

# **Buffer solution induced high crystalline sodium-rich Prussian blue for sodium storage**

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## **Synthesis of Prussian blue**

The sodium iron hexacyanoferrate was synthesized by hydrothermal method in acetic acid-sodium acetate (HAc-NaAc, 1:1, pH =4.75) buffer solution. Typical synthesis process is as follows: 2 mmol of  $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ , 1mmol of sodium ascorbate and 5g of NaCl were added to a 60 mL 0.2 M HAc-NaAc buffer solution, stirred and ultrasonicated until completely dissolved. Then the solution was transferred to a 100mL Teflon reactor for hydrothermal reaction at 120°C for 24h. The precipitates collected by centrifugation were washed several times with deionized water and ethanol and dried in a 120°C vacuum oven for 12h. The obtained sample was named PB-B. For comparison, a dilute hydrochloric acid solution (pH=4.75) was adopted to take the place of the buffer solution to prepare the sample PB-H. In order to study the effect of the hydrothermal temperature on the morphology and the crystal structure of the sample, a series of PBAs were prepared at different temperature. In the raw materials, sodium ascorbate and NaCl works as antioxidant for  $\text{Fe}^{2+}$  ions and Na source for the Na-rich PBAs, respectively.

## **Material characterization**

The morphologies and microstructure of as-synthesized samples were observed by field emission scanning electron microscopy (FESEM, JSM-7001F, 10 kV). Crystalline structures of materials were characterized in the range of 5-80° (2 $\theta$ ) through Bruker D8 Advance X-ray diffractometer (XRD) using Cu K $\alpha$  ( $\lambda=1.54056 \text{ \AA}$ ) radiation. The Iron ion valence and chemical compositions of these samples were investigated by the X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific, USA). Raman spectra were performed by a confocal laser micro-Raman spectrometer (HORIBA, Lab RAM HR Evolution). ICP-MS (ELAN 9000) was used to test the sodium and iron content in the samples. Elemental analyzer (VARIO ELIII) was used to characterize the carbon and nitrogen content in the sample.

## **Electrochemical measurements**

The electrochemical properties of the obtained PB-B and PB-H materials were tested by assembling CR2032 coin cells in an Ar-filled glovebox (MIKROUNA, Super 1220/750/900, H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm) using PB-B or PB-H as the working electrode, sodium metal as the counter electrode, 1.0 M NaClO<sub>4</sub> dissolved in a mixture of EC, DMC and EMC (1:1:1, vol.%) with 2 vol.% FEC as electrolyte, and Whatman glass fiber as separator. The working electrodes were fabricated as follows: first, the obtained PB materials were mixed with Ketjen black (as conductive agent), and poly(vinylidene fluoride) (PVDF, as binder) in a mass ratio of 8:1:1, the mixture was dispersed in N-methyl-2-pyrrolidone (NMP) to form homogeneous slurry, and then the resulting slurry was uniformly coated on aluminum foil and dried at 120 °C for 12 h in a vacuum oven. Finally, the PB coated Al foils were punched into 14 mm disks to obtain the working electrodes. The loading mass of active material was about 1 mg. The electrochemical measurements, including constant current charge-discharge testing, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using Land battery testing system (CT4008TNn-5V10mA-164, China) and an electrochemical workstation (CHI660e, China), respectively. The cells were galvanostatically charged and discharged between 2.0 and 4.0 V at various current densities. The capacity was calculated according to the mass of the active material in the electrode, excluding the mass of conductive carbon (Ketjenblack).

Galvanostatic intermittent titration (GITT) measurement was used to evaluate the Na<sup>+</sup> diffusion coefficient (*D*) of the PB-B and PB-H. *D* can be calculated by using Fick's second law as follows:

$$D = \frac{4}{\pi\tau} \left( \frac{V_M m_B}{SM_B} \right)^2 \left( \frac{\Delta E_s}{\Delta E_\tau} \right)^2$$

where *V<sub>M</sub>*, *m<sub>B</sub>*, *M<sub>B</sub>*, and *S* are molar volume, mass, molar mass, and electrode area, respectively. *τ* is the pulse time (s). *ΔE<sub>s</sub>* and *ΔE<sub>τ</sub>* are the differences of voltage and time, respectively.

Table S1. The ICP-MS and element analysis for PB-B and PB-H.

Samples	Element weight percentage content (%)			
	Na	Fe	C	N
PB-B	12.65	32.19	20.35	23.96
PB-B(150) <sup>a</sup>	11.78	31.04	19.19	22.61
PB-H	8.31	28.87	18.04	20.84

<sup>a</sup> synthesized at 150 °C

Table S2. Valence states of Fe.

Samples	Fe 2p	
	Fe <sup>3+</sup>	Fe <sup>2+</sup>
PB-B	35.97%	64.03%
PB-H	39.88%	60.12%

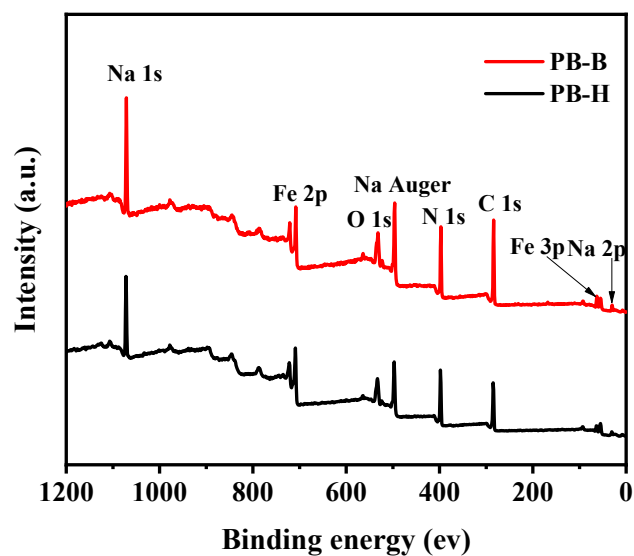


Fig. S1 The full XPS spectra of PB-B and PB-H

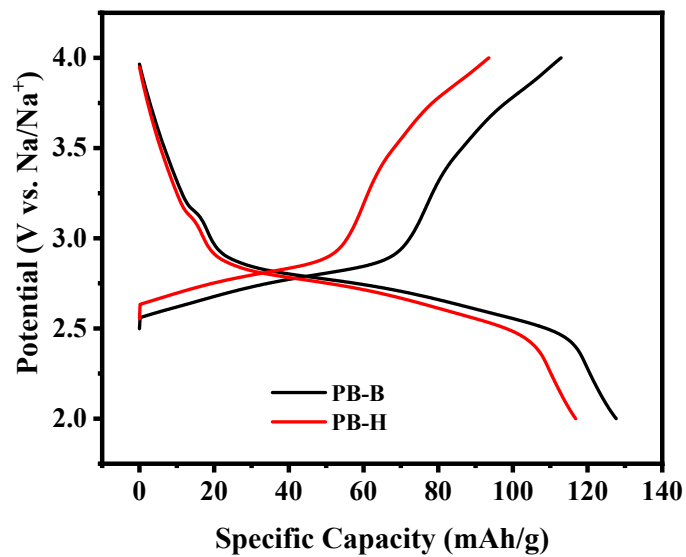


Fig. S2 The initial charge/discharge curves of PB-B and PB-H.

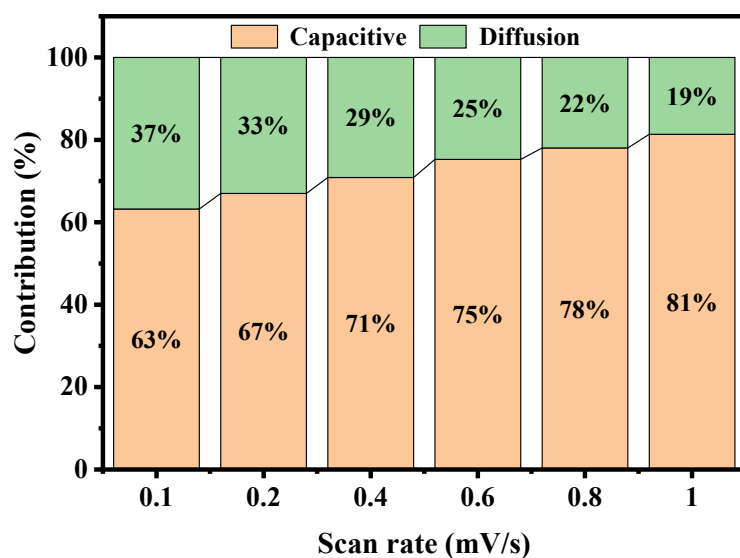


Fig. S3 Contribution ratio of the capacitive and diffusion-controlled charge versus scan rate

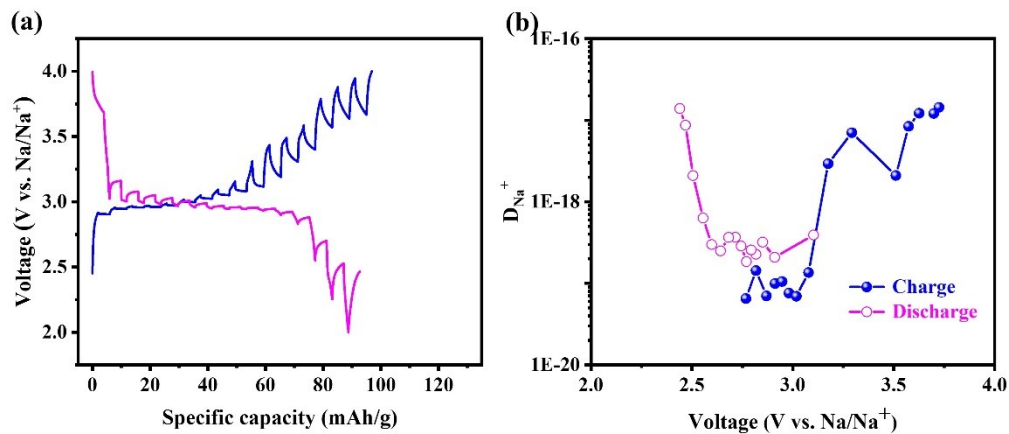


Fig. S4 (a) The GITT curves and (b) sodium-ion diffusion coefficient of PB-H as a function of discharge and charge process.