

## Support information

### High-crystallinity and high-rate Prussian blue analogues synthesized at oil-water interface

Ceheng Duan,<sup>a</sup> Yan Meng,<sup>a</sup> Yujue Wang,<sup>b</sup> Zhaokun Zhang,<sup>c</sup> Yunchen Ge,<sup>b</sup> Xiaopeng, Li,<sup>a</sup> Yong Guo<sup>\*b,c</sup> and Dan Xiao<sup>\*a,b,c</sup>

*a. School of Chemical Engineering, Sichuan University, Chengdu, 610065, China*

*b. Institute of New Energy and Low-Carbon Technology (INELT), Sichuan University, Chengdu, 610207, China*

*c. College of Chemistry, Sichuan University, Chengdu 610064, China*

\* *xiaodan@scu.edu.cn; guoy@scu.edu.cn*

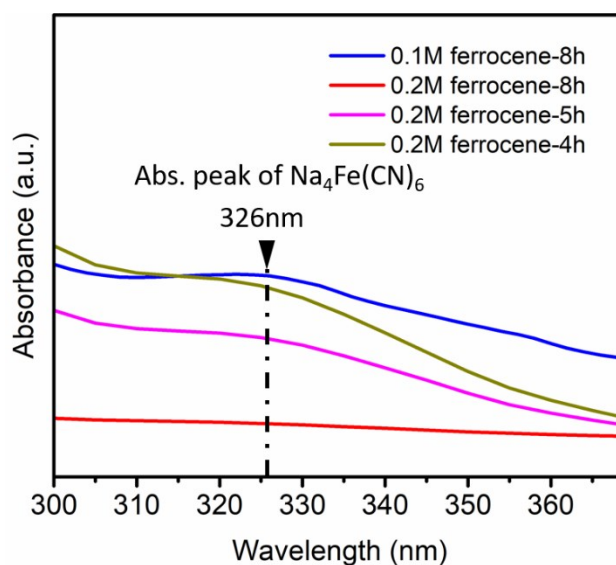


Fig. S1 the comparison of the UV-vis absorption spectra of the water phase after reacting with different concentration ferrocene at different reaction time

Fig.S1 shows the comparison of the UV-vis absorption spectra of the water phase after reacting with different concentration ferrocene at different reaction time. It can be seen that the absorption intensity of sodium ferrocyanide after reacting with 0.1 M ferrocene solution is much higher than that of 0.2 M ferrocene solution through 8 h reaction, and its absorption intensity of sodium ferrocyanide is equivalent to the solution after 4 hours of reaction with 0.2 M ferrocene.

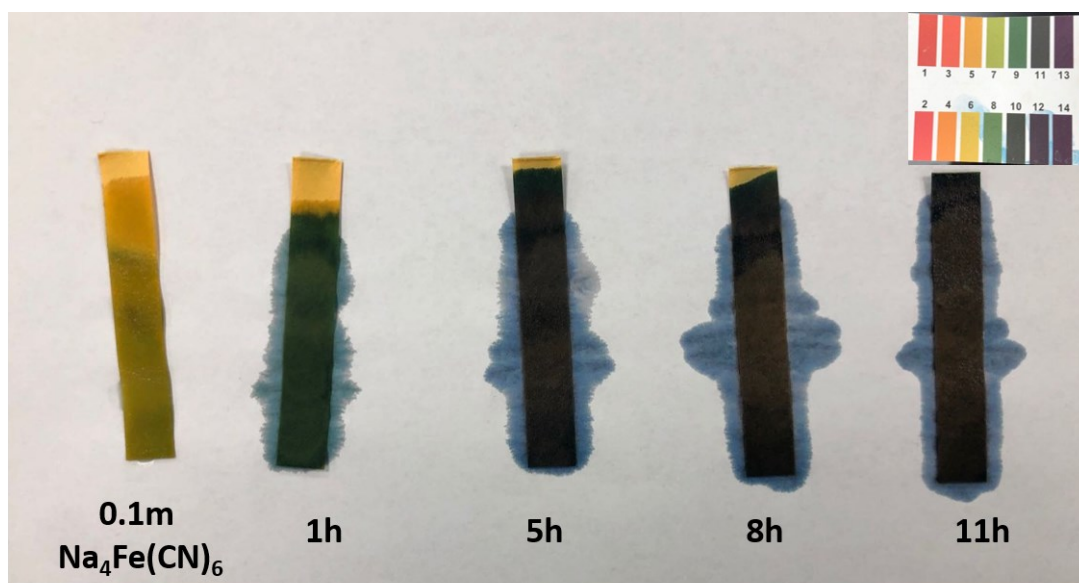


Fig. S2 pH test paper results of water phase with different reaction times (0 h, 1 h, 5 h, 8 h, 11 h)

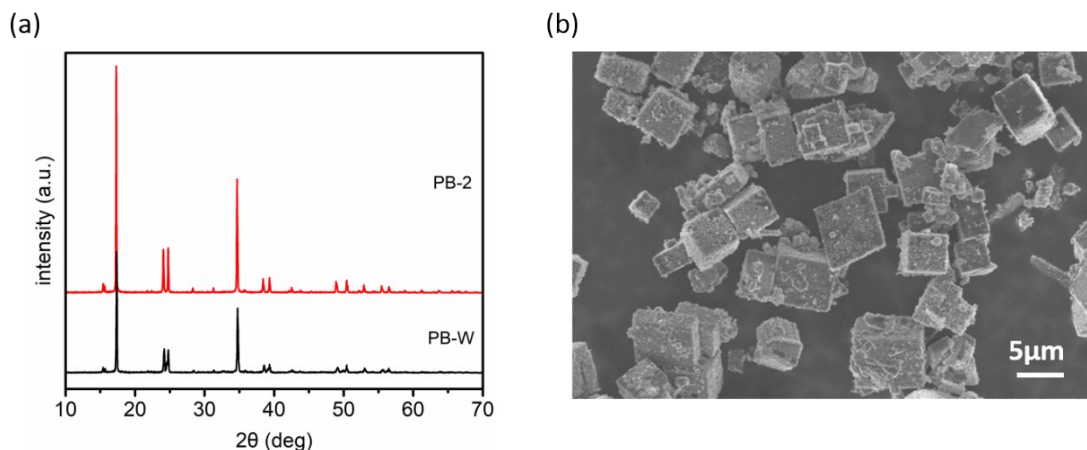


Fig. S3 (a) the XRD pattern of the PB-2 and the PB-w (synthesized in water phase for 8 h) (b) the SEM image of the PB-W

Fig. S3a shows the comparison of the XRD pattern of PB-2 and PB-w (synthesized in water phase for 8 h). The angles of the characteristic diffraction peaks of the two samples are basically the same, indicating that the crystal structures are both the monoclinic structure. However, it can be clearly observed that the overall diffraction peaks intensity of the PB-2 sample are higher, manifesting that the crystallinity of the sample synthesized by the two-phase method is significantly higher. Combined with the SEM picture in Fig. S3b, it is found that the particle regularity of the PB-W is worse and the average size is smaller. According to the environment of water phase synthesis, since the ferrocene is hardly soluble in water, it is suspended above the water phase when it reacts with sodium ferrocyanide. In this way, the contact between ferrocene and water is not uniform, resulting the nucleation concentration of different areas on the water surface varies greatly. In addition, both the solid-liquid mass transfer rate which is much lower than that of liquid-liquid interface and the by-product cyclopentadiene floating on the water are not conducive to the nucleation and growth of the reaction process. As a result, the crystallinity of the crystal grain obtained by the reaction of the aqueous phase system is poor and the yield is also much lower than that of the two-phase system.

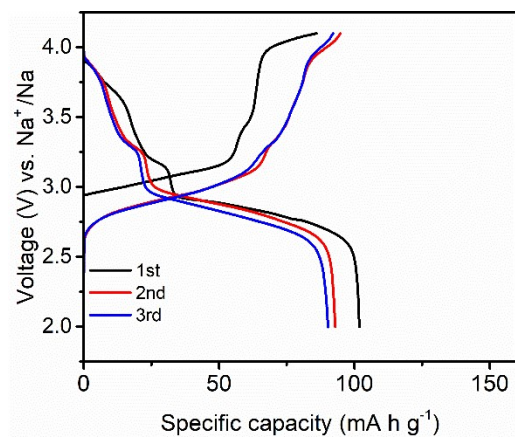


Fig. S4 The charge and discharge curves of PB-W at 0.2C (1 C=170 mA g<sup>-1</sup>)

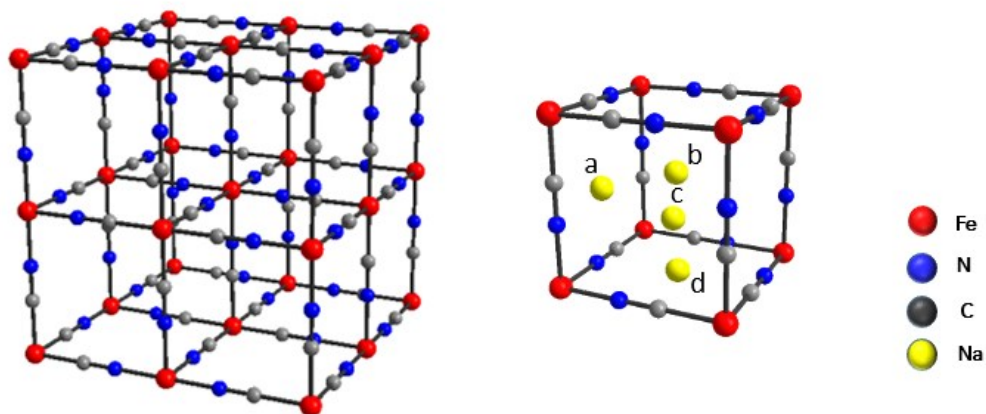


Fig. S5 Possible interstitial sites of  $\text{Na}^+$  ions in the cubic structure of  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$

Fig. S5 displays the possible interstitial sites of  $\text{Na}^+$  in the cubic structure of  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$ , which involves the position where Na ions are extracted and inserted in PB with different Na contents during charging and discharging process. As shown in Fig S1, a represents 8c site (body-center), b stands for 24d site (face-center), c is 32f site (displaced from 8c sites along a  $[1\ 1\ 1]$  axis toward N-coordinated corner), and d means 32f' site (displaced from 8c sites along a  $[100]$  axis toward C-coordinated corner).<sup>1</sup>

Table S1 The fitted Mössbauer parameters of pristine three PB samples.

	PB-1			PB-2			PB-3		
	Center Shift (mm s <sup>-1</sup> )	Quadrupole Splitting (mm s <sup>-1</sup> )	Site Populatinos	Center Shift (mm s <sup>-1</sup> )	Quadrupole Splitting (mm s <sup>-1</sup> )	Site Populatinos	Center Shift (mm s <sup>-1</sup> )	Quadrupole Splitting (mm s <sup>-1</sup> )	Site Populatinos
(Low spin) Fe <sup>2+</sup>	-0.127	0.106	26.4	-0.121	0.105	29.7	-0.125	0.072	23
(High spin) Fe <sup>3+</sup>	0.268	0.601	48.8	0.294	0.64	40	0.226	0.606	48
(High spin) Fe <sup>2+</sup>	1.10	0.53	24.8	0.98	0.84	30	0.9	0.4	30

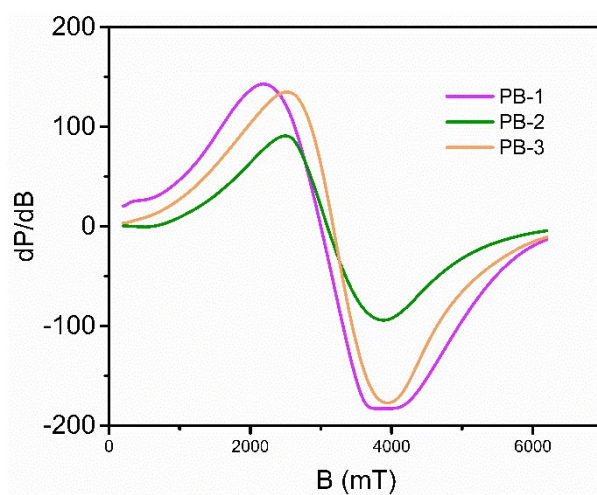


Fig. S6 The electron paramagnetic resonance (EPR) results of three PB samples

Table S2 List of the performance characteristics of the representative PBAs materials for sodium-ion batteries.

Samples	Reversible capacity	Rate capability	Cycling stability	Refs.
$\text{Na}_{1.56}\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 3.1\text{H}_2\text{O}$	103.6 mA h g <sup>-1</sup> at 20 mA g <sup>-1</sup>	90 mA h g <sup>-1</sup> at 100 mA g <sup>-1</sup>	97% after 400 cycles at 20 mA/g	[2]
$\text{Na}_{1.02}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.95}$	140 mAh g <sup>-1</sup> at 0.1 C	51 mAh g <sup>-1</sup> 10 C	95.8 % at 1C after 500 cycles	[3]
$\text{Na}_{1.73}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.98} \cdot 0.02$	123 mA h g <sup>-1</sup> at 100 mA g <sup>-1</sup>	78 mA h g <sup>-1</sup> at 8 C	73% after 200 cycles at 1 C	[4]
$\text{Na}_{0.61}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.94} \cdot 2.79\text{H}_2\text{O}$	170 mA h g <sup>-1</sup> at 25 mA g <sup>-1</sup>	70 mA h g <sup>-1</sup> at 4 C	100% after 150 cycles at 0.2 C	[5]
$\text{Na}_{1.93}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.93}$	120 mAh g <sup>-1</sup> at 50 mA g <sup>-1</sup>	60 mAh g <sup>-1</sup> 1.6 A g <sup>-1</sup>	80 % at 100 mA g <sup>-1</sup> after 280 cycles	[6]
$\text{Na}_{1.58}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.92}$	142 mAh g <sup>-1</sup> at 0.1 C	80 mAh g <sup>-1</sup> 10 C	90 % at 2C after 800 cycles	[7]
$\text{Na}_{1.09}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.86} \cdot 1.55\text{H}_2\text{O}$	140 mAh g <sup>-1</sup> at 0.2C	110 mAh g <sup>-1</sup> 10C	84% at 2C after 200cycles	this work



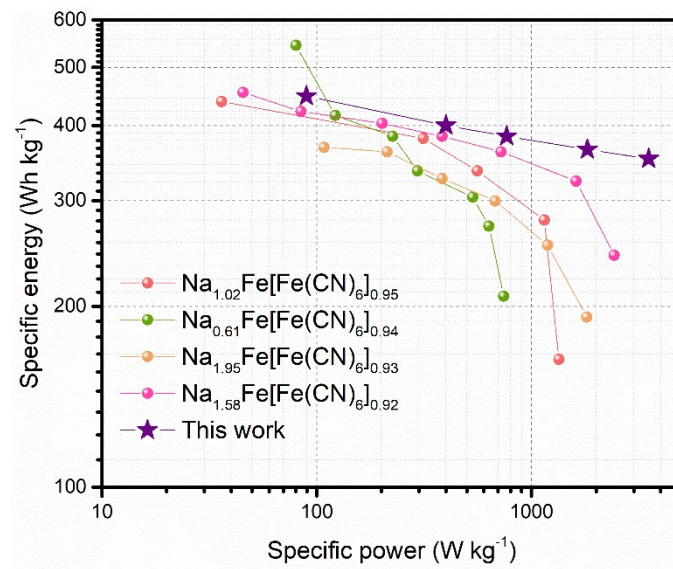


Fig. S7 Comparison of Ragone plots of the reported PBAs materials to this work

Table S3 the fitting values of EIS of Three PB samples

Sample	R1/ $\Omega$	R2/ $\Omega$	R3/ $\Omega$
PB-1	2.813	11.03	175.1
PB-2	2.358	9.814	168.5
PB-3	2.607	176.6	291.2

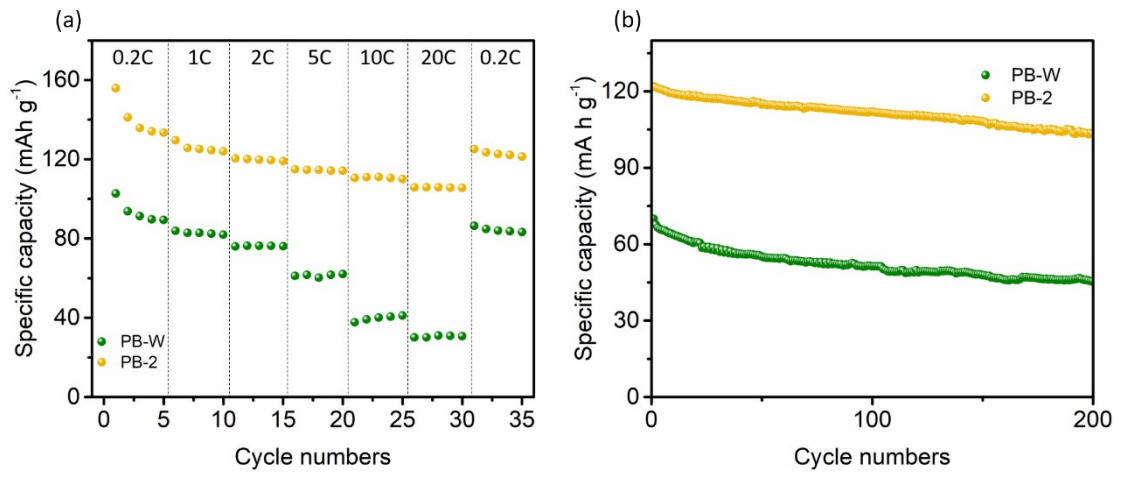


Fig. S8 (a) the rate performance of PB-W and PB-2; (b) the cycle performance of PB-W and PB-2 at a rate of 2C in a range of 2.0-4.1 V.

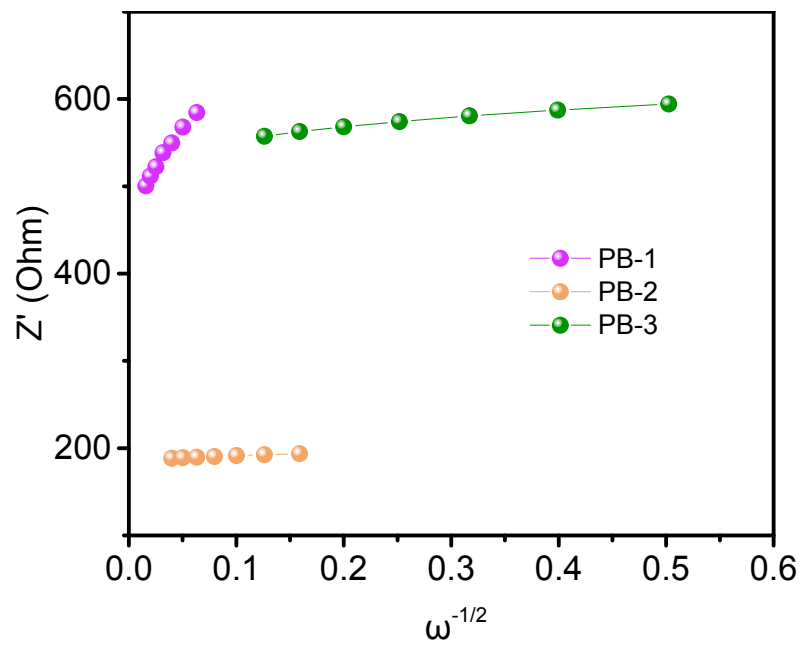


Fig. S9 the linear fit between  $Z'$  and  $\omega^{-1/2}$  at low frequencies

- 1 C. Yang, A. Zhao, F. Zhong, X. M. Feng, W. H. Chen, J. F. Qian, X. P. Ai, H. X. Yang, Y. L. Cao, A low-defect and Na-enriched Prussian blue lattice with ultralong cycle life for sodium-ion battery cathode, *Electrochim. Acta*, 2020, **332**, 135533.
- 2 W. J. Li, S. L. Chou, J. Z. Wang, Y. M. Kang, J. L. Wang, Y. Liu, Q. F. Gu, H. K. Liu, S. X. Dou, Facile method to synthesize Na-enriched  $\text{Na}_{1+x}\text{FeFe}(\text{CN})_6$  frameworks as cathode with superior electrochemical performance for sodium-ion batteries, *Chem. Mater.*, 2015, **27**, 1997-2003.
- 3 H. Hu, W. F. Liu, M. L. Zhu, Y. S. Lin, Y. Liu, J. W. Zhang, T. Chen, K. Y. Liu, Yolk-shell Prussian blue nanoparticles with fast ion diffusion for sodium-ion battery, *Mater. Lett.*, 2019, **249**, 206–209.
- 4 Y. Yang, E. Liu, X. M. Yan, C. R. Ma, W. Wen, X. Z. Liao, Z. F. Ma, Influence of structural imperfection on electrochemical behavior of Prussian blue cathode materials for sodium ion batteries, *J. Electrochem. Soc.*, 2016, **163**, A2117-A2123.
- 5 Y. You, X. L. Wu, Y. X. Yin, Y. G. Guo, High-quality Prussian blue crystals as superior cathode materials for room-temperature sodium-ion batteries, *Energy Environ. Sci.*, 2014, **7**, 1643-1647.
- 6 Y. X. Huang, M. Xie, J. T. Zhang, Z. H. Wang, Y. Jiang, G. H. Xiao, S. J. Li, L. Li, W. Feng, R. J. Chen, A novel border-rich Prussian blue synthesized by inhibitor control as cathode for sodium ion batteries, *Nano Energy*, 2017, **39**, 273–283.
- 7 X. Tang, H. Liu, D. Su, P. H. L. Notten, G. X. Wang, Hierarchical sodium-rich Prussian blue hollow nanospheres as high-performance cathode for sodium-ion batteries, *Nano Res.*, 2018, **11**, 3979–3990.