

Electronic Supplementary Information for

## Spinel Compounds as Multivalent Battery Cathodes: A Systematic Evaluation Based on *ab initio* Calculations

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Fig. S1 shows an example of how the energy above the hull<sup>1-3</sup> is determined for the spinel  $\text{Mn}_2\text{O}_4$ . In the Mn-O compositional phase diagram, by connecting the lowest formation energy compounds (solid blue dots) that cannot be decomposed to reduce the energy, a convex hull is constructed (solid black lines). Adding the spinel  $\text{Mn}_2\text{O}_4$  energy and composition in the plot appears a red circle  $\sim 32\text{meV}/\text{atom}$  above the convex hull. Hence, the energy above hull of spinel  $\text{Mn}_2\text{O}_4$  is  $32\text{meV}/\text{atom}$ .

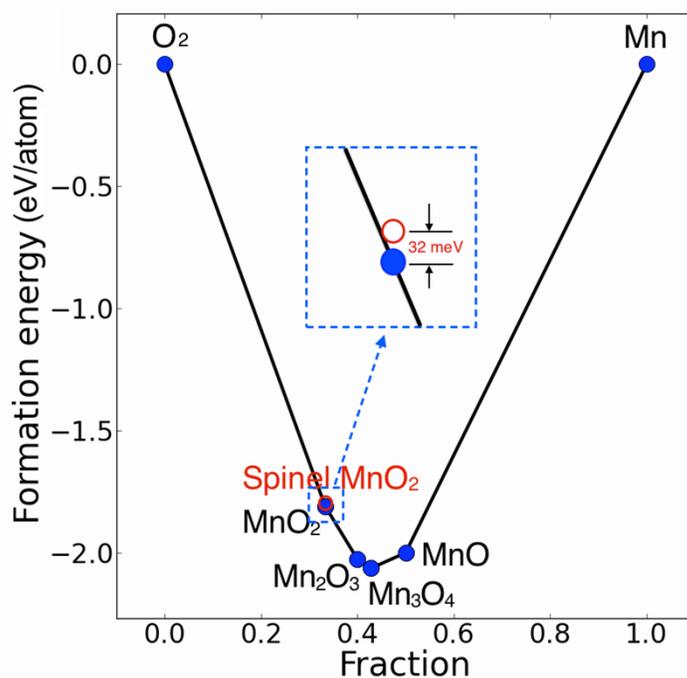


Fig. S1 The energy above hull is calculated as the formation energy difference between a compound and the convex hull trace (black line). As an example, the energy above hull for the spinel  $\text{MnO}_2$  is calculated as the energy difference between spinel  $\text{Mn}_2\text{O}_4$  (marked as a red open circle) and the most stable  $\text{MnO}_2$  polymorph.

Several approaches were applied to address the temperature effect. We found that the entropy term of a reaction is dominated by the entropy of the gas. Therefore, for a solid-state reaction that does not involve any gas phase on both sides of the stoichiometric equation, the temperature effect (entropy term) is much smaller than the enthalpy, hence the temperature effect should be not prominent at a room temperature<sup>4</sup>. For those stoichiometric reaction that involves gas phases, the O<sub>2</sub> gas energy has been taken into account with a gas phase energy correction, which uses the corrected O<sub>2</sub> chemical potential, to adjust all the phase diagram to standard ambient condition.

Wang *et al.* shows that the energy of O<sub>2</sub> gas at 0 K includes an error to overestimate the O<sub>2</sub> bonding.<sup>5</sup> Such error arises from the overbinding of the O<sub>2</sub> molecule in GGA as well as an additional GGA error associated with adding electrons to the oxygen *p* orbital when O<sup>2-</sup> is formed from O<sub>2</sub>. They also showed that such error can be corrected through a constant shift of -1.36 eV per O<sub>2</sub> molecule, which includes the PΔV contribution to the oxygen enthalpy by comparing with the experimental thermodynamic data for O<sub>2</sub> at 0.1 MPa at 298K, as obtained from the JANAF thermochemical tables<sup>6</sup>. Following this convention, we have applied this same shift to the calculated energy of the O<sub>2</sub> molecule to gauge the convex hull energies.

For the thermal stability calculation, the temperature effect is taken into account by adjusting the entropy term (-TΔS) of the O<sub>2</sub> chemical potential at corresponding temperature based on Ong *et al.*<sup>1</sup>. The reaction Gibbs free energy is  $\Delta G = \Delta H - T\Delta S$ , where as ΔG is exclusively given by the -TΔS term, where ΔS corresponds to the oxygen gas entropy. The entropy term of O<sub>2</sub> gas as a function of temperature can be solved iteratively based on the JANAF thermochemistry data.<sup>6</sup> Using the ΔS at the desired temperature allows us to access the thermal stability at given temperature.<sup>5</sup>

To test the inversed spinel stability we performed DFT calculations for a small cell with cation inversion for Ca/Mg/Zn spinels with a transition metal selected from the B={Ti, V, Cr, Mn, Co, Fe, Ni} set. This treatment, which is similar to that employed by Bhattacharya *et al.*<sup>7</sup>, ignores some of the randomness of inverse spinel, but gives a reliable trend. Fig S2. shows the energy difference between inverse spinel and normal spinel at a given composition. All the energy differences are positive, which indicates that the normal spinel is more energetically favorable compared to the inverse spinel.

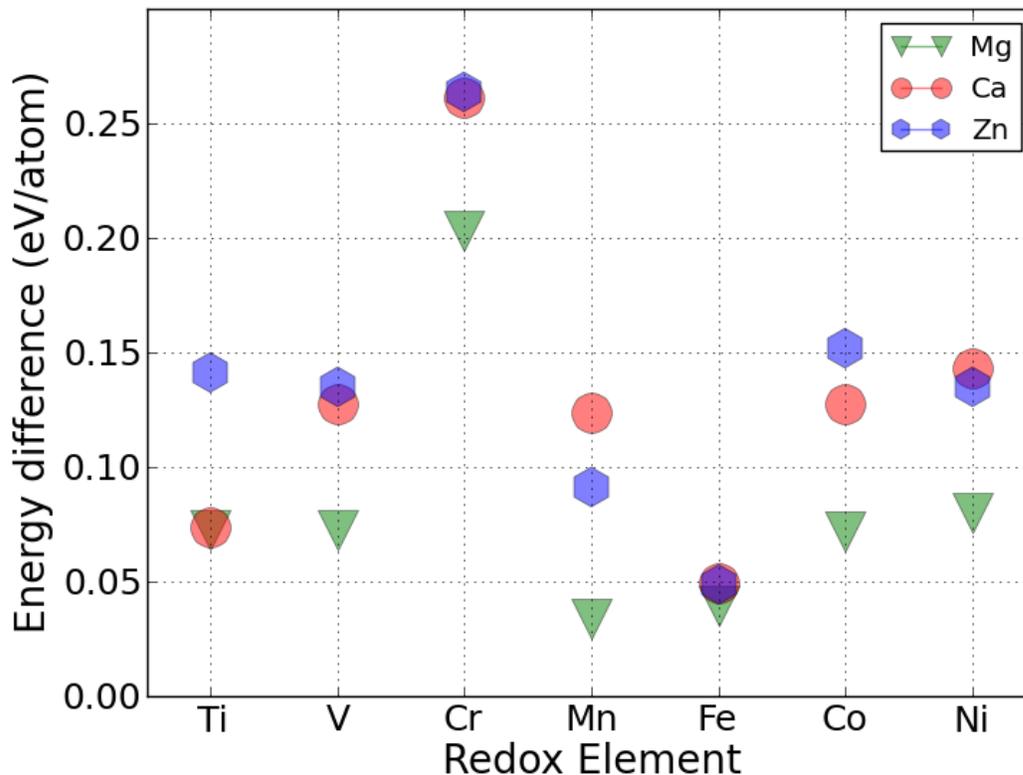


Fig. S2 the energy difference between inverse spinel and normal spinel at a given composition. A positive value indicates that the normal spinel phase is more energetically stable than inverse spinel.

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- (2) Ong, S. P.; Jain, A.; Hautier, G.; Kang, B.; Ceder, G. Thermal Stabilities of Delithiated Olivine MPO<sub>4</sub> (M=Fe, Mn) Cathodes Investigated Using First Principles Calculations. *Electrochem. commun.* **2010**, *12*, 427–430.
- (3) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; *et al.* Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater.* **2013**, *1*, 011002.
- (4) Wang, L.; Maxisch, T.; Ceder, G. A First-Principles Approach to Studying the Thermal Stability of Oxide Cathode Materials. **2007**, 543–552.
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- (6) M. W. Chase. *NIST-JANAF Thermochemical Tables*; American Chemical Society: New York, 1998; p. 2013.
- (7) Bhattacharya, J.; Wolverton, C. Relative Stability of Normal vs. Inverse Spinel for 3d Transition Metal Oxides as Lithium Intercalation Cathodes. *Phys. Chem. Chem. Phys.* **2013**, *15*, 6486–6498.