Sodium iron hexacyanoferrate with high Na content as a Na-rich cathode material for Na-ion batteries

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Sodium iron hexacyanoferrate with high Na content (~1.63 per molecule) is obtained employing a facile and effective protection strategy, which shows high Coulombic efficiency and impressive cycling stability as promising Na-rich cathode materials for full Na-ion cells.

Sodium iron hexacyanoferrate with high Na content as a Na-rich cathode material for Na-ion batteries

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ABSTRACT

Owing to the worldwide abundance and low-cost of Na, room-temperature Na-ion batteries are emerging as attractive energy storage systems for large-scale grids. Increasing the Na content in cathode material is one of the effective ways to achieve high energy density. Prussian blue and its analogues (PBAs) are promising Na-rich cathode materials since they can theoretically store two Na ions per formula. However, increasing the Na content in PBAs cathode materials is a big challenge in the current. Here we show that sodium iron hexacyanoferrate with high Na content could be obtained by simply controlling the reducing agent and reaction atmosphere during synthesis. The Na content can reach as high as 1.63 per formula, which is the highest value for sodium iron hexacyanoferrate. This Na-rich sodium iron hexacyanoferrate demonstrates a high specific capacity of 150 mA h g⁻¹ and remarkable cycling performance with 90% capacity retention after 200 cycles. Furthermore, the Na intercalation/de-intercalation mechanism is systematically studied by *in situ* Raman, X-ray diffraction and X-ray absorption spectroscopy analysis for the first time. The Na-rich sodium iron hexacyanoferrate could function as a plenteous Na reservoir and has great potential as a cathode material toward practical Na-ion batteries.

1 Introduction

Developing large-scale electric energy storage systems is a crucial issue in efforts towards the utilization of the sustainable energy [1-7]. For grid scale storage, rechargeable batteries based on plenteous resources as well as low-cost, high safety and long lifespan are highly desired. Among the

candidates, room-temperature Na-ion batteries have again aroused great attention because Na is a worldwide abundance material with low-cost, which is able to satisfy the large-scale and long-term requirement [8-18].

Similar with Li-ion batteries, room-temperature rechargeable Na-ion batteries follow a working principle of the “rocking chair” storage mechanism

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[19-26]. In a typical full-cell configuration, cathodes are composed of Na-sufficient materials while anodes are composed of Na-deficient materials. Although many cathode materials, such as MF_3 ($\text{M} = \text{Fe}, \text{Ti}, \text{Co}, \text{Mn}$) [27], $\text{Na}_{0.44}\text{MnO}_2$ [28], and $\text{Fe}_2(\text{MoO}_4)_3$ [29] exhibit high discharge capacity in half-cells, the first charge capacity (charging first) is too low to be used in full-cells due to their low initial Na content. Similar with developing lithium-excess cathode materials in Li-ion batteries, increasing the Na content in cathode material is one of the effective ways to achieve high energy density. Therefore, it is in urgent need of exploring Na-rich cathode materials.

As good hosts for Li, Na, and K ions, Prussian blue analogues ($\text{A}_x\text{M}[\text{Fe}(\text{CN})_6]_{1-y}\square_y\bullet m\text{H}_2\text{O}$; A, alkaline metal; M, transitional metal; $\square$, $[\text{Fe}(\text{CN})_6]$ vacancies; $0 < x < 2$, $y < 1$; denoted as PBAs) have attracted immense interest as cathode materials in rechargeable batteries [30-34]. PBAs have the perovskite-type structure in which the transitional metal centers are bridged by cyanides to form a rigid framework. The large interstitial sites inside their frameworks are suitable for hosting Na ions and form a three dimensional (3D) channel for fast transporting of Na ions [35-39]. Most importantly, PBAs are able to store two Na ions per formula at most, making them appealing as Na-rich cathode materials. Unfortunately, many reported PBAs still exhibit low Na content [40]. Recently, some Na-rich PBAs, such as $\text{Na}_{1.4}\text{Cu}_{1.3}\text{Fe}(\text{CN})_6$ and $\text{Na}_{1.94}\text{Ni}_{1.03}\text{Fe}(\text{CN})_6$ have been investigated in aqueous Na-ion batteries [41,42]. However, the electrochemical process of these PBAs is based on one-electron reaction. Thus the capacity is limited within 70 mA h g^{-1} . $\text{Na}_{1.72}\text{MnFe}(\text{CN})_6$ were obtained through introducing a large amount of NaCl by Goodenough *et al* [43]. Introducing Mn element could improve the capacity given the two-electron reaction process, however, the cycling performance was limited, which might be resulted from the Jahn-Teller effect of Mn^{3+} [44]. High-quality sodium iron hexacyanoferrate nanocrystals, $\text{Na}_{0.61}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.94}$ exhibited high cycling stability as well as high specific capacity in half-cells employing Na foil as anode, making it quite attractive candidates toward room-temperature Na-ion batteries [45]. However, the Na content in

$\text{Na}_{0.61}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.94}$ is only 0.61 per molecule and the theoretical specific capacity is limited to only *ca.* 61 mA h g^{-1} (based on 0.61 Na ions intercalation/de-intercalation) when used in full-cells employing Na-deficient anode. Unfortunately, $\text{Na}_x\text{FeFe}(\text{CN})_6$ with high Na content ($x > 1$) is rarely reported since Fe^{2+} are easily being oxidized, further leading to a high average valance state of Fe and a low content of Na. Therefore, how to obtain Na-rich sodium iron hexacyanoferrate is still a great challenge.

Here, we show that sodium iron hexacyanoferrate with high Na content $\text{Na}_{1.63}\text{Fe}_{1.89}(\text{CN})_6$ can be obtained under ascorbic acid (VC) or nitrogen environment, further leads to a high charge capacity in the first cycle. When applying VC and N_2 simultaneously, $\text{Fe}^{2+} / [\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ oxidation could be effectively suppressed and the Na content can reach as high as 1.63 per formula, which is the highest value in sodium iron hexacyanoferrate materials so far. This Na-rich sodium iron hexacyanoferrate exhibits the highest Coulombic efficiency in the first cycle ($\sim 98\%$) and the following cycles ($\sim 100\%$), high specific capacity (150 mA h g^{-1}), and superior capacity retention (90% after 200 cycles).

2 Experimental

2.1 Synthesis

Synthesis of $\text{NaFe}(0.83)$ and $\text{NaFe}(1.03)$. In a typical synthesis for $\text{NaFe}(0.83)$, 4 mmol of $\text{NaFe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ was dissolved in 100 mL of hydrochloric acid aqueous solution of 1 M. For $\text{NaFe}(1.03)$, 1 mmol ascorbic acid was also added. The obtained solution was maintained at 80°C for 4 h under vigorous stirring. The obtained dark blue precipitates were collected by centrifugation, washed by water and ethanol for several times and dried at 100°C in a vacuum oven for 24 h.

Synthesis of $\text{NaFe}(1.24)$ and $\text{NaFe}(1.63)$. In a typical synthesis for $\text{NaFe}(1.24)$, 4 mmol of $\text{NaFe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ was dissolved in 100 mL of hydrochloric acid aqueous solution of 1 M. For $\text{NaFe}(1.63)$, 1 mmol ascorbic acid was also added. The obtained solution was bubbled with pure nitrogen for 30 minutes to eliminate the oxygen dissolved in water. Then the solution was transferred

under N₂ protection and maintained at 80 °C for 4 h with vigorous stirring. The light blue precipitates were collected by centrifugation, washed by water and ethanol for several times and dried at 100 °C in a vacuum oven for 24 h.

2.2 Structural characterizations

The morphology and size of the obtained samples were examined by scanning electronic microscopy (SEM, JEOL 6701F) operated at 10 kV. Powder X-ray diffraction (XRD) were carried out on a Rigaku D/max-2500 diffractometer with a filtered Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). Raman spectra were performed on a DXR Raman Microscope (Thermo Scientific) with a laser wavelength of 532 nm. The chemical composition was examined by the elemental analysis (Flash EA 1112) for C and N elements and by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPE-9000) for Fe and Na elements. ⁵⁷Fe Mössbauer spectroscopy was obtained by MS-500 Mössbauer at room temperature. ⁷Co/Pd was used as Mössbauer source. The isomer shifts reported here are relative to α -Fe⁵⁷. *In situ* XRD experiments were carried out at beamline X14A of the National Synchrotron Light Source (NSLS) at Brookhaven national laboratory (BNL) using a linear position sensitive silicon detector with a wavelength of 0.7788 Å. For easy comparison with the results presented in the literature, the 2θ has been converted to the values that correspond to the more common laboratory Cu K α radiation ($\lambda=1.54 \text{ \AA}$). X-ray absorption spectra were collected at beamlines X18A and X19A using a Si(111) double-crystal monochromator. The experimental details are described in our previous works [46]. X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) data were analyzed by ATHENA software package [47]. The extracted EXAFS signal was weighted by k^2 and Fourier-transformed in k -ranges of 3.2 – 13.0 Å⁻¹ using a Hanning window function to obtain the magnitude plots of the EXAFS spectra in R-space (Å). The Fourier-transformed peaks were not phase corrected, and thus the actual bond lengths are approximately 0.2 – 0.4 Å longer.

2.3 Electrochemical characterizations

The working electrode was prepared by casting a

mixture of PB, ketjen black, and poly(vinyl difluoride) (PVDF, Aldrich) binder at a weight ratio of 7:2:1 onto aluminum foil (99.6%, Goodfellow). The working electrodes were dried at 80 °C in a vacuum oven for 24h. **The average mass loading of the active materials is about 10 mg cm⁻².** Two-electrode Swagelok-type cells were assembled in an argon-filled glove box. A pure Na foil (10 mm in diameter) was used as counter electrode and a porous glass fiber (GF/D) was used as separator. The electrolyte was saturated NaPF₆ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) at 1:1 volume ratio. Galvanostatic tests were carried out between voltage range of 2.0 – 4.2 V vs. Na⁺/Na using an Arbin BT2000 system. ***In situ* Raman tests were conducted employing an especially designed two-electrode cell with a glass window on the side of working electrode.**

3 Results and discussion

3.1. Preparation and characterizations of sodium iron hexacyanoferrates

In order to increase the Na content in sodium iron hexacyanoferrate, reducing agent and inert atmosphere were employed in this work. It is found that the reaction environment significantly influences the Na content of the finally obtained samples (Table 1), the formulas of which are determined by the elemental analyzer for C and N elements and ICP-AES for Fe and Na elements. Based on the elemental analysis of Na, Fe, C and N, sodium iron hexacyanoferrate synthesized under air only, VC and air, nitrogen only, and VC and nitrogen atmospheres are described by the formula of Na_{0.83}Fe_{1.97}(CN)₆ (NaFe(0.83)), Na_{1.03}Fe_{1.95}(CN)₆ (NaFe(1.03)), Na_{1.24}Fe_{1.94}(CN)₆ (NaFe(1.24)) and Na_{1.63}Fe_{1.89}(CN)₆ (NaFe(1.63)) , respectively. It is obvious that under VC or N₂ protection, the Na content in PBAs can be notably increased to as high as 1.63 per formula. This phenomenon is mainly because that VC and N₂ can prevent Fe²⁺/[Fe^{II}(CN)₆]⁴⁻ from being oxidized to Fe³⁺/[Fe^{III}(CN)₆]³⁻, further resulting in a decreased average valance of Fe and increased content of Na. XRD patterns in Fig. 1(a) show that NaFe(0.83) exhibits a typical cubic face-centered structure [35]. With the increase of Na content to 1.03 and 1.24 per

formula, XRD peaks shift gradually toward lower diffraction angles, indicating an increase of the lattice parameters. For NaFe(1.63), the crystal structure has been identified as rhombohedral rather than cubic, demonstrating that the crystal tend to form low symmetry structure to contain more Na ions [48]. Raman spectra (Fig. 1(b)) are used to identify the average valance state of Fe because the frequency of the cyanide stretching vibration mode, ν (CN), is sensitive to the surrounding chemical environment [49]. Cyanide coordinated to Fe^{II} exhibits lower wavenumber peaks than that coordinated to Fe^{III} [50]. It is obvious that ν (CN) shift gradually toward low wavenumber positions from NaFe(0.83) to NaFe(1.63), revealing a decrease of the average valance state of Fe, which is consistent with the obtained chemical compositions. In spite of the different compositions and structures, NaFe(0.83), NaFe(1.03), NaFe(1.24) and NaFe(1.63) all exhibit similar morphologies (Fig. 1(c)-(f)). The sizes of NaFe(1.24) and NaFe(1.63) are larger than NaFe(0.83) and NaFe(1.03), indicating that the crystals tend to grow with larger size under N_2 atmosphere. Above all, by simply controlling the reducing agent and reaction atmosphere, the Na content and average valance state of Fe in sodium iron hexacyanoferrate can be tailored.

^{57}Fe Mössbauer spectra at 298 K were performed to further identify the effects of VC and N_2 protection on the detailed compositions and structures of the obtained samples (Fig. 2). The black dots and red solid lines in Fig. 2 correspond to the experimental and best-fitted results, respectively. The detailed fitting parameters are shown in Table S1 in the Electronic Supplementary Material (ESM), where δ is the isomer shift, Q_s is the quadrupole splitting and the area ratio represents the weight ratio of iron at different sites [51]. The best-fitted curve is composed of one singlet sub-spectrum and three doublet sub-spectra (two for NaFe(0.83)). The singlet sub-spectrum with a zero value of Q_s is assigned to the low spin symmetrical octahedral $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, while the other double sub-spectra are assigned to Fe^{2+} , Fe^{3+} and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ [52-54]. Q_s of $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ is less than that of Fe^{3+} due to a more symmetrical coordination environment. There is no Fe^{2+} observed in NaFe(0.83), demonstrating that Fe^{2+} from the decomposition of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ are completely re-oxidized to Fe^{3+} under air atmosphere. However,

Table 1 Compositions of the obtained PB samples under different synthetic conditions.

Sample	Synthetic conditions	Compositions
NaFe(0.83)	Air; without VC	$\text{Na}_{0.83}\text{FeFe}_{0.97}(\text{CN})_6$
NaFe(1.03)	Air; with VC	$\text{Na}_{1.03}\text{FeFe}_{0.91}(\text{CN})_6$
NaFe(1.24)	N_2 ; without VC	$\text{Na}_{1.24}\text{FeFe}_{0.94}(\text{CN})_6$
NaFe(1.63)	N_2 ; with VC	$\text{Na}_{1.63}\text{FeFe}_{0.89}(\text{CN})_6$

Figure 1 (a) XRD patterns, (b) Raman spectra of PB samples. 1: NaFe(0.83); 2: NaFe(1.03); 3: NaFe(1.24); 4: NaFe(1.63). SEM images of (c) NaFe(0.83); (d) NaFe(1.03); (e) NaFe(1.24) and (f) NaFe(1.63).

under VC or N_2 protection, the oxidation is noticeably suppressed. From NaFe(0.83) to NaFe(1.63), the Fe^{2+} content increases while the Fe^{3+} and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ content decreases. The weight percentage of each Fe^{III} and Fe^{II} component and $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ratio are calculated and listed in Table 2. The $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ratios for NaFe(0.83), NaFe(1.03), NaFe(1.24) and NaFe(1.63) are 3.31, 1.84, 0.96, and 0.71, respectively, indicating that VC and N_2 can effectively suppress the $\text{Fe}^{2+}/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ oxidation. This result is well consistent with the Raman results. The application of VC and N_2 protection during synthesis not only has great influence on the Na content and Fe valance, but also on the geometric symmetry around iron atoms. The calculated Q_s values of both Fe^{3+} and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ increase from

NaFe(0.83) to NaFe(1.63), indicating a more distorted coordination environment of Fe [53]. This disordered environment is induced by the Na displacement along cubic [111] axis at higher Na concentration [43].

Figure 2 The 295 K ^{57}Fe Mossbauer spectra of (a) NaFe(0.83); (b) NaFe(1.03); (c) NaFe(1.24) and (d) NaFe(1.63).

Table 2 The calculated weight contents of Fe^{III} and Fe^{II} in the obtained samples.

Sample	Fe^{III} (wt%)	Fe^{II} (wt%)	$\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$
NaFe(0.83)	76.8	23.2	3.31
NaFe(1.03)	64.8	35.2	1.84
NaFe(1.24)	49.1	50.9	0.96
NaFe(1.63)	41.4	58.6	0.71

3.2 Electrochemical performance of sodium iron hexacyanoferrates

The electrochemical performance of the obtained four samples as cathodes for room-temperature Na-ion batteries were tested by galvanostatic charging and discharging as shown in Fig. 3. The open-circuit voltages (OCV) of NaFe(0.83), NaFe(1.03), NaFe(1.24), and NaFe(1.63) were 3.14 V, 3.04 V, 2.96 V and 2.93 V, respectively, consistent with a decreasing average valence state of Fe. In the first cycle, NaFe(0.83), NaFe(1.03), NaFe(1.24), and NaFe(1.63) exhibit a charge capacity of 81, 82, 122 and 153 mA h g^{-1} , respectively. The increasing charge capacity is in good agreement with the increasing Na contents. The charge capacity during the first cycle is

Figure 3 Electrochemical tests of the obtained samples at a current density of 25 mA g^{-1} . (a) Galvanostatic voltage profiles and (b) cycling performance of NaFe(0.83). (c) Galvanostatic voltage profiles and (d) cycling performance of NaFe(1.03). (e) Galvanostatic voltage profiles and (f) cycling performance of NaFe(1.24). (g) Galvanostatic voltage profiles and (h) cycling performance of NaFe(1.63).

very important since it directly represents how much Na ions are available in full-cells employing Na-deficient anodes. The high Na content in NaFe(1.63) is also proved by a low discharge capacity of 33 mA h g^{-1} when discharging first (Fig. S1 in the ESM). NaFe(0.83) with less cations delivered a discharge capacity of 100 mA h g^{-1} (Fig. S2 in the ESM). The high cation content in NaFe(1.63) ensures that it is promising for applications as Na sufficient cathode materials without any pre-treatment. **Due to the decomposition of interstitial water, the Coulombic efficiency is not high in the first, but still could reach ~100% after a few cycles.** For NaFe(1.63), an excellent cycling stability was obtained with 90% capacity retention after 200 cycles. Although NaFe(0.83) can also deliver a high specific capacity

and no obvious capacity fading for 200 cycles, it is worth noting that when combined with Na deficient anodes, the capacity would be very low based on its initial low Na content. The capacity for NaFe(1.24) is little lower (135 mA h g^{-1}) than other three samples, which is might due to its larger size results in a decreased electrochemical activity. *Ex situ* SEM images of four samples after cycling are shown in Fig. S3 (in the ESM). The cube morphology could be preserved after cycling, indicating the well structure stability.

3.3 Na storage mechanism of NaFe(1.63)

To gain more specific insight into the Na intercalation/de-intercalation mechanism, *in situ* synchrotron XRD patterns of NaFe(1.63) electrode were recorded during first charge/discharge process. The structure changes are monitored by the shift of the major diffraction peaks (Fig. 4(a)) selected from the full XRD patterns shown in Fig. S4 (in the ESM). The peak intensities of the initial rhombohedral phase gradually decreased while the new peaks of the final cubic phase emerged during the early stage of Na extraction (i.e. charging). The peaks of the cubic phase monotonically shifted towards high two-theta angle positions upon further charging up to 3.3 V, suggesting Na^+ extraction among cubic phase is through solid-solution reaction during the first charging process. The phase transitions proceeded in a reverse manner when Na ions were re-inserted. The initial rhombohedral structure was restored at the end of discharge at 2.0 V. This result suggests the highly reversible structural changes during the Na^+ extraction/insertion process, which is responsible for its superior cycling stability.

In situ Raman spectra (Fig. 4(b)) of NaFe(1.63) were analyzed to show the valance state change of Fe during the first charge/discharge process. It is observed that the positions of the original peaks at 2135, 2109 and 2070 cm^{-1} gradually shifted towards high wavenumber positions when Na ions were extracted, indicating that the iron center was predominantly oxidized. When charged to 4.3 V, a new Raman peak at 2150 cm^{-1} appeared, suggesting a complete oxidation of Fe^{II} to Fe^{III} [55]. By the backward stepwise shift of electrode potential, the reduction process of iron proceeded in a reverse

manner and peaks at 2128, 2090, and 2070 cm^{-1} were finally observed when discharged to 2.0 V. Compared with original Fe states, these peaks are at lower wavenumber positions, indicating that the average valance state of Fe after Na^+ intercalation was lower. The $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ redox couple was highly reversible during the second cycle as well (Fig. S5 in the ESM).

Figure 4 (a) *In situ* XRD patterns of NaFe(1.63) electrode collected during first charge and discharge. The major diffraction peaks selected from the full XRD patterns are plotted to clearly show the phase transitions between the pristine rhombohedral and cubic phases. The charge and discharge curves are shown on the right column respectively. (b) *In situ* Raman spectra of NaFe(1.63) electrode during the first charge and discharge process.

More fundamental information about electronic structure of Fe was revealed by X-ray absorption spectra (XAS). XANES measurements at the Fe K-edge were performed to quantitatively determine the average valance state of Fe in the charged/discharged NaFe(1.63) electrodes and their spectra are shown in Fig. 5(a). All XANES features are similar to those of Prussian blue analogs reported in the literature [56]. The spectra for the pristine and discharged (2.0 V) ones display small hump in the

beginning of the absorption ramp (about 7118 eV~7120 eV) which can be assigned to a shakedown process involving the 1s to 4p transition followed by ligand-to-metal charge transfer (LMCT). Appearance of this peak suggests strong covalent bonding nature of Fe ions with CN ligands [57]. A strong main absorption peaks at around 7127 eV for Na inserted (i.e., discharged) samples and around 7132 eV for Na extracted (i.e., charged) samples are ascribed to the purely dipole-allowed 1s to 4p transition. The pre-edge features seen in most transition metal oxides due to dipole forbidden 1s to 3d transition are less discernible in our samples due to either the weak signal/noise ratio and/or overlapping with the LMCT features.

Figure 5 (a) *Ex situ* Fe K-edge XANES and (b) Fourier-transformed magnitude of Fe K-edge EXAFS spectra of NaFe(1.63) electrode collected at different charge and discharge states.

The XANES for the Fe K-edge after Na extraction (i.e. 3.3 V and 4.4 V states) showed a clear edge shift to higher energy indicating an increased average valance state of Fe. The energy of the absorption maxima (7131eV) for the fully charged electrode (4.4V) is similar to that of the $K_3Fe(CN)_6$, which confirms that most of Fe in the charged states are in

the Fe^{III} state [58]. For the electrode after one cycle (2.0 V), the edge position even shifted below the pristine material's position, indicating the further reduction of Fe is close to +2. This phenomenon is in good agreement with the higher specific capacity obtained at the low voltage region during first discharge and subsequent cycles. *In situ* XANES experiment was also performed on NaFe(1.63) electrode during the first charge process as shown in Fig. S6 (in the ESM). The half-height energy position [59] was used to track the average valance state of Fe. Clear continuous increase in edge energy was observed during charging up to 3.3 V. The edge energy increase became slower with further charging above 3.3 V to the end of the charge (4.3 V). This indicates that the major redox reaction of Fe took place at the low voltage plateau region.

Fourier transformed magnitudes of the Fe K-edge EXAFS spectra of the pristine, fully charged and discharged samples are shown in Fig. 5(b). Three dominant peaks were observed in all the spectra; the peaks at 1.5, 2.5, and 4.4–4.8 Å can be ascribed to the Fe-C, Fe-N, and Fe-Fe shells, respectively [60]. The significant split of the Fe-C and Fe-N peaks for the pristine and discharged samples reveals an irregular or distorted iron octahedral environment due to lower symmetry of rhombohedral structure which agrees well with XRD results. The intensities of these peaks increased for the fully sodium extracted sample (4.4 V), which agrees well with the XRD observation of the phase transformation from rhombohedral to high symmetry cubic phase upon Na^+ extraction. An obvious change of the peak attributed to the Fe-Na interaction (3.0 Å) can also be observed at pristine and fully discharged electrodes in which sufficient Na^+ occupy the interstitial sites in the lattice.

4 Conclusions

In summary, Na content in sodium iron hexacyanoferrate could be incredibly increased by applying reducing agent and inert atmosphere. VC and N_2 are found to effectively protect $Fe^{2+}/[Fe^{II}(CN)_6]^{4-}$ from being oxidized to $Fe^{3+}/[Fe^{III}(CN)_6]^{3-}$, further lead to a decreased average valance of Fe and a increased content of Na. A highest Na content for sodium iron hexacyanoferrate

(1.63 per molecule) is achieved when applying VC and N₂ protection at the same time. The obtained sodium iron hexacyanoferrate with high Na content exhibits high discharge capacity (150 mA h g⁻¹), superior cycling performance (90% capacity retention for 200 cycles) and impressive Coulombic efficiency (~ 100%) as a cathode material in room-temperature Na-ion batteries. Most importantly, the high Na content ensures that it could function as a plentiful Na reservoir and is quite attractive as Na-rich cathode materials from the practical point of view. In addition, NaFe(1.63) undergoes a rhombohedral ↔ cubic phase transition and the main Na intercalation/de-intercalation process occurs mainly at low voltage region (< 3.7 V), as revealed by the *in situ* XRD and XAS analysis. The protection strategy for synthesis is simple yet very effective. This synthetic method may also open a new insight into the preparation of PBAs with high Na contents and can be extended to synthesize other cathode materials.

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Electronic Supplementary Material

Sodium iron hexacyanoferrate with high Na content as a Na-rich cathode material for Na-ion batteries

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Table S1 The detailed fitting parameters of four sodium iron hexacyanoferrate samples

Sample	structure	$\delta(\text{mm/s})$	$Qs(\text{mm/s})$	$HWHM(\text{mm/s})$	Area Ratio(%)
NaFe(0.83)	$[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$	-0.13 ± 0	0	0.13 ± 0	23.2
NaFe(1.03)		-0.10 ± 0	0	0.14 ± 0	22.5
NaFe(1.24)		-0.07 ± 0	0	0.11 ± 0	15.8
NaFe(1.63)		-0.05 ± 0	0	0.12 ± 0	19.5
NaFe(0.83)	Fe^{2+}	/	/	/	/
NaFe(1.03)		1.01 ± 0.01	0.97 ± 0.02	0.39 ± 0.01	12.7
NaFe(1.24)		0.80 ± 0	1.43 ± 0.01	0.39 ± 0.01	35.1
NaFe(1.63)		0.84 ± 0	1.27 ± 0.02	0.45 ± 0.01	39.1
NaFe(0.83)	$[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$	0.21 ± 0	0.39 ± 0	0.21 ± 0	36.0
NaFe(1.03)		0.19 ± 0	0.51 ± 0	0.20 ± 0	33.5
NaFe(1.24)		0.25 ± 0	0.60 ± 0	0.17 ± 0	22.3
NaFe(1.63)		0.28 ± 0	0.64 ± 0	0.17 ± 0	19.7
NaFe(0.83)	Fe^{3+}	0.36 ± 0	0.68 ± 0	0.21 ± 0	40.8
NaFe(1.03)		0.36 ± 0	0.65 ± 0	0.23 ± 0	31.3
NaFe(1.24)		0.40 ± 0	0.87 ± 0	0.22 ± 0	26.8
NaFe(1.63)		0.40 ± 0	0.90 ± 0	0.21 ± 0	21.7

Figure S1 Galvanostatic voltage profiles of NaFe(1.63) under a current density of 25 mA g⁻¹ by discharging first.

Figure S2 Galvanostatic voltage profiles of NaFe(0.83) under a current density of 25 mA g⁻¹ by discharging first.

Figure S3 *Ex situ* SEM images of (a) NaFe(0.83), (b) NaFe(1.03), (c) NaFe(1.24) and (d) NaFe(1.63) electrode after 30 cycles.

Figure S4 *In situ* XRD patterns of the NaFe(1.63) collected during first charge and discharge, respectively.

Figure S5 *In situ* Raman spectra of NaFe(1.63) electrodes during the second cycle.

Figure S6 *In situ* Fe K-edge XANES spectra of NaFe(1.63) collected during first charge process. (Current density: 12 mA g^{-1}) The half-height energy positions of the XANES spectra are plotted and correlated with the charge curve.