

## Supporting Information

### Rechargeable Aqueous Proton Battery Based on Dipyridophenazine Anode and Indium Hexacyanoferrate Cathode

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## **Experimental**

### **Materials**

Dipyridophenazine (DPPZ, CAS 19535-47-8, >98%) was purchased from TCI Chemicals. Indium nitrate trihydrate ( $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ ) was purchased from Sigma-Aldrich. Potassium ferrocyanide ( $\text{K}_4[\text{Fe}(\text{CN})_6]$ ), anhydrous ethanol and sulphuric acid ( $\text{H}_2\text{SO}_4$ ) were obtained from Sinopharm Group Chemical Co., Ltd. All chemicals were all analytical reagents and used as received without further purification.

### **Preparation of InHCF**

InHCF was prepared via a facile co-precipitation approach. Two types of solutions, 50 mM indium nitrate trihydrate ( $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ ) and 25 mM potassium ferrocyanide ( $\text{K}_4[\text{Fe}(\text{CN})_6]$ ), were used for the precipitation. The volume of both solutions is 30 mL. Then, both solutions were slowly added to 15 mL deionized water under vigorous stirring with the aid of a pumping machine to maintain a constant molar ratio of  $\text{In}(\text{NO}_3)_3$  to  $\text{K}_4\text{Fe}(\text{CN})_6$  during the co-precipitation process. After complete mixing, the mixture was heated and kept at 60 °C for 6 h under a nitrogen atmosphere, and then allowed to stand for 24 h. The precipitates were collected by vacuum filtration and then washed with ethanol and deionized water in turn to remove the residual chemicals. Finally, the powdered InHCF sample was obtained by dried in a vacuum at 60 °C for 24 h.

## **Characterization**

<sup>1</sup>H NMR spectra were recorded on a Bruker ARX-500 type NMR spectrometer using CDCl<sub>3</sub> as the solvent. The FTIR spectra were recorded on a Nexus 670 FTIR spectrometer (Thermo Nicolet). X-ray powder diffraction (XRD) measurements were carried out on a Rigaku D/max-2500 diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.5418$  Å). The microstructure of samples was characterized using field emission scanning electron microscope (FESEM, Supra 55, Carl Zeiss) and transmission electron microscope (TEM, JEOL JEM-2100). Elemental composition and oxidation states were analysed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) using Al K $\alpha$  radiation.

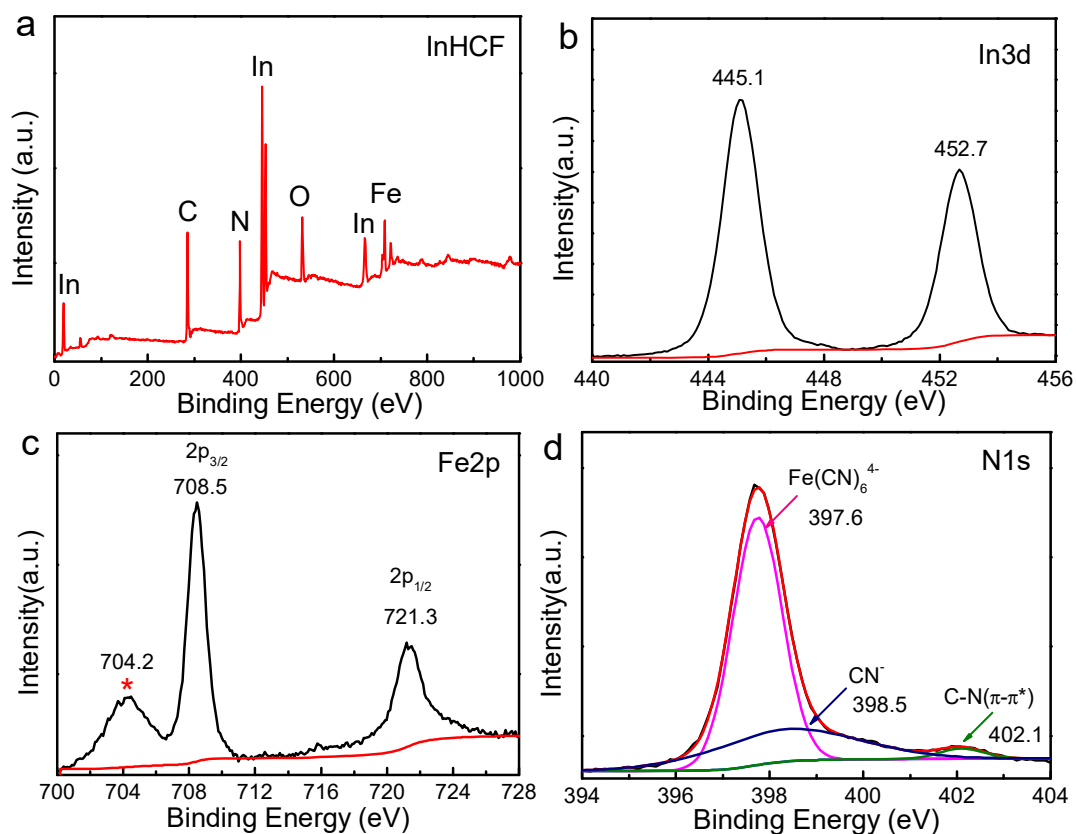
## **Electrochemical measurements**

All electrochemical measurements were performed on a CHI 660B potentiostat (CH Instruments) with a three-electrode cell at 23 $\pm$ 1 °C. The sample (2 mg) and carbon black (Ketjen Black, 2 mg) were mixed and then dispersed into a mixture containing Nafion ionomer (5 wt.%, 75  $\mu$ L), deionized water (0.5 mL) and isopropanol (0.5 mL) to form a homogeneous suspension. Then, 3  $\mu$ L of the suspension was dropped on a pre-polished glassy carbon electrode with a 3 mm diameter, and left to dry at 60 °C for about 8 h to serve as working electrode. Saturated calomel electrode (SCE) and platinum foil electrode were used as the reference electrode and counter electrode, respectively. All potentials were

measured versus the SCE but are reported versus the standard hydrogen electrode (SHE).

### **Full cell measurements**

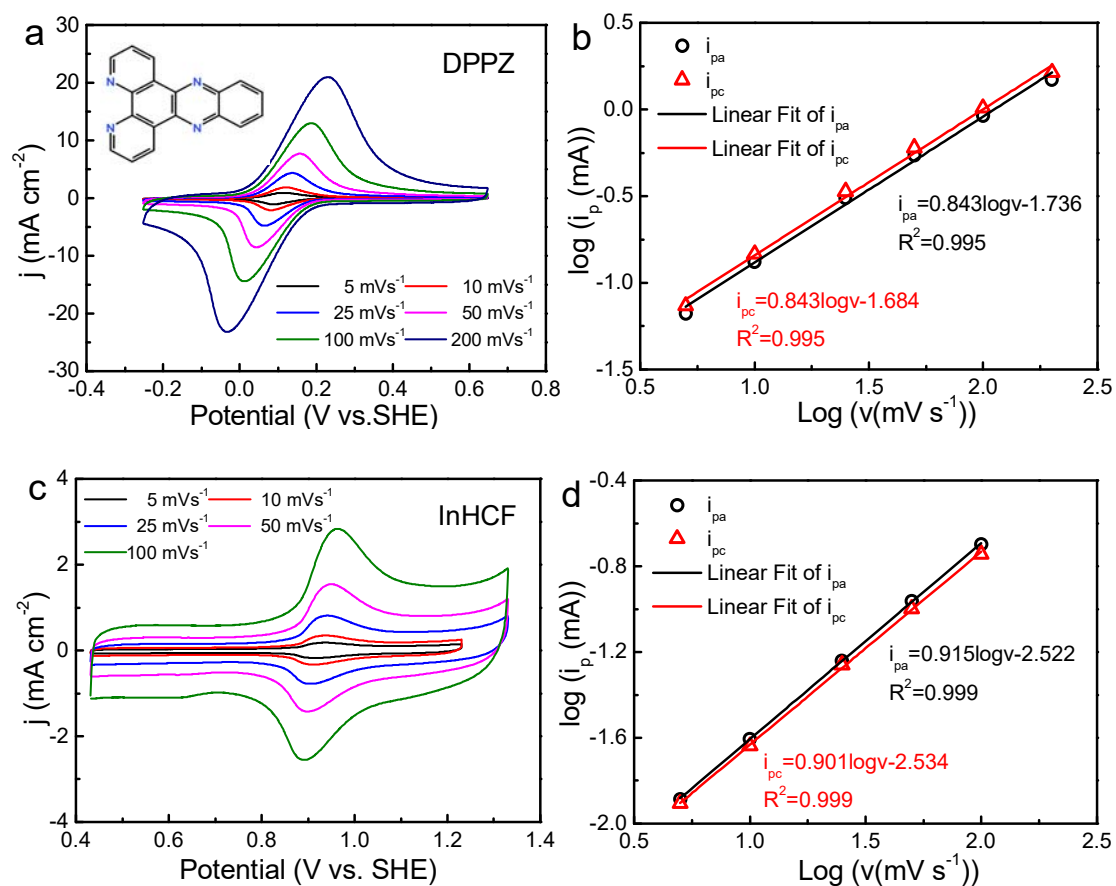
The aqueous proton battery was fabricated using a static battery configuration with the active area of 5 cm<sup>2</sup> in which the DPPZ and InHCF were used as the anode and cathode materials, respectively. A 0.05 M H<sub>2</sub>SO<sub>4</sub> solution (pH=1) was utilized as the anolyte. The DPPZ anode was prepared by mixing DPPZ, Ketjen Black and Nafion ionomer at a weight ratio of 6:3:1 in an isopropanol-water solution, and then transferring them onto the surface of hydrophilic-pre-treated Toray TGP-H-060 carbon paper <sup>[S1]</sup> by a drop-coating method. The loading of DPPZ is 0.4 mg cm<sup>-2</sup>. The InHCF cathode was made by mixing InHCF sample, carbon black and Nafion ionomer at a weight ratio of 7:2:1 in an isopropanol-water solution, and then coating them onto the surface of hydrophilic-pre-treated Toray TGP-H-060 carbon paper. A piece of Fumasep FKS-30 cation exchange membrane (30 μm) sandwiched between the anode and cathode. The galvanostatic charge-discharge and cycling stability were carried out on an Interface 1000 battery system (Gamry) with voltage cut-offs of 0.2 and 1.5 V at room temperature. The current density is calculated based on the weight of DPPZ.



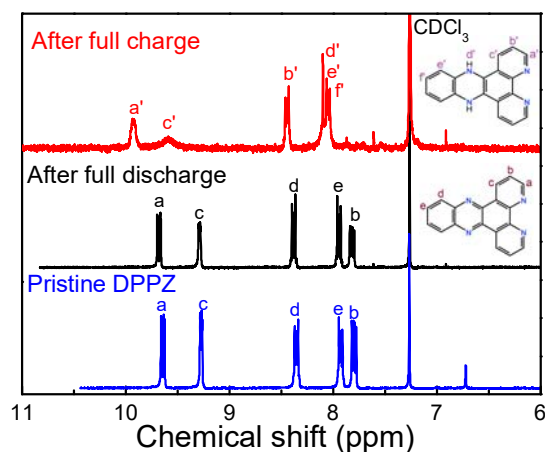
**Fig. S1** XPS survey spectrum (a) of InHCF with the high resolution In 3d (b), Fe 2p (c) and N1s (d) spectra.

**Table S1** Elemental contents in InHCF from XPS.

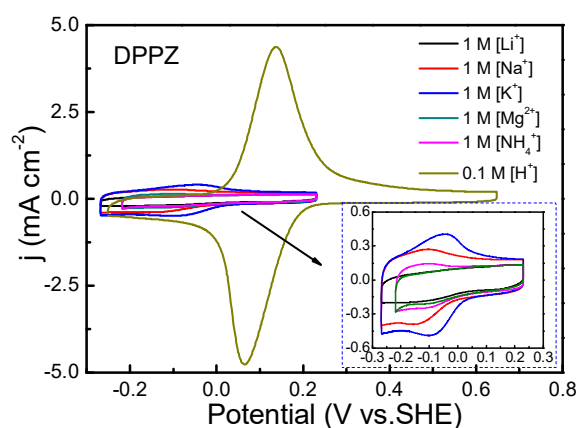
Sample	K (at.%)	In (at.%)	Fe (at.%)	O (at.%)
InHCF	1.29	5.82	6.44	13.97



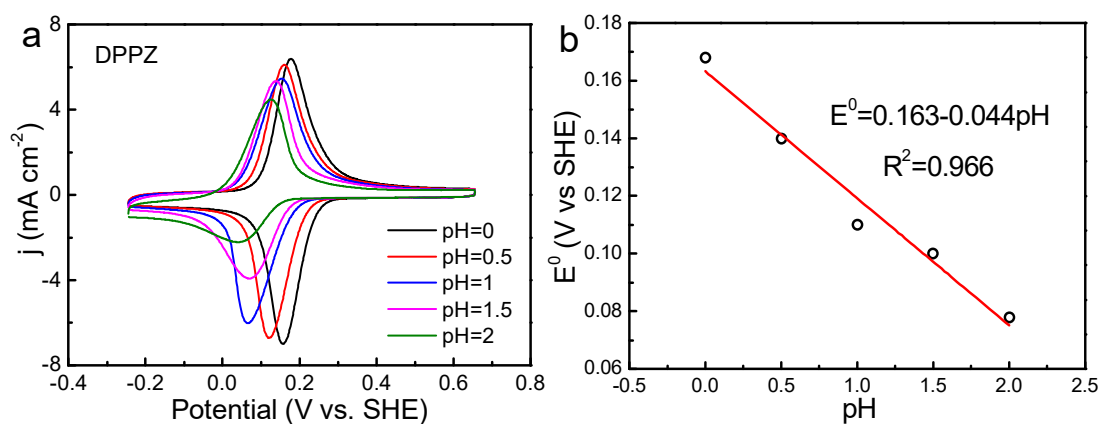
**Fig. S2** (a) CV curves of DPPZ electrode at different scan rates ( $v$ ) in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution (pH=1). (b) corresponding plots of  $\log i_p$  versus  $\log v$  for DPPZ electrode. (c) CV curves of InHCF electrode at different scan rates ( $v$ ) in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution (pH=1). (d) corresponding plots of  $\log i_p$  versus  $\log v$  for InHCF electrode.



**Fig. S3**  $^1\text{H}$  NMR spectra of pristine DPPZ (blue line) and the anode materials after full discharge (black line) and charge (red line). Solvent:  $\text{CDCl}_3$ .

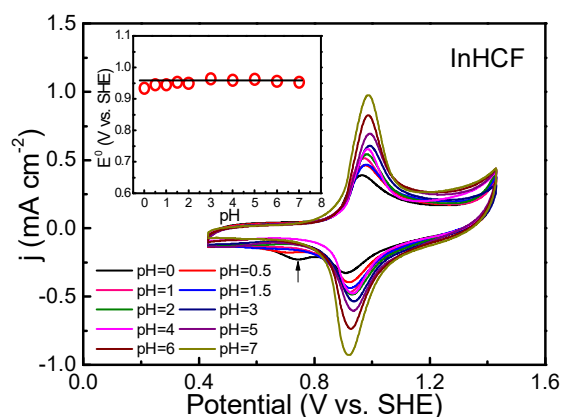


**Fig. S4** (a) CV curves of DPPZ electrode at  $25 \text{ mV s}^{-1}$  in electrolyte solutions containing different cations.

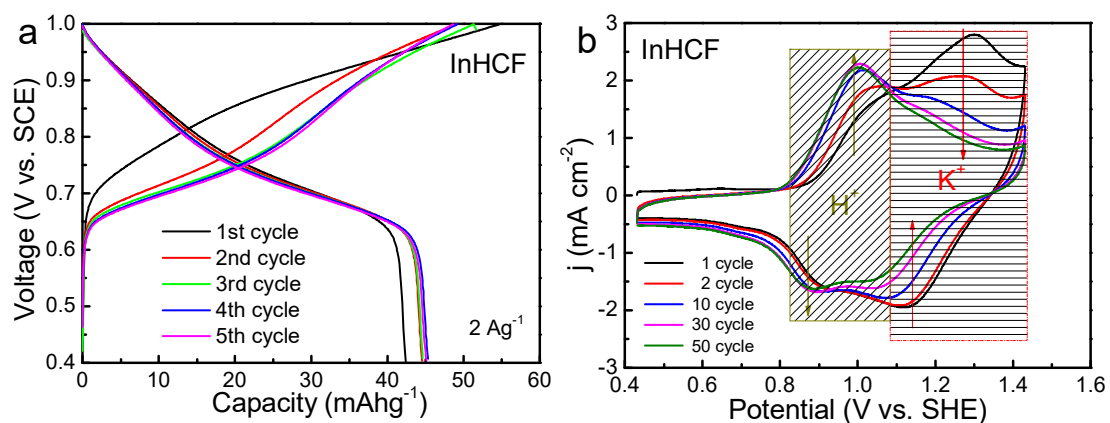


**Fig. S5** (a) CV curves of DPPZ electrode at  $25 \text{ mVs}^{-1}$  in pure  $\text{H}_2\text{SO}_4$  solutions with

different pH values. (b) Pourbaix diagram ( $E^0$  vs pH).



**Fig. S6** (a) CV curves of InHCF electrode at  $25 \text{ mVs}^{-1}$  in different pH solutions with  $0.1 \text{ M KCl}$  as the supporting electrolyte. The inset is Pourbaix diagram ( $E^0$  vs pH).



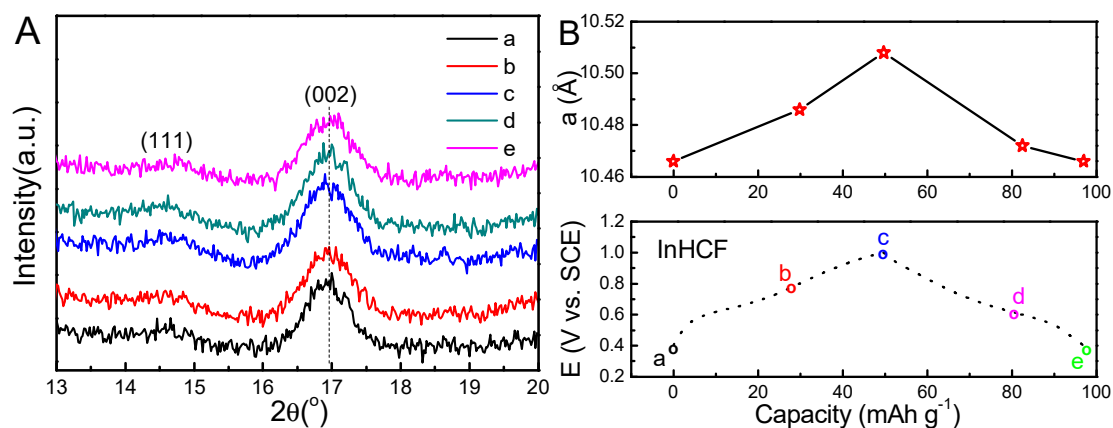
**Fig. S7** (a) Galvanostatic charge-discharge curves of InHCF at  $2 \text{ Ag}^{-1}$ . (b) CV curves of the InHCF electrode with Vulcan XC72R carbon black as a conductive agent in  $0.05 \text{ M H}_2\text{SO}_4$  (pH=1) solution at a scan rate of  $100 \text{ mV s}^{-1}$ .



**Table S2** A performance summary of some aqueous proton batteries (APBs) and air batteries. OCV, open circuit voltage. AQDS, anthraquinone-2,7-disulfonate. CRP, conducting redox polymer. NA, not applicable.

Battery type	OCV (V)	Specific capacity (mAhg <sup>-1</sup> )*	Energy density (Wh kg <sup>-1</sup> )	Coulomb efficiency	Energy efficiency	Capacity retention
Alizarin//Alizarin APBs <sup>[S2]</sup>	1.04	81.5 (at ~1.6 A g <sup>-1</sup> )	~77	95% (at 10 C)	>80% (at 10 C)	47% at 10 C (~1.6 A g <sup>-1</sup> ) for 100 cycles (99.25% per cycle)
Alizarin//2,3-CH <sub>3</sub> -quinizarin APBs <sup>[S2]</sup>	1.16	NA	NA	~88% (at 10 C)	NA	55% at 10 C for 500 cycles (99.88% per cycle)
AQDS//tiron APBs <sup>[S3]</sup>	<0.7	54 (at ~0.27 A g <sup>-1</sup> )	~26	99.4% (at 5 C)	78% (at 5 C)	70% at 5 C (~0.27 A g <sup>-1</sup> ) for 600 cycles (99.94% per cycle)
CRP-based APBs <sup>[S4]</sup>	0.4	74 (at 0.18 A g <sup>-1</sup> )	~18	NA	NA	85% at 3C (0.18 A g <sup>-1</sup> ) for 500 cycles (99.968% per cycle)
CRP-air batteries <sup>[S5]</sup>	~0.96	76 (at ~0.4 A g <sup>-1</sup> )	~34	~100% (at 5 C)	~45% (at 5 C)	97% at 5 C (~0.4 A g <sup>-1</sup> ) for 100 cycles (99.97% per cycle)
DPPZ//InHCF APBs (this work)	0.82	37 (at 1 A g <sup>-1</sup> )	~28	99.7% (at 6 Ag <sup>-1</sup> )	69.5% (at 6 Ag <sup>-1</sup> )	76.1% at 6 A g <sup>-1</sup> (~52 C) for 3000 cycles (99.991% per cycle)

\*Based on the total mass of cathode and anode active materials.



**Fig. S8** (A) Ex situ XRD patterns of InHCF with cycling. (B) Changes of lattice parameter of InHCF during cycling. a, 0.4 V, b, 0.8 V, c, 1.0 V, d, 0.6 V and e, 0.4 V, five states are selected for comparison.

## References

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