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The electronic structure change during the reversible Li-ion storage reaction in a bimetallic MnFe-Prussian blue analogue (Li$_2$K$_{0.14}$Mn$_{1.43}$[Fe(CN)$_6$]·6H$_2$O) was investigated by soft x-ray absorption spectroscopy. The Mn L$_{2,3}$-edge spectra revealed the unchanged Mn$^{2+}$ high-spin state regardless of Li-ion concentration (x). On the other hand, the Fe L$_{2,3}$-edge spectra clearly revealed a reversible redox behavior as Fe$^{3+}$ ↔ Fe$^{2+}$ states with Li-ion insertion/extraction. Experimental findings suggested strong metal-to-ligand charge transfer in accompany with ligand-to-metal one. The resulting charge delocalization between the Fe and CN is considered to contribute to the high reversibility of the Li-ion storage process.

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I. INTRODUCTION

Electronic properties of coordination polymers have attracted considerable attention since they have the unique potential of wide applications for spintronics, guest separation, and ion storage\cite{1-3}. In particular, coordination polymer electrodes for Li-ion batteries exhibit the solid-state redox of the host framework during charge/discharge process\cite{4-6} as their drastic changes in orbital occupation and energy levels of transition metals (TMs) and bridging ligands.

Recently, we demonstrated that the cyanide-bridged coordination polymer, Prussian blue analogue (PBA), undergoes electrochemical Li-ion insertion/extraction (discharge/charge) reactions with high reversibility\cite{7}. PBAs generally have a perovskite structure bridged by cyanide groups: A$_n^+$M$_{b}^{2+}$[M$_{3}^{3+}$(CN)$_{6}$]·nH$_2$O (A: alkali metal, M$_a$ and M$_3$: TMs) (Fig. 1(a)). As indicated in the formula, there are Schottky defects at A and [M$_3$(CN)$_6$] sites because alkali-metal ions with small ionic radii such as K-ion cannot stably occupy the large pore in PBAs. Thus, in contrast to M$_a$ ions in the M$_3$(CN)$_6$ coordination environment, M$_a$ ions form an M$_a$(NC)$_{6-δ}$(OH)$_2$$_δ$ octahedron (0 < δ < 2) that has a weak and slightly distorted ligand field in contrary to a perfect M$_a$(NC)$_6$ octahedron. By using this host framework, the following electrochemical reaction can be achieved: xLi$^+$ + xe$^-$ + (PBA)$^{0}$ ↔ Li$_{x}^{+}$(PBA)$^{x-}$.

Figure 1(a) shows schematic electrochemical reaction and crystal structure of Li$_2$K$_{0.14}$Mn$_{1.43}$[Fe(CN)$_6$]·6H$_2$O (Li$_2$MnFe-PBA) which exhibits high reversibility over 100 charge/discharge cycles\cite{7}. During the reaction completely via solid solution state, the Li concentration x continuously changes within each particle, and electrons are simultaneously supplied/removed by an electric current (Fig. 1(a)), resulting in charge/discharge process at a specific redox voltage (Fig. 1(b)).

According to the previous reports, Fe-CN-Mn PBA framework (e.g. Rb salt: Rb$_3$Mn$$_2$[Fe(CN)$_6$]·nH$_2$O) exhibits rich physical properties such as inter-metallic charge transfer transition due to the strong interaction among the Mn $t_{2g}$, Fe $t_{2g}$, and CN $p_z$ orbitals\cite{8-10}. This suggested that MnFe-PBA could have the class II mixed valence state with electron delocalization over the entire framework, therefore the investigation of the electronic structure of MnFe-PBA during Li-ion insertion/extraction is highly intriguing. Furthermore, understanding the corresponding electronic-structure change during the redox reaction would shed light on material designs to improve the performance of the coordination polymer electrodes. Consequently, it is crucial for the research field of not only basic science but also technological applications to perform element-selective investigations of the electronic structures of PBAs.

For an element-selective observation of 3d electronic structures of TMs, soft x-ray absorption spectroscopy (XAS) is a powerful technique. Concerning hexacyanometalates, Cartier dit Moulin et al.\cite{12} and Hocking et al.\cite{13} showed that Fe L$_{2,3}$-edge (2p$_{1/2,3}$ → 3d absorption) XAS for K$_3$[Fe$^{III}$(CN)$_6$] and K$_4$[Fe$^{III}$(CN)$_6$] in combination with the charge transfer multiplet (CTM) calculations could clarify not only the Fe oxidation state but
The color change shows Li-ion concentration within a MnFe-PBA particle. (b) Discharge (Li-ion insertion)/charge (Li-ion extraction) curves. Li-ion concentration, $x$, was calculated from the integrated electric current through the electrochemical cell. The inset in (b) indicates cyclability of the discharge capacity during 100 cycles$^7$.

also the degrees of donation and back-donation between the Fe and cyanide ligand. Thus, XAS is an appropriate method to investigate the electronic-structure change of PBAs during the charge/discharge process. Here, we report XAS investigations of the electrochemical reversible Li-ion storage reaction in MnFe-PBA.

II. EXPERIMENT

We synthesized MnFe-PBA using the precipitation method and performed elemental analyses as previously reported$^7$. X-ray diffraction measurements confirmed that the compound had a conventional cubic PBA structure without any impurity phases. For electrochemical experiments, MnFe-PBA (75 wt%), acetylene black (20 wt%), and polytetrafluoroethylene (5 wt%) were ground into a paste. The electrochemical Li-ion insertion/extraction has been performed according to Ref.$^7$. As Figure 1(b) displays, MnFe-PBA can store Li ions up to $x = 0.9$, so that we prepared samples of as-pasted (MnFe-PBA, before Li-ion insertion), fully Li-ion inserted (Li$_{0.9}$MnFe-PBA), and fully Li-ion extracted (Li$_{0}$MnFe-PBA) states.

XAS measurements were performed at BL-7A of the Photon Factory (PF). The total electron-yield (TEY) mode was employed. The resolution was $E/\Delta E \sim 1500$. The pressure was maintained at the order of $10^{-8}$ Torr. All the XAS measurements were performed at room temperature. In advance of the XAS measurements at PF, we had done preliminary XAS measurements at BL7.0.1 of the Advanced Light Source.

III. RESULTS AND DISCUSSION

Figure 2 shows photon flux-normalized XAS spectra of Li$_x$MnFe-PBA at the Mn $L_{2,3}$ edges. The Mn $L_{2,3}$-edge XAS spectra of all the samples were nearly the same, which suggested that the electronic structure of Mn remains unchanged during Li-ion insertion/extraction. To analyze the spectra in detail, we also performed CTM calculations$^{12-16}$. The calculated spectrum is also shown in Fig. 2. Using the parameters for Mn$^{2+}$ high-spin (HS) state with $3d^5$ and $3d^6L$ (where, $L$ denotes ligand hole) configurations in $O_h$ symmetry$^{15-19}$, we could reproduce the experimental XAS. Figure 2 shows a calculated Mn$^{2+}$ HS spectrum with the crystal-field splitting $10Dq$ of 0.8 eV, while the charge-transfer (CT) energy $\Delta$, the on-site 3d-3d Coulomb energy $U_{dd}$, and the core-hole potential $U_{pd}$ were respectively fixed to 6.5, 5.2, and 6.2 eV in the calculations. The $10Dq$ of 0.8 eV is smaller than that for Mn$^{11}$N$_6$ octahedron in MnNCN ($\sim$1 eV)$^{20}$. This is consistent with the weak crystal-field splitting of the Mn(NC)$_{6-\delta}$(OH)$_2\delta$ octahedron in MnFe-PBA.

Here, we note the evaporation effect of coordinating water for the Mn 3d electronic structure. It is well known that the coordinated water molecules in Mn(NC)$_{6-\delta}$(OH)$_2\delta$ can evaporate in vacuum to form Mn(NC)$_{6-\delta}$.$^{21}$ Therefore, the estimated $10Dq$ based on the spectra could be slightly different from that for the actual state. Nevertheless, the value on the Mn site was small (0.8 eV) compared to Mn$^{11}$N$_6$ octahedron ($\sim$1 eV)$^{20}$. Therefore, in the present study, the evaporation effect may not be significant.

Figure 3 shows photon-flux-normalized Fe $L_{2,3}$-edge XAS spectra of Li$_x$MnFe-PBA. The spectrum of MnFe-PBA is similar to that of K$_3$[Fe$^{11+}$(CN)$_6$] (Fig. 3(b)), indicating the Fe$^{3+}$ low-spin (LS) states$^{12,13}$. As Li-ion was inserted (Li$_{0.9}$MnFe-PBA), the spectral shape drastically changed and the shape became similar to that of
K$_3$[Fe$^{III}$(CN)$_6$] (Fig. 3(c))$^{12,13}$. The peak at 706 eV disappeared upon Li-ion insertion can be ascribed to the states consisting mainly of Fe $t_{2g}$ orbital. The other two peaks in the $L_3$ region (at 709.2 and 710.8 eV) could be attributed to the unoccupied $e_g$ states. Thus, the Fe atoms were reduced as Fe$^{3+}$ LS $\rightarrow$ Fe$^{2+}$ LS by Li-ion insertion. Furthermore, the Fe $L$-edge spectrum completely returned to the initial shape after Li-ion extraction (Fig. 3(a)). Therefore, the reversible redox reaction occurs mainly on the Fe $t_{2g}$ orbital during Li-ion insertion/extraction.

According to the previous study by Hocking $et$ $al.$$^{13}$, the Fe $L$-edge spectra of [Fe$^{III}$(CN)$_6$]$^{3-}$ and [Fe$^{II}$(CN)$_6$]$^{4-}$ could be explained only when the metal-to-ligand charge transfer (MLCT) (i.e., $\pi$ back-donation, Fig. 4(a)) was taken into account in addition to the ligand-to-metal charge transfer (LMCT) (i.e., $\pi/\sigma$ back-donation, Fig. 4(a)) in the CTM calculations. Figures 3(b) and 3(c) respectively show the calculated results for Fe$^{3+}$ and Fe$^{2+}$ states with/without MLCT. The Fe $L$-edge spectra of [Fe$^{III}$(CN)$_6$]$^{3-}$ and [Fe$^{II}$(CN)$_6$]$^{4-}$ quoted from Ref.$^{13}$ are also shown. In the LMCT-only calculation, the parameters of $10Dq = 4.0$ eV, $\Delta = 1.0$ eV, $U_{dd} = 2.0$ eV, and $U_{pd} = 1.0$ eV were used for both Fe$^{3+}$ and Fe$^{2+}$ states. In regard to the LMCT-MLCT combined CTM calculation, the CT energy, i.e., the energy difference between $d^n$, $d^{n+1}L$, and $d^{n-1}L^-$ configurations is given by ground-state energies of EG2 ($d^{n-1}L^-$ and $d^n$ (MLCT)) and EG3 ($d^{n-1}L^-$ and $d^{n+1}L$, (relating to LMCT)) and final-state energies EF2 and EF3. The hopping (i.e., mixing) energies for the $t_{2g}$ and $e_g$ symmetries ($V_{t_{2g}}$, $V_{e_g}$) were also taken into account in the LMCT-MLCT combined CTM calculation$^{13}$.

As shown in Fig. 3, the experimental spectra could not be reproduced by the LMCT-only calculations for both Fe$^{3+}$ and Fe$^{2+}$ states, even if the electronic parameters are varied largely. In contrast, the LMCT-MLCT combined calculations well reproduced the spectra. The electronic structure parameters for the best reproduced results are summarized in Table I. This indicated that MnFe-PBA has strong MLCT similar to $K_3$[Fe$^{III}$(CN)$_6$] and $K_4$[Fe$^{II}$(CN)$_6$]. However, it should be emphasized that there are slight differences between the Fe $L$-edge XAS spectra for the isolated complexes ($K_3$[Fe$^{III}$(CN)$_6$] and $K_4$[Fe$^{II}$(CN)$_6$]) and coordination polymers (Li$_x$MnFe-PBA). For example, two peak intensities in the Fe $L_3$-edge for Li$_{10.9}$MnFe-PBA are almost same. On the other hand, the peak intensity at 710.8 eV is larger than that at 709.2 eV for $K_4$[Fe$^{II}$(CN)$_6$] (Fig. 3(c)). This can be explained by using the LMCT-MLCT combined CTM calculations. By tuning the LMCT and MLCT parameters, e.g., increasing $V_{e_g}$ for MLCT (case 2 in Fig. 3(c)), the peak at 710.8 eV became weaker to reproduce the spectra for Li$_{10.9}$MnFe-PBA. This implied that the $\sigma$ donating character of CN ligand in Li$_{10.9}$MnFe-PBA is enhanced by the orbital hybridization with Mn.

As for the Fe$^{3+}$ state, the peak intensity at 706 eV for MnFe-PBA is relatively weaker than that for $K_3$[Fe$^{III}$(CN)$_6$] (Fig. 3(b)). As mentioned above, the peak at 706 eV can be attributed to the density of unoccupied states mainly consisting of Fe $t_{2g}$ orbital. Since the Fe $t_{2g}$ orbital well hybridizes with the CN $\pi$ orbital (Fig. 4(b)), the weaker peak intensity at 706 eV indicates that the $\pi$ donation to the Fe $t_{2g}$ orbital is larger than that in $K_3$[Fe$^{III}$(CN)$_6$]. In other words, $3d^6\pi$ character is enhanced in MnFe-PBA while the $\sigma$ donating character is enhanced in Li$_{10.9}$MnFe-PBA.

Now, the Fe $L$-edge XAS for Li$_x$MnFe-PBA clarified the hybridization between the Fe and CN orbitals, and suggested the enhanced $\sigma/\pi$ donation compared to the isolated complexes. Since the strong orbital hybridization should result in the electron delocalization, the changes in the C or N $K$-edge XAS during the charge/discharge process are also expected. However, changes in the C $K$-edge XAS among Li$_x$MnFe-PBA could hardly be observed during Li-ion insertion/extraction because the C $K$-edge XAS spectra also included a large amount of background signals from acetylenelblack and PTFE (Fig. 5(a)). On the other hand, the N $K$-edge XAS showed a slight change with Li-ion insertion (Figs. 5(b)). Although it was hard to elucidate quantitatively, the small peak at 397.3 eV, which could be the $\pi$ orbital hybridized with the Fe $t_{2g}$ orbital, almost disappeared and the main peak of $\pi^*$ orbital at 400.8 eV decreased with Li-ion insertion. Thus, by Li-ion insertion, the $\pi/\pi^*$ orbitals should be reduced in accompany with the Fe $t_{2g}$ orbital, suggesting the electron delocalization on the hybridized Fe $t_{2g}$ and CN $\pi/\pi^*$ orbitals. As for the O $K$-edge XAS studies of TM-oxide such as Li$_{1-x}$CoO$_2$ and Li$_{1-x}$FePO$_4$, their spectral changes were much larger than those in the present C and N $K$-edge XAS$^{22-24}$. This may be due to the difference in the or-
Comparison of Fe

As for MnFe-PBA, electron localization would induce a large lattice strain that deteriorates the electrode. Nevertheless, it is apparent that the hybridization between the Fe and CN orbitals plays an important role in the orbital hybridization mechanism. Since the O 2p (2p_{x,y,z}) orbitals which form wide band around the Fermi level (E_F) well hybridize any TM 3d orbital through the large transfer integrals of (pdσ) and (pdπ) (i.e. σ/π donation), the O K-edge XAS spectra of TM oxides generally include much contribution from the TM's unoccupied 3d states in addition to the O 2p state. For example, the valence band of LiCoO_2 (Co^{3+} LS state (t_{2g}^6)) which directly corresponds to the redox behavior (LiCoO_2 ↔ Li_{1-x}CoO_2), was reported to consist of ~37% Co t_{2g} and ~60% O 2p. Thus, the O K-edge XAS of Li_{1-x}CoO_2 has a character of the hole created in the valence band as a result of the strong hybridization, resulting in the large spectral change depending on the Li concentration. In contrast, the molecular orbital of CN consists of separated and narrow π/σ bands. The frontier orbital (lowest unoccupied molecular orbital, LUMO) of [Fe^{3+}(CN)_6]^{3-} was reported to consist of 77% Fe t_{2g} and 23% CN π orbitals as a result of LMCT and MLCT. Thus, the small changes in the C and N K-edge XAS should originate from the weak partial density of states of CN on the narrow LUMO. Therefore, the orbital hybridization mechanism in MnFe-PBA (LMCT and MLCT on the narrow CN π band) is different from that in the TM oxides (strong LMCT (σ/π donation) on the wide O 2p band). Nevertheless, it is apparent that the hybridization between the Fe and CN orbitals plays an important role in the electronic structure of MnFe-PBA.

Finally, we address the robustness of MnFe-PBA against the Li-ion insertion/extraction cycles. As Férey et al. suggested, the charge delocalization during the Li-ion insertion/extraction might be indispensable for the robust and flexible framework for Li-ion storage, since electron localization would induce a large lattice strain that deteriorates the electrode. As for MnFe-PBA, ex situ x-ray diffraction measurement revealed that the experimental spectra of TM oxides generally include much contribution from the TM's unoccupied 3d states in addition to the O 2p state. For simplicity, only the hybridization between the Fe t_{2g} and CN π* orbitals is depicted.

FIG. 3: (Color online) (a) XAS spectra at the Fe L_{2,3}-edge of Li$_2$MnFe-PBA. For comparison, CTM-calculated spectra and the experimental spectra of K$_2$[Fe^{III}(CN)$_6$] and K$_2$[Fe^{II}(CN)$_6$] quoted from Ref. 13 are also displayed in (b) (for Fe$^{3+}$) and (c) (for Fe$^{2+}$). In (c), two LMCT-MLCT combined CTM-calculated spectra with different V$_{ex}$ in LMCT (1.40 eV for case 1 and 1.85 eV for case 2) are plotted.

FIG. 4: (Color online) (a) Schematic drawings of the possible CTs between Fe and CN. (b) Energy diagram among the Fe$^{3+}$, CN, Mn$^{2+}$ states. For simplicity, only the hybridization between the Fe t_{2g} and CN π* orbitals is depicted.
The relationship between the final- and ground-state energies are given by \( EF = EG + U_{dd} (3d-3d \text{Coulomb energy}) - U_{pd} \text{ (core-hole potential)} \).

### TABLE I: Electronic structure parameters used in the LMCT-MLCT combined CTM calculations.

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<th>( 10Dq )</th>
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<th>LMCT</th>
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<tr>
<td></td>
<td>( V_{d2g} )</td>
<td>( V_{e_g} )</td>
<td>( V_{d2g} )</td>
</tr>
<tr>
<td>Fe(^{3+}) (3d(^5)) (eV)</td>
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<td>1.0</td>
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<tr>
<td>Fe(^{2+}) (3d(^6)) (eV)</td>
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<td>2.1</td>
<td>1.6</td>
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\[ 1.85 \text{ (case 2)} \]

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**IV. CONCLUSION**

XAS was applied to the study on the electronic structure change of MnFe-PBA during various stages of Li-ion insertion/extraction process. The Mn ions were determined to be Mn\(^{2+}\) HS state regardless of the Li-ion concentration. CTM calculations revealed that the Mn ions were under the weak crystal field. On the other hand, the Fe \( L \)-edge XAS spectra revealed that Li-ion insertion caused redox reaction of Fe\(^{3+}\) \( \leftrightarrow \) Fe\(^{2+}\) \( L \)-states. The spectral shapes of the Fe\(^{3+}\) \( L \)-states and Fe\(^{2+}\) \( L \)-states are respectively analogous to those of \( K_3[Fe^{III}(CN)_6] \) and \( K_4[Fe^{II}(CN)_6] \) of which could be reproduced with MLCT as well as LMCT. However, the degree of LMCT was slightly enhanced by the polymerization. Although the orbital hybridization mechanism was different from that for the TM oxides, the bidirectional CTs between the Fe and CN suggest strong charge delocalization there, leading to the stable Li-ion-storage properties of MnFe-PBA.

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