

Supplementary Information

An Aqueous Rechargeable Copper Ammonium Hybrid Battery with Good
Cycling Performance

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Experimental section

Materials

$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (analytical reagent, 99.0%), anhydrous CuSO_4 (analytical reagent, 99.0%) and polyvinylpyrrolidone (PVP10, K29-32) were purchased from Macklin. KCl (guaranteed reagent, $\geq 99.8\%$), $(\text{NH}_4)_2\text{SO}_4$ (analytical reagent, $\geq 99.0\%$) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (analytical reagent, 99.0-102.0%) were purchased from Sinopharm. None of the chemicals were further purified before usage.

Preparation of N-CuHCF

In this research, a viable two-step synthesis was adopted to fabricate NH_4^+ -rich copper hexacyanohydroferrate (N-CuHCF). In the first step, $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$ was typically prepared via co-precipitation. Initially, 2.1123 g $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ was dissolved in 50 mL deionized (DI) water, labeled solution A. Subsequently, 0.8775 g anhydrous CuSO_4 , 3.7276 g KCl , and 4.0005 g PVP10 were mixed with 50 mL DI water, stirring until clear solution B was afforded. Afterwards, solution A was added dropwise into solution B under magnetic stirring. After 6 h of reaction, the resulting russet precipitate was collected by centrifugation and washed with DI water and ethanol several times, and then dried in vacuum at 80 °C overnight to obtain $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$. The second step was to prepare $(\text{NH}_4)_2\text{Cu}[\text{Fe}(\text{CN})_6]$ by utilizing ion-exchange method. Firstly, 0.1769 g $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$ was added into 50 mL DI water and ultrasonically dispersed for 20 min, labeled solution C. Following that, 1.3210 g $(\text{NH}_4)_2\text{SO}_4$ was solubilized in 50 mL DI water to form solution D. Eventually, solution C was added dropwise into solution D under magnetic stirring and kermesinus precipitate extracted immediately. The mixture was stirred 6 h, and the precipitate was collected by centrifugation, washed repeatedly with DI water and ethanol, and then vacuum-dried at 80 °C overnight to obtain $(\text{NH}_4)_2\text{Cu}[\text{Fe}(\text{CN})_6]$.

Preparation of electrolyte

Under magnetic stirring, 6.6072 g $(\text{NH}_4)_2\text{SO}_4$ and 1.2081 g $\text{Cu}(\text{NO}_3)_2$ were dissolved in 50 mL DI water to obtain homogeneous solution of 1 M $(\text{NH}_4)_2\text{SO}_4$ and 0.1 M $\text{Cu}(\text{NO}_3)_2$, in which 0.1 M $\text{Cu}(\text{NO}_3)_2$ was served as additive of electrolyte.

Material characterization

The crystal structure of obtained N-CuHCF sample was investigated by X-ray diffraction (XRD, Bruker D8 Advance) using Cu-K α radiation ($\lambda = 0.154$ nm) at 40 kV and 40 mA with 2θ range of 10 to 80°. The morphology of composite was observed by scanning electron microscopy (SEM, JEOL JSM-6390) and transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin). The thermogravimetric analysis (TGA, PerkinElmer TGA 7) data were collected under N₂ flow at a ramp-up rate of 5 °C min⁻¹ from 25-600 °C. To determine the chemical state and composition of the cathode material, X-ray photoelectron spectroscopy (XPS) was carried out on PerkinElmer PHI 550. Fourier transform infrared (FTIR) spectra were measured by NICOLET 6700 in the range of 1000-4000 cm⁻¹ via KBr disk method.

Electrochemical measurements

The N-CuHCF working electrode was prepared by mixing in a mass ratio of 60% N-CuHCF, 30% acetylene black and 10% polytetrafluoroethylene (PTFE, Macklin) to obtain a homogeneous slurry, which was coated on carbon paper current collectors and then dried in vacuum at 60 °C overnight. Each carbon paper was loaded with at least 2 mg cm⁻² of active material. Three-electrode cell and full cell were assembled for electrochemical measurements. The three-electrode cell contained 1 M (NH₄)₂SO₄ per 0.1 M Cu(NO₃)₂ electrolyte, a N-CuHCF working electrode, a Pt counter electrode and a Ag/AgCl reference electrode ($E = 0.1989$ V vs. normal hydrogen electrode, NHE) while the full cell used 1 M (NH₄)₂SO₄ and 0.1 M Cu(NO₃)₂ homogeneous solution as electrolyte, N-CuHCF on a carbon paper as cathode and a copper sheet (20×15 mm) as anode. Cyclic voltammetry (CV) tests were carried out by BioLogic VSP electrochemical workstation from 0.5 to 1 V at various scan rates of 0.1 mV s⁻¹, 0.2 mV s⁻¹, 0.3 mV s⁻¹, 0.4 mV s⁻¹ and 0.5 mV s⁻¹. The cycling and rate performance were conducted within 0.5-1 V using a multichannel LANHE, CT2001A battery test instrument. The specific capacity of Cu-(N-CuHCF) battery was based on the active material mass of working electrode.

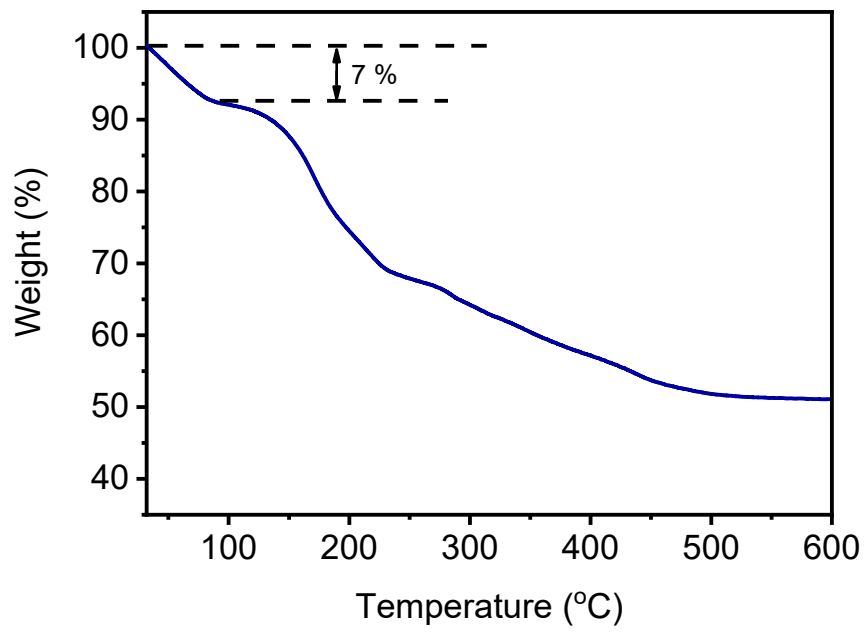


Figure S1 TG curve of N-CuHCF.

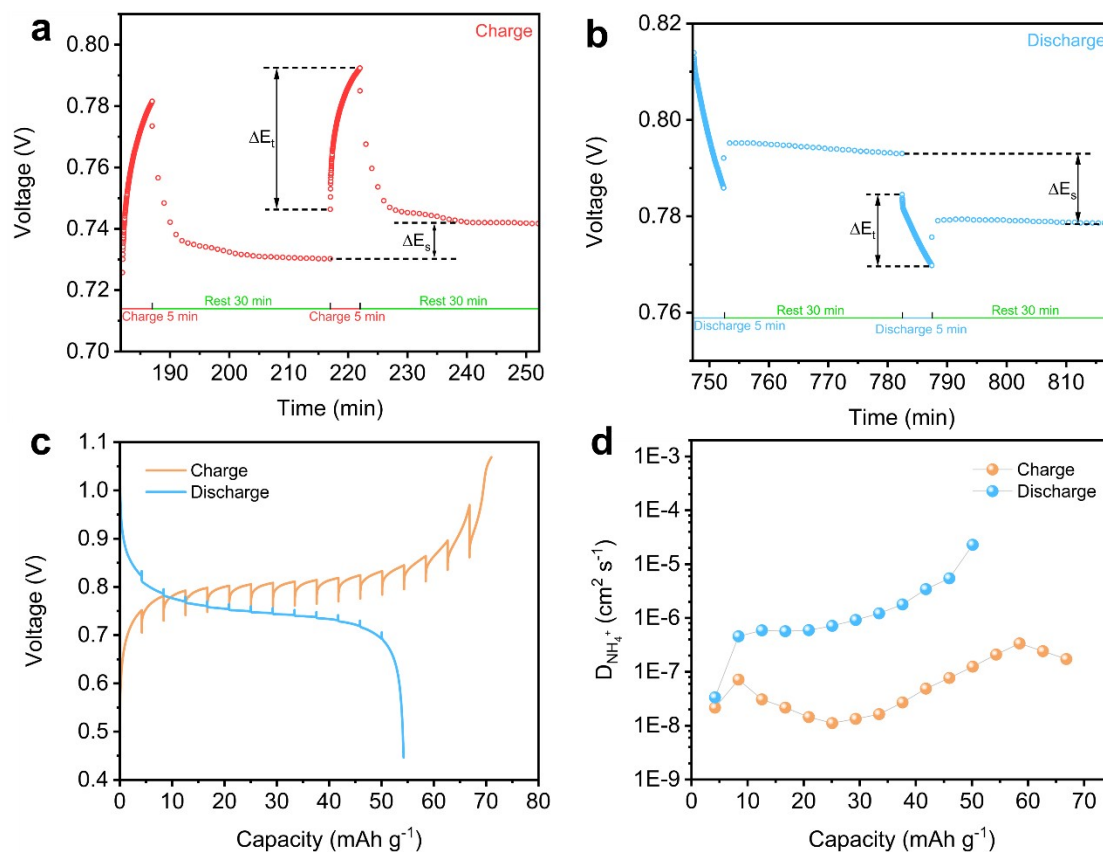


Figure S2. (a, b) Schematic illustration for selected steps of the GITT curves of Cu/N-CuHCF full battery during charge/discharge process. (c) Charge/discharge GITT curves for the N-CuHCF electrode at 0.2 A g⁻¹. (d) The NH₄⁺ diffusion coefficient calculated from GITT.

The Galvanostatic Intermittent Titration Technique (GITT) measurements are performed at the first discharge-charge curves at 0.2 A g⁻¹. Subsequently, a galvanostatic pulse (charge or discharge) for 5 min and then rest for 30 min to reach the voltage equilibrium until 1.0 V (0.5 V). The NH₄⁺ ion diffusion coefficients can be calculated based on the following formula:

$$D_{NH_4^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2$$

where τ is the duration time of current pulse, m_B , M_B and V_M correspond to the mass of the active material (g), molecular weight (g mol⁻¹) and molar volume (cm³ mol⁻¹), respectively. A represents the total contacting area between electrode and electrolyte (cm²). ΔE_τ is the voltage change in the over cell voltage upon each current pulse, while ΔE_s is the voltage change about steady state voltage between two adjacent steps.

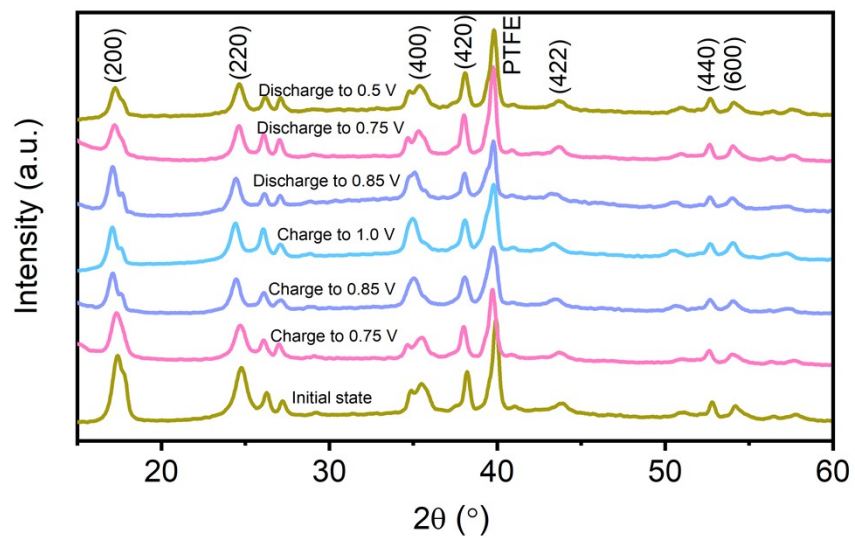


Figure S3. XRD patterns of N-CuHCF collected at different charge/discharge states.

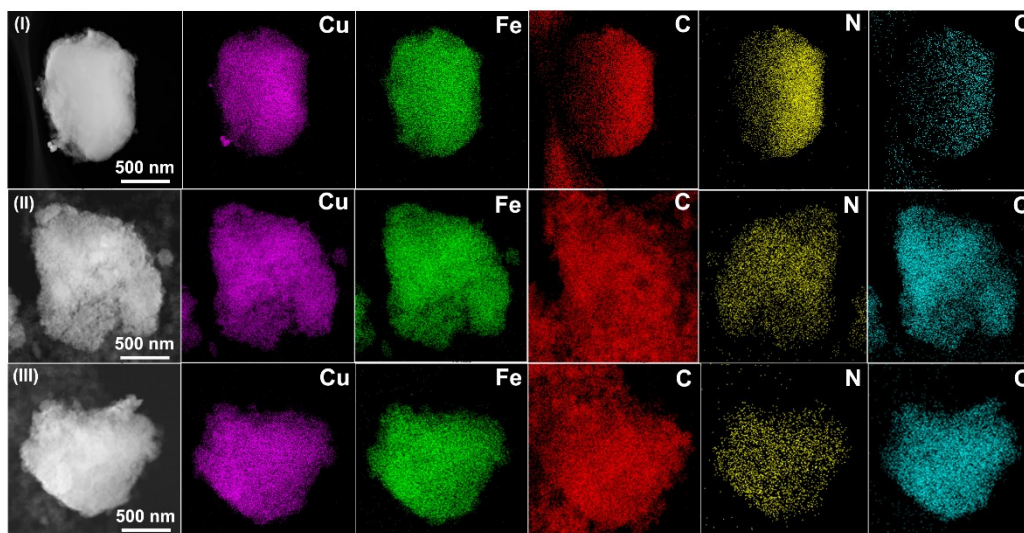


Figure S4. EDS mapping of elemental distributions (Cu, Fe, C, N, O) on N-CuHCF electrode: (I) pristine, (II) discharged and (III) charged states.

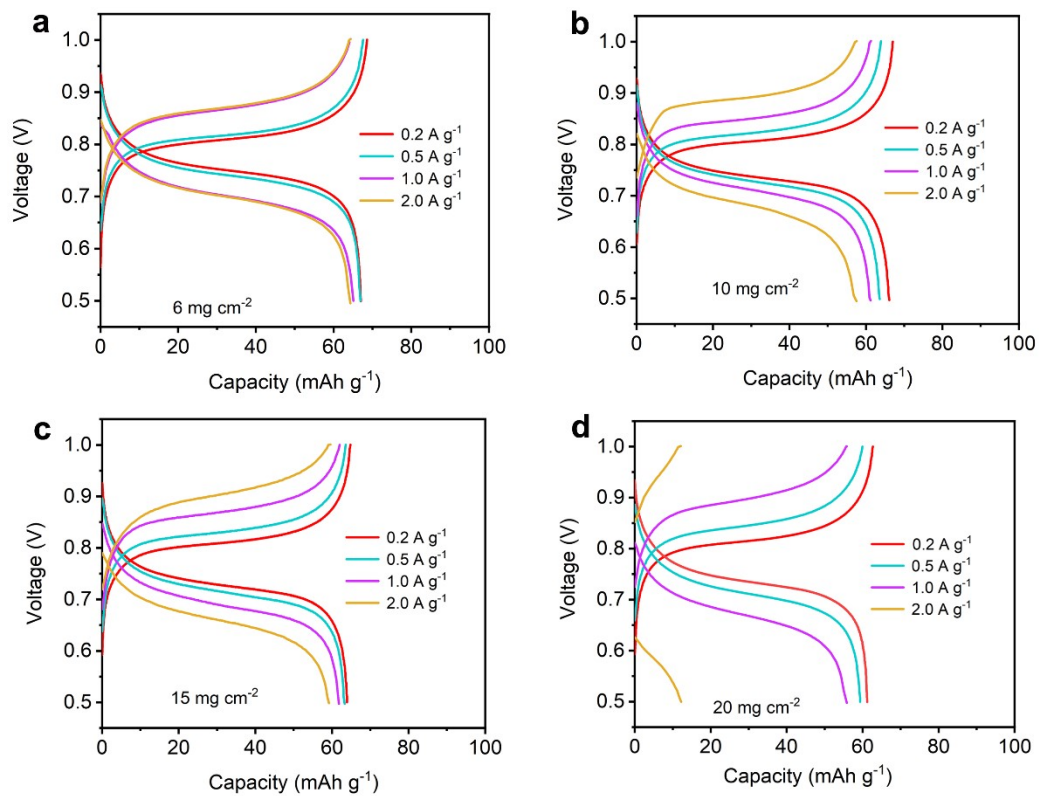


Figure S5. Rate performances of Cu//N-CuHCF cells with various mass-loadings (from 6 mg cm⁻² to 20 mg cm⁻²) in N-CuHCF cathode.

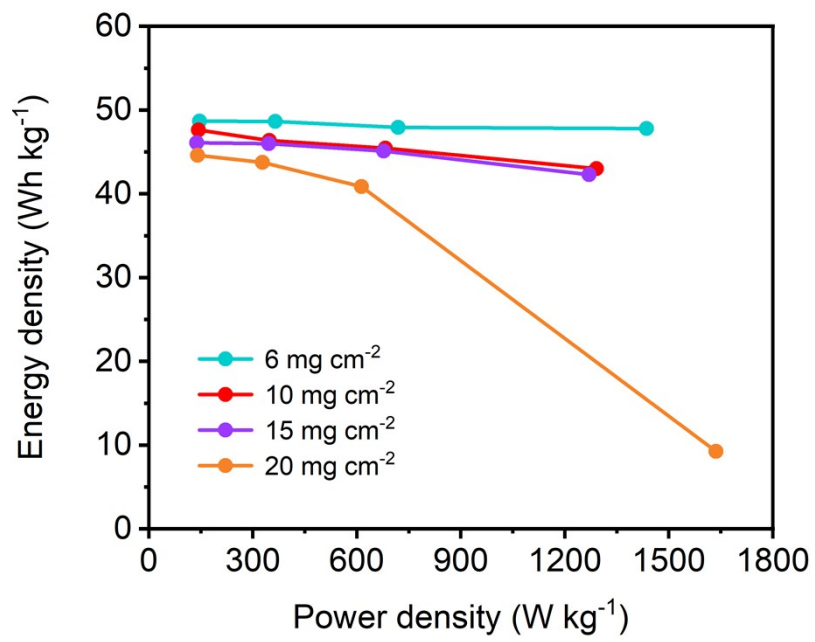


Figure S6. Ragone plot with different mass-loadings.

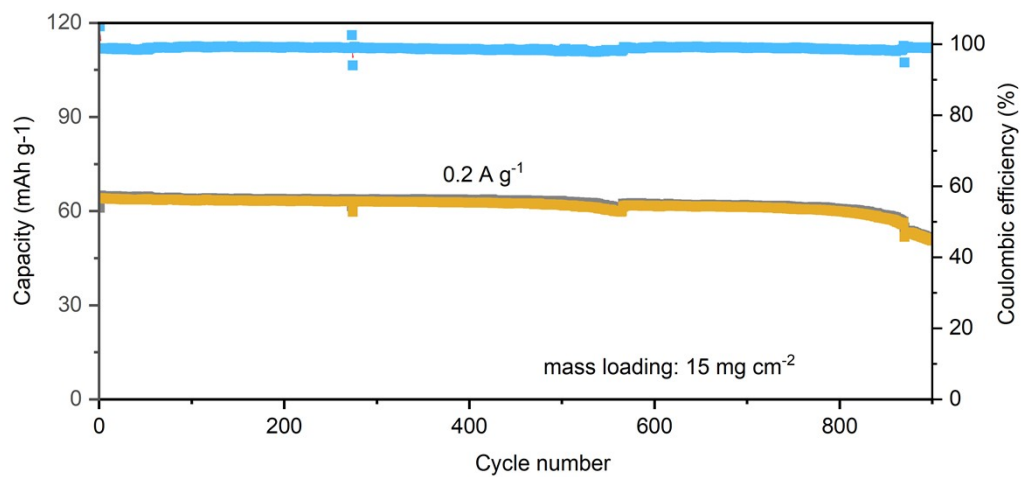


Figure S7. Cycle performance of the Cu//N-CuHCF battery with mass-loading of 15 mg cm⁻².

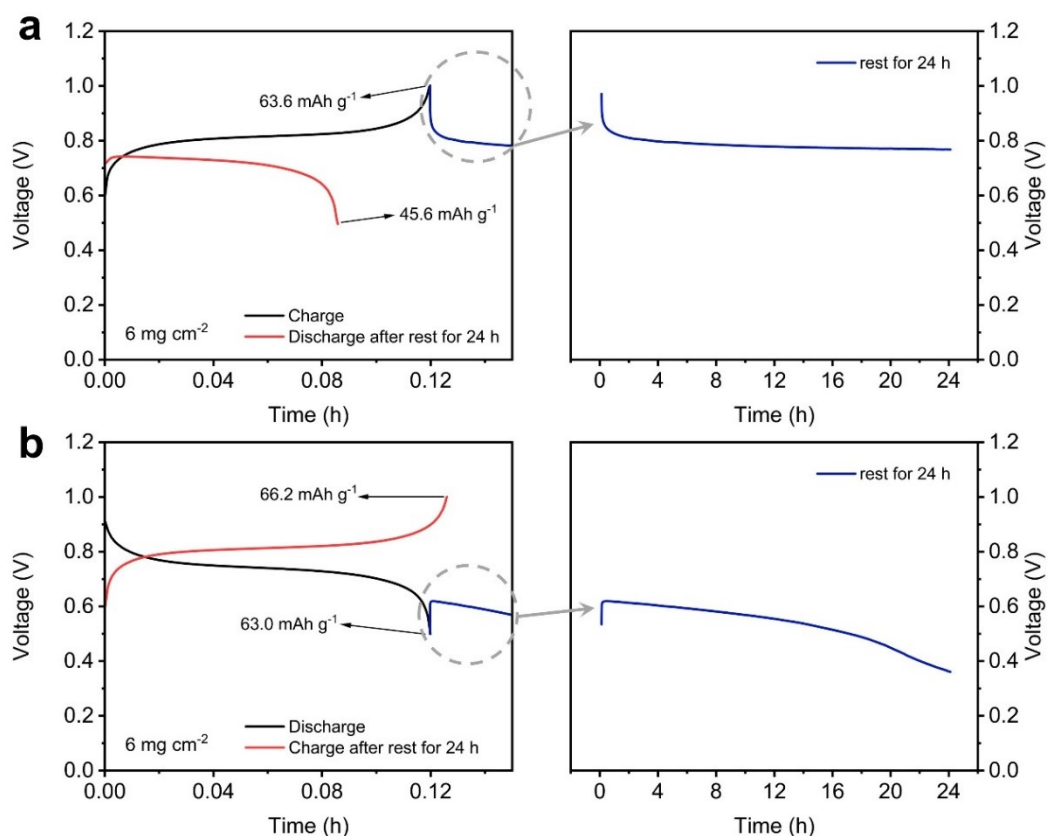


Figure S8. Self-discharge behavior tested at a current density of 0.5 A g^{-1} . (a) when firstly charged to 1.0 V, and then discharged to 0.5 V after rest for 24 hours. (b) when firstly discharged to 0.5 V, and then charged to 1.0 V after rest for 24 hours.

Firstly, we investigated the self-discharge at fully charged condition. In this test, the cell was fully charged to 1.0 V at 0.5 A g^{-1} followed by a rest step of 24 h, which was then discharged to 0.5 V at the same current. The discharge after rest delivers a capacity of 45.6 mAh g^{-1} , which is $\sim 72 \%$ of that (63.6 mAh g^{-1}) on charge (**Figure S8a**). The state-of-charge test was also investigated with the similar process. After discharged to 0.5 V, the cell experienced a 24 h rest. The consequent recharge shows a capacity of 66.2 mAh g^{-1} , which is slightly higher than that (63 mAh g^{-1}) on discharge (**Figure S8b**). This phenomenon may be caused by the self-discharge of N-CuHCF electrode.