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Electronic structure change of $Li_xK_{0.14}Mn_{1.43}[Fe(CN)_6]\cdot 6H_2O$ during Li insertion/extraction

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Introduction

Prussian blue analogue (PBA) is a new-class electrode materials for Li-ion batteries. We have found that $K_{0.14}Mn_{1.43}[Fe(CN)_6]\cdot 6H_2O$ (MnFe-PBA) could store $0.9Li^+$ in the unit cell [1]. However, the redox reaction on the transition metals has not been clear. To element-selectively clarify the electronic structure change during Li insertion/extraction, we performed soft x-ray absorption spectroscopy (XAS) [2]. Charge-transfer-multiplet (CTM) calculations [3] were also carried out to understand the experimental results [2].

Experimental

The samples of $K_{0.14}Mn_{1.43}[Fe(CN)_6]\cdot 6H_2O$ (MnFe-PBA, before Li insertion), $Li_{0.9}K_{0.14}Mn_{1.43}[Fe(CN)_6]\cdot 6H_2O$ ($Li_{0.9}$MnFe-PBA, fully Li-inserted state), and $Li_0K_{0.14}Mn_{1.43}[Fe(CN)_6]\cdot 6H_2O$ (Li_0MnFe-PBA after Li extraction) were fabricated in the same manner of Ref. 1. The *ex situ* XAS measurements were carried out at BL-7A of the Photon Factory. The total electron-yield mode was employed. The energy resolution was $E/\Delta E$ ~1500. The pressure was maintained at the order of 10^{-8} Torr. All the measurements were performed at room temperature.

Results and discussion

The Mn $L_{2,3}$-edge XAS spectra for Li_xMnFe-PBA did not change regardless of the Li concentration x (not shown) [2]. CTM calculations including ligand-to-metal charge transfer (LMCT) revealed that the unchanged spectra were attributed to Mn^{2+} high-spin state with crystal-field splitting $10Dq$ = 0.8 eV. The small $10Dq$ is consistent with that Mn forms $Mn(NC)_{6-\delta}(OH_2)_\delta$ ($\delta < 2$) octahedron having a weak crystal-field splitting. Although the evaporation of the zeolitic and coordinating H_2O in vacuum cannot be neglected (i.e., formation of $Mn(NC)_{6-\delta}$), the evaporation effect could not be significant because the small $10Dq$ cannot be largely different from the real state of $Mn(NC)_{6-\delta}(OH_2)_\delta$.

On the other hand, the Fe $L_{2,3}$-edge XAS showed drastic changes during Li insertion/extraction (Fig. 1(a)). The spectral shapes of MnFe-PBA and Li_0MnFe-PBA are very similar to that of $K_3[Fe(CN)_6]$ which is of the Fe^{3+} low-spin (LS) state with strong metal-to-ligand CT (MLCT) in addition to LMCT [4]. For $Li_{0.9}$MnFe-PBA, the peak at 706 eV of the t_{2g} orbital disappeared and the spectral shape was nearly the same as $K_4[Fe(CN)_6]$ which is of the Fe^{2+} LS state with LMCT and strong MLCT [4]. Therefore, the Fe was reduced/oxidized by Li insertion/extraction. Furthermore, as shown in Fig. 1(b), we could reproduce those experimental spectra by CTM calculations including MLCT and LMCT [2]. The electronic structure parameters such as CT energies for both MLCT and LMCT were slightly different from those of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ [4].

The bidirectional CT between Fe and CN should make the Fe-CN-Mn framework robust. In fact, MnFe-PBA could store $0.9Li^+$ even after 100 Li-insertion/extraction cycles [1], i.e., MnFe-PBA is highly stable against Li insertion/extraction. The present results well agree with the stability.

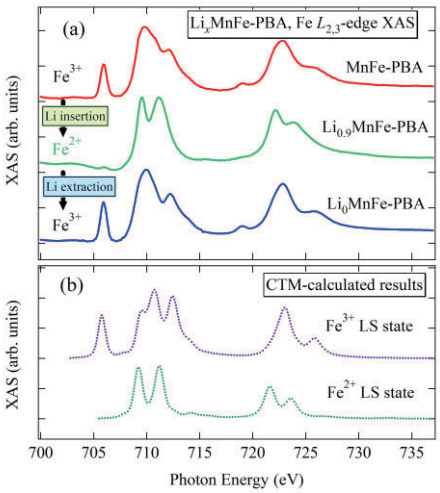

Figure 1: (a) The Fe $L_{2,3}$-edge XAS spectra for Li_xMnFe-PBA. (b) CTM-calculated results for Fe^{3+} and Fe^{2+} LS states with MLCT and LMCT.

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