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A Coordination Chemistry Strategy of Ammonia Molecular Pillaring for Structurally Reinforced Prussian Blue Cathodes in Sodium-Ion Batteries

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Experimental Section

Synthesis of FeHCF: In a typical synthesis, 12 mmol $Na_4Fe(CN)_6{\cdot}10H_2O$ and 15 g sodium citrate were dissolved in 200 mL deionized water to obtain a homogenous solution, labeled as solution A. Then, 15 g sodium citrate and 12 mmol $Na_4Fe(CN)_6{\cdot}10H_2O$ were dissolved in 200 mL deionized water, labeled as solution B. Solution A and B were then transferred quickly into a constant pressure drop funnel and into a three-neck flask (under Ar/N_2), respectively. Then, solution A was added dropwise into solution B, and the mixture was kept stirring at 800 rpm for 6 h and aged for 1 h before filtration. The precipitate was washed with deionized water and ethanol 3-5 times (200 mL each time), and finally, the wet powder was dried in a vacuum oven at 100 °C for 24 h.

Synthesis of FeHCF-HT: FeHCF was subjected to Ar at room temperature for 1 hour, then heated to 270 ℃ at a rate of 5 ℃/min, and annealed under Ar for 2 hours to obtain the HT sample.

Synthesis of FeHCF-HT-NH_3: The ammonia solution was prepared by diluting 50 mL of concentrated ammonia (25 wt%) with deionized water to a total volume of 300 mL. Then maintain the diluted concentrated ammonia solution at 60 ℃ for 6 hours, and connect the outlet to a tube furnace containing the HT sample. React at room temperature for 6 hours under Ar to obtain the secondary treated sample.

Material Characterization: Compositions and chemical states of the samples were characterized by X-ray diffraction (XRD, Bruker D8-Focus). Structures of all the as-prepared samples were characterized by scanning electron microscopy (SEM, HITACHI S4800). The Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Scientific Nicolet iS 50. The water content was obtained from thermogravimetric (TG) (NETZSCH TG 209 F3 Tarsus) measurement in N_2 atmosphere. XPS was measured on Thermo ESCALAB 250Xi with an Al-Kα (hv=1486.6eV) radiation source.

Electrochemical Characterization: The assembled CR 2032 coin-type cells in Ar filled glovebox were used to analyze the electrochemical performances of the as-prepared materials. The cathode consisted of active materials, Super P carbon, and polyvinyl difluoride (PVDF) binder at a weight ratio of 7:2:1, coated on an aluminum foil. After drying at 100 °C for 12 h, the electrodes were cut into circular pieces. The mass loading of the active materials was about 2.5 mg·cm^{-2}. 1 M $NaClO_4$ dissolved in EC/DMC (1:1 vol ratio) solvent with 5 vol% FEC was used as electrolyte. A glass fiber (Whatman) separator was used to isolate the cathode and sodium metal anode. The galvanostatic charge/discharge tests were carried out on a Neware Battery Testing System between 2.0 and 4.0 V. The cyclic voltametry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI660E electrochemical workstation. CV was performed in a potential window of 2.0-4.0 V (vs. Na^+/Na) at 0.1 mV·s^{-1}. EIS was conducted in the frequency range from 0.01 to 10^5 Hz.

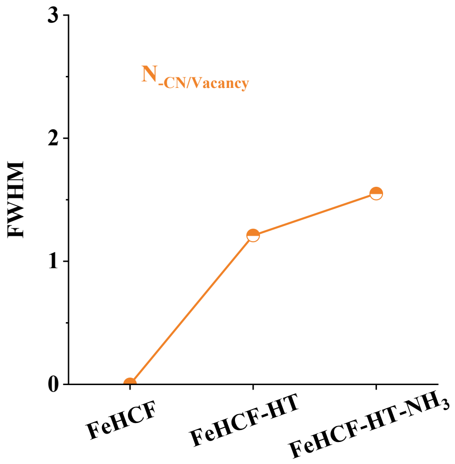

Fig. S1. Comparison of the full width at half maximum (FWHM) values of the characteristic -CN/vacancy peaks derived from the N 1s XPS spectra of FeHCF, FeHCF-HT, and FeHCF-HT-NH_3.

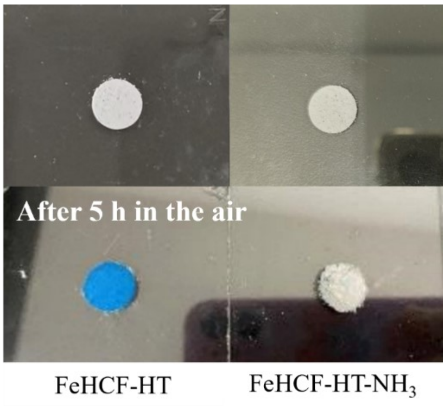

Fig. S2. Macroscopic visual evaluation of rehydration resistance.

Digital photographs displaying the color evolution of dehydrated FeHCF-HT and FeHCF-HT-NH$_3$ after exposure to ambient air for 5 h. The FeHCF-HT sample undergoes a noticeable color reversion to its original blue hue, indicative of spontaneous moisture reabsorption and the gradual restoration of the hydrated phase. In contrast, the FeHCF-HT-NH$_3$ sample largely preserves its initial color state. This observation suggests that the successful occupation of water sites by ammonia molecules significantly hinders the re-entry of atmospheric water, thereby enhancing the environmental stability of the framework.

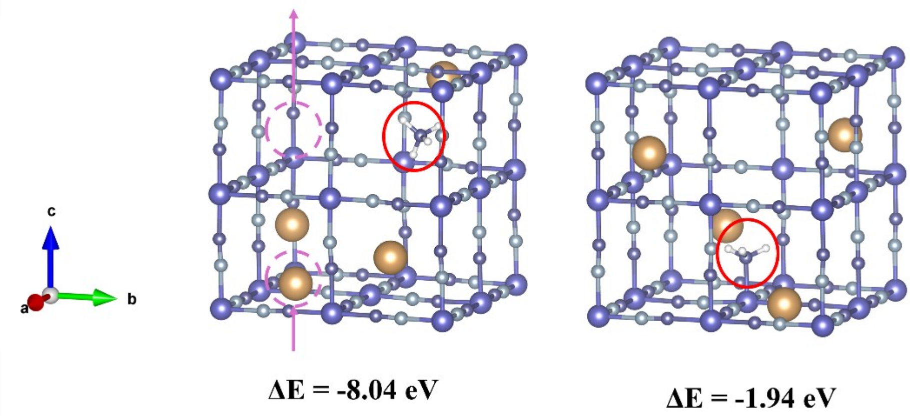

Fig. S3. DFT calculation of binding energies and structural configurations for interstitial NH_4^+ and vacancy NH_3.

The calculations reveal a significantly high binding affinity for NH_4^+ (ΔE = -8.04 eV) within the interstitial cages. The optimized structures illustrate the repulsion and resultant displacement of neighboring Na^+ ions upon the insertion of the bulky NH_4^+ guest (indicated by arrows and dashed circles).