Supporting Information

On the Mechanism of the Improved Operation Voltage of Rhombohedral Nickel Hexacyanoferrate as Cathodes for Sodium-Ion Batteries

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Table S1 ICP-OES test the metal contents of r-NiHCF and c-NiHCF materials

	Na	K	Ni	Fe
r-NiHCF	10.93%	-	19.07%	15.05%
c-NiHCF	-	0.59%	21.24%	13.64%

Table S2 EA test the C, N and H contents of r-NiHCF and c-NiHCF materials

	C	N	H
r-NiHCF	19.42%	22.66%	1.43%
c-NiHCF	17.61%	20.54%	2.93%

By ICP calibration of Na, K, Ni, Fe contents and C, N, H elemental analysis, the composition of the r-NiHCF and c-NiHCF can be determined as $Na_{1.46}Ni[Fe(CN)_6]_{0.83}\square_{0.17}\cdot 2.2H_2O$ and $K_{0.04}Ni[Fe(CN)_6]_{0.67}\square_{0.33}\cdot 4.0H_2O$, respectively.

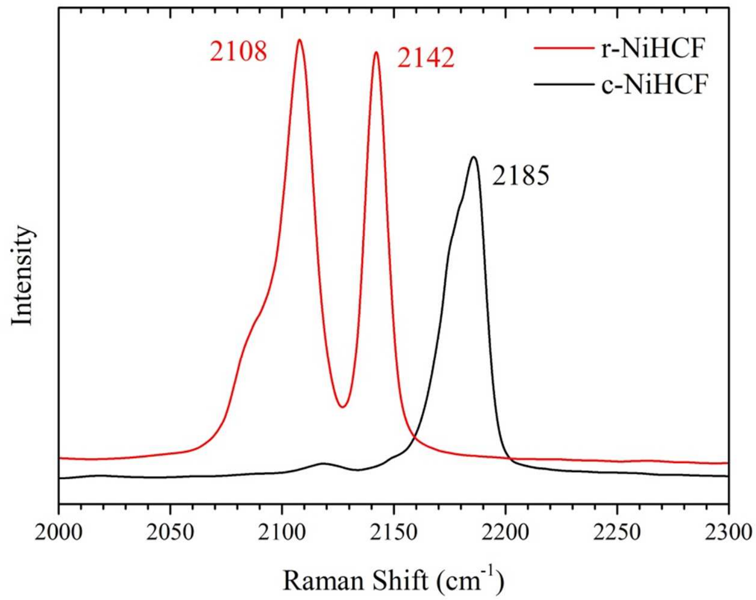

Figure S1. The Raman spectrum of r- and c-NiHCF.

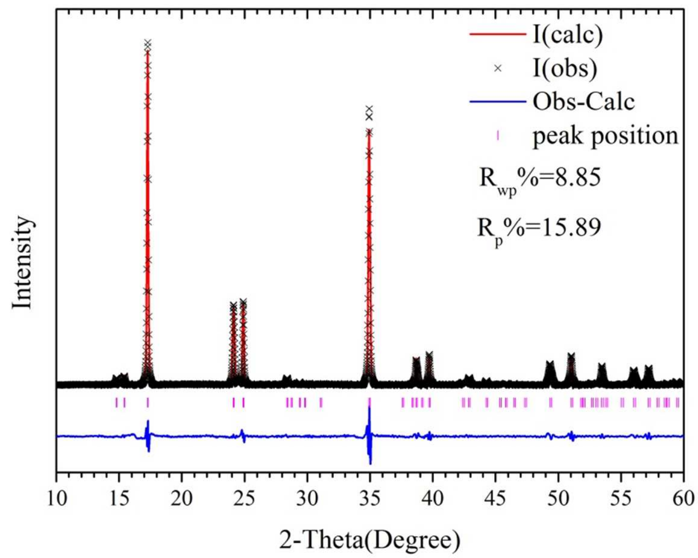

Figure S2. The indexing result of r-NiHCF.

The Powder diffraction pattern of r-NiHCF was first indexed by DICVOL04, which generates a rhombohedral unit cell. A Pawley refinement[1] was successively carried out using the pseudo-Voigt profile function (2 parameters) and the Berar-Baldinozzi asymmetry correction (4 parameters and 20 background coefficients). The zero-point shift of the diffraction pattern was also adjusted. Finally, the cell parameters (a=b=7.386 Å, c=17.279 Å; α=β=90°, γ=120°) and an R-3 space group were obtained, which match well with the XRD profile with the low R_{wp} of 8.85% and R_p of 15.89%.

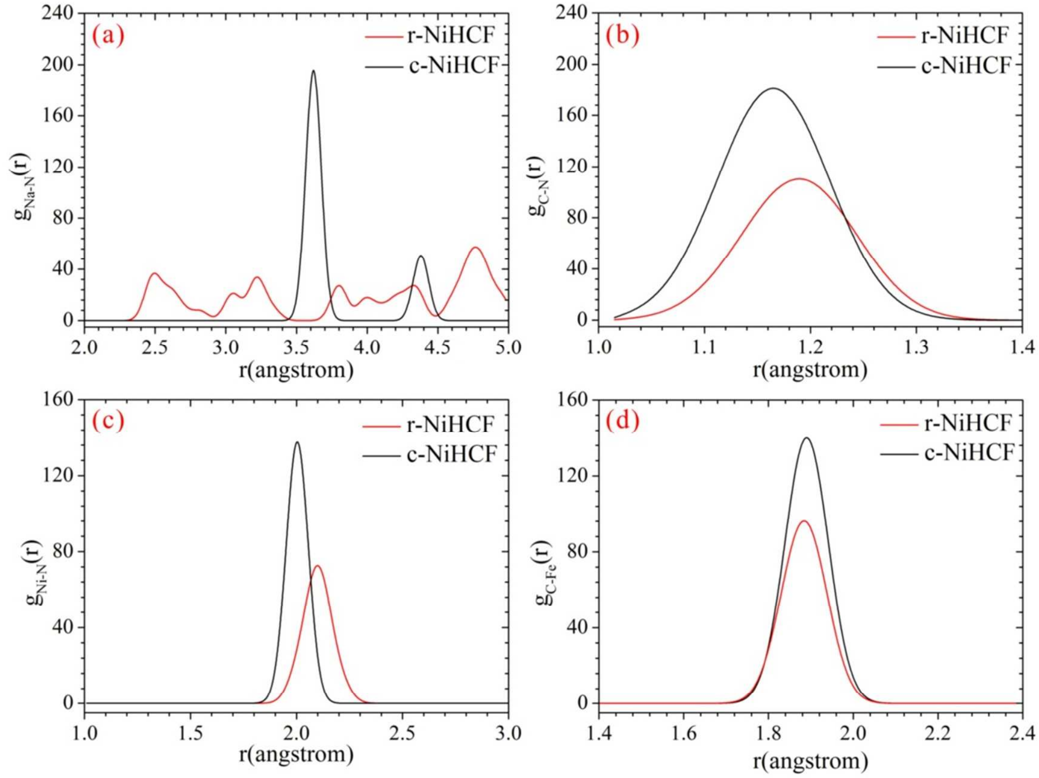

Figure S3. The radial distribution function (RDF) of Na-N (a); C-N (b); Ni-N (c); C-Fe (d) in r- and c-NiHCF.

Table S3. Charge/discharge voltages of current reported cubic NiFe-PBA as the cathode materials of room-temperature Na-ion batteries.

Materials	Charge/discharge voltage (V)
$Na_{1.014}Ni[Fe(CN)_6]_{0.818}\cdot 3.53H_2O$[2]	3.19 / 3.15
$Na_2NiFe(CN)_6$[3]	3.30 / 3.22
$K_{0.09}Ni[Fe(CN)_6]_{0.71}\cdot 6H_2O$[4]	3.25 / 2.95
KNiFe[5]	3.33 / 3.13
$Na_{1.01\sim1.41}Ni[Fe(CN)_6]_{1.02\sim0.91}$[6]	~3.2

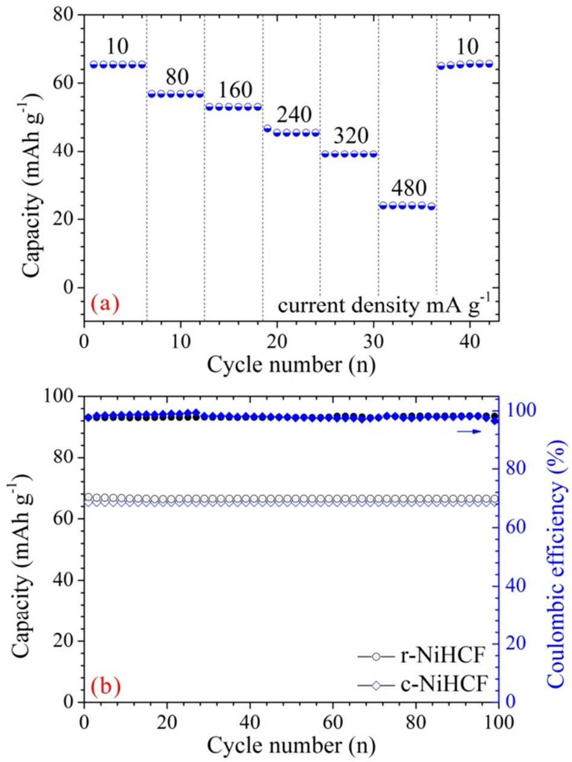

Figure S4. The rate capability of c-NiHCF (a); cycle performance of r-NiHCF and c-NiHCF under current density of 10 mA g^{-1} (b).

Fig. S4a shows that, at low current density (10 mA g^{-1}), the discharge capacity of c-NiHCF level out around 65.4 mAh g^{-1}. As the current density increases to 80 mA g^{-1}, 160 mA g^{-1}, 240 mA g^{-1}, 320 mA g^{-1} and 480 mA g^{-1}, it delivers the available discharge capacity of 56.8 mAh g^{-1}, 53.0 mAh g^{-1}, 46.7 mAh g^{-1}, 39.1 mAh g^{-1} and 24.0 mAh g^{-1}, respectively, and recovers to 65.0 mAh g^{-1} as the current density shifts back to 10 mA g^{-1}, indicating poor rate capability compared with r-NiHCF, which should result from bigger particle size (300-600 nm) of c-NiHCF than that of r-NiHCF (30-50 nm). Long-term charge/discharge (Fig. S4b) shows that, both r-NiHCF and c-NiHCF exhibits excellent cycling stability that there is no capacity loss after 100 cycles at a current ~~rate of~~ density of 10 mA g^{-1}.

References

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