**Supplementary Information**

# Unlocking the Potential of Ni-Rich $LiNi_{0.9}Co_{0.1}O_2$ Cathodes: A DFT Investigation of Performance-Limiting Factors

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## Supercell Convergence

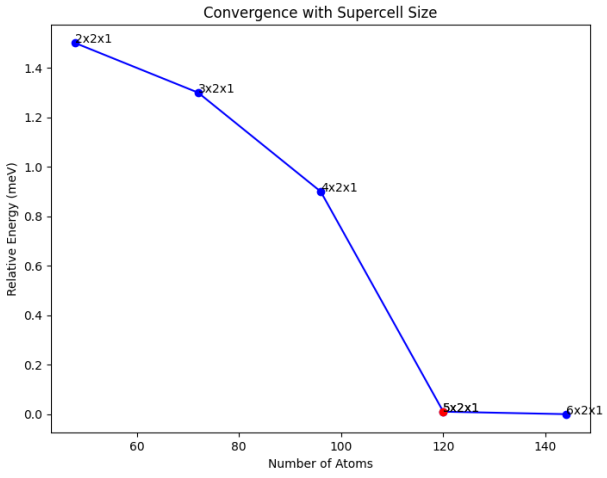


Figure S1: Supercell convergence plot

# Effect of Hubbard U parameter changes on the structural properties and Li vacancy formation energy in NC91

Table S1: Effect of changes to Hubbard U parameter for Ni to the structural properties of NC91

| U value | Unit cell volume (Å$^3$) |
|---|---|
| 4.5 | 104.044 |
| 5.0 | 104.09 |
| 5.5 | 103.161 |
| 6.0 | 102.669 |
| 6.5 | 102.687 |
| 7.0 | 102.295 |
| 7.5 | 102.181 |

Table S2: Effect of changes to Hubbard U parameter for Ni to the vacancy formation energy in NC91

| U value | Vacancy Formation energy (eV) |
|---|---|
| 4.5 | 5.57 |
| 5.0 | 5.67 |
| 6.0 | 5.44 |
| 6.5 | 6.16 |

# Effect of London Dispersion

Table S3: Comparison of Bulk Properties with and without Dispersion

| Property | PBE (no dispersion) | PBE-D3 (with dispersion) | Difference ($\Delta$) |
|---|---|---|---|
| Unit cell volume (Å$^3$) | 98.11 | 97.86 | 0.25 |
| Total Energy (eV) | -157.56 | -157.64 | 0.08 |

Table S4: Defect Formation Energies with and without Dispersion Defect considered: Oxygen vacancy (neutral charge state).

| Material | Method | $E_{defect}$ (eV) | Difference ($\Delta E$, eV) |
|---|---|---|---|
| $LiCoO_3$ | PBE | 2.32 | |
| | PBE-D3 | 2.38 | 0.06 |
| $LiNiO_3$ | PBE | 2.45 | |
| | PBE-D3 | 2.46 | 0.01 |

# Chemical Potentials for $LiMO_2$ (M = Co, Ni, $Ni_{0.9}Co_{0.1}$)

The choice of chemical potentials is influenced by equilibrium conditions and constraints that prevent the precipitation of secondary phases. To form stable configurations of LNO and LCO, the chemical potentials must satisfy the following conditions:

$$\Delta\mu_{Li} + \Delta\mu_{Co} + 2\Delta\mu_O = \Delta\mu_{E_f}(LCO), \tag{1}$$

$$\Delta\mu_{Li} + \Delta\mu_{Ni} + 2\Delta\mu_O = \Delta\mu_{E_f}(LNO). \tag{2}$$

Where,

$$\Delta\mu_i = \mu_i - \mu_i^o \tag{3}$$

In addition, to prevent the precipitation of secondary phases, the following need to be considered as boundaries of the chemical potentials:[1]

For LCO:

$$2\Delta\mu_{Li} + \Delta\mu_O \leq -5.75eV/fu...(Li_2O), \tag{4}$$

$$2\Delta\mu_{Li} + 2\Delta\mu_O \leq -5.84eV/fu...(Li_2O_2) \tag{5}$$

$$3\Delta\mu_{Co} + 4\Delta\mu_O \leq -9.94eV/fu...(Co_3O_4) \tag{6}$$

$$6\Delta\mu_{Li} + \Delta\mu_{Co} + 4\Delta\mu_O \leq -20.62eV/fu...(Li_6CoO_4) \tag{7}$$

$$\Delta\mu_{Co} + 2\Delta\mu_O \leq -3.13eV/fu...(CoO) \tag{8}$$

For LNO:

$$\Delta\mu_{Ni} + 2\Delta\mu_O \leq -2.89eV/fu...(NiO) \tag{9}$$

$$2\Delta\mu_{Li} + \Delta\mu_{Ni} + 2\Delta\mu_O \leq -8.76eV/fu...(Li_2NiO_2) \tag{10}$$

$$\Delta\mu_{Li} + \Delta\mu_{Ni} + 3\Delta\mu_O \leq -9.1eV/fu...(Li_NiO_3), \tag{11}$$

$$2\Delta\mu_{Li} + \Delta\mu_O \leq -5.75eV/fu...(Li_2O) \tag{12}$$

To prevent the emergence of single metal phases in LNO and LCO, the following boundaries were used:

$$\Delta\mu_{Li} \leq E_{Li} \tag{13}$$

$$\Delta\mu_{Ni} \leq E_{Ni} \tag{14}$$

$$\Delta\mu_O \leq E_O \tag{15}$$

Table S5: Formation Enthalpies at 0 K used for stability diagram (from ref. [1])

| System | Crystal Structure | Formation enthalpy (eV) |
|---|---|---|
| $Li_2O$ | Cubic | -5.75 |
| $Li_2O_2$ | Hexagonal | -5.84 |
| $Li_2NiO_2$ | Trigonal | -8.76 |
| $Li_2NiO_3$ | Monoclinic | -9.10 |
| $Li_6CoO_4$ | Tetragonal | -20.62 |
| NiO | Cubic | -2.89 |
| CoO | Hexgaonal | -3.13 |
| $Co_3O_4$ | Cubic | -9.94 |

Table S6: Chemical Potentials for points A-K in Fig 2 for LCO

| Phase | Symbol | $\Delta\mu Li$ | $\Delta\mu Co$ | $\Delta\mu O$ |
|---|---|---|---|---|
| $Li_2O$ | A | 0.00 | -4.54 | - 5.75 |
| | B | -2.88 | -4.09 | 0.00 |
| $Li_2O_2$ | C | 0.00 | -1.12 | -2.92 |
| | D | -2.92 | -4.04 | 0.00 |
| CoO | E | -0.70 | 0.00 | -3.13 |
| | F | -3.83 | -3.13 | 0.00 |
| $Co_3O_4$ | G | -1.99 | 0.00 | -2.49 |
| | H | -3.65 | -3.31 | 0.00 |
| $Li_6CoO_4$ | I | 0.00 | -6.70 | -6.83 |
| | J | -1.68 | 0.00 | -2.64 |
| | K | -2.73 | -4.23 | 0.00 |

Table S7: Chemical Potentials for points A-G in Fig 2 for LNO

| Phase | Symbol | $\Delta\mu Li$ | $\Delta\mu Co$ | $\Delta\mu O$ |
|---|---|---|---|---|
| NiO | A | -0.32 | 0.00 | -2.89 |
| | B | -3.21 | -2.89 | 0.00 |
| $Li_2NiO_2$ | C | -2.66 | 0.00 | -1.72 |
| | D | -2.66 | -3.44 | 0.00 |
| $Li_2NiO_3$ | E | 0.00 | -0.10 | -3.00 |
| | F | -0.10 | 0.00 | -3.10 |
| | G | -3.00 | -3.10 | 0.00 |

Table S8: Chemical Potentials for points A-N in Fig 2 for NC91

| Phase | Symbol | $\Delta\mu Li$ | $\Delta\mu Co$ | $\Delta\mu O$ |
|---|---|---|---|---|
| CoO | A | -0.70 | 0.00 | -3.13 |
| | B | -3.83 | -0.31 | 0.00 |
| $Co_3O_4$ | C | -1.99 | 0.00 | -2.49 |
| | D | -3.65 | -0.33 | 0.00 |
| $Li_6CoO_4$ | E | 0.00 | -0.67 | -6.83 |
| | F | -1.68 | 0.00 | -2.64 |
| | G | -2.73 | -0.42 | 0.00 |
| NiO | H | -0.32 | 0.00 | -2.89 |
| | I | -3.21 | -2.60 | 0.00 |
| $Li_2NiO_2$ | J | -2.66 | 0.00 | -1.72 |
| | K | -2.66 | -3.10 | 0.00 |
| $Li_2NiO_3$ | L | 0.00 | -0.09 | -3.00 |
| | M | -0.10 | 0.00 | -3.10 |
| | N | -3.00 | -2.79 | 0.00 |

# References

(1) Hoang, K.; Johannes, M. D. Defect chemistry in layered transition-metal oxides from screened hybrid density functional calculations. *Journal of Materials Chemistry A* **2014**, *2*, 5224–5235.