

**A Redlich–Kister type free energy model for
Li-intercalation compounds with variable lattice
occupation numbers**

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Abstract

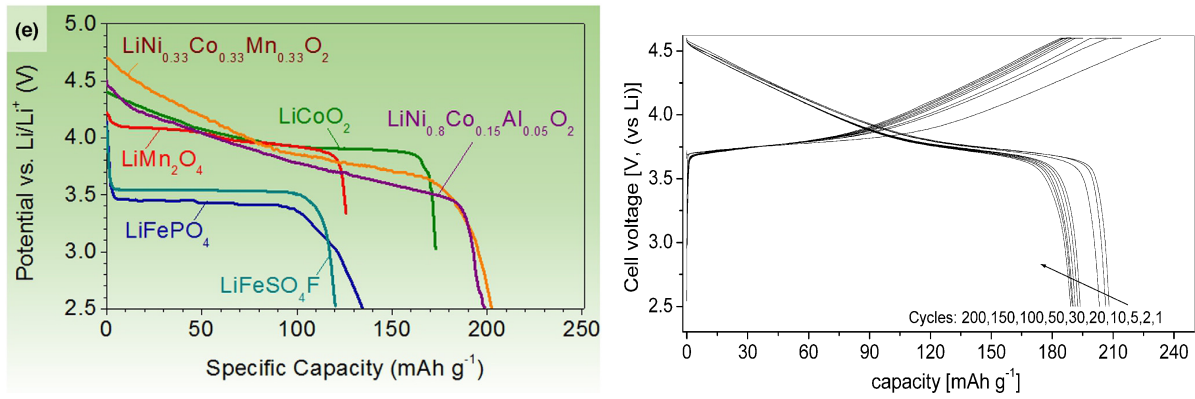
One of the central quantities of a lithium ion intercalation compound is the open circuit potential, the voltage a battery material delivers in thermodynamic equilibrium. This voltage is related to the chemical potential of lithium in the insertion material and in general a non-linear function of the mole fraction of intercalated lithium. Experimental data shows further that it is specific for various materials. The open circuit voltage is a central ingredient for mathematical models of whole battery cells, which are used to investigate and simulate the charge and discharge behavior and to interpret experimental data on non-equilibrium processes. However, since no overall predictive theoretical method presently exists for the open circuit voltage, it is commonly fitted to experimental data. Simple polynomial fitting approaches are widely used, but they lack any thermodynamic interpretation. More recently systematically and thermodynamically motivated approaches are used to model the open circuit potential. We provide here an explicit free energy density which accounts for variable occupation numbers of Li on the intercalation lattice as well as Redlich–Kister-type enthalpy contributions. The derived chemical potential is validated by experimental data of $\text{Li}_y(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ and we show that only two parameters are sufficient to obtain an overall agreement of the non-linear open circuit potential within the experimental error.

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1 Introduction

In this study we want to derive and discuss a free energy density function ψ for lithium ion intercalation compounds like the high energy density material $\text{Li}_y(\text{Ni}_{z_1}\text{Mn}_{z_2}\text{Co}_{z_3})\text{O}_2$, ($y \in (0, 1)$, $z_1 + z_2 + z_3 = 1$) [1]. The chemical potential μ of intercalated lithium in such materials



(a) OCP during discharge for various intercalation compounds (Fig. 4.e) of [5], reprinted with permission of Elsevier). (b) OCP during charge and discharge for macro-porous $\text{Li}_y(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (Fig. 3 of [6], reprinted with permission of Wiley-VCH).

Figure 1: Non-linear E^{OCP} as function of the capacity, which is direct proportional to y .

is related to measurable open circuit potential E in a half cell with metallic Li as counter electrode [2–4], i.e.

$$E(y) = \frac{1}{e_0} (\mu_{\text{Li}} - \mu(y)) \quad \text{with} \quad \mu_{\text{Li}} = \text{const.} \quad (1)$$

where y is the mole fraction of intercalated lithium. The open circuit potential (OCP) is in general a non-linear function of y (or the capacity) and the central characteristic quantity of the respective intercalation material. Fig. 1a shows typically measured functions of various materials[5] and Fig. 1b especially of $\text{Li}_y(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ [6].

Quite commonly, the OCP is tabulated [7–9] or *fitted* to some polynomial [2, 10–13], rational, exponential [14], piecewise polynomials [15], or combination of these functions [16–19]. Despite that this entails in general a huge amount of parameters to capture the non-linear behavior of the OCP, it lacks any thermodynamic interpretation.

However, since the *origin* of the OCP, and especially its concentration dependency, is of pure thermodynamic nature, this is a major shortcoming. Hence more recent attempts try to overcome these conventional *fitting approaches* by more elaborate thermodynamic models of the chemical potential μ [20–22]. They rely essentially on an entropic contribution to the chemical potential of an ideal lattice in combination with an enthalpy of mixing [23, 24], commonly called regular solution [25, 26]. The thermodynamics of mixtures and their deviation from *ideality* is a longstanding topic of physical chemistry, and we refer to [27–29] for details.

In this work we provide a systematic thermodynamic modeling of a free energy density ψ and the corresponding chemical potential μ for a general lithium intercalation compound. Three central aspects enter the free energy modeling, the reference contribution ψ^R (yielding the constant E^0), the entropy of mixing contribution ψ^S and the enthalpy contribution ψ^H , i.e.

$$\psi = \psi^R + \psi^S + \psi^H. \quad (2)$$

For the entropic contribution, we extend the common ideas of lattice mixtures to more realistic and flexible scenarios of variable occupation numbers on a lattice. For the enthalpy contribution, we extend the common ideas of regular solutions to a specific Redlich-Kister type expression. Overall, this leads to a free energy model with a rather small amount of interpretable parameters showing a remarkable agreement to experimental data of the OCP.

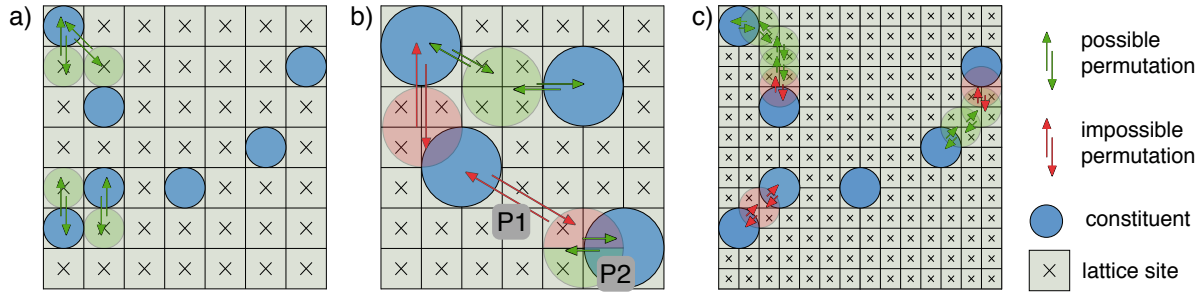


Figure 2: Sketch of possible configurations and permutations on a lattice. a) occupation number $\omega = 1$, which corresponds to an ideal lattice mixture, b) with an occupation number $\omega = 4$ and larger species A on the same lattice, c) $\omega = 4$ but similar sized particles as in a). Note that for a fixed lattice site one permutation with this site could be possible while another one is forbidden, e.g. in b) the permutation P1 is impossible while P2 is possible.

2 Entropy of Mixing with variable occupation number

For the entropy of mixing we consider a mixture on a lattice, where N indistinguishable Li constituents mix on N_ℓ lattice sites. However, we assume that each particle requires ω sites of the lattice, see Fig. 2. The origin for the uptake of ω lattice sites are diverse. One could consider that a mobile ionic species on the lattice *solvates* vacancies, or that ion-ion interactions prohibit a closer arrangement. For ion conducting materials it is well known that far more interstitial sites in a crystal structure can exist than the maximum number of ions on a lattice [30, 31]. However, the sake of this work is not to actually discuss the origin of the occupation number ω , but the thermodynamic consequences.

The number of vacancies on the lattice is then

$$N_V = N_\ell - \omega \cdot N \quad (3)$$

and the number of mixing particles is

$$N^{\text{mix}} = N + N_V = N_\ell + (1 - \omega)N. \quad (4)$$

This yields for the configurational entropy

$$S = k_B \ln \left(\frac{N, N_V}{N^{\text{mix}}} \right) \approx k_B \left(N \cdot \ln \left(\frac{N}{N^{\text{mix}}} \right) + k_B T N_V \cdot \ln \left(\frac{N_V}{N^{\text{mix}}} \right) \right), \quad (5)$$

where the Stirling approximation for large N 's was used. It is crucial that number of mixing particles N^{mix} enters the configurational entropy in the denominator and not the total number N_ℓ of lattice sites. This accounts, for example, for the effect that a permutation of a particle with an empty lattice is forbidden if the particle would require adjacent lattice sites that are already occupied (see Fig. 2.b the permutation P1). However, the very same position is available for the particle which previously prohibited the permutation (Fig 2.b permutation P2).

This yields for the entropic free energy contribution

$$\Psi_A^S = k_B T N \cdot \ln \left(\frac{N}{N^{\text{mix}}} \right) + k_B T N_V \cdot \ln \left(\frac{N_V}{N^{\text{mix}}} \right) \quad (6)$$

and in the transition to densities

$$\frac{N}{V} \rightarrow n, \frac{N_V}{V} \rightarrow n_V \quad \text{and} \quad \frac{\Psi_A^S}{V} \rightarrow \psi^S \quad (7)$$

the configurational entropic free energy density

$$\psi^S = k_B T (n \cdot \ln(c) + n_V \cdot \ln(c_V)) \quad (8)$$

with

$$c = \frac{n}{n^{\text{mix}}} = \frac{n}{n_\ell + (1 - \omega)n} \quad \text{and} \quad c_V = \frac{n_V}{n^{\text{mix}}} = \frac{n_\ell - \omega n}{n_\ell + (1 - \omega)n}. \quad (9)$$

Note that for $\omega = 1$ the classical entropy of mixing on a lattice is obtained [22, 31]. We assume that the number density of lattice sites is constant, which corresponds to an incompressibility constraint [32], i.e. $n_\ell = \text{const.}$, and call

$$y = \frac{n}{n_\ell^\omega} \in (0, 1). \quad (10)$$

with $n_\ell^\omega := \frac{1}{\omega} n_\ell$ mole fraction of Li. Note that the maximum amount N^{max} of species A on the lattice is thus $N^{\text{max}} = \frac{1}{\omega} N_\ell$.

The chemical potential contribution of the entropy of mixing is

$$\mu^S = \frac{\partial \psi^S}{\partial n} = k_B T \ln(c) - k_B T \omega \ln(c_V) \quad (11)$$

with

$$c = \frac{\frac{n}{n_\ell}}{1 + (1 - \omega)\frac{n}{n_\ell}} = \frac{y}{\omega + (1 - \omega)y} = \hat{c}(y) \quad (12)$$

and

$$c_V = \frac{n_\ell - \omega n}{n_\ell + (1 - \omega)n} = \frac{1 - y}{1 + \frac{1 - \omega}{\omega} y} = \hat{c}_V(y) \quad (13)$$

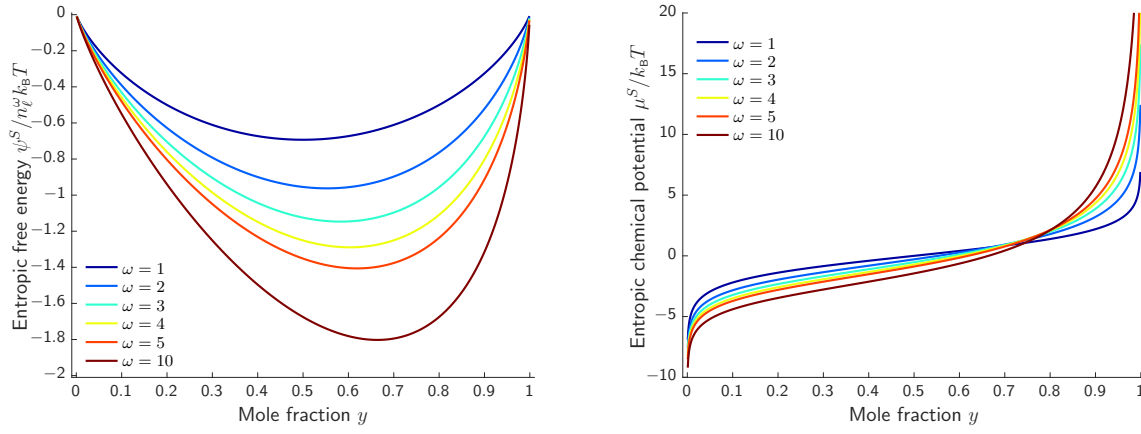
satisfying $c + c_V = 1$. Note that in the variables c and c_V the entropy of mixing *looks like* an ideal mixture. However, since we actually *control* $y = \frac{n}{n_\ell^\omega}$, i.e. the amount of particles on the lattice, the entropic contribution μ^S is *non-ideal*. A similar effect was found recently for the impact of the solvation shell on the entropy of mixing in liquid electrolytes [33]. One could thus also consider the occupation number ω as solvation shell of vacancies on a lattice.

Rewriting the configurational entropy (8) and the chemical potential contribution (11) explicitly in terms of y , by inserting the representations in (11), yields

$$\psi^S = n_\ell^\omega k_B T \cdot \left(y \cdot \ln \left(\frac{y}{\omega + (1 - \omega)y} \right) + \omega(1 - y) \cdot \ln \left(\frac{1 - y}{1 + \frac{1 - \omega}{\omega} y} \right) \right) \quad (14)$$

and

$$\mu^S = k_B T \left(\ln \left(\frac{y}{\omega + (1 - \omega)y} \right) - \omega \cdot \ln \left(\frac{1 - y}{1 + \frac{1 - \omega}{\omega} y} \right) \right). \quad (15)$$



(a) Entropic free energy density ψ^S as function of the mole fraction y . (b) Entropic chemical potential contribution μ_A^S as function of the mole fraction y .

Figure 3: Influence of the occupation number ω on the free energy density and the chemical potential.

These are the configurational entropy contributions with variable occupation number ω and considerably the generalization of the classical entropy of mixing on a lattice. Fig. 3a displays the entropic contribution of free energy density and Fig. 3b the entropy contribution to the chemical potential as function of the mole fraction y and the occupation number ω .

The influence of the occupation number ω on the free energy and the chemical potential becomes evident for $y \rightarrow 1$, since the lattice becomes then completely filled. This decreases the free energy, quite similar as in a solvation shell mixture [32, 33], since the *competition* for vacant sites increases. In the chemical potential contribution, the impact of the occupation number becomes well marked for $y > 0.8$ and broadens the tail of function. This is of special importance as we shall see in the overall comparison to experimental data.

3 Redlich–Kister type enthalpy

Next we consider an enthalpy of mixing (or excess enthalpy) ψ^H contribution to of the free energy. For a *simple* regular solution [23–26] a contribution of

$$\psi_A^H = n_\ell^\omega k_B T \gamma \cdot y \cdot (1 - y) \quad (16)$$

is frequently considered as enthalpy term. This yields for $\gamma < 2.5$ a phase separation, which has an enormous impact on the overall behavior of a many particle electrode [34]. Here, however, we focus on $\gamma > 2.5$, whereby no phase separation occurs and the intercalated lithium is actually a solid solution.

A consecutive extension of this approach was proposed by Redlich and Kister [35] as

$$\psi^H = n_\ell^\omega k_B T \gamma \left(y(1 - y) \cdot h^{\text{RK}}(y) \right) \quad (17)$$

with

$$h^{\text{RK}}(y) = \sum_{k=1}^K A_k (2 \cdot y - 1)^{k-1}. \quad (18)$$

We focus in the following exclusively on a very specific version of the coefficients and refer to [21] for a discussion on the general Redlich–Kister equation.

For the following discussion, we assume

$$A_k = \frac{(-1)^k}{k} \quad (19)$$

yielding

$$h = \sum_{k=1}^K \frac{(-1)^k}{k} (2 \cdot y - 1)^{k-1} \quad (20)$$

and thus an enthalpy free energy density contribution

$$\psi_{\text{A}}^H = n_{\ell}^{\omega} k_{\text{B}} T \gamma y (1 - y) \left(\sum_{k=1}^K \frac{(-1)^k}{k} (2 \cdot y - 1)^{k-1} \right). \quad (21)$$

This function has essentially two parameters, the interaction energy γ and the Redlich–Kister degree K . The corresponding chemical potential contribution is

$$\mu^H = \frac{\partial \psi^H}{\partial n} = k_{\text{B}} T \gamma \cdot ((1 - 2y)h(y) + y(1 - y) \cdot \partial_y h(y)) = k_{\text{B}} T \gamma \cdot g(y) \quad (22)$$

with

$$\partial_y h(y) = 2 \sum_{k=2}^K (k - 1) \frac{(-1)^k}{k} (2y - 1)^{k-2} \quad (23)$$

and

$$g(y) = (1 - 2y) \sum_{k=1}^K A_k (2 \cdot y - 1)^{k-1} + y(1 - y) 2 \sum_{k=2}^K (k - 1) \frac{(-1)^k}{k} (2y - 1)^{k-2} \quad (24)$$

$$= \left((2y - 1) + \sum_{k=2}^K \left(2(k + 1)y(1 - y) - 1 \right) \frac{(-1)^k}{k} (2 \cdot y - 1)^{k-2} \right) \quad (25)$$

Especially for $K = 1, 2, 3$ we have

$$\frac{\mu^H}{k_{\text{B}} T} = \gamma \cdot \begin{cases} (2y - 1), & \text{for } K = 1 \\ (2y - 1) + \frac{1}{2} (6y(1 - y) - 1), & \text{for } K = 2 \\ (2y - 1) + \frac{1}{2} (6y(1 - y) - 1) - \frac{1}{3} (8y(1 - y) - 1)(2y - 1) & \text{for } K = 3 \end{cases} \quad (26)$$

Fig. 4a displays the corresponding free energy density contribution and Fig. the chemical potential contribution 4b for various values of γ .

4 Discussion and conclusion

For the overall free energy density we obtain thus

$$\psi = n \cdot g^R + n_{\ell}^R k_{\text{B}} T \left(y \cdot \ln \left(\frac{\frac{1}{\omega} y}{1 + \frac{1-\omega}{\omega} y} \right) + \omega(1 - y) \ln \left(\frac{1 - y}{1 + \frac{1-\omega}{\omega} y} \right) + \gamma \cdot y(1 - y) \cdot h(y) \right) \quad (27)$$

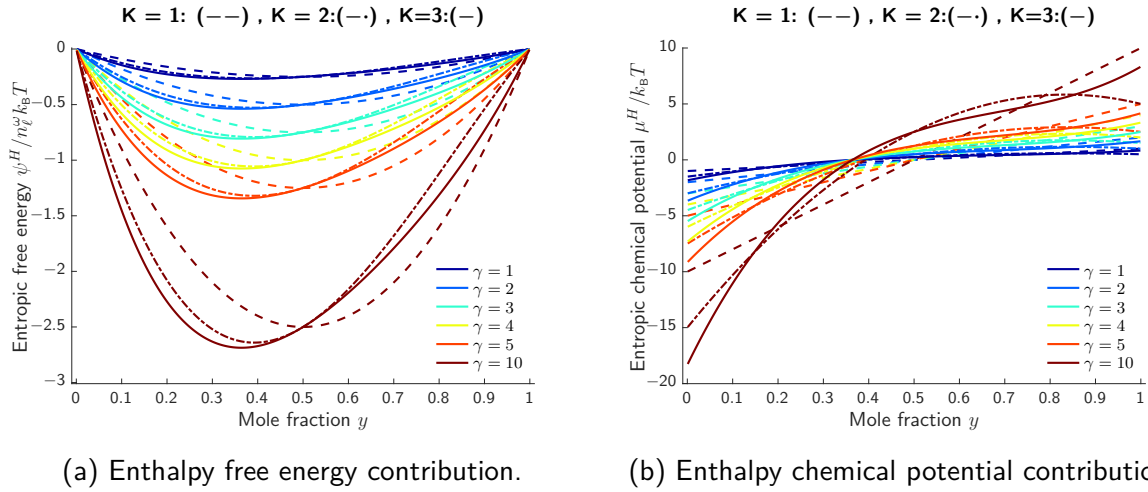


Figure 4: The Redlich–Kister-type contributions for various values of γ and N .

with reference free energy density $\psi^R = n \cdot g^R$ and correspondingly for the chemical potential

$$\mu = g^R + k_B T f(y) \quad \text{with} \quad f(y) = \ln \left(\frac{\frac{1}{\omega} y}{1 + \frac{1-\omega}{\omega} y} \right) - \omega \cdot \ln \left(\frac{1-y}{1 + \frac{1-\omega}{\omega} y} \right) + \gamma \cdot g(y) \quad (28)$$

with $g(y)$ according to eq. (24). For the open circuit potential we have thus

$$E(y) = E^0 - \frac{k_B T}{e_0} f(y) \quad \text{with} \quad E^0 = \frac{1}{e_0} (\mu_{\text{Li}} - g^R). \quad (29)$$

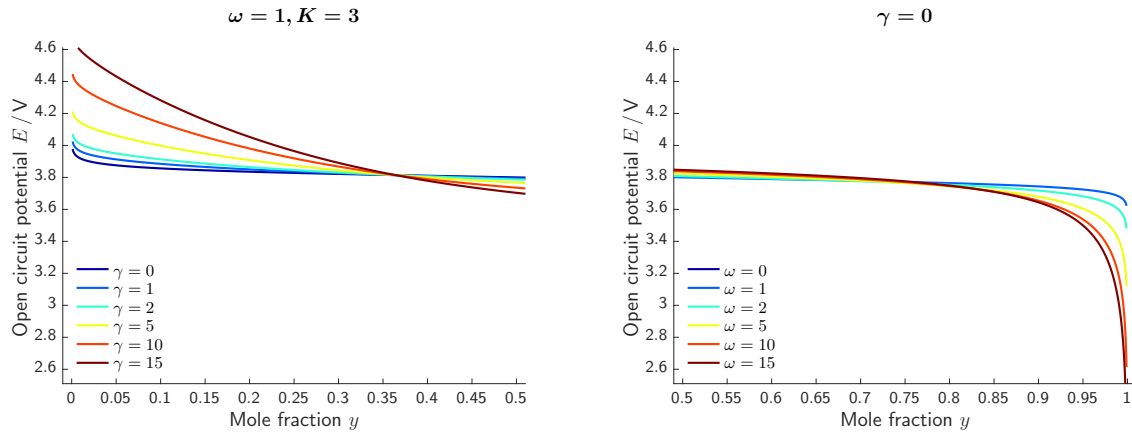
For the following discussion, we set $E^0 = 3.95 / V$ whereby we have three parameters, the interaction energy γ and the number of occupation sites ω , and the Redlich–Kister degree K , which are combined as $\vec{p} = (\omega, \gamma, K)$.

Figure 5a shows a computation of the OCP for $y \in (0, 0.5)$ and a variation of γ (with $\omega = 1$ and $N = 3$), while Fig. 5b shows the OCP for $y \in (0.5, 1)$ with a variation of ω (and $\gamma = 0$). It turns out that the Redlich–Kister type enthalpy mainly influences the OCP in the region $y \in (0, 0.5)$, where an increasing values of γ increases the potential of the discharged state $y = 0$. The occupation number has a minor contribution in the range $y \in (0, 0.5)$ since for *diluted* mixtures on lattice the occupation number ω becomes negligible. However, for $y \in (0.5, 1)$ the occupation number becomes expectably dominant, yielding an earlier decay of the cell voltage with respect to y for increasing values of ω . We can thus conclude that γ mainly impacts the cell voltage in the region $y \in (0, 0.5)$ and especially the voltage $E|_{y \rightarrow 0}$ while the occupation number broadens the voltage decay for $y \in (0.5, 1)$. By comparison to Fig. 1 we would thus expect $\omega > 1$ and $\gamma > 0$ and we discuss several parameter combinations $\vec{p}_j$ in the following.

Note that we can measure the absolute error ΔE^{OCP} and relative error Δr^{OCP} to measurable data $(\check{y}_m, \check{E}_m)$, $m = 1, \dots, M$, where M is the number of measured points, as

$$\varepsilon^E = \sqrt{\frac{1}{M} \sum_{m=1}^M (\check{E}_m - E(\check{y}_m))^2} \quad \text{and} \quad \delta^E = \sqrt{\frac{1}{M} \sum_{m=1}^M \left(\frac{\check{E}_m - E(\check{y}_m)}{\check{E}_m} \right)^2}. \quad (30)$$

For the following validation study of $\text{Li}_y(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (NMC) we rely on data of P. Bruce *et. al* [6] and N. Nitta *et. al* [5]. The data-points $\check{E}^{\text{Bruce}}$ were extracted from Fig. 3 of



(a) Ideal lattice mixture with variation of the regular solution parameter γ . (b) Variation of the occupation number ω with vanishing enthalpy contribution.

Figure 5: Open circuit potential according to (29).

[6] (1st-cycle) and $\check{E}^{\text{Nitta}}$ from Fig. 4.e of [5] ($\text{Li}_y(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$). First note that the experimental errors between the two data sets are

$$\varepsilon_{\text{Bruce}, \text{Nitta}}^E = 0.120 / \text{V} \quad \text{and} \quad r_{\text{Bruce}, \text{Nitta}}^E = 3.65\% . \quad (31)$$

We seek thus an approximation within the range of the absolute and relative experimental error.

Fig. 6 displays the computed open circuit voltage E for various parameter vectors $\vec{p}_j, j = 1, \dots, 4$, which are summarized in table 1.

Table 1: Overview of the parameter study $\vec{p}_j, j = 1, \dots, 4$ and the corresponding approximation errors to measured data of Bruce and Nitta.

Parameter	ω	γ	K	$\varepsilon_{\text{Bruce}}^E$	δ_{Bruce}^E	$\varepsilon_{\text{Nitta}}^E$	δ_{Nitta}^E
$\vec{p}_1$	1	0	0	0.270 / V	7.200%	0.35546 / V	10.420%
$\vec{p}_2$	1	13	1	0.113 / V	3.369%	0.18617 / V	5.958%
$\vec{p}_3$	5	13	2	0.059 / V	2.012%	0.14713 / V	4.958%
$\vec{p}_4$	10	13	3	0.064 / V	1.860%	0.09652 / V	3.167%

Expectably, the most common and simple model of an ideal lattice, *i.e.*

$$\mu(y; \vec{p}_1) = k_{\text{B}} T \ln \left(\frac{y}{1-y} \right) , \quad (32)$$

yields large deviations to the experimental data, *c.f.* Tab. 1, with relative errors of 7% and 10% in the standard quadratic norm. Accounting for a regular solution term in the chemical potential, *i.e.*

$$\mu(y; \vec{p}_2) = k_{\text{B}} T \ln \left(\frac{y}{1-y} \right) + k_{\text{B}} T \gamma (1-2y) \quad \text{with} \quad \gamma = 13 , \quad (33)$$

halves the absolute and relative error compared to an ideal lattice. However, the qualitative difference to the experimental data manifests in absolute errors of 0.113 / V (and 0.186 / V).

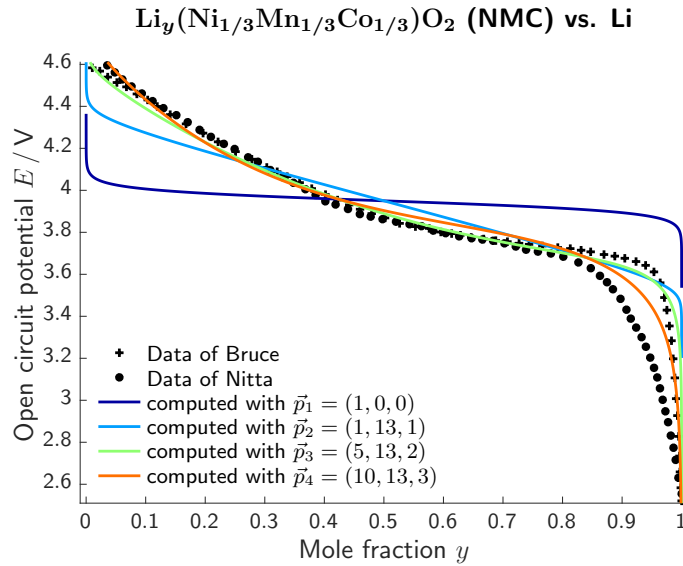


Figure 6: Comparison between the measured open circuit voltage of $\text{Li}_y(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (+) Data of [5], (•) Data of [5], and computations according to eq. (29) with various parameters $\vec{p}_j$.

Accounting for an occupation number of $\omega > 1$ further decreases the deviation to experimental data, yielding for $\omega = 1$ and $\gamma = 13$ (with $K = 2$) already absolute errors in the order of the experimental error. For $\omega = 10$, $\gamma = 13$ and $K = 3$ we yield finally also relative errors below the experimental errors, whereby we propose

$$\mu = k_B T \left(\ln \left(\frac{\frac{1}{\omega} y}{1 + \frac{1-\omega}{\omega} y} \right) - \omega \cdot \ln \left(\frac{1-y}{1 + \frac{1-\omega}{\omega} y} \right) + \gamma \cdot g(y) \right) \quad (34)$$

with

$$g(y) = (2y-1) + \frac{1}{2}(6y(1-y) - 1) - \frac{1}{3}(8y(1-y) - 1)(2y-1) \quad (35)$$

as a simple (in the sense that the model has only two parameters) but efficient and thermodynamically sound material function for $\text{Li}_y(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ with $\gamma = 13$ and $\omega = 10$. Of course, the preceding discussion can be adapted to other non-phase separating materials, forming solid solutions of intercalated lithium. The combination of Redlich–Kister-type enthalpy terms and a variable lattice occupation turns out to be a simple but effective *toolbox* to model the free energy density of a lithium intercalation compound and thus the corresponding open circuit potential.

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