

## Electronic Supplementary Information

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

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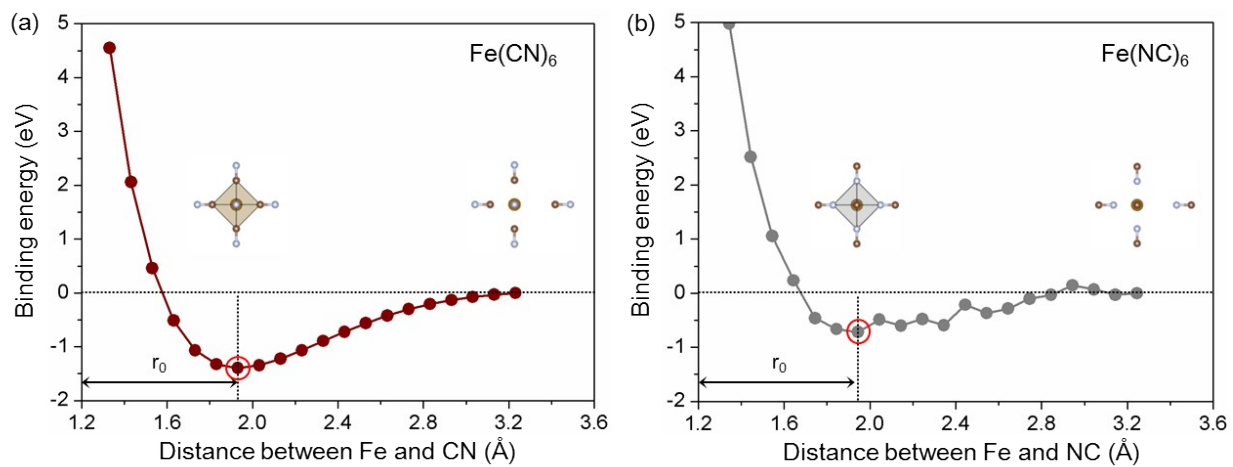
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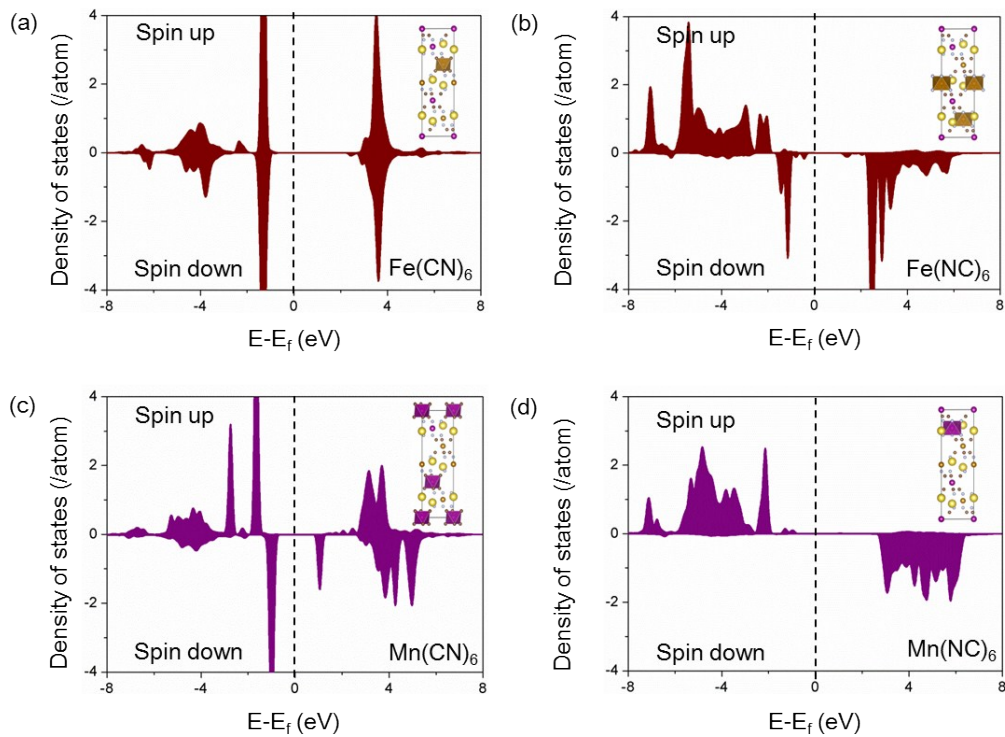
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Compound	Lattice parameters				R <sub>wp</sub>	R <sub>exp</sub>
	a (Å)		c (Å)			
	Exp.	DFT	Exp.	DFT		
NFMCN	6.5788	6.5803	18.9286	19.4447	5.77	6.42

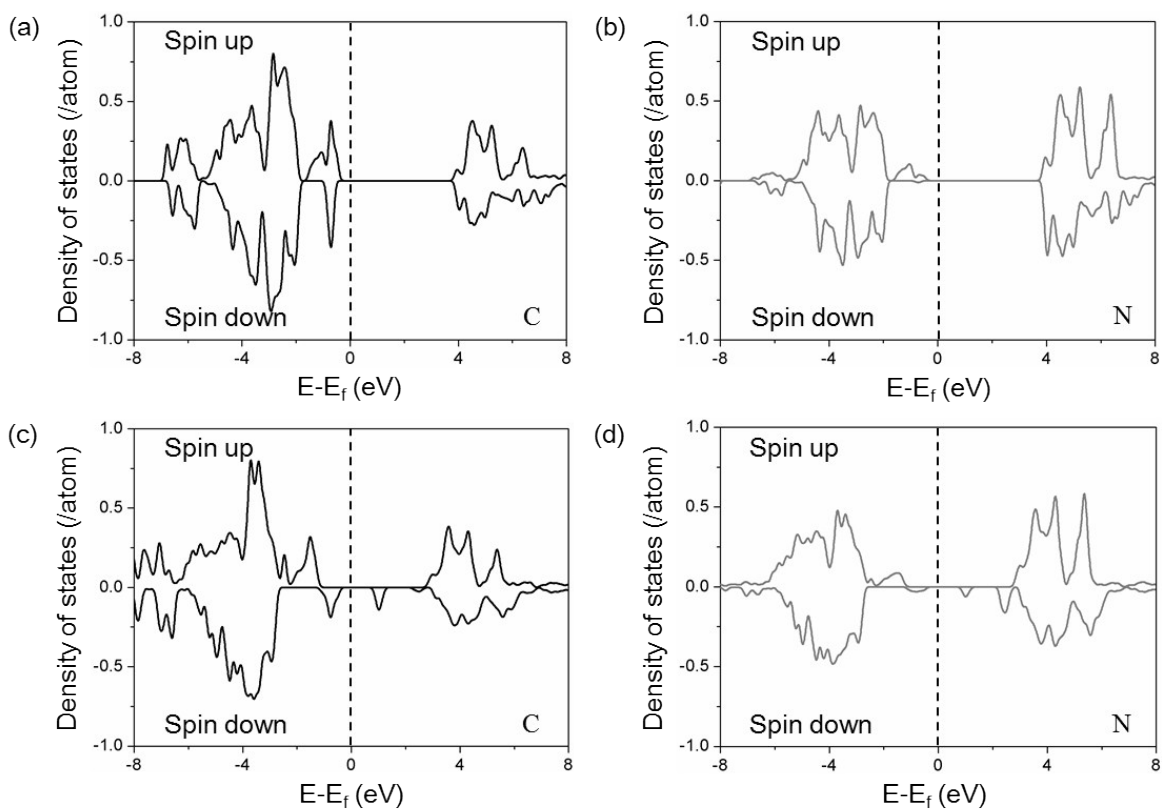
**Table S1** Comparison of lattice parameters of NFMCN obtained from Rietveld refinement results and First-principles calculation.



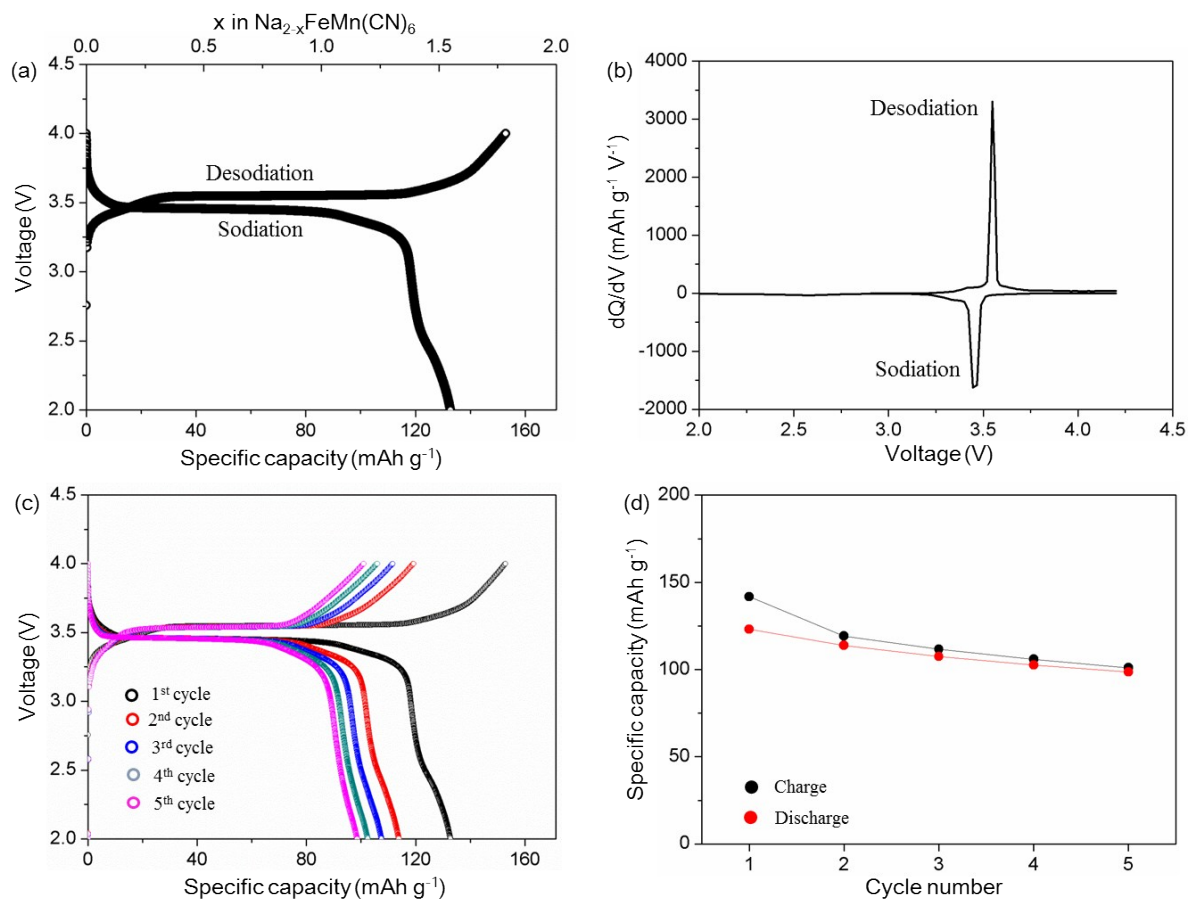
**Fig. S1** Binding energy curves as a function of distance between Fe and (a) CN and (b) NC.  $r_0$  refers to the distance at equilibrium state indicated as red circle.



**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  $\text{Na}_2\text{FeMn}(\text{CN})_6$  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  $\text{Na}_2\text{FeMn}(\text{CN})_6$ .



**Fig. S4** (a) Initial charge (desodiation) and discharge (sodiation) curves between 2.0 V vs. 4.0 Na/Na<sup>+</sup> 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.