Redox-coupled alkali-metal ion transport mechanism in binder-free films of Prussian blue nanoparticles

Manabu Ishizaki,*a Hideo Ando,*a Noboru Yamada,*a Kai Tsumoto,*a Kenta Ono,b Hikaru Sutoh,*a Takashi Nakamura,b Yoshihide Nakaoc and Masato Kuriharad,b

a. Faculty of Science, Yamagata University, 1-4-12 Kojirakawa-machi, Yamagata, Yamagata 990-8560, Japan.
b. National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino-ku, Sendai, Miyagi 983-8551, Japan.
c. Faculty of Life Science, Kyushu Sangyo University, 2-3-1 Matsukadai, Higashi-ku, Fukuoka 813-8503, Japan.

E-mail: manabu-ishizaki@sci.kj.yamagata-u.ac.jp, ando@sci.kj.yamagata-u.ac.jp
Experimental

Materials

All reagents and solvents were obtained from commercial suppliers and used as received. Fe(NO$_3$)$_3$·9H$_2$O (>99.0%, Kanto Chemical Co., Inc.), Na$_4$[Fe(CN)$_6$]·10H$_2$O (>98.0%, Kanto Chemical Co., Inc.). The perfect lattice PB (PB-p) was supplied from Dainichiseika Colour & Chemicals Mfg. Co., Ltd., and the formula of PB-p was determined to be (NH$_4$)$_{0.70}$Fe$^{III}_{1.10}$[Fe$^{II}$(CN)$_6$]·1.7H$_2$O with the elemental analysis. LiCl (Guaranteed reagent, Nacalai Tesque, Inc.), KCl (>99.5%, Kanto Chemical Co., Inc.), Li(CF$_3$SO$_2$)$_2$N (>99.7%, Kanto Chemical Co., Inc.), K(CF$_3$SO$_2$)$_2$N (>99.8%, Kanto Chemical Co., Inc.), propylene carbonate (>99.5% for electrochemistry, Kanto Chemical Co., Inc.), and ITO glass substrates (Furuuchi Chemical Co., 10 Ω/sq).

Apparatus

The centrifugation and spin coating processes were carried out using a Kubota 2800 and Mikasa MS-A100, respectively. The plasma treatment of an ITO glass was performed using a Meiwafosis SEDE. The low-temperature annealing of the PB NP spin-coated thin films was carried out using a constant temperature oven (Yamato DK 240S). The XRD patterns of the PB NP powder were recorded using a Rigaku MiniFlexII (Cu K$_{α_1}$ radiation) with a semiconductor detector (D/teX). The FT-IR spectra of the PB NPs were recorded on a Thermo Fisher Scientific Nicolet6700 equipped with an attenuated total reflection (ATR) unit. The dynamic light-scattering (DLS) particle sizes of the PB NPs were measured with an Otsuka ELSZ-1000 particle size analyser. The SEM images were obtained using a JEOL JSM-7600F. The TG-Mass analyses of the PB NP powder were carried out using a JEOL JMS-Q1050GC (Electron Ionization mass spectrometer) and TA instrument SDT Q600, where the powdery PB NPs were heated at a rate of 10 °C/min under a stream of He (100 mL/min). CO$_2$ adsorption abilities were measured for pore size analysis using a Belsorp Max (BEL Japan, Inc.). The humidity-controlled thermogravimetric (TG) analyses were performed using a Rigaku Thermo
plus EVO2 and HUM-1.

The electrochromic properties of the PB NP thin films were measured with an ALS1100P electrochemical analyser using quartz cell (T-3-UV40, Tosoh Quartz Co., Ltd.). The time course change of the electrochromism was monitored with an Agilent 8453 photodiode array spectrometer.

**Preparation of PB-d**

The defect lattice PB (PB-d) was synthesised as previous reports. An aqueous solution (260 mL) of Fe(NO$_3$)$_3$・9H$_2$O (113 g, 0.280 mmol) was added to an aqueous solution (420 mL) of Na$_4$[Fe(CN)$_6$]・10H$_2$O (102 g, 0.210 mmol), and the as-mixed solution was stirred for 30 min. After centrifugation for 5 min (4000 rpm, 2740 G), the blue precipitate was washed with water nine times and methanol three times, and dried under reduced pressure. Finally, we obtained the PB-d, Fe$_4$[Fe(CN)$_6$]$_3$・15H$_2$O, whose number of waters of crystallization was determined through thermogravimetric (TG) analysis (see the following figure).

![Figure](image)

**Figure**  TG-mass analyses of (a) PB-d NPs and (b) PB-p NPs.
Preparation of suspension solution of PB

Water (20 ml) was added to the PB-d NPs (3.00 g, 2.66 mmol) or PB-p NPs (3.00 g, 3.82 mmol). Ultrasonic waves were then applied to obtain suspensions. The as-prepared water-suspension solutions were further diluted so as to obtain thin films of similar thickness later. Dynamic light scattering measurements revealed that both PB NPs made small aggregates dispersed in water (approximately 100 nm, Fig. S3).

Fabrication of spin coated film of PB on ITO

The as-prepared water-suspension solution (150 μl) of PB NPs was spread on a plasma-treated ITO glass using two-step spin coating procedures (1st step, spin speed accelerates from 5 rpm up to 2000 rpm in 15 sec; 2nd step, 2500 rpm for 10 sec). The spin-coated thin films were then heated at a low temperature (100 °C) for 60 min in a constant-temperature oven (i.e. annealing process). The annealing process resulted in tight connections among the PB NPs. The surface water ligands of Fe^{III}-OH$_2$ were thermally eliminated, and the as-generated unsaturated (nonoctahedral) Fe^{III} sites on the NP surface were then coordinated by the dangling CN ligands of Fe^{II}-CN on adjacent NPs surface. All insoluble PB NPs thin films had a similar thickness (ca. 100 nm) (Fig. S4).

Electrochemical properties

As electrolyte solutions, we used aqueous solutions of LiCl and KCl (0.1 M) and nonaqueous PC solutions of LiTFSI and KTFSI (0.1 M). Pt wire and an as-prepared PB NP film on an ITO glass were used as counter and working electrodes, respectively. The reference electrodes employed in aqueous and PC electrolyte solutions were Ag/AgCl and Ag/Ag$^+$, respectively. Cyclic voltammograms were measured using the three-electrode method, and the scan rate was 10 mV/sec.
Quantum chemical model and calculation

We employed a local structure model of the PW cage (Fig. 5a), consisting of 36 cyano groups, four singlet-state Fe$^{II}$ centres, and four quintet-state Fe$^{II}$ centres. The singlet-state Fe$^{II}$ centres and the quintet-state Fe$^{II}$ centres are octahedrally coordinated by C atoms and by N atoms, respectively. Considering that the antibonding $e_g$-orbital occupation of the Fe centres in the PW model is the same as that in the PB crystal, the structural parameters were taken from the X-ray crystallography data of the PB crystal. The Fe$^{II}$–C, Fe$^{II}$–N, and C–N bond lengths are 1.923, 2.029, and 1.131 Å, respectively. We ignored the Jahn-Teller distortion at the quintet-state Fe$^{II}$ centres because the distortion originating from uneven occupancy of $t_{2g}$ orbitals is typically weak. The PW model thus belongs to the $T_d$ point group. Inside the PW model, a bare Li$^+$ or K$^+$ cation moves. We placed 24 point charges of +0.792 $e$ at the very locations of the absent Fe$^{II}$ centres next to 24 dangling cyano groups to model the Fe$^{II}$ centres and to guarantee that the whole clathrates, PW·Li$^+$ and PW·K$^+$, are electrically neutral.

Using unrestricted Kohn-Sham density functional theory (DFT), we calculated the electronic states of the PW·Li$^+$ and the PW·K$^+$ models in 17tet spin multiplicity ($S_z = 8$). The B3LYP functional was employed throughout this work, which is adequate to study low-lying states of iron compounds. While Wojdeł et al. and Hegner et al. have theoretically suggested that the diamagnetic singlet state is also stable in PW, we verified that the spin-multiplicity difference did not notably affect the energy profile of Li$^+$ adsorption (Fig. S14). For the Fe atoms, we used (7511/6711/411) basis set along with the effective core potentials by Christiansen group, which is of triple-$\zeta$ quality for valence 4$s$, 4$p$, and 3$d$ electrons. For the Li, C, and N atoms and for the K atom, we employed cc-pVDZ basis sets and cc-pVDZ-PP basis set with the Stuttgart/Cologne effective core potentials (ECP10MDF) respectively. There are six square faces of the cubic PW cage, and each has a channel gate through which Li$^+$ or K$^+$ moves to a neighbouring PW cage (Fig. 5a).
Freezing the geometry of the whole PW framework, we investigated two kinds of Li\(^+\) (K\(^+\)) transport pathways: linear transport path and energetically favourable transport path (Fig. 5). The origin of the Cartesian \(xyz\) coordinates is at the channel gate on a PW face centre, shown at the left-hand side in Fig. 5a. From the channel gate, the linear transport path \((x)\) leads to the front channel gate across the PW cage centre (Fig. 5a). The potential energy curves were evaluated with varying the Li\(^+\) (K\(^+\)) coordinate at every interval of \(\Delta x = 0.2542\ \text{Å}\). This path \(x\) is on a \(C_2\) rotation axis of the PW model.

The energetically favourable transport path was obtained with DFT(B3LYP) optimisation of the Li\(^+\) (K\(^+\)) position in every \(yz\) plane at different \(x\) coordinates (\(\Delta x = 0.2542\ \text{Å}\)). This path was explored up to the vicinity of a stationary adsorption site, and then projected by \(T_d\) symmetry operations so as to construct the whole transport network in PW. Along the energetically favourable path toward the adsorption site, frequency analysis in the constrained subspace for optimisation (i.e. \(y\) and \(z\)) confirmed that there was no imaginary frequency mode in every \(yz\) plane, indicating that the path was successfully optimised. We performed self-consistent-field stability analysis\(^{16,17}\) and spin contamination check along both pathways to confirm that the electronic states we obtained were reliable stable electronic configurations.

For in-depth study of the interaction between Li\(^+\) and the PW and PB frameworks, we focused on a \(C_3\) rotation axis of the local structure model (i.e. space diagonal line in Fig. 5a). In the PW model, the Li\(^+\) cation moves from the quintet-state Fe\(^{III}\) position toward the singlet-state Fe\(^{III}\) position along the \(C_3\) axis. To evaluate the relevant potential energy curve, the Li\(^+\)···Fe\(^{III}\) (quintet) distance was elongated at every interval of 0.2554 Å. We also investigated a PB model and another PW model whose eight Fe\(^{III}\) atoms were replaced by Zn\(^{II}\) atoms (called PW(Zn) model in text), and compared the potential energies and the electronic states modulated by Li\(^+\) migration. In the PB model, surrounded by 24 point charges of +0.625 e, we studied the electronic state in 21tet spin multiplicity (\(S_z = 10\)). For the Zn atoms, we employed (7511/6711/411) basis set and the effective
core potentials by Christiansen group.10,11 All quantum chemical calculations were carried out with Gaussian 0918 and molecular visualization with Chemcraft 1.8.19

Natural spin density of Fe centres in the PW, PB, and PB(IVCT) frameworks

Net natural spin density (NSD) at each atomic site provides a clear picture of spin distributions throughout the molecular system. A detailed description of the NSD concept in the natural population analysis is available elsewhere.20 We analysed the electronic states calculated with the unrestricted DFT method in terms of the NSD to evaluate excess $\alpha$-spin density at each Fe centre in the PW-Li$,^+$, PB-Li$,^+$, and PB(IVCT)-Li$,^+$ clathrate models (Fig. S19). In the classical ionic limit, the ideal values for singlet-, doublet-, quintet-, sextet-spin states are 0, 1, 4, and 5 $e$, respectively.

In the PW-Li$^+$ model (Fig. S19a), the NSD values of C-coordinated Fe centres and those of N-coordinated Fe centres were close to 0 and 4 $e$, respectively; note that the NSD values of N-coordinated Fe centres lay below 4 $e$ mainly due to metal-ligand bonding. This indicates that the C-coordinated Fe centres were in a singlet Fe$^{II}$ state and the N-coordinated Fe centres were in a quintet Fe$^{II}$ state. All NSD values were not largely affected by the Li$^+$ location, showing that the Li$^+$ transport did not rearrange the spin distributions of the PW cage, for example, through charge transfer.

As compared to the PW-Li$^+$ model, the NSD values of the C-coordinated Fe centres were only slightly increased and those of the N-coordinated Fe centres were greatly increased in the PB-Li$^+$ model (Fig. S19b). The C-coordinated Fe centres thus remained in a singlet Fe$^{II}$ state and the N-coordinated Fe centres were in a sextet Fe$^{III}$ state. Also in the PB-Li$^+$ model, we found that the Li$^+$ transport accompanied neither significant spin redistributions nor intervalence charge transfer (IVCT) between the Fe$^{II}$ and the Fe$^{III}$ centres.
In the PB(IVCT)-Li⁺ model, the Li⁺ transport accompanied spin redistributions (Fig. S19c). We first focus on the region where the Li⁺⋯Fe₆ distance is shorter than 5 Å. The transport-hub and the cage-centre geometries are located in this region. As compared to the PB·Li⁺ model (Fig. S19b), the NSD values of the C-coordinated Fe centres were increased to about 1 e, while those of the N-coordinated Fe centres were decreased as compensation (Fig. S19c). The NSD values of the N-coordinated Fe centres in the PB(IVCT)-Li⁺ model were on a similar level to those in the PW·Li⁺ model (Fig. S19a). These indicate that IVCT occurred in the PB(IVCT) cage so that the C-coordinated Fe centres had a doublet Fe^{III} character and the N-coordinated Fe centres had a quintet Fe^{II} character. In the remaining region, where the Li⁺⋯Fe₆ distance is longer than 5 Å and the hub-II geometry is located, the NSD value of the C-coordinated Fe³ centre dropped to about 0 e and the NSD values of the N-coordinated Fe centres were slightly increased as compensation (Fig. S19c). As the Li⁺ cation approaches the Fe³ centre, it thus took on a less-electropositive singlet Fe^{II} character.

All these support the discussion on the electronic states in text.
**Fig. S1**  XRD patterns of (a) PB-d NPs and (b) PB-p NPs.

**Fig. S2**  SEM images of (a) PB-d NPs and (b) PB-p NPs.
**Fig. S3** Number-averaged dynamic light-scattering (DLS) particle-size distributions of (a) PB-d and (b) PB-p NPs dispersion solutions.

**Fig. S4** The SEM cross-section images of (a) PB-d and (b) PB-p NP spin-coated thin films on ITO glass substrates.
UV-Vis-NIR absorption spectra of (a) PB-d and (b) PB-p NP films before (black line) and after (red line) the low-temperature annealing at 100°C.

In panel (a), the significantly blue-shifted peak of the Fe$^{II} \rightarrow$ Fe$^{III}$ charge transfer is presumably attributed to the \{Fe$^{III}$–(NC)Fe$^{II}$(CN)$_5$$^{4-}$–Fe$^{III}$\} bonds that are newly formed due to the annealing. PB-d shows a larger peak shift than PB-p. PB-p has a slightly bigger particle size; therefore, the grain boundary effects on the PB-p properties are limited.
Fig. S7  CO$_2$ adsorption properties and pore sizes of (a) PB-d and (b) PB-p NPs. The pore size distribution was estimated by analyzing CO$_2$ adsorption isotherms with the Non Localised Density Functional Theory/Grand Canonical Monte Carlo (NLDFT/GCMC) method.

Fig. S8  Humidity-controlled TG analyses of (a) PB-d and (b) PB-p NPs. (c) Decrease in weight (%) during the humidity decrease from 90 to 5% RH (the reference weight 100% is the sample weight at 90% RH).
Fig. S9  Cyclic voltammograms and redox cyclability of PB-d and PB-p NP films in aqueous and nonaqueous PC electrolyte solutions. (a) PB-d in LiCl (aq) and KCl (aq), (b) PB-d in Li·TFSI (PC) and K·TFSI (PC), (c) PB-p in LiCl (aq) and KCl (aq), (d) PB-p in Li·TFSI (PC) and K·TFSI (PC). The scan rate is 10 mV/s.
Fig. S10  FT-IR spectra of (a) PB-p NP film and (b) PB-p NP film after electrochemical measurement in an aqueous solution of KCl.
**Fig. S11** UV-Vis-NIR absorption spectra simultaneously measured with the PB → PW reduction of PB-d NP film in aqueous solution and nonaqueous PC solution. (a) LiCl (aq), (b) KCl (aq), (c) Li·TFSI (PC), (d) K·TFSI (PC).
**Fig. S12**  UV-Vis-NIR absorption spectra simultaneously measured with the PB → PW reduction of PB-p NP film in aqueous solution and nonaqueous PC solution. (a) LiCl (aq), (b) KCl (aq), (c) Li·TFSI (PC), (d) K·TFSI (PC).
Reduced PB NP films were immersed in methanol for removing the physically attached PC solvent from the PB NP film surfaces and for protection against air oxidation. The FT-IR spectrum of reduced PB was measured without drying. In panel (a), the marker bands of PC and those of methanol are in the purple regions and the orange regions, respectively. The vertical dotted line corresponds to the $\nu(C=\equiv N)$ stretching band of PB. In panel (b), the region of the $\nu(C=O)$ stretching band of PC (around 1780 cm$^{-1}$) is magnified.
Fig. S14  Potential energy curves of Li+ moving along a C3 axis of the PW17tet and PWsinglet models. The PW17tet model has 17tet spin multiplicity ($S_z = 8$), which in text we call PW model for short. The PWsinglet model has singlet spin multiplicity ($S_z = 0$), whose all FeII centres are in a singlet state. Except for the spin multiplicity, there is no difference between the two models. Along the C3 coordinate (Fig. 5a), a Li+ cation moves from the quintet-state (singlet-state) FeII position at 0.0 Å to the singlet-state FeII position at 8.804 Å in the PW17tet (PWsinglet) cage. The energy curves are plotted against the reference energy level, at which Li+ occupies the channel gate.
Fig. S15  Change of Li$^+$ coordinates $y$ and $z$ along the energetically favourable path from the PW channel gate up to the Li$^+$ transport hub. The transport hub at $(x, y, z) = (1.51 \text{ Å}, 1.03 \text{ Å}, -1.03 \text{ Å})$ and the transport path were obtained with DFT(B3LYP) optimisation (Fig. 5b, 5c, and 6a). The sum of the $y$ and $z$ values is almost zero along the energetically favourable path, indicating that the path lies on a mirror $\sigma_d$ plane of the PW cage. See Fig. 5b and c for the $xyz$ frame and the mirror plane.
Fig. S16   Natural charges of C and N atoms in (a) PW and (b) PW(Zn) frameworks, which are affected by Li$^+$ migration along the $C_3$ axis. Ignoring the natural charges of the dangling cyano groups, we plot the average charge of three C (N) atoms at each framework corner; for example, C(Fe$^1$) is the average charge of the three C atoms which coordinate the Fe$^1$ centre (Fig. S17a). Owing to the approaching Li$^+$ cation, the N(Fe$^6$) and N(Zn$^6$) charges become more negative at the transport hub (2.61 Å), and the C(Fe$^3$) and C(Zn$^3$) charges slightly lose their positive values at the transport hub II (5.93 Å). See Fig. S17a for the $C_3$ coordinate and the Fe/Zn number notation.
Fig. S17 Natural atomic charges of the Fe centres in the PW and PB frameworks, which are affected by Li$^+$ migration along the $C_3$ axis. (a) Side view of the framework with the Fe number notation. Along the $C_3$ coordinate, the Li$^+$ cation moves from the Fe$^6$ position (0.0 Å) to the Fe$^3$ position (8.804 Å). The transport hub, the cage centre, and the transport hub II in the PW model are located at 2.61, 4.40, and 5.93 Å, respectively. The Fe$^1$, Fe$^2$, Fe$^3$, and Fe$^4$ centres are coordinated by C atoms, whereas the Fe$^5$, Fe$^6$, Fe$^7$, and Fe$^8$ centres are coordinated by N atoms. By comparison with the natural atomic charges of the reference PB·Li$^+$ state (Fig. 8a), we plot the relative atomic charges of (b) PW·Li$^+$, (c) PB·Li$^+$, and (d) PB(IVCT)·Li$^+$ models.
Electronic state of the PB-Li\textsuperscript{+} clathrate without exhibiting IVCT. The relevant potential energy curve is the less stable curve (black) shown in Fig. 7. In the cage-centre geometry, the reference spin density is depicted, which does not exhibit IVCT. In the hub and the hub II geometry, the spin density difference almost disappears and the change in natural atomic charge of every Fe centre is close to zero (see also Fig. S17c). This indicates that the IVCT is very minor also at the hub and hub II geometries. The density surfaces were generated by using the isosurface contour values of 0.07 e/Bohr\textsuperscript{3} (yellow) and −0.07 e/Bohr\textsuperscript{3} (blue).
Fig. S19  Natural spin density (i.e. excess $\alpha$ spin) of every Fe centre in (a) PW, (b) PB, and (c) PB(IVCT) frameworks. The ideal (ionic-limit) spin densities of singlet-, doublet-, quintet-, and sextet-spin states are 0, 1, 4, and 5 $e$, respectively. To a greater or lesser extent, the calculated spin density is affected by Li$^+$ migration along the $C_3$ axis. The transport hub, the cage centre, and the transport hub II in the PW model are located at 2.61, 4.40, and 5.93 Å, respectively. The Fe$^1$, Fe$^2$, Fe$^3$, and Fe$^4$ centres are coordinated by C atoms, whereas the Fe$^5$, Fe$^6$, Fe$^7$, and Fe$^8$ centres are coordinated by N atoms (Fig. S17a).
References

1 Calcd (Found) (%): C, 22.76 (22.53); H, 1.97 (1.96); N, 29.64 (29.77).


18  M. J. Frisch, *et al.*, Gaussian 09 (Revision C.01), Gaussian Inc., Wallingford CT, 2016.

19  G. A. Zhurko, Chemcraft 1.8 (Build 180), Ivanovo, Russia, 2016.