Supporting Information

Part I: Experimental details, Calculations & Discussions

S-1-1: Preparation of KCoFe-PBA HMC-OAs

The KCoFe-PBA HMC-OAs sample was prepared by a simple coprecipitation strategy and all the raw materials used in this work were directly purchased from commercial resources. In a typical process, cobalt acetate tetrahydrate, sodium citrate dehydrates and sodium dodecyl sulfates (SDS) were dissolved in 40 ml distilled water to form solution A. On the other hand, the potassium hexacyanoferrate was dissolved in 60 ml distilled water to form solution B. Solution B was mixed with solution A under magnetic stirring for 1 min, which followed by aged at 55 °C for 24 h. After washed with water and ethanol and dried under vacuum, the final product was achieved.

S-1-2: Preparation of RA reference sample

The RA reference sample was prepared by the same procedure to the KCoFe-PBA HMC-OAs. The difference between two strategies is the absence of SDS in the synthetic process.

S-1-3: Preparation of SCR reference sample

The IAR reference sample was prepared by the same procedure to the KCoFe-PBA HMC-OAs. The difference between two strategies is the absence of sodium citrate dehydrates in the synthetic process.

S-1-4: Preparation of IAR reference sample

The IAR reference sample was prepared by the same procedure to the KCoFe-PBA HMC-OAs. The difference between two strategies is the absence of SDS and sodium citrate dehydrates in the synthetic process.

S-1-5 Preparation of RM and IC reference samples

i) RM reference sample

The RM reference samples were prepared by a simple coprecipitation strategy and all the raw materials used in this work were directly purchased from commercial resources. In a typical process, cobalt nitride was dissolved in 50 ml distilled water to form solution A at room temperature. The potassium hexacyanoferrate was dissolved in 50 ml distilled water to form solution B at room temperature. Solution B was mixed with solution A under magnetic stirring for 1 min, which followed by aged at room temperature for 24 h. After washed with water and ethanol and dried under vacuum, the final product was achieved.

ii) IC reference sample

The IC reference samples were prepared by a simple coprecipitation strategy as reported in previous study [S1]. All the raw materials used in this work were directly purchased from commercial resources. In a typical process, cobalt nitride was dissolved in 50 ml distilled water to form solution A. The potassium hexacyanoferrate was dissolved in 50 ml distilled water to form solution B. Then both solution A and B were froze at -10 °C overnight. The frozen solution A and solution B were mixed (Figure S8) and aged for 24 h in an icebox at 2 °C. After washed with water and ethanol and dried under vacuum, the final product was achieved.

S-2: Materials characterizations

Powder X-ray diffraction (XRD, Bruker D8/Germany) using Cu Kα radiation was employed to identify the crystalline phase of the material. The morphology was observed with a scanning electron microscope (SEM, HITACHIS-4700) and a transmission electron microscope (TEM, JEOS-2010 PHILIPS). The element distribution of the sample was confirmed by energy dispersive X-ray detector (EDX). X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was employed to measure the chemical or electronic state of each element. Thermogravimetric analysis (TGA, NETZSCH STA 449C) was used to investigate the carbon content of the sample. Nitrogen adsorption-desorption isotherms were measured using a Micromeritics ASAP 2010. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method.

S-3: Electrochemical measurements

S-3-1: Electrochemical properties of the cathode

The electrochemical characteristics of the cathode were carried out in a three-electrode system. The working electrode was prepared by mixing the KCoFe-PBA, Ketjen black and polytetrafluoroethylene (PTFE) at a weight ratio of 7:2:1. The mixture was dissolved in the distilled water and the slurry was pressed on to a titanium foil under the pressure. After dried at 50 °C in a vacuum oven, the working electrode was prepared. The carbon electrode was used as counter electrode and the Ag/AgCl electrode was used as reference electrode. The water-in-salt (WiS, 22 M KCF₃SO₃) electrolyte was prepared by dissolving 22 mol KCF₃SO₃ salt in 1 L distilled water. Cyclic voltammetry (CV) was conducted using a Zivelab electrochemical workstation. Galvanostatic charge/discharge tests were performed using a Land battery testing system (Wuhan, China).

S-3-2: Electrochemical properties of the full battery

The both full coin cells and the pouch type cells, the KCoFe-PBA HMC-OAs electrode as cathodes and PTCDI as the anode. The Ti mesh was used as current collectors and the WIS electrolyte (22 M KCF₃SO₃) was used as the electrolyte. Galvanostatic charge/discharge tests were performed using a Land battery testing system (Wuhan, China).

S-4: Calculation of the capacitive contribution

In the CV curves, the current is believed to originate from two independent and distinct parts: the surface-induced capacitive process and the diffusion-controlled process. As described in the following equation,

$$i = a \times v^b \tag{1}$$

Where i is the measured current; v is the scan rate. Determined from the slope of the curve between the log*i* versus log*v*, the *b* values of different peaks can be achieved.

$$\log i = \log a + b \log v \tag{2}$$

To further characterize each contribution to the total properties, the measured current (i) at a fixed potential can be separated into two parts, *i. e.* the contribution from the capacitive and the diffusion processes as described in the following equation,

$$i = k_1 v + k_2 v^{1/2} \tag{3}$$

Where k_1v and $k_2v^{1/2}$ correspond to the capacitive and diffusion contributions, respectively. Based on the above equation, the ratios of the capacitive contribution ratios at various scan rates can be quantitatively achieved.

S-5 Computational methods

The theoretical calculations were carried out using the density functional theory and the plane-wave pseudpotential method. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) exchange correlation function was adopted. All geometric optimizations and energy calculations were performed using periodic boundary conditions with adjacent adsorbents and adsorbents to prevent configurational interactions.

Part II: Supporting Figures



Figure S1 SEM image of the RA reference sample.



Figure S2 (a) SEM and (b) TEM images of IAR reference sample.



Figure S3 (a) SEM and (b) TEM images of SCR reference sample.

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Figure S4



Figure S4 XRD patterns of SCR and IAR reference samples. The standard pattern of KCoFe-PBA (PDF: 75-0038) is displayed as reference.



Figure S5 (a) N_2 adsorption/desorption isotherms and (b) pore-size distribution of the

SCR and IAR reference samples and the HMC-OAs sample.

Figure S6



Figure S6 Charge/discharge profiles of (a) the HMC-OAs, (b) SCR and (c) IAR reference

samples.



Figure S7 XRD patterns of HMC-OAs sample after different cycles. The standard pattern

of KCoFe-PBA (PDF: 75-0038) is displayed as reference.



Figure S8 Digital photo of the experimental process for preparation of the IC reference sample, where the upper ice is cobalt nitrate and the lower one is potassium hexacyanoferrate.

Figure S9



Figure S9 XRD patterns of (a) IC and (b) RM reference samples.



Figure S10 SEM images of (a) RM and (b) IC reference samples.



Figure S11 Rate cycling properties of RM and IC reference samples.

Figure S12



Figure S12 XRD pattern of PTCDI sample.



Figure S13 SEM image of PTCDI sample.

Figure S14



Figure S14 Galvanostatic charge/discharge plots of PTCDI electrode.





Figure S15 The conductivity of WIS electrolyte (22 M KCF₃SO₃) in a wide temperature range from -20 to 45 °C.

Part III: Supporting references

[S1] J. Peng, W. Zhang, Z. Hu, L. F. Zhao, C. Wu, G. Peleckis, Q. F. Gu, J. Z. Wang, H. K. Liu, S. X. Dou, S. L. Chou, Ice-Assisted Synthesis of Highly Crystallized Prussian Blue Analogues for All-Climate and Long-Calendar-Life Sodium Ion Batteries. *Nano Lett.* 2022, *22*, 1302-1310.