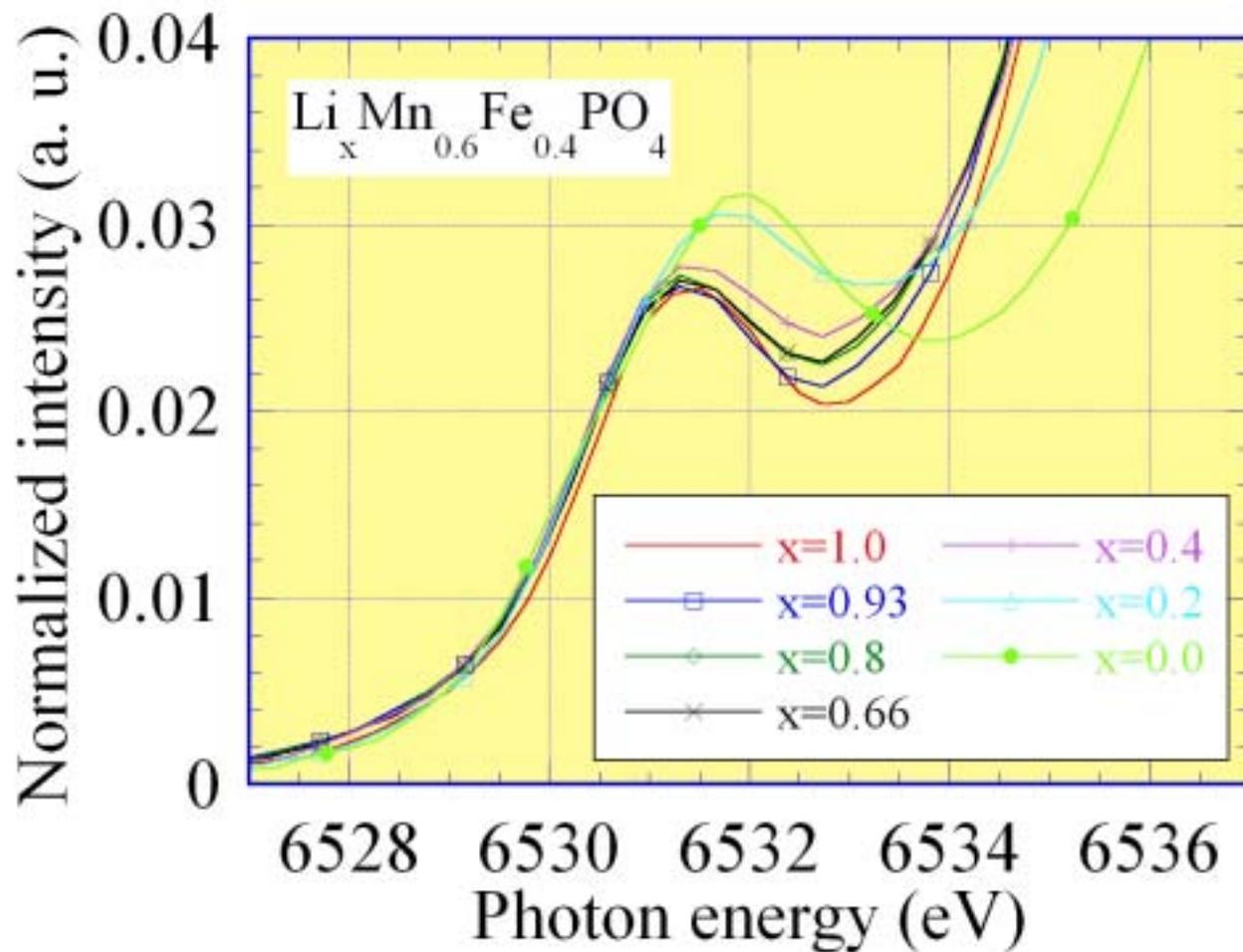
OCV measured for $\text{Li}_x\text{Mn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ ($0 < x < 1$).

XANES spectra at the Mn K edge



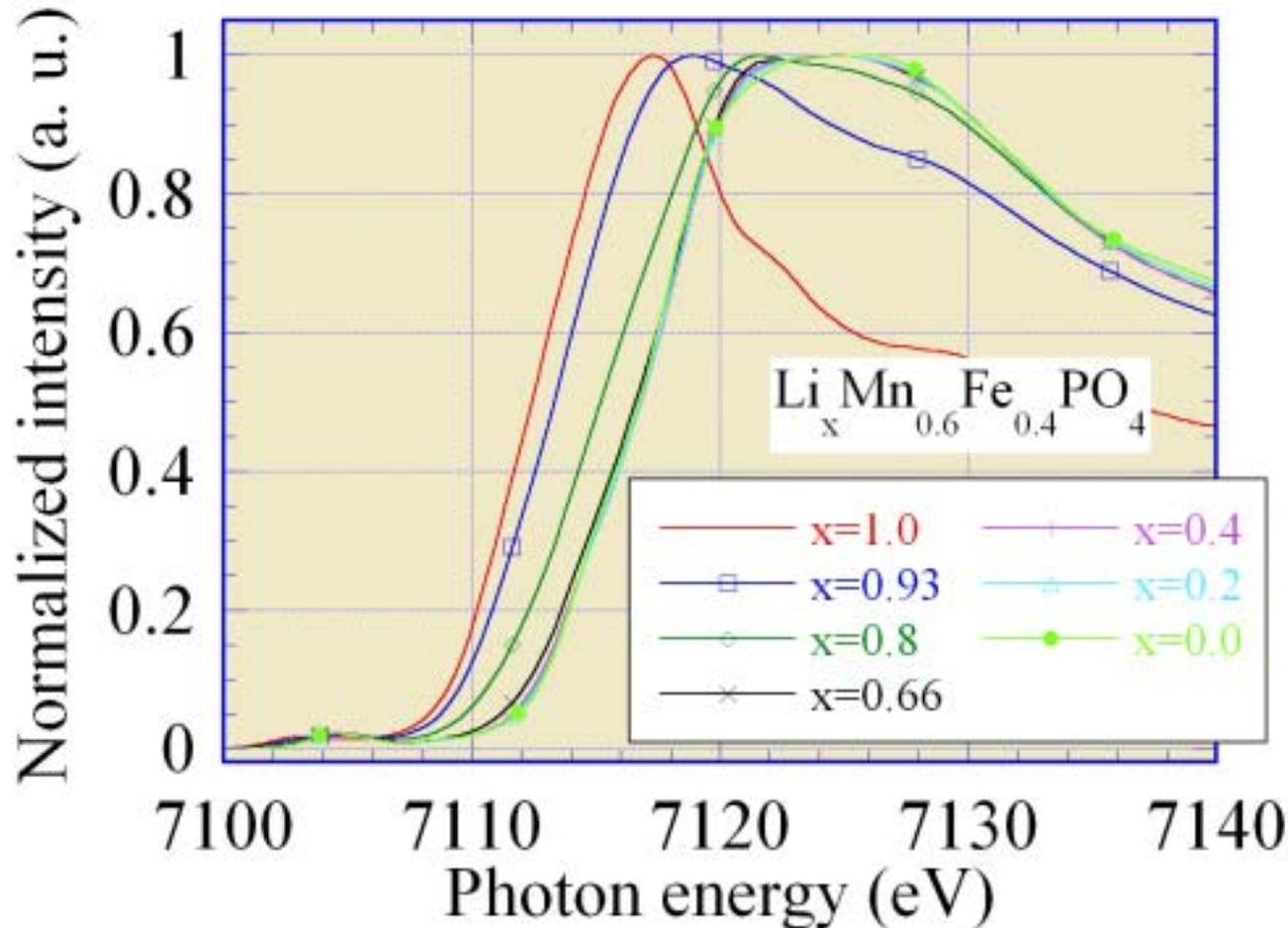
The spectra were normalized by the main peak intensity. For Mn K-edge in region I ($0 < x < 0.6$), the edge shifts in accordance with the manganese valence are clearly seen. The change in the absorption intensity at the higher energy region is also clear.

Pre-edge structures for Mn



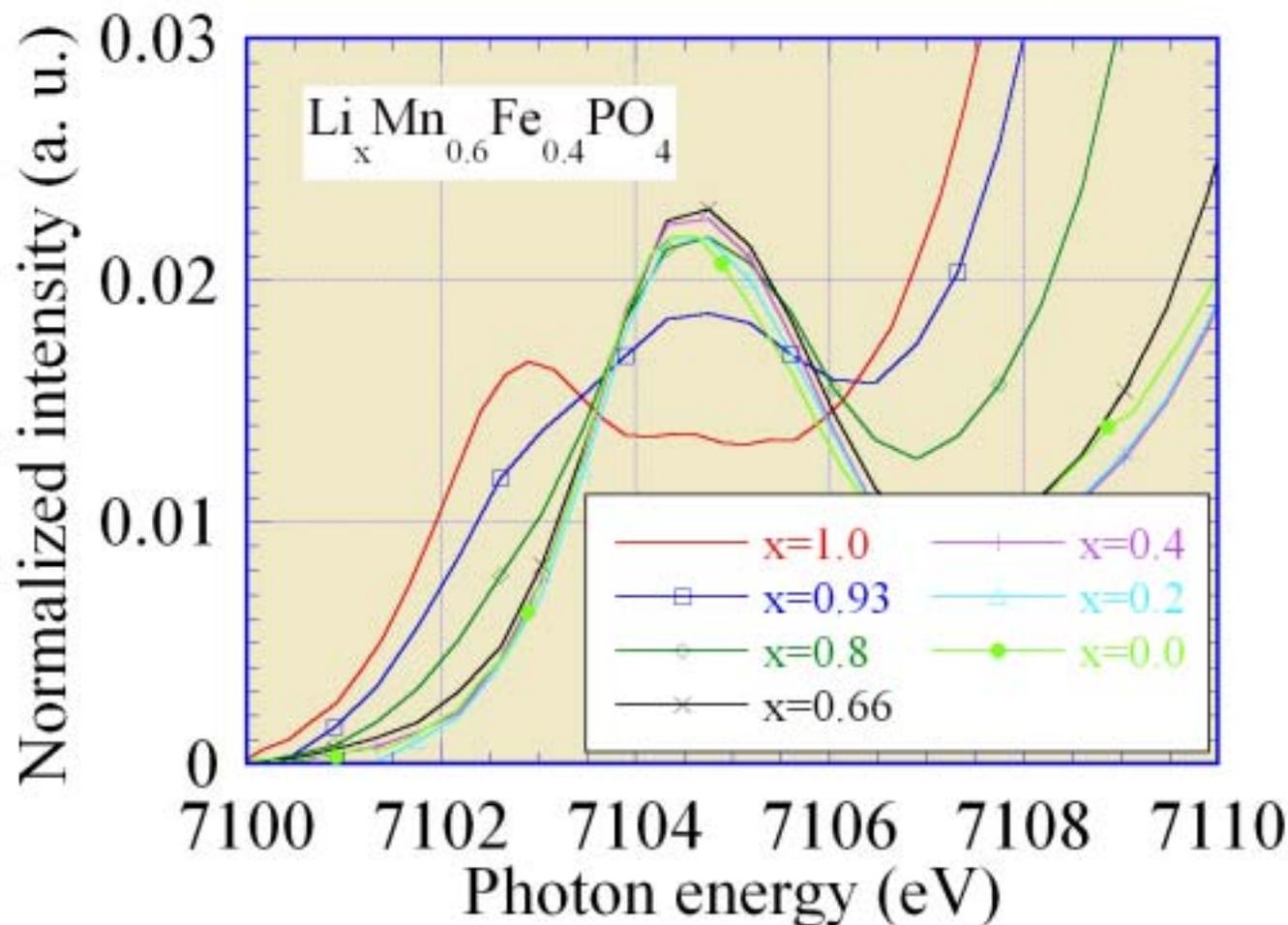
The intensity of the pre-edge peaks originating from the Mn 1s to 3d transition increases with the formal manganese valence, reflecting the increase in vacancy of the 3d state. The shift of the peak position shows the same trend as that of the main absorption.

XANES spectra at the Fe K edge



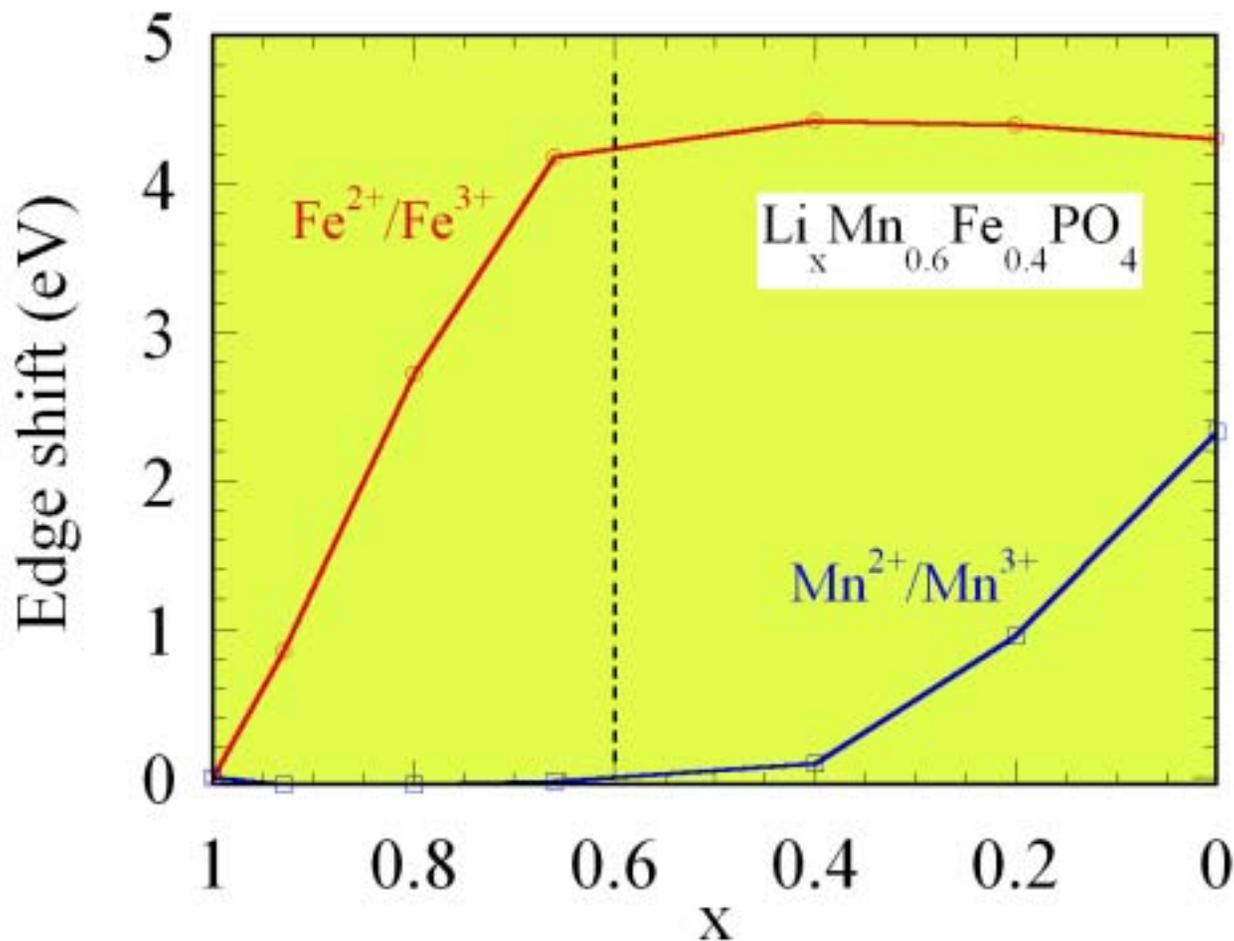
The spectra at the Fe K-edge in region II ($0.6 < x < 1$) show clear contrast to those of region I ($0 < x < 0.6$). In region II, significant chemical shifts in the spectra for Fe but almost identical spectra for Mn were observed.

Pre-edge structures for Fe



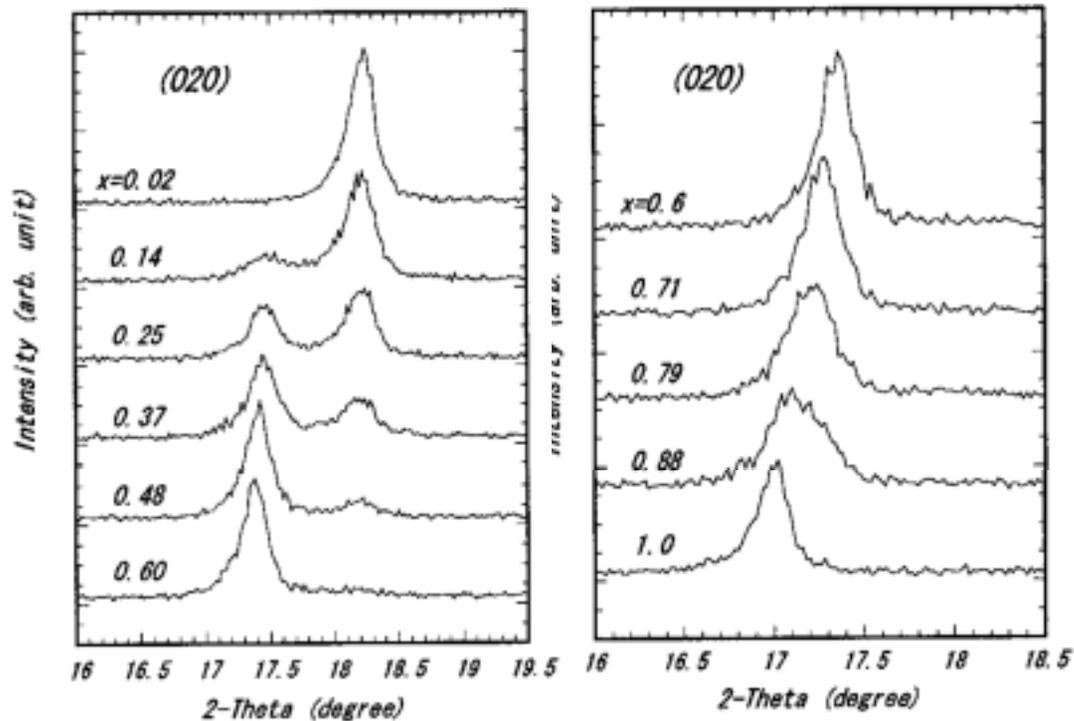
The intensity of the pre-edge peaks originating from the Fe 1s to 3d transition increases with the formal iron valence, reflecting the increase in vacancy of the 3d state. The shift of the peak position shows the same trend as that of the main absorption.

Chemical shifts of Mn and Fe K edges in XANES



The chemical shifts in XANES are defined at the midpoint of the absorption edge and referenced to the values for $x=0$, though they provide only the qualitative tendency of the valence change.

XRD peaks



The x-ray diffraction (XRD) experiments were also performed in laboratory. The left figure shows the changes in the (020) peaks in region I ($0 \leq x \leq 0.6$). In the intermediate compositional range of $0 \leq x \leq 0.6$, a two-phase reaction proceeds from the single phase at $x=0$ to another single phase at $x=0.6$.

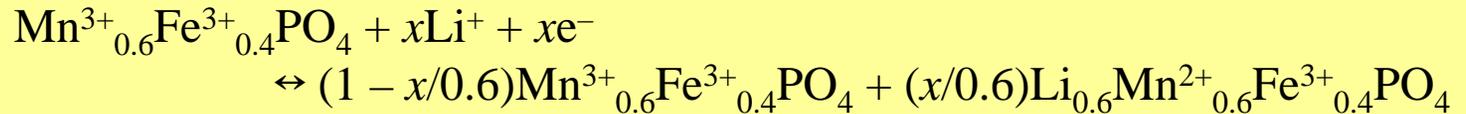
The right figure shows the changes in the (020) peaks in region II ($0.6 \leq x \leq 1$). In contrast to region I, the peak was analyzed by a single-phase orthorhombic $Pmnb$.

Conclusions

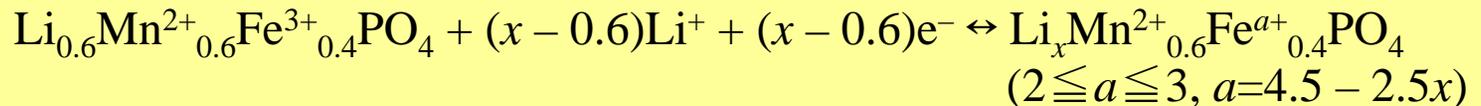
The charge-discharge reaction mechanism of the olivine-type $\text{Li}_x\text{Mn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ ($0 \leq x \leq 1$) cathode material for lithium ion batteries is concluded as described below:

- 1) A two-phase reaction occurs in region I ($0 \leq x \leq 0.6$) and single-phase reaction occurs in region II ($0.6 \leq x \leq 1$), and
- 2) $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox occurs in region I and $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox occurs in region II.

Region I ($0 \leq x \leq 0.6$, 4.1V, $\text{Mn}^{3+}/\text{Mn}^{2+}$, two-phase)



Region II ($0.6 \leq x \leq 1$, 3.5V, $\text{Fe}^{3+}/\text{Fe}^{2+}$, single-phase)



These features show significant differences from the reaction mechanism of Li_xFePO_4 ($0 \leq x \leq 1$), in which the whole $\text{Fe}^{3+}/\text{Fe}^{2+}$ reaction proceeds in a two-phase manner ($\text{LiFePO}_4\text{-FePO}_4$) with a flat voltage profile at 3.4V.