Introduction

The PBAs, $A_xM_y[Fe(CN)_z]_wH_2O$ ($A$ and $M$ are alkali and transition metals, respectively), are promising cathode materials for LIBs. Imanishi et al. reported Li† intercalation behaviors in $M[Fe(CN)_z]_w$ ($M = V$, Mn, Fe, Ni, Cu). However, their charge/discharge cyclability is far from satisfactory. Cyclability is fairly improved in $K_{0.10}[Fe(CN)_z]_{0.70}H_2O$ and $Rb_{0.61}[Fe(CN)_z]_{0.37}H_2O$. Matsuda and Morimoto synthesized a thin film of manganese hexacyanoferrate, $Li_{1.32}Mn_2[Fe(CN)_z]_{0.83}5.5H_2O$, by means of electrochemical deposition. They reported that the thin-film electrode exhibits a high capacity of 128mAh/g and an average operating voltage of 3.6V against Li with good cyclability. Kurihara et al. improved the capacity of Mn-PBA by increasing the Fe concentration ($x$): the discharge capacity increases from 115mAh/g at $x = 0.83$ ($Li_{1.32}Mn_2[Fe(CN)_z]_{0.83}5.5H_2O$) to 143mAh/g at $x = 0.93$ ($Li_{1.72}Mn_2[Fe(CN)_z]_{0.92}2.3H_2O$). On the other hand, Takachi et al. reported that the $Li_{1.96}Co_2[Fe(CN)_z]_{0.90}2.9H_2O$ film electrode exhibits a high capacity of 132mAh/g and an average operating voltage of 3.6V against Li with good cyclability.

The high capacity of Mn-PBA is ascribed to the two reduction processes for Mn and Fe,[7] which form two plateaus at 3.8V (Mn) and 3.4V (Fe) in the discharge curve of LIB. The substitions was performed by charge/discharge cycles of the as-grown films in an ethylene carbonate (EC)/diethyl carbonate (DEC) solution containing 1 mol/L LiClO$_4$.

The Li concentration ($x$) of the film was controlled by the charge/discharge process described above. The magnitude of $x$ was calculated from the total current under the assumption that $Li_{42.52}[Fe(CN)_z]_{1-x}^z$ is in the discharge state and $Li_{0.06}[Fe(CN)_z]_{0.94}$ is in the charge state. Except for the high-$x$ region, the film is stable in air. The high-$x$ films were carefully and rapidly sealed in a glass capillary. The film was carefully removed from the ITO glass substrate with a microspatula, and then fine powder was filled into a 300µm glass capillary. The powder diffraction pattern was detected with an imaging plate (IP). The exposure time was 5 min. The X-ray wavelength was calibrated using the lattice constant ($a \approx 5.41112Å$) of standard CeO$_2$ powder. Thus-obtained power diffraction patterns were analyzed by the Rietveld method (Rietan-FP).[8]

Ex situ XAS measurements were performed at the 9C beamline of the PF, KEK. XAS spectra were measured in a fluorescent yield mode with a Lytle detector at 300 K. The X-ray was monochromized with a Si(111) double-crystal monochromator. In the XAS measurement for respective elements, e.g., Mn, Co, and Fe, the monochromator was calibrated by the K-edge of the respective metal foils. The background subtraction, normalization, and component decomposition were performed with the ATHENA program.[9] The self-absorption effect is negligible because the penetration depths ($\lambda > 40µm$) of the compounds at the fluorescence and absorption energies of the Mn, Fe, and Co K-edges are much larger than the thickness of the films ($= 0.5 µm$).

Experiment

Thin films of $NaMn_{1-x}Co_x[FeII(CN)_z]_w$H$_2O$ were synthesized by electrochemical deposition on an indium–tin oxide (ITO) transparent electrode under potentiostatic conditions at 10.45V vs a standard Ag/AgCl electrode in an aqueous solution containing $K_{0.10}H_2O$, $MnICl_2$, $CoICl_2$, and 5 mol/L NaCl. The deposition time was 5 min. The thickness of the films was 0.5 µm. Before the film growth, the surface of the ITO electrode was purified by the electrolysis of water for 5 min. The chemical composition of the films was determined by inductively coupled plasma (ICP) measurement. The magnitudes of $x$ and $z$ were determined so as to minimize the sum of the squares of the residual error under the charge neutrality condition ($x + 2 - 4z = 0$). The Li compounds, $Li_{1.32}[Fe(CN)_z]_{0.83}5.5H_2O$, were obtained by the electrochemical substitution of Li† for Na†. The substitutions was performed by charge/discharge cycles of each film in an ethylene carbonate (EC)/diethyl carbonate (DEC) solution containing 1 mol/L LiClO$_4$.

Ex situ XAS measurements were performed at the 9C beamline of the PF, KEK. XAS spectra were measured in a fluorescent yield mode with a Lytle detector at 300 K. The X-ray was monochromized with a Si(111) double-crystal monochromator. In the XAS measurement for respective elements, e.g., Mn, Co, and Fe, the monochromator was calibrated by the K-edge of the respective metal foils. The background subtraction, normalization, and component decomposition were performed with the ATHENA program.[9] The self-absorption effect is negligible because the penetration depths ($\lambda > 40µm$) of the compounds at the fluorescence and absorption energies of the Mn, Fe, and Co K-edges are much larger than the thickness of the films ($= 0.5 µm$).

Results and Discussion

Figure 1(a) shows the XRD patterns of $Li_{1.32}Mn_{0.89}[Fe(CN)_z]_{0.93}3.1H_2O$ ($y = 0.11$) against $x$. Except at $x = 0.00$, the XRD patterns can be indexed with the fcc setting. The cell parameter $a$ was refined by Rietveld analysis with the fcc (Fm3m; $Z = 4$) model. At $x = 0.00$, doublet features are observed in the (200), (220), and (400) reflections. The features indicate a phase
separation into two fcc phases. The cell parameter $a$ of the respective phase was refined with a two-phase model. Similar two-phase features are observed in the low-$x$ region at $y = 0.22$ (not shown).

**Fig. 1** XRD patterns of (a) Li$_{x}$Mn$_{0.89}$Co$_{0.11}$[Fe(CN)$_{6}$]$_{0.89}$3.1H$_2$O, (b) Li$_{x}$Mn$_{0.18}$Co$_{0.82}$[Fe(CN)$_{6}$]$_{0.91}$3.4H$_2$O, and (c) Li$_{x}$Co[Fe(CN)$_{6}$]$_{0.92}$4.6H$_2$O. Values in parentheses represent indexes in the fcc setting. The subscript R indicates the rhombohedral setting.

Figure 1(b) shows the XRD patterns of Li$_{x}$Mn$_{0.18}$Co$_{0.82}$[Fe(CN)$_{6}$]$_{0.91}$3.4H$_2$O ($y = 0.82$). All the XRD patterns can be indexed with the fcc setting. The cell parameter $a$ was refined with the fcc (Fm3m; $Z = 4$) model. Figure 1(c) shows the XRD patterns of Li$_{x}$Co[Fe(CN)$_{6}$]$_{0.92}$4.6H$_2$O ($y = 1.00$). Except at $x = 1.68$, the XRD patterns can be indexed with the fcc setting. The cell parameter $a$ was refined with the fcc (Fm3m; $Z = 4$) model. At $x = 1.68$, a doublet feature is observed at 11°, indicating a rhombohedral distortion. The cell parameters $a$ and $c$ at $x = 1.68$ were refined with the rhombohedral (R$3m$; $Z = 4$) model.

**Fig. 2.** XAS of Li$_{x}$Mn$_{0.89}$Co$_{0.11}$[Fe(CN)$_{6}$]$_{0.89}$3.1H$_2$O against $x$ around the (a) Mn K-, (b) Co K-, and (c) Fe K-edges. The broken vertical lines in (c) represent the peak energies of Fe$^{2+}$ and Fe$^{3+}$. Figure 2(a) shows the XAS spectra of Li$_{x}$Mn$_{0.18}$Co$_{0.82}$[Fe(CN)$_{6}$]$_{0.91}$3.1H$_2$O ($y = 0.11$) against $x$ around the Mn K-edge. The spectra show negligible changes with $x$, indicating that the Mn valence essentially remains 2+. Figure 2(b) shows the XAS spectra of the films against $x$ around the Co K-edge. The XAS spectrum at $x = 0.0$ nearly coincides with that of low-spin (LS) Co$^{3+}$, while the spectrum at 1.56 coincides with that of HS Co$^{2+}$. The systematic spectral change in Fig. 2(b) indicates that the average Co valence changes from 3+ to 2+ with an increase in $x$. Figure 2(c) shows the XAS spectra of the films against $x$ around the Fe K-edge. The broken vertical lines represent the peak energies of Fe$^{2+}$ and Fe$^{3+}$. The red shift of the peak indicates that the average Fe valence changes from 3+ to 2+ with an increase in $x$.

**Fig. 3.** X-ray absorption spectra of Li$_{x}$Mn$_{0.89}$Co$_{0.11}$[Fe(CN)$_{6}$]$_{0.89}$3.1H$_2$O against $x$ around the (a) Mn K-, (b) Co K-, and (c) Fe K-edges. The broken vertical lines in (c) represent the peak energies of Fe$^{2+}$ and Fe$^{3+}$.

Figure 3(a) shows the XAS spectra of Li$_{x}$Mn$_{0.18}$Co$_{0.82}$[Fe(CN)$_{6}$]$_{0.91}$3.4H$_2$O against $x$ around the Mn K-edge. The XAS spectrum at $x = 0.0$ is due to Mn$^{3+}$, while the spectrum at 1.64 is due to Mn$^{2+}$. The spectral change in Fig. 3(a) indicates that the average Mn valence changes from 3+ to 2+ with an increase in $x$. Figure 3(b) shows the XAS spectra of the films against $x$ around the Co K-edge. The spectral change indicates that the average Co valence changes from 3+ to 2+ with an increase in $x$. Figure 3(c) shows the XAS spectra of the films against $x$ around the Fe K-edge. The red shift of the peak indicates that the average Fe valence changes from 3+ to 2+ with an increase in $x$.

Figure 4 shows the XAS spectra of Li$_{x}$Co[Fe(CN)$_{6}$]$_{0.92}$4.6H$_2$O against $x$ around the (a) Co K- and (b) Fe K-edges. The broken vertical lines in (b) represent the peak energies of Fe$^{2+}$ and Fe$^{3+}$.
Figure 4(a) shows the XAS spectra of Li$_x$Co[Fe(CN)$_6$]$_{0.92}$$H_2$O ($y = 1.00$) against $x$ around the Co K-edge. The spectral change indicates that the average Co valence changes from 3+ to 2+ with increase in $x$. Figure 4(b) shows the XAS spectra of the films against $x$ around the Fe K-edge. The red shift of the peak indicates that the average Fe valence changes from 3+ to 2+ with an increase in $x$.

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