



# The phase transition behaviors of $\text{Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ during lithium extraction studied by *in situ* X-ray absorption and diffraction techniques

Kyung-Wan Nam<sup>a</sup>, Won-Sub Yoon<sup>b,\*</sup>, Karim Zaghib<sup>c</sup>, Kyung Yoon Chung<sup>d</sup>, Xiao-Qing Yang<sup>a</sup>

<sup>a</sup> Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

<sup>b</sup> School of Advanced Materials Engineering, Kookmin University, 861-1 Jeongneung-dong, Seongbuk-gu, Seoul 136-702, Republic of Korea

<sup>c</sup> Institut de Recherche d'Hydro-Québec (IREQ), Varennes, Quebec, Canada J3X 1S1

<sup>d</sup> Battery Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

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## ABSTRACT

How the structural changes take place in  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ -type cathode materials during lithium extraction/insertion is an important issue, especially on if they go through the single-phase reaction (i.e., solid solution reaction) or the two-phase reaction regions. Here we report the studies on the phase transition behaviors of a carbon coated  $\text{Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  ( $\text{C-Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ ,  $0.0 \leq x \leq 1.0$ ) sample during the first charge using *in situ* X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) techniques. The combination of *in situ* XAS and XRD results clearly identify two two-phase coexistence regions at two voltage plateaus of 3.6 ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) and 4.2 V ( $\text{Mn}^{2+}/\text{Mn}^{3+}$ ) and a narrow intermediate region which proceeds via single-phase reaction in between two two-phase regions. In addition, simultaneous redox reactions of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Mn}^{2+}/\text{Mn}^{3+}$  in the narrow single-phase region are reported and discussed for the first time.

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## 1. Introduction

$\text{LiMPO}_4$ -type materials with an ordered olivine structure have been extensively studied in the last decade as promising cathode materials due to their excellent electrochemical and thermal stability [1–7]. Among them,  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$  solid solution is considered as one of the promising cathode materials because of its favored operation voltage between 3.5 and 4.2 V, low material cost and environmental compatibility. The structural changes of  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$  during charge–discharge cycling have been studied using *ex situ* and *in situ* X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and Mössbauer spectroscopy [8–13]. The charge curve reflecting the electrochemical lithium extraction from  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$  exhibits two voltage plateaus at  $\sim 3.6$  and 4.2 V, corresponding to the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox couples, respectively. Nevertheless, the debate about if the phase transitions are based on the single-phase reaction (i.e., solid solution reaction) or the two-phase reaction in  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$  during lithium extraction/insertion is still going on. Based on the extensive studies on the  $\text{Li}_{1-x}\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$  ( $0.0 \leq x, y \leq 1.0$ ) systems, Yamada et al. reported that the first plateau ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) at  $\sim 3.5$  V can be attributed to the single-phase reaction whereas the second plateau ( $\text{Mn}^{2+}/\text{Mn}^{3+}$ ) at  $\sim 4.2$  V is reflecting a phase transition through the two-phase reaction [8,9]. These conclusions were drawn from their

*ex situ* XRD analysis obtained from the chemically delithiated samples. On the other hand, a single-phase reaction mode during electrochemical lithium extraction of  $\text{Li}_{1-x}\text{Mn}_{0.45}\text{Fe}_{0.55}\text{PO}_4$  in the whole lithium composition range ( $0.0 \leq x \leq 1.0$ ) was reported by Molenda et al. using *ex situ* XRD study [10,11]. Recently, Bramnik et al. showed that there are two two-phase reaction regions during lithium extraction for both  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox couples in  $\text{Li}_{1-x}\text{Fe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$  using high resolution synchrotron *in situ* XRD study [13]. They also showed that the existence of a narrow single-phase region (i.e.,  $0.33 \leq x \leq 0.45$  in  $\text{Li}_{1-x}\text{Fe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ ), represented by an intermediate phase, located in between the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox reaction regions [13]. The single-phase reaction in  $\text{Li}_{1-x}\text{MPO}_4$ -type cathodes is considered to be very important and beneficial both for the charge movement and the subsequent phase boundary movement [14,15]. Therefore, clear understanding on the phase transition behavior of  $\text{Li}_{1-x}\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$  during lithium extraction/insertion is quite important for the development of  $\text{Li}_{1-x}\text{MPO}_4$ -type cathodes with enhanced power and energy density. Here, we report our observation on the phase transition behavior during electrochemical lithium extraction of carbon coated  $\text{Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  (i.e.,  $\text{C-Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ ) studied by combined *in situ* XAS and XRD techniques.

## 2. Experimental

$\text{C-LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  powders were provided from Institut de Recherche d'Hydro-Québec (IREQ) and the detailed synthesis

\* Corresponding author. Tel.: +82 2 9104664; fax: +82 2 9104320.

E-mail address: [wsoon@kookmin.ac.kr](mailto:wsoon@kookmin.ac.kr) (W.-S. Yoon).

procedures were described elsewhere [16]. The electrodes were prepared by mixing the  $\text{C-LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  with carbon black and PVDF at a weight ratio of 8:1:1 first, slurring it in a NMP (*n*-methyl pyrrolidone) solution, then coating the slurry onto an Al foil. The cathodes were incorporated into the spectroelectrochemical cells for *in situ* XAS and XRD experiments with a Li foil as negative electrode and a Celgard separator as described in our prior publication [17]. The electrolytes used were 1.2 M  $\text{LiPF}_6$  dissolved in ethylene carbonate and ethyl methyl carbonate solution (EC:EMC = 3:7, volume).

*In situ* XAS spectra were collected in transmission mode at beamline X19A at the National Synchrotron Light Source (NSLS) using a Si(1 1 1) double-crystal monochromator. Reference spectrum of each element was simultaneously collected with the corresponding spectrum of the *in situ* cells using Mn and Fe reference foils. *In situ* XRD patterns were collected at beamline X18A of the NSLS using a position sensitive detector (PSD) with the wavelength of 0.9999 Å. For easy comparison, the two theta angles of all the XRD patterns have been recalculated and converted to the corresponding angles for  $\lambda = 1.54 \text{ \AA}$  (Cu- $K_\alpha$  radiation).

### 3. Results and discussions

Fig. 1a shows the first charge profile of  $\text{C-Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  during *in situ* XAS experiments using a slow current rate (i.e., C/20 based on theoretical capacity of  $168 \text{ mAh g}^{-1}$ ), which is close to the quasi-equilibrium state. The lithium composition,  $x$  in  $\text{C-Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ , was calculated from the charge and mass of the active material, by assuming that all the current passed was due to lithium extraction. Two voltage plateaus at around 3.6 and 4.2 V marked as I and II are clearly observed in the charge profile. *In situ* metal K-edge X-ray absorption near edge structure (XANES) spectroscopy was used to study the charge compensation mechanism of these two voltage plateaus and the results at Fe and

Mn K-edges are shown in Fig. 1b and c. Composition change ( $\Delta x$ ) in  $\text{C-Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  during each scan was  $\sim 0.01$ . Fig. 1b and c clearly show that the edge shifts toward higher energy takes place mainly in the Fe K-edge during the first plateau, while the shifts in the Mn K-edge relayed in the second plateau, indicating the two voltage plateaus around 3.6 and 4.2 V are mainly originated from the redox reactions of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Mn}^{2+}/\text{Mn}^{3+}$ , respectively. This result agrees well with previous *ex situ* XAS studies on the  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$  ( $0.0 \leq y \leq 0.8$ ) [8,12]. However, there are two interesting observations to be pointed out in the *in situ* XANES result. The first one is the existence of two single isosbestic points (marked as red arrows in the insets of Fig. 1b and c) in some Fe and Mn K-edge XANES spectra. The second one is the existence of a narrow composition range (i.e.,  $\sim 0.4 \leq x \leq \sim 0.5$  in  $\text{C-Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ ) where both of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox reactions take place simultaneously. These are described in more details below.

The spectra with the composition ranges of  $0.00 \leq x \leq 0.38$  for Fe K-edge and  $0.49 \leq x \leq 1.00$  for Mn K-edge in  $\text{C-Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  have single isosbestic points at  $\sim 7130$  and  $\sim 6558$  eV, respectively. Isosbestic points are common in spectroscopic data. The presence of an isosbestic point indicates that only two species with changing ratios of their concentration in the mixture contribute to the absorption around the isosbestic point [18]. The normalized Fe and Mn K-edge spectra having a single isosbestic point were fitted using principal component analysis (PCA). The spectra for two end members of  $\text{Li}_{1.00}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  and  $\text{Li}_{0.62}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  (i.e.,  $x = 0.00$  and  $0.38$  in  $\text{Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ ) were used for Fe K-edge spectra fitting whereas the spectra for the  $\text{Li}_{0.51}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  and  $\text{Li}_{0.00}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  (i.e.,  $x = 0.49$  and  $1.00$  in  $\text{Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ ) were used for Mn K-edge spectra fitting. As shown in Fig. 2a and b, excellent fits could be obtained using linear combinations of the spectra for end members at each edge. For example, a PCA result for the Mn K-edge spectrum of  $\text{Li}_{0.28}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  (i.e.,  $x = 0.72$  in  $\text{C-Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ ) shown in Fig. 2a reveals that the observed spectrum is composed of 53% of

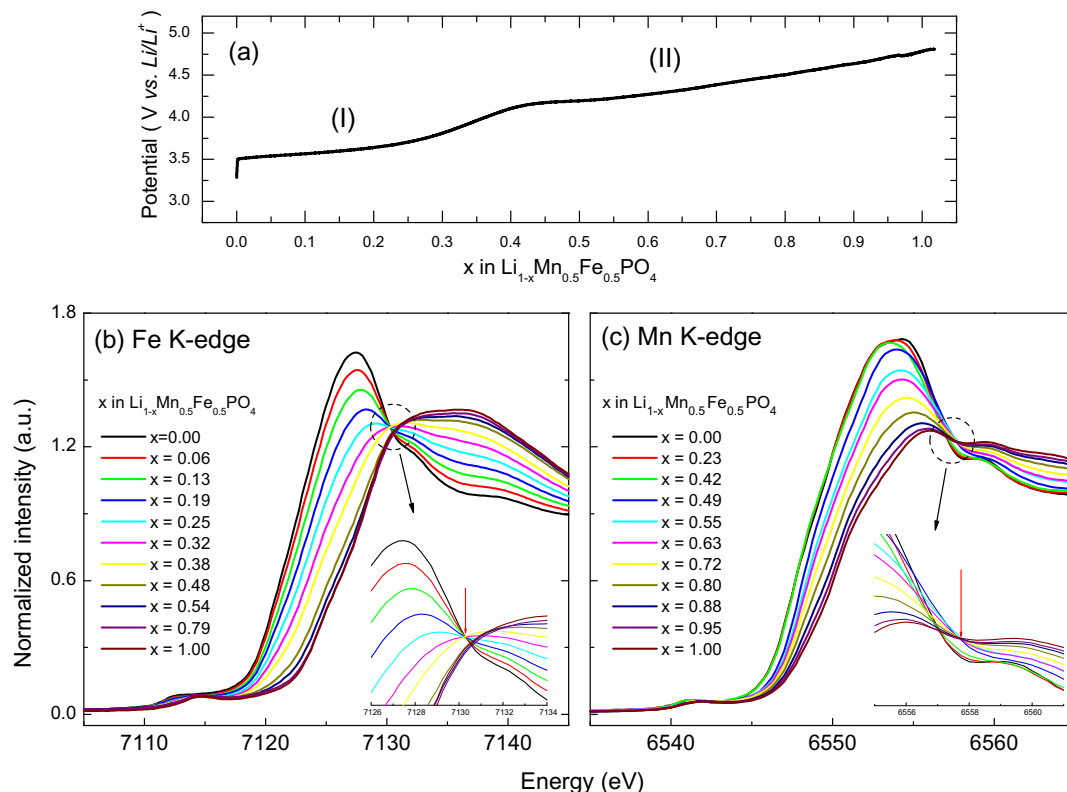


Fig. 1. (a) First charge curves of  $\text{C-Li}_{1-x}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  at a C/20 rate and corresponding *in situ* (b) Fe and (c) Mn K-edge XANES spectra.

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