The role of potassium ions in iron hexacyanoferrate as a cathode material for hybrid ion batteries

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Abstract

The synthesis of $\text{Na}_x\text{K}_y\text{Fe}[\text{Fe}(\text{CN})_6]$ through a simple co-precipitation method and the application of these nanoparticles in sodium-ion batteries are presented. $\text{K}_{1.90}\text{Fe}[\text{Fe}(\text{CN})_6]$ with a cubic structure shows low volumetric change during electrochemical cycling. It is clarified by ex-situ X-ray diffraction and cyclic voltammetry curves that K^+ influences the intercalation sites of the neighboring Na^+ . More significantly, this hexacyanoferrate delivers a high capacity of 137.0 mAh g^{-1} at a current density of 14 mA g^{-1} and superior cyclability with 94% capacity retention after 120 cycles, showing great promise for sodium-ion battery applications.

Keywords: potassium; iron hexacyanoferrate; interstitial site; phase transition; sodium-ion batteries.

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1. Introduction

Recently, prussian blue analogues (PBAs): $A_{2-x}M_a[M_b(CN)_6]_{1-y} \cdot zH_2O$ (A: alkali cations, M: metal ions) have attracted much attention as cathode materials for secondary batteries, due to their special structure that support a reversible extraction of Li^+ , Na^+ and K^+ ions [1-5], especially for the sodium-ion batteries (SIB) in terms of low cost and resource abundance. For instance, You et al. has demonstrated $Na_{0.84}Ni[Fe^{II}(CN)_6]_{0.71}$ as a zero-strain insertion cathode material with an excellent cycling stability [6]. High-quality $Na_{0.61}Fe[Fe(CN)_6]_{0.94}$ crystals show excellent electrochemical properties as a cathode of SIB, yet an initial sodium insertion process is needed due to the low sodium content [7]. Lee et al. have demonstrated sodium manganese hexacyanomanganate ($Na_{1.96}Mn^{II}[Mn^{II}(CN)_6]_{0.99}$) with extremely high capacity ($\sim 209 \text{ mAh g}^{-1}$) [8]. Wang et al. has synthesized rhombohedral prussian white ($Na_{1.92}Fe[Fe(CN)_6]$) with few vacancies that delivers high specific capacity and good rate performance, which can be partly attributed to the high Na concentration [9]. On the other hand, these sodium-rich materials usually suffer from obvious capacity fading during the first ten cycles owing to the phase transition from monoclinic/rhombohedral to cubic structure during the Na^+ extraction [6, 10].

The phase transition occurs as the less covalent M_a^{II} can accommodate a reduced bond angle $\angle M_b-CN-M_a$ and minimize void space, when the size of insertion cation is relatively small [11]. For example, $A_2Mn^{II}[Mn^{II}(CN)_6]$ with the lattice parameter about $10.6 \text{ \AA}$, rhombohedral structure can be observed (A=Na, K, Rb) except for the cubic $Cs_2Mn^{II}[Mn^{II}(CN)_6]$ [11, 12]. Thus, the cubic-rhombohedral structural phase

transition is related to the occupation of small cations at other interstitial positions (in the $\langle 111 \rangle$ directions towards the four tetrahedral sites, 32f) [13, 14]. While the lattice parameter of iron hexacyanoferrate (FeHCF) is smaller ($\sim 10.18 \text{ \AA}$) [15], Ling et al. have calculated that the most stable Na^+ interstitial site in $\text{Fe}[\text{Fe}(\text{CN})_6]$ is face-centered site (24d). As for large cations such as K^+ , Rb^+ and Cs^+ , they usually prefer to occupy the body-center (8c) site of the empty cube. Even more, the large space of 8c site is capable of accommodating the insertion of K^+ without too much structural deformation [16]. Liu et al. have also suggested that multiple Na^+ intercalation sites can be confirmed in the Na-rich $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6]$; Na^+ may intercalate into 8c site or 24d site, which leads to bizarre charge/discharge curves [17].

The co-intercalations of alkali and alkaline earth cations such as Mg-Li [18], Mg-Na [19], have been reported in literature. However, it is difficult to synthesize MgFeHCF through a precursor-based method. Instead, it is obtained via an electrochemical way in which Mg^{2+} ions are introduced from electrolyte or Mg counter electrode during a discharge process. Moreover, the average voltage of a MgFeHCF electrode is usually less than 3.0 V. In this paper, alkali iron hexacyanoferrates with different contents of sodium and potassium ($\text{Na}_x\text{K}_y\text{FeHCF}$) are synthesized via a co-precipitation method. The FeHCF with an average voltage of about 3.3 V shows an interesting cation selectivity ($\text{K}^+ > \text{Na}^+$) so that K^+ in the electrolyte can reinsert into the structure during the electrochemical cycling despite of its low concentration. Also, its charge/discharge curves and cycling performance are found to be improved with K^+ in the structure.

2. Experimental

2.1 Materials synthesis

Synthesis of $\text{Na}_x\text{K}_y\text{FeHCF}$ was carried out as described elsewhere in the literature by a typical co-precipitation method [17], with slight modification. Solution A: 5 mmol of $\text{A}_4\text{Fe}(\text{CN})_6$ ($\text{A}=\text{Na}$ or K) was dissolved in 100 mL of deionized water. Solution B: 5 mmol of FeCl_2 and 6.7 mmol of sodium/potassium citrate were dissolved in 100 mL of deionized water, 0.5 g of ascorbic acid was used to avoid the oxidation of Fe^{2+} . The solution A was slowly added into the solution B under vigorous stirring, and then maintained at room temperature for 10 h. The molar ratios of $\text{Na}:\text{K}$ were 0:1, 1:1, 3:1, 7:1 and 1:0, respectively, for both of the two precursor solutions. The products were washed for several times with deionized water and ethanol, and finally dried at 100 °C in a vacuum oven for 24 h. The as-obtained products are marked as NKFF-X ($\text{X}=1, 2, 3, 4, 5$), where X increases along with the sodium content.

2.2 Characterization

The phase of as-obtained samples was characterized by an X-ray diffractometer (Philips X'Pert Pro Super, $\text{Cu K}\alpha$ radiation). The morphology of the samples was studied by scanning electron microscopy (SEM, Sirion 2000, FEI) and transmission electron microscope (TEM, H-800 Hitachi). The elemental compositions were analyzed by energy dispersive X-ray spectroscopy (EDS) attached to the SEM instrument. Thermogravimetric analysis (TGA) was performed at a heating rate of

10 °C min⁻¹ in the temperature range of 30-700 °C under flowing N₂ (DTG-60H, Shinadzu).

2.3 Electrochemical evaluation

The electrochemical properties of the obtained FeHCF materials were evaluated in coin-type cells (CR2032 size). The electrode laminates consisted of the active material (70 wt. %), acetylene black (20 wt. %) and PVDF (10 wt. %) binder on an aluminium foil collector. The typical electrode mass was about 2 mg cm⁻². For the fabrication of sodium half cells, sodium metal was used as the counter electrode and 1 mol L⁻¹ NaClO₄ in EC/DMC (1:1 in volume)/1% FEC was used as the electrolyte. For lithium half cells, the sample NKFF-1 with the best Na half-cell performance was used as the working electrode, lithium foil as the counter electrode and 1 mol L⁻¹ LiPF₆ in EC/DEC (1:1 in volume) as the electrolyte. In both of the cells, a Whatman glass-fiber separator was used. The coin-cells were assembled in an argon-filled glove box (O₂ and H₂O contents were 2 and 1ppm, respectively), and then aged for 10 h before charge/discharge to ensure full infiltration of electrolyte into the electrodes. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the cells were conducted on a CHI 604A electrochemical workstation. The CV was measured in a voltage range from 2.0 to 4.2 V at a scan rate of 0.1 mV s⁻¹. The cells were also galvanostatically cycled on a multi-channel battery test system (Neware BTS-2300, Shenzhen) in the voltage range from 2.0 to 4.2 V.

2.4 Ex-situ EDS

Na half cells for ex-situ EDS measurements were specially-made. The NKFF-1 electrode mass was 1.91 ± 0.03 mg, 0.4 mL 1 mol L⁻¹ NaClO₄ in EC/DMC (1:1 in volume, without FEC) was used as the electrolyte (the molar ratio of K:Na was about 1:40). The cells were charged and discharged at a low current of 14 mA g⁻¹ (0.1 C) to a certain voltage, and then were disassembled and washed by DMC in the glove box.

3. Results and discussion

The initial color of the as-obtained samples is pale blue, while they slowly become darken during the washing process as a result of the oxidation of Fe^{II} and Na/K loss.

The (Na+K) contents of freshly synthesized NKFF-X samples are expected theoretically to be (Na+K)/Fe=1. However, if Fe^{II} is gradually oxidized to Fe^{III} when it is exposed to air, the same amount of alkali cation should be lost for the sake of charge neutrality. **Table 1** shows the Na and K contents (molar) of NKFF-X samples

obtained by EDS analysis, and all the metal contents are normalized to the Fe content. Obviously, the total alkali cation (Na+K) contents decrease from NKFF-1 to NKFF-5, which means the KFeHCF is more air-stable. And the K contents (NKFF-2, 3, 4) higher than expected can be attributed to the cation selectivity of FeHCF. The TEM images (**Fig. 1a**) show the samples are composed of nanoparticles with sizes of 20–40 nm. The samples with high Na contents (e.g. NKFF-5) possess a cubic-like morphology due to the strong chelating ability of citrate and slower precipitation rate [17, 20]. HR-TEM images (**Fig. 1c and 1d**) show the lattice fringes of NKFF-1 and

NKFF-5, in which (200) and (400) planes can be identified and the lattice parameter are about 10.1 Å and 10.2 Å, respectively.

The XRD patterns of all the samples shown in [Fig. 2a](#) are readily indexed to the face-centered-cubic structure of prussian blue (JCPDS No: 52–1907). In accord with their morphology, the high Na content samples show better crystallinity. The expanded XRD patterns from 15° to 20° are shown in [Fig. 2b](#). The diffraction peaks slightly shift to the lower angles, indicating that the lattice parameter increases with sodium content, especially for the potassium-free sample (NKFF-5). The lattice parameter of the NKFF-1 sample is calculated to be $a=10.13$ Å ([Fig. 2c](#)), being close to the result of HR-TEM. It means the potassium ions prevent the volumetric expansion, and even slightly reduce the lattice parameter. Similar changes during the insertion of K^+ in CuHCF and FeHCF have been reported [[4](#), [21–23](#)]. [Fig. 3](#) show the TG and DTA curves. The weight loss below 190°C can be assigned to the elimination of absorbed and/or interstitial waters [[24](#)]. The NKFF-1 sample shows the lowest water content (absorbed and interstitial water), due to the existence of relatively high content of alkali ions at interstitial site [[22](#)]. Nevertheless, some of NKFF samples (e.g. NKFF-5) start to decompose when the temperature reaches to about 160°C, as confirmed by the change of DTA curves. The sharp weight loss occurring at about 300°C can be attributed to the decomposition of NaKFeHCF to $Fe(CN)_2$, CN and A_2O ($A=Na$ or K , the O atom comes from coordinated water) [[25](#)]. The last weight loss step occurring in the range of 500°C to 700°C due to the decomposition of $Fe(CN)_2$

into Fe, C and N₂. Thus, the highest decomposition temperatures of NKFF-1 measured here evidences its stable structure.

Fig. 4a and 4b compare the first and second charge/discharge profiles of NKFF-1 and NKFF-5 samples in a Na half-cell with a current density of 0.1 C (1 C=140 mA g⁻¹). The charge/discharge curves of other samples are shown in **Fig. S1**, where the curves of NKFF-4 are close to that of Piernas-Muñoz's work [26]. The NKFF-1 sample delivers the highest initial charge capacity, due to its highest alkali cation content, while all the initial discharge capacity are close to 140 mAh g⁻¹. Furthermore, the NKFF-1 electrode exhibits two plateaus, corresponding to the two kinds of Fe^{III}/Fe^{II} (low-spin FeC₆ and high-spin FeN₆) redox reactions, respectively. The main CV curves (**Fig. 4d**) demonstrate two pairs of oxidation/redox peaks at 3.18/2.77 V (Na₁↔Na₂) and 3.74/3.43 V (Na₀↔Na₁) for NKFF-1, and a little deviation with the charge/discharge voltage plateaus is resulted from the polarization at a higher current density. The similar charge/discharge profiles are shown in other potassic samples (NKFF-2, 3, 4). However, the NKFF-5 electrode exhibits three uneven plateaus during the second charge process, clarified by the three oxidation peaks of CV curves. This peculiar double peak phenomenon at high voltage is a consequence of Na⁺ intercalation into both 8c and 24d sites, and the calculated voltages to extract Na⁺ from these two sites are 3.72 and 4.15 V, respectively [17]. As for potassic samples, the single peak at 3.74 V demonstrates that only 8c site is permitted when there is K⁺ neighboring (**Fig. 4c**). The higher voltage plateaus of 8c site and lower polarization of potassic samples increase the energy density.

The reversible intercalation and de-intercalation of K^+ in NKFF-1 are directly proved by the ex-situ EDS analysis, which is consistent with the results of Piernas-Muñoz et al. [26]. As shown in Fig. 5c, the contents of Na+K show an approximately linear change during the discharge/charge process (Fig. 5a). However, the K^+ is the dominant cation, opposite to the initial cation concentration in the electrolyte. The K^+ ratio of fully discharged electrode is 0.87 (obtained by ex-situ EDS), which means 92% of K^+ are remained. The cation selectivity ($K^+ > Na^+ > Li^+$) of PB in both of aqueous and propylene carbonate solutions have been demonstrated by Crumbliss et al [27]. This is in reverse order to ionic radius and in the order of increasing solvated radius (K^+ , 2.75 Å; Na^+ , 3.10 Å; Li^+ , 3.37 Å)[28] determined by ionic mobility, activation energy for interfacial charge transfer[29] and strong interaction with PB [26, 30]. In addition, the detection limit of K^+ for some PBAs is below 1×10^{-4} M, with the potentiometric selectivity coefficient of the potassium ion-selective electrode based on the CoHCF film-modified electrode is 2×10^{-2} ($K_{K,Na}^{pot}$) and 1×10^{-3} ($K_{K,Li}^{pot}$), respectively [31-33]. The selectivity coefficient $K_{K,B}^{pot}$ is calculated from the following equation[34] recommended by IUPAC:

$$K_{K,B}^{pot} = a_K(e^{\Delta E Z_K F / RT} - 1) / (a_B)^{Z_K / Z_B}$$

Therefore, the FeHCF supports a reversible extraction of K^+ in Na half cells, as a low concentration of K^+ in the electrolyte can reinsert into the structure. Nevertheless, there are some residual K^+ ions even the electrode is fully charged. It implies the K^+ ions in FeHCF are two types: (i) the internal potassium ions, within the crystalline structure and (ii) the surface potassium ions [35]. Both internal and surface sites of

FeHCF show cation selectivity, and the Na^+ at surface site is more unstable. Furthermore, one of the NKFF-1 electrodes was first charged and washed by DMC to complete internal K^+ extraction, and then reassembled. The charge/discharge profiles (Fig. S2) similar to NKFF-5 (without even plateaus) evidence the K^+ ions at surface sites are electrochemical inactive. Thus, the rapid variation of charge/discharge profiles of NKFF-4 (Fig. S1c) are related to increase of the residual Na and K contents of fully charged NKFF-4 during cycles (Fig. S3). It can be ascribed to the low concentration of internal K^+ gradually gathering at the surface (as shown in Fig. 6) and losing the effect. For other potassic samples, the surface sites are obviously not enough for all of the K^+ ions. Fig. 5b are ex-situ XRD patterns of NKFF-1 electrodes at various discharge and charge states. During the K^+ and Na^+ insertion process, the (200) peak intensity relative to that of the (220) peak decrease, together with the slight shift of the positions of XRD peaks toward bigger angle (decrease of the lattice parameter). This finding differs from the single Na^+ insertion process, where the lattice parameter increases and the crystal structure changes from cubic to rhombohedral [7, 15, 17]. The phase transition is suppressed, as K^+ ions are too large to move along the cubic [111] axis towards 32f site. The decrease of lattice parameter by 1.1% ($10.23 \rightarrow 10.12 \text{ \AA}$, Fig. 7) is a combined effect of (i) a shortening of the $\text{Fe}^{\text{HS}}\text{--N}$ bond distance and (ii) the extra electron introduced to the $\text{Fe}^{\text{LS}}\text{--C--N--Fe}^{\text{HS}}$ π bonding system upon reduction of $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ to $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ [4, 21, 23], while the insertion of Na^+ to small site (such as 24d) plays a more prominent role to lattice expansion. As a result, the change of the unit cell volume after the insertion of K^+ is

around 3%, smaller than Na^+ (around 6%) [16]. Ex-situ Raman spectroscopy (Fig. 5d) illustrates the valance state change of Fe. The ex-situ Raman spectroscopy of fully discharged electrode shows three peaks at 2150, 2127 and 2080 cm^{-1} (Fig. 5d, spectrum 5), indicating a total of two ions transfer during the discharge process. Nevertheless, the peak at 2080 cm^{-1} is not very obvious because the electrode is exposed to air during the Raman testing. Similar phenomenon has been observed by Samain et al [36]. The $\nu(\text{CN})$ bands shift gradually toward low wave number positions during the discharge process, indicating the redox of Fe^{3+} and Fe^{2+} [7].

Fig. 8 show the cycling and rate performances of NKFF-X in Na half cells. During the charge and discharge at a low current density of 0.1 C (Fig. 8a), the capacity of NKFF-1 slightly decreases from 137.0 mAh g^{-1} initially to 134.7 mAh g^{-1} after 30 cycles, while the cycling stability get worse when the K content decrease. The long cycling stability of NKFF-1 is shown in Fig. 8b, 94.0% of capacity retention after 120 cycles is excellent compared with other alkali ion rich samples [8, 9, 17]. Unfortunately, the rate performance of potassic samples are relatively poor (as shown in Fig. 8c). The Na and K molar ratio (normalized to Fe content) of NKFF-1 electrode fully discharged at 2 C is 0.19 and 0.47, respectively (the ratio is 0.12 and 0.87 at 0.1 C). It may result from the low concentration and sluggish kinetics of K^+ . Fig. 8d shows discharge curves of the NKFF-1/Na half-cell at different current densities, a superior rate capability at the low voltage plateau is contributed by the $\text{Fe}^{\text{HS}}\text{-N}$ couple, as the K/Na-inserted $\text{FeFe}(\text{CN})_6$ behaves more like a metallic system with increased electronic conduction [37].

Furthermore, we fabricated Li half cells to investigate the co-insertion mechanism of K^+ and Li^+ . However, only the first charge process (de-intercalation of K^+) is similar to Na half cells (**Fig. S4**). The rapid capacity fading and gradually uneven plateaus are like the lithium PB cells as reported [5]. It can be attributed to the lower standard redox potential of Li/Li^+ than K/K^+ , and the replacement of K by Li. The deposition of K metal at anode is non-activated. For Na half cells, no K metal deposits as the potential of Na/Na^+ is higher.

4. Conclusions

In summary, Na_xK_yFeHCF with different Na and K contents are successfully synthesized by a simple co-precipitation process. As a potassium ion-selective material, low concentration of K^+ is able to reinsert into FeHCF structure in Na half cells. The intercalation sites of Na^+ are influenced by neighboring K^+ , so that the potassic samples exhibit two even plateaus. The reversible extraction of K^+ at 8c site prevents the phase transition and volumetric expansion, corresponds to a good cycling stability with 94.0% of capacity retention after 120 cycles. Therefore, the potassium ions play an important role in FeHCF, and make it a promising cathode material for K^+/Na^+ hybrid ion batteries.

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Appendix A. Supplementary data

Supplementary data related to this article.

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Figure captions

Table 1 Molar metal element ratios of NKFF-X (normalized to the Fe content).

Fig. 1 TEM images of (a) NKFF-1, (b) NKFF-5; HR-TEM images of (c) NKFF-1, (d) NKFF-5.

Fig. 2 (a) XRD patterns and (b) the expanded XRD patterns between 15° and 20° of NKFF-X, (c) lattice parameter (Å) of NKFF-X samples.

Fig. 3 TGA and DTA of (a) NKFF-1, (b) NKFF-2, (c) NKFF-3, (d) NKFF-4, (e) NKFF-5 in flowing N₂ at a heating rate of 10 °C min⁻¹.

Fig. 4 The first and second galvanostatic charge and discharge profiles of NKFF-1 (a) and NKFF-5 (b) at a current density of 14 mA g⁻¹ (0.1 C). (c) Crystal structure of iron hexacyanoferrate (high-spin Fe is pink, low-spin Fe is green, C is gray, N is blue, intercalated K⁺ is purple, intercalating Na⁺ is yellow and interstitial sites are white). (d) CV curves of the NKFF-X electrodes from 2.0 to 4.2 V at a scan rate of 0.1 mV s⁻¹.

Fig. 5 (a) Different states of NKFF-1 during the first discharge and the second charge process. Ex-situ (b) XRD patterns, (c) EDS analysis and (d) Raman spectroscopy at these states.

Fig. 6 Schematic of gathering K⁺ at the surface sites during charge and discharge processes.

Fig. 7 The change of lattice parameter during the discharge/charge process.

Fig. 8 (a) Cycling performances of NKFF-X at 0.1 C (1 C=140 mA g⁻¹). (b) Long-term cycling performance of NKFF-1 at 0.5 C. (c) Rate performance of NKFF-1 and NKFF-5. It was charged at low currents 0.5 C (except 0.1 C and 0.2 C), and

discharged at different currents. (d) Discharge curves of the NKFF-1/Na half-cell at different currents.

Figure 1

Figure 2(a)

Figure 2(b)

Figure 2(c)

sample	lattice parameter (Å)
NKFF-1	10.13
NKFF-2	10.14
NKFF-3	10.15
NKFF-4	10.16
NKFF-5	10.28
FeFe(CN)₆	10.18 (Ref. 15)

Figure 3(a)

Figure 3(b)

Figure 3(c)

Figure 3(d)

Figure 3(e)

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1

sample	Na	K	Na+K
NKFF-1	0	0.95	0.95
NKFF-2	0.08	0.69	0.77
NKFF-3	0.12	0.48	0.60
NKFF-4	0.17	0.35	0.52
NKFF-5	0.46	0	0.46