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## Supplementary Information for

The Ni/Li Disordering Evolution Mechanisms in Ni-Based Layered Cathode

# Materials: Insights from First-Principles Calculations

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#### **METHODOLOGY**

All the first-principles calculations based on the density functional theory (DFT) framework are implemented in the Vienna *ab initio* simulation package (VASP) code.<sup>1</sup> The projector-augmented wave (PAW) method is used for the pseudopotentials of atomic cores.<sup>2</sup> A plane-wave basis set <sup>3</sup> with an energy cutoff of 400 eV is used. The spin-polarization is considered. The Brillouin zone is sampled with the  $5 \times 5 \times 2$  kpoint mesh using the Monkhorst-Pack scheme.<sup>4</sup> The exchange-correlation functional is counted by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) version.<sup>5</sup> The strong correlation effect of transition metal is addressed with the Hubbard U correction (GGA+U).<sup>6,7</sup> The U value for the 3d state of Ni is 4.05 eV, which is taken from previous theoretical works.<sup>8</sup> The energy convergence criterion for self-consistent calculations is set to be 10<sup>-5</sup> eV. The force convergence criterion for structural relaxations is set to be 0.01 eV/Å. The Ni ion migration in LiNiO2 is performed in a 2  $\times$  2  $\times$  1 supercell containing 48 atoms. The Li<sub>27</sub>Ni<sub>9</sub>Co<sub>9</sub>Mn<sub>9</sub>O<sub>54</sub>, Li<sub>27</sub>Ni<sub>27</sub>O<sub>54</sub>, and Li<sub>10</sub>Ni<sub>6</sub>Co<sub>2</sub>Mn<sub>2</sub>O<sub>20</sub> supercells are used for NCM111, LNO, and NCM622 materials in Li<sub>Ni</sub> anti-site calculations, respectively. Uniaxial strain (ε) was calculated by dividing the lattice deformation ( $\Delta \alpha$ ) by the initial lattice constant ( $\alpha$ ) in that orientation (i.e.,  $\varepsilon = \Delta \alpha / \alpha$ ). The Ni/Li anti-site configurations were generated by exchanging the positions of Ni and Li ions, followed by structural optimization. The anti-site formation energy ( $\Delta E$ ) is defined as:

$$\Delta E = E(\text{defect}) - E(\text{pristine})$$

Where E(defect) and E(pristine) are the total energies of the configuration with Ni/Li anti-site defect and the pristine configuration, respectively.

### SUPPLEMENTARY FIGURES



**Fig. S1** (a) The orange and green bar charts represent the Ni<sup>3+</sup> and Ni<sup>4+</sup> content, respectively. And the average magnetic moment of Ni ion in Li<sub>1-x</sub>NiO<sub>2</sub> structures for x = 0.00, 0.25, 0.50, 0.75.

The contents of Ni<sup>3+</sup> and Ni<sup>4+</sup> cations are determined by the atomic magnetic moments. It can be observed that the proportion of Ni<sup>3+</sup> ions decreases with an increase in x, while the proportion of Ni<sup>4+</sup> ions increases. The average magnetic moment of Li<sub>1-x</sub>NiO<sub>2</sub> increases with the growth of x.



**Fig. S2** (a) The PDOS of Ni<sup>2+</sup>, Ni<sup>3+</sup>, and Ni<sup>4+</sup> ions. Schematic diagram of the 3*d* electron configurations (b) and the NiO<sub>6</sub> octahedron local structures (c). The blue and red spheres represent Ni and O atoms, respectively.



**Fig. S3** (a) The optimized structure of  $\text{LiNiO}_2$ . The Li/vacancy configurations for the  $\text{Li}_{1-x}\text{NiO}_2$  of (b) x = 0.00, (c) x = 0.25, (d) x = 0.50, and (e) x = 0.75. The purple and blue spheres represent Li and Ni atoms, respectively.



Fig. S4 Difference between the interlayer spacing of Li and Ni layers under strain.



**Fig. S5** The relationship between  $d_{LiO}$ - $d_{NiO}$  and the migration energy of Ni<sup>3+</sup> migrate to the octahedral site (a) and tetrahedral site (b) of the Li layer. The relationship between  $d_{LiO}$ - $d_{NiO}$  and the migration energy of Ni<sup>4+</sup> migrate to the octahedral site (c) and tetrahedral site (d) of the Li layer.



**Fig. S6** Difference between the LiO and NiO slab distances before and after Ni migration. The LiO slabs with and without Ni ion are marked as "slab A" and "slab B", respectively.



**Fig. S7** Two migration paths for the coordinated migration of Li ions and Ni ions in  $Li_{0.5}NiO_2$ . Path 1 and path 2 represent the migration of Li ions from the original site (a) to octahedral (b) and tetrahedral (c) sites in the Ni layer when Ni ions migrate to the octahedral site in the Li layer, respectively.

	Initial magnetic moment (µB)	Optimized magnetic moment (µB)
Ni <sup>2+</sup>	0 (low spin)	1.7(high spin)
	2 (high spin)	1.7(high spin)
Ni <sup>3+</sup>	3 (high spin)	1.0 (low spin)
	1 (low spin)	1.0 (low spin)
Ni <sup>4+</sup>	4 (high spin)	0.0 (low spin)
	0 (low spin)	0.0 (low spin)

Table S1 The initial and optimized magnetic moments of Ni<sup>2+</sup>, Ni<sup>3+</sup>, and Ni<sup>4+</sup> ions.

Both the high-spin and low-spin configurations of Ni<sup>2+</sup>, Ni<sup>3+</sup>, and Ni<sup>4+</sup> ions were tested by setting different initial magnetic moments. The result revealed that different initial spin configurations consistently converged to the same spin configurations after selfconsistent field (SCF) iteration, as listed in Table S1. The optimized electronic states of Ni<sup>2+</sup>, Ni<sup>3+</sup>, and Ni<sup>4+</sup> ions are as follows: Ni<sup>2+</sup> exhibits a high-spin state  $(t_{2g}^{6}e_{g}^{2})$  with a magnetic moment of about 2 µB, Ni<sup>3+</sup> shows a low-spin state  $(t_{2g}^{6}e_{g}^{1})$  with a magnetic moment of about 1 µB, and Ni<sup>4+</sup> displays a low-spin state  $(t_{2g}^{6})$  with a magnetic moment of about 0 µB.

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