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Redox Reactions in Prussian Blue Analogue Films with Fast Na⁺ Intercalation

Masamitsu Takachi¹, Tomoyuki Matsuda¹, and Yutaka Moritomo^{1,2*}

¹Graduate School of Pure and Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

²Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan E-mail: moritomo.yutaka.gf@u.tsukuba.ac.jp

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Electronic state of cobalt and manganese Prussian blue analogues were systematically investigated against Na⁺ intercalation by means of the infrared and X-ray absorption spectroscopies. The spectroscopies revealed that 3.8 and 3.4 V plateaus in the discharge curve of Na_xCo[Fe(CN)₆]_{0.90}2.9H₂O (denoted as NCF90) are ascribed to the reduction processes of Fe³⁺ and Co³⁺, respectively. On the other hand, 3.6 and 3.2 V plateaus of Na_xMn[Fe(CN)₆]_{0.83}3.5H₂O (NMF83) are ascribed to the reduction processes of Mn³⁺ and Fe³⁺, respectively. We found that the film electrodes with a thickness of 1.1 µm exhibit fast Na⁺ intercalations: the discharge capacity at 60 C of the NCF90 (NFM83) film was 90% (45%) of the open-circuit-voltage (OCV) value. Thus, Prussian blue analogue films are promising cathode candidates for sodium-ion secondary batteries. © 2013 The Japan Society of Applied Physics

S odium-ion secondary batteries (SIBs) are promising candidates for next-generation batteries with safe, environmentally friendly, and low-cost characteristics.^{1,2)} These battery device stores the electric energy by utilizing the intercalation/deintercalation process of abundant Na⁺ (Clark number: 2.63). In this sense, the SIBs are suitable for large-scale batteries for the stable use of solar and/or window energies. Recently, Komaba et al.³⁾ have found that hard carbon exhibits a repeatable Na⁺ intercalation behavior, and demonstrated that a coin-type full SIB with a hard carbon/NaNi_{0.5}Mn_{0.5}O₂ configuration exhibits a high capacity of more than 200 mAh/g (anode basis) and an average operating voltage of \approx 3 V with a good cyclability.³⁾

Coordination polymer and metal organic framework (MOF) compounds are promising cathode materials for SIB, reflecting their nanoporous host framework. Among them, Prussian blue analogues (PBAs), $Na_x M[Fe(CN)_6]_y$ (M is a transition metal), exhibit a three-dimensional (3D) jungle-gym-type host framework and cubic nanopores, 5 Å at the edge.⁴⁾ Imanishi et al.^{5,6)} reported Li⁺ intercalation behaviors in $M[Fe(CN)_6]_v$ (M = V, Mn, Fe, Ni, Cu), even though their cyclability is far from satisfactory. Cyclability is fairly improved in $K_{0.10}Mn^{II}$ [Fe^{III}(CN)₆]_{0.70}4.2H₂O and Rb_{0.61}Mn^{II}[Fe^{III}(CN)₆]_{0.87}2.2H₂O.⁷⁾ Recently, Goodenough's group⁸⁾ has reported Na⁺ intercalation behaviors in a $K-M-Fe(CN)_6$ system (M = Mn, Fe, Co, No, Cu, Zn). However, their coulomb efficiency ($\sim 60\%$ for M = Fe), i.e., the ratio of discharge capacity to charge capacity, is very low. Matsuda et al.⁹ investigated electrochemical properties of film electrodes of Na_{1,32}Mn^{II}[Fe^{II}(CN)₆]_{0,83}-3.5H₂O, and reported a high capacity of 109 mAh/g and an average operating voltage of 3.4 V against Na, with a good cyclability. Takachi et al.¹⁰ reported that a Na_{1.60}- $Co^{II}[Fe^{II}(CN)_6]_{0.90}2.9H_2O$ film electrode exhibits a high capacity of 135 mAh/g and an average operating voltage of 3.6 V against Na, with a good cyclability. In both compounds, the jungle-gym-type host framework is fairly robust: the host structure remains cubic (Fm3m: Z = 4) against Na⁺ intercalation, without showing structural phase transition or phase separation.

In this study, by the infrared spectroscopy of the CN stretching mode and the X-ray absorption spectroscopy around the Fe and Co K-edges, we systematically investigated the redox process of $Na_xCo[Fe(CN)_6]_{0.90}2.9H_2O$ (denoted as NCF90) and $Na_xMn[Fe(CN)_6]_{0.83}3.5H_2O$

(NMF83). The spectroscopies revealed that 3.8 and 3.4 V plateaus of NCF90 are ascribed to the reduction processes of Fe³⁺ and Co³⁺, respectively. On the other hand, 3.6 and 3.2 V plateaus of NMF83 are ascribed to the reduction processes of Mn^{3+} and Fe³⁺, respectively. The discharge capacity at 60 C of the NCF90 (NMF83) film was 90% (45%) of the open-circuit voltage (OCV) value.

Films of NCF90 (NMF83) were synthesized by electrochemical deposition on an indium-tin oxide (ITO) transparent electrode¹¹⁾ under potentiostatic conditions at -0.50 V vs a standard Ag/AgCl electrode in an aqueous solution, containing 0.8 mM K₃[Fe(CN)₆], 0.5 mM Co(NO₃)₂, and 5.0 MNa(NO₃), 1.0 mM K₃[Fe(CN)₆], 1.5 mM MnCl₂, and 1.0 M NaCl. The chemical composition of the films was determined by the inductively coupled plasma (ICP) method and CHN organic elementary analysis. The film thickness (L) was 1.1 μ m, which was measured with a profilometer (Dektak3030). The NCF90 film consists of needle like crystals whose diameters are $\sim 0.4 \,\mu m$,¹²⁾ while the NMF83 film consists of crystalline grains whose diameters are $\sim 1 \,\mu m$.¹³⁾ We further synthesized thicker films of NCF90 (L = 5, 15, and 20 μ m) and NMF83 (L = 5 and 10 μ m). We, however, cannot investigate the electrochemical properties of the thicker films, because they were removed from the ITO substrate in the first charge run. An improvement of the film synthesis process is needed before the actual use of the film.

The electrochemical properties of the films were investigated in a beaker-type cell using Na as the anode. The electrolyte used was 1 M NaClO₄ in propylene carbonate (PC). The active area of the films was about 2.0 cm^2 . The cut off voltage was in the range of 2.0 to 4.0 V. The charge rate was fixed at 0.6 C. The mass of each film was measured using a conventional electronic weighing machine after the film was carefully removed from the ITO glass with a microspatula. The experimental error for the mass, and hence the capacity, was $\approx 10\%$. The magnitude of x of the films was controlled by the charge/discharge process in a beakertype cell. We confirmed that the discharge capacities of the NCF90 (= 135 mAh/g) and NMF83 (= 130 mAh/g) films were close to the ideal values (125 and 109 mAh/g, respectively). The sodium ion concentration (x) was calculated from the total current under the assumption that the fully charged NCF90 and NMF83 films are Co[Fe(CN)₆]_{0.90}-2.9H₂O (x = 0.0) and Mn[Fe(CN)₆]_{0.83}3.5H₂O (x = 0.0), respectively.



Fig. 1. (Color online) Discharge curve measured at 0.6 C, lattice constant (*a*), valence of the constituent transition metals of (a) $Na_xCo[Fe(CN)_6]_{0.90}$ -2.9H₂O and (b) $Na_xMn[Fe(CN)_6]_{0.83}$ 3.5H₂O against *x*. For convenience of explanation, we defined plateaus I and II. Open (filled) marks mean that the data were obtained in the discharge (charge) process. Lattice constants in (a) indicated by squares (circles) were determined in this work (cited from¹⁰⁾). Lattice constants in (b) were cited from Ref. 9. Valence data in (a) indicated by circles (squares) were determined by infrared (X-ray) absorption spectroscopies. Valence data in (b) were determined by infrared absorption spectroscopies.

Ex situ X-ray absorption measurements around the Fe and Co K-edges were performed at the 7C beamline of the Photon Factory, KEK. The spectra of the NCF90 films were recorded by a Lytle detector in a fluorescent yield mode with a Si(111) double-crystal monochromator at 300 K. The background subtraction, normalization, and component decomposition were performed with the ATHENA¹⁴ program. Ex situ infrared absorption spectra were measured with a conventional Fourier transform infrared (FTIR) spectrometer. Ex situ X-ray powder diffraction measurements were performed at the BL02B2 beamline¹⁵⁾ of SPring-8. The obtained fine powder samples were filled and sealed in a glass capillary. The X-ray diffraction patterns were detected with an imaging plate (IP). The exposure time was 5 min. The wavelength of the X-ray (= 0.499406 Å) was calibrated from the cell parameter of standard CeO₂ powders. The lattice constants (a) were refined by Rietveld analysis (Rietan-FP¹⁶⁾ program) with the face-centered cubic model $(Fm\bar{3}m; Z = 4)$. Thus, the obtained lattice constants are plotted as square symbols in the middle panel of Fig. 1(a).

The top panel of Fig. 1(a) shows the discharge curve of the NCF90 film measured at 0.6 C. The discharge curve can be regarded as an OCV curve, because no rate dependence was observed in the rate region. The discharge curve exhibits two plateaus at 3.8 (plateau I) and 3.4 V (plateau II). Similarly, the discharge curve of the NMF83 film [Fig. 1(b)] exhibits two plateaus at 3.6 (plateau I) and 3.2 (plateau II) V. The middle panels of Fig. 1 show the lattice constants indicated by circles were cited from the literature.^{9,10} In the NCF90 film [Fig. 1(a)], the magnitude of *a* is nearly constant in plateau I ($x \le 0.6$), while it steeply increases in plateau II



Fig. 2. (Color online) Infrared absorption spectra around the CN stretching mode of (a) $Na_x Co[Fe(CN)_6]_{0.90} 2.9H_2O$ and (b) $Na_x Mn[Fe(CN)_6]_{0.83}$ -3.5H₂O against *x*. The spectra were obtained in the discharge process.



Fig. 3. (Color online) X-ray absorption spectra of $Na_xCo[Fe(CN)_6]_{0.90}$ -2.9H₂O around the (a) Fe and (b) Co K-edges. The spectra were obtained in the charge process.

 $(x \ge 0.6)$. In the NMF83 film [Fig. 1(b)], the magnitude of *a* steeply increases in plateau I ($x \le 0.3$), while it slightly decreases in plateau II ($x \ge 0.3$).

In PBA, the energy and relative intensity of the CN stretching mode are sensitive indicators of the valence state of the neighboring transition metals. Figure 2(a) shows infrared absorption spectra of the NCF90 films against *x*. The CN stretching mode gradually shifts to the lower energy side with *x*. In cobalt PBA, Igarashi et al.¹⁷⁾ reported an empirical relation between the energy ($\hbar\omega$) and the Co valence (s_{Co}): $\hbar\omega$ (cm⁻¹) = 2006.10 + 40.48 $\cdot s_{Co}$. With the use of this empirical relation, we derived s_{Co} against *x* and plotted s_{Co} by circles in the bottom panel of Fig. 1(a).

Figure 3(a) shows X-ray absorption spectra of the NCF90 films against *x* around the Fe K-edge. In $x \le 0.6$ (plateau I), the absorption exhibits a slight redshift with *x* (see open triangles), indicating the variation of the Fe valence. The peak energy (= 7123.8 eV) at x = 1.6 coincides with that of low-spin (LS) Fe²⁺.¹⁸⁾ In addition, Yokoyama et al.¹⁹⁾ reported that the peak energy of LS Fe²⁺ is 1 eV lower than that of LS Fe³⁺. Thus, we estimated the Fe valence (s_{Fe}) from the peak energy ($\hbar\omega$): $\hbar\omega$ (eV) = 7123.8 + ($s_{\text{Fe}} - 2$). Figure 3(b) shows X-ray absorption spectra around the Co K-edge. At $x \ge 0.6$ (plateau II), the absorption [$\phi(x)$] exhibits a significant profile change, indicating the variation of the Co valence. The spectral profiles, $\phi(0.0)$ and $\phi(1.6)$, at x = 0.0 and 1.6 coincide with those of LS Co³⁺ and high-

Table I. Interrelationship between plateaus and redox sites in $Na_x Co[Fe(CN)_6]_{0.90} 2.9H_2O$ and $Na_x Mn[Fe(CN)_6]_{0.83} 3.5H_2O$. *V* is the discharge voltage vs Na.

Material	Plateau	V	Redox site
Na _x Co[Fe(CN) ₆] _{0.90} 2.9H ₂ O	Ι	\approx 3.8 V	Fe
$Na_x Co[Fe(CN)_6]_{0.90} 2.9 H_2 O$	II	\approx 3.4 V	Co
Na _x Mn[Fe(CN) ₆] _{0.83} 3.5H ₂ O	Ι	$\approx 3.6 \text{ V}$	Mn
$Na_xMn[Fe(CN)_6]_{0.83}3.5H_2O$	II	$\approx 3.2 \text{ V}$	Fe

spin (HS) Co²⁺, respectively.¹⁸⁾ In the intermediate *x*-region, we estimated the Co valence (s_{Co}) by the spectral decomposition of $\phi(x)$ into $\phi(0.0)$ and $\phi(1.6)$:

$$\phi(x) = (s_{\rm Co} - 2) \cdot \phi(0.0) + (3 - s_{\rm Co}) \cdot \phi(1.6).$$
(1)

Thus, the obtained s_{Fe} and s_{Co} are plotted by square symbols in the lower panel of Fig. 1(a). The infrared and X-ray absorption spectroscopies clearly indicate that the plateaus I and II are ascribed to the reduction processes of Fe³⁺ and Co³⁺, respectively.

Figure 2(b) shows the infrared absorption spectra of the NCF83 film against *x*. The spectra show two CN stretching modes at 2070 and 2150 cm⁻¹, which are ascribed to the CN stretching modes in the $[Fe^{II}(CN)_6]^{4+}$ and $[Fe^{III}(CN)_6]^{3+}$ units, respectively.²⁰⁾ Then, the Fe valence (s_{Fe}) can be estimated from the intensities, $I_{2070cm^{-1}}$ and $I_{2150cm^{-1}}$, of the 2070 and 2150 cm⁻¹ modes: $s_{Fe} = 2 + I_{2150cm^{-1}}/(I_{2070cm^{-1}} + I_{2150cm^{-1}})$. Thus, the obtained s_{Fe} is plotted by circles in the bottom panel of Fig. 1(b). The infrared spectroscopy suggests that the plateaus I and II are ascribed to the reduction processes of Mn³⁺ and Fe³⁺, respectively. Similarly, the discharge curve of Li_xMn[Fe(CN)₆]_{0.83}-3.5H₂O exhibits two plateaus at 3.9 and 3.5 V against Li⁺ intercalation. The 3.9 and 3.5 V plateaus are ascribed to the reduction processes of Mn³⁺ and Fe³⁺, respectively.²¹

Now, let us discuss the interrelationship between the redox process and the response of the host framework. In Table I, we summarize redox sites of the respective plateaus. In the Fe redox plateaus, i.e., plateaus I of the NCF90 film and plateau II of the NMF83 film, a negligibly changes with x. This is probably because the ionic radius ($r_{\text{FeIII}} = 0.55 \text{ Å}$) of LS Fe³⁺ is nearly the same as that $(r_{\text{FeII}} = 0.61 \text{ Å})$ of LS Fe^{2+} . In the Co redox plateau, i.e., plateau II of the NCF90 film, a significantly increases from 9.95 Å at x = 0.6 to 10.20 Å = at 1.6 [see Fig. 1(a)]. Such a lattice expansion is ascribed to the ionic radius ($r_{\text{CoII}} = 0.745 \text{ Å}$) of HS Co²⁺ being larger than that $(r_{\text{CoIII}} = 0.545 \text{ Å})$ of LS Co^{3+} . Roughly, the lattice expansion is expected to be $2 \times 1.0 \times$ $(r_{\text{CoII}} - r_{\text{CoIII}})$, since the nominal Co valence at x = 0.6 (1.6) is 3.0 (2.0). The expected value (= 0.40 Å) is close to the observed lattice expansion (= 0.25 Å). In the Mn redox plateau, i.e., plateaus I of the NMF83 film, a steeply increases from 10.40 Å at x = 0.0 to 10.58 Å at 0.4 [see Fig. 1(b)]. Such a lattice expansion is ascribed to the ionic radius $(r_{\text{MnII}} = 0.830 \text{ Å})$ of HS Mn²⁺ being larger than that $(r_{\text{CoIII}} =$ 0.645 Å) of HS Mn³⁺. The lattice expansion is expected to be $2 \times 0.4 \times (r_{\text{CoII}} - r_{\text{CoIII}})$, since the nominal Mn valence at x = 0.0 (0.4) is 2.4 (2.0). The expected value (= 0.11 Å) is close to the observed lattice expansion (= 0.18 Å).

Figure 4(a) shows the rate (r) dependence of the discharge curve of the NCF90 film ($L = 1.1 \,\mu$ m). The discharge curve



Fig. 4. (Color online) Rate dependence of discharge curves of film electrodes of (a) $Na_x Co[Fe(CN)_6]_{0.90} 2.9H_2O$ and (b) $Na_x Mn[Fe(CN)_6]_{0.83} 3.5H_2O$. The charge rate was fixed at 0.6 C. Broken curve is the discharge curve at 0.6 C measured after the *r*-dependence.



Fig. 5. (Color online) Discharge rate (*r*) dependence of capacity (*Q*) of film electrodes of (a) $Na_xCo[Fe(CN)_6]_{0.90}2.9H_2O$ and (b) $Na_xMn[Fe(CN)_6]_{0.83}3.5H_2O$. Squares represent the boundaries between plateaus I and II. The solid and broken curves are merely guides for the eyes.

is discernible even at 300 C. The discharge rate (= 300 C) is comparable to that (= 340 C) of the film electrode of $\text{Li}_x \text{Mn}[\text{Fe}(\text{CN})_6]_{0.83} 3.5 \text{H}_2\text{O}$ ($L = 1.2 \,\mu\text{m}$).²²⁾ The discharge capacity [broken curve in Fig. 4(a)] measured after the *r* dependence is nearly the same as the initial value. To investigate the *r* dependence of the respective plateaus, the boundaries between plateaus I and II were determined by the local minima of the *Q* derivative of the discharge curves. In Fig. 5(a), we plotted the discharge capacity (circles) and the capacity (squares) of plateau I against *x*. The discharge capacity at 60 C is 93% of the OCV value. This indicates that the plateau I is slightly robust against *r* as compared with plateau II. This is probably because plateau I exhibits a negligible lattice expansion with *x* [see Fig. 1(a)].

Figure 4(b) shows *r* dependence of the discharge curve of the NMF83 film ($L = 1.1 \,\mu$ m). The discharge curve is discernible even at 120 C. In Fig. 5(b), we plot the discharge capacity (circles) and the capacity (squares) of plateau I against *x*. The discharge capacity at 60 C is 45% of the OCV value. We found that the capacity of plateau I steeply decreases and eventually disappears at \approx 60 C. In plateau I, the reduction process of Mn³⁺ causes a significant expansion of the ionic radius and the switching of the Jahn–Teller

activity, and hence a considerable local lattice relaxation. Such a lattice relaxation requires time and cannot follow the fast Na^+ intercalation.

In summary, we spectroscopically investigated the valence state of the constituent transition metals in the NCF90 and NMF83 films as a function of sodium content. The spectroscopy revealed that both the PBA films exhibit well-defined redox reactions with Na⁺ intercalation. In particular, the NCF90 film exhibits excellent rate properties (discharge capacity at 60 C is 90% of the OCV value). Thus, Prussian blue analogue films are promising cathode candidates for SIB.

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