Electronic Supplementary Information

Iron Phosphate Hydroxide Hydrate as a Novel Anode Material for Advanced Aqueous Full Potassium-Ion Batteries

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Experimental Section

Synthesis of $Fe_{1.19}PO_4(OH)_{0.18}(H_2O)_{0.3}$ (IPHH): All chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd (China) and were used without further treatment. The $Fe_{1.19}PO_4(OH)_{0.18}(H_2O)_{0.3}$ were synthesized through a typical hydrothermal method. Firstly, 1 mmol ferric citrate powder (98%), 8 g citric acid (AR), and 20 mL ethylene glycol (AR) were added to 20 mL deionized water with continuous magnetic stirring at room temperature for 0.5 h. Then 3.5 g phosphoric acid (AR, ≥85 wt%) was added to the above solution with continuous magnetic stirring for another 0.5 h. The obtained solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 24 h. Finally, the obtained pale green powder was collected by centrifugation, washed with deionized water, and dried at 80 °C for 12 h.

Synthesis of $K_2Zn_3(Fe(CN)_6)_2$ (KZF): In a typical procedure, 1 mmol $ZnSO_4$ powder (AR) and 15 mmol potassium citrate powder (AR) were dissolved into 100 mL deionized water (solution A). 1 mmol $K_4Fe(CN)_6{\cdot}3H_2O$ powder (AR) was dissolved into 100 mL deionized water (solution B). Then solution B was dropped into solution A slowly with continuous magnetic stirring for 24 h. Finally, the obtained white powder was

collected by centrifugation, washed with deionized water for three times, and dried at 110 °C for 12 h.

Preparation of (20+30) m "water-in-salt" electrolyte: Typically, 20 mmol KCF_3SO_3 powder (97%) and 30 mmol KFSI powder (99%) were dissolved into 1.0 g deionized water to obtain (20+30) m "water-in-salt" electrolyte (H_2O: K^+ = 1.11: 1 in a mole ratio).

Materials Characterization: The crystal structures of anode and cathode samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) with Cu K_α (λ = 1.5418 Å). The morphologies and size of all samples were characterized by scanning electron microscopy (SEM, ZEISS SUPRA®55) and transmission electron microscope (TEM, JEM-3200FS) with an energy dispersive spectrometer (EDS) for elemental analysis. The chemical compositions of the as-prepared IPHH sample were examined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY2000-2 HORIBA JOBIN YVON) for K and Fe elements and thermogravimetric analysis (TGA) with the heating rate of 5 °C min^{-1} in a nitrogen atmosphere. The valence of Fe element in IPHH sample in pristine, fully discharged, and full charged states were analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific, Escalab 250Xi).

Electrochemical Characterization: The electrochemical properties of the IPHH sample were performed at room temperature using a half-cell configuration, and the electrochemical properties of the IPHH//KZF full cell were performed using CR2032-type coin cells. To prepare the IPHH electrodes, IPHH samples were mixed with conductive material (Ketjen black) and binder (polytetrafluoroethylene, PTFE) at a weight ratio of 7:2:1 with the diluent of isopropyl alcohol. The mixture was pressed into a film to cut into disks and then dried at 110 °C for 12 h under vacuum. After dying, these disks were pressed onto Ti mesh. The average mass loading of the electrodes is about 2 mg cm^{-2}. The KZF electrode and carbon electrode were prepared in the same way. The cyclic voltammetric (CV) tests and galvanostatic measurements of the IPHH samples were carried out in (20+30) m "water-in-salt" electrolyte by using a three-electrode system. The system consists of the above IPHH electrode (working

electrode), carbon electrode (counter electrode), and Hg/Hg_2SO_4 reference electrode. The test voltage range is -1.7 to -0.2 V (*vs.* Hg/Hg_2SO_4). For galvanostatic measurements of the full battery, the IPHH electrode and KZF electrode were assembled into a coin cell CR2032, in which the IPHH electrode was used as the working electrode while the KZF electrode was used as both counter electrode and reference electrode. The amount of electrolyte used in CR2032-type coin cells is 100 μL. Glass microfiber filter (Whatman) is used as the separator. The test voltage range is 0 to 2.5 V. The CV measurements were conducted at various scan rates on a CHI660D electrochemical workstation (Chenhua Instrument Company, Shanghai, China). The electrochemical tests were measured on a NEWARE battery test system. All electrochemical tests were performed at atmospheric pressure and room temperature.

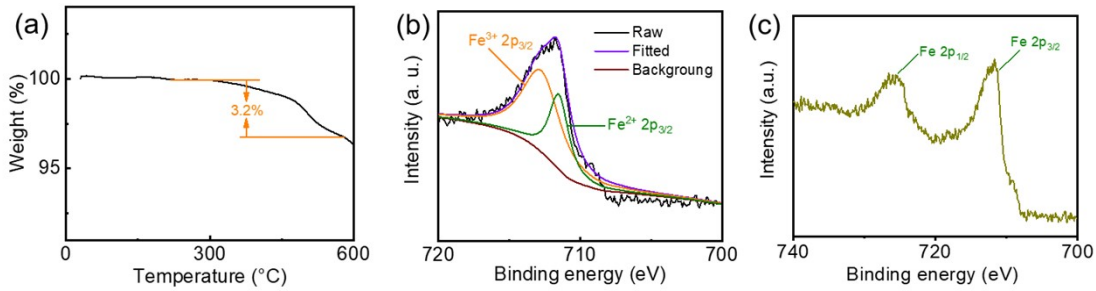

Fig. S1 (a) TGA curve, (b) Fe $2p_{3/2}$ XPS spectra and (c) Fe 2p XPS spectra of IPHH sample.

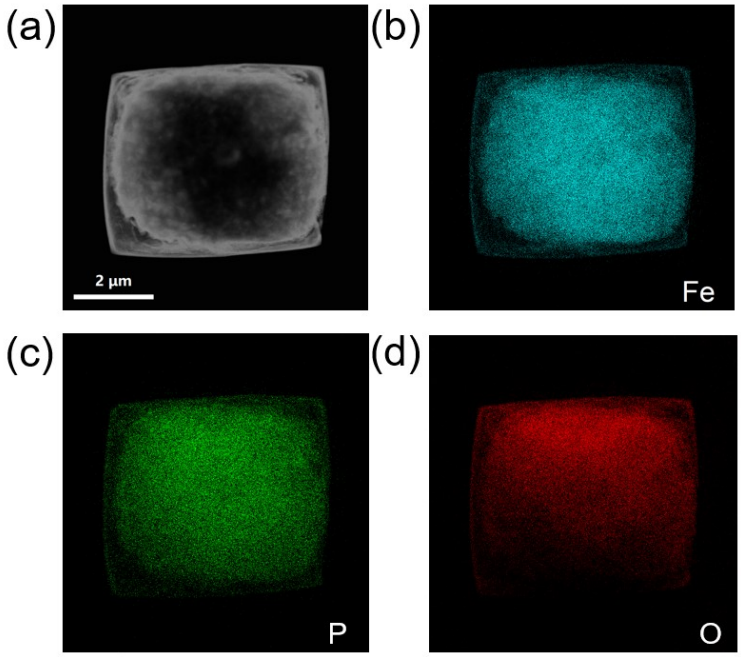

Fig. S2 EDX images of IPHH sample.

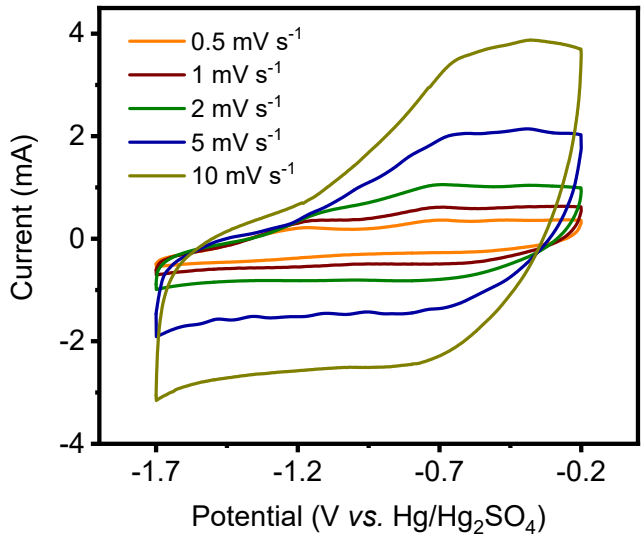

Fig. S3 CV curves of IPHH electrode at different scanning rates.

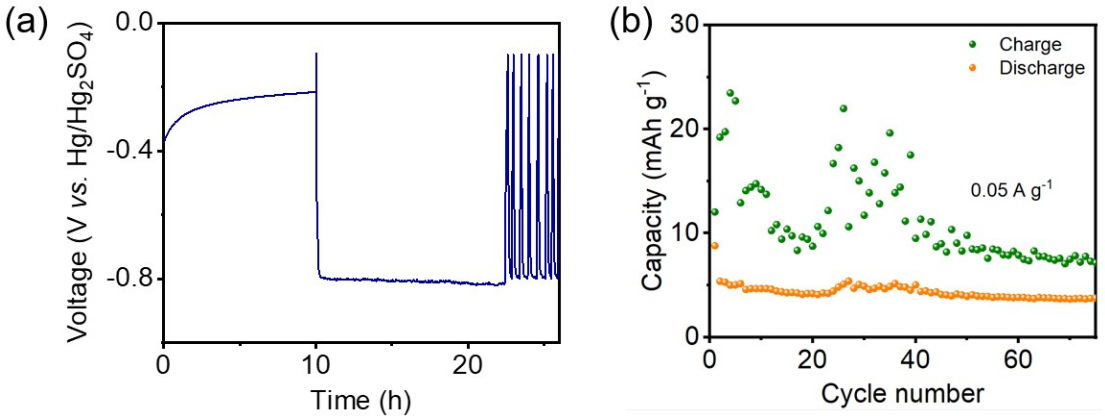

Fig. S4 Electrochemical performance of IPHH in 3 m KFSI electrolyte. (a) V-t curve of IPHH electrode. (b) Cycling performance of IPHH electrode at 0.05 A g^{-1}.

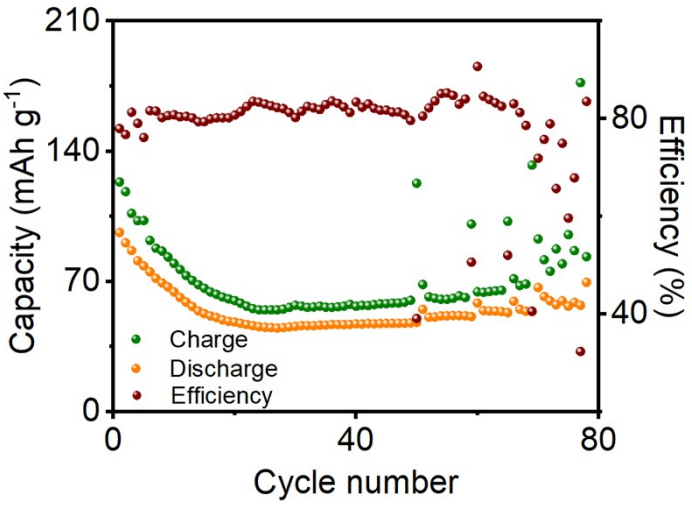

Fig. S5 Cycling performance of IPHH electrode in 30 m KFSI electrolyte at 0.05 A g^{-1}.

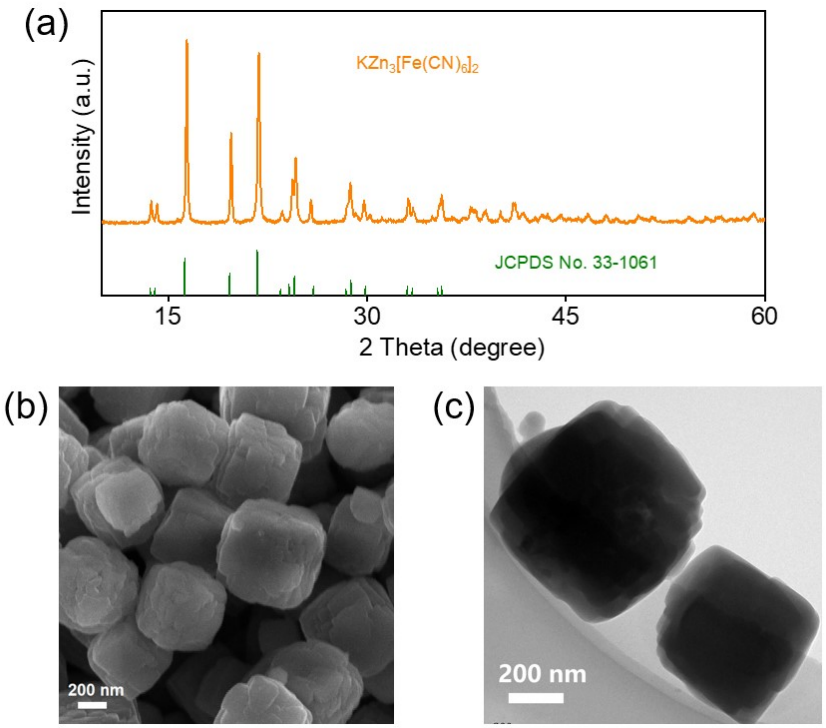

Fig. S6 Characterizations of cathode material KZF sample: (a) XRD pattern, (b) SEM image, and (c) TEM image.

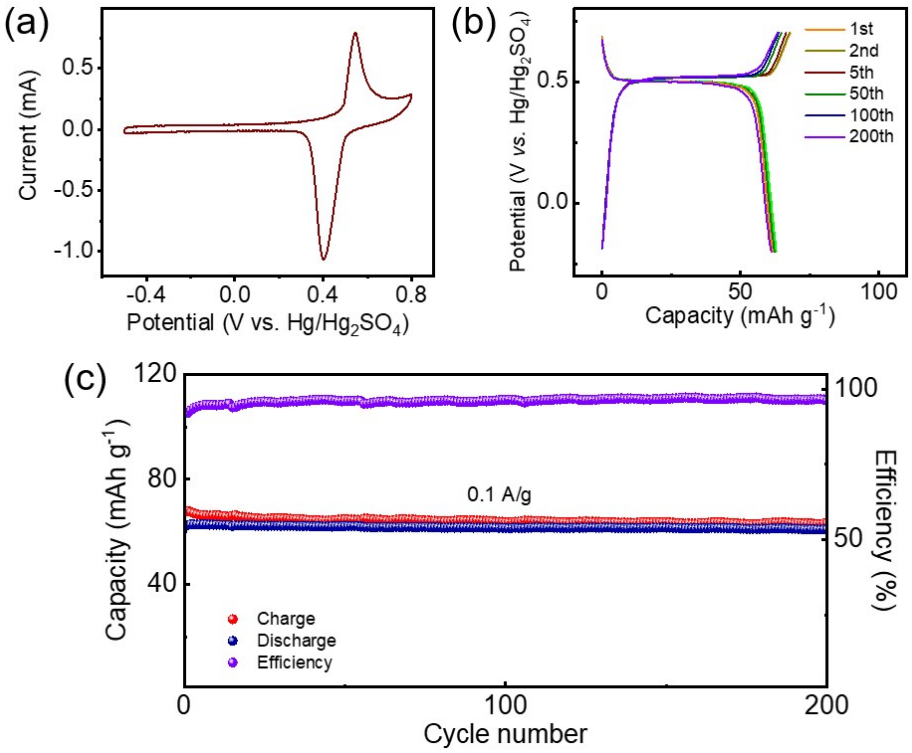

Fig. S7 Electrochemical performances of KZF in (20+30) m electrolyte. (a) CV curve of KZF at a scan rate of 0.5 mV s^{-1}. (b) Galvanostatic charge/discharge curves of KZF at a current density of 0.05 A g^{-1}. (c) Long-term cycle performance of KZF at 0.1 A g^{-1}.

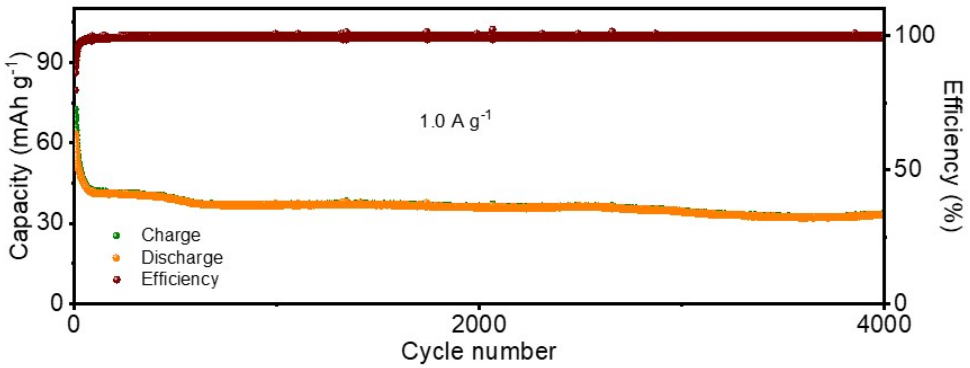

Fig. S8 Long-term cycle performance of the battery at 1.0 A g^{-1}.

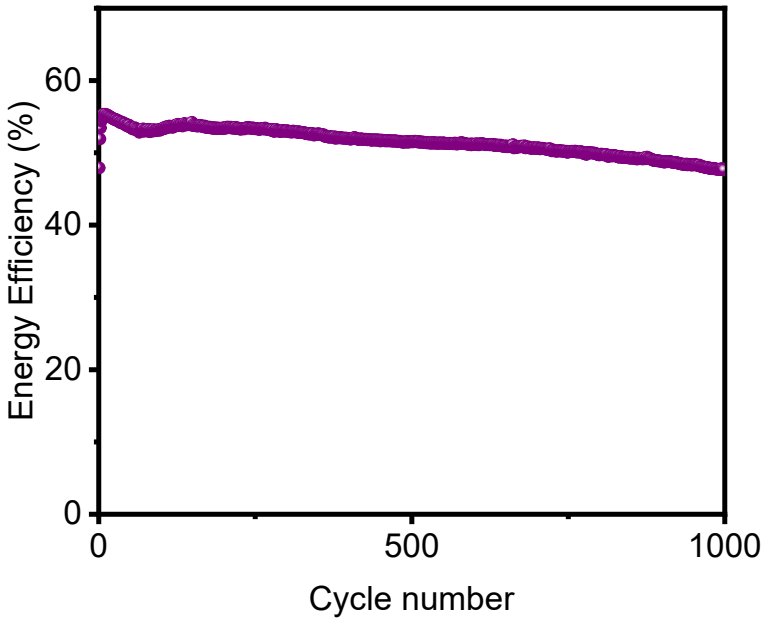

Fig. S9 Energy efficiency of the battery at a current density of 0.2 A g^{-1}.

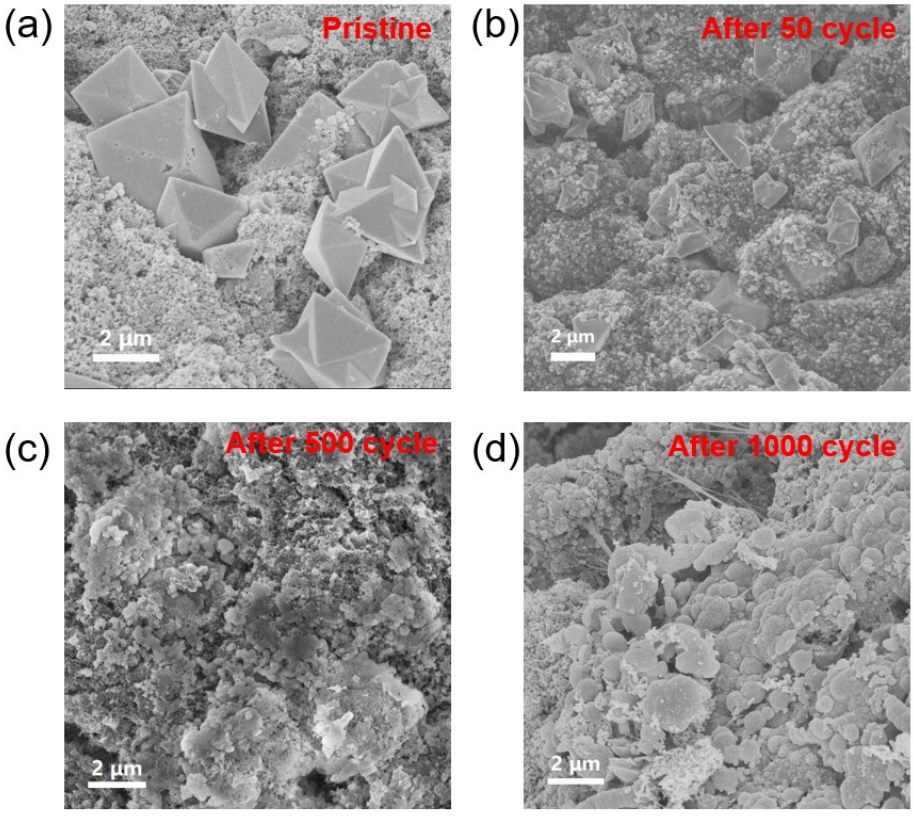

Fig. S10 SEM images of IPHH electrode after different cycles: (a) pristine, (b) 50 cycles, (c) 500 cycles and (d) 1000 cycles.

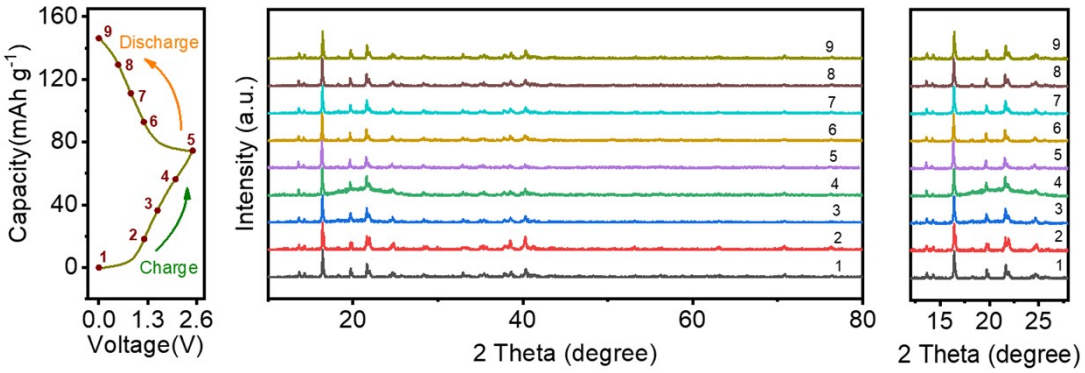

Fig. S11 Ex-situ XRD patterns of KZF electrode collected at various charged/discharged states.

Table S1 ICP result for IPHH sample.

Element	P	Fe
Concentration (mg L^{-1})	8.83	18.88

Table S2 Element analysis result for IPHH electrode in the fully charged state.

Element	K	Fe
Concentration (mg L^{-1})	2.74	7.80