Electronic Supplementary Information

Hexacyanometallates for Sodium-Ion Batteries: Insights into Higher Redox Potentials Using $d$
Electronic Spin Configurations

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<table>
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<th>Compound</th>
<th>Lattice parameters</th>
<th></th>
<th></th>
<th>R_{exp}</th>
<th>R_{wp}</th>
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<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>Exp.</td>
<td>DFT</td>
<td>Exp.</td>
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<tr>
<td>NFMCN</td>
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<td>6.5803</td>
<td>18.9286</td>
<td>19.4447</td>
<td>5.77</td>
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**Table S1** Comparison of lattice parameters of NFMCN obtained from Rietveld refinement results and First-principles calculation.
Fig. S1 Binding energy curves as a function of distance between Fe and (a) CN and (b) NC. $r_0$ refers to the distance at equilibrium state indicated as red circle.
**Fig. S2** The projected partial density of states (PDOS) of $3d$ electrons based on a sampled intermediate phase between the lowest and highest mixing enthalpy in Na$_2$FeMn(CN)$_6$ from Fig. 2a.
Fig. S3 The projected partial density of states (PDOS) of 2p electrons based on the phase of lowest mixing enthalpy ((a) C and (b) N) and the phase of highest mixing enthalpy ((c) C and (d) N) from Fig. 2a in Na$_2$FeMn(CN)$_6$. 
**Fig. S4** (a) Initial charge (desodiation) and discharge (sodiation) curves between 2.0 V vs. 4.0 Na/Na$^+$ with a constant specific current of 0.1 C rate, and (b) corresponding dQ/dV profiles. (c) Charge and discharge curves from the first to fifth cycles under the same condition as (a). (d) The corresponding specific capacities as a function of cycle number.