



Core-shell hexacyanoferrate for superior Na-ion batteries



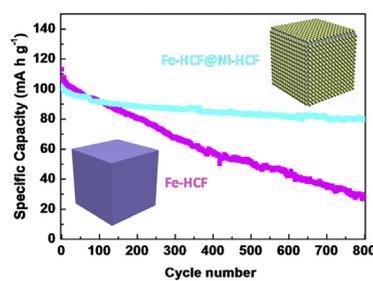
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HIGHLIGHTS

- Core-shell structured Fe-HCF@Ni-HCF was synthesized via a facile solution method.
- The Fe-HCF@Ni-HCF composite integrates the advantages of both Fe-HCF and Ni-HCF.
- Ni-HCF coating improves the electron conductivity and suppresses the side reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Sodium iron hexacyanoferrate (Fe-HCF) is regarded as a potential cathode material for sodium-ion batteries (SIBs) due to its high specific capacity, low cost, facile synthesis and environmentally friendly. However, Fe-HCF always suffers from poor electronic conductivity, low crystallinity and side reactions with electrolyte, leading to poor rate performance, low coulombic efficiency and deterioration of cycling stability. Herein, we report a green and facile synthesis to encapsulate Fe-HCF microcubes with potassium nickel hexacyanoferrate (Ni-HCF). The core-shell Fe-HCF@Ni-HCF composite delivers a reversible capacity of 79.7 mAh g⁻¹ at 200 mA g⁻¹ after 800 cycles and a high coulombic efficiency of 99.3%. In addition, Fe-HCF@Ni-HCF exhibits excellent rate performance, retaining 60 mAh g⁻¹ at 2000 mA g⁻¹. The results show that Fe-HCF@Ni-HCF integrates the advantages of both Fe-HCF and Ni-HCF, making it electrochemically stable as cathode material for SIBs.

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1. Introduction

In recent years, sodium ion batteries (SIBs) have received increasing research attentions as alternative for lithium ion batteries in the application of large-scale electric energy storage (EES) [1–4]. SIBs have the advantages of high sodium abundance and low

cost, and plenty of materials are investigated for sodium ion storage, such as layered oxides and tunneled oxides [5–10]. Except these, Prussian blue and its derivatives (PBAs) with the merits of high specific capacity, facile synthesis and low cost, are also identified as promising electrode materials for SIBs [11–17].

PBAs usually have a face-centered cubic structure: A_xM₁[M₂(CN)₆]_y□_{1-y}•nH₂O (0 < x < 2, 0 < y < 1), in which A represents alkali cations, M transition metal ions, and □ the vacancies of [M₂(CN)₆] occupied by coordinated H₂O [18]. The 3D open framework of PBAs can provide large interstitial sites for fast Na⁺ insertion/extraction. Among these PBAs, sodium iron

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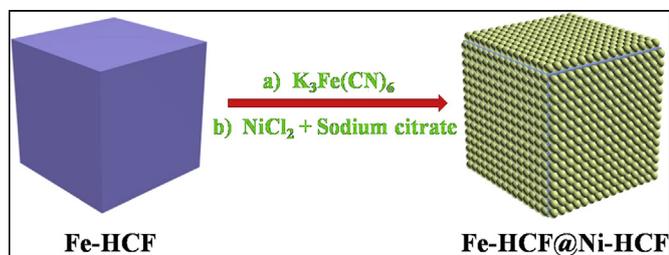


Fig. 1. Schematic representation of synthesis procedure of Fe-HCF@Ni-HCF composite.

hexacyanoferrate ($A = \text{Na}$, $M_1 = M_2 = \text{Fe}$, Fe-HCF) has two electrochemically active sites, which leads to a high theoretical specific capacity of 170 mAh g^{-1} [19]. However, Fe-HCF always suffers from low coulombic efficiency and poor cycling stability due to the lattice vacancies in the crystal structure and the side reactions between Fe-HCF and electrolyte [20–22].

In order to solve these drawbacks of Fe-HCF, it is desirable to synthesize high-quality Fe-HCF with few lattice vacancies via a single iron source method [23–25]. You et al. used this method to synthesize the highly crystalline $\text{Na}_{0.61}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.94}$. The reversible specific capacity is about 170 mAh g^{-1} under 25 mA g^{-1} , and coulombic efficiency is nearly 100% [23]. Wang et al. also synthesized the sodium-rich and stable $\text{Na}_{1.92}\text{Fe}[\text{Fe}(\text{CN})_6]$ with high capacity (157 mAh g^{-1} at 15 mA g^{-1}), long cycle life (80% after 750

cycles) and excellent rate capability (145 mAh g^{-1} at 1500 mA g^{-1}) [24]. Jiang et al. synthesize PB@C composite which shows superior rate performance and remarkable cycling stability [25]. However, the single iron source method may release highly toxic $[\text{CN}]^-$ anions and the yield is quite low, which is not suitable for the mass production. Recently, our group used the double iron sources to synthesize high-quality Fe-HCF nanocubes with high yield [26]. We also modified the surface of Fe-HCF microcubes by PPY coating, and the obtained Fe-HCF@PPy exhibits excellent rate capability and improved cycling stability [22]. However, the coulombic efficiency of Fe-HCF@PPy is 97%, which is still not satisfied for the practical applications. Therefore, it is still a challenge to develop a non-toxic and high-yield method to prepare Fe-HCF with high coulombic efficiency and excellent cyclability.

On the other side, potassium nickel hexacyanoferrate (Ni-HCF) and sodium nickel hexacyanoferrate with low capacity of 60 mAh g^{-1} and 70 mAh g^{-1} are highly stable during redox cycling because the inactive Ni^{2+} can stabilize the crystal lattice [27,28]. Daisuke Asakura et al. designed a core-shell structure by coating $\text{K}_{0.1}\text{Cu}[\text{Fe}(\text{CN})_6]_{0.73.5}\text{H}_2\text{O}$ (Cu-HCF) core with Ni-HCF shell [20], and such heterostructure delivered enhanced lithium storage performance over the sum of the individual components. Masashi Okubo et al. investigated Cu-HCF@Ni-HCF as cathode material for SIBs [29]. It was found that Ni-HCF could effectively inhibit the formation of over-sodiated insulating surface, and hence obviously improve the rate performance of Cu-HCF. Inspired by the above strategies, it is supposed that the cycling stability and coulombic efficiency of Fe-HCF can also be improved via a coating of Ni-HCF.

Herein, we propose a facile co-precipitation method to synthesize core-shell structured Fe-HCF@Ni-HCF with outstanding electrochemical performance as cathode material for SIBs. Compared with our previous work [22], the high-quality Fe-HCF@Ni-HCF integrates the advantages of both Fe-HCF and Ni-HCF, which exhibits high specific capacity, excellent cycling stability and promoted rate performance. It retains 78% capacity at 200 mA g^{-1} after 800 cycles and delivers an average coulombic efficiency of approximately 100% during cycling. The result further proves that Fe-HCF is a promising cathode material in the practical application of SIBs.

2. Experimental

Fe-HCF microcubes were prepared by a co-precipitation method as reported in our previous work [22]. Typically, $1.67 \text{ g FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $15 \text{ g sodium citrate}$ were dissolved in $200 \text{ mL deionized (DI) water}$, while $1.94 \text{ g Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ was dissolved into 200 mL DI water . The above two precursor solutions were then mixed at 25°C for 6 h . The precipitates were collected by centrifugation, washed thoroughly with DI water and alcohol, and finally dried in a vacuum oven at 70°C for 12 h . Ni-HCF nanocubes were synthesized by following process. Briefly, $4.29 \text{ g NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $9.9 \text{ g sodium citrate}$ were dissolved in 600 mL DI water . $3.96 \text{ g K}_3\text{Fe}(\text{CN})_6$ was dissolved into 600 mL DI water . The above two precursor solutions were then mixed at 25°C under continuous stirring for 24 h . The precipitates were collected by centrifugation, washed thoroughly with DI water and alcohol, and finally dried in a vacuum oven at 70°C for 12 h .

The synthetic procedure for core-shell structured Fe-HCF@Ni-HCF composites is illustrated in Fig. 1. Firstly, 0.5 g Fe-HCF was dissolved into 60 mL DI water and ultrasonically stirred for 20 min , and then $0.396 \text{ g K}_3\text{Fe}(\text{CN})_6$ was added under continuous stirring for 30 min , marked as solution A. $0.429 \text{ g NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $0.99 \text{ g sodium citrate}$ were dissolved in 60 mL DI water to form solution B. Subsequently, solution B was added into solution A, and the mixed solution was stirred at room temperature for 24 h . The precipitates

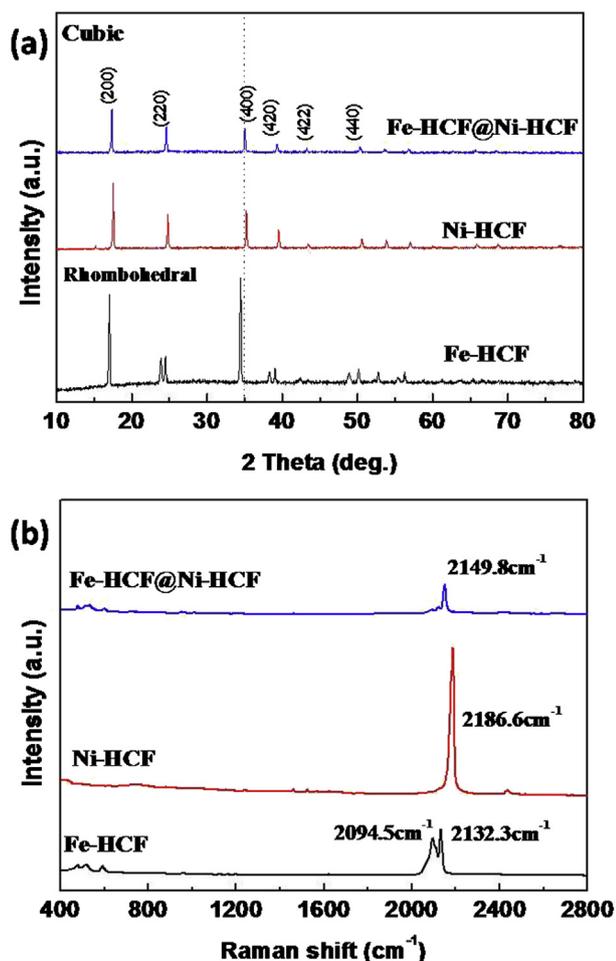


Fig. 2. XRD patterns (a) and Raman spectra (b) of Ni-HCF, Fe-HCF and Fe-HCF@Ni-HCF.

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