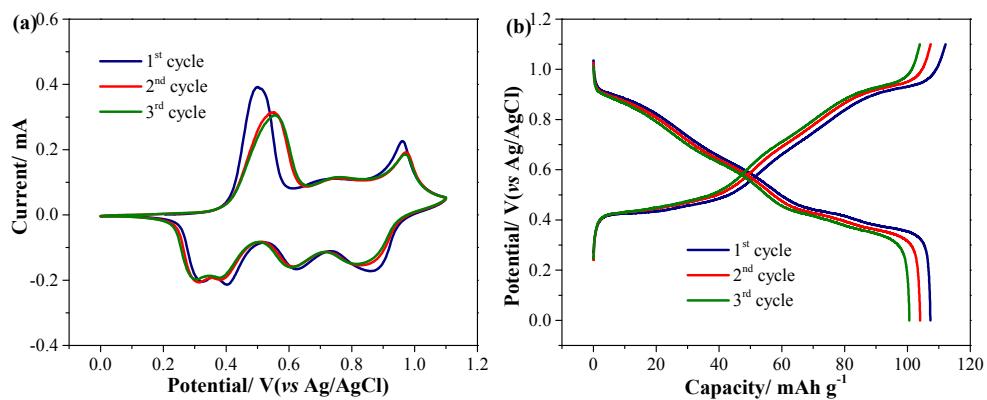


*Supporting Information*

**Insight into electrochemical properties and reaction mechanism of cobalt-rich Prussian blue analogue cathode in  $\text{NaSO}_3\text{CF}_3$  electrolytes for aqueous sodium-ion batteries**

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**Figure S1.** Electrochemical properties of  $\text{Na}_2\text{Co}_{0.8}\text{Ni}_{0.2}[\text{Fe}(\text{CN})_6]$  in 2 M  $\text{Na}_2\text{SO}_4$  electrolytes: a) cyclic voltammograms at the scanning rate of  $0.1 \text{ mV s}^{-1}$  and b) charge/discharge profiles at the current of  $50 \text{ mA g}^{-1}$ .

**Table S1.** Performance comparison of Prussian-blue cathodes for aqueous SIBs reported in this work and literatures

Materials	Reversible capacity (mAh g <sup>-1</sup> )	Working potential (V vs Ag/AgCl)	Specific energy# (Wh kg <sup>-1</sup> )	Cycling performance
Na <sub>0.44</sub> MnO <sub>2</sub> <sup>1</sup>	45 (5.6 mA g <sup>-1</sup> )	0.41	54	96% capacity retention after 1000 cycles at 180 mA g <sup>-1</sup>
Na <sub>0.5</sub> Mn <sub>0.5</sub> Ti <sub>0.5</sub> O <sub>2</sub> <sup>2</sup>	46 (30 mA g <sup>-1</sup> )	0.41	56	95% capacity retention after 100 cycles at 60 mA g <sup>-1</sup>
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>3</sup>	94.5 (1176 mA g <sup>-1</sup> )	0.4	113	20% capacity retention after 30 cycles at 2352mA g <sup>-1</sup>
Na <sub>3</sub> VTi(PO <sub>4</sub> ) <sub>3</sub> <sup>4</sup>	56 (62 mA g <sup>-1</sup> )	0.42	68	92% capacity retention after 500 cycles at 310 mA g <sup>-1</sup>
Na <sub>3</sub> MnTi(PO <sub>4</sub> ) <sub>3</sub> <sup>5</sup>	58.4 (29.35 mA g <sup>-1</sup> )	0.6	82	98% capacity retention after 100 cycles at 58.7 mA g <sup>-1</sup>
Na <sub>2</sub> Ni[Fe(CN) <sub>6</sub> ] <sup>6</sup>	65 (65 mA g <sup>-1</sup> )	0.48	83	93% capacity retention after 500 cycles at 325 mA g <sup>-1</sup>
Na <sub>2</sub> Cu[Fe(CN) <sub>6</sub> ] <sup>7</sup>	59 (60 mA g <sup>-1</sup> )	0.61	83	93% capacity retention after 500 cycles at 300 mA g <sup>-1</sup>
Na <sub>2</sub> Co[Fe(CN) <sub>6</sub> ] <sup>8</sup>	110.8 (240 mA g <sup>-1</sup> )	0.53	147	72% capacity retention after 100 cycles at 240 mA g <sup>-1</sup>
NaFe[Fe(CN) <sub>6</sub> ] <sup>9</sup>	61 (18.432 mA g <sup>-1</sup> )	0.23	63	84% capacity retention after 200 cycles at 92.16 mA g <sup>-1</sup>
Na <sub>2</sub> Fe[Fe(CN) <sub>6</sub> ] <sup>10</sup>	113 (25 mA g <sup>-1</sup> )	0.53	150	79% capacity retention after 500 cycles at 200 mA g <sup>-1</sup>
Na <sub>2</sub> Fe <sub>1-x</sub> Ni <sub>x</sub> [Fe(CN) <sub>6</sub> ] <sup>11</sup>	106 (10 mA g <sup>-1</sup> )	0.59	147	96% capacity retention after 100 cycles at 10mA g <sup>-1</sup>
Na <sub>2</sub> Co <sub>0.6</sub> Ni <sub>0.4</sub> [Fe(CN) <sub>6</sub> ] <sup>12</sup>	85 (35 mA g <sup>-1</sup> )	0.62	121	90% capacity retention after 100 cycles at 70 mA g <sup>-1</sup>
Na <sub>2</sub> Co <sub>0.8</sub> Ni <sub>0.2</sub> [Fe(CN) <sub>6</sub> ] (this work)	116.4 (50 mA g <sup>-1</sup> )	0.67	171	88% capacity retention after 100 cycles at 100 mA g <sup>-1</sup>

#: specific energy is calculated based on the NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> anode (-0.8 V vs Ag/AgCl).

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