

## Symmetry switch of cobalt ferrocyanide framework by alkali cation exchange

Nanoporous coordination polymers are attracting increasing interest from materials scientists, because they can be utilized in various devices, for example, Li ion batteries, electrochromic devices, hydrogen storage devices, molecular sensors and molecular filters. Among nanoporous materials, Prussian blue analogues, represented as  $A_xM[Fe(CN)_6]_y \cdot zH_2O$  (where  $A$  and  $M$  are an alkali metal and a transition metal, respectively), form a nanoporous three-dimensional (3D) framework (-  $M$ -NC-Fe-CN- $M$ -). In Fig. 1, we schematically show the framework structure, together with the guest alkali cation  $A^+$ . A significant feature of the compounds is the controllability of the guest concentration ( $x$ ) by an electrochemical method [1] or by adjusting external voltage on all solid devices [2,3]. Imanishi *et al.* reported lithium intercalation into the host framework as well as the charge-discharge behavior in a series of cyano-bridged transition metal compounds with  $M = V, Mn, Co, Ni$  and  $Cu$ . The average discharge potential for the  $V$  compound is about 3.6 V, corresponding to the reduction of the  $V^{3+}$  ion, while those for the  $Mn, Co, Ni$  and  $Cu$  compounds are around 3.3 V, corresponding to the reduction of the  $Fe^{3+}(CN)_6$  unit. The charge capacity of the  $Cu$  compound reaches  $140 \text{ mAhg}^{-1}$ , which is comparable to that of the actually used material,  $LiCoO_2$  (capacity,  $140 \text{ mAhg}^{-1}$ ). Thus, the compounds are quite promising as positive electrode materials. In order to extract better electrode performance from the compounds, an exhaustive structural investigation is needed to clarify the interaction between the guest cations and the host framework.

Now, let us discuss the interrelation between the ionic size of  $A^+$  and the interval ( $\sim 0.5 \text{ nm}$ ) of the

framework (see Fig. 1). The ionic radius  $r$  of  $A^+$  increases with atomic number:  $r = 0.092 \text{ nm}$  for  $Li^+$ ,  $r = 0.182 \text{ nm}$  for  $Na^+$ ,  $r = 0.151 \text{ nm}$  for  $K^+$ ,  $r = 0.161 \text{ nm}$  for  $Rb^+$ , and  $r = 0.174 \text{ nm}$  for  $Cs^+$ . Here, we emphasize that the transition metal ions are bridged by CN groups, and hence the 'frame' is rather thick. Recently, Moritomo *et al.* [4] have investigated the cation channel in the cobalt ferrocyanide framework. They confirmed that the  $Na^+$  ions go through the square window of the framework, while the larger ions, i.e., the  $K^+$  and  $Rb^+$  ions, take a detour channel along the vacancies. The cation dependent behavior is well reproduced by the cation potential, which is calculated by *ab initio* total energy calculation with use of a WIEN2k program. The cation dependence of the channel suggests that the nanopores of the host framework are rather large for the  $Na^+$  and  $Li^+$  ions, but fit well for the  $K^+$ ,  $Rb^+$  and  $Cs^+$  ions.

We investigated the crystallographic symmetry of the cobalt ferrocyanide framework while changing  $A^+$ . The cobalt ferrocyanide with larger cations, i.e.,  $A^+ = K^+, Rb^+, \text{ and } Cs^+$  belongs to the face-centered cubic lattice ( $Fm\bar{3}m$ ;  $Z=4$ ), while the cobalt ferrocyanide with smaller  $Na^+$  ions belongs to the rhombohedral lattice ( $R\bar{3}m$ ;  $Z=2$ ). We suspect that the displacement of the  $Na^+$  ion is the origin for the rhombohedral distortion. In the nanopore, the  $Na^+$  ion is surrounded by our  $[Fe(CN)_6]^{4-}$  ions and four  $Co^{2+}$  ions, and hence, feels an asymmetric ( $T_d$  symmetry) electrostatic potential. Then, the local potential minimum is not at the central position of the cube, but at the tetrahedral sites toward the four  $Fe(CN)_6]^{4-}$  ions. Then, a cooperative displacement of the  $Na^+$  ion can cause the rhombohedral distortion.

We further found that a simple dipping

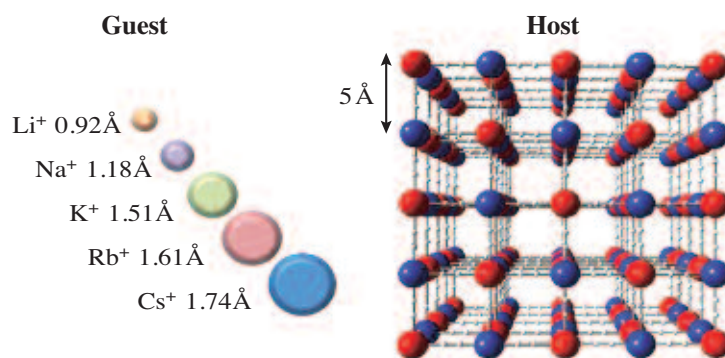
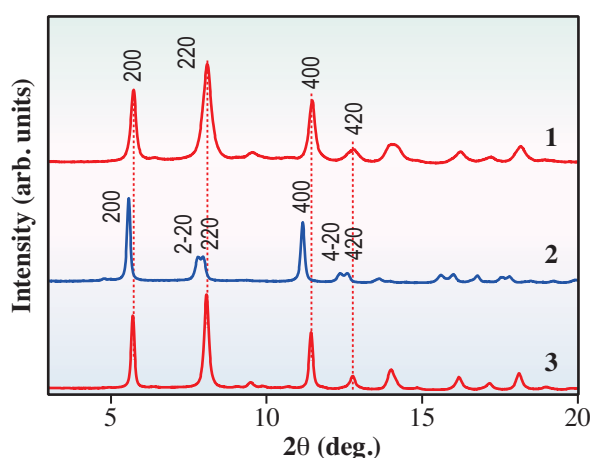


Fig. 1. Schematic pictures of the guest alkali cations and host framework for Prussian blue compounds.

procedure can exchange the guest alkali cation between  $K^+$  and  $Na^+$ , and switch the symmetry of the framework between cubic and rhombohedral ones [5]. **Figure 2** shows the X-ray powder diffraction patterns for  $K_{1.88}Co[Fe(CN)_6]_{0.97} \cdot 3.8H_2O$  (**1**),  $Na_{1.52}K_{0.04}Co[Fe(CN)_6]_{0.89} \cdot 3.9H_2O$  (**2**) and  $Na_{0.04}K_{1.48}Co[Fe(CN)_6]_{0.88} \cdot 2.6H_2O$  (**3**), obtained at **BL02B2** beamline. **2** was obtained by dipping **1** in 1 mol  $dm^{-3}$  of NaCl solution, and **3** was obtained by dipping **2** in 1 mol  $dm^{-3}$  KCl solution. The wavelength of the X-ray was 0.50243 Å, which was calibrated by the lattice constant of standard  $CeO_2$  powder. We performed Rietveld analysis to determine the lattice symmetry and lattice constant. **1** shows a face-centered-cubic structure with a lattice constant  $a = 10.057(7)$  Å. In contrast, the diffraction pattern of **2** was different from that of **1**. We could index the pattern with a rhombohedral structure:  $a = 10.340(2)$  Å and  $\alpha = 91.32^\circ$ . Again, **3** shows a face-centered-cubic structure with a lattice constant  $a = 10.082(3)$  Å. The elemental analysis by ICP-AES spectrometry after respective dipping procedures revealed nearly complete cation exchange at least for 8 cycles (**Fig. 3**).

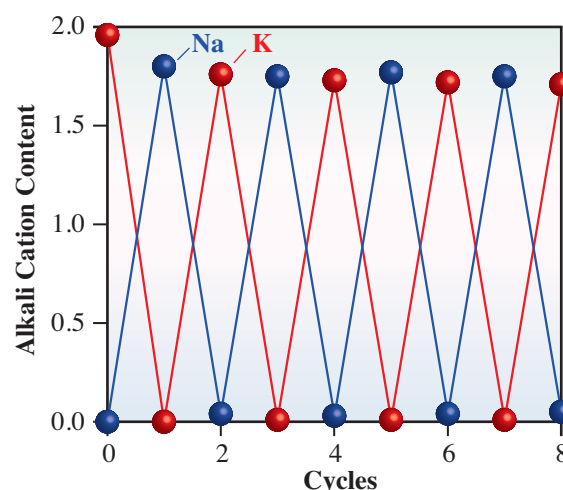
We investigated the valence states of **1** and **2** using infrared (IR) spectra and the magnetic susceptibility. The CN stretching peaks of  $[Fe^{II}(CN)_6]$  were observed at 2079.9  $cm^{-1}$  in **1** and at 2086.6  $cm^{-1}$  in **2**. The products of the magnetic susceptibility ( $\chi_M$ ) and temperature ( $T$ ) plots are observed at 300 K and are almost equal to the expected spin-only values of 3.0, i.e., 3.06 (**1**) and 3.02  $cm^3 K mol^{-1}$  (**2**). These data indicate that the valence states are the same, i.e.,  $Co^{II}_{hs}-Fe^{II}_{ls}$ . Thus, the symmetry switch observed in the present system has a purely structural



**Fig. 2.** X-ray powder diffraction patterns for **1** (upper), **2** (middle), and **3** (bottom) measured at **BL02B2** beamline. X-ray wavelength was 0.50243 Å.

origin. We further investigated the diffuse reflectance spectra. The cation exchange alters the position of the absorption band from 520 nm (**1**) to 610 nm (**2**). The rather sharp 610 nm band in **2** can be ascribed to the  $d-d$  transition of  $Co^{II}_{hs}$ . The rhombohedral distortion of the framework can dipole-activate such a  $d-d$  transition.

In summary, we found a reversible symmetry switch of the cobalt ferrocyanide framework by alkali cation exchange. The symmetry change switches the optical properties of the compound. We suspect that the displacement of the  $Na^+$  ion is the origin of rhombohedral distortion. The  $Li^+$  substitution effect on structural properties is the key to the comprehensive understanding of the guest-host interaction of the Prussian blue analogues.



**Fig. 3.** Reversible alkali cation exchanges. The Na and K contents determined by ICP-AES are plotted after respective cation exchanges.

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