ELECTRONIC SUPPLEMENTARY INFORMATION

Non-aqueous synthesis of high-quality Prussian blue analogues for Na-ion batteries

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Experimental Section:

Material synthesis

The synthesis of NaFeHCF adopts the traditional synthesis method with slight modification.0.4 mmol $Na_4Fe(CN)_6$ and 0.2 ml hydrochloric acid (37%) were dissolved in 20 ml absolute ethanol. Transfer the above solution to a microwave tube, and then heat the solution in a microwave synthesizer (Anton Paar Monowave 400) at 80 °C for 4 hours, 100 °C for 2 hours, 100 °C for 4 hours, 120 °C for 2 hours, 120 °C for 4 hours. After cooling to room temperature, the sample was collected by centrifugation, washed 3 times with deionized water and ethanol, and then dried under vacuum at 100 °C overnight.

Physical characterization

X-ray diffraction (XRD) data was based on a Rigaku Miniflex 600 desktop by Cu Karadiaton. A Quanta FEG250 was used to study the surface morphology of anodes via Scanning electron microscopy (SEM). The ESCALAB250Xi (Thermal Science) spectrometer is equipped with a monochromatic Al Ka x-ray source (hv = 1486.6 eV) working at 150 W to obtain the x-ray photoelectron spectroscopy (XPS) of the sample. Using PerkinElmer Frontier Mid IR FTIR spectrometer to obtain Fourier transform infrared spectra (FTIR) of NaFeHCF samples under different preparation conditions. PerkinElmer TG 209 F3 thermogravimetric analyzer was used to test the thermal stability of NaFeHCF. Test temperature range is 40-500 °C, and the heating rate is 10 °C min^{-1}. The sample weighed 5.0 ± 0.1 mg for analysis and were heated in a nitrogen atmosphere.

Electrochemical evaluation

NaFeHCF electrodes were mixed according to the weight ratio of NaFeHCF: Super P: PVDF=7:2:1 and then coated on aluminum foil. NaFeHCF electrodes were vacuum dried at 100 °C. The NaFeHCF electrodes and Na foil were assembled in CR2032 coin cells with 1 M $NaClO_4$ in propylene carbonate (PC) and ethylene carbonate (EC) (1:1 vol/vol) electrolyte. All batteries were tested at room temperature by land CT2001 multichannel battery tester. Cyclic voltammetry (CV) tests were measured on the Ivium electrochemical workstation between 2.0 V and 4.3 V vs. Na/Na^+ at a scan rate increases from 0.1 mV s^{-1} to 1 mV s^{-1}.

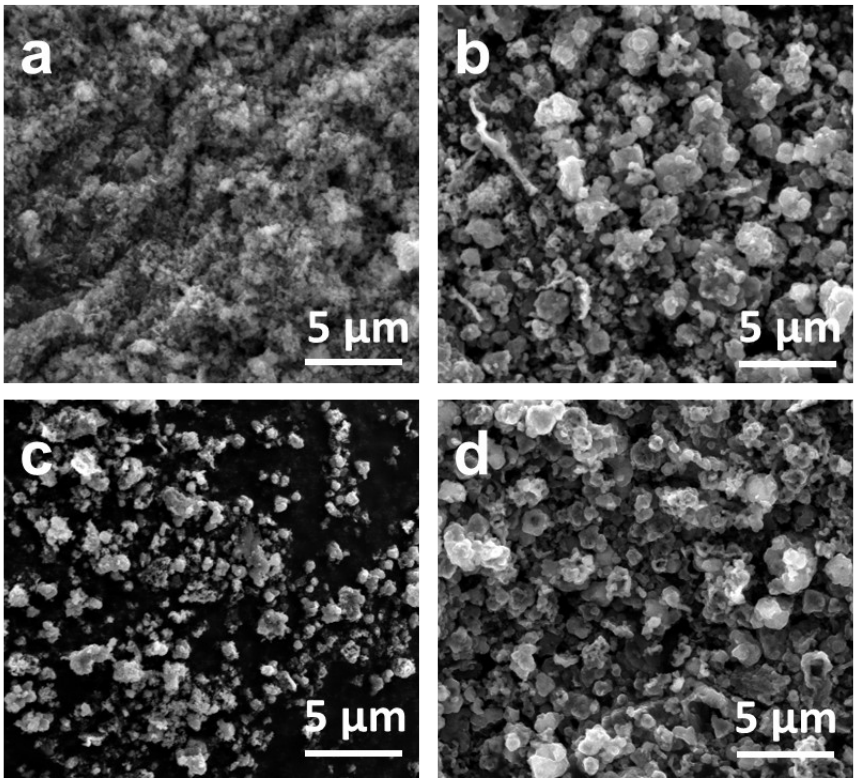

Fig. S1. SEM images of (a) NaFeHCF80-4, (b) NaFeHCF100-2, (c) NaFeHCF120-2, (d) NaFeHCF120-4.

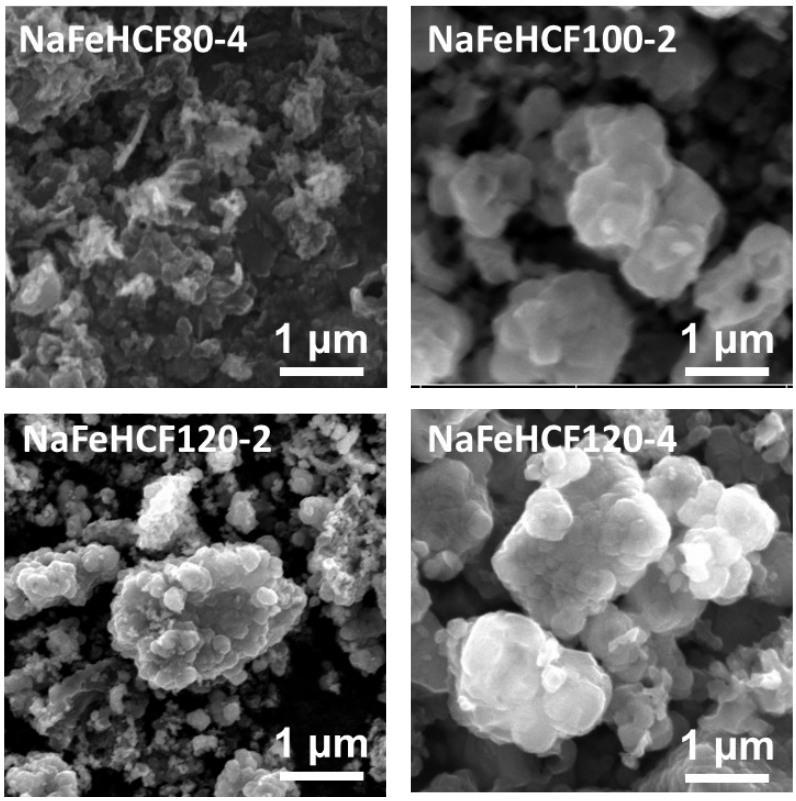

Fig. S2. SEM images of partial enlarged (a) NaFeHCF80-4, (b) NaFeHCF100-2, (c) NaFeHCF120-2, (d) NaFeHCF120-4.

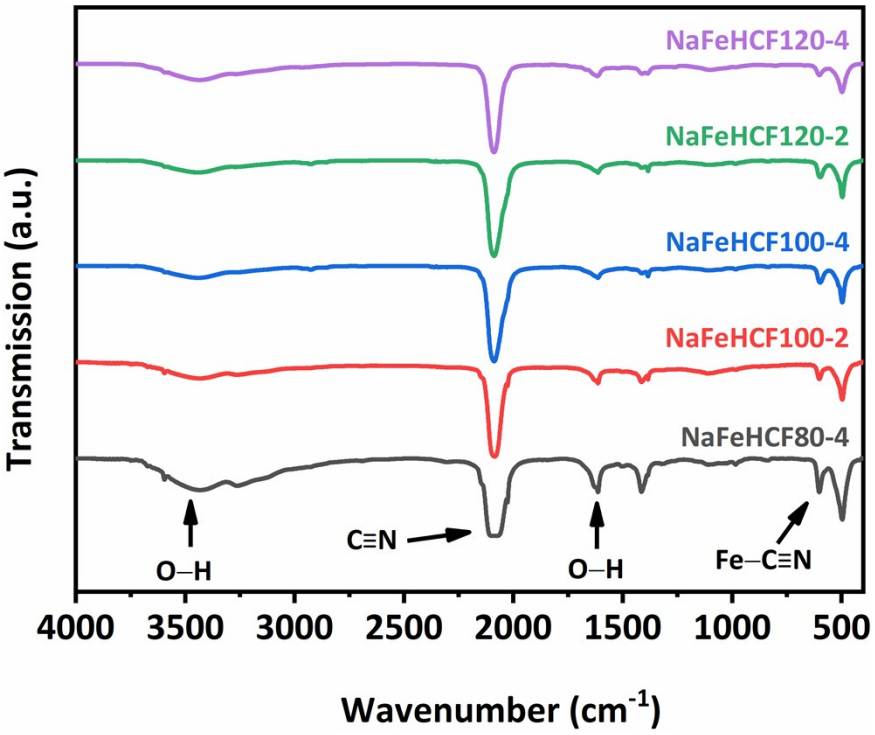

Fig. S3. FTIR spectra of NaFeHCF under different synthesis conditions.

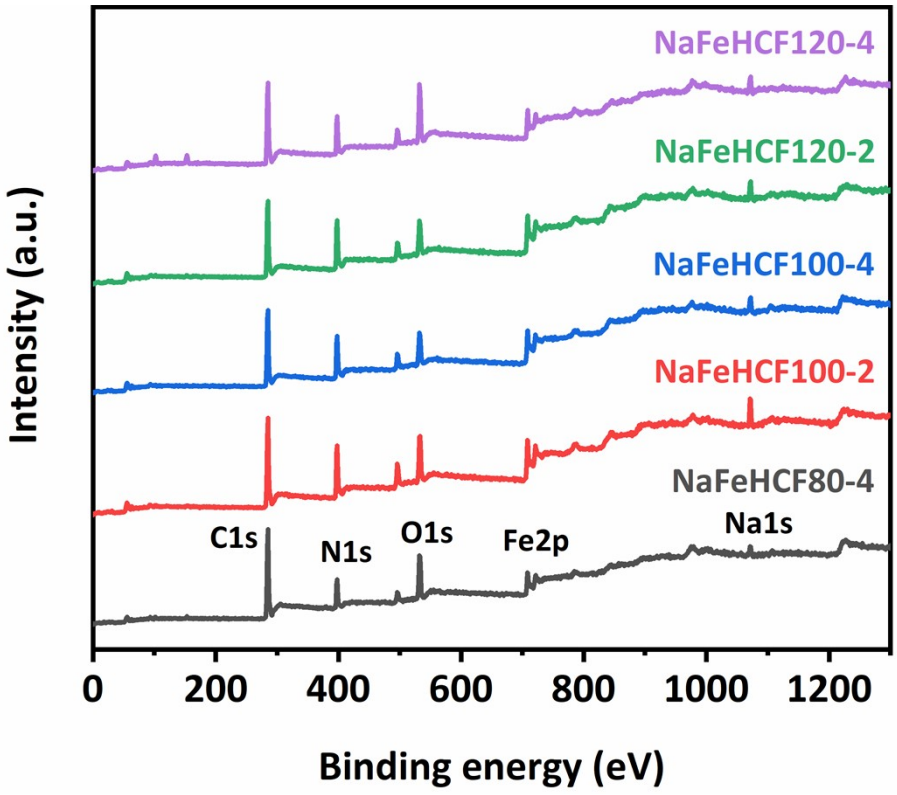

Fig. S4. XPS spectra of NaFeHCF under different synthesis conditions.

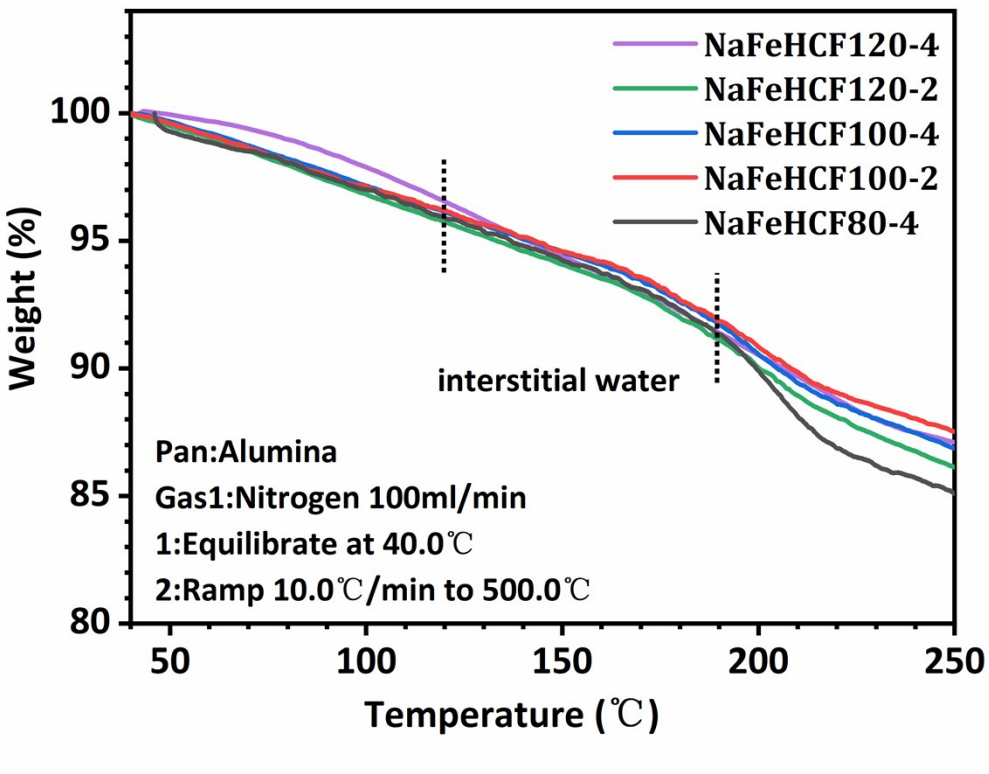

Fig. S5. TGA curves of NaFeHCF under different synthesis conditions.

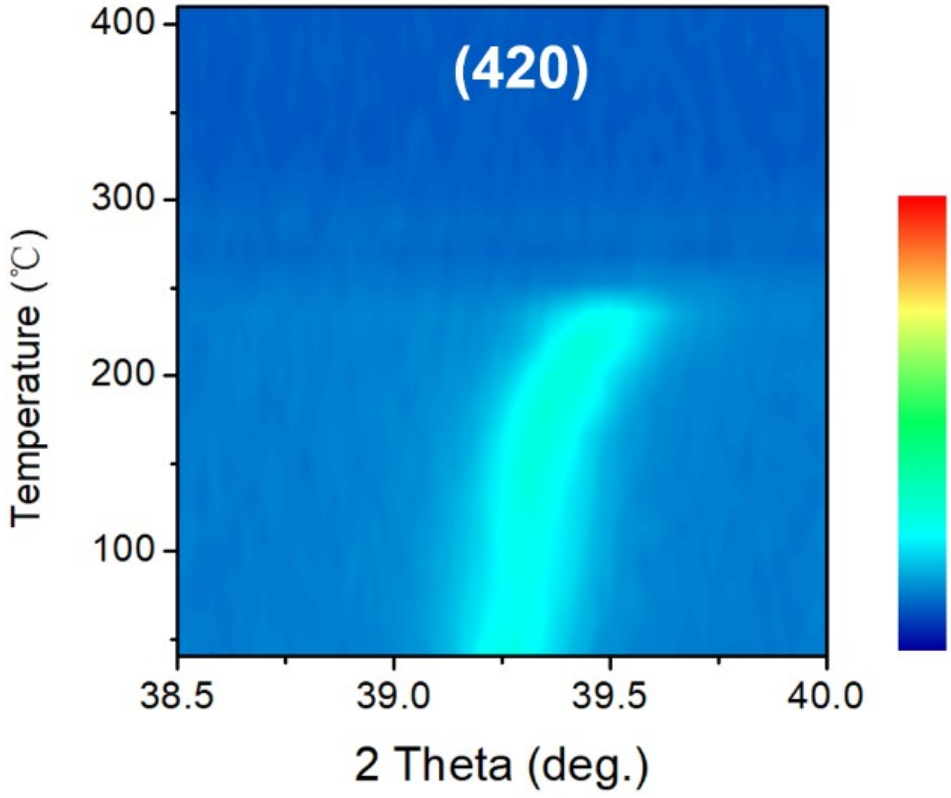

Fig. S6. In-situ XRD of NaFeHCF100-4 of the (420) crystal plane.

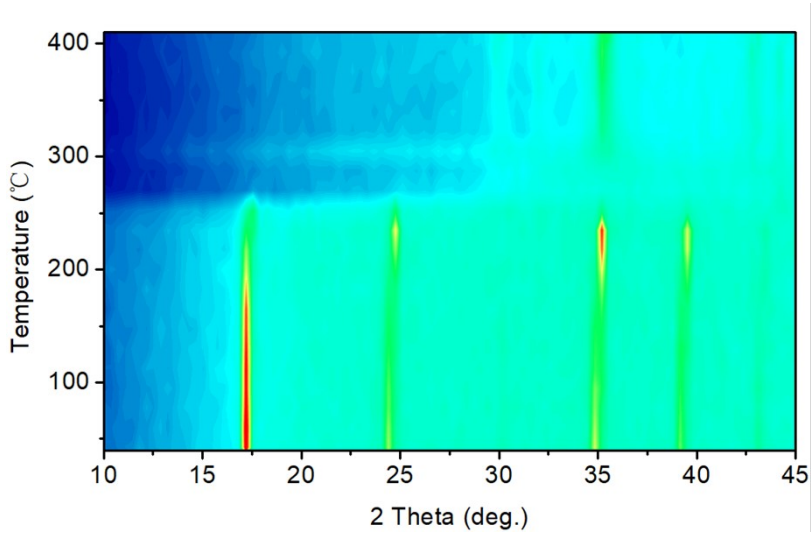

Fig. S7. In-situ XRD of NaFeHCF100-4.

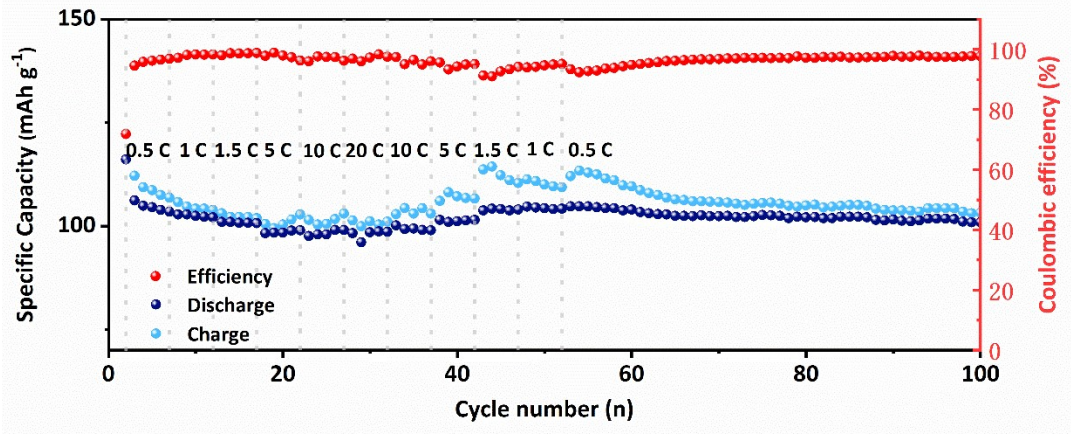

Fig. S8. Charge and discharge capacity of NaFeHCF100-4 electrode at different current densities.

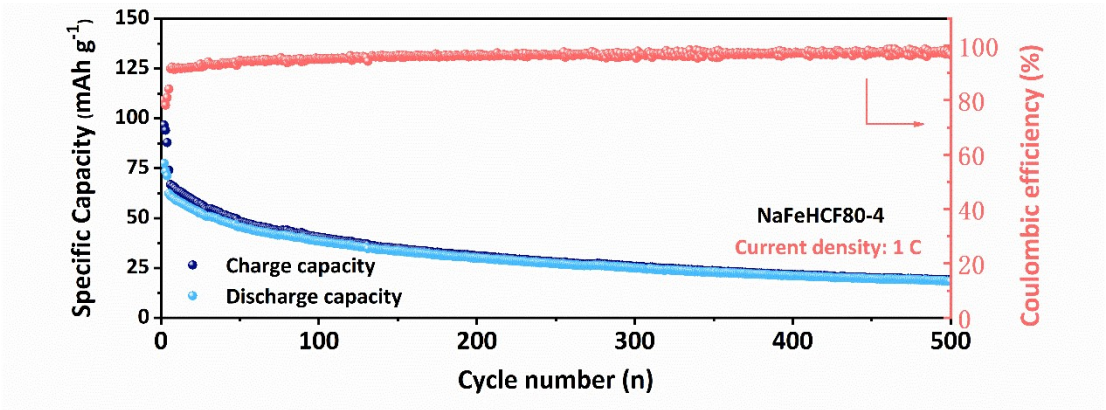

Fig. S9. Cycle performance of NaFeHCF80-4.

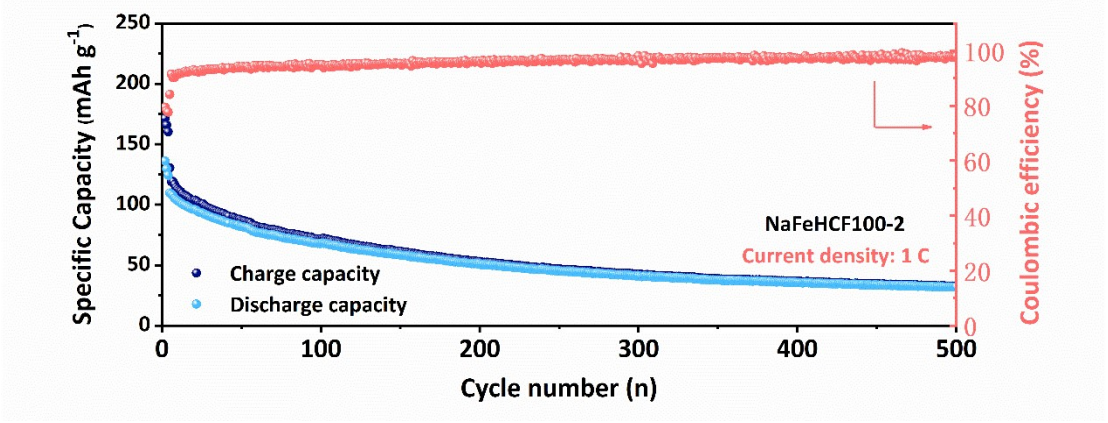

Fig. S10. Cycle performance of NaFeHCF100-2.

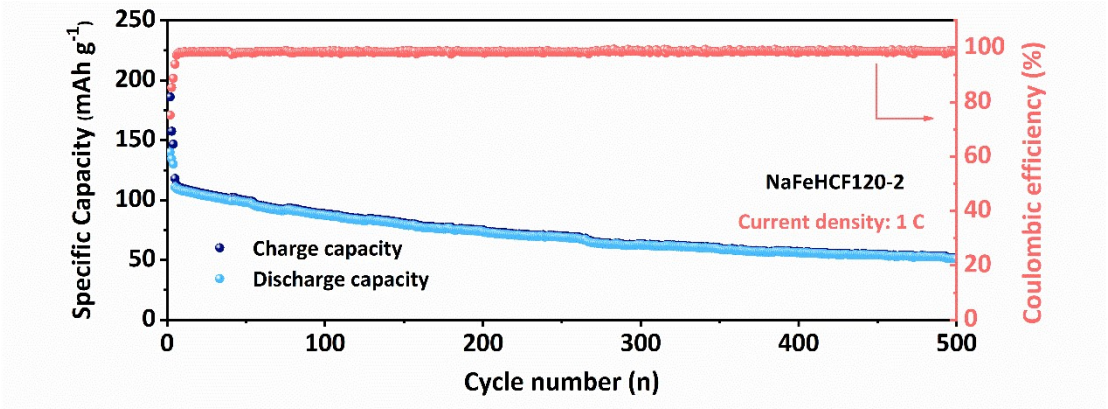

Fig. S11. Cycle performance of NaFeHCF120-2.

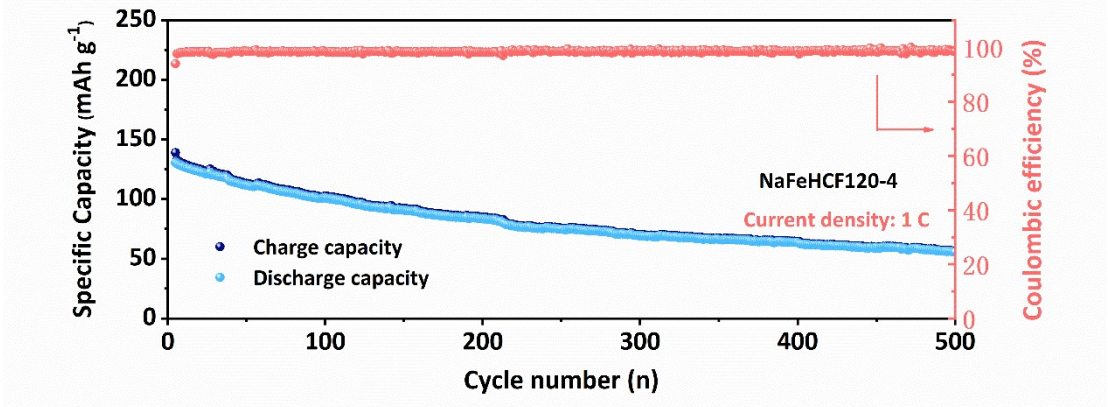

Fig. S12. Cycle performance of NaFeHCF120-4.

Table S1. Comparison of electrochemical properties of NaFeHCF synthesized from aqueous solution and anhydrous ethanol.

Samples	Synthetic medium	Specific capacity (mAh g^{-1})	Current density (mA g^{-1})
BR-FeHCF[1]	water	120	50
YSPB[2]	water	140	17
HQ-NaFe[3]	water	170	25
NFFCN-4M NaCl-160 °C[4]	water	92.5	50
Our work	anhydrous ethanol	150	17

References

1. Y. Huang, M. Xie, J. Zhang, Z. Wang, Y. Jiang, G. Xiao, S. Li, L. Li, F. Wu, R. Chen, *Nano Energy*, 2017, **39**, 273-283.
2. H. Hu, W. Liu, M. Zhu, Y. Lin, Y. Liu, J. Zhang, T. Chen, K. Liu, *Mater. Lett.*, 2019, **249**, 206-209.
3. Y. You, X. Wu, Y. Yin, Y. Guo, *Energy Environ. Sci.*, 2014, **7**, 1643-1647.
4. J. Sun, H. Ye, J. A. S. Oh, A. Plewa, Y. Sun, T. Wu, Q. Sun, K. Zeng, L. Lu, *Energy Storage Mater.*, 2021, **43**, 182-189.