Lithium intercalation properties in manganese-iron Prussian blue analogues

T Matsuda¹, Y Kurihara¹ and Y Moritomo¹,²

¹ Graduated School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571, Japan
² Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, Tsukuba 305-8571, Japan

E-mail: moritomo@sakura.cc.tsukuba.ac.jp

Abstract. We investigated the electronic states and structural properties of LiₓMn[Fe(CN)₆]₀.₈₃·₃.₅H₂O, and LiₓMn[Fe(CN)₆]₀.₈₇·₂.₆H₂O, which have different amount of [Fe(CN)₆] vacancies. X-ray absorption spectra near the Fe and Mn K-edges revealed that the Li intercalation/deintercalation process is two-electron reaction, i.e. Mn II—NC—Fe II, Mn II—NC—Fe III, and MnIII—NC—Fe III. The crystal structure of LiₓMn[Fe(CN)₆]₀.₈₃·₃.₅H₂O remains cubic and single phase throughout the Li intercalation/deintercalation process. The crystal structure of LiₓMn[Fe(CN)₆]₀.₈₇·₂.₆H₂O is also cubic, while phase separation of Li⁺-rich phase and Li⁺-poor phase was observed during the MnII/MnIII reduction/oxidation process.

1. Introduction
Nanoporous materials are attracting the increasing interests from materials scientists, since such materials can be utilized in various devices, e.g., Li ion secondary batteries, electrochromic devices, hydrogen storage devices, molecular sensors, and molecular filters. Among nanoporous materials, Prussian blue analogues [1-16], AₓMA[MB(CN)₆]₀.₃/₃·zH₂O (MA and MB are transition metal ions, and A is an alkali metal ion), have three-dimensional nanoporous frameworks of cyano-bridged transition metal ions. In the interstitial site of the nanoporous framework, the alkali cations and the part of the water molecules (zeolitic waters) are located, and the alkali cation concentration (x) can be electrochemically controlled via the electronic states of the transition metal ions to maintain charge neutrality[3,4]. The remaining water molecules (ligand waters) coordinate to the MA ion at the vacancy sites of [MB(CN)₆]. As for the crystal structure, the typical compounds show face-centered cubic structures (Fm−3m) in MA[MB(CN)₆]₀.₂/₃·zH₂O. In a stoichiometric compound, AMₐ[MB(CN)₆]₀.₃, the compounds show several space groups by the ordering of the alkali cations [5]. Moreover, by the utilization of the cooperative Jahn-Teller instability inherent to MnIII and CuII, the compounds exhibit the tetragonal structures (I−4m2) in RbMn[Fe(CN)₆], CsCu[Co(CN)₆], and CsCu[Cr(CN)₆] [5-7].

Recently, Okubo et al. reported the reversible Li ion intercalation properties in K₀.₁₄Mn₁.₄₃[Fe(CN)₆]·₆H₂O and Rb₀.₉Mn₁.₁₅[Fe(CN)₆]·₂.₅H₂O [14]. We have also demonstrated that a thin film of Li₁.₃₂Mn[Fe(CN)₆]₀.₈₃·₃.₅H₂O shows a large charge capacity (= 128 mA h g⁻¹) as well as excellent cyclability, which indicates that the Prussian blue analogues are one of the promising...
cathode materials for the Li ion secondary batteries [15,16]. In this Li ion intercalation process, Mn^{II}/Mn^{III} reduction/oxidation occurs and the cooperative Jahn-Teller instability can be expected. In this work, we prepared two Li$_x$Mn[Fe(CN)$_6$]$_{y}$·$z$H$_2$O, which have different amount of [Fe(CN)$_6$] vacancy sites and investigated the electronic states and structural properties.

2. Experimental

2.1. Preparation of Li$_x$Mn[Fe(CN)$_6$]$_{y}$·$z$H$_2$O

Thin films of Na$_{1.32}$Mn[Fe(CN)$_6$]$_{0.83}$·$3.5$H$_2$O and Na$_{1.48}$Mn[Fe(CN)$_6$]$_{0.87}$·$2.6$H$_2$O were electrochemically synthesized on an indium tin oxide (ITO) transparent electrode under potentiostatic conditions at −0.50 V vs a standard Ag/AgCl electrode in an aqueous solution containing K$_3$[Fe(CN)$_6$] (1.0 mmol dm$^{-3}$), MnCl$_2$·$6$H$_2$O (1.5 mmol dm$^{-3}$), and NaCl (1 and 3 mol dm$^{-3}$). Before the film growth, the surface of the ITO electrode was purified by electrolysis of water for 3–5 min. The obtained film was transparent with a thickness of around 1 μm. Chemical compositions of the films were determined by the inductively coupled plasma (ICP) method and CHN organic elementary analysis (Perkin-Elmer 2400 CHN Elemental Analyzer). The Na ions were electrochemically substituted by Li ions, using lithium metal as the reference and counter electrode, and ethylene carbonate (EC) / diethyl carbonate (DEC) solution containing LiClO$_4$ (1 mol dm$^{-1}$) as an electrolyte. We electrochemically contained the Li concentration ($x$), and thus obtained thin films of Li$_x$Mn[Fe(CN)$_6$]$_{0.83}$·$3.5$H$_2$O (L$_x$MF83), and Li$_x$Mn[Fe(CN)$_6$]$_{0.87}$·$2.6$H$_2$O (L$_x$MF87).

2.2. X-ray absorption measurements

The electronic states of the Mn and Fe sites of L$_x$MF83 against $x$ were determined by the ex-situ X-ray absorption spectra (XAS) around the Mn and Fe K-edge. The XAS measurements were conducted at the beamline 7C of the Photon Factory, KEK. The XAS spectra were recorded by a Lytle detector in a fluorescent yield mode with a Si(111) double-crystal monochromator at 300 K. The background subtraction and normalization were conducted by ATHENA program [17].

2.3. Powder X-ray diffraction measurements

The ex-situ powder X-ray diffraction (XRD) measurements of L$_x$MF83, and L$_x$MF87 against $x$ were performed at the beamline 8A of KEK-PF, equipped with an imaging plate detector. The samples were washed with DEC, and carefully removed from the ITO glasses. The obtained powders were sealed in 300 μm glass capillaries. XRD patterns were measured at 300 K and the exposure time was 5 min. Wavelength of the X-ray were 0.77516 Å for L$_x$MF 83, and 0.77476 Å for L$_x$MF 87, respectively. The lattice constants of each compounds were refined by the RIETAN-FP program [18].

3. Results

3.1. Voltage dependence and electronic states on Li ion intercalation processes

Figure 1 shows the voltage against Li metal dependence on $x$ of Li$_x$Mn[Fe(CN)$_6$]$_{0.83}$·$3.5$H$_2$O (L$_x$MF83) and Li$_x$Mn[Fe(CN)$_6$]$_{0.87}$·$2.6$H$_2$O (L$_x$MF87) during the Li ion intercalation process. Here, the possible $x$ regions are 0 $\leq$ $x$ $\leq$ 1.32 for L$_x$MF83 and 0 $\leq$ $x$ $\leq$ 1.48 for L$_x$MF87 due to the charge neutrality. On both films, the electrochemical reactions were observed at around 3.8, and 3.4 V.

The electronic states for each electrochemical reactions are studied by the Mn and Fe K-edge XAS spectra of L$_x$MF83 against $x$. Figure 2 shows the Mn K-edge XAS spectra of L$_x$MF83 against $x$ [16]. The peak around 6549 eV, which is ascribed to Mn$^{II}$ [10-12], was observed in the whole-$x$ region. On the contrary, the shoulder peak around 6552 eV, which is ascribed to Mn$^{III}$ [10-12], was observed in the small-$x$ region. These spectra indicate the reduction/oxidation of Mn (high-spin Mn$^{II}$, and high-spin Mn$^{III}$) occurs in the small-$x$ region. Figure 3 shows the Fe K-edge XAS spectra of L$_x$MF83 against $x$ [16]. The absorption peak energies ($E$) in the Fe K-edge spectra show clear blue shift with decrease in $x$, and saturate below $x$ = 0.41. These data indicates blue shift is ascribed to the oxidation...
of Fe (low-spin Fe$^{II} \rightarrow$ low-spin Fe$^{III}$) [10-13], and indicates the reduction/oxidization of Fe takes place in the large-$x$ region. Considering the formula and the range of $x$, the reduction/oxidization of Fe occurs in $0.49 \leq x \leq 1.32$ region, while the reduction/oxidization of Mn occurs in $0 \leq x \leq 0.49$ region in L$_x$MF83. The same scenario can also be applied to L$_x$MF87, and the reduction/oxidization of Fe occurs in $0.61 \leq x \leq 1.48$ region, while the reduction/oxidization of Mn occurs in $0 \leq x \leq 0.61$ region. Hence, the first plateau in Figure 1 corresponds to the Mn$^{3+}$/Mn$^{2+}$ reduction process, and the second plateau in Figure 1 corresponds to [Fe$^{III}$(CN)$_6$]$^{3-}$/[Fe$^{II}$(CN)$_6$]$^{4-}$ reduction process. We can control $x$ at will by using these data.

3.2. Structural properties.

Figure 4a shows the XRD patterns of L$_x$MF83 [16]. The peak patterns are all similar, which indicates that the lattice structure remains the face-centered cubic ($Fm$–$3m$; $Z = 4$) throughout whole $x$ region. Figure 4b shows the magnified 200 peak, and the reflection shifts to the lower-angle side above $x = 0.41$ while shifts to the lower-angle side below $x = 0.41$. The value of $x = 0.41$ is close to the value of $x = 0.49$ where reduction/oxidation switch between Mn and Fe occurs.

Figure 5a shows the XRD patterns of L$_x$MF87. The lattice structures were the face-centered cubic ($Fm$–$3m$; $Z = 4$) above $x = 0.61$. In $x = 0.15$, each reflection peaks were split into two, which indicates the occurrence of the phase separation, and again, the face-centered cubic structure ($Fm$–$3m$; $Z = 4$)
was observed in \( x = 0.00 \). Figure 5b shows the magnified 200 peak, and the reflection shifts to the lower-angle side above \( x = 0.61 \). The new peak appeared at the higher angle side in \( x = 0.15 \), and the peak at the lower angle side disappeared in \( x = 0.00 \). Overall feature of the XRD patterns of \( x = 0.15 \) can be reproduced by two cubic \((\overline{Fm}3m; Z = 4)\) phases model with different lattice constants. The value of \( x = 0.61 \) is where reduction/oxidation switch between Mn and Fe occurs, and the phase separation occurs in the reduction/oxidation of Mn region.

**Figure 4.** (a) The powder XRD patterns for Li\(_x\)Mn[Fe(CN)\(_6\)]\(_{0.83}\)·3.5H\(_2\)O (L\(_x\)MF83). (b) Magnified 200 peaks. The ticks indicate the reflection peak positions. The wavelength of the X-ray is 0.77516 Å.

**Figure 5.** (a) The XRD patterns for Li\(_x\)Mn[Fe(CN)\(_6\)]\(_{0.87}\)·2.6H\(_2\)O (L\(_x\)MF87). (b) Magnified 200 peaks. The ticks indicate the reflection peaks of Mn\(^{II}\) phase and the stars indicate the reflection peaks of Mn\(^{III}\) phase. The wavelength of the X-ray is 0.77476 Å.
Figure 6a shows the lattice constants against $x$ of $L_x$MF83 refined by the Rietveld analyses. In the reduction/oxidation of Fe region ($0.49 \leq x \leq 1.32$), the lattice constants decreases with $x$. The decrease is ascribed to the smaller size of $[\text{Fe}^{\text{II}}(\text{CN})_6]^-$ as compared with that of $[\text{Fe}^{\text{III}}(\text{CN})_6]^-$.

In the reduction/oxidation of Mn region ($0 \leq x \leq 0.49$), the lattice constants increase with $x$. The increase is ascribed to the larger ionic radius of high-spin Mn$^{\text{II}}$ (0.83 Å) than high-spin Mn$^{\text{III}}$ (0.645 Å).

Figure 6b shows the lattice constants against $x$ of $L_x$MF87 refined by the Rietveld analyses. In the reduction/oxidation of Fe region ($0.61 \leq x \leq 1.48$), the lattice constants decreases with $x$ as observed in $L_x$MF83. On the contrary, in the reduction/oxidation of Mn region ($0 \leq x \leq 0.61$), the phase separation occurred and two cubic phase appeared. The lattice constants of larger volume phase is almost same as $x = 0.61$, while the lattice constants of the smaller volume phase is similar as $x = 0$ of $L_x$MF83, i.e., $\text{Mn}^{0.57}\text{Mn}^{\text{III}}_{0.43}[\text{Fe}^{\text{III}}(\text{CN})_6]_{0.83}^\cdot 3.5\text{H}_2\text{O}$. Hence, the larger volume phase can be ascribed to the Mn$^{\text{II}}$-rich, or Li$^+$-rich phase, and the smaller volume phase can be ascribed to the Mn$^{\text{III}}$-rich, or Li$^+$-poor phase. This phase separation was caused by the volume change for the difference in the ionic radii of Mn$^{\text{II}}$ and Mn$^{\text{III}}$.

4. Discussion

Here, we discuss the crystal structures of Prussian blue analogues with Jahn-Teller active sites. The crystals structures of RbMn[Fe(CN)$_6$], CsCu[Co(CN)$_6$]$_2$, and CsCu[Cr(CN)$_6$]$_2$ are tetragonal due to the cooperative Jahn-Teller instability inherent to Mn$^{\text{III}}$ and Cu$^{\text{II}}$ in [4-6]. The crystal structure dependences against the amounts of [Fe(CN)$_6$] sites ($y$) and Mn$^{\text{III}}$ sites are inreported in $Rb_3yMn[Fe(CN)_6]y\cdot z\text{H}_2\text{O}$, and $Cs_xMn[Fe(CN)_6]_x\cdot z\text{H}_2\text{O}$ systems [6-9]. In $Rb_3yMn[Fe(CN)_6]y\cdot z\text{H}_2\text{O}$, the tetragonal crystal structure ($I-4m2$) can be observed in $y > 0.95$, and the driving force of the structural distortion is ascribed to the cooperative Jahn-Teller instability of the Mn$^{\text{III}}$ sites. On the contrary, the cubic structure ($Fm-3m$) appeared in $y = 0.91$, because the Jahn-Teller elongation of Mn$^{\text{III}}$ cannot occur in only one direction of the lattice due to the low Mn$^{\text{III}}$/ (Mn$^{\text{II}}$ + Mn$^{\text{III}}$) ratio of 0.65 and much [Fe(CN)$_6$] vacancies of 9%. The same cubic structures were observed in $Cs_xMn[Fe(CN)_6]_x\cdot z\text{H}_2\text{O}$ due to the low Mn$^{\text{III}}$/ (Mn$^{\text{II}}$ + Mn$^{\text{III}}$) ratio.

In $L_x$MF87, the maximum of Mn$^{\text{III}}$/ (Mn$^{\text{II}}$ + Mn$^{\text{III}}$) ratio is 0.61 in $x = 0$ and [Fe(CN)$_6$] vacancy sites of 13% exists. These values are close to that of $y = 0.91$ compound in $Rb_3yMn[Fe(CN)_6]y\cdot z\text{H}_2\text{O}$. Hence, Mn$^{\text{III}}$-rich phase in $L_x$MF87 is cubic structure. Moreover, $L_x$MF83 which have lower Mn$^{\text{III}}$/ (Mn$^{\text{II}}$ + Mn$^{\text{III}}$) ratio of 0.49 and more [Fe(CN)$_6$] vacancy sites of 17% is also cubic, and the suppression of the phase separation may be due to much [Fe(CN)$_6$] vacancy sites.

5. Conclusions

In summary, we investigated the Li ion intercalation properties of $Li_xMn[Fe(CN)_6]_{0.83}^\cdot 3.5\text{H}_2\text{O}$ and $Li_xMn[Fe(CN)_6]_{0.87}^\cdot 2.6\text{H}_2\text{O}$. The XAS spectra clearly indicates the two-electron reduction/oxidation of
Mn and Fe. The crystal structure of Li$_{\chi}$Mn[Fe(CN)$_6$]$_{0.83}$$\cdot$3.5H$_2$O remains cubic and single phase throughout the Li intercalation/deintercalation process. The crystal structure of Li$_{\chi}$Mn[Fe(CN)$_6$]$_{0.87}$$\cdot$2.6H$_2$O was also cubic, while the phase separation of Mn$^{II}$-rich, or Li$^+$-rich phase and Mn$^{III}$-rich, or Li$^+$-poor phase was observed during the Mn$^{II}$/Mn$^{III}$ reduction/oxidization process. The phase separation observed in Li$_{\chi}$Mn[Fe(CN)$_6$]$_{0.87}$$\cdot$2.6H$_2$O is ascribed to the difference in the ionic radii of Mn$^{II}$ and Mn$^{III}$. The cubic structure observed in Mn$^{III}$-rich, or Li$^+$-poor phase is ascribed to the Jahn-Teller elongation is randomly oriented by the [Fe(CN)$_6$] vacancy sites.

Acknowledgements
This work was supported by a Grant-in-Aid (21244052) for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology. Elementary analysis was performed at Chemical Analysis Division, Research Facility Center for Science and Engineering, University of Tsukuba. The X-ray powder diffraction and X-ray absorption experiments were performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2010G502 and 2011G501).

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