

Water-in-Salt Electrolyte Avoiding Organic Material Dissolution and Enhanced Kinetics Property for Aqueous Potassium Ion Batteries

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Experimental section:

Materials and Chemicals: Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA, 98%, Aladdin), potassium bis(fluorosulfonyl) imide (KFSI, 99.9%, Suzhou Fluolyte Co., Ltd), Potassium hexacyanoferrate (II) trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$, Sigma-Aldrich, $\geq 99\%$), hydrochloric acid (Sigma-Aldrich, 36.5-38%), ethylene glycol (Sigma-Aldrich, 99.8%) and glass microfiber separator (GF/C, Cat no. 1822-090, Whatman) were used.

Synthesis of β -PTCDA: β -PTCDA was synthesized by annealing PTCDA at 450 °C for 4 h under Ar with a heating rate of 5 °C min⁻¹.

Synthesis of KFHCF: The synthetic method is consistent with previous report by Wang et al. [S1] Potassium hexacyanoferrate (II) trihydrate (0.25 mmol) was added to a 0.1 M solution of hydrochloric acid in ethylene glycol (50 mL). A clear solution was obtained upon stirring and the mixture was transferred into a Teflon-lined stainless steel autoclave, which was subsequently heated at 80 °C for 24 h. The resultant blue solid was collected by filtration and washed several times with distilled water and then with ethanol and dried in a vacuum oven at 60 °C overnight.

Physical Characterization: X-ray diffraction (XRD) patterns of the β -PTCDA were recorded using a Bruker D8 Advance Diffractometer with Cu K α radiation. Bruker VERTEX 70 were used to conduct the FTIR. JEOL JSM-6700F was used for SEM images.

Preparation of "Water-in-Salt" Electrolytes: The electrolytes were made by dissolving 1 m, 10 m, 20 m and 30 m KFSI in deionized H₂O. The 30 m electrolyte was warmed to 80 °C to facilitate the complete dissolution of KFSI in H₂O.

Electrochemical Characterization: For fabrication of anode electrodes, the active material β -PTCDA, Super P conductive additive and polyvinylidene fluoride (PVDF) binder were prepared into slurry with N-Methyl-2-pyrrolidone (NMP) with a weight ratio of 7: 2: 1, then coat on titanium foil to make working electrodes. The counter electrodes were self-standing films of activated carbon, which were composed of 90 wt.% activated-carbon, and 10 wt.% poly tetra fluoroethylene (PTFE) as binder. The

electrochemical performance was tested in a three-electrode Swagelok cell (a T-cell), which comprised β -PTCDA as the working electrode, activated carbon as the counter electrode, an Hg/Hg₂Cl₂ reference electrode (sat. KCl, 0.241 V vs. SHE), and Whatman filter paper as separators. The GITT data were collected at a current density of 200 mA g⁻¹ for 1 min and a rest interval of 30 min. Aqueous full potassium-ion batteries (AFKIBs) were likewise tested in a T-cell, with preactivated cathodes and anodes materials. For preactivation, a half cell was first established using the active material as the working electrode, which was then charged-discharged for 5 cycles at 0.2 A g⁻¹. Then the cells were disassembled, and a AFKIB was assembled employing the preactivated anode and cathode. The anode to cathode mass ratio was 1: 1. In a half cell, the mass loading for active materials without the Super P conductive additive and binder is ≈ 1 mg cm⁻². All the electrochemical tests were carried out at room temperature. Galvanostatic discharge-charge cycling was performed on Land-2001A (Wuhan, China) automatic battery tester. Cyclic voltammetry (CV) was carried with a VSP multichannel potentiostatic-galvanostatic system (Bio-Logic SAS, France). Electrolyte conductivity experiments were carried out using a Multi 3500i conductivity tester (Xylem Analytics).

For the detection of dissolved PTCDA, the cycled separators were soaked in 1 ml NaOH solution with concentration of 2 mol L⁻¹. As is known that NaOH would destroy the structure of the anhydride in β -PTCDA and turns color from red to green.^[S2]

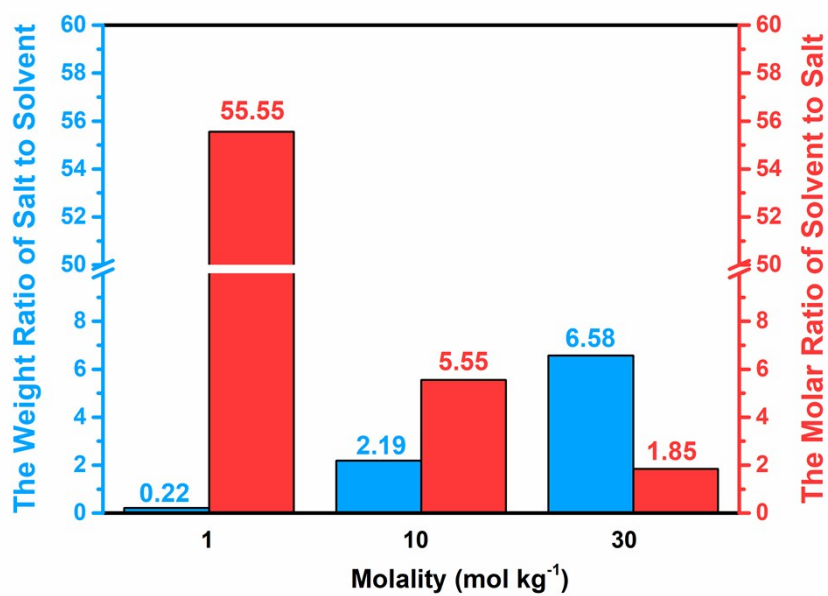


Fig. S1 The weight and molar ratio of KFSI and H₂O in KFSI-H₂O binary system.

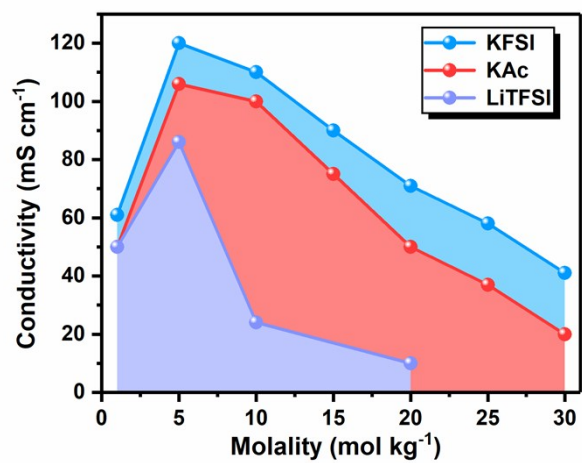


Fig. S2 Measured conductivity of KFSI, KAc and LiTFSI.

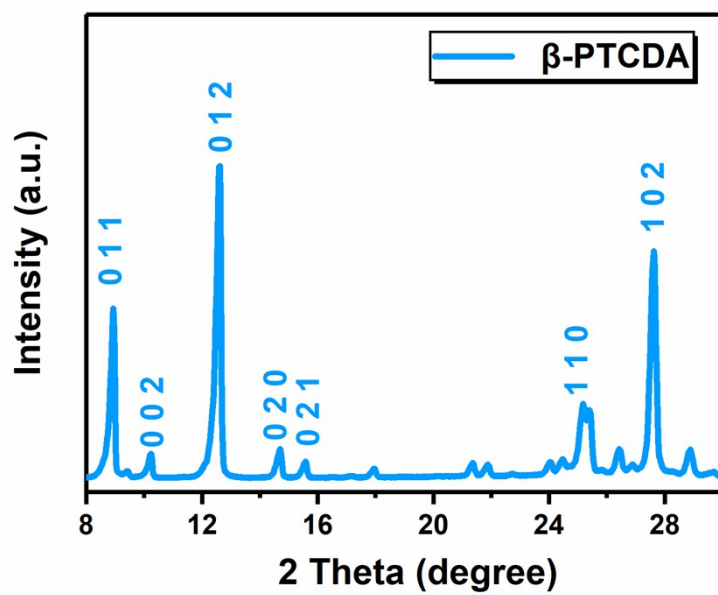


Fig. S3 XRD pattern of β -PTCDA. [S3]

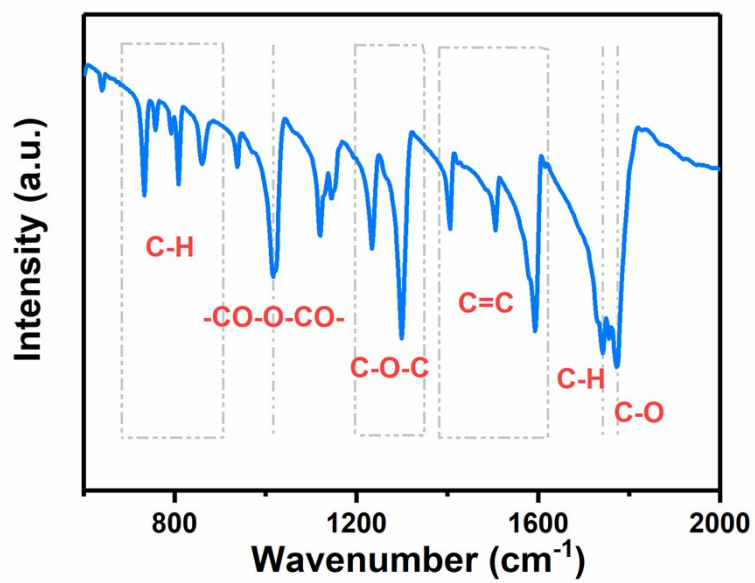


Fig. S4 FTIR spectra of β -PTCDA. ^[S3]

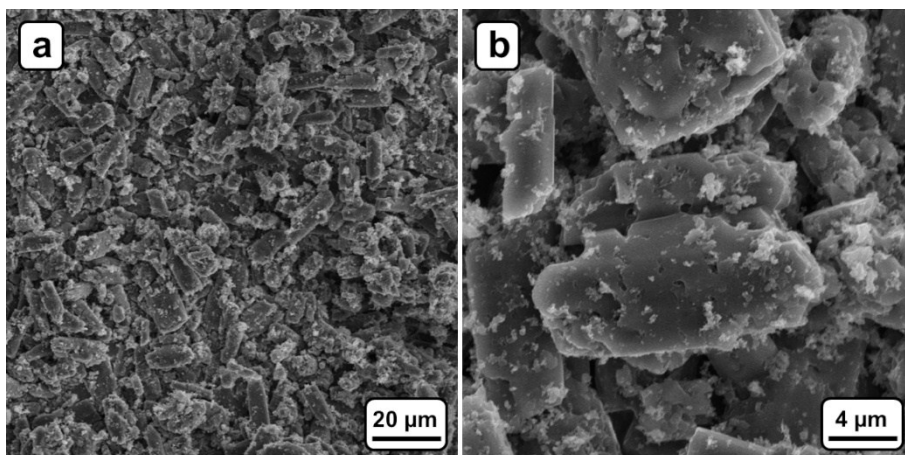


Fig. S5 SEM of β -PTCDA.

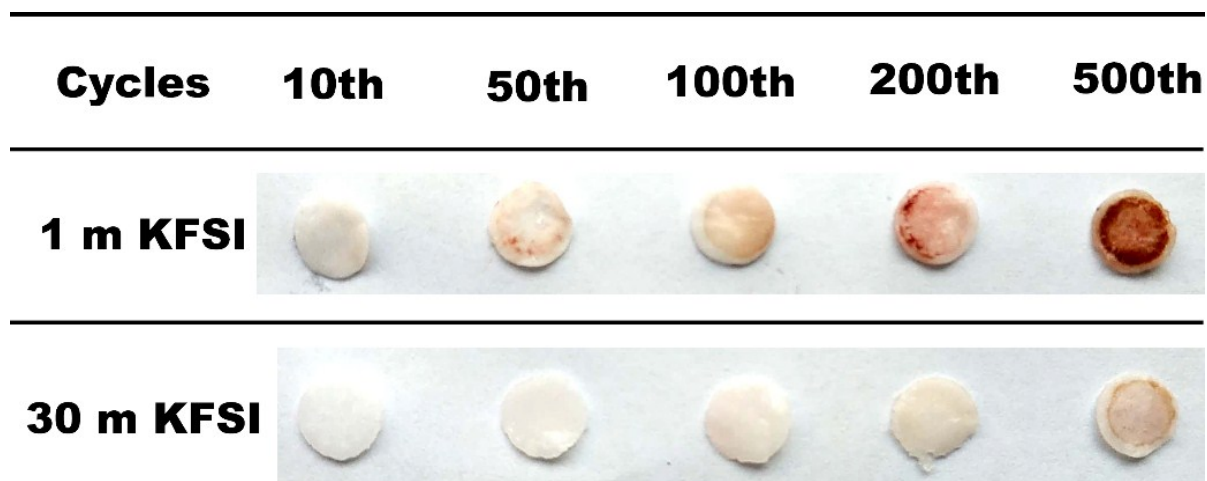


Fig. S6 The digital photographs of the separators with adsorbed electrolyte of KFSI (1m) and KFSI (30 m) after different cycles.

As shown in Fig. S4, after 500 cycles with the electrolyte of 1 m KFSI, the active material dissolved in electrolyte badly, which would cause the rapid capacity fading. But with the electrolyte of 30 m KFSI, the active material dissolved in electrolyte slightly after 500 cycles.

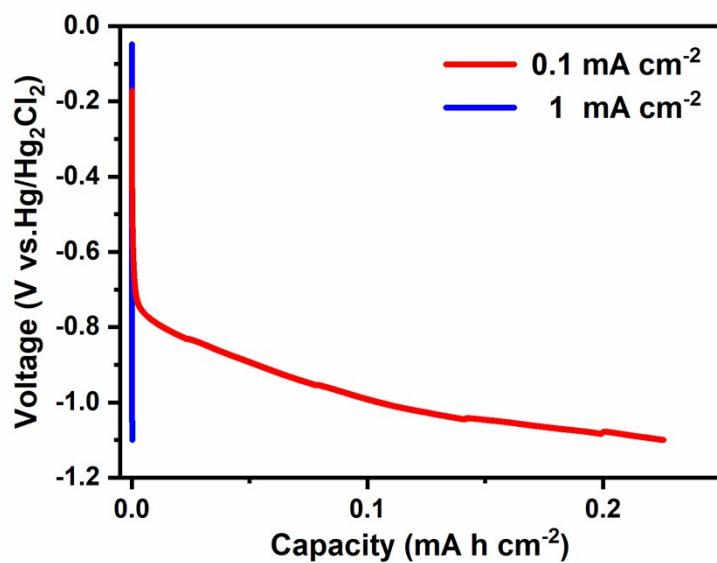


Fig. S7 Discharge capacities of three-electrode battery using inert Ti working electrode at small and large current density.

Activated carbon is used as counter electrode, Hg/Hg₂Cl₂ is used as reference electrode and 1 m KFSI solution is used as electrolyte. The capacity at low voltage range could be attributed to hydrogen evolution reaction.



Fig. S8 Desolved K₂PTCDA in water.

After discharged to -1.1 V, the electrode was put in water and shaken. Obviously dissolution could be observed.

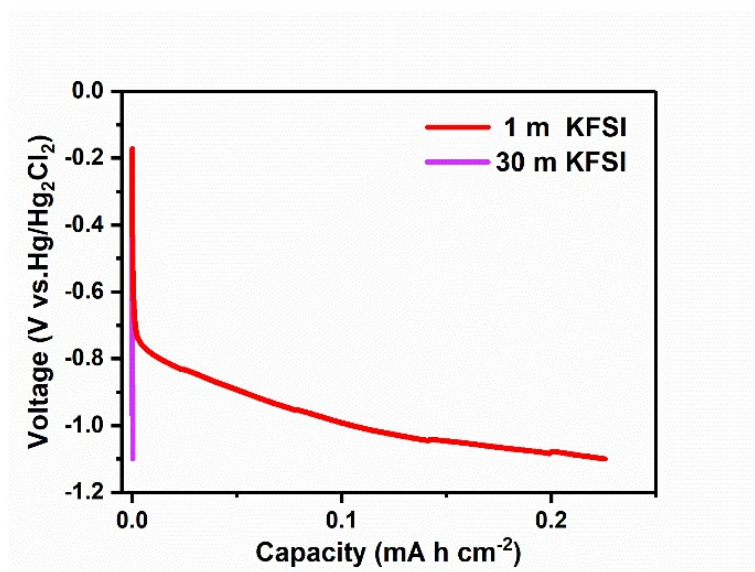


Fig. S9. The discharge capacities of three-electrode battery using inert Ti working electrode and KFSI electrolyte with different concentration (1 m and 30 m).

Activated carbon is used as counter electrode, Hg/Hg₂Cl₂ is used as reference electrode. The current density is 0.1 mA cm⁻². The capacity at low voltage range could be attributed to hydrogen evolution reaction. Thus it could be seen that hydrogen evolution is suppressed by high concentration KFSI electrolyte.

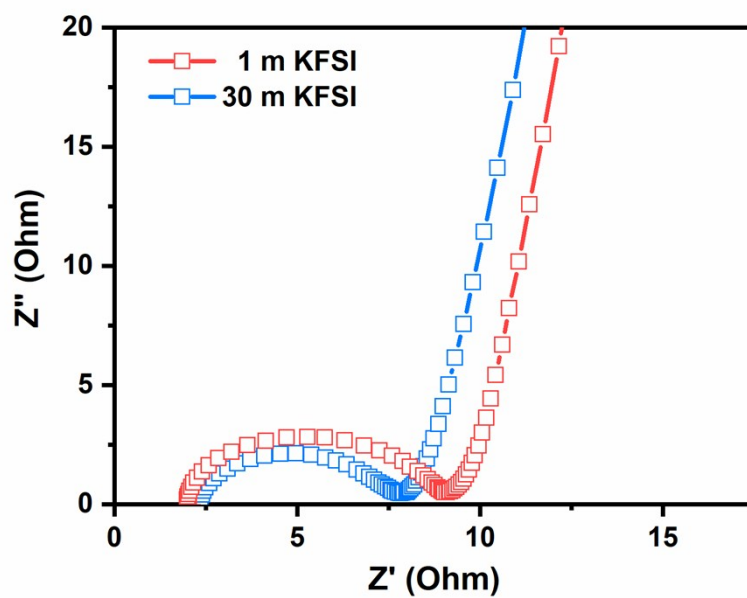


Fig. S10 Electrochemical impedance spectra of β -PTCDA after 5 cycles with 1 m KFSI electrolyte and 30 m KFSI electrolyte.

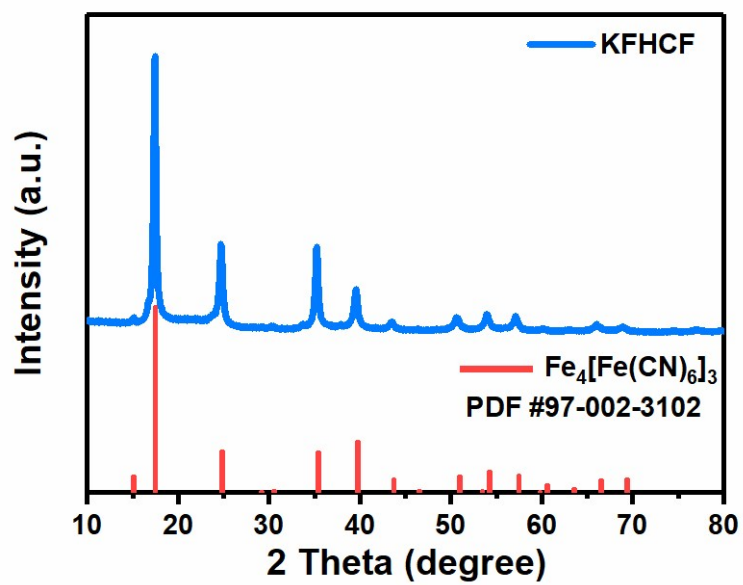


Fig. S11 XRD pattern of KFHCF.

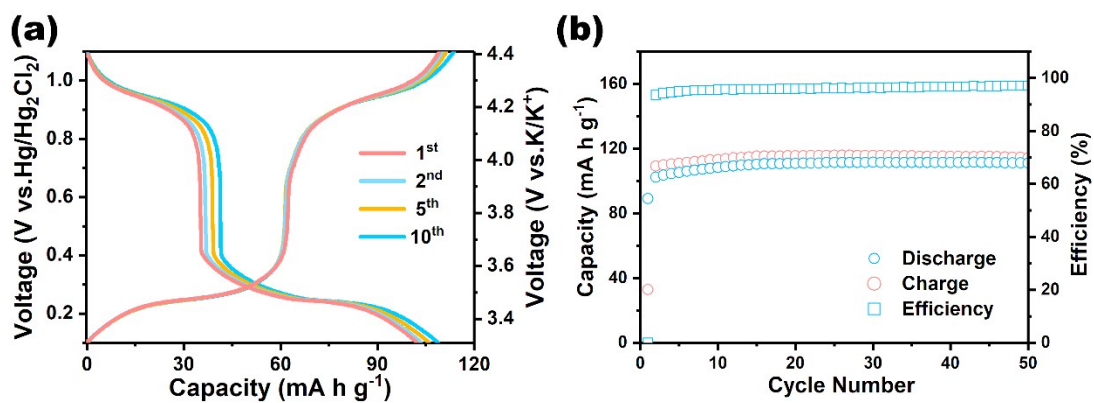


Fig. S12 (a) Galvanostatic discharge/charge curves of KFHCF at a current density of 0.2 A g^{-1} in the voltage range of $0.1 \text{ V} - 1.1 \text{ V}$ vs $\text{Hg}/\text{Hg}_2\text{Cl}_2$ with 30 m KFSI electrolyte. (b) Cycle performance of KFHCF at a current density of 0.2 A g^{-1} with 30 m KFSI electrolyte. The performance of KFHCF is tested in three-electrode battery.

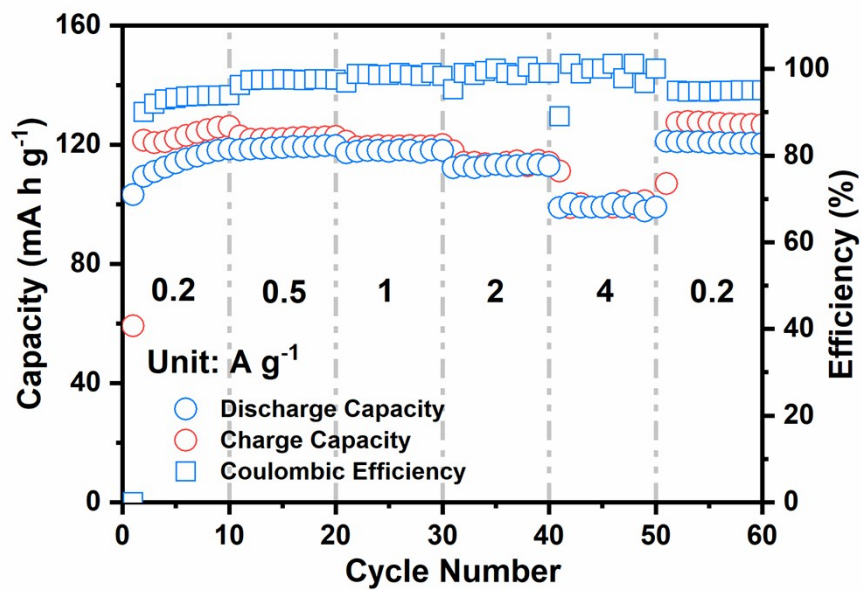


Fig. S13 Rate performance for KFHCF at different current densities with 30 m KFSI electrolyte in a three-electrode battery.

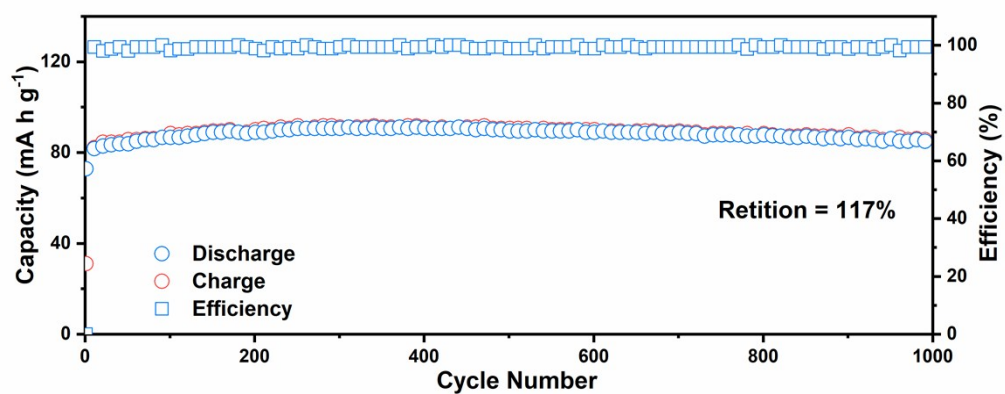


Fig. S14 Cycle performance for KFHCF at current density of 2 A g⁻¹ with 30 m KFSI electrolyte in three-electrode battery.

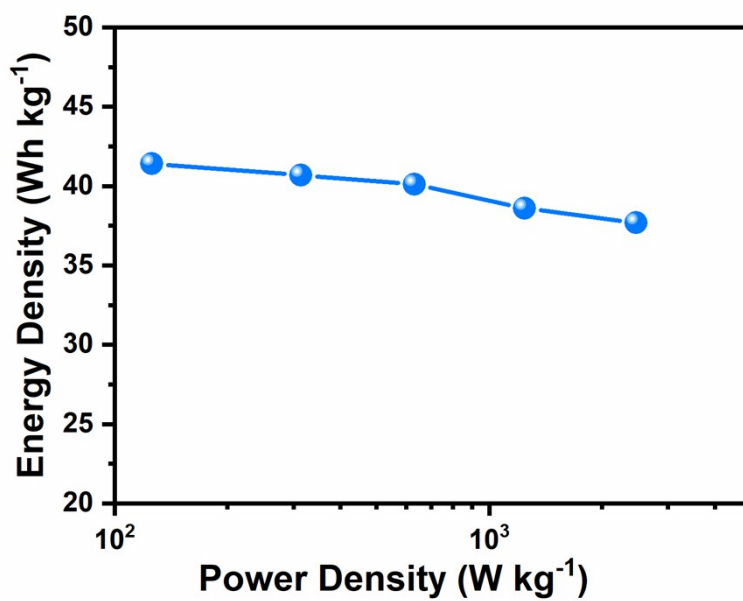


Fig. S15 Ragone plot of the aqueous full K-ion battery.

Notes and references

- [S1] D. Su, A. McDonagh, S. Z. Qiao and G. Wang, *Adv Mater*, 2017, **29**, 1604007.
- [S2] T. Yang, Y. Cui, Z. Li, H. Zeng, S. Luo, W. Li, *J. Hazard. Mater*, 2018, **357**, 475.
- [S3] L. Fan, R. Ma, J. Wang, H. Yang and B. Lu, *Adv Mater*, 2018, **30**, 1805486.