

# Electronic structure of $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$ for lithium-ion battery studied by resonant photoemission spectroscopy

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**Abstract.** In order to clarify changes in the electronic structures, especially Fe partial density of states (DOS), of  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  with Mn substitution, we have performed x-ray absorption spectroscopy and resonant photoemission spectroscopy (RPES) experiments for  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$ . Using RPES techniques, we have succeeded in extracting the  $\text{Fe}^{2+}$  partial DOS. We have found the systematic shift to higher binding energy and broadening of Fe 3d  $t_{2g}$  down-spin states accompanying with the Mn substitution. The peak shift of the Fe 3d  $t_{2g}$  down-spin states is matched very well to the change of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox potential, suggesting that the origin of high  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox potential in  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  is the shift of the Fe 3d  $t_{2g}$  down-spin states to the higher binding energy with Mn substitution.

## 1. Introduction

A pyrophosphate iron compound  $\text{Li}_2\text{FeP}_2\text{O}_7$  is a newly designed polyanionic-cathode material for a Li-ion battery [1]. Compared to olivine formula  $\text{LiFePO}_4$  [2, 3],  $\text{Li}_2\text{FeP}_2\text{O}_7$  has some superior characteristics such as high redox voltage of 3.5 eV, reversible electrochemical activity without any particle-downsizing/carbon coating, a two-dimensional channel for Li-diffusion, and the potential of a 2-electron redox reaction. In addition, recently it has been reported that the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox potential upshifts to 4 V with partial substitution of Mn for Fe sites in  $\text{Li}_2\text{FeP}_2\text{O}_7$  [4]. Since the possibility of  $\text{Mn}^{3+}/\text{Mn}^{2+}$  redox reaction below 4 V has been ruled out,

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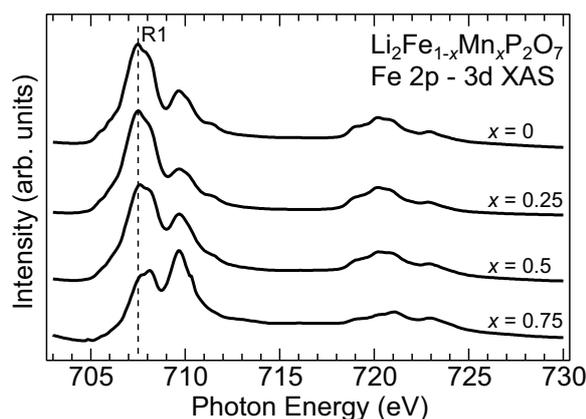
the upshift of the redox potential in  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  is thought to be derived from changes in the Fe states with Mn substitution. In order to clarify changes in the electronic structures, especially Fe partial density of states (DOS), of  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  with Mn substitution, we have performed x-ray absorption spectroscopy (XAS) and resonant photoemission spectroscopy (RPES) experiments for  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$ .

## 2. Experimental

The mixed-metal pyrophosphate  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  ( $x = 0, 0.25, 0.5, \text{ and } 0.75$ ) powders were synthesized by conventional solid state reactions [4] using  $\text{Li}_2\text{CO}_3$ ,  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{MnC}_2\text{O}_4$ , and  $(\text{NH}_4)_2\text{HPO}_4$ . Stoichiometric amounts of precursors and optional 10 wt% Ketjen black carbon additives for improvement of electron conductivity were thoroughly mixed and then sintered at  $600^\circ\text{C}$  for 12 h under Ar gas flow. The formation of  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  crystals were confirmed by powder x-ray diffraction measurements.

Before soft x-ray spectroscopic measurements, we performed electrochemical charge/discharge cycles for characterization and control of Li concentration. Working electrodes were formulated with mixing the  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7/\text{C}$  composites, additional carbon black, and polyvinylidene fluoride binder in a minimal amount of N-methylpyrrolidone solvent. The cells were charged and discharged over the potential range from 2.0 V to 4.5 V in an Ar-filled glove box and we confirmed that galvanostatic cycling profiles were the same as those in the previous reports [4]. After the several charge/discharge cycles, each cell was charged up to 2.0 V for full lithiation.

Spectroscopic measurements were performed at BL-2C of the Photon Factory in High Energy Accelerator Research Organization. In order to avoid moisture air exposure, we enclosed the electrode samples in an Ar-filled transfer chamber at the inside of the glove box and connected the transfer chamber to a sample entry of measurement chamber without any exposure to air. The total energy resolution of XAS and RPES measurements was set to 200 meV. The binding energies were calibrated using an Au 4f core-level peak on a gold foil reference and a C 1s core-level peak on carbon black additives in the samples.

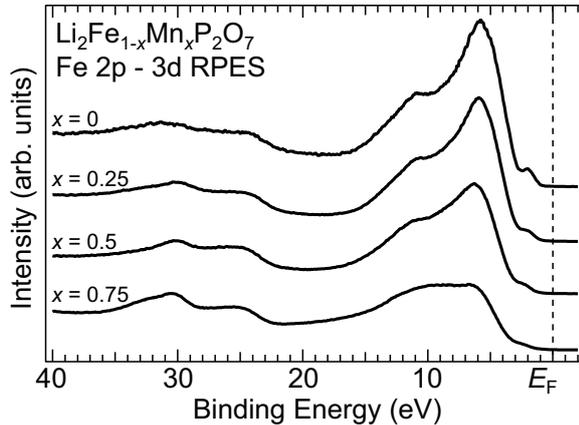


**Figure 1.** Fe 2p - 3d XAS spectra for  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$ . A dashed line labeled R1 corresponds to the photon energy used for RPES measurements in Fig. 2.

## 3. Results and Discussion

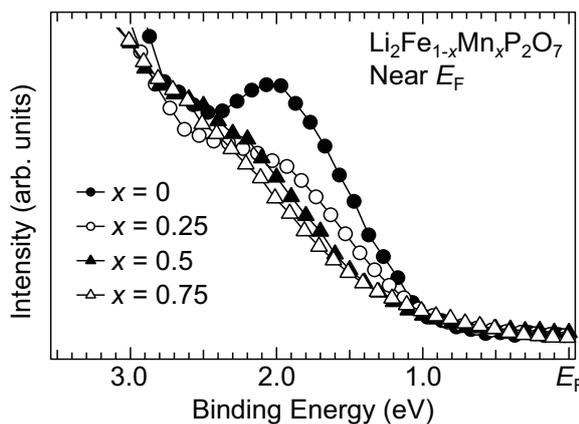
Figure 1 shows Fe 2p - 3d XAS spectra for  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$ . The XAS spectra on  $\text{Li}_2\text{FeP}_2\text{O}_7$  and  $\text{Li}_2\text{Fe}_{0.75}\text{Mn}_{0.25}\text{P}_2\text{O}_7$  are very similar to those on olivine-type  $\text{LiFePO}_4$  [5] and  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  [6] with  $\text{Fe}^{2+}$  states. With increasing Mn concentration,  $\text{Fe}^{3+}$  components slightly increase [5]. Since the Mössbauer spectra, which are completely sensitive to bulk conditions, show only small signal of  $\text{Fe}^{3+}$  impurity without any Mn-concentration dependence [4], the origin of the  $\text{Fe}^{3+}$  components is probably a slight desorption of Li ions at the surface.

By the slight Li desorption, the valencies of Fe ions are more strongly affected for samples with less amount of Fe such as  $x = 0.75$ . because the valencies of Mn ions hardly change. In order to extract the  $\text{Fe}^{2+}$  contribution in the valence band, we have performed RPES measurements at the excitation energy R1 (a dashed line in Fig. 1) corresponding to the absorption edge of  $\text{Fe}^{2+}$  states.

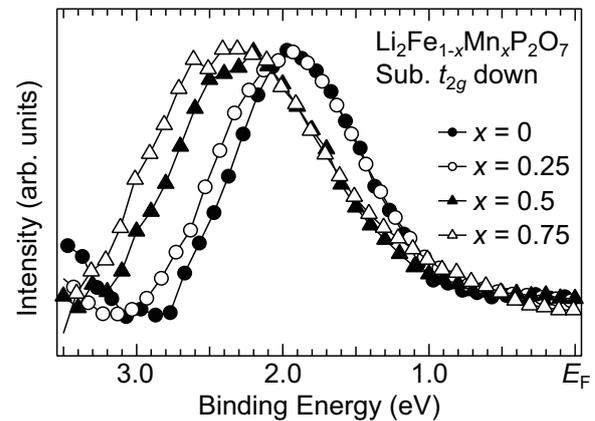


**Figure 2.** Fe  $2p - 3d$  RPES spectra for  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  measured at the excitation energy R1 (a dashed line in Fig. 1). The spectral intensity is normalized by the area of O  $2s$  core-level peaks around 25 eV.

Figure 2 shows Fe  $2p - 3d$  RPES spectra for  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  measured at the excitation energy R1. The RPES spectrum on  $\text{Li}_2\text{FeP}_2\text{O}_7$  is also very similar to that for olivine-type  $\text{LiFePO}_4$  [5] with  $\text{Fe}^{2+}$  states, suggesting that Li-Fe pyrophosphate and olivine materials have similar electronic structures. A distinctive feature around 2 eV corresponding to the Fe  $3d t_{2g}$  down-spin states in  $\text{Fe}^{2+}$  [7] is clearly observed. With decreasing Fe concentration, although the intensity of resonant valence band spectra decreases, Fe  $3d t_{2g}$  down-spin states still remain observable.



**Figure 3.** The expanded RPES spectra near  $E_F$  for  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$ .



**Figure 4.** The extracted Fe  $3d t_{2g}$  down-spin states obtained by subtracting the contribution from the other states from the RPES spectra for  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$ .

The expanded RPES spectra near  $E_F$  are shown in Fig. 3. We note that the Fe  $3d t_{2g}$  down-spin states gradually shift to higher binding energy with increasing Mn concentration. In order to analyze the shift of the Fe  $3d t_{2g}$  down-spin states in detail and quantitatively, we extract the Fe  $3d t_{2g}$  down-spin states by subtracting the contribution from the other states, as shown

in Fig. 4. The systematic peak shift and broadening accompanying with the Mn substitution is observed more clearly in the extracted Fe 3d  $t_{2g}$  down-spin states. Thus, we have determined that the center of the peak position at  $x = 0, 0.25, 0.5,$  and  $0.75$  is 1.9 eV, 2.0 eV, 2.3 eV, and 2.4 eV, respectively. The peak shift between 1.9 eV at  $x = 0$  and 2.4 eV at  $x = 0.75$  is matched very well to the difference of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox potential between 3.5 eV for  $\text{Li}_2\text{FeP}_2\text{O}_7$  and around 4 eV for  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  with high Mn concentration [4]. These results suggests that the origin of high  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox potential in  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  is the change in the electronic structures of  $\text{Fe}^{2+}$  partial DOS, namely the shift of the Fe 3d  $t_{2g}$  down-spin states to the higher binding energy with Mn substitution. Possible explanations for the Mn-induced change in the Fe 3d electronic structure are enhancements of Fe - O bond length and Fe ionicity resulting from the lattice volume expansion [8], and development of destabilization and higher Gibbs free energy due to strong electrostatic repulsion between  $\text{Li}^+$  and  $\text{Fe}^{3+}$  (or, lithium vacancy and  $\text{Mn}^{2+}$ ) in oxidized  $\text{Fe}^{3+}$  and unreacted  $\text{Mn}^{2+}$  surrounding the remaining  $\text{Li}^+$  ions [9].

In conclusion, we have investigated the changes in the electronic structures, especially Fe partial DOS, of  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  with Mn substitution using XAS and RPES techniques. We have found the systematic shift to higher binding energy and broadening of Fe 3d  $t_{2g}$  down-spin states accompanying with the Mn substitution. The peak shift of the Fe 3d  $t_{2g}$  down-spin states is matched very well to the change of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox potential, suggesting that the origin of high  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox potential in  $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{P}_2\text{O}_7$  is the shift of the Fe 3d  $t_{2g}$  down-spin states to the higher binding energy with Mn substitution.

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### References

- [1] Nishimura S, Nakamura M, Natsui R and Yamada A 2010 *J. Am. Chem. Soc.* **132** 13596
- [2] Padhi A K, Nanjundaswamy K S and Goodenough J B 1997 *J. Electrochem. Soc.* **144** 1188
- [3] Yamada A, Kudo Y and Liu K Y 2001 *J. Electrochem. Soc.* **148** A1153
- [4] Furuta N, Nishimura S, Barpanda P and Yamada A 2012 *Chem. Mater.* **24** 1055
- [5] Kurosumi S, Nagamura N, Toyoda S, Horiba K, Kumigashira H, Oshima M, Furutsuki S, Nishimura S, Yamada A and Mizuno N 2011 *J. Phys. Chem. C* **115** 25519
- [6] Kurosumi S, Horiba K, Nagamura N, Toyoda S, Kumigashira H, Oshima M, Furutsuki S, Nishimura S, Yamada A and Mizuno N 2013 *J. Power Sources* **226** 42
- [7] Augustsson A, Zhuang G V, Butorin S M, Osorio-Guillen J M, Dong C L, Ahuja R, Chang C L, Ross P N, Nordgren J and Guo J H 2005 *J. Chem. Phys.* **123** 184717
- [8] Yamada A, Takei Y, Koizumi H, Sonoyama N, Kanno R, Itoh K, Yonemura T and Kamiyama T 2006 *Chem. Mater.* **18** 804
- [9] Padhi A K, Nanjundaswamy K S, Masquelier C, Okada S and Goodenough J B 1997 *J. Electrochem. Soc.* **144** 1609