Thermodynamic dataset of electrode materials in lithium ion batteries

Keke Chang, Bengt Hallstedt, Denis Music

chang@mch.rwth-aachen.de
RWTH Aachen University

Julian Fischer, Carlos Ziebert, Sven Ulrich, Hans J. Seifert

Karlsruhe Institute of Technology (KIT)

Outline

Li ion batteries

Background

Ab initio and empirical method

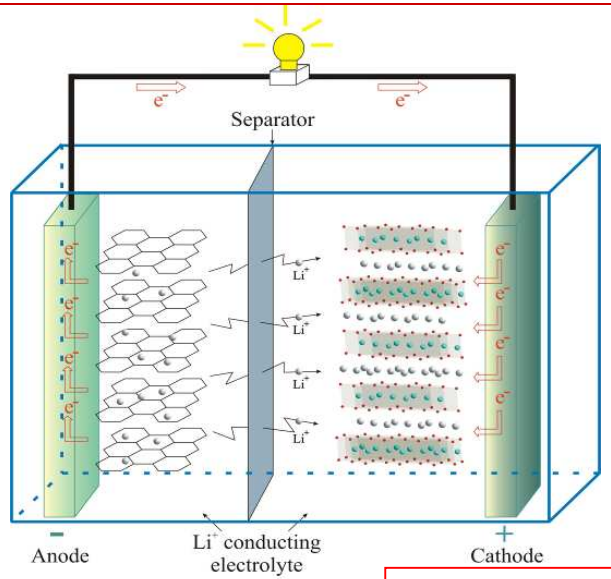
CALPHAD and thermodynamic description

- The $LiNiO_2$–NiO_2 system
- The $LiCoO_2$–CoO_2 system
- The $Li(Co,Ni)O_2$–$(Co,Ni)O_2$ system

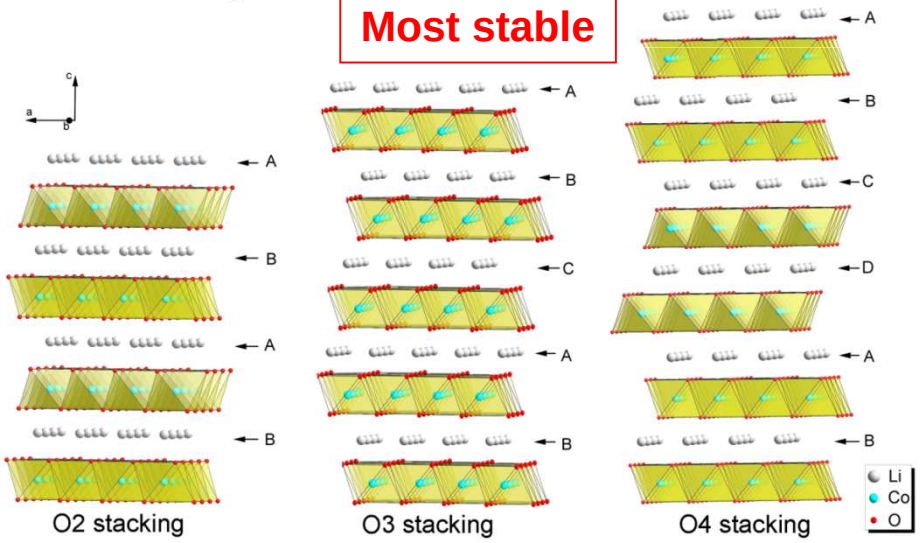
Cell voltages of Li ion cells

Summary and outlook

Background



Most stable



Crystal structures of $LiCoO_2$ with different stacking of Li layers.

- **Phase changes in cycling of Li/O3-$LiCoO_2$:**

O3, O3' (ordered), M, H1-3 and O1

O3-$LiCoO_2$	O3-$LiNiO_2$
- High price	- Difficult to synthesize
- Safety problem	

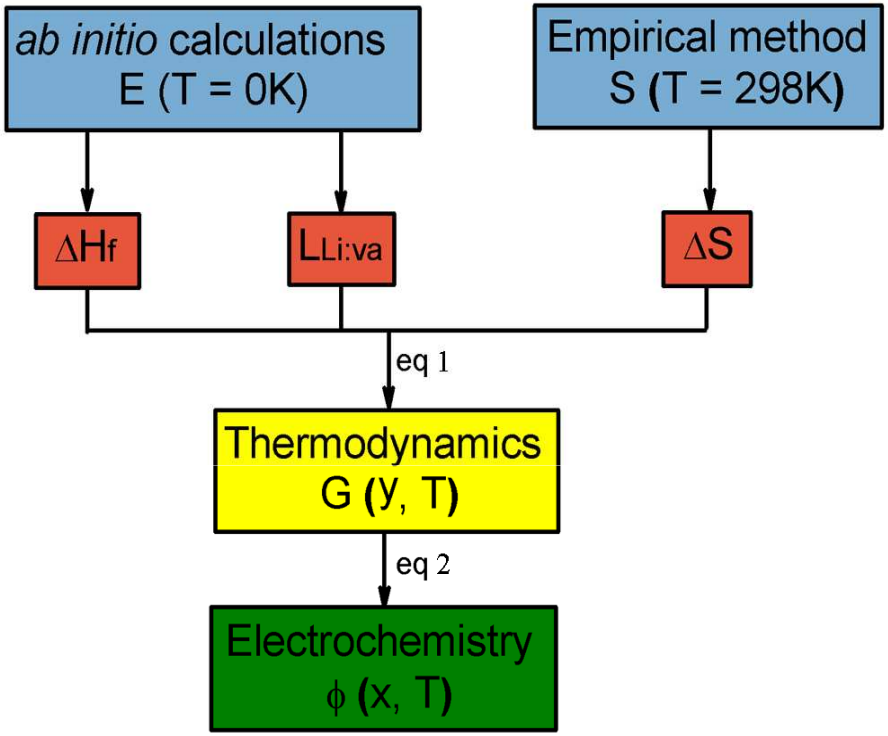
O3-Li(Co, Ni)O_2

- Co and Ni have unlimited solid solubility;

- Can be deintercalated to O3-$Li_{0.4}$(Co, Ni)O_2;

- Can remain as the layered O3 structure.

Ab initio and empirical method



The flow chart of the present theoretical approaches.

Gibbs energy function:

$$ {}^{o}G_{m}^{Li_xCo_yO_z} - x_{Li}\,{}^{o}G_{Li}^{BCC\_A2} - x_{Co}\,{}^{o}G_{Co}^{HCP\_A3} - 0.5\cdot x_O\,{}^{o}G_{O_2}^{GAS} = \Delta H - \Delta S\cdot T \qquad (1) $$

Cell voltage of a Li/Li$^+$ cell:

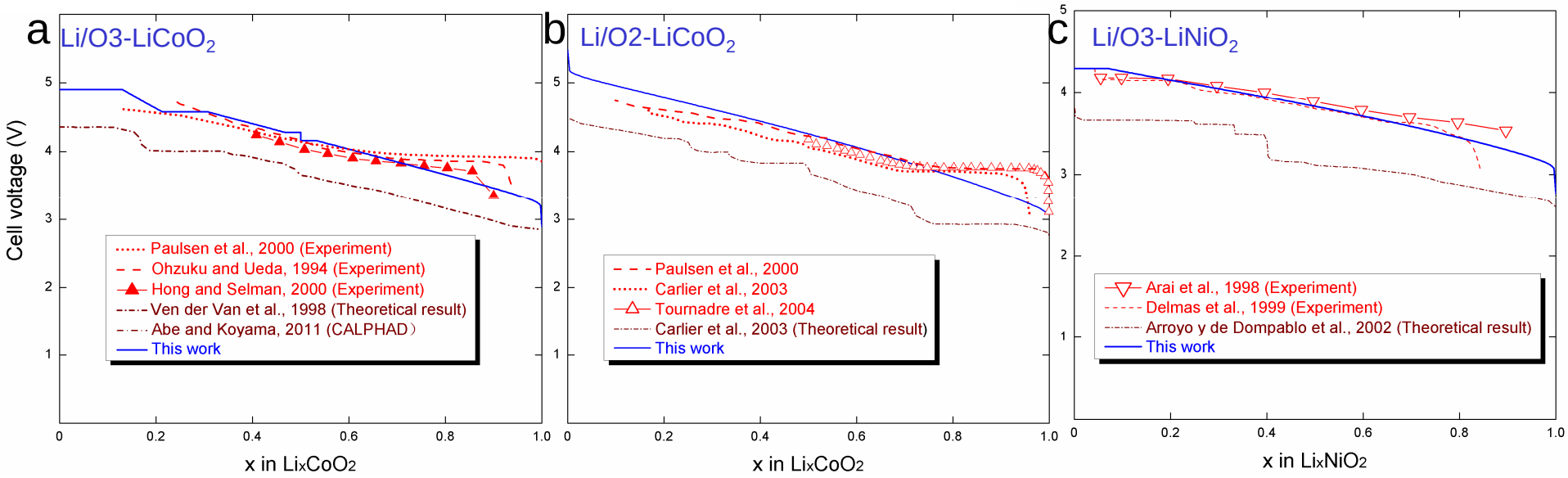
$$ V = -\frac{\mu_{Li}^{Cathode}}{F} \qquad (2) $$

[Ref] K. Chang, B. Hallstedt, D. Music, Chem. Mater. 24 (2012) 97-105.

Ab initio and empirical method

Evaluation of thermodynamic and electrochemical properties using *ab initio* and empirical methods
(Simple models for the phases)

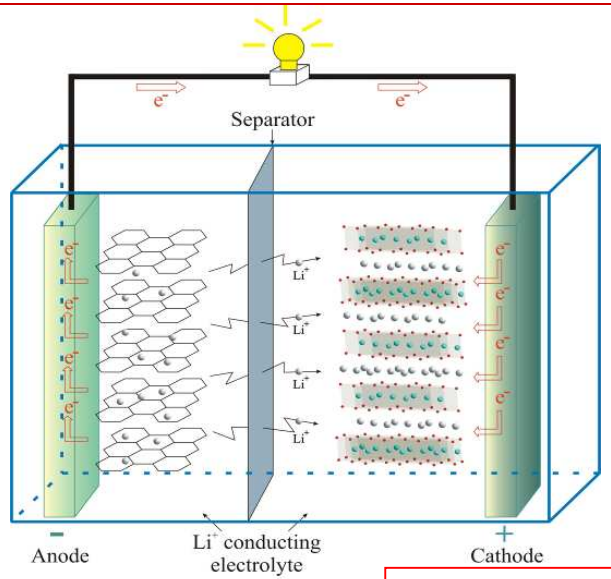
CALPHAD method
(More appropriate models)



Calculated cell voltages at 300 K compared to the experimental data, CALPHAD calculation and the previous theoretical results.

[Ref] K. Chang, B. Hallstedt, D. Music, Chem. Mater. 24 (2012) 97-105.

Background



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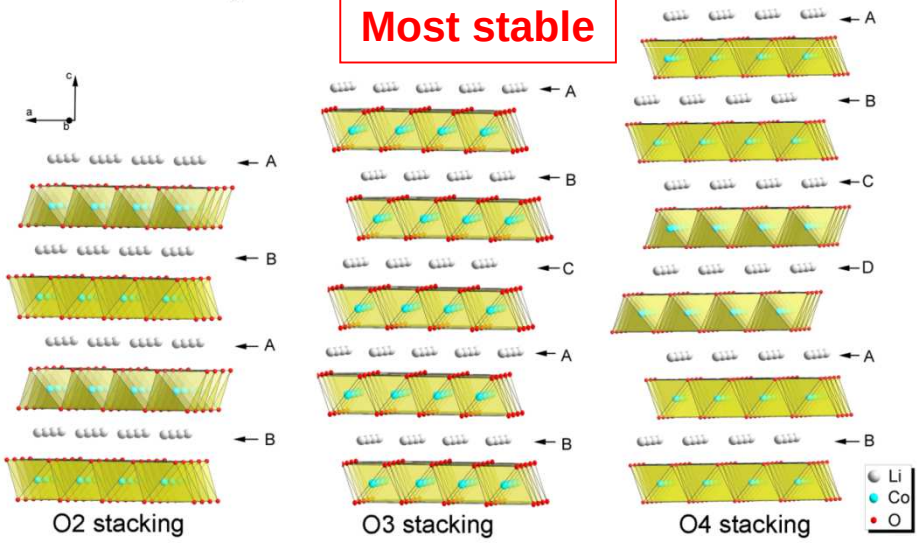

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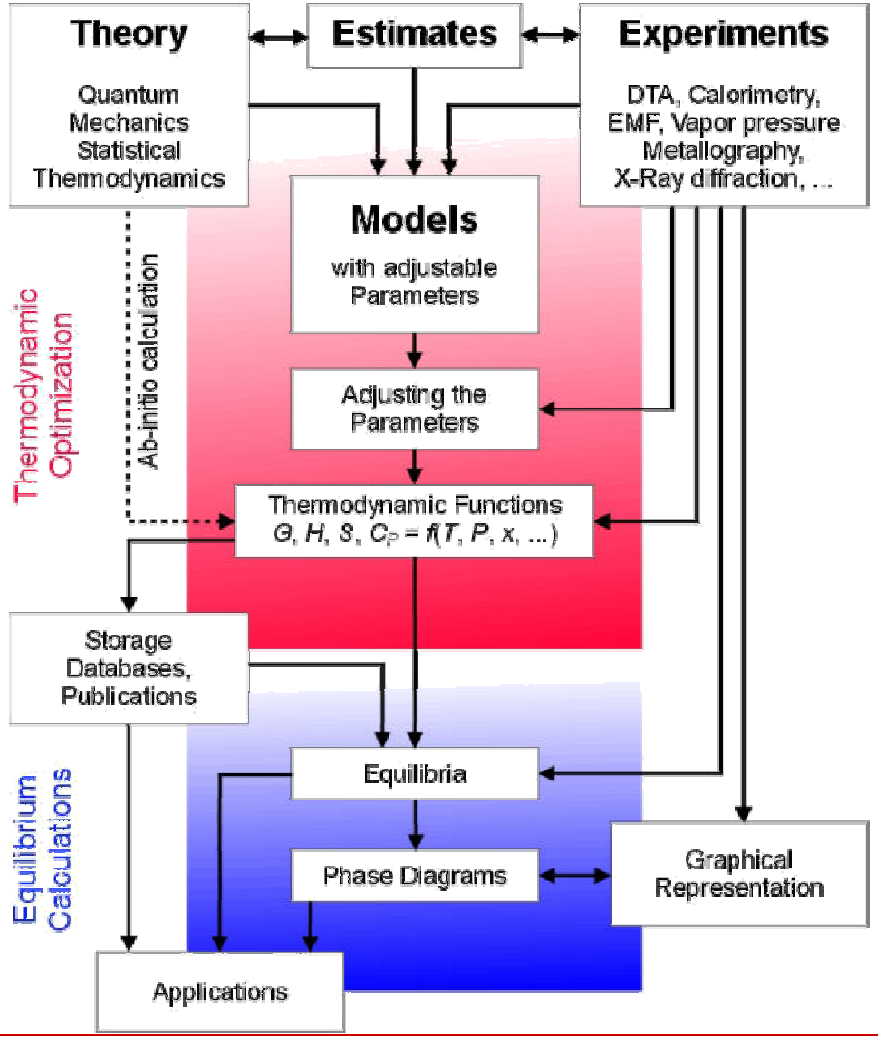
CALPHAD



CALculation of PHAse Diagrams

Models for individual phases:

(1) Ordered and disordered phases

$$G_m^{\mathrm{Ord}} = G_m^{\mathrm{Dis}}(x_i) + G_m^{\mathrm{Ord}}(y_i^s) - G_m^{\mathrm{Ord}}(y_i^s = x_i)$$

(2) End-member compound (C_p well-defined)

$${}^{\circ}G_m^{\mathrm{O3\text{-}LiCoO_2}} - H_{\mathrm{Li}}^{\mathrm{SER}} - H_{\mathrm{Co}}^{\mathrm{SER}} - 2H_{\mathrm{O}}^{\mathrm{SER}} = A + B\cdot T + C\cdot T\cdot \ln T + D\cdot T^2 + E\cdot T^{-1}$$

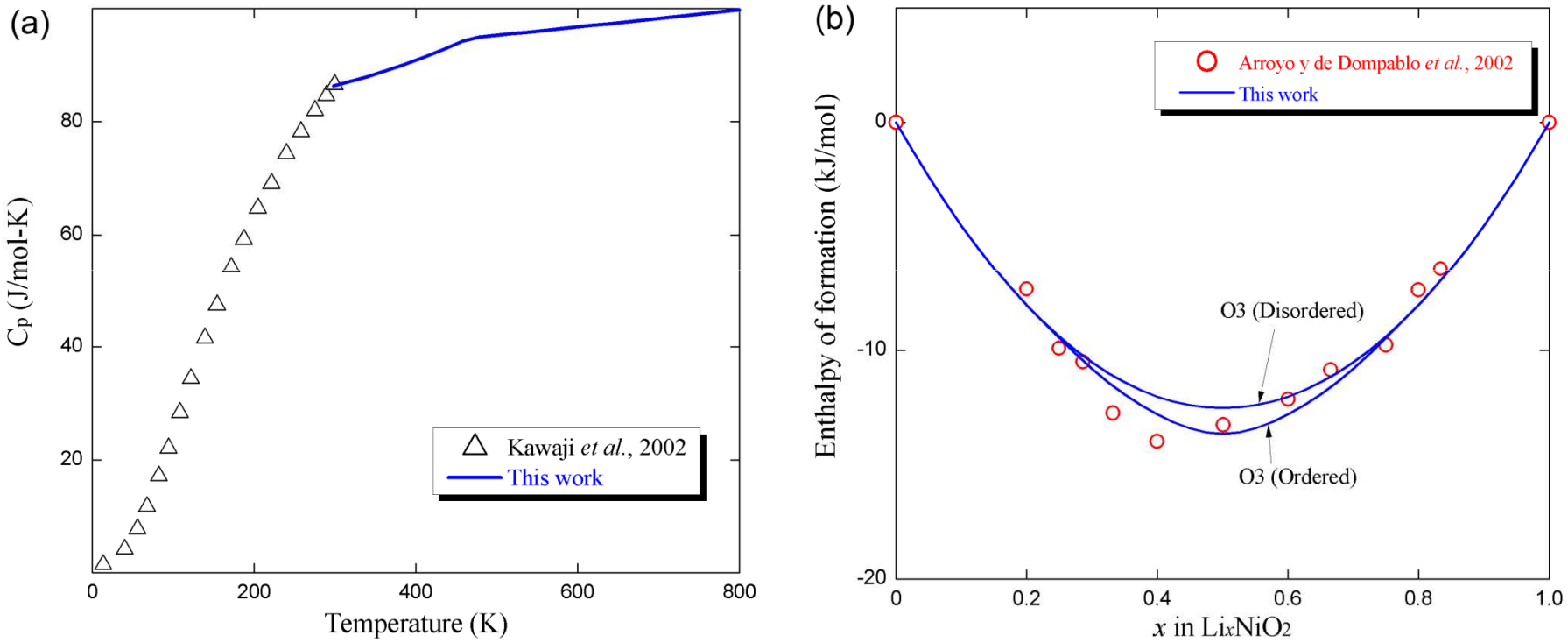
(3) End-member compound (Neumann-Kopp rule)

$${}^{\circ}G_m^{\mathrm{O3\text{-}CoO_2}} - H_{\mathrm{Co}}^{\mathrm{SER}} - 2\,H_{\mathrm{O}}^{\mathrm{SER}} = A + B\cdot T + {}^{\circ}G_m^{\mathrm{Co}} + {}^{\circ}G_m^{\mathrm{O_2}}$$

[Ref 1] http://www.sgte.org/
[Ref 2] M. Hillert, J. Alloys Compd. 320 (2001) 161-176.
[Ref 3] I. Ansara, N. Dupin, H.L. Lukas, B. Sundman, J. Alloys Compd. 247 (1997) 20-30.

Thermodynamic description

I. $LiNiO_2$–NiO_2 system

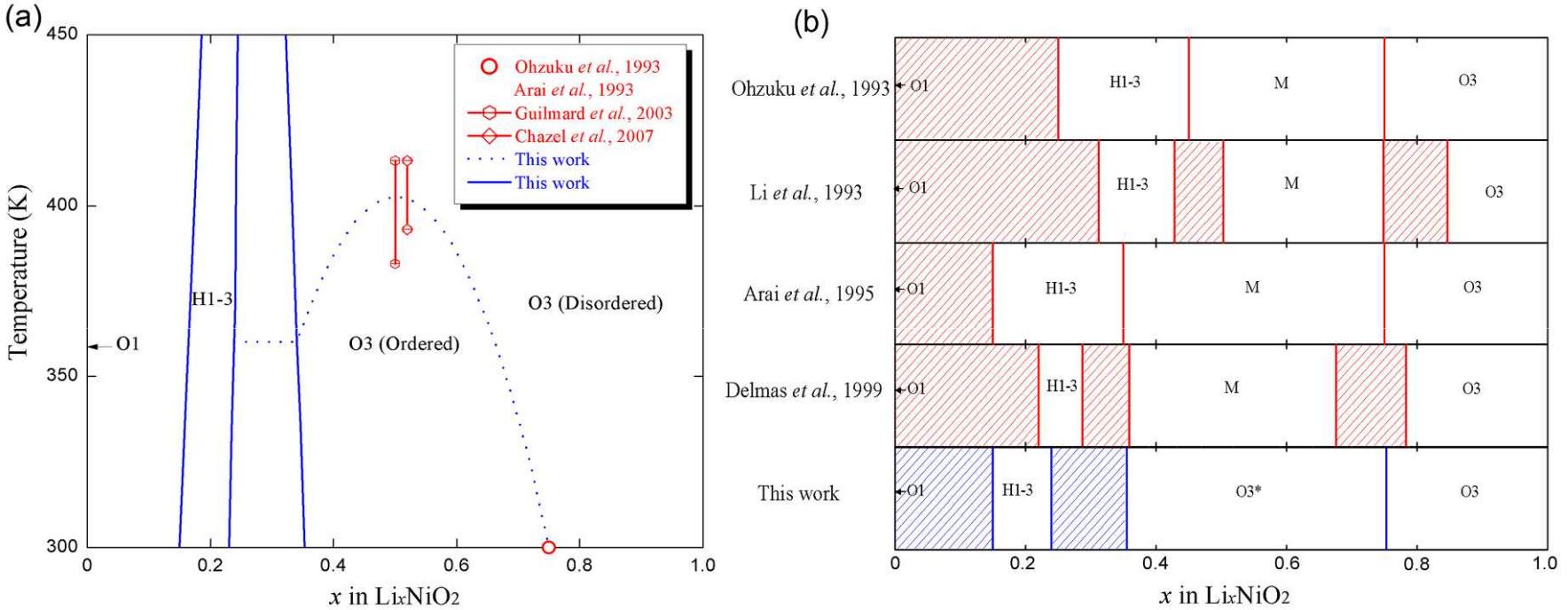


Calculated thermodynamic properties compared with the literature data: (a) Heat capacity of O3-$LiNiO_2$; (b) Enthalpies of formation for O3-Li_xNiO_2 ($0 < x < 1$) relative to O3-NiO_2 and O3-$LiNiO_2$.

[Ref] K. Chang, B. Hallstedt, D. Music, CALPHAD 37 (2012) 100-107.

Thermodynamic description

I. $LiNiO_2$–NiO_2 system



Calculated phase diagram of the $LiNiO_2$–NiO_2 pseudo-binary system compared with the experimental data: (a) from 300 K to 450 K; (b) at 298 K.

[Ref] K. Chang, B. Hallstedt, D. Music, CALPHAD 37 (2012) 100-107.

Thermodynamic description

II. $LiCoO_2$–CoO_2 system

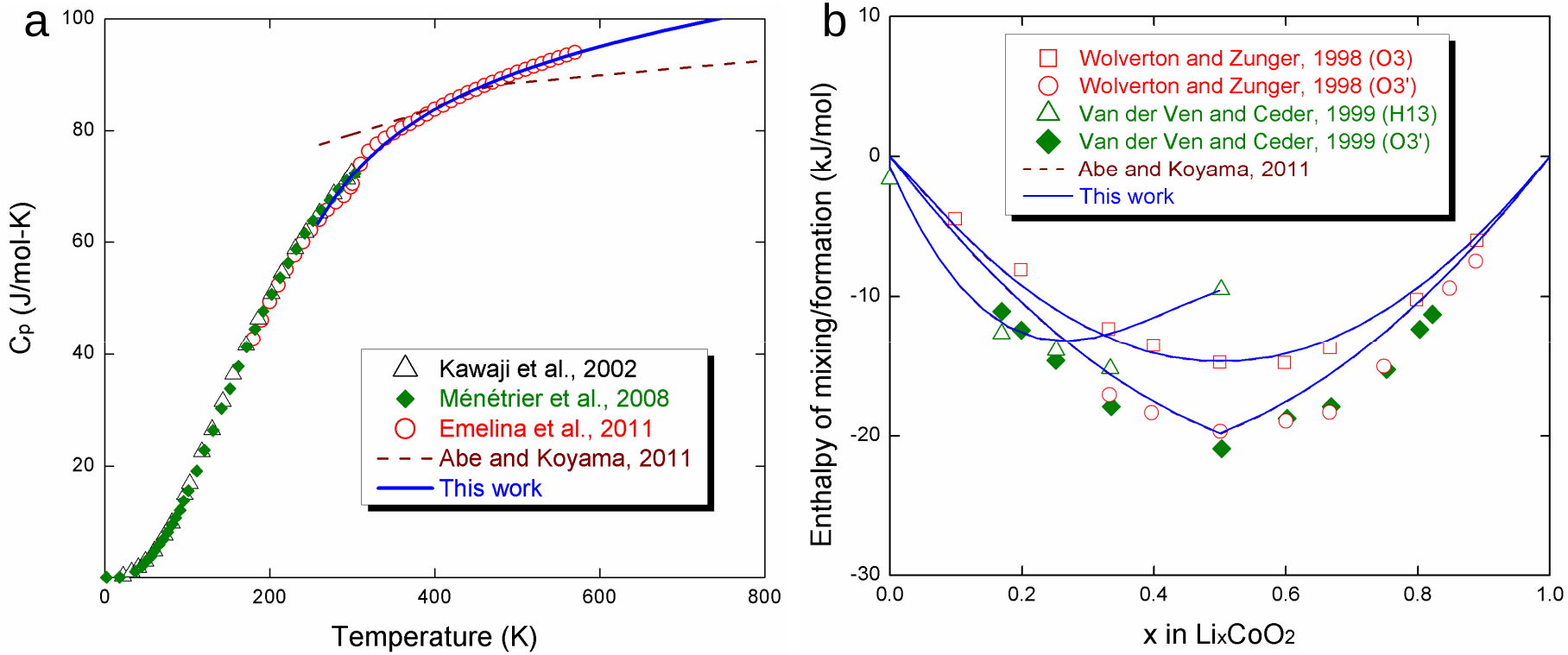


Fig. (a) Heat capacity data of O3-$LiCoO_2$ from literature compared with the C_p function used in this work. The result from the Neumann-Kopp rule [Ref] is also presented. (b) Calculated enthalpies of formation for O3-, O3'-, and H1-3 relative to O3-$LiCoO_2$ and O3-CoO_2 compared with literature data.

[Ref] K. Chang, B. Hallstedt, D. Music, J. Fischer, C. Ziebert, S. Ulrich, H.J. Seifert, CALPHAD 41 (2013) 6

Thermodynamic description

III. The O3 structural $Li(Co,Ni)O_2$–$(Co,Ni)O_2$ system

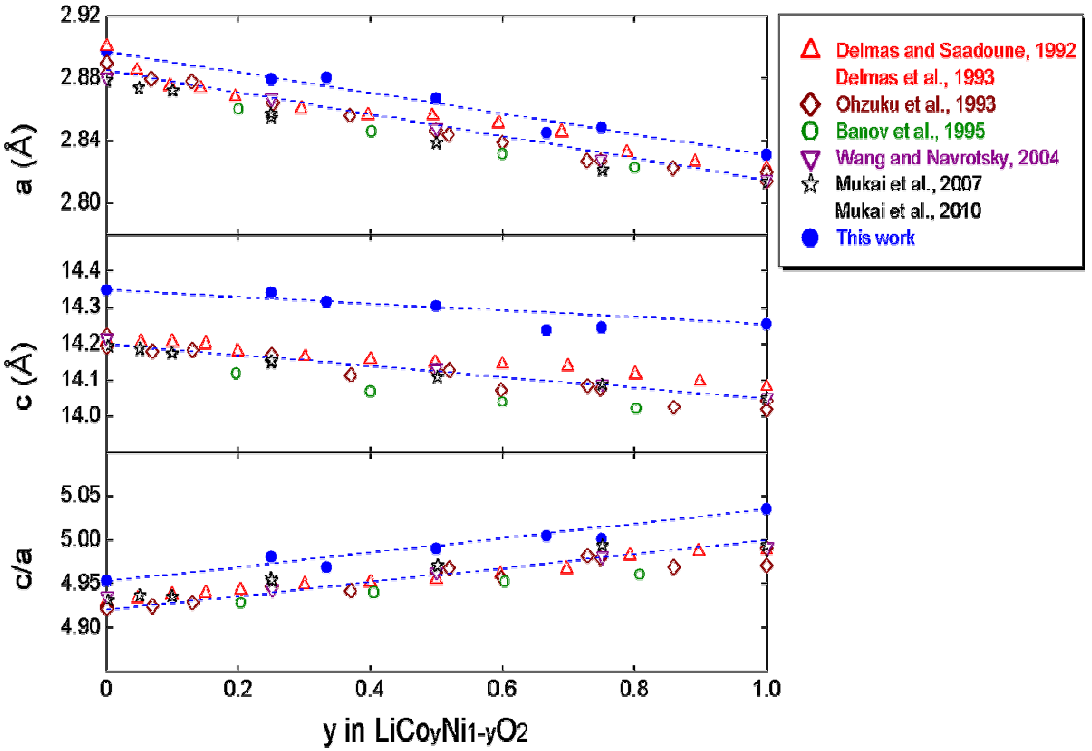


Fig. Cell parameters and c/a ratio vs. *y* in $LiCo_yNi_{1-y}O_2$.

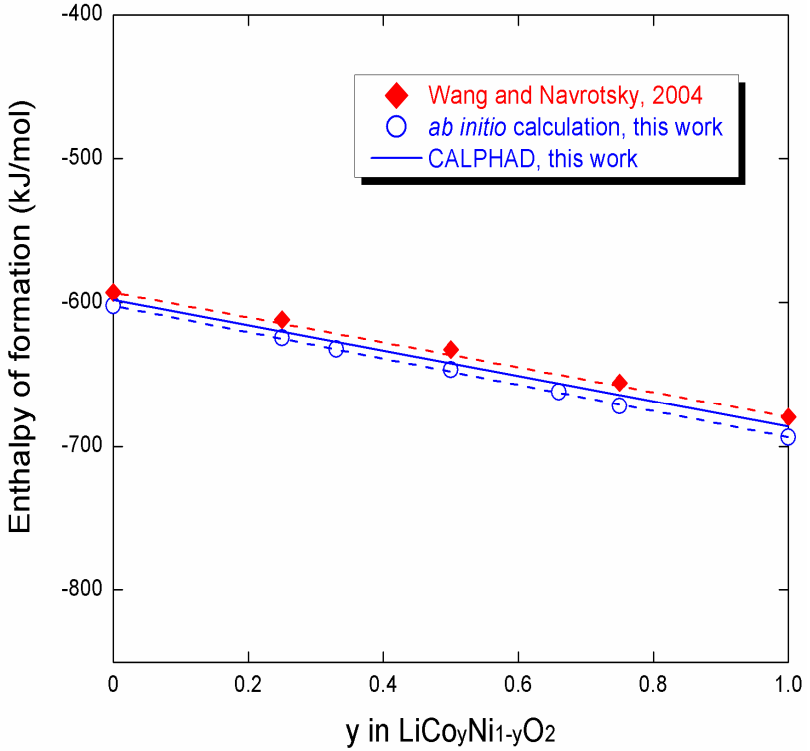


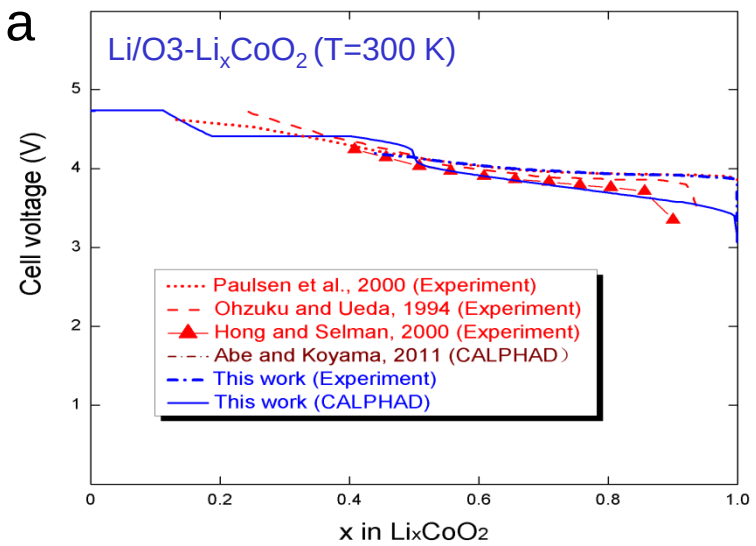
Fig. Experimental and calculated enthalpies of formation for $LiCo_yNi_{1-y}O_2$.

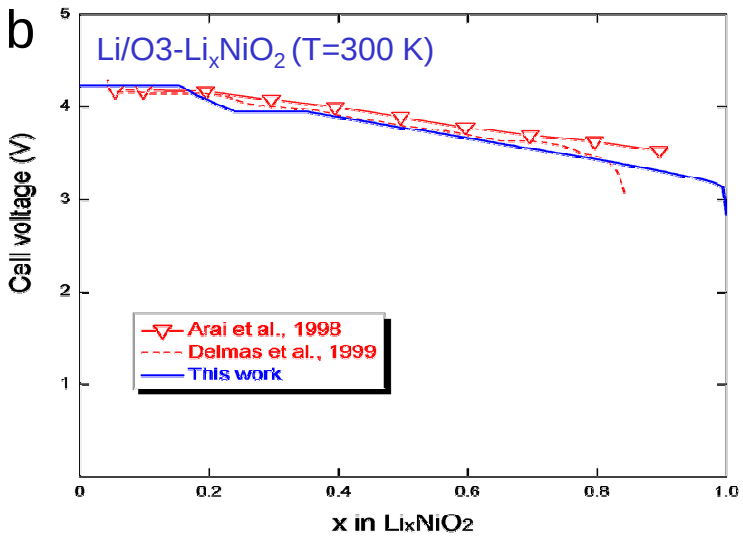
➔ The $LiCoO_2$–CoO_2 and $LiNiO_2$–NiO_2 systems are considered to be ideally mixing.

[Ref] K. Chang, B. Hallstedt, D. Music, CALPHAD 37 (2012) 100-107.

Cell voltages of Li ion cells

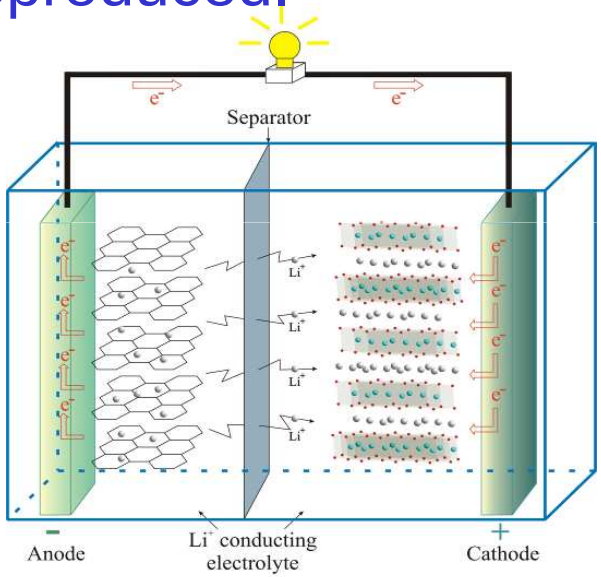
Cell voltage of a Li/Li$^+$ cell: $$V = -\frac{\mu_{\mathrm{Li}}^{\mathrm{Cathode}}}{F}$$





Summary

- ✓ Thermodynamic dataset obtained.
- ✓ Experimental and *ab initio* data well reproduced.
- ✓ Cell voltage predicted.



Outlook

- ❑ Amorphous anode
- ❑ Thin film electrode for LIB
- ❑ Thermodynamic dataset of Si-based systems

Acknowledgement:

WeNDeLIB
SPP 1473 DFG
DFG Deutsche Forschungsgemeinschaft
GTT - TECHNOLOGIES
FactSage

Thank you for your attention!