Electronic Supplementary Information

Prussian Blue Analogue as a Long Life Cathode for Liquid-State and Solid-State Sodium-Ion Batteries

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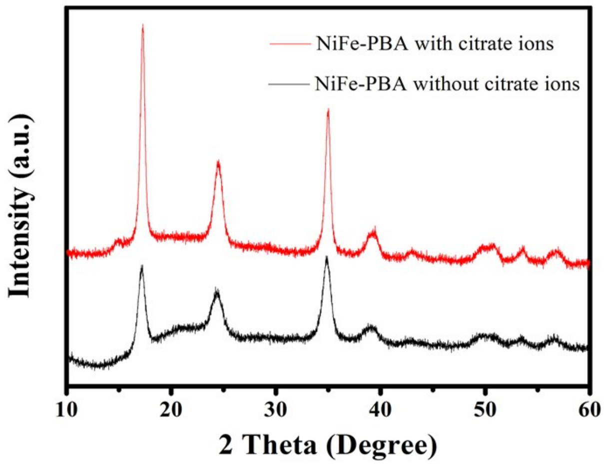

Fig. S1 XRD patterns of two NiFe-PBA materials synthesized with/without citrate ions.

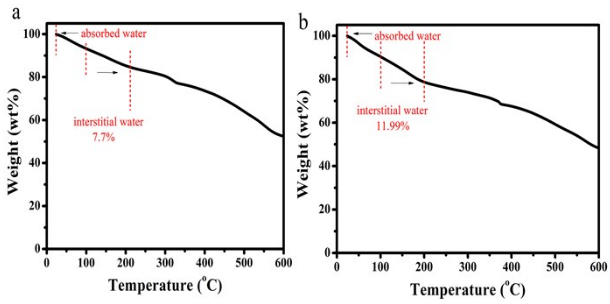

Fig. S2 TGA curves of two NiFe-PBA materials synthesized (a) with citrate ions, (b) without citrate ions at a rate of 10 °C/min in N_2 atmosphere.

The surface adsorbed water are evaporated from room temperature to 100 °C, while the weight loss in temperature range of 100 to 200 °C was ascribed to the interstitial water. As displayed in Fig. S2, the water content of the NiFe-PBA with citrate ions (7.7%) is smaller than that of sample prepared without citrate ions (11.99%). This is an indication that the citrate dehydrate may reduce material defects. Therefore, it is beneficial to improve the electrochemical performance of the NiFe-PBA.

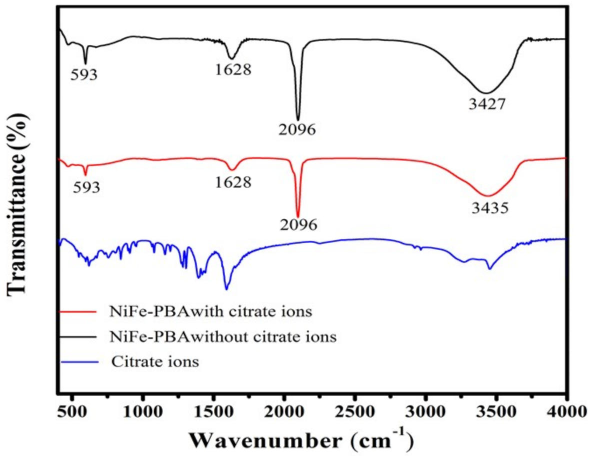

Fig. S3 Infrared spectrum of two NiFe-PBA materials synthesized with/without citrate ions.

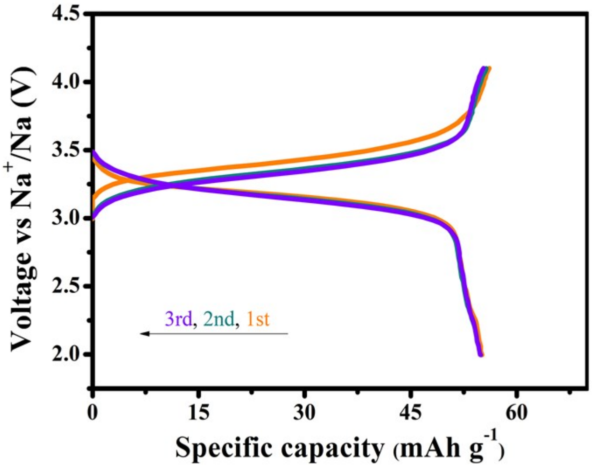

Fig. S4 The first three charge/discharge profiles of NiFe-PBA without citrate ions electrode at a current density of 0.1 A g^{-1}.

The initial discharge specific capacity of the NiFe-PBA without citrate ions is only 55.1 mAh g^{-1}, which is much lower than that of the NiFe-PBA with citrate ions (70.9 mAh g^{-1}).

Table S1. ICP results of two NiFe-PBA materials synthesized with/without citrate ions.

	Na	Fe	Ni
As-prepared NiFe-PBA	0.395mg/L	0.47 mg/L	0.55 mg/L
NiFe-PBA without citrate ions	0.196 mg/L	0.292 mg/L	0.351 mg/L

According to ICP results, the chemical formulas of two NiFe-PBA materials synthesized with/without citrate ions are $Na_{1.82}Ni[Fe(CN)_6]_{0.90} \cdot 2.7H_2O$ and $Na_{1.42}Ni[Fe(CN)_6]_{0.85} \cdot 6.7H_2O$, respectively. It can also be found from the value of the defect in the chemical formula, the increase of $Fe(CN)_6$ vacancies reduces the content of Na in the crystal lattice and therefore also reduces the initial charge capacity.

Table S2. The sodium storage properties of reported Prussian Blue Analogues.

Materials	Electrolyte	Rate /A g^{-1}	Cycle Number (capacity retention)	Final capacity /m Ah g^{-1}
$Na_{1.82}Ni[Fe(CN)_6]_{0.89}$ • $4.8H_2O$	1.0 M $NaClO_4$ in EC: DEC=1:1 with 5% FEC	0.1	1120	60.8
$Na_{1.76}Ni[Fe(CN)_6]_{0.94}$[1]	1.0 M $NaClO_4$ in EC: PC=1:1 with 5% FEC	0.1	500	＜55
$Na_{1.46}Ni[Fe(CN)_6]_{0.83}$ • $2.2H_2O$[2]	1.0 M $NaClO_4$ in EC: DEC=1:1	0.08	200	66.8
$K_{0.09}Ni[Fe(CN)_6]_{0.71}$ • $6H_2O$[3]	1 M $NaPF_6$ in EC: PC=1:1	0.02	200	66
$Na_{1.01\sim1.41}Ni[Fe(CN)_6]_{1.02\sim0.91}$[4]	1.0 M $NaClO_4$ in EC: DEC=1:1	0.1	200	＜60
$Na_{1.014}Ni[Fe(CN)_6]_{0.818}$· $3.53H_2O$[5]	1.0 M $NaClO_4$ in EC: DEC=1:1	0.01	100	68
$Na_{1.20}Ni[Fe(CN)_6]_{0.65}$[6]	/	0.03	50	66

References

1. W. Zhang, Y. Zhao, V. Malgras, Q. Ji, D. Jiang, R. Qi, K. Ariga, Y. Yamauchi, J. Liu, J.-S. Jiang and M. Hu, Synthesis of Monocrystalline Nanoframes of Prussian Blue Analogues by Controlled Preferential Etching, *Angewandte Chemie International Edition*, 2016, **55**, 8228-8234.
2. Z. Ji, B. Han, H. Liang, C. Zhou, Q. Gao, K. Xia and J. Wu, On the Mechanism of the Improved Operation Voltage of Rhombohedral Nickel Hexacyanoferrate as Cathodes for Sodium-Ion Batteries, *ACS Applied Materials & Interfaces*, 2016, **8**, 33619-33625.
3. Y. You, X.-L. Wu, Y.-X. Yin and Y.-G. Guo, A zero-strain insertion cathode material of nickel ferricyanide for sodium-ion batteries, *Journal of Materials Chemistry A*, 2013, **1**, 14061-14065.
4. Y. Yue, A. J. Binder, B. Guo, Z. Zhang, Z.-A. Qiao, C. Tian and S. Dai, Mesoporous Prussian Blue Analogues: Template-Free Synthesis and Sodium-Ion Battery Applications, *Angewandte Chemie International Edition*, 2014, **53**, 3134-3137.
5. S. Yu, Y. Li, Y. Lu, B. Xu, Q. Wang, M. Yan and Y. Jiang, A promising cathode material of sodium iron–nickel hexacyanoferrate for sodium ion batteries, *Journal of Power Sources*, 2015, **275**, 45-49.
6. X. Bie, K. Kubota, T. Hosaka, K. Chihara and S. Komaba, Synthesis and electrochemical properties of Na-rich Prussian blue analogues containing Mn, Fe, Co, and Fe for Na-ion batteries, *Journal of Power Sources*, 2018, **378**, 322-330.