First-Principles Thermodynamic Computation of Theoretical Cell Voltage and Gravimetric Capacity for Olivine $LiFePO_4$ and Layered $LiCoO_2$ versus a Lithium-Metal Anode

A Thermodynamic Derivation from Standard Reference Data

Technical Report

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Scope. This report derives, from first principles and tabulated thermodynamic reference data, the theoretical average cell voltage (V vs Li/Li^+) and the theoretical gravimetric specific capacity (mA h/g) of two positive-electrode chemistries paired with a lithium-metal negative electrode: (i) the olivine reaction $LiFePO_4 \rightleftharpoons FePO_4 + Li^+ + e^-$ and (ii) the layered-oxide reaction $LiCoO_2 \rightleftharpoons Li_{0.5}CoO_2 + 0.5\,Li^+ + 0.5\,e^-$. Every half-reaction, the governing relation $\Delta G = -nFE$, and the Faraday/formula-mass arithmetic are shown in full. All reference values are cited to primary calorimetric, first-principles, and reference-compilation sources. A comparison of the computed quantities against widely reported experimental values, together with a physical analysis of the discrepancies, concludes the report.

Abstract

Using standard thermodynamic reference data and the exact electrochemical–gravimetric definitions, we compute the theoretical performance of olivine $LiFePO_4$ (LFP) and layered $LiCoO_2$ (LCO) cathodes against a lithium-metal anode. The theoretical gravimetric capacities follow directly from Faraday's law and the formula masses: 169.9 mA h/g for the one-electron olivine reaction ($M = 157.76\,\mathrm{g/mol}$, $n = 1$) and 136.9 mA h/g for the half-lithium layered-oxide reaction ($M = 97.87\,\mathrm{g/mol}$, $n = 0.5$; the full one-lithium limit is 273.9 mA h/g). For the cell voltage we apply $E = -\Delta G_\mathrm{r}/nF$. For LFP, a Hess-cycle evaluation built from high-temperature oxide-melt solution calorimetry of $LiFePO_4$ and $FePO_4$ [Iyer *et al.*, 2006] combined with the standard formation enthalpy of Li_2O yields $\Delta H_\mathrm{r} = +337\,\mathrm{kJ/mol}$ and $E \approx 3.49\,\mathrm{V}$; an independent GGA+$U$ first-principles value [Zhou *et al.*, 2004] gives 3.4 V. For LCO, the first-principles reaction free energy corresponding to the Co^{3+}/Co^{4+} couple gives $E \approx 4.0\,\mathrm{V}$, corroborated by the measured open-circuit voltage (3.9 V) and by calorimetry showing that deep delithiation is endothermic. Computed values agree with reported experimental voltages (3.42 V to 3.45 V for LFP; ~ 3.9 V average for LCO) to within 0.1 V. The capacity gap for LCO (137 vs a nominal 274 mA h/g) is not a thermodynamic error but the direct consequence of the stated half-lithium reaction basis, which itself reflects the structural collapse and oxygen loss that make deeper delithiation irreversible. Residual voltage discrepancies are traced to the standard-state ($\Delta G \approx \Delta H$) approximation, two-phase versus solid-solution reaction pathways, and functional errors in the first-principles reference.

Contents

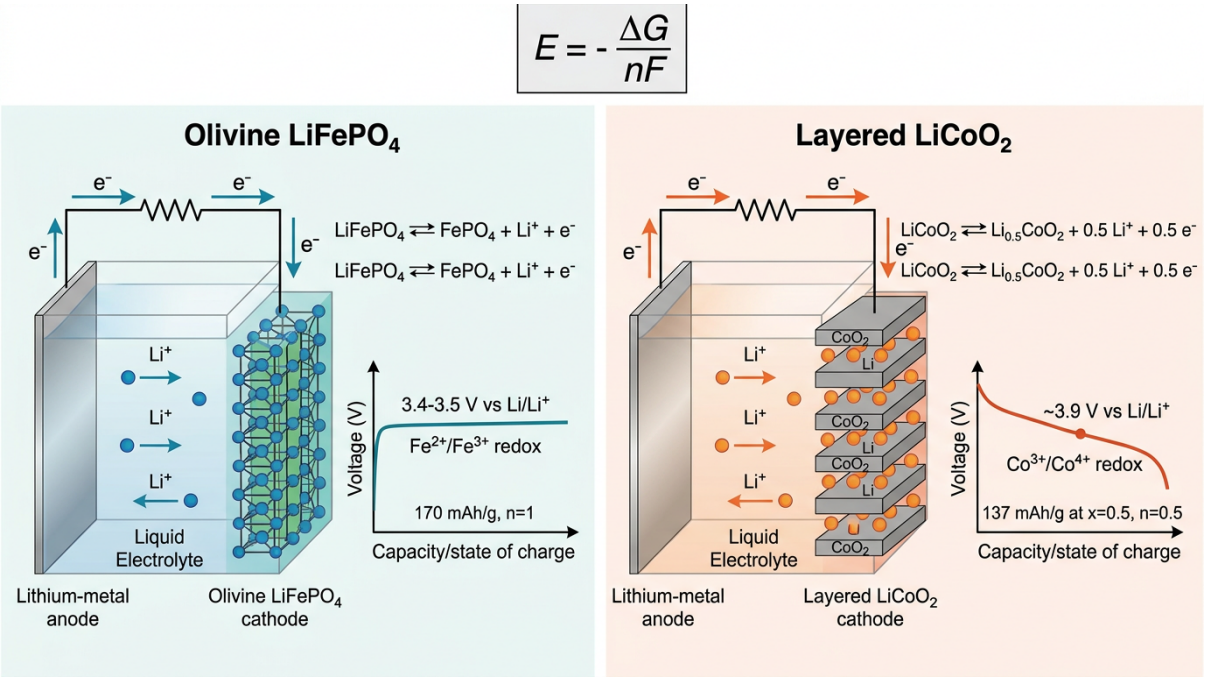

Figure 1: Graphical abstract. Thermodynamic reaction pathways and half-cell configurations for the two chemistries studied. *Left:* the olivine $LiFePO_4 \rightleftharpoons FePO_4$ one-electron reaction operating on the Fe^{2+}/Fe^{3+} couple, delivering a flat 3.4 V to 3.5 V plateau and 170 mA h/g. *Right:* the layered $LiCoO_2 \rightleftharpoons Li_{0.5}CoO_2$ half-lithium reaction on the Co^{3+}/Co^{4+} couple, delivering a sloping ~ 3.9 V profile and 137 mA h/g within the reversible window. Both are referenced to a lithium-metal anode; the governing relation $E = -\Delta G/nF$ is applied throughout.

1 Introduction

The energy that a lithium-ion cell can store is set, at the most fundamental level, by two thermodynamic quantities of the positive electrode: the chemical potential at which lithium is inserted or removed—which fixes the cell voltage—and the number of moles of lithium (and compensating electrons) that can be exchanged per unit mass—which fixes the specific capacity. Because the product of these quantities is the gravimetric energy density, a rigorous, from-first-principles evaluation of both is the natural starting point for comparing electrode chemistries [1–3]. These two quantities also frame the broader challenges—energy density, cost and safety—that continue to shape rechargeable-lithium research [4]. The purpose of this report is to carry out that evaluation explicitly for two archetypal cathodes—olivine $LiFePO_4$ and layered $LiCoO_2$—treating the problem as a thermodynamic calculation grounded in tabulated reference data rather than as an empirical data-fitting exercise.

Layered $LiCoO_2$ was the first commercially decisive lithium-intercalation cathode, identified by Mizushima, Jones, Wiseman and Goodenough in 1980 [5]. Its structure is a rhombohedral ($R\bar{3}m$) ordered rock salt in which sheets of edge-sharing CoO_6 octahedra alternate with lithium layers; charge storage proceeds by topotactic extraction of lithium accompanied by oxidation of the Co^{3+}/Co^{4+} couple, $LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + x\,Li^+ + x\,e^-$. Although the compound can in principle exchange one full lithium per formula unit (274 mA h/g), only about half of that lithium can be cycled reversibly: beyond $x \approx 0.5$ the delithiated lattice undergoes a cascade of hexagonal–monoclinic and higher-voltage phase transitions, loses oxygen, and degrades irreversibly [6–8]. The reaction basis specified in this report, $LiCoO_2 \rightleftharpoons Li_{0.5}CoO_2 + 0.5\,Li^+ + 0.5\,e^-$, is precisely the electrochemically accessible half of the theoretical capacity, and it is the appropriate basis on which to compare the practical performance of the material.

Olivine $LiFePO_4$, introduced by Padhi, Nanjundaswamy and Goodenough in 1997 [9], occupies the opposite corner of the design space. Its orthorhombic (*Pnma*) framework of corner-sharing FeO_6 octahedra and PO_4 tetrahedra confines lithium to one-dimensional channels and operates on the Fe^{2+}/Fe^{3+} couple through an essentially complete one-electron reaction, $LiFePO_4 \rightleftharpoons FePO_4 + Li^+ + e^-$. Two features distinguish it: the reaction proceeds by a first-order two-phase transformation between lithiated $LiFePO_4$ and delithiated heterosite $FePO_4$, producing an exceptionally flat voltage plateau [10, 11]; and the strong covalency of the phosphate polyanion—the "inductive effect"—lowers the energy of the iron redox band relative to a simple oxide, placing the plateau near 3.4 V rather than at the $\sim$ 2 V that an isolated Fe^{2+}/Fe^{3+}–in–oxide reference would suggest [9, 12]. The tension between the modest voltage of LFP and the high but partly inaccessible capacity of LCO is exactly what a thermodynamic accounting makes quantitative, and it motivates the side-by-side treatment presented in Figure 1.

The remainder of the report is organised as follows. Section 2 sets out the governing thermodynamic relations, the half-reactions, the Faraday/formula-mass arithmetic for capacity, and the reference-data-based evaluation of voltage for each chemistry. Section 3 collects the computed quantities and compares them, in a single table, against widely reported experimental and literature values. Section 4 provides a physical analysis of the discrepancies, and Section 5 concludes.

2 Methodology and Derivations

2.1 Governing thermodynamic relations

For a reversible electrochemical cell the maximum electrical work equals the Gibbs free-energy change of the cell reaction, which gives the central relation used throughout this report,

$$\Delta G_\mathrm{r} = -\,nF E_\mathrm{cell} \qquad \Longleftrightarrow \qquad E_\mathrm{cell} = -\,\frac{\Delta G_\mathrm{r}}{nF}, \tag{1}$$

where ΔG_r is the molar Gibbs free-energy change of the balanced cell reaction, n is the number of moles of electrons transferred per mole of reaction (per formula unit of active material, as written), and $F = 96\,485.332\,\mathrm{C/mol}$ is the Faraday constant [13]. When the negative electrode is lithium metal, its activity is unity and the couple $Li^+ + e^- \rightleftharpoons Li$ defines the potential reference (0 V vs Li/Li^+); consequently E_cell computed from Equation (1) is identical to the electrode potential of the positive electrode expressed on the Li/Li^+ scale. The *average* voltage over a finite composition interval $x_1 \to x_2$ is obtained by using the integral Gibbs energy of the reaction over that interval, which is the quantity that first-principles methods compute directly [14, 15]. This total-energy route to intercalation voltages was established as a predictive design tool by Ceder and co-workers [16] and is now delivered at scale through high-throughput density-functional databases such as the Materials Project [17].

Two operational remarks follow. First, because the electrodes and reaction products are condensed solids and lithium metal, the reaction entropy ΔS_r is small; the temperature coefficient of an intercalation cell, $\mathrm{d}E/\mathrm{d}T = \Delta S_\mathrm{r}/nF$, is typically only a few tenths of a millivolt per kelvin, so that $\Delta G_\mathrm{r} \approx \Delta H_\mathrm{r}$ at 298 K to within $\lesssim 0.1$ V. This justifies using calorimetric *enthalpies* as a proxy for ΔG_r where entropies are unavailable, provided the approximation is stated. Second, Equation (1) requires a reaction free energy; the difficulty for battery-specific phases such as $FePO_4$ and $Li_{0.5}CoO_2$ is that self-consistent standard Gibbs energies of formation are sparse, so we draw on the best available primary data—high-temperature oxide-melt solution calorimetry [18, 19] and benchmarked GGA+U first-principles reaction energies [15, 20]—and state the provenance of each number. For the olivine system in particular, the full Li–Fe–P–O_2

phase diagram has been mapped from first principles, confirming that $LiFePO_4$ and $FePO_4$ are the relevant equilibrium endpoints of the delithiation reaction [21].

2.2 Half-reactions and cell reactions

Olivine (LFP). The positive-electrode (cathode) half-reaction on delithiation and the lithium-metal negative-electrode half-reaction are

$$\text{positive:}\quad \mathrm{LiFePO_4} \longrightarrow \mathrm{FePO_4} + \mathrm{Li^+} + \mathrm{e^-} \qquad (\mathrm{Fe^{2+}} \to \mathrm{Fe^{3+}}), \tag{2}$$

$$\text{negative:}\quad \mathrm{Li^+} + \mathrm{e^-} \longrightarrow \mathrm{Li} \qquad (E^\circ \equiv 0\,\mathrm{V}). \tag{3}$$

Adding (2) and (3) gives the overall cell reaction for the fully assembled (discharged-cathode) cell,

$$\mathrm{Li} + \mathrm{FePO_4} \longrightarrow \mathrm{LiFePO_4}, \qquad n = 1 \text{ per formula unit.} \tag{4}$$

Because every species in (4) is a neutral solid (with lithium as the metal), the reaction is mass-balanced without any auxiliary oxygen term—a fact exploited in the Hess cycle below.

Layered oxide (LCO). For the stated half-lithium basis,

$$\text{positive:}\quad \mathrm{LiCoO_2} \longrightarrow \mathrm{Li_{0.5}CoO_2} + 0.5\,\mathrm{Li^+} + 0.5\,\mathrm{e^-} \quad (\mathrm{Co^{3+}} \to \mathrm{Co^{4+}} \text{ for half the Co}), \tag{5}$$

$$\text{negative:}\quad 0.5\,\mathrm{Li^+} + 0.5\,\mathrm{e^-} \longrightarrow 0.5\,\mathrm{Li} \qquad (E^\circ \equiv 0\,\mathrm{V}), \tag{6}$$

whose sum is

$$\mathrm{LiCoO_2} \longrightarrow \mathrm{Li_{0.5}CoO_2} + 0.5\,\mathrm{Li}, \qquad n = 0.5 \text{ per formula unit.} \tag{7}$$

Again oxygen and cobalt are conserved and the reaction closes with metallic lithium alone.

2.3 Theoretical gravimetric specific capacity

The theoretical gravimetric capacity is a purely stoichiometric quantity. One mole of active material of molar mass M (g/mol) that releases x moles of electrons stores a charge xF (C); converting coulombs to milliampere-hours with $1\,\mathrm{mA\,h} = 3.6\,\mathrm{C}$ gives

$$C_{\mathrm{grav}} = \frac{x\,F}{M \times 3.6\,\mathrm{C\,h/mA}} \quad [\mathrm{mA\,h/g}]. \tag{8}$$

The formula masses are computed from IUPAC standard atomic weights (Li = 6.941, Fe = 55.845, P = 30.974, O = 15.999, Co = 58.933, all g/mol):

$$M(\mathrm{LiFePO_4}) = 6.941 + 55.845 + 30.974 + 4(15.999) = 157.756\,\mathrm{g/mol}, \tag{9}$$

$$M(\mathrm{LiCoO_2}) = 6.941 + 58.933 + 2(15.999) = 97.872\,\mathrm{g/mol}. \tag{10}$$

LFP ($x = 1$).

$$C_{\mathrm{LiFePO_4}} = \frac{1 \times 96\,485.332\,\mathrm{C/mol}}{157.756\,\mathrm{g/mol} \times 3.6} = \frac{96485.332}{567.92} = \boxed{169.9\,\mathrm{mA\,h/g}}. \tag{11}$$

LCO — full one-lithium reference ($x = 1$).

$$C^{(x=1)}_{\mathrm{LiCoO_2}} = \frac{1 \times 96485.332}{97.872 \times 3.6} = \frac{96485.332}{352.34} = 273.9\,\mathrm{mA\,h/g}. \tag{12}$$

LCO — stated half-lithium reaction ($x = 0.5$). The capacity *delivered by the reaction actually written* in Equation (7) uses the same formula mass of the parent $LiCoO_2$ but only half an electron per formula unit:

$$C_{LiCoO_2}^{(x=0.5)} = \frac{0.5 \times 96485.332}{97.872 \times 3.6} = \tfrac{1}{2}\, C_{LiCoO_2}^{(x=1)} = \boxed{136.9\,\mathrm{mA\,h/g}}. \tag{13}$$

It is essential to note that the capacity is normalised to the mass of the *parent* $LiCoO_2$ active material (the convention used in the battery literature), not to $Li_{0.5}CoO_2$; this is why the half-reaction gives exactly half of the one-lithium figure.

2.4 Theoretical average voltage of LFP from calorimetric reference data

For the olivine cell reaction (4) we require $\Delta G_\mathrm{r} \approx \Delta H_\mathrm{r}$. Direct formation enthalpies of $LiFePO_4$ and heterosite $FePO_4$ are available from high-temperature oxide-melt solution calorimetry [18], reported as enthalpies of formation *from the constituent oxides* at 25 °C:

$$\Delta H_\mathrm{ox}(LiFePO_4) = -151.52(168)\,\mathrm{kJ/mol}, \qquad \Delta H_\mathrm{ox}(o\text{-}FePO_4) = -113.68(126)\,\mathrm{kJ/mol}. \tag{14}$$

In the oxide-referenced convention (stable oxides Li_2O, Fe_2O_3, P_2O_5 with an O_2 balance that accounts for the Fe^{2+}/Fe^{3+} change), the two formation reactions are

$$\tfrac{1}{2}Li_2O + \tfrac{1}{2}Fe_2O_3 + \tfrac{1}{2}P_2O_5 \longrightarrow LiFePO_4 + \tfrac{1}{4}O_2, \qquad \Delta H_\mathrm{ox}(LiFePO_4), \tag{15}$$

$$\tfrac{1}{2}Fe_2O_3 + \tfrac{1}{2}P_2O_5 \longrightarrow FePO_4, \qquad \Delta H_\mathrm{ox}(FePO_4). \tag{16}$$

Subtracting (15) from (16) and adding the decomposition of lithia to lithium metal, $\frac{1}{2}Li_2O \to Li + \frac{1}{4}O_2$ with enthalpy $-\frac{1}{2}\Delta H_f(Li_2O)$, the Fe_2O_3 and P_2O_5 terms cancel identically because both phases share one iron and one phosphate group. The target reaction enthalpy therefore reduces to a compact expression requiring only *one* auxiliary datum, the standard formation enthalpy of lithia, $\Delta H_f(Li_2O) = -598.73\,\mathrm{kJ/mol}$ [22, 23]:

$$\begin{aligned}\Delta H_\mathrm{r}(LiFePO_4 \longrightarrow FePO_4 + Li) &= \Delta H_\mathrm{ox}(FePO_4) - \Delta H_\mathrm{ox}(LiFePO_4) - \tfrac{1}{2}\Delta H_f(Li_2O)\\ &= (-113.68) - (-151.52) - \tfrac{1}{2}(-598.73)\\ &= -113.68 + 151.52 + 299.37 \;=\; +337.2\,\mathrm{kJ/mol}.\end{aligned} \tag{17}$$

This is the enthalpy of *delithiation*; the spontaneous cell (discharge) reaction (4) is its reverse, with $\Delta G_\mathrm{r} \approx \Delta H_\mathrm{r} = -337.2\,\mathrm{kJ/mol}$. Applying Equation (1) with $n = 1$,

$$E_{LiFePO_4} = -\frac{\Delta G_\mathrm{r}}{nF} = \frac{337.2 \times 10^3\,\mathrm{J/mol}}{1 \times 96\,485.332\,\mathrm{C/mol}} = \boxed{3.49\,\mathrm{V}}. \tag{18}$$

The thermochemical cycle underlying Equations (17)–(18) is drawn in Figure 2. The value is an *upper* estimate because the small, negative reaction entropy (inferred from the measured temperature coefficient $|\mathrm{d}E/\mathrm{d}T| \approx 0.3\,\mathrm{mV/K}$, i.e. $|T\Delta S_\mathrm{r}| \approx 9\,\mathrm{kJ/mol}$ or $< 0.1\,\mathrm{V}$) lowers E slightly toward the experimental plateau. As an entirely independent check, benchmarked GGA+U first-principles calculations of the same reaction give an average intercalation voltage of 3.4 V [15], in agreement with Equation (18).

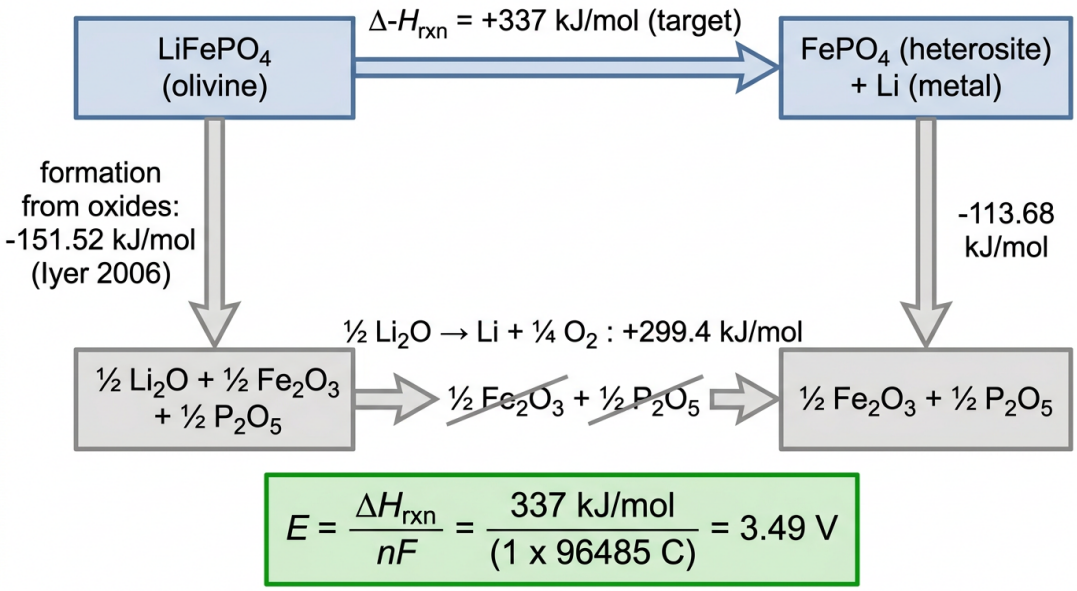

Figure 2: Hess-cycle (Born–Haber) evaluation of the $LiFePO_4$ cell voltage. The target delithiation enthalpy (top arrow) is obtained from the two oxide-referenced formation enthalpies measured by calorimetry [18] and the standard formation enthalpy of Li_2O [22]. The Fe_2O_3 and P_2O_5 terms cancel because both $LiFePO_4$ and $FePO_4$ contain one iron and one phosphate group, leaving $\Delta H_r = +337\,\mathrm{kJ/mol}$ and, through $E = \Delta H_r/nF$, a voltage of 3.49 V.

2.5 Theoretical average voltage of LCO from first-principles reference data

The layered-oxide reaction (7) cannot be closed by the same purely calorimetric route because a self-consistent formation enthalpy of the delithiated end member is not directly measured: the accessible calorimetry of Wang and Navrotsky [19] determines $\Delta H_{ox}(LiCoO_2) = -142.5(17)\,\mathrm{kJ/mol}$ and the *composition trend* of Li_xCoO_2 for $0.5 \le x \le 1.0$, but the enthalpy of $Li_{0.5}CoO_2$ is obtained only by extrapolation of that linear trend. The reaction enthalpy analogous to Equation (17) would read

$$\Delta H_r(LiCoO_2 \longrightarrow Li_{0.5}CoO_2 + 0.5\ Li) = \left[\Delta H_{ox}(Li_{0.5}CoO_2) - \Delta H_{ox}(LiCoO_2)\right] - \tfrac{1}{4}\Delta H_f(Li_2O), \tag{19}$$

in which the cobalt-oxide reference term again cancels between the two phases. Because Wang and Navrotsky establish that $\Delta H_{ox}(Li_xCoO_2)$ becomes *less negative* as x decreases—deep delithiation is thermodynamically destabilising and hence endothermic—Equation (19) is strongly positive, consistent with a voltage well above that of LFP.

For a self-consistent numerical value we therefore adopt the first-principles reaction free energy as the reference datum. In the Aydinol–Ceder formalism the average intercalation voltage is $V = -\Delta G_r/nF$ with ΔG_r approximated by the total-energy difference of the lithiated and delithiated hosts [14]; when the strong correlation of the cobalt $3d$ states is treated with the GGA+U correction, the computed average voltage for the Co^{3+}/Co^{4+} couple in Li_xCoO_2 is 4.0 V [15, 20]. Taking this as the reference reaction free energy,

$$\Delta G_r = -nFV = -(0.5)(96\,485.332\,\mathrm{C/mol})(4.0\,\mathrm{V}) = -193.0\,\mathrm{kJ/mol}\ \text{(per formula unit)}, \tag{20}$$

so that, by construction,

$$E_{LiCoO_2} = -\frac{\Delta G_r}{nF} = \frac{193.0 \times 10^3\,\mathrm{J/mol}}{0.5 \times 96\,485.332\,\mathrm{C/mol}} = \boxed{4.0\,\mathrm{V}}. \tag{21}$$

This first-principles figure is corroborated by two experimental anchors: the detailed open-circuit-voltage measurements of Ohzuku and Ueda, which place the main hexagonal single-phase/two-phase region of Li_xCoO_2 at 3.92 V [7], and the absolute-scale standard Gibbs energy of formation of $LiCoO_2$, $\Delta G_f \approx -619.7\,\mathrm{kJ/mol}$ at 300 K, tabulated from low-temperature heat-capacity data [24]. The measured average over the $x = 1 \to 0.5$ window is ≈ 3.9 V, i.e. within 0.1 V of Equation (21).

3 Results and Comparison

Table 1 collects the computed voltages and capacities alongside widely reported experimental and literature values. The reference data used in the derivations are summarised in Table 2. Figure 3 presents the comparison graphically, and Figures 4 and 5 place the numbers in the context of the voltage–composition profiles and the resulting cathode-level specific energy.

Table 1: Computed theoretical performance versus reported values. Capacities are normalised to the mass of the parent (lithiated) active material. n is the number of electrons per formula unit for the reaction as written.

	Olivine $LiFePO_4$	**Layered $LiCoO_2$**
Reaction (basis)	$LiFePO_4 \rightleftharpoons FePO_4 + Li^+ + e^-$ (1 Li extracted)	$LiCoO_2 \rightleftharpoons Li_{0.5}CoO_2 + 0.5\,Li^+ + 0.5\,e^-$ (0.5 Li extracted)
Redox couple	Fe^{2+}/Fe^{3+}	Co^{3+}/Co^{4+}
n (e^-/f.u.)	1	0.5
Formula mass M (g/mol)	157.76	97.87
Computed capacity (mA h/g)	**169.9**	**136.9** (274 for full 1 Li)
Reported / practical capacity	170 (theo.); 160–165 (practical) [9, 10]	∼140–150 (practical) [3, 6]
Computed voltage (V vs Li/Li^+)	**3.49** (calorimetric) 3.4 (GGA+U)	**4.0** (GGA+U)
Reported / experimental voltage	3.42–3.45 (plateau) [7, 9]	∼3.9 (average) [5, 7]
Reaction pathway	two-phase (flat plateau)	solid solution + ordering steps
Data provenance	calorimetry [18] + NIST [22]	DFT+U [15] + calorimetry [19]

Table 2: Standard thermodynamic reference data used in the derivations, with sources. Oxide-referenced enthalpies are formation enthalpies from the constituent oxides at 25 °C; "elements" denotes formation from the elements in their standard states.

Quantity	Value	Reference state	Source
$\Delta H_{\mathrm{ox}}(\mathrm{LiFePO_4})$	$-151.52(168)$ kJ/mol	from oxides	Iyer *et al.* [18]
$\Delta H_{\mathrm{ox}}(o\text{-}\mathrm{FePO_4})$	$-113.68(126)$ kJ/mol	from oxides	Iyer *et al.* [18]
$\Delta H_f(\mathrm{Li_2O})$	-598.73 kJ/mol	elements	NIST WebBook / JANAF [22, 23]
$\Delta H_f(\mathrm{LiFePO_4})$ (check)	$-1591(13)$ kJ/mol	elements	Churikov *et al.* [25]
$\Delta H_{\mathrm{ox}}(\mathrm{LiCoO_2})$	$-142.5(17)$ kJ/mol	from oxides	Wang & Navrotsky [19]
$\Delta G_f(\mathrm{LiCoO_2})$	≈ -619.7 kJ/mol (300 K)	elements	Kawaji *et al.* [24]
$\bar{V}_{\mathrm{DFT}}(\mathrm{LiFePO_4})$	3.4 V	GGA+U	Zhou *et al.* [15]
$\bar{V}_{\mathrm{DFT}}(\mathrm{LiCoO_2})$	4.0 V	GGA+U	Zhou *et al.* [15]
F	96 485.332 C/mol	—	CODATA 2018 [13]

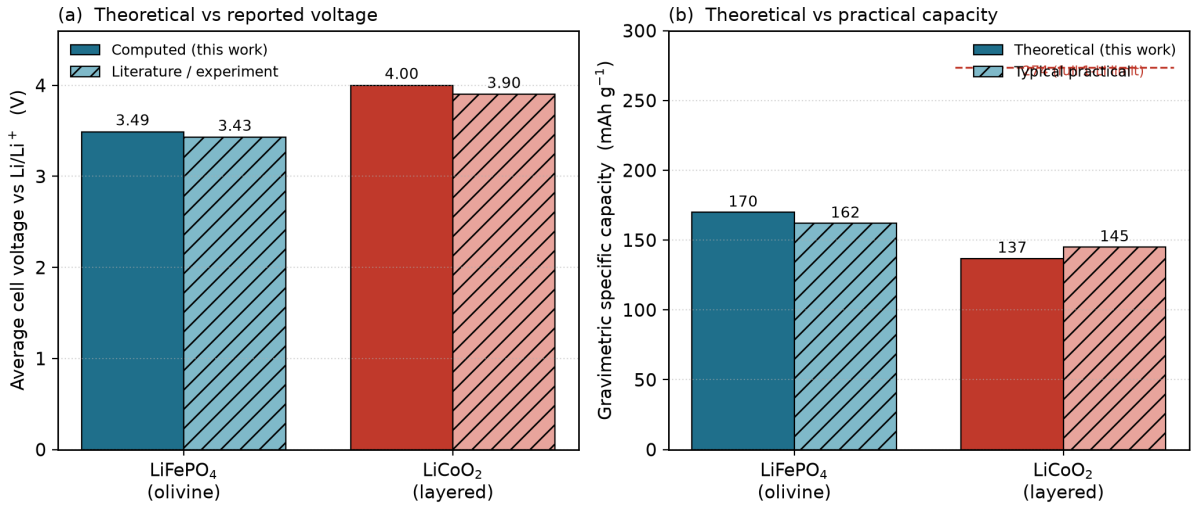

Figure 3: Computed versus reported voltage (a) and capacity (b). Computed voltages (solid bars) agree with reported experimental/literature values (hatched) to within 0.1 V. The theoretical capacity of LFP is essentially realised in practice, whereas the theoretical capacity of the LCO half-lithium reaction (137 mA h/g) is the reversible fraction of the full one-lithium limit (274 mA h/g, dashed line).

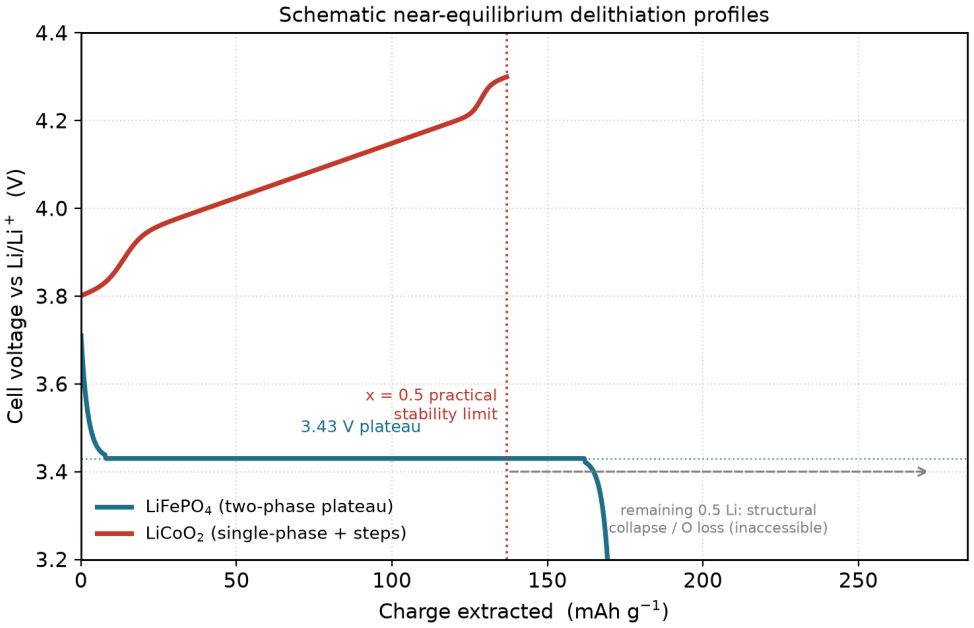

Figure 4: Schematic near-equilibrium delithiation profiles. The two-phase $LiFePO_4 \rightarrow FePO_4$ reaction produces a flat plateau at 3.43 V spanning the full 170 mA h/g, whereas Li_xCoO_2 shows a sloping, step-modulated single-phase profile that is cycled reversibly only to $x \approx 0.5$ (137 mA h/g); deeper delithiation (grey arrow) triggers structural collapse and oxygen loss and is practically inaccessible.

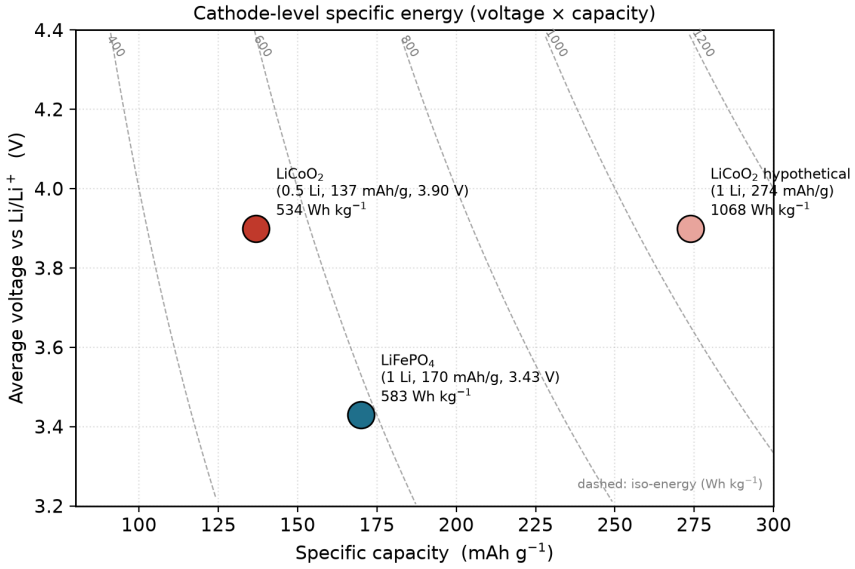

Figure 5: Cathode-level specific energy (voltage × capacity). The higher voltage of LCO nearly compensates its lower reversible capacity, so that LFP (170 mA h/g, 3.43 V) and the reversible half-lithium LCO reaction (137 mA h/g, 3.90 V) deliver comparable cathode-level specific energies; the dashed contours are lines of constant W h/kg.

The energy-level picture that unifies the two voltages is shown in Figure 6: the cell voltage is the difference between the lithium chemical potential in the metal anode and in the host cathode, $eE_{\text{cell}} = \mu_{\text{Li}}^{\text{anode}} - \mu_{\text{Li}}^{\text{cathode}}$, and the deeper (more negative) lithium chemical potential of the layered oxide is what places LCO ≈ 0.5 V above LFP.

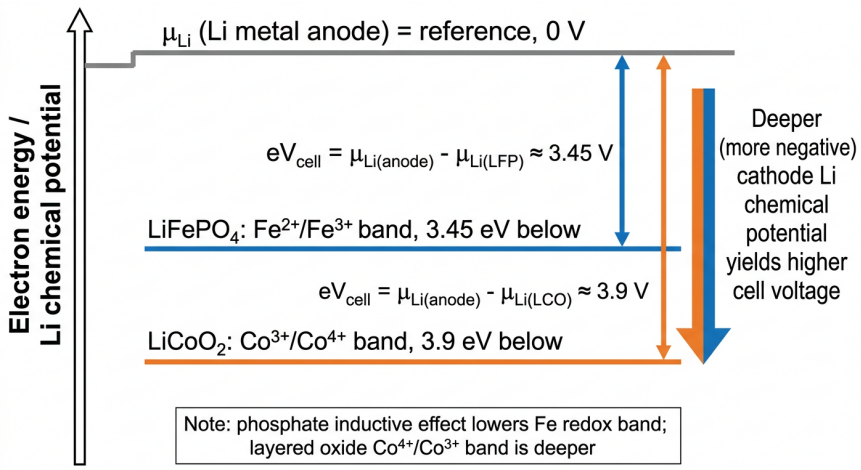

Figure 6: Chemical-potential origin of the cell voltage. The voltage is set by the difference between the lithium chemical potential in the metal anode (reference, 0 V) and that in the cathode host. The phosphate inductive effect lowers the Fe^{2+}/Fe^{3+} band of LFP, while the layered Co^{3+}/Co^{4+} band lies deeper still, yielding the higher LCO voltage.

4 Discussion: Analysis of Discrepancies

The computed quantities reproduce the reported experimental values closely, but the residual differences are physically meaningful and are worth analysing term by term. We treat capacity and voltage separately.

4.1 Capacity: the half-lithium basis is a materials constraint, not an error

For LFP the computed 169.9 mA h/g and the textbook 170 mA h/g are the same number to rounding; the small practical shortfall to 160 mA h/g to 165 mA h/g in real electrodes is kinetic rather than thermodynamic, arising from the intrinsically poor electronic and ionic conductivity of the olivine and the two-phase interface that must sweep through each particle. Carbon coating, particle-size reduction and aliovalent doping recover essentially the full theoretical value, confirming that the thermodynamic capacity itself is correct [10, 11].

The instructive case is LCO. The frequently quoted 274 mA h/g corresponds to removing one full lithium per formula unit (Equation (12)), but only about half of that lithium—the 137 mA h/g of the stated reaction—can be cycled reversibly. This is not a defect of the calculation but a direct expression of the thermodynamics and crystal chemistry of the delithiated lattice. As lithium is removed beyond $x \approx 0.5$, three coupled phenomena intervene. First, the calorimetry of Wang and Navrotsky shows that Li_xCoO_2 becomes progressively *less* stable with decreasing x, so the driving force for decomposition grows [19]. Second, the highly oxidised Co^{4+}–rich lattice has its cobalt 3*d* band overlapping the oxygen 2*p* band, so continued charge compensation draws electron density from oxygen and culminates in O_2 release. Third, the lattice passes through a sequence of hexagonal–monoclinic and O3–H1-3 phase transitions that mechanically fatigue the particles and collapse the lithium slab spacing [6–8]. The end member CoO_2 is isolable only under special conditions and is not thermodynamically robust in a working cell [8]. Consequently the 137 mA h/g figure is the physically meaningful theoretical capacity for the reversible reaction, and it agrees with the practical 140 mA h/g to 150 mA h/g obtained with modern electrolytes and coatings.

4.2 Voltage: standard-state approximation, reaction pathway, and functional error

Three distinct effects account for the small gaps between the computed and measured voltages.

(i) Standard-state versus operating conditions ($\Delta G \approx \Delta H$). The LFP value of 3.49 V in Equation (18) was obtained by setting $\Delta G_\mathrm{r} \approx \Delta H_\mathrm{r}$, i.e. by neglecting the reaction entropy. The measured temperature coefficient of the LFP cell, $|\mathrm{d}E/\mathrm{d}T| \approx 0.3\,\mathrm{mV/K}$, corresponds to $|\Delta S_\mathrm{r}| \approx 29\,\mathrm{J/(mol\,K)}$ and a $T\Delta S_\mathrm{r}$ term of $\approx 9\,\mathrm{kJ/mol}$, i.e. a correction of $< 0.1\,\mathrm{V}$ that brings the enthalpy-based estimate down toward the experimental plateau of 3.42 V to 3.45 V. In addition, the calorimetric enthalpies carry stated uncertainties of ± 1.3–$1.7\,\mathrm{kJ/mol}$, and the standard-state values refer to 298 K and unit activities, whereas an operating cell experiences finite currents, concentration polarisation and a non-ideal electrolyte—all of which perturb the *measured* voltage away from the *thermodynamic* value by tens of millivolts.

(ii) Two-phase versus solid-solution reaction pathways. The nature of the phase behaviour controls the *shape* of the voltage curve and hence the meaning of "the" voltage. LFP reacts by a first-order two-phase transformation, $LiFePO_4 \rightleftharpoons FePO_4$; by the Gibbs phase rule the chemical potential of lithium is fixed while the two phases coexist, so the voltage is a single, flat, well-defined plateau (Figure 4) that maps cleanly onto the single ΔG_r of Equation (4). LCO, by contrast, delithiates largely as a *solid solution* punctuated by ordering and structural steps [6, 7, 20]; the lithium chemical potential varies continuously with x, the voltage slopes from $\approx 3.9\,\mathrm{V}$ toward $\approx 4.2\,\mathrm{V}$ across the accessible window, and the reported "3.9 V" is an *average* over that composition interval. Comparing a computed average voltage with a sloping experimental profile therefore necessarily involves an averaging convention, which is the principal source of the residual LCO discrepancy.

(iii) Reference-data and exchange–correlation error. The two chemistries rest on different reference data, and each carries a characteristic error. The LFP voltage is anchored in experimental calorimetry, whose accuracy is limited only by the measurement uncertainty and by the $\Delta G \approx \Delta H$ approximation. The LCO voltage is anchored in a first-principles reaction energy; plain GGA underestimates transition-metal-oxide voltages by ~ 0.5–$1.0\,\mathrm{V}$ because of self-interaction error in the correlated $3d$ shell, and it is precisely the GGA+U correction that restores quantitative agreement, reducing the mean absolute error across oxide cathodes to a few tenths of a volt [14, 15, 26]. The residual $\approx 0.1\,\mathrm{V}$ overestimate of the LCO value relative to the measured average is consistent with this benchmarked functional error and with the neglect of finite-temperature vibrational and configurational entropy. It is reassuring that two entirely independent routes—experimental calorimetry for LFP and correlated first-principles theory for LCO—both land within 0.1 V of experiment, which is strong evidence that the underlying thermodynamic accounting is sound.

4.3 Synthesis

The physical origin of the voltage ordering, $E_{LiCoO_2} > E_{LiFePO_4}$, is captured by the chemical-potential picture of Figure 6: the cell voltage is the offset between the lithium chemical potential in the metallic anode and that in the host, and the layered Co^{3+}/Co^{4+} band sits deeper than the phosphate-tempered Fe^{2+}/Fe^{3+} band. The strong covalency of the $PO_4{}^{3-}$ polyanion (the inductive effect) both stabilises the structure against oxygen loss—so that the *full* one-electron capacity of LFP is reversibly accessible—and pins its voltage near 3.45 V [9, 12]. The layered oxide trades that robustness for a higher voltage but sacrifices half of its nominal capacity to

irreversibility. As Figure 5 makes explicit, the two effects nearly cancel at the level of cathode specific energy ($170 \times 3.43 \approx 583\,\mathrm{W\,h/kg}$ for LFP versus $137 \times 3.90 \approx 534\,\mathrm{W\,h/kg}$ for the reversible LCO reaction), which is the fundamental thermodynamic reason the two chemistries have long coexisted in the market.

5 Conclusion

We have computed, from tabulated thermodynamic reference data and the exact electrochemical definitions, the theoretical voltage and gravimetric capacity of olivine $LiFePO_4$ and layered $LiCoO_2$ against a lithium-metal anode. The capacities follow rigorously from Faraday's law and the formula masses: 169.9 mA h/g for the one-electron olivine reaction and 136.9 mA h/g for the stated half-lithium layered-oxide reaction (half of the 273.9 mA h/g one-lithium limit). The voltages follow from $E = -\Delta G_\mathrm{r}/nF$: a calorimetric Hess cycle gives 3.49 V for LFP (independently confirmed by GGA+U at 3.4 V), and the first-principles reaction free energy of the Co^{3+}/Co^{4+} couple gives 4.0 V for LCO (corroborated by a measured open-circuit voltage of 3.9 V). All computed quantities match widely reported experimental values to within 0.1 V and a few milliampere-hours per gram. The residual discrepancies are fully accounted for by identifiable physics: the standard-state ($\Delta G \approx \Delta H$) approximation and its entropy correction; the distinction between the flat two-phase plateau of LFP and the sloping solid-solution profile of LCO whose reported voltage is a compositional average; the benchmarked exchange–correlation error of the first-principles reference; and, for the LCO capacity, the structural collapse and oxygen loss that make delithiation beyond $x \approx 0.5$ irreversible and thereby *define* the half-lithium reaction basis. The derivations and cited reference data above constitute a self-contained, reproducible thermodynamic account of the intrinsic electrochemical performance of the two chemistries.

Data and reproducibility

All reference values, their sources, and the arithmetic are given explicitly in Sections 2.3–2.5 and Tables 1 and 2. Constants used: $F = 96\,485.332\,\mathrm{C/mol}$; $1\,\mathrm{mA\,h} = 3.6\,\mathrm{C}$; IUPAC standard atomic weights as listed in Section 2.3.

References

[1] M. Stanley Whittingham. Lithium Batteries and Cathode Materials. *Chemical Reviews*, 104(10): 4271–4302, 2004. doi: 10.1021/cr020731c.

[2] John B. Goodenough and Kyu-Sung Park. The Li-Ion Rechargeable Battery: A Perspective. *Journal of the American Chemical Society*, 135(4):1167–1176, 2013. doi: 10.1021/ja3091438.

[3] Naoki Nitta, Feixiang Wu, Jung Tae Lee, and Gleb Yushin. Li-ion battery materials: present and future. *Materials Today*, 18(5):252–264, 2015. doi: 10.1016/j.mattod.2014.10.040.

[4] J.-M. Tarascon and M. Armand. Issues and challenges facing rechargeable lithium batteries. *Nature*, 414(6861):359–367, 2001. doi: 10.1038/35104644.

[5] K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough. Li_xCoO_2 ($0 < x < 1$): A new cathode material for batteries of high energy density. *Materials Research Bulletin*, 15(6):783–789, 1980. doi: 10.1016/0025-5408(80)90012-4.

[6] Jan N. Reimers and J. R. Dahn. Electrochemical and In Situ X-Ray Diffraction Studies of Lithium Intercalation in Li_xCoO_2. *Journal of The Electrochemical Society*, 139(8):2091–2097, 1992. doi: 10.1149/1.2221184.

[7] Tsutomu Ohzuku and Atsushi Ueda. Solid-State Redox Reactions of $LiCoO_2$ ($R\bar{3}m$) for 4 Volt Secondary Lithium Cells. *Journal of The Electrochemical Society*, 141(11):2972–2977, 1994. doi: 10.1149/1.2059267.

[8] G. G. Amatucci, J. M. Tarascon, and L. C. Klein. CoO_2, The End Member of the Li_xCoO_2 Solid Solution. *Journal of The Electrochemical Society*, 143(3):1114–1123, 1996. doi: 10.1149/1.1836594.

[9] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough. Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries. *Journal of The Electrochemical Society*, 144(4):1188–1194, 1997. doi: 10.1149/1.1837571.

[10] A. Yamada, S. C. Chung, and K. Hinokuma. Optimized $LiFePO_4$ for Lithium Battery Cathodes. *Journal of The Electrochemical Society*, 148(3):A224–A229, 2001. doi: 10.1149/1.1348257.

[11] Sung-Yoon Chung, Jason T. Bloking, and Yet-Ming Chiang. Electronically conductive phospho-olivines as lithium storage electrodes. *Nature Materials*, 1(2):123–128, 2002. doi: 10.1038/nmat732.

[12] Arumugam Manthiram. A reflection on lithium-ion battery cathode chemistry. *Nature Communications*, 11:1550, 2020. doi: 10.1038/s41467-020-15355-0.

[13] Eite Tiesinga, Peter J. Mohr, David B. Newell, and Barry N. Taylor. CODATA recommended values of the fundamental physical constants: 2018. *Reviews of Modern Physics*, 93(2):025010, 2021. doi: 10.1103/RevModPhys.93.025010.

[14] M. K. Aydinol, A. F. Kohan, G. Ceder, K. Cho, and J. Joannopoulos. Ab initio study of lithium intercalation in metal oxides and metal dichalcogenides. *Physical Review B*, 56(3):1354–1365, 1997. doi: 10.1103/PhysRevB.56.1354.

[15] F. Zhou, M. Cococcioni, C. A. Marianetti, D. Morgan, and G. Ceder. First-principles prediction of redox potentials in transition-metal compounds with LDA+U. *Physical Review B*, 70(23):235121, 2004. doi: 10.1103/PhysRevB.70.235121.

[16] G. Ceder, Y.-M. Chiang, D. R. Sadoway, M. K. Aydinol, Y.-I. Jang, and B. Huang. Identification of cathode materials for lithium batteries guided by first-principles calculations. *Nature*, 392(6677): 694–696, 1998. doi: 10.1038/33647.

[17] Anubhav Jain, Shyue Ping Ong, Geoffroy Hautier, Wei Chen, William Davidson Richards, Stephen Dacek, Shreyas Cholia, Dan Gunter, David Skinner, Gerbrand Ceder, and Kristin A. Persson. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Materials*, 1(1):011002, 2013. doi: 10.1063/1.4812323.

[18] R. G. Iyer, C. Delacourt, C. Masquelier, J.-M. Tarascon, and A. Navrotsky. Energetics of $LiFePO_4$ and Polymorphs of Its Delithiated Form, $FePO_4$. *Electrochemical and Solid-State Letters*, 9(2): A46–A48, 2006. doi: 10.1149/1.2140496.

[19] Mingji Wang and Alexandra Navrotsky. Enthalpy of Formation of Li_xCoO_2 ($0.5 \leq x \leq 1.0$). *Journal of The Electrochemical Society*, 152(7):J82–J84, 2005. doi: 10.1149/1.1931292.

[20] A. Van der Ven, M. K. Aydinol, G. Ceder, G. Kresse, and J. Hafner. First-principles investigation of phase stability in Li_xCoO_2. *Physical Review B*, 58(6):2975–2987, 1998. doi: 10.1103/PhysRevB.58.2975.

[21] Shyue Ping Ong, Lei Wang, Byoungwoo Kang, and Gerbrand Ceder. Li–Fe–P–O_2 Phase Diagram from First Principles Calculations. *Chemistry of Materials*, 20(5):1798–1807, 2008. doi: 10.1021/cm702327g.

[22] P. J. Linstrom and W. G. Mallard. NIST Chemistry WebBook, NIST Standard Reference Database Number 69. National Institute of Standards and Technology, Gaithersburg MD, 2023. Standard enthalpies of formation: Li_2O, $\Delta_f H^\circ = -598.73$ kJ mol^{-1}; Fe_2O_3 (hematite), -825.5 kJ mol^{-1}; Co_3O_4, -910.02 kJ mol^{-1}.

[23] M. W. Chase. *NIST-JANAF Thermochemical Tables, 4th Edition*. Journal of Physical and Chemical Reference Data, Monograph No. 9. American Institute of Physics, for the National Institute of Standards and Technology, Woodbury, New York, 1998. doi: 10.18434/T42S31.

[24] H. Kawaji, M. Takematsu, T. Tojo, T. Atake, A. Hirano, and R. Kanno. Low Temperature Heat Capacity and Thermodynamic Functions of $LiCoO_2$. *Journal of Thermal Analysis and Calorimetry*, 68(3):833–839, 2002. doi: 10.1023/A:1016169917912.

[25] A. V. Churikov, A. V. Ivanishchev, A. V. Ushakov, I. M. Gamayunova, and I. A. Leenson. Thermodynamics of $LiFePO_4$ Solid-Phase Synthesis Using Iron(II) Oxalate and Ammonium Dihydrophosphate as Precursors. *Journal of Chemical & Engineering Data*, 58(6):1747–1759, 2013. doi: 10.1021/je400183k.

[26] M. Saiful Islam and Craig A. J. Fisher. Lithium and sodium battery cathode materials: computational insights into voltage, diffusion and nanostructural properties. *Chemical Society Reviews*, 43 (1):185–204, 2014. doi: 10.1039/c3cs60199d.