

Supporting Information

for

How Lithium-Ion Batteries Work Conceptually: Thermodynamics of Li Bonding in Idealized Electrodes

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1. Lithiation of FePO₄ and Delithiation of LiFePO₄

The details of the process of phase transformation between FePO₄ (lithium-free) and LiFePO₄ (fully lithiated) have been the subject of a long debate. Initially, the “shrinking core” model was proposed by Padhi, Goodenough and co-workers,¹ with a radius-dependent conversion of LiFePO₄ to FePO₄ during delithiation. It was proposed that during delithiation, the surface area (and radius) of the FePO₄/LiFePO₄ interface shrinks through each particle while the lithiated core is converted to the delithiated phase.

Since the inception of the “shrinking core” model, other groups have continued their research into lithium insertion and have ultimately concluded that this model was incomplete. A mosaic variant was introduced by Andersson et al.,² who proposed that lithium atoms can intercalate into FePO₄ at many specific sites in the particle, not just at the interface of a growing core with the lithium-free shell. This leaves small regions of LiFePO₄ or FePO₄ during deintercalation and intercalation, respectively. Other groups also proposed new models of insertion, such as the domino-cascade and the spinodal-decomposition models.^{3,4} Several publications⁵⁻⁷ have emphasized the anisotropic nature of intercalation and deintercalation, which is incompatible with the isotropic mechanism proposed by Padhi et al.¹ This was noted early on by Ceder and coworkers,⁸ who found a very high ionic conductivity in the *b*-direction, while ionic conductivity was nearly unnoticeable in other directions.⁸ This gives evidence to the fact that intercalation occurs through tunnels or channels along the *b*-direction of the FePO₄ lattice, which was later confirmed by Laffont and co-workers⁷ using high resolution electron energy loss spectroscopy (HREELS). In the model developed by Laffont et al.,⁷ there are distinct lithium-free and lithiated regions, with a sharp phase boundary between the two. Upon intercalation, lithium is inserted into the channels along the *b*-direction of the crystal structure and parallel to the phase boundary, which moves perpendicular to the direction of insertion (see Figure S1).

To understand how this process occurs, one must consider the interfacial region⁷, where the lithiated and lithium-free phases co-exist along the phase boundary. Between the two phases, there is a lattice mismatch due to the differences in the Fe^{III}PO₄ and LiFe^{II}PO₄ crystal structures around the transition metal in its different oxidation states. This mismatch locally strains the crystal structure, which is thought to facilitate the lithiation and delithiation processes at the interface.⁶ When lithium deintercalates along the *b*-direction, a lithium ion and an electron

coming from Fe^{2+} (which transitions to Fe^{3+}) very quickly diffuse out of the cathode,⁶ resulting in the formation of the next layer of the lithium-free FePO_4 region and a displacement of the phase boundary along the a -direction.^{5,6} Where the FePO_4 crystal structure has adopted its undistorted bulk form, it is difficult for the lithium ion and the electron to reenter the cathode.⁶ The experimental data clearly show that in the absence of a phase boundary, lithium ions and electrons are not able to diffuse back into nearly empty channels of FePO_4 . Similarly, during delithiation, lithium is unable to leave a full channel of LiFePO_4 except at the phase boundary.

For the intercalation and deintercalation processes, the domino-cascade model of Delmas et al.⁶ proposes that, once nucleated, the phase boundary moves along the a -direction in a “wave-like” manner, requiring little energy to proceed.⁶ The insertion process may be more nuanced, see Figures S1(a): lithium fills empty channels of FePO_4 near the phase boundary with LiFePO_4 starting from the particle edge in contact with the lithium-rich electrolyte.⁷ The phase boundary may be sharp⁷ or an interfacial solid solution zone (SSZ) of up to 20 nm thickness.⁹ A model that accounts for all observations of intercalation and deintercalation should explain the required high electronic conductivity to and at the phase boundary.

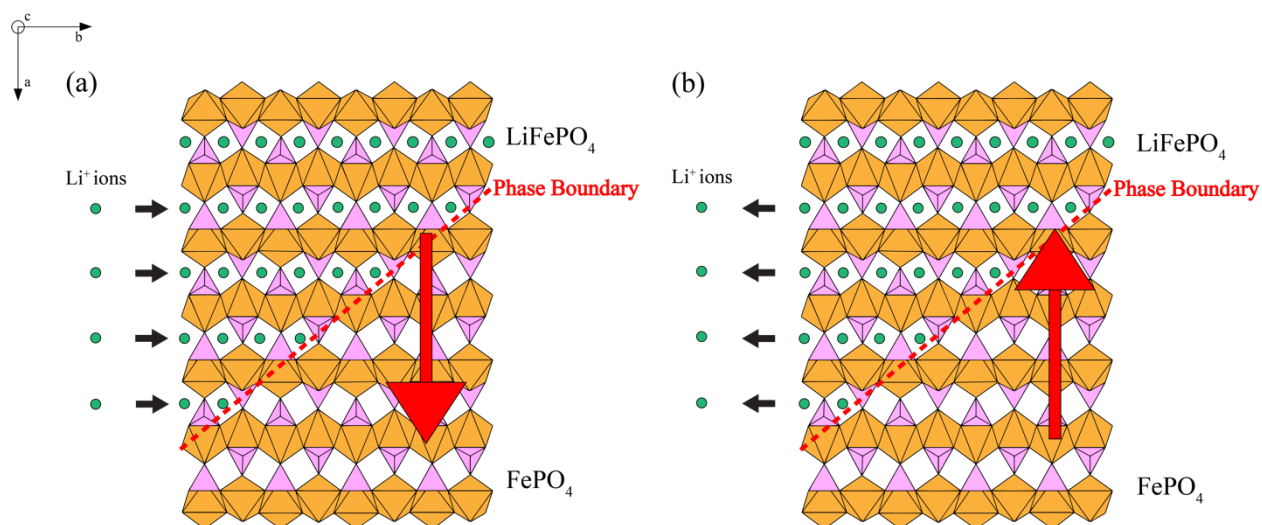


Figure S1. (a) Lithiation process as deduced from HREELS,⁷ at the phase boundary between two distinct phases, LiFePO_4 and FePO_4 . Lithium is inserted into channels or tunnels of FePO_4 along the b -direction (horizontal, indicated by black arrows), and the lithiated phase grows perpendicular to this local direction of insertion (vertical in the figure). Lithium ions are indicated as green spheres. (b) The delithiation process according to HREELS.⁷ Lithium leaves the channels in the b -direction and the phase boundary moves along the red arrow perpendicular to this local direction of deintercalation. Lithium ions are indicated as green spheres.

2. Equations for Electrical-Energy Release by an Electrochemical Cell

Quantifying the electrical energy released by a discharging electrochemical cell such as a LIB is a goal of chemical thermodynamics. It is widely accepted that at constant T and P , the electrical energy released by an electrochemical cell, also known as electrical work, is equal to the free-energy change in the electrochemical reaction,

$$w_{\text{ele}} = \Delta G \quad (\text{S1})$$

Strictly speaking, however, this equality applies only for a *reversible* electrochemical cell; for an irreversibly discharging cell, the second law leads to $\Delta G < w_{\text{ele}}$. Here we show how a useful approximate alternative to eq.(S1) for a slowly but irreversibly discharging cell can be derived.

A reversible cell is problematic because it is more contrived than is widely recognized: it must have an applied voltage, from an attached external voltage source, to ensure reversibility between discharging and charging by an infinitesimal change in the applied voltage. We would like to instead describe an electrochemical cell without attached external voltage source discharging slowly through a large resistance in the external circuit, but this is an irreversible process and therefore more difficult to analyze.

We can make progress towards an analysis of an irreversibly discharging cell by a first-law analysis of the internal-energy change ΔU of a general electrochemical cell, at constant pressure $P = P_{\text{ext}}$ and variable volume V , due to work w and heat q exchanged with the surroundings, which gives us

$$\Delta U = q + w = q - P \Delta V + w_{\text{ele}} \quad (\text{S2})$$

Using this equality and the definition $H = U + PV$, still at constant pressure, we obtain

$$\begin{aligned} \Delta_r H &= \Delta H = \Delta U + \Delta(PV) = \Delta U + P \Delta V \\ &= q - P \Delta V + w_{\text{ele}} + P \Delta V = q + w_{\text{ele}} \end{aligned} \quad (\text{S3})$$

to be solved for

$$w_{\text{ele}} = \Delta_r H - q \quad (\text{any cell at constant } P) \quad (\text{S4})$$

This general and useful result, derived without assuming reversibility, tells us that we can obtain the electrical-energy release as $\Delta_r H$, which is mostly the change in bond energies, corrected for heat loss (usually; rarely heat gain). It shows that dissipative heat loss by the cell, discussed in more detail below, reduces the magnitude of the electrical energy released, in accordance with expectations based on the principle of conservation of energy.

We first apply eq.(S4) to a reversible process at constant T (and still P), where the equality of Clausius applies,

$$\Delta_r S = q_{\text{rev}}/T \quad (\text{reversible cell at constant } T) \quad (\text{S5})$$

recovering the well-known eq.(S1)

$$w_{\text{ele}} = \Delta_r H - T \Delta_r S = \Delta_r G \quad (\text{reversible cell at constant } T \text{ and } P) \quad (\text{S6})$$

Next we consider a cell irreversibly discharging with a small current I through a large resistance in the external circuit, at constant T and P . A small ionic current of the same magnitude I flows through the small internal resistance R_{cell} of the cell for a period of time Δt , and dissipates a small amount of ‘Ohmic’ heat according to

$$q_{\text{diss}} = - R_{\text{cell}} I^2 \Delta t < 0 \quad (\text{S7})$$

Since the temperature of the cell is constant, this energy is given off (hence its negative sign) as heat to the constant-temperature (heat-bath) surroundings. Next we assume that this small heat dissipation does not significantly alter the heat given off or taken up by the chemical reaction in the reversible case, so we can add the two types of heat,

$$q \approx q_{\text{rev}} + q_{\text{diss}} = T \Delta_r S + q_{\text{diss}} \quad (\text{S8})$$

This immediately leads to

$$w_{\text{ele}} \approx \Delta_r H - (T \Delta_r S + q_{\text{diss}}) = \Delta_r G - q_{\text{diss}} \quad (\text{S9})$$

an eminently reasonable result: The energy lost through dissipative resistive heating in the cell directly reduces the magnitude of the electrical-energy release into the external circuit. It is commonly assumed that q_{diss} can be neglected relative to $\Delta_r G$. With $R_{\text{cell}} = 10^{-2} \Omega$, $I = 0.1$ Amp, and $\Delta t = 10^6$ s in eq.(S7), indeed $q_{\text{diss}} = - 0.1$ kJ is small in magnitude compared to $\Delta_r G \approx - 300$ kJ. All three quantities in eq.(S9) are negative, and we can also write

$$|w_{\text{ele}}| \approx |\Delta_r G| - |q_{\text{diss}}| \quad (\text{S10})$$

The second-law requirement $\Delta G < w_{\text{ele}}$ is fulfilled because $(- q_{\text{diss}}) > 0$ in eq.(S9) makes w_{ele} less negative than ΔG .

3. Electrode Terminology

Negative/positive electrode vs. anode/cathode. Two terminologies for electrodes are common in electrochemistry: negative/positive electrode and anode/cathode. There is universal agreement that the anode is the electrode where oxidation (loss of electrons) occurs. In a discharging battery, this is the negative electrode since it releases negatively charged electrons into the external circuit. The cathode is the electrode where reduction (gain of electrons) happens and it is the positive electrode in a working battery. We prefer “negative electrode” for several reasons (for instance, it can be understood without memorization of a definition that in turn requires an understanding of oxidation) and use it in the initial, conceptual sections of our paper.

The negative electrode remains negative whether the battery is discharging or charging, in the first case because the electrochemical reaction releases excess electrons at this electrode, see Figure S2a, and in the second case because the external voltage source pushes excess electrons into this electrode, see Figure S2b. By contrast, because the electrochemical reaction is reversed from the discharging to the charging condition, the anode in a discharging battery becomes the cathode upon switch to the charging state (while remaining the negative electrode).

Unfortunately, “negative electrode” has the serious drawback of being too long in technical analyses: for instance, “negative electrode” does not work well as a subscript, while “anode” or some shortened form of it is convenient. Furthermore, the battery literature refers almost exclusively to anode and cathode. For these reasons, we switch to anode and cathode in the later, technical sections of this paper.

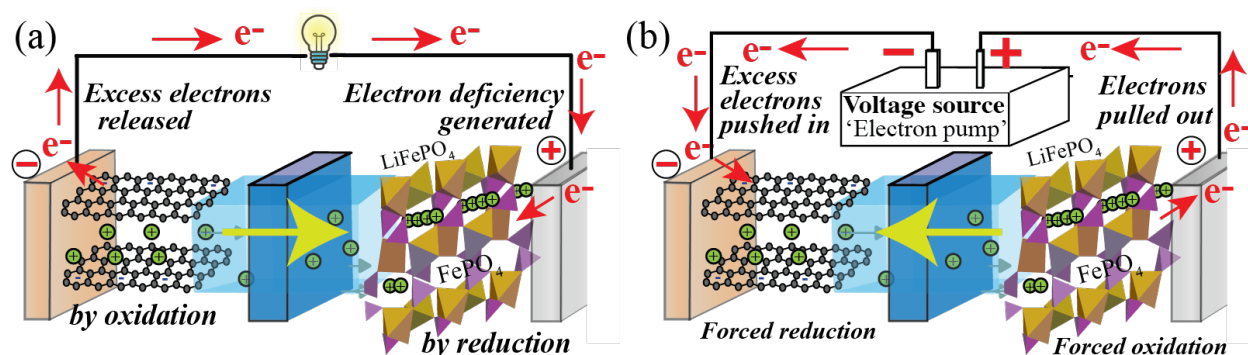


Figure S2. Cartoons of a lithium-ion battery, with an emphasis on electron flow and electrode polarity, (a) while discharging and (b) while being charged by an external voltage source. In a), electron flow is driven by the spontaneous electrochemical reaction, in b) by the external voltage source which acts like an electron pump, pushing electrons into the negative and pulling them out of the positive electrode. In both cases, the left electrode has an electron excess and is therefore negative.

4. Calculation of Molar Enthalpies and Gibbs Free Energies

Calculating the energy released in a lithium iron phosphate battery. Using thermodynamic data presented by Phan et al.,¹⁰ taken from an earlier source,¹¹ we obtain the enthalpy and free energy of reaction as well as the cell voltage of a lithium-ion battery with a lithium-metal anode and iron-phosphate cathode:



$$\Delta_f H_i^\circ \quad 0 \quad + \quad -1279 \quad -1616 \quad \text{kJ/mol} \quad \Delta_r H^\circ = -337 \text{ kJ/mol} \quad (\text{S11b})$$

$$S_i^\circ \quad 29.1 \quad 122 \quad 131 \quad \text{J/mol K} \quad \Delta_r S^\circ = -20 \text{ J/mol K} \quad (\text{S11c})$$

$$\Delta_r G^\circ = \Delta_r H^\circ - 298 \text{ K } \Delta_r S^\circ = \mathbf{-331 \text{ kJ/mol}} \quad (\text{S11d})$$

$$E_{\text{cell}}^\circ = -\Delta_r G^\circ / F = \mathbf{3.43 \text{ V}} \quad (\text{S1e})$$

Calculating cohesive energies from enthalpies of formation. As shown in the supporting information of reference,¹² the cohesive (free) energy of a compound *i* with the elemental composition $C_c H_h O_o N_n S_s P_p Li_l Fe_{fe} Mn_{mn} Co_{co}$ relative to the unbonded, free atoms at the same temperature can be calculated from the enthalpy or free energy of formation according to:

$$\begin{aligned} H_i^\circ = \Delta_f H_i^\circ - \\ (716.7 c + 218.0 h + 249.2 o + 472.7 n \\ + 278.8 s + 314.64 p + 159.4 li + 416.3 fe \\ + 281.0 mn + 425.0 co) \text{ kJ/mol} \end{aligned} \quad (\text{S12})$$

The coefficients are the bond energies per atom in the elements in their standard states, e.g. 436 kJ/mol/2 for hydrogen or -498.4 kJ/mol/2 for oxygen. Similarly,

$$\begin{aligned} G_i^\circ = \Delta_f G_i^\circ - \\ (671.3 c + 203.3 h + 231.8 o + 455.6 n \\ + 238.3 s + 278.3 p + 126.7 li + 370.7 fe \\ + 173.6 mn + 380.3 co) \text{ kJ/mol} \end{aligned} \quad (\text{S13})$$

Technically, the molar energies multiplying the elemental coefficients are the standard enthalpies (or free energies) of formation of the gaseous (unbonded) atoms¹³ (from the elements in their standard state). For example, this yields the cohesive energies of iron phosphate and lithium iron phosphate:

$$H_{\text{FePO}_4}^{\circ} = -1279 \text{ kJ/mol} - (249.2 \times 4 + 314.64 + 416.3) \text{ kJ/mol} = -3007 \text{ kJ/mol} \quad (\text{S14})$$

$$H_{\text{LiFePO}_4}^{\circ} = -1616 \text{ kJ/mol} - (249.2 \times 4 + 314.64 + 159.4 + 416.3) \text{ kJ/mol} = -3503 \text{ kJ/mol} \quad (\text{S15})$$

The cohesive energy H_i° , molar entropy S_i° , and cohesive free energy G_i° of a compound $\text{Li}_i\text{Fe}_f\text{P}_p\text{O}_o$ are related as follows:

$$G_i^{\circ} = H_i^{\circ} - 298 \text{ K} (S_i^{\circ} - (160.95 o + 163.08 p + 180.38 fe + 138.66 li) \text{ J/molK}) \quad (\text{S16})$$

Here, the molar entropies before the elemental coefficients are the molar entropies of the gaseous atoms.¹³ We can thus obtain the cohesive free energies of iron phosphate and lithium iron phosphate:

$$G_{\text{FePO}_4}^{\circ} = -3007 \text{ kJ/mol} - 298 \text{ J/mol} (122.21 - 160.95 \times 4 - 163.08 - 180.38) = -2749.2 \text{ kJ/mol} \quad (\text{S17})$$

$$G_{\text{LiFePO}_4}^{\circ} = -3503 \text{ kJ/mol} - 298 \text{ J/mol} (130.95 - 160.95 \times 4 - 163.08 - 180.38 - 138.66) = -3206.5 \text{ kJ/mol} \quad (\text{S18})$$

Cohesive energies of CoO_2 and LiCoO_2 were calculated from the equations given above based on the enthalpies of formation reported as

$$\Delta_f H_{\text{CoO}_2}^{\circ} = -290 \text{ kJ/mol}^{14}$$

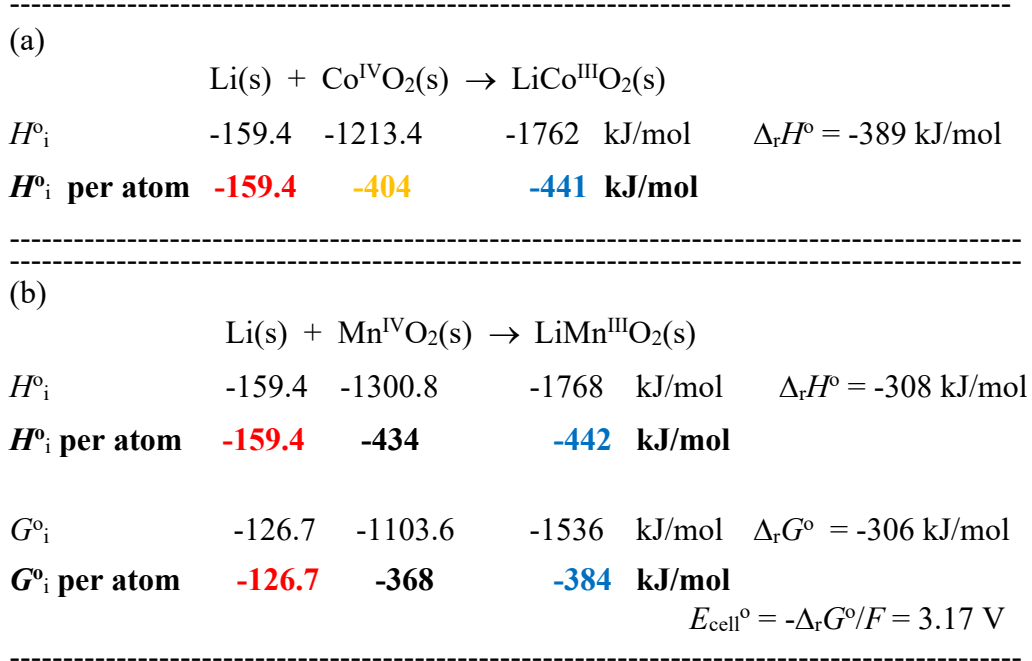
$$\Delta_f H_{\text{LiCoO}_2}^{\circ} = -679 \pm 3 \text{ kJ/mol}^{8, 14-16}$$

This yields the cohesive energies of cobalt oxide and lithium cobalt oxide according to eqs.(S12) and (S13):

$$H_{\text{CoO}_2}^{\circ} = -290 \text{ kJ/mol} - (425 \text{ kJ/mol} + (249.2 \text{ kJ/mol}) \times 2) = -1213.4 \text{ kJ/mol} \quad (\text{S19})$$

$$H_{\text{LiCoO}_2}^{\circ} = -679 \text{ kJ/mol} - (159.4 \text{ kJ/mol} + 425 \text{ kJ/mol} + (2)(249.2 \text{ kJ/mol})) = -1761.8 \pm 3 \text{ kJ/mol} \quad (\text{S20})$$

The comparison of the cohesive energy per atom in Scheme S1a shows that $\text{Co}^{\text{IV}}\text{O}_2(\text{s})$ is relatively weakly bonded (and consequently quite unstable), which contributes to the large energy release.



Scheme S1. Cohesive (free) energies in a metal-oxide-based battery with a lithium-metal anode. (a) CoO_2 . (b) MnO_2 . High (i.e. only slightly negative) energy values are highlighted in red and orange.

Cohesive energies of MnO_2 and LiMnO_2 were calculated from the enthalpies and free energies of formation reported as

$$\Delta_f H_{\text{MnO}_2}^\circ = -521.4 \text{ kJ/mol}^{17}, \Delta_f G_{\text{MnO}_2}^\circ = -466.4 \text{ kJ/mol}^{17}$$

$$\Delta_f H_{\text{LiMnO}_2}^\circ = -829 \text{ kJ/mol}^{18}, \Delta_f G_{\text{LiMnO}_2}^\circ = -772 \text{ kJ/mol}^{18}$$

Using eqs.(S12) and (S13), we obtain

$$H_{\text{MnO}_2}^\circ = -521.4 \text{ kJ/mol} - (281 \text{ kJ/mol} + (2)(249.2 \text{ kJ/mol})) = -1300.8 \text{ kJ/mol} \quad (\text{S21a})$$

$$G_{\text{MnO}_2}^\circ = -466.4 \text{ kJ/mol} - (173.6 \text{ kJ/mol} + (2)(231.8 \text{ kJ/mol})) = -1103.6 \text{ kJ/mol} \quad (\text{S21b})$$

$$\begin{aligned} H_{\text{LiMnO}_2}^\circ &= -829 \text{ kJ/mol} - (159.4 \text{ kJ/mol} + 281 \text{ kJ/mol} + (2)(249.2 \text{ kJ/mol})) \\ &= -1767.8 \text{ kJ/mol} \quad (\text{S22a}) \end{aligned}$$

$$\begin{aligned} G_{\text{LiMnO}_2}^\circ &= -772 \text{ kJ/mol} - (126.7 \text{ kJ/mol} + 173.6 \text{ kJ/mol} + (2)(231.8 \text{ kJ/mol})) \\ &= -1535.9 \text{ kJ/mol} \quad (\text{S22b}) \end{aligned}$$

The comparison of the cohesive (free) energy per atom is shown in Scheme S1b. The cell voltage of a lithium-ion battery with a lithium-metal anode and manganese-oxide cathode can be approximately calculated from the cohesive free energies:

$$E_{\text{cell}}^{\circ}(x_{\text{Li}} = 0.5) \approx -(-1536 - (-127 - 1104)) \text{ kJ} / 96.5 \text{ kC} = 3.17 \text{ V} \quad (\text{S23})$$

Thermodynamic data for graphite and lithiated graphite. From the free energy of formation of graphite $\Delta_f G^{\circ}_{\text{C(s)}} = 0$, we find from eq.(S13)

$$G^{\circ}_{\text{C(s)}} = \Delta_f G^{\circ}_{\text{C(s)}} - 671.3 \text{ kJ/mol} = - 671.3 \text{ kJ/mol}. \quad (\text{S24})$$

Each C-atom has 4 half bonds or two full bonds, so per bond, the cohesive free energy is

$$(-671 \text{ kJ/mol})/2 \text{ bonds} = -336 \text{ kJ/(mol of bonds)} \quad (\text{S25})$$

which is reasonable with -359 kJ/mol C-C bond-formation energy and a ~6% entropic contribution.

The value for $G^{\circ}_{\text{LiC}_6(\text{s})}$ can be found as follows: The average potential of a cell with a graphite cathode and a Li(s) anode is $E^{\circ}_{\text{cell}} = 0.15 \pm 0.06 \text{ V}$.¹⁹ This gives

$$\Delta_r G^{\circ} = -FE^{\circ}_{\text{cell}} = -15 \pm 6 \text{ kJ/mol} \quad \text{for} \quad \text{Li} + 6 \text{ C(s)} \rightleftharpoons \text{LiC}_6 \quad (\text{S26})$$

One can solve $\Delta_r G^{\circ} = G^{\circ}_{\text{LiC}_6(\text{s})} - (G^{\circ}_{\text{Li(s)}} + 6 G^{\circ}_{\text{C(s)}})$ for $G^{\circ}_{\text{LiC}_6(\text{s})}$ and obtain the cohesive free energy of lithiated graphite:

$$\begin{aligned} G^{\circ}_{\text{LiC}_6(\text{s})} &= \Delta_r G^{\circ} + G^{\circ}_{\text{Li(s)}} + 6 G^{\circ}_{\text{C(s)}} \\ &= (-15 - 126.7 + 6 \times (-671.3)) \text{ kJ/mol} = -4169 \text{ kJ/mol} \end{aligned} \quad (\text{S27})$$

In this case, the enthalpy or free energy of bonding per atom is less informative than usual since the C-C bonding is so much stronger than the graphite–lithium bonding.

Calculation of the lattice (free) energy of NaCl and LiCl. According to the principles laid out above, see eqs.(S12) and (S13), we can calculate the cohesive energies of NaCl and LiCl from their enthalpies of formation as follows:

$$\begin{aligned}
H_{\text{NaCl}}^{\circ} &= \Delta_f H_{\text{NaCl}}^{\circ} - (107.32 \text{ na} + 121.68 \text{ cl}) \text{ kJ/mol} \\
&= (-411.15 - 107.32 - 121.68) \text{ kJ/mol} = -640 \text{ kJ/mol}
\end{aligned} \tag{S28}$$

$$\begin{aligned}
G_{\text{NaCl}}^{\circ} &= \Delta_f G_{\text{NaCl}}^{\circ} - (76.8 \text{ na} + 105.71 \text{ cl}) \text{ kJ/mol} \\
&= (-384.15 \text{ kJ/mol} - 76.8 - 105.71) \text{ kJ/mol} = -566 \text{ kJ/mol}
\end{aligned} \tag{S29}$$

$$\begin{aligned}
H_{\text{LiCl}}^{\circ} &= \Delta_f H_{\text{LiCl}}^{\circ} - (159.4 \text{ li} + 121.68 \text{ cl}) \text{ kJ/mol} \\
&= (-408.61 - 159.4 + 121.68) \text{ kJ/mol} = -689.7 \text{ kJ/mol}
\end{aligned} \tag{S30}$$

$$\begin{aligned}
G_{\text{LiCl}}^{\circ} &= \Delta_f G_{\text{LiCl}}^{\circ} - (126.7 \text{ li} + 105.71 \text{ cl}) \text{ kJ/mol} \\
&= (-384.39 \text{ kJ/mol} - 126.7 - 105.71) \text{ kJ/mol} = -616.8 \text{ kJ/mol}
\end{aligned} \tag{S31}$$

Other quantities shown in Figure 4 were obtained as follows:

$$\text{Lattice enthalpy} = \text{enthalpy of sublimation} + \frac{1}{2} \text{BondE} + \text{IE} - \text{EA} - \Delta_f H^{\circ} \tag{S32}$$

$$\text{Lattice enthalpy of LiCl} = (159.4 + 121.68 + 520 - 349 - (-408.61)) \text{ kJ/mol} = 861 \text{ kJ/mol}$$

$$\text{Entropy of LiCl(s)} = 59.33 \text{ J/molK}^{13}$$

$$\text{Entropy of Li(g)} + \text{Cl(g)} = (138.7 + 165.1) \text{ J/molK}^{13}$$

5. Chemical Potentials in Lithium-Ion Batteries

Basic aspects of chemical potentials. The electrochemical potential of a chemical species i can be defined as

$$\tilde{\mu}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} \tag{S33a}$$

which is the rate of change in Gibbs free energy $G = U + PV - TS$ (of the system) with a small change in the amount of species i at fixed temperature and pressure as well as fixed amounts of all other species. From this, the chemical potential can be obtained as²⁷

$$\mu_i = \tilde{\mu}_i - z_i F \phi \tag{S33b}$$

where z_i is the charge of species i , $F = 96.5$ kC/mol, and ϕ is the Galvani electrical potential. For neutral species such as the lithium atom, $z_{\text{Li}} = 0$ and therefore $\mu_{\text{Li}} = \tilde{\mu}_{\text{Li}}$.

Equation (S33a) can be shown²⁰ to lead to

$$G = \sum_{\text{species } i} \tilde{\mu}_i n_i \quad (\text{S34})$$

where the sum is over a full set of species, of amounts n_i in mole, in the system. Note that there is no restriction to constant T and P , or to a closed system, for eq.(S34). The chemical potential is therefore the partial molar Gibbs free energy of a species i . For instance, the Gibbs free energy of a cathode consisting of 2 moles of FePO_4 and 1.5 moles of LiFePO_4 is

$$\begin{aligned} G_{\text{cathode}} &= 2 \text{ mol } \mu_{\text{FePO}_4} + 1.5 \text{ mol } \mu_{\text{LiFePO}_4} \\ &= 2 (-2749 \text{ kJ}) + 1.5 (-3206.5 \text{ kJ}) = -10,308 \text{ kJ} \end{aligned} \quad (\text{S35})$$

Traditional thermodynamics in terms of free energies of formation usually cannot really quantify chemical potentials, but only their differences. Our thermodynamics in terms of individual (molecular/atomic/compound) enthalpies H_i^0 and free energies $G_i^{0,12,21}$ has overcome this limitation.

For pure solids of constant composition, there is no concentration dependence of the chemical potential and we have simply

$$\mu_{\text{pure solid}} = G_{\text{pure solid}}^0 \quad (\text{S36})$$

With $\mu_i = G_i^0 + RT \ln a_i$,²⁰ this is equivalent to stating that the activity a_i of a pure solid is

$$a_{\text{pure solid}} = 1. \quad (\text{S37})$$

Chemical potential of lithium in coexisting phases. In diffusion equilibrium, the chemical potential of any diffusible species is uniform throughout the system. For instance, for coexisting $\text{Li}_{0.02}\text{FePO}_4$ and $\text{Li}_{0.98}\text{FePO}_4$, the chemical potential of lithium or of iron is the same in both phases:

$$\mu_{\text{Li}}(\text{Li}_{0.02}\text{FePO}_4) = \mu_{\text{Li}}(\text{Li}_{0.98}\text{FePO}_4) = \mu_{\text{Li}}(\text{Li}_{0.02}\text{FePO}_4 \text{ coexisting with } \text{Li}_{0.98}\text{FePO}_4) \quad (\text{S38a})$$

$$\mu_{\text{Fe}}(\text{Li}_{0.02}\text{FePO}_4) = \mu_{\text{Fe}}(\text{Li}_{0.98}\text{FePO}_4) \quad (\text{S38b})$$

Otherwise, the system could achieve a reduction in Gibbs free energy, $\Delta G < 0$, by lithium atoms (or ions plus electrons) diffusing from high to low partial molar Gibbs free energy (i.e. from high to low chemical potential). This would be in violation of diffusion equilibrium.

Chemical potential of lithium in coexisting iron phosphates. As mentioned above, it is a well-known fundamental property of chemical potentials that in Li-diffusion equilibrium between two phases, e.g. FePO_4 and LiFePO_4 , the chemical potential of lithium is the *same* in both phases. In a consistent analysis, presented in the following, this requires at least a small amount of lithium in FePO_4 , e.g. $\text{Li}_{0.02}\text{FePO}_4$; we show below how this low-level lithium incorporation is entropically favored. The uniform chemical potential of lithium can be expressed as

$$\mu_{\text{Li}}(\text{Li}_{0.02}\text{FePO}_4) = \mu_{\text{Li}}(\text{Li}_{0.98}\text{FePO}_4) \quad (\text{S39})$$

We can repeat the calculations of eqs.(7) and (8) in the main text, with

$$n_{\text{Li}} = 0.98 n_{\text{Li}_{0.98}\text{FePO}_4} + 0.02 n_{\text{Li}_{0.02}\text{FePO}_4} \quad (\text{S40})$$

$$n_{\text{Li}_{0.02}\text{FePO}_4} + n_{\text{Li}_{0.98}\text{FePO}_4} = n_{\text{Fe}}$$

These equations can be solved for

$$n_{\text{Li}_{0.02}\text{FePO}_4} = (n_{\text{Fe}} - n_{\text{Li}})/0.96$$

$$n_{\text{Li}_{0.98}\text{FePO}_4} = n_{\text{Fe}} - (n_{\text{Fe}} - n_{\text{Li}})/0.96$$

to give the dependence of G on the chemical potential of lithium

$$\begin{aligned} G_{\text{sys}} &= \sum_i \mu_i n_i = \mu_{\text{Li}_{0.98}\text{FePO}_4} n_{\text{Li}_{0.98}\text{FePO}_4} + \mu_{\text{Li}_{0.02}\text{FePO}_4} n_{\text{Li}_{0.02}\text{FePO}_4} \\ &= \mu_{\text{Li}_{0.98}\text{FePO}_4} (n_{\text{Fe}} - (n_{\text{Fe}} - n_{\text{Li}})/0.96) + \mu_{\text{Li}_{0.02}\text{FePO}_4} (n_{\text{Fe}} - n_{\text{Li}})/0.96 \end{aligned} \quad (\text{S41})$$

Taking the derivative gives

$$\mu_{\text{Li}}(\text{cathode}) = (\partial G_{\text{sys}}/\partial n_{\text{Li}})_{T,P,n'} = (\mu_{\text{Li}_{0.98}\text{FePO}_4} - \mu_{\text{Li}_{0.02}\text{FePO}_4})/0.96 \quad (\text{S42})$$

We can combine eqs. (S42) and (S38a) to relate four chemical potentials, two of which are the same:

$$\mu_{\text{Li}(\text{Li}_{0.02}\text{FePO}_4)} = \mu_{\text{Li}(\text{Li}_{0.98}\text{FePO}_4)} = (\mu_{\text{Li}_{0.98}\text{FePO}_4} - \mu_{\text{Li}_{0.02}\text{FePO}_4})/0.96 \quad (\text{S43})$$

Given the approximately linear dependence of the chemical potential of the cathode on the lithium fraction, see Figure S3a and eq.(S63) below,¹⁰

$$\begin{aligned} \mu_{\text{Li}_x\text{FePO}_4} &\approx \mu_{\text{FePO}_4} + x_{\text{Li}} (\mu_{\text{LiFePO}_4} - \mu_{\text{FePO}_4}) \\ &= -2749 \text{ kJ/mol} - x_{\text{Li}} 458 \text{ kJ/mol} \end{aligned} \quad (\text{S44a})$$

the factor of 0.96 cancels out and

$$\begin{aligned} \mu_{\text{Li}(\text{Li}_{0.02}\text{FePO}_4)} &= \mu_{\text{Li}(\text{Li}_{0.98}\text{FePO}_4)} \approx \mu_{\text{LiFePO}_4} - \mu_{\text{FePO}_4} \\ &= G^\circ_{\text{LiFePO}_4} - G^\circ_{\text{FePO}_4} = -458 \text{ kJ/mol} \end{aligned} \quad (\text{S44b})$$

essentially the same as obtained in the main text, eq.(17), using the simplifying model of stoichiometric phases.

Specifying the species *i* of the chemical potential is important; for instance, we need to distinguish between the chemical potential of $\text{Li}_{0.98}\text{FePO}_4$ and the chemical potential of *lithium in* $\text{Li}_{0.98}\text{FePO}_4$, which are not at all equal:

$$\mu_{\text{Li}_{0.98}\text{FePO}_4} = G^\circ_{\text{Li}_{0.98}\text{FePO}_4} = -3206.5 \text{ kJ/mol} + 0.02 \times 458 \text{ kJ/mol} \quad (\text{S45a})$$

$$\mu_{\text{Li}(\text{Li}_{0.98}\text{FePO}_4)} = -458 \text{ kJ/mol} \quad (\text{S45b})$$

One is the rate of change in Gibbs free energy with a small change in the amount of $\text{Li}_{0.98}\text{FePO}_4$, with a value according to eq.(S44a), the other the rate of change in Gibbs free energy with a small change in the amount of lithium in $\text{Li}_{0.98}\text{FePO}_4$, with the numerical value shown in eq.(34b). We will show that in the single-phase region, the two chemical potentials in eq.(S45) are related through $\mu_{\text{Li}(\text{Li}_x\text{FePO}_4)} = (\partial \mu_{\text{Li}_x\text{FePO}_4} / \partial x)$, see eq.(S62a) below.

6. Cell Voltage from Thermodynamics

Cell voltage and the slope of $G(\xi)$. At constant T and P , the cell voltage E_{cell} relates to the change in Gibbs free energy with the extent of reaction:

$$\sum_i \mu_i \tilde{\nu}_i = (\partial G_{\text{chem}}/\partial \xi)_{T,P} = -\nu_e F E_{\text{cell}} \quad (\text{S46})$$

This important relation has been presented in some textbooks (though with $(\partial G/\partial \xi)_{T,P}$ often misleadingly replaced by $\Delta_r G$) and was recently derived carefully from first principles.²² Instead of repeating this derivation, we link eq.(S46) to the much more familiar Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - RT/(\nu_e F) \ln Q \quad (\text{S47})$$

in effect running part of a derivation of the Nernst equation in reverse. The reaction quotient Q also appears in

$$(\partial G_{\text{chem}}/\partial \xi)_{T,P} = \Delta_r G^\circ + RT \ln Q \quad (\text{S49})$$

a frequently presented equation in the thermodynamic theory of chemical equilibrium²⁰ that could conceptually follow soon after $(\partial G_{\text{chem}}/\partial \xi)_{T,P} = \sum_i \mu_i \tilde{\nu}_i$. After multiplying the Nernst equation with $-\nu_e F$, it becomes

$$-\nu_e F E_{\text{cell}} = -\nu_e F E_{\text{cell}}^\circ + RT \ln Q \quad (\text{S50})$$

Given that $\Delta_r G^\circ = -\nu_e F E_{\text{cell}}^\circ$, which is the widely used relation between standard Gibbs free energy change and standard cell voltage, we can replace the first term on the right-hand side of eq.(S50):

$$-\nu_e F E_{\text{cell}} = \Delta_r G^\circ + RT \ln Q \quad (\text{S51})$$

Given that the right-hand sides of eqs.(S49) and (S51) are the same, their left-hand sides must be equal, too, so

$$(\partial G_{\text{chem}}/\partial \xi)_{T,P} = -\nu_e F E_{\text{cell}} \quad (\text{S52})$$

confirming eq.(S46).

Cell voltage and lithium chemical potential difference. The thermodynamic analysis of lithium-intercalation batteries relies heavily on the relation between the cell voltage and the chemical potential of lithium atoms:^{8, 15, 23-25}

$$E_{\text{cell}} = -\Delta\mu_{\text{Li}}/F = -(\mu_{\text{Li}(\text{cathode})} - \mu_{\text{Li}(\text{anode})})/F \quad (\text{S53})$$

Here we review the classical derivation of this equation by McKinnon and Haering²⁴ with added interpolations and standard chemistry notation: since the Li^+ ions remain inside the system throughout the process, only the electrons do work in the thermodynamic sense, which is energy transferred between system and surroundings. The work done is just $w_{\text{ele}} = -e E_{\text{cell}} < 0$ for each electron (of charge $-e$). Based on

$$\Delta_r G = w_{\text{nonPV}} \quad \text{at constant } T \text{ and } P \quad (\text{S54})$$

this work is the change in Gibbs free energy due to the chemical reaction,

$$\Delta_r G = w_{\text{ele}} = -e E_{\text{cell}} \quad (\text{S55})$$

More rigorously,²² in electrochemical thermodynamics for a reversible cell, with the extent of reaction ξ , one finds (see eq.(S52))

$$" \Delta_r G " = (\partial G_{\text{chem}}/\partial \xi)_{T,P} = -\nu_e F E_{\text{cell}} = -F E_{\text{cell}} \quad (\text{S56})$$

with $\nu_e = 1$ for singly-charged lithium ions. From 1 mol electrons = 6×10^{23} electrons, striking electrons on both sides, we obtain 1 mol = 6×10^{23} and therefore²⁶

$$F = 96500 \text{ C}/(1 \text{ mol}) = 96500 \text{ C}/(6 \times 10^{23}) = 1.6 \times 10^{-19} \text{ C} = e \quad (\text{S57})$$

As a result, equations (S55) and (S56) are recognized as identical.

Next, one can relate the Gibbs free energy change to the lithium chemical potential difference. If we write the intercalation reaction as



then according to standard chemical thermodynamics of the approach to equilibrium,²⁷

$$" \Delta_r G " = (\partial G_{\text{chem}}/\partial \xi)_{T,P} = \sum_i \mu_i \tilde{\nu}_i = \mu_{\text{Li}(\text{cathode})} - \mu_{\text{Li}(\text{anode})} \quad (\text{S59})$$

This tells us that the molar Gibbs free energy change is the difference in chemical potential of Li in cathode and anode; inserting this eq.(S59) into eq.(S56), we obtain

$$F E_{\text{cell}} = - (\mu_{\text{Li}(\text{cathode})} - \mu_{\text{Li}(\text{anode})})$$

which is equivalent to eq.(S53), completing the derivation.

Cell voltage and the slope of $G_{\text{cath}}(x_{\text{Li}})$. The mole fraction of lithium, $x_{\text{Li}} \equiv x$, in an iron-phosphate cathode of average composition Li_xFePO_4 can be related to amounts of lithium and iron (both in mol) according to

$$x_{\text{Li}} = n_{\text{Li}}/n_{\text{Fe}} \quad (\text{S60})$$

Then, the slope of the molar Gibbs free energy of the cathode,

$$G_{\text{cath}}/n_{\text{Fe}} = \mu_{\text{cath}} = \mu_{\text{Li}_x\text{FePO}_4} \quad (x < 0.02 \ \& \ x > 0.98) \quad (\text{single phase}) \quad (\text{S61a})$$

$$G_{\text{cath}}/n_{\text{Fe}} = \mu_{\text{cath}} = \mu_{\text{Li}_{0.02}\text{FePO}_4} + (x_{\text{Li}} - 0.02)/0.96 (\mu_{\text{Li}_{0.98}\text{FePO}_4} - \mu_{\text{Li}_{0.02}\text{FePO}_4}) \quad (\text{two phases}) \quad (\text{S61b})$$

as a function of $x \equiv x_{\text{Li}}$ gives the chemical potential of lithium, according to its definition and using eqs. (S60) and (S61),

$$\mu_{\text{Li}(\text{cath})} = (\partial G_{\text{cath}}/\partial n_{\text{Li}}) = (\partial(G_{\text{cath}}/n_{\text{Fe}})/\partial x_{\text{Li}}) = (\partial\mu_{\text{cath}}/\partial x_{\text{Li}}) \quad (\text{S62a})$$

$$= (\partial\mu_{\text{Li}_x\text{FePO}_4}/\partial x) \quad (\text{single phase}) \quad (\text{S62b})$$

$$= (\mu_{\text{Li}_{0.98}\text{FePO}_4} - \mu_{\text{Li}_{0.02}\text{FePO}_4})/0.96 \quad (\text{two phases}) \quad (\text{S62c})$$

as indicated by Phan et al.¹⁰ To illustrate eq.(S61), the dependence of the molar free energy (or chemical potential) of an iron phosphate-based cathode on lithium mole fraction according to Phan et al.¹⁰ is presented in Figure S3a, and its slope (matching eq.(S62)) in Figure S3b. The corresponding cell voltage in a battery with a lithium metal anode is shown on the right axis. A 0.09 V shift relative to the corresponding plot of Phan et al.¹⁰ can be traced back to a referencing error as discussed below.

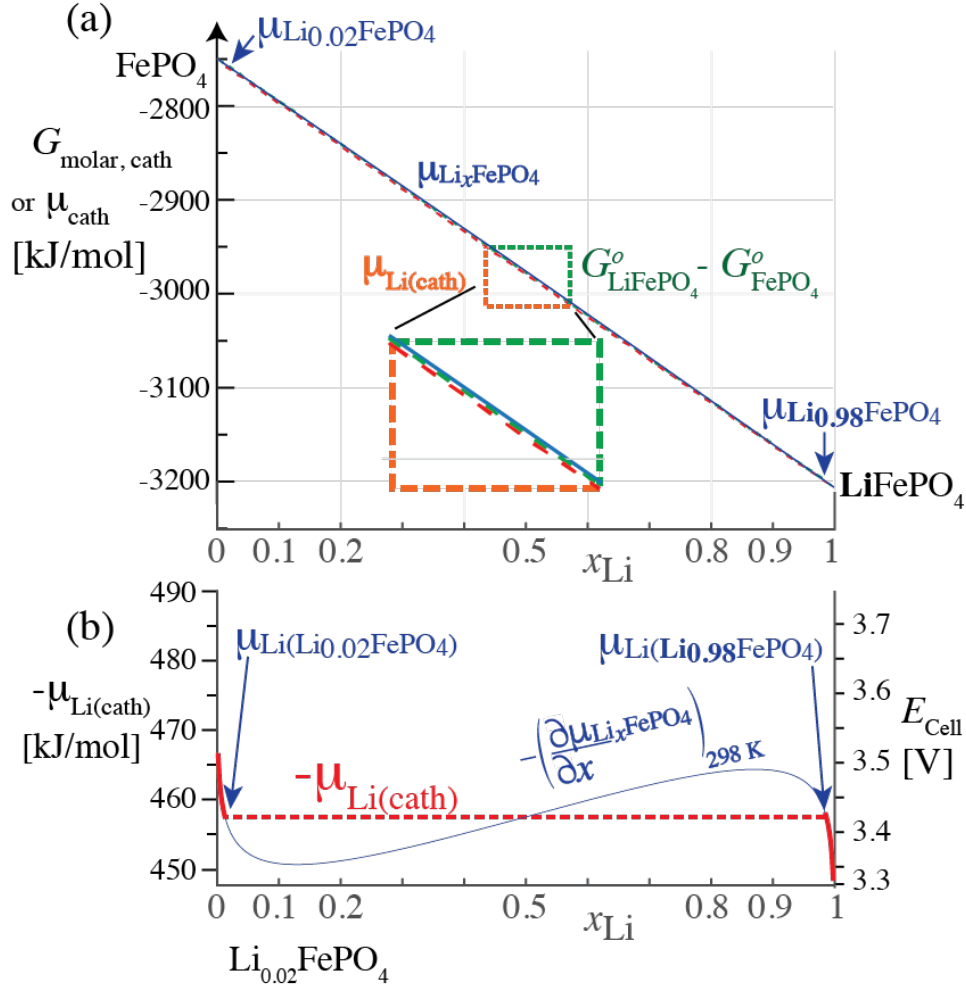


Figure S3. Plots of the molar Gibbs free energy of, and of the chemical potential of lithium in, an iron-phosphate-based cathode as a function of lithium content according to Phan et al.¹⁰ and eq.(S63). (a) Blue curve: molar Gibbs free energy (or chemical potential) of a hypothetical single-phase Li_xFePO_4 cathode, $\mu_{\text{Li}_x\text{FePO}_4}$, according to eq.(S63) on a scale with the unbonded atoms at zero free energy. The red dashed-line double tangent to the single-phase Gibbs free energy curve (in blue) marks the molar Gibbs free energy of coexisting $\text{Li}_{0.02}\text{FePO}_4$ and $\text{Li}_{0.98}\text{FePO}_4$, which has the lowest G_{molar} at most values of x_{Li} . In this miscibility gap, the fraction of $\text{Li}_{0.98}\text{FePO}_4$ increases from left to right, while the fraction of $\text{Li}_{0.02}\text{FePO}_4$ decreases. In the center of the figure, the equality of the slope μ_{Li} of the red-dashed double tangent with $\Delta_r G^\circ$, the slope of the green dashed line connecting the standard molar free energies $G^\circ_{\text{FePO}_4}$ and $G^\circ_{\text{LiFePO}_4}$, is quite apparent. (b) Thin blue curve: magnitude of the slope $(\partial\mu_{\text{Li}_x\text{FePO}_4}/\partial x)$ of a hypothetical single-phase Li_xFePO_4 cathode from a); thick red line: slope of the curve of lowest molar G in a) (mostly of the double tangent in a): dashed), which is the magnitude of the chemical potential μ_{Li} of lithium in the cathode, see eq.(S62). The cell voltage with a lithium-metal anode is shown on the right axis.

Initial voltage drop and entropic driving force. There is a large entropic driving force for lithium incorporation when $\text{Fe}^{\text{III}}\text{PO}_4$ is completely free of lithium.¹⁰ This is the reason for the initial high voltage commonly observed for $x_{\text{Li}} = 0$ and disproves the claim made by Liu et al.²⁸ that entropy is always negligible, which applies only for phases of fixed composition.

When a phase is devoid of a component or species, the chemical potential of that species is negative infinity. This can be seen in statistical mechanics of the multiplicity of lithium in lattice models, which are directly applicable here and used in advanced analyses, e.g. of Phan et al.¹⁰ In a regular-solution model that fits the phase diagram at moderate temperatures,¹⁰ the molar Gibbs free energy, or chemical potential, of a hypothetical single-phase Li_xFePO_4 cathode depends on the lithium mole fraction $x_{\text{Li}} \equiv x$ according to

$$\begin{aligned} \mu_{\text{Li}_x\text{FePO}_4} = & G_{\text{FePO}_4}^{\circ} + x_{\text{Li}} (G_{\text{LiFePO}_4}^{\circ} - G_{\text{FePO}_4}^{\circ}) + x_{\text{Li}} (1-x_{\text{Li}}) 22 \text{ kJ/mol} \\ & + RT (x_{\text{Li}} \ln x_{\text{Li}} + (1-x_{\text{Li}}) \ln(1-x_{\text{Li}})) \end{aligned} \quad (\text{S63})$$

as plotted in Figure S3a (blue curve). Then, certainly for small mole fractions x_{Li} , according to eq.(S62b) and as shown in Figure S3b,

$$\begin{aligned} \mu_{\text{Li}(\text{cath})}(x_{\text{Li}}) = & (\partial \mu_{\text{Li}_x\text{FePO}_4} / \partial x) = (G_{\text{LiFePO}_4}^{\circ} - G_{\text{FePO}_4}^{\circ}) \\ & + 22 \text{ kJ/mol} - x_{\text{Li}} 44 \text{ kJ/mol} + RT (\ln(x_{\text{Li}}) - \ln(1-x_{\text{Li}})) \end{aligned} \quad (\text{S64})$$

For $x_{\text{Li}} = 0$, the fourth term in the sum ($RT \ln(0) = -\infty$) diverges and therefore

$$\mu_{\text{Li}}(x_{\text{Li}} = 0) = -\infty. \quad (\text{S65})$$

This quantifies the very strong entropic driving force, traditionally summarized as “nature abhors a vacuum”, for incorporating a dilute solute. The infinity does not make the Gibbs free energy of the system diverge because lithium’s contribution $\mu_{\text{Li}} n_{\text{Li}}$ to G_{sys} is zero due to the vanishing amount $n_{\text{Li}} = 0$. Furthermore, this is not a strong infinity: even with just one Li atom/ion in a mole of FePO_4 , $x_{\text{Li}} = 10^{-24}$, the entropic voltage contribution has dropped from infinity to 1.4 V (added to $(G_{\text{LiFePO}_4}^{\circ} - G_{\text{FePO}_4}^{\circ}) + 22 \text{ kJ/mol}$ from the difference in bonding). There is correspondingly a reverse entropic driving force as lithium empties out of a graphite anode.

No simple chemical reaction can be written here, so the lithium chemical potential formalism is needed. Still, one can *explain* the chemical potential of lithium, in this case in terms of an entropic driving force.

Erroneous cell voltage due to neglected entropy of solid lithium. The cell voltage shown in Figure 3 of the informative paper by Phan et al.¹⁰ is 3.52 V, while the useful thermodynamic data compiled in their Table 1 give only 3.43 V. The moderate discrepancy can be traced to an inconsistent treatment of the standard molar entropy of metallic Li. Its value is 29.1 J/mol K, so $-T S_{\text{Li(s)}}^{\circ} = -298 \times 29.1 \text{ J/mol} = -8.7 \text{ kJ/mol}$ at 298 K, which corresponds to $-8.7 \text{ kJ/mol}/96.5 \text{ kC/mol} = -0.09 \text{ V}$, the numerical value of the discrepancy. In effect, this error is due to a pitfall of standard thermodynamics that has been remarked upon too little, namely that

$$\Delta_f G_{\text{Li(s)}}^{\circ} \neq \Delta_f H_{\text{Li(s)}}^{\circ} - T S_{\text{Li(s)}}^{\circ} \quad (\text{S66})$$

Specifically, Phan et al.¹⁰ defined $G_i^{\circ} = \Delta_f H_i^{\circ} - T S_i^{\circ}$ for the two stoichiometric phases i of the cathode. For consistency, this definition would need to be applied to all reactants, including metallic Li:

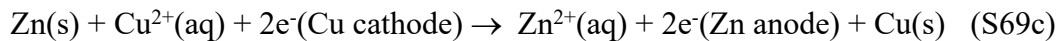
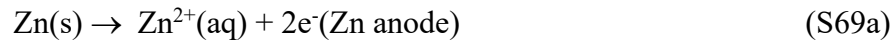
$$G_{\text{Li(s)}}^{\circ} = \Delta_f H_{\text{Li(s)}}^{\circ} - T S_{\text{Li(s)}}^{\circ} = 0 - 298 \times 29.1 \text{ J/mol} = -8.7 \text{ kJ/mol} \quad (\text{S67})$$

However, below their eq.(9), Phan et al.¹⁰ set

$$G_{\text{Li(s)}}^{\circ} = \mu_{\text{Li(s)}} = 0 \quad (\text{S68})$$

The inconsistency between the two values for $G_{\text{Li(s)}}^{\circ}$, from the use of two different free-energy scales, gave rise to a minor 0.09 V error in their Figure 3.

Thermodynamics of an open electrochemical cell. We use a $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$ as a simple, familiar example of a galvanic cell here. For an *open* cell, electrons do show up in the overall reaction:



$$\begin{aligned} (\partial G / \partial \xi)_{T,P} = \sum_{i=1}^6 \tilde{\mu}_i \tilde{\nu}_i = \sum_{i=1}^4 \mu_i \tilde{\nu}_i + \tilde{\mu}_{e^{-}(\text{anode})} - \tilde{\mu}_{e^{-}(\text{cathode})} = \sum_{i=1}^4 \mu_i \tilde{\nu}_i \\ + 2 \mu_{e^{-}(\text{Zn(s)})} - 2 F \phi(\text{Zn anode}) - 2(\mu_{e^{-}(\text{Cu(s)})} - F \phi(\text{Cu cathode})) \end{aligned} \quad (\text{S69d})$$

Note that the electromotive force is *not* equal to $\phi(\text{Zn anode}) - \phi(\text{Cu cathode})$. Rather, the zinc electrode needs to be placed in contact with a (second) piece of copper.²⁴ Then, in diffusion equilibrium, the electrochemical potential of the electrons is the same in zinc and the connected piece of copper,

$$\tilde{\mu}_{e^-(\text{anode})} = 2 \mu_{e^-}(\text{Zn(s)}) - 2 F \phi(\text{Zn anode}) = 2 \mu_{e^-}(\text{Cu(s)}) - 2 F \phi(\text{Cu anode}) \quad (\text{S70})$$

With the difference in electron electrochemical potential (using the conventional “cathode minus anode” definition), inserting eq.(S70) in the third step, we obtain

$$\begin{aligned} \Delta \tilde{\mu}_{e^-} &= \tilde{\mu}_{e^-(\text{cathode})} - \tilde{\mu}_{e^-(\text{anode})} \\ &= 2 \mu_{e^-}(\text{Cu(s)}) - 2 F \phi(\text{Cu cathode}) - 2 (\mu_{e^-}(\text{Zn(s)}) - F \phi(\text{Zn anode})) \\ &= 2 \mu_{e^-}(\text{Cu(s)}) - 2 F \phi(\text{Cu cathode}) - 2 (\mu_{e^-}(\text{Cu(s)}) - F \phi(\text{Cu anode})) \\ &= 2F (\phi(\text{Cu anode}) - \phi(\text{Cu cathode})) \end{aligned} \quad (\text{S71})$$

This gives the open circuit voltage, or OCV, as a “natural” potential difference of

$$E_{\text{cell}} = \text{OCV} = \phi(\text{Cu cathode}) - \phi(\text{Cu anode}) = - \Delta \tilde{\mu}_{e^-} / 2F \quad (\text{S72})$$

Since electrons do not flow through an external circuit here, no electrical work is done by an open cell, $w_{\text{ele}} = 0$, and therefore in equilibrium

$$0 = (\partial G / \partial \xi)_{T,P} = \sum_{i=1}^4 \mu_i \tilde{\nu}_i + \Delta \tilde{\mu}_{e^-} = \Delta_r G^\circ + RT \ln Q + \tilde{\mu}_{e^-(\text{anode})} - \tilde{\mu}_{e^-(\text{cathode})} \quad (\text{S73})$$

Solving this equation for $\Delta \tilde{\mu}_{e^-} = \tilde{\mu}_{e^-(\text{cathode})} - \tilde{\mu}_{e^-(\text{anode})}$ as defined in eq.(S71), we find

$$E_{\text{cell}} = \Delta \tilde{\mu}_{e^-} / (-2F) = \Delta_r G^\circ / (-2F) - (RT/2F) \ln Q \quad (\text{S74})$$

which is the Nernst equation with $\nu_e = 2$.²⁷

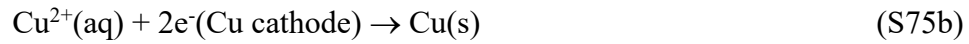
Thermodynamics of a continuously working electrochemical cell. For a very short initial period of time, the working galvanic cell behaves like an open cell. It usually produces some

electrons in the anode and consumes some in the cathode, which generates a charge difference and resulting voltage. During this time, no electrons flow through the external circuit, so no electrical work is produced.

In a continuously working cell, including a reversible one, electrons are only intermediates. The electrons generated at the anode travel through the external circuit, performing electrical work, and end up in the cathode:



The electrons are consumed in the reaction at the cathode:



Therefore, the net reaction does not show electrons.



$$(\partial G/\partial \xi)_{T,P} = \sum_i \tilde{\mu}_i \tilde{\nu}_i = \sum_i \mu_i \tilde{\nu}_i = \Delta_r G^\circ + RT \ln Q \quad (\text{S75d})$$

If the process is made reversible by an applied external voltage that matches the cell voltage,

$$w_{\text{ele}} = \Delta_r G \approx |\Delta n_{\text{Li(s)}}| (\partial G/\partial \xi)_{T,P} \quad (\text{S76})$$

The voltage drop across a large external resistance can, in effect, act like a nearly matched applied voltage.

7. Plots with the Chemical Potential of the Electron in Metal-Oxide Electrodes

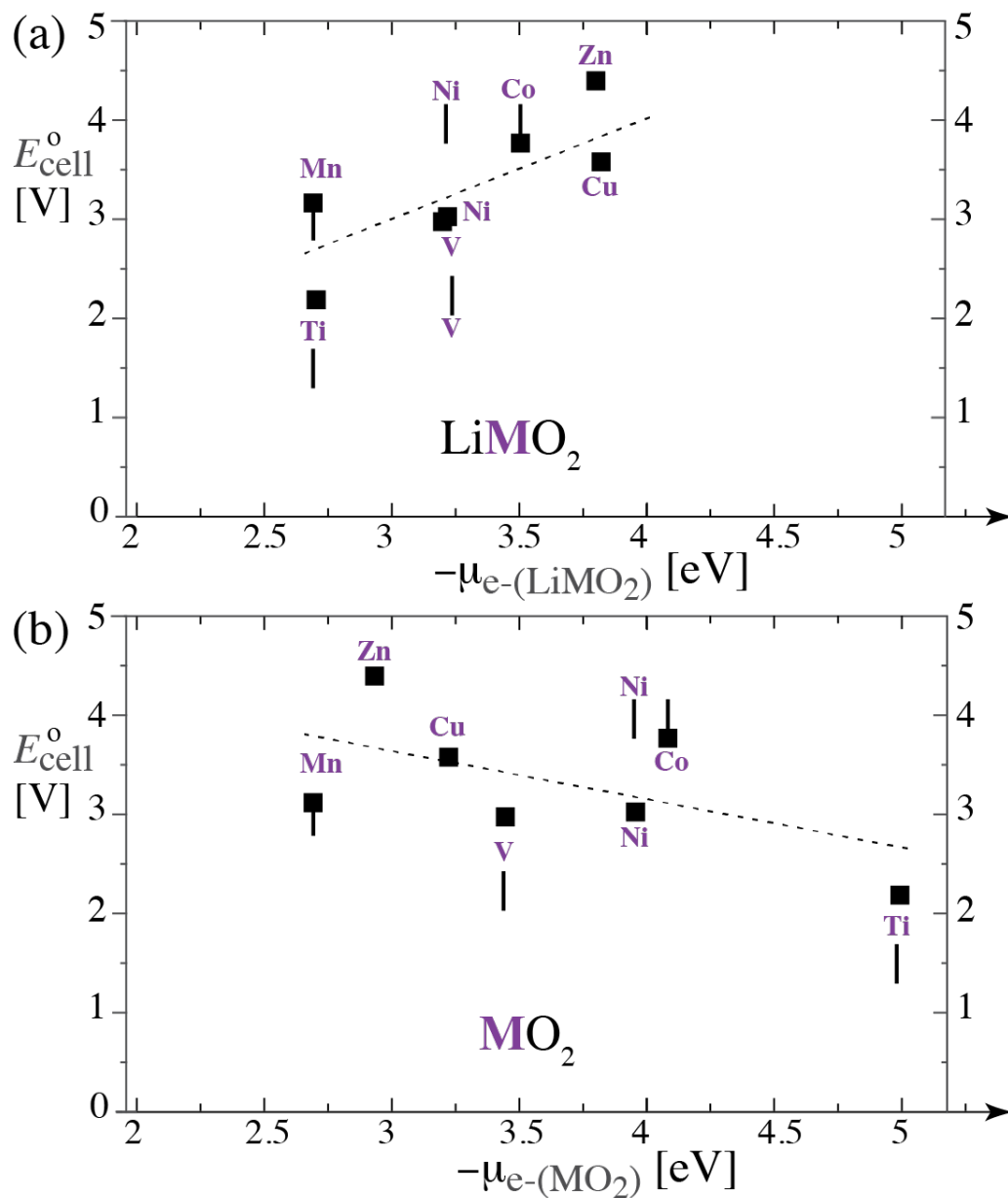


Figure S4. Plot of calculated (squares) and measured (vertical bars) cell voltages with a MO_2 cathode (with metal M as indicated) and Li(s) anode as a function of the calculated Fermi level μ_{e^-} in (a) lithiated transition-metal oxides; (b) lithium-free transition-metal oxides. Little correlation is observed, in particular in b). Data were obtained from highly cited Aydinol et al.¹⁵ The coefficients of determination are moderate at best: in a), $R^2 = 0.68$ for the predicted and 0.54 for the experimental voltages, while b) shows a weak anticorrelation with $R^2 = 0.40$ and 0.24 for predicted and experimental voltages, respectively.

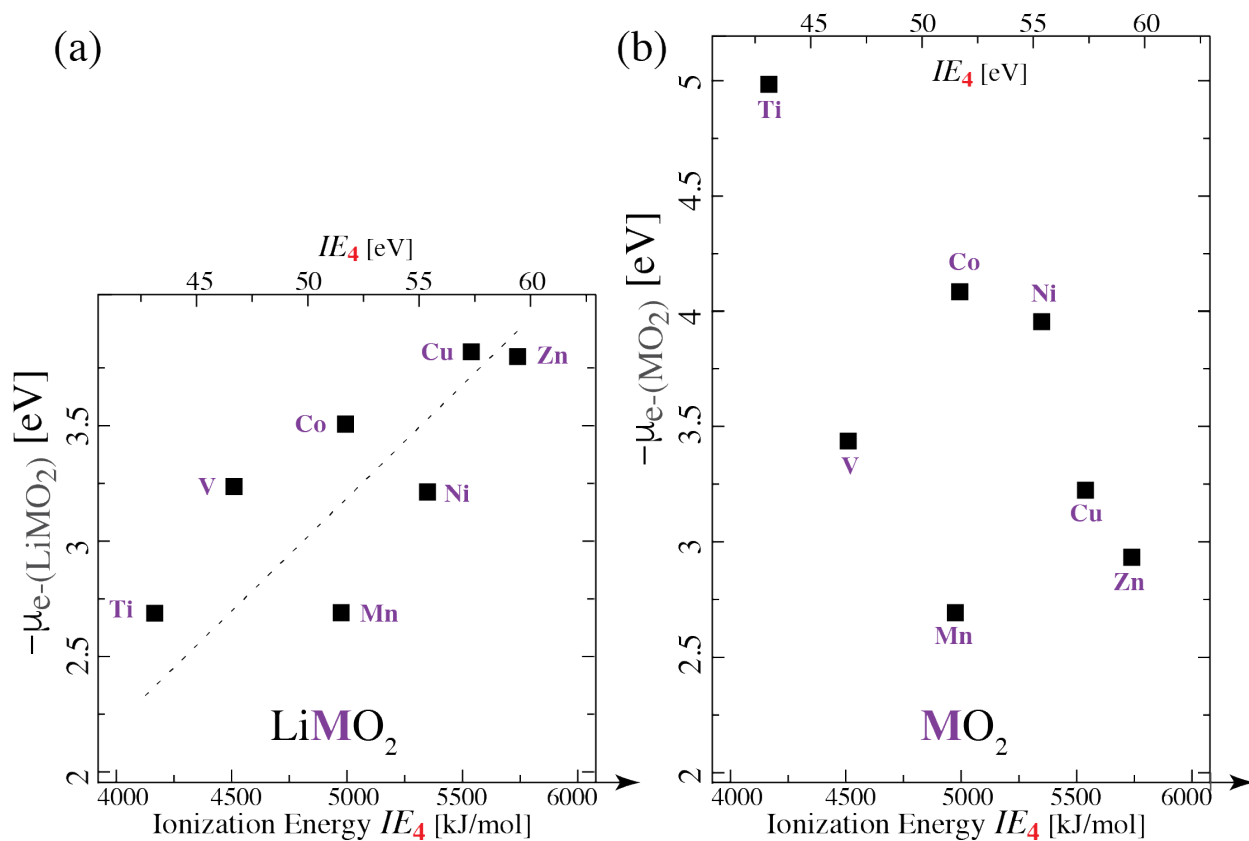


Figure S5. Plot of the chemical potential of electrons in (a) LiMO_2 and (b) MO_2 (with metal M as indicated), estimated by quantum-chemical simulations,¹⁵ as a function of the 4th ionization energy of the transition metal M. The coefficients of determination are moderate, $R^2 = 0.58$ in a), and $R^2 = 0.42$ in b) for a weak anticorrelation.

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