Electronic Supplementary Material (ESI) for Materials Advances.

Machine Learning of Phase Diagrams: Supplemental Information

J. Lund[†], H. Wang[†], R. Braatz[‡], and R.E. García[†,∗]
†: School of Materials Engineering,
Purdue University, West Lafayette, IN 47907 USA
‡: Department of Chemical Engineering,
Massachusetts Institute of Technology, Cambridge, MA 02139 USA
∗: Corresponding author; email: redwing@purdue.edu

February 19, 2022

Supplementary Information

S1 Table of Symbols

Table S1: Glossary of symbols.

Name	Definition	Units
a	leftmost end member of pseudo-binary PD	—
a_j	temperature independent portion of jth Redlich Kister parameter	J/mol
b	rightmost end member of pseudo-binary PD	—
b_j	temperature dependent portion of jth Redlich Kister parameter	J/(mol K)
c_i	concentration of the ith component of the system	mol fraction
c_p	heat capacity	J/(mol K)
$c_\circ$	stable concentration of stoichiometric compound	mol fraction
$\mathcal{F}$	Faraday's constant	C/mol
$g^{(i)}$	Gibbs free energy function of ith phase	J/mol
g_{form}	formation energy	J/mol
$g_{\max}$	maximum deviation from equilibrium	J/mol
$g_{\text{mix,ideal}}$	ideal mixing energy due to configurational entropy	J/mol
$g_{\text{mix,xs}}$	excess free energy of mixing	J/mol
$H_{T_\circ}$	enthalpy of transformation at $T_\circ$	J/mol
k	number of nearest neighbors considered in knnalgorithm	—
L	total number of Redlich-Kister mixing parameters	—
L_j	jth Redlich-Kister excess mixing parameter	J/mol
$L^{(s)}_{l_1:l_2:\cdots:l_{s-1}:j,k:l_{s+1}:\cdots:l_S}$	binary interaction parameter between the jth and kth species on sublattice s with every other sublattice, m, filled with species l_m	J/mol
$\mathscr{L}$	distance metric between proposed and desired equilibrium properties	—
M	number of phases present in material system	—
n	L-norm used to weight outliers in phase diagram metric	—
$n^{(s)}$	fractional stoichiometric ratio of the sublattice, s	—
N	number of components in the system	—
P	number of phases at equilibrium	—
$p^{(i)}$	ith phase of the material system	—
Q	number of dimensions in free energy parameter space	—
R	universal gas constant	J/(mol K)
S	total number of sublattices	—
$S_{T_\circ}$	entropy of transformation at $T_\circ$	J/(mol K)
T	temperature	K

continued on next page

Table S1: *continued...*

Name	Definition	Units
T_m	transformation temperature	K
$T_{m,i}$	transformation temperature of ith component	K
$T_\circ$	reference temperature	K
w_i	weight of or confidence in given boundary on phase diagram	—
x	fraction of lithium in cathode material	mol fraction
$y_j^{(s)}$	site fraction of the jth species found on the s sublattice	—
z	charge valence	—
Δc	analyzed composition range	mol fraction
$\Delta g_{\text{form}}^{(i)}$	transformation energy between reference phase and ith phase	J/mol
$\Delta g_{j:k:\cdots:l}^{\text{form}}$	end-member formation energy of species $j, k, \cdots l$ on their respective sublattices	J/mol
ΔH_i	transformation enthalpy of ith component	J/mol
ΔT	analyzed temperature range	K
Θ	stability of stoichiometric compound	J/mol
κ	gradient energy coefficient	J/m
λ	characteristic wavelength for spinodal decomposition	m
$\mu^{(i)}$	chemical potential of the ith phase	J/mol
Φ	equilibrium voltage	V
σ_{property}	metric for a given equilibrium property	—
$\Omega^{(i)}$	excess free energy of mixing parameter for regular solution model	J/mol

S2 Model Implementation

S2.1 Regular Solution Model

The phase diagrams reported by Pelton and Thompson [1] were reproduced using the α phase as the reference phase, *i.e.*, $\Delta H_a^{(\alpha)} = \Delta H_b^{(\alpha)} = 0$. $T_{m,a}^{(\alpha)}$ and $T_{m,b}^{(\alpha)}$ were arbitrarily assigned to a very large number.

Table S2: Optimized parameters for the diagrams reported by Pelton and Thompson [1]. The Ω values in the header for each row and column indicate the values used by Pelton and Thompson to generate the phase diagrams whereas the parameters in each cell are the ones found in this work. The formation enthalpies used to generate the diagrams are $\Delta H_a^{(\beta)} = 8$ kJ/mol and $\Delta H_b^{(\beta)} = 12$ kJ/mol.

		$\Omega^{(\beta)}$ kJ/mol				
		-20	-10	0	10	20
$\Omega^{(\alpha)}$ kJ/mol	30	$\Delta H_a^{(\beta)} = 8.0$ $\Delta H_b^{(\beta)} = 11.9$ $\Omega^{(\alpha)} = -19.8$ $\Omega^{(\beta)} = 30.4$	$\Delta H_a^{(\beta)} = 7.9$ $\Delta H_b^{(\beta)} = 11.7$ $\Omega^{(\alpha)} = -9.5$ $\Omega^{(\beta)} = 26.6$	$\Delta H_a^{(\beta)} = 7.6$ $\Delta H_b^{(\beta)} = 11.3$ $\Omega^{(\alpha)} = 0.8$ $\Omega^{(\beta)} = 25.8$	$\Delta H_a^{(\beta)} = 7.5$ $\Delta H_b^{(\beta)} = 11.1$ $\Omega^{(\alpha)} = 10.2$ $\Omega^{(\beta)} = 25.3$	$\Delta H_a^{(\beta)} = 10.0$ $\Delta H_b^{(\beta)} = 11.2$ $\Omega^{(\alpha)} = 19.9$ $\Omega^{(\beta)} = 26.9$
	15	$\Delta H_a^{(\beta)} = 8.3$ $\Delta H_b^{(\beta)} = 12.3$ $\Omega^{(\alpha)} = -20.6$ $\Omega^{(\beta)} = 25.6$	$\Delta H_a^{(\beta)} = 7.9$ $\Delta H_b^{(\beta)} = 11.7$ $\Omega^{(\alpha)} = -9.6$ $\Omega^{(\beta)} = 13.6$	$\Delta H_a^{(\beta)} = 7.2$ $\Delta H_b^{(\beta)} = 11.4$ $\Omega^{(\alpha)} = 0.5$ $\Omega^{(\beta)} = 14.5$	$\Delta H_a^{(\beta)} = 7.2$ $\Delta H_b^{(\beta)} = 12.5$ $\Omega^{(\alpha)} = 9.4$ $\Omega^{(\beta)} = 14.8$	$\Delta H_a^{(\beta)} = 7.8$ $\Delta H_b^{(\beta)} = 8.7$ $\Omega^{(\alpha)} = 20.2$ $\Omega^{(\beta)} = 14.9$
	0	$\Delta H_a^{(\beta)} = 7.4$ $\Delta H_b^{(\beta)} = 11.2$ $\Omega^{(\alpha)} = -17.5$ $\Omega^{(\beta)} = 0.8$	$\Delta H_a^{(\beta)} = 6.4$ $\Delta H_b^{(\beta)} = 9.3$ $\Omega^{(\alpha)} = -4.7$ $\Omega^{(\beta)} = 3.0$	$\Delta H_a^{(\beta)} = 7.7$ $\Delta H_b^{(\beta)} = 9.6$ $\Omega^{(\alpha)} = 1.0$ $\Omega^{(\beta)} = 0.4$	$\Delta H_a^{(\beta)} = 7.5$ $\Delta H_b^{(\beta)} = 10.9$ $\Omega^{(\alpha)} = 9.9$ $\Omega^{(\beta)} = 0.7$	$\Delta H_a^{(\beta)} = 7.6$ $\Delta H_b^{(\beta)} = 11.8$ $\Omega^{(\alpha)} = 20.3$ $\Omega^{(\beta)} = 1.4$
	-15	$\Delta H_a^{(\beta)} = 5.9$ $\Delta H_b^{(\beta)} = 8.8$ $\Omega^{(\alpha)} = -12.4$ $\Omega^{(\beta)} = -8.8$	$\Delta H_a^{(\beta)} = 6.4$ $\Delta H_b^{(\beta)} = 13.1$ $\Omega^{(\alpha)} = -10.1$ $\Omega^{(\beta)} = -13.2$	$\Delta H_a^{(\beta)} = 8.1$ $\Delta H_b^{(\beta)} = 12.1$ $\Omega^{(\alpha)} = -3.3$ $\Omega^{(\beta)} = -18.1$	$\Delta H_a^{(\beta)} = 7.8$ $\Delta H_b^{(\beta)} = 11.8$ $\Omega^{(\alpha)} = 9.3$ $\Omega^{(\beta)} = 14.4$	$\Delta H_a^{(\beta)} = 8.2$ $\Delta H_b^{(\beta)} = 12.6$ $\Omega^{(\alpha)} = 16.7$ $\Omega^{(\beta)} = 17.6$

S2.2 Electrolyte Systems

The ten electrolyte phase diagrams were modeled using stoichiometric line compounds for the solid phases and a Redlich-Kister for the liquid phase:

$$\begin{aligned}
\Delta g^{(l)}(c,T) &= RT\big(c\ln(c) + (1-c)\ln(1-c)\big) \\
&\quad + c(1-c)\left(L_\circ^{(l)} + L_1^{(l)}(2c-1) + L_2^{(l)}(2c-1)^2\right) \\
\Delta g^{(s,a)}(c,T) &= \Delta H^{(s,a)}\left(1 - T/T_m^{(s,a)}\right) + \Theta c^2 \\
\Delta g^{(s,b)}(c,T) &= \Delta H^{(s,b)}\left(1 - T/T_m^{(s,b)}\right) + \Theta(1-c)^2 \\
\Delta g^{(\text{DMC-II})}(c,T) &= \Delta H^{(\text{DMC-II})}\left(1 - T/T_m^{(\text{DMC-II})}\right) + \Theta(1-c_{\text{DMC-II}})^2
\end{aligned} \tag{S1}$$

where the liquid phase has already been simplified as the reference phase. The formation enthalpies and transformation temperatures were taken from experiments reported in literature [2].

Table S3: Optimized parameters for electrolyte systems.

DMC+EC	EMC+EC	DEC+EC	PC+EC	PC+DMC
$L_\circ^{(l)} = 3504$	$L_\circ^{(l)} = 2442$	$L_\circ^{(l)} = 3504$	$L_\circ^{(l)} = -1310$	$L_\circ^{(l)} = 3504$
$L_1^{(l)} = -292$	$L_1^{(l)} = -434$	$L_1^{(l)} = -292$	$L_1^{(l)} = 889$	$L_1^{(l)} = -292$
$L_2^{(l)} = -429$	$L_2^{(l)} = -558$	$L_2^{(l)} = -429$	$L_2^{(l)} = -1943$	$L_2^{(l)} = -429$
PC+EMC	PC+DEC	EMC+DMC	DEC+DMC	DEC+EMC
$L_\circ^{(l)} = 1075$	$L_\circ^{(l)} = 1165$	$L_\circ^{(l)} = -569$	$L_\circ^{(l)} = -429$	$L_\circ^{(l)} = -207$
$L_1^{(l)} = 920$	$L_1^{(l)} = 601$	$L_1^{(l)} = 250$	$L_1^{(l)} = 1$	$L_1^{(l)} = 78$
$L_2^{(l)} = 577$	$L_2^{(l)} = 665$	$L_2^{(l)} = -506$	$L_2^{(l)} = -256$	$L_2^{(l)} = -162$

S2.3 Lithium Iron Phosphate System

The LFP system was modeled with three different sublattice models, SRO, LRO and T-LRO:

$$
\begin{aligned}
g^{(\mathrm{SRO})}(c,T) = \quad & -c^2 T \Delta S^{(\mathrm{SRO})}_{\mathrm{Li^+Fe^{+2}}} + c(1-c)\left(\Delta H^{(\mathrm{SRO})}_{\mathrm{Va:Fe^{+2}}} - T\Delta S^{(\mathrm{SRO})}_{\mathrm{Va:Fe^{+2}}}\right) \\
& -(1-c)^2 T \Delta S^{(\mathrm{SRO})}_{\mathrm{Va:Fe^{+3}}} + c(1-c)\Delta H^{(\mathrm{SRO})}_{\mathrm{Li^+:Fe^{+3}}} \\
& + 2RT\Bigg(c\ln(c) + (1-c)\ln(1-c)\Bigg) \\
& + c^2(1-c)^2\Big(a^{(\mathrm{SRO})}_\circ + b^{(\mathrm{SRO})}_\circ)T + (2c-1)(a^{(\mathrm{SRO})}_{1/2} + b^{(\mathrm{SRO})}_{1/2})T)\Big)
\end{aligned}
\tag{S2}
$$

$$
\begin{aligned}
g^{(\text{T-LRO})}(c,T) = \min_{\frac{3}{5}y^{(\circ)}_{\text{Li}^+}+\frac{2}{5}y^{(1)}_{\text{Li}^+}=c} \Bigg(& y^{(\circ)}_{\text{Li}^+} y^{(1)}_{\text{Li}^+} (1-c)\left(\Delta H^{(\text{T-LRO})}_{\text{LiFePO}_4^+} - T\Delta S^{(\text{T-LRO})}_{\text{LiFePO}_4^+}\right) \\
& + \frac{1}{5} y^{(\circ)}_{\text{Li}^+}\left(1-y^{(1)}_{\text{Li}^+}\right)(1-c)\left(3\Delta H^{(\text{T-LRO})}_{\text{LiFePO}_4^+} - 3T\Delta S^{(\text{T-LRO})}_{\text{LiFePO}_4^+} + \Delta G^{(\text{T-LRO})}_{\text{adjust}_2}\right) \\
& + \frac{2}{5}\left(1-y^{(\circ)}_{\text{Li}^+}\right) y^{(1)}_{\text{Li}^+}(1-c)\left(\Delta H^{(\text{T-LRO})}_{\text{LiFePO}_4^+} - T\Delta S^{(\text{T-LRO})}_{\text{LiFePO}_4^+}\right) \\
& + \frac{1}{5} y^{(\circ)}_{\text{Li}^+}\left(1-y^{(1)}_{\text{Li}^+}\right) c\left(2\Delta H^{(\text{T-LRO})}_{\text{FePO}_4^-} - 2T\Delta S^{(\text{T-LRO})}_{\text{FePO}_4^-} + \Delta G^{(\text{T-LRO})}_{\text{adjust}_1}\right) \\
& + \frac{3}{5}\left(1-y^{(\circ)}_{\text{Li}^+}\right) y^{(1)}_{\text{Li}^+} c\left(\Delta H^{(\text{T-LRO})}_{\text{FePO}_4^-} - T\Delta S^{(\text{T-LRO})}_{\text{FePO}_4^-}\right) \\
& + \frac{1}{5}\left(1-y^{(\circ)}_{\text{Li}^+}\right)\left(1-y^{(1)}_{\text{Li}^+}\right) c\left(\Delta H^{(\text{T-LRO})}_{\text{FePO}_4^-} - T\Delta S^{(\text{T-LRO})}_{\text{FePO}_4^-}\right) \\
& + \frac{1}{5}RT\Bigg(3y^{(\circ)}_{\text{Li}^+}\ln\left(y^{(\circ)}_{\text{Li}^+}\right) \qquad +3\left(1-y^{(\circ)}_{\text{Li}^+}\right)\ln\left(1-y^{(\circ)}_{\text{Li}^+}\right) \\
& \qquad + 2y^{(1)}_{\text{Li}^+}\ln\left(y^{(1)}_{\text{Li}^+}\right) \qquad +2\left(1-y^{(1)}_{\text{Li}^+}\right)\ln\left(1-y^{(1)}_{\text{Li}^+}\right) \\
& \qquad + 5c\ln(c) \qquad\qquad +5(1-c)\ln(1-c)\Bigg)\Bigg)
\end{aligned}
\tag{S3}
$$

where LRO is obtained by setting $\Delta S^{(\text{T-LRO})}_{\text{LiFePO}_4^+} = \Delta S^{(\text{T-LRO})}_{\text{FePO}_4^-} = 0$. In SRO, higher order inter-sublattice interactions have been accounted for using the method described by Hillert [3]. In addition, compound energy formalism [3, 4] is used to relate the formation energy of the end-members, *e.g.* $\Delta g^{\text{form}}_{j:k:\cdots:l}(T)$, to each other based on their physical similarities, see [5] for more details.

Table S4: Search ranges and optimized parameters for each model for the `LFP` system. Values reported from Lee [6] and Phan *et al.* [7] and used to reproduce their work are included in the literature column.

model	parameter	lower	upper	literature	**O**	**D**	**P**	units
SRO	$\Delta H^{(\text{SRO})}_{\text{Li}^+:\text{Fe}^{+3}}$	-1000	0	-420	-310	-98	-336	kJ/mol
	$\Delta H^{(\text{SRO})}_{\text{Va:Fe}^{+2}}$	-1000	0	-100	-202	-430	-218	kJ/mol
	$\Delta S^{(\text{SRO})}_{\text{Li}^+\text{Fe}^{+2}}$	-100	100	-19	30	83	97	J/(mol K)
	$\Delta S^{(\text{SRO})}_{\text{Va:Fe}^{+3}}$	-100	100	-32	-60	-6	-46	J/(mol K)
	$\Delta S^{(\text{SRO})}_{\text{Va:Fe}^{+2}}$	-100	100	-3	-93	41	59	J/(mol K)
	$a^{(\text{SRO})}_{\circ}$	-100	100	-74	-67	-62	-16	kJ/mol
	$b^{(\text{SRO})}_{\circ}$	-100	100	81	64	58	-20	J/(mol K)
	$a^{(\text{SRO})}_{1/2}$	-100	100	5	15	4	-12	kJ/mol

continued on next page

Table S4: *continued...*

model	parameter	lower	upper	literature	**O**	**D**	**P**	units
	$b^{(\mathrm{SRO})}_{1/2}$	-100	100	-19	-39	-19	17	J/(mol K)
LRO	$\Delta H^{(\mathrm{LRO})}_{\mathrm{LiFePO}_4^+}$	-100	100	15	0.8	5	-55	kJ/mol
	$\Delta H^{(\mathrm{LRO})}_{\mathrm{FePO}_4^-}$	-100	100	15	29	25	85	kJ/mol
	$\Delta G^{(\mathrm{LRO})}_{\mathrm{adjust}_1}$	-100	100	-20	-19	-21	-20	kJ/mol
	$\Delta G^{(\mathrm{LRO})}_{\mathrm{adjust}_2}$	-100	100	-29	-29	-31	-30	kJ/mol
T-LRO	$\Delta H^{(\mathrm{T\text{-}LRO})}_{\mathrm{LiFePO}_4^+}$	-100	100	—	—	58	-39	kJ/mol
	$\Delta H^{(\mathrm{T\text{-}LRO})}_{\mathrm{FePO}_4^-}$	-100	100	—	—	-6	86	kJ/mol
	$\Delta G^{(\mathrm{T\text{-}LRO})}_{\mathrm{adjust}_1}$	-100	100	—	—	-26	-24	kJ/mol
	$\Delta G^{(\mathrm{T\text{-}LRO})}_{\mathrm{adjust}_2}$	-100	100	—	—	-36	-33	kJ/mol
	$\Delta S^{(\mathrm{T\text{-}LRO})}_{\mathrm{LiFePO}_4^+}$	-100	100	—	—	63	-56	J/(mol K)
	$\Delta H^{(\mathrm{T\text{-}LRO})}_{\mathrm{FePO}_4^-}$	-100	100	—	—	-27	85	J/(mol K)

Voltages reported for SRO and LRO were taken from literature [6, 7] whereas the T-LRO had its two-phase chemical potential optimized to ±0.2 mV of the reported two-phase region [8].

S2.4 Lithium Cobalt Oxide System

The LCO system had four phases modeled:

$$\begin{aligned}
\Delta g^{(\mathrm{O1})}(c,T) &= \Delta G^{(\mathrm{O1})} + \Theta c^2 \\
\Delta g^{(\mathrm{H13})}(c,T) &= \Delta G^{(\mathrm{H13})}_{\mathrm{CoO}_3}(1-2c) + \Delta G^{(\mathrm{H13})}_{\mathrm{LiCoO}_3} 2c \\
&\quad + \tfrac{1}{2}RT\left(2c\ln(2c) + (1-2c)\ln(1-2c)\right) \\
&\quad + 2c(1-2c)\Big((a^{(\mathrm{H13})}_{\circ} + b^{(\mathrm{H13})}_{\circ}T) + (a^{(\mathrm{H13})}_{1} + b^{(\mathrm{H13})}_{1}T)(4c-1)\Big) \\
\Delta g^{(\mathrm{O3})}(c,T) &= RT\big(c\ln(c) + (1-c)\ln(1-c)\big) \\
&\quad + c(1-c)\Big((a^{(\mathrm{O3})}_{\circ} + b^{(\mathrm{O3})}_{\circ}T) + (a^{(\mathrm{O3})}_{1} + b^{(\mathrm{O3})}_{1}T)(2c-1)\Big) \\
\Delta g^{(\mathrm{I})}(c,T) &= \Delta G^{(\mathrm{I})}_{\mathrm{CoO}_3}(1-c) + \Delta G^{(\mathrm{I})}_{\mathrm{LiCoO}_3} c \\
&\quad + RT\big(c\ln(c) + (1-c)\ln(1-c)\big) \\
&\quad + c(1-c)\Omega^{(\mathrm{I})}
\end{aligned} \tag{S4}$$

In the parameter optimization, the equilibrium voltage profile was included by calculating the residual of the root mean squared error between predicted and experimental data after using it to optimize the chemical potential of LCO relative to lithium.

Table S5: Search ranges and optimized parameters for the LCO system. The *gibbs*.ML header indicates the phase diagram and associated free energy proposed in this work.

	search bounds		without (I) phase			with (I) phase			
parameter	lower	upper	[9]	[10]	*gibbs*.ML	[9]	[10]	*gibbs*.ML	units
$\Delta G^{(\mathrm{O1})}$	−10	0	−3.4	−2.9	−4.6	−4.0	−2.1	−4.3	kJ/mol
$\Delta G^{(\mathrm{H13})}_{\mathrm{CoO_3}}$	−10	0	−0.3	0.3	−1.6	−2.1	1.4	−1.0	kJ/mol
$\Delta G^{(\mathrm{H13})}_{\mathrm{LiCoO_3}}$	0	10	1.5	3.4	−0.4	3.0	−3.0	0.1	kJ/mol
$a_\circ^{(\mathrm{H13})}$	−50	−10	−44.6	−50.7	−49.3	−55.4	−52.6	−49.0	kJ/mol
$b_\circ^{(\mathrm{H13})}$	0	100	−17.2	10.9	10.1	5.9	73.1	6.7	J/(mol K)
$a_1^{(\mathrm{H13})}$	0	30	10.0	−1.1	3.2	−6.4	26.9	7.1	kJ/mol
$b_1^{(\mathrm{H13})}$	0	100	−13.5	32	−2.4	−7.5	36.0	14.0	J/(mol K)
$a_\circ^{(\mathrm{O3})}$	−70	−10	−59.7	−61.6	−61.2	−63.9	−63.2	−61.7	kJ/mol
$b_\circ^{(\mathrm{O3})}$	0	100	−2.3	13.1	22.7	24.0	20.1	17.5	J/(mol K)
$a_1^{(\mathrm{O3})}$	−30	30	−32.8	−13.0	16.5	2.9	9.0	15.7	kJ/mol
$b_1^{(\mathrm{O3})}$	0	100	21.6	75.7	3.1	16.0	1.2	7.9	J/(mol K)
$\Delta G^{(\mathrm{I})}_{\mathrm{CoO_3}}$	−2	10	—	—	—	−1.0	1.5	0.5	kJ/mol
$\Delta G^{(\mathrm{I})}_{\mathrm{LiCoO_3}}$	−5	−1	—	—	—	−2.8	−2.7	−2.2	kJ/mol
$\Omega^{(\mathrm{I})}$	−30	30	—	—	—	−28.0	−34.8	−28.4	kJ/mol

References

[1] A. D. Pelton and W. T. Thompson. “Phase diagrams.” *Prog. Solid State Chem.*, 10, 119, 1975.

[2] M. S. Ding. “Excess Gibbs energy of mixing for organic carbonates from fitting of their binary phase diagrams with nonideal solution models.” *J. Solution Chem.*, 34, 343, 2005.

[3] M. Hillert. “The compound energy formalism.” *J. Alloys Compd.*, 320, 161, 2001.

[4] J.-O. Andersson, A. Guillermet, M. Hillert, B. Jansson, and B. Sundman. “A compound-energy model of ordering in a phase with sites of different coordination numbers.” *Acta Metall.*, 34, 437, 1986.

[5] G. Cacciamani. “An Introduction to the Calphad method and the compound energy formalism (CEF).” *Tecnol. em Metal. Mater. e Mineração*, 13, 16, 2016.

[6] S. H. Lee. “A study of ionic materials for the energy applications through first-principles calculations and Calphad modeling.” Doctor of philosophy, Penn State, 2011.

[7] A. T. Phan, A. E. Gheribi, and P. Chartrand. “Modelling of phase equilibria of $LiFePO_4$-$FePO_4$ olivine join for cathode material.” *Can. J. Chem. Eng.*, 97, 2224, 2019.

[8] A. Yamada, H. Koizumi, S. I. Nishimura, N. Sonoyama, R. Kanno, M. Yonemura, T. Nakamura, and Y. O. Kobayashi. “Room-temperature miscibility gap in Li_xFePO_4.” *Nat. Mater.*, 5, 357, 2006.

[9] T. Abe and T. Koyama. “Thermodynamic modeling of the $LiCoO_2$-CoO_2 pseudo-binary system.” *Calphad Comput. Coupling Phase Diagrams Thermochem.*, 35, 209, 2011.

[10] K. Chang, B. Hallstedt, D. Music, J. Fischer, C. Ziebert, S. Ulrich, and H. J. Seifert. “Thermodynamic description of the layered O3 and O2 structural $LiCoO_2$-CoO_2 pseudo-binary systems.” *Calphad Comput. Coupling Phase Diagrams Thermochem.*, 41, 6, 2013.