

## Supporting Information

### Nickel ferrocyanides for aqueous ammonium ion batteries

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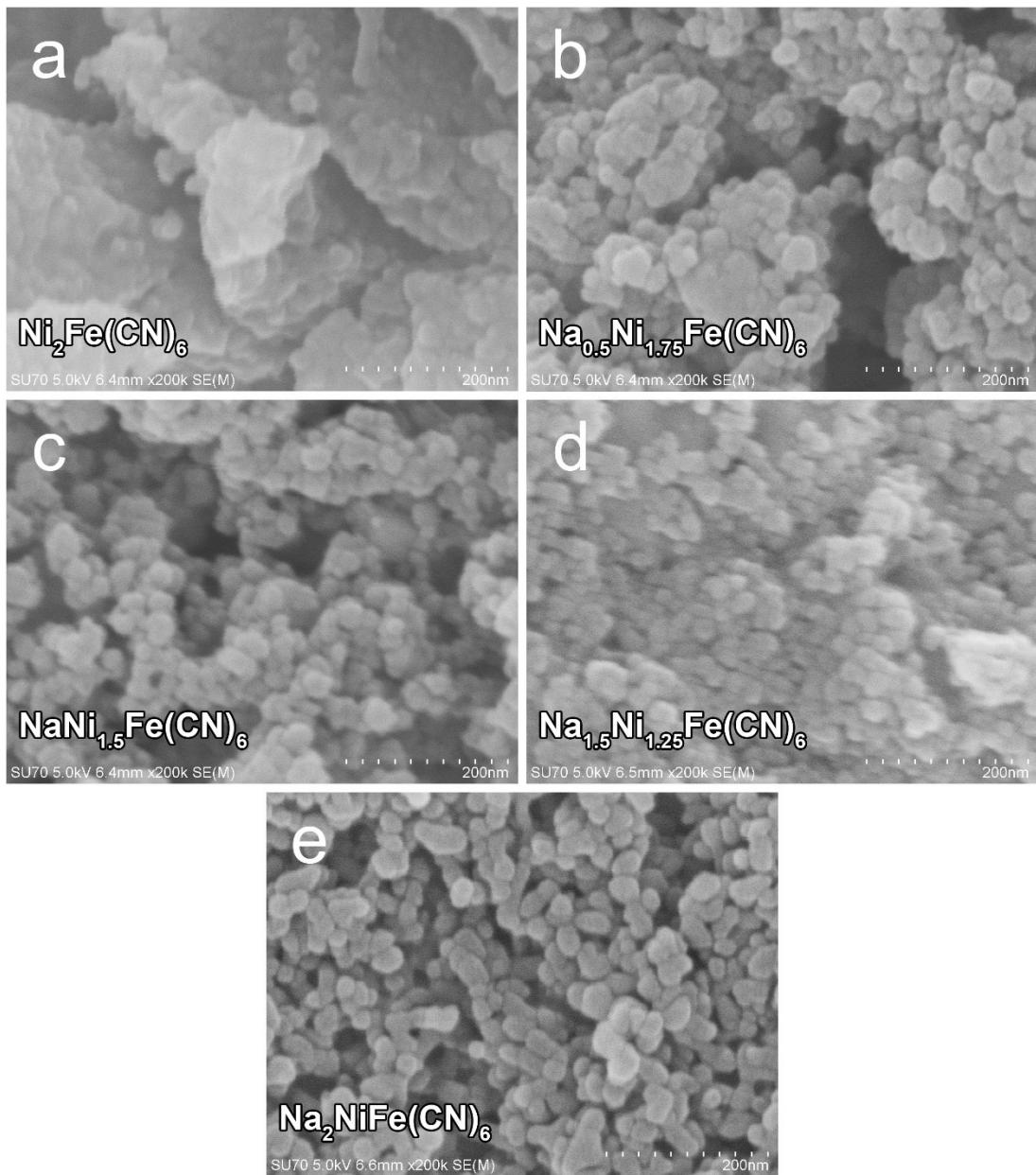
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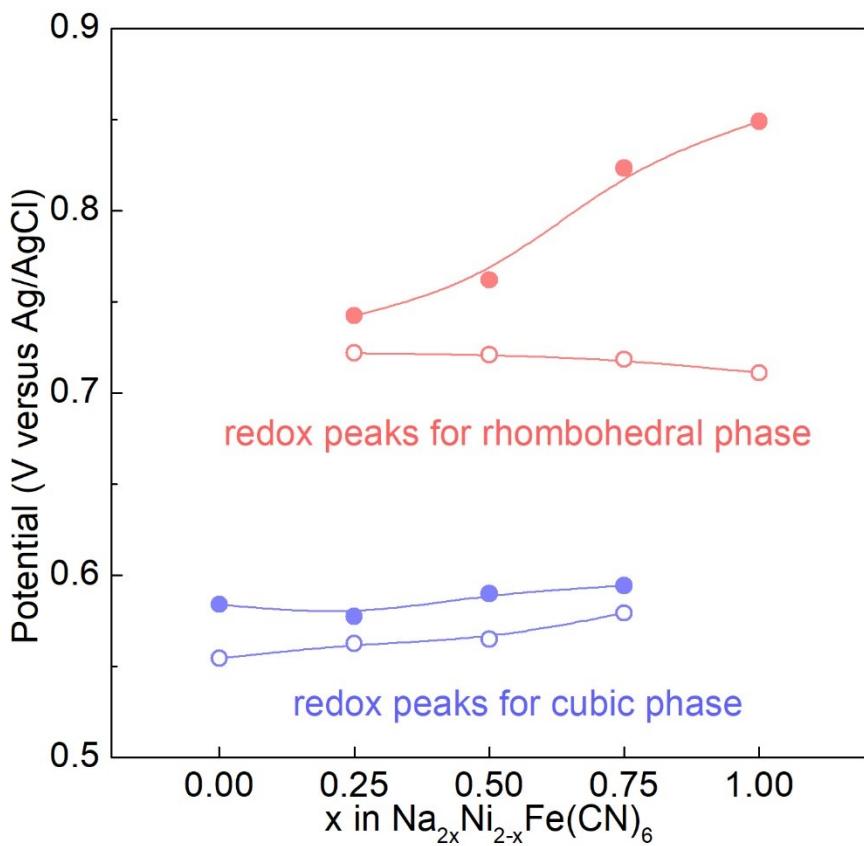
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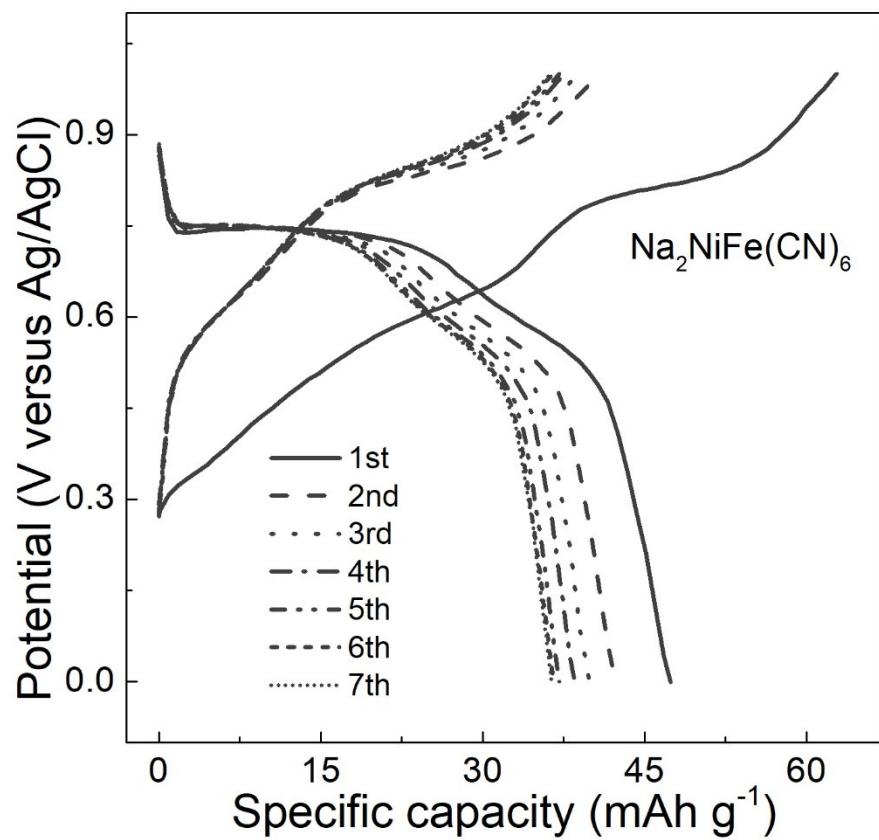
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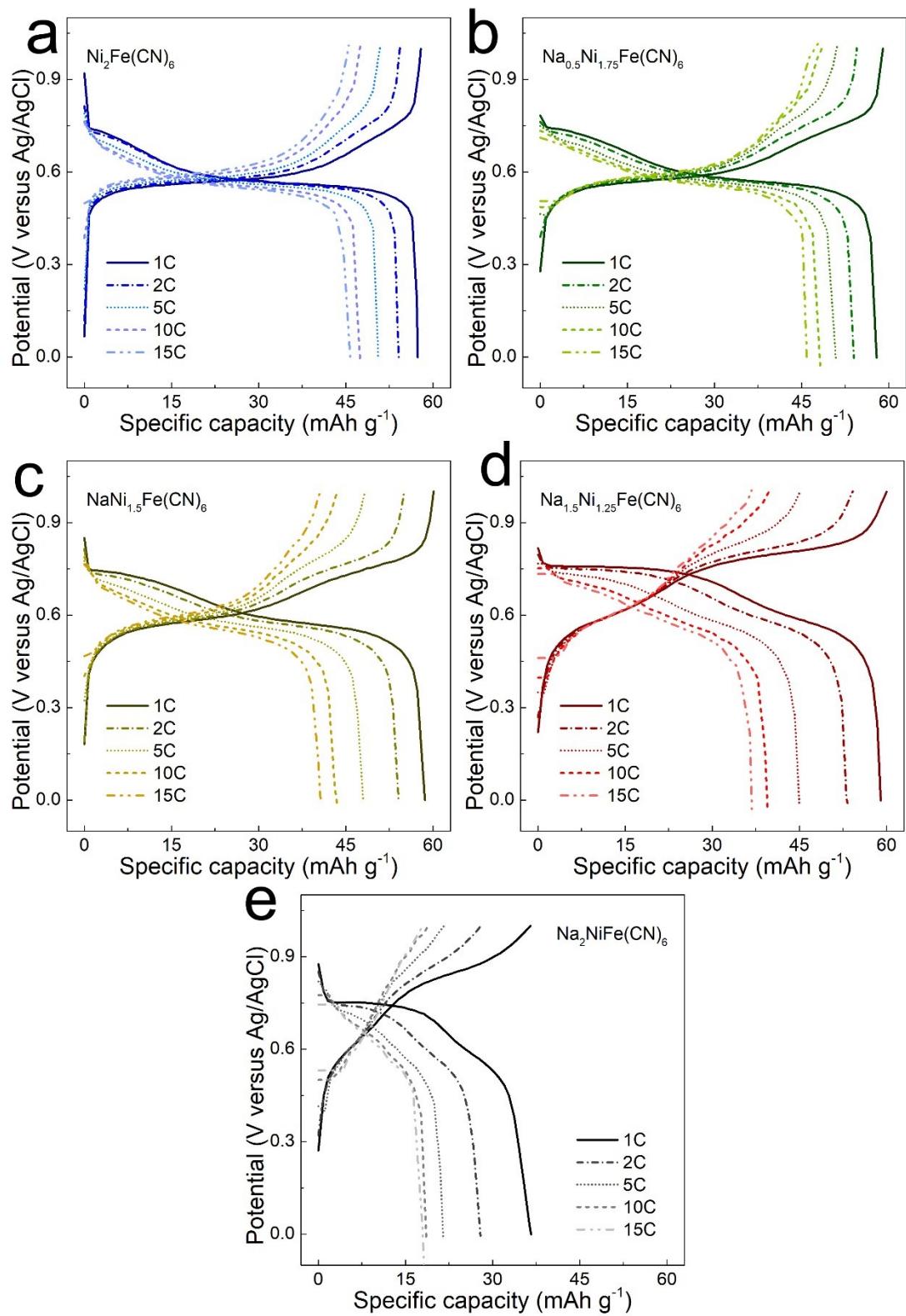
**Figure S1.** SEM images with large magnification of (a)  $\text{Ni}_2\text{Fe}(\text{CN})_6$ ; (b)  $\text{Na}_{0.5}\text{Ni}_{1.75}\text{Fe}(\text{CN})_6$ ; (c)  $\text{NaNi}_{1.5}\text{Fe}(\text{CN})_6$ ; (d)  $\text{Na}_{1.5}\text{Ni}_{1.25}\text{Fe}(\text{CN})_6$ ; (e)  $\text{Na}_2\text{NiFe}(\text{CN})_6$ .



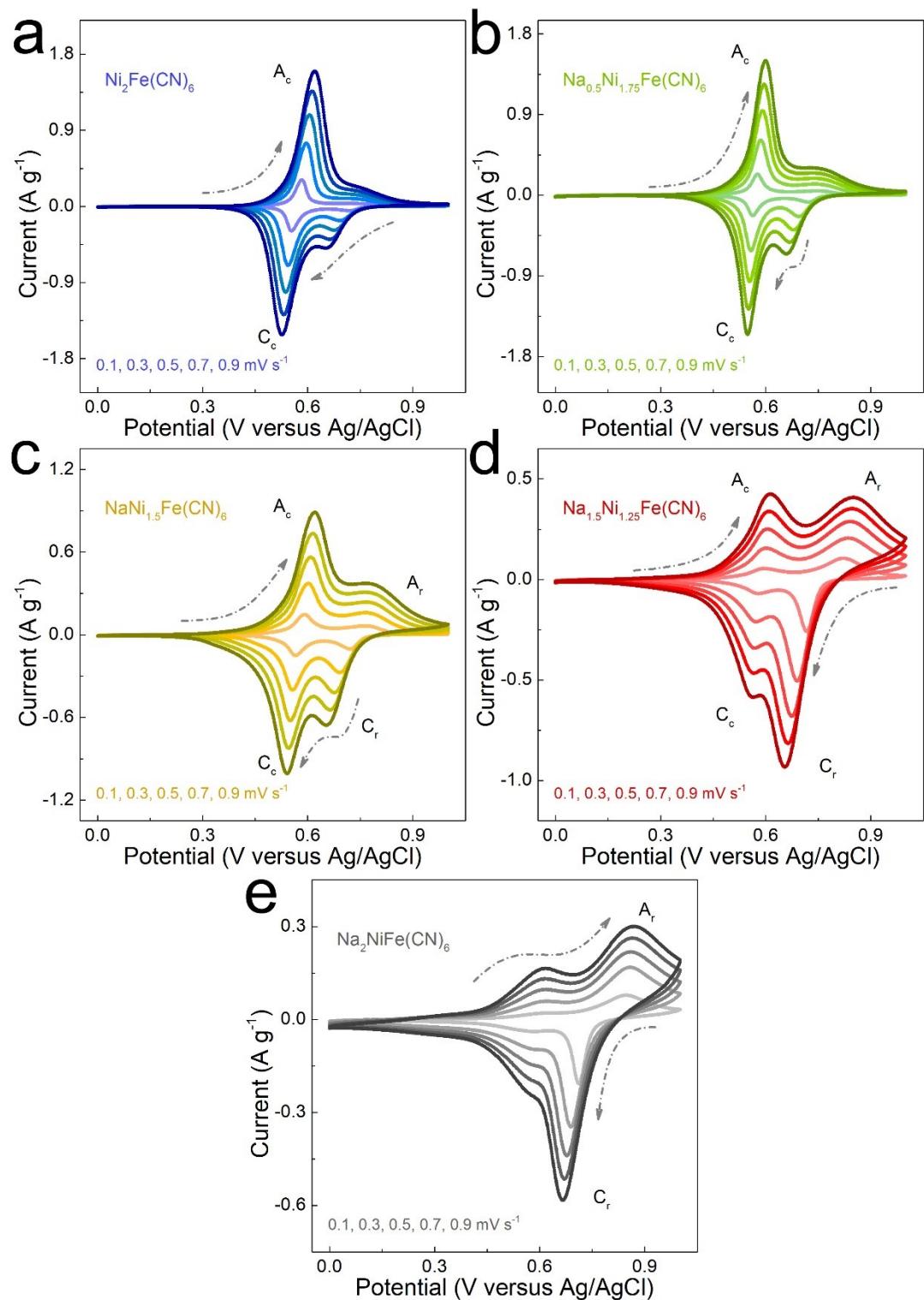
**Figure S2.** Graph of the redox peak plotted against  $x$  in  $\text{Na}_{2x}\text{Ni}_{2-x}\text{Fe}(\text{CN})_6$  ( $x = 0, 0.25, 0.5, 0.75$ , and  $1$ ).



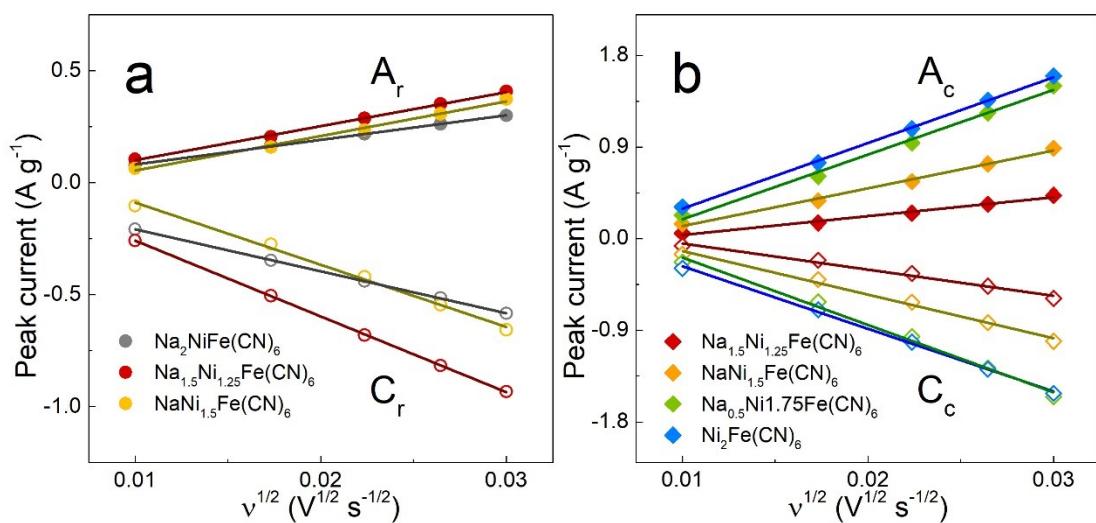
**Figure S3.** First seven potential curves of  $\text{Na}_2\text{NiFe}(\text{CN})_6$  at 1 C.



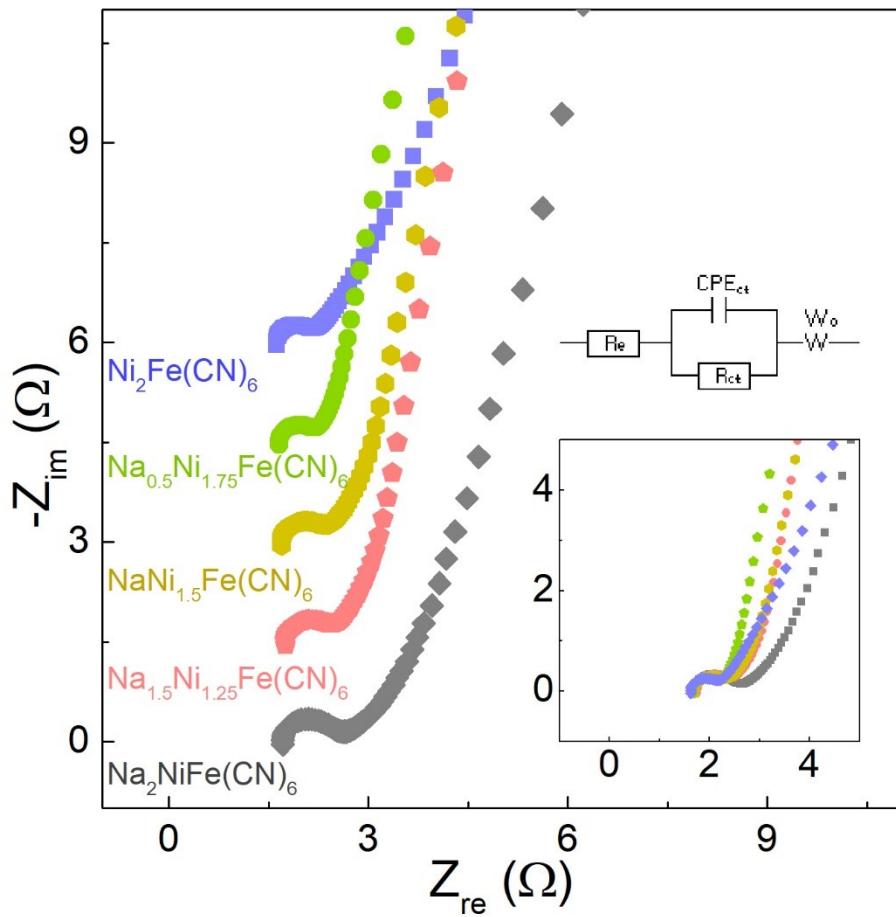
**Figure S4.** Galvanostatic potential profiles of (a) Ni<sub>2</sub>Fe(CN)<sub>6</sub>; (b) Na<sub>0.5</sub>Ni<sub>1.75</sub>Fe(CN)<sub>6</sub>; (c) NaNi<sub>1.5</sub>Fe(CN)<sub>6</sub>; (d) Na<sub>1.5</sub>Ni<sub>1.25</sub>Fe(CN)<sub>6</sub>; (e) Na<sub>2</sub>NiFe(CN)<sub>6</sub> at various current rates.



**Figure S5.** CV profiles of (a)  $\text{Ni}_2\text{Fe}(\text{CN})_6$ ; (b)  $\text{Na}_{0.5}\text{Ni}_{1.75}\text{Fe}(\text{CN})_6$ ; (c)  $\text{NaNi}_{1.5}\text{Fe}(\text{CN})_6$ ; (d)  $\text{Na}_{1.5}\text{Ni}_{1.25}\text{Fe}(\text{CN})_6$ ; (e)  $\text{Na}_2\text{NiFe}(\text{CN})_6$  at different scan rates.



**Figure S6.** Linear relationship of the peak current and the square root of scan rate ( $v^{1/2}$ ) for (a) rhombohedral phase and (b) cubic phase of  $\text{Na}_{2x}\text{Ni}_{2-x}\text{Fe}(\text{CN})_6$  ( $x = 0, 0.25, 0.5, 0.75$ , and 1).



**Figure S7.** Nyquist plots of  $\text{Na}_{2x}\text{Ni}_{2-x}\text{Fe}(\text{CN})_6$  ( $x = 0, 0.25, 0.5, 0.75$ , and  $1$ ). The inset shows an enlargement of Nyquist plots and an equivalent circuit.

**Table S1.** ICP-OES analysis of  $\text{Ni}_2\text{Fe}(\text{CN})_6$ ,  $\text{Na}_{0.5}\text{Ni}_{1.75}\text{Fe}(\text{CN})_6$ ,  $\text{NaNi}_{1.5}\text{Fe}(\text{CN})_6$ ,  $\text{Na}_{1.5}\text{Ni}_{1.25}\text{Fe}(\text{CN})_6$ , and  $\text{Na}_2\text{NiFe}(\text{CN})_6$ .

	<b>Na</b>	<b>Ni</b>	<b>Fe</b>
<b><math>\text{Ni}_2\text{Fe}(\text{CN})_6</math></b>	4.3549%	23.1807%	11.6106%
<b><math>\text{Na}_{0.5}\text{Ni}_{1.75}\text{Fe}(\text{CN})_6</math></b>	5.6718%	23.6330%	13.7176%
<b><math>\text{NaNi}_{1.5}\text{Fe}(\text{CN})_6</math></b>	6.5047%	21.0285%	13.4359%
<b><math>\text{Na}_{1.5}\text{Ni}_{1.25}\text{Fe}(\text{CN})_6</math></b>	7.0720%	14.3564%	10.8211%
<b><math>\text{Na}_2\text{NiFe}(\text{CN})_6</math></b>	7.6944%	11.9442%	9.9176%

**Table S2.** Comparison of rate capacities of  $\text{Na}_{2x}\text{Ni}_{2-x}\text{Fe}(\text{CN})_6$  ( $x = 0, 0.25, 0.5, 0.75$ , and 1).

	Capacity (mAh g <sup>-1</sup> )				
	1 C	2 C	5 C	10 C	15 C
<b>Ni<sub>2</sub>Fe(CN)<sub>6</sub></b>	57.4	54.1	50.6	47.5	45.8
<b>Na<sub>0.5</sub>Ni<sub>1.75</sub>Fe(CN)<sub>6</sub></b>	57.9	54.0	50.9	48.2	45.9
<b>NaNi<sub>1.5</sub>Fe(CN)<sub>6</sub></b>	58.6	54.1	48.0	43.5	40.7
<b>Na<sub>1.5</sub>Ni<sub>1.25</sub>Fe(CN)<sub>6</sub></b>	59.0	53.3	45.0	39.5	36.8
<b>Na<sub>2</sub>NiFe(CN)<sub>6</sub></b>	36.6	27.9	21.5	18.6	18.2

**Table S3.** Diffusion coefficients calculated from CV.

	D for Rhombohedral phase		D for Cubic phase	
	(cm <sup>2</sup> s <sup>-1</sup> )		(cm <sup>2</sup> s <sup>-1</sup> )	
	A <sub>r</sub> <sup>*</sup>	C <sub>r</sub> <sup>*</sup>	A <sub>c</sub> <sup>*</sup>	C <sub>c</sub> <sup>*</sup>
<b>Ni<sub>2</sub>Fe(CN)<sub>6</sub></b>	-- <sup>#</sup>	-- <sup>#</sup>	2.85×10 <sup>-9</sup>	2.58×10 <sup>-9</sup>
<b>Na<sub>0.5</sub>Ni<sub>1.75</sub>Fe(CN)<sub>6</sub></b>	-- <sup>#</sup>	-- <sup>#</sup>	2.76×10 <sup>-9</sup>	2.99×10 <sup>-9</sup>
<b>NaNi<sub>1.5</sub>Fe(CN)<sub>6</sub></b>	1.63×10 <sup>-10</sup>	5.27×10 <sup>-10</sup>	9.42×10 <sup>-10</sup>	1.25×10 <sup>-9</sup>
<b>Na<sub>1.5</sub>Ni<sub>1.25</sub>Fe(CN)<sub>6</sub></b>	1.57×10 <sup>-10</sup>	7.82×10 <sup>-10</sup>	2.35×10 <sup>-10</sup>	4.52×10 <sup>-10</sup>
<b>Na<sub>2</sub>NiFe(CN)<sub>6</sub></b>	8.25×10 <sup>-11</sup>	2.40×10 <sup>-10</sup>	-- <sup>#</sup>	-- <sup>#</sup>

\* A<sub>r</sub>: anodic peak current for rhombohedral phase; C<sub>r</sub>: cathodic peak current for rhombohedral phase; A<sub>c</sub>: anodic peak current for cubic phase; C<sub>c</sub>: cathodic peak current for rhombohedral phase.

<sup>#</sup> The values can hardly be calculated because the corresponding peak currents are difficult to identify.