

Report

Summary of the preliminary work on the Project “Design of cathode materials for improved capacity, stability and safety for lithium ion batteries based on the system LiMO₂ (M=Co, Mn, Ni)”

Keke Chang, Bengt Hallstedt, Denis Music

Materials Chemistry, RWTH Aachen University

Hans Seifert, Sven Ulrich

Karlsruhe Institute of Technology

1. Thermodynamic assessment of the Li–O system using CALPHAD approach

The Li–O system has been investigated by means of CALPHAD approach. The phase equilibria and thermodynamic data of this system are critically reviewed and assessed. The liquid phase and two stable lithium oxides, Li₂O and Li₂O₂, are modeled. A set of self-consistent thermodynamic parameters for this system is obtained by considering reliable data from literature. The Li–O phase diagram at 1 bar total pressure is established for the first time, as shown in Fig. 1(a). Figure 1(b) shows the calculated solubility of O in liquid, which agrees well with the experimental data. The phase equilibria and thermodynamic data in the literature are also satisfactorily accounted for by the present thermodynamic description.

More detailed information can be found in Ref. [1].

[1] K. Chang, B. Hallstedt, Thermodynamic assessment of the Li–O system, *Calphad*, 2011; 35: 160-4.

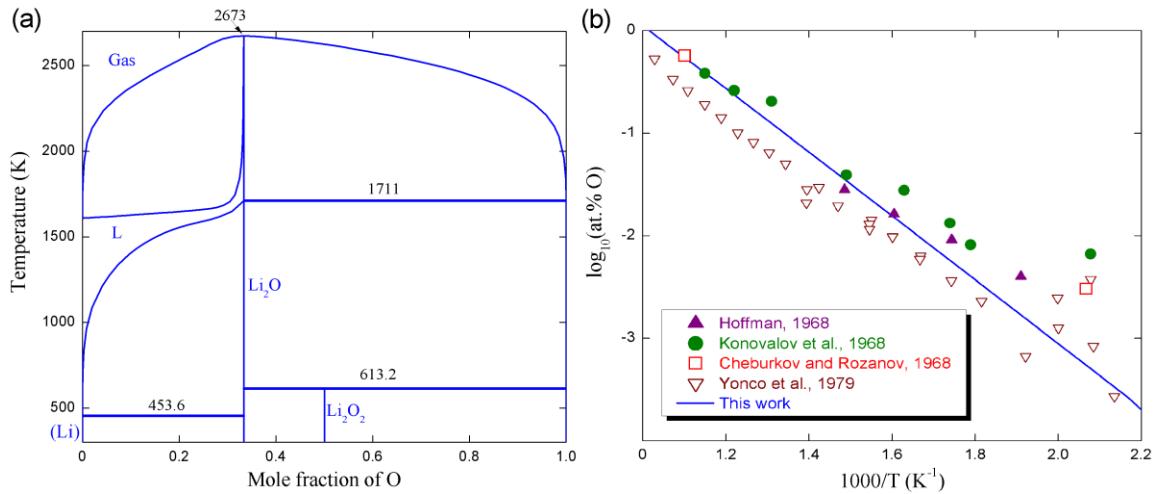


Fig. 1. (a) Calculated Li–O phase diagram including the gas phase at 1 bar total pressure; (b) Calculated solubility of O in liquid compared with the experimental data.

2. Thermodynamic and electrochemical properties of the Li–Co–O and Li–Ni–O systems studied by *ab initio* and empirical methods

In this work, the thermodynamic and electrochemical properties of the Li–Co–O and Li–Ni–O systems have been studied. An approach to accurately calculate enthalpies of formation for transition metal-containing oxides is proposed. The Gibbs energy functions of binary and ternary oxides in the Li–Co–O and Li–Ni–O systems are obtained based on the *ab initio* calculations and empirical predictions. For the oxides of transition metals with valence state +2.7 or +3, the calculated enthalpies of formation at 0 K agree well with available experimental data, as shown in Fig. 2(a). However, for oxides of transition metals with valence state of +2 and +4, the data are inconsistent, see Fig. 2(b). We propose that the accurate enthalpy of formation per mole metal can be obtained by correcting the pristine GGA data with -0.8 and +0.8 eV shifts for oxides of transition metals with valence state of +2 and +4, respectively. This corrects inaccurately strong correlations of localized and hybridized *d* transition

metal states and provides an alternative to the Hubbard approach or the GW approximation.

To prove the accuracy of this thermodynamic model, we calculate the cell voltages of lithium ion batteries. The cell voltages of $\text{Li}/\text{O}_3\text{-Li}_x\text{MO}_2$ ($\text{M} = \text{Co}, \text{Ni}; 0 \leq x \leq 1$) are shown in Fig. 3 as examples. Compared to the previously calculated results, which underestimate the cell voltages of lithium ion batteries, our calculations are in good agreement with the experimental data. The present theoretical approaches are reliable to evaluate the thermodynamic and electrochemical properties of lithium-containing transition metal oxides.

More detailed information can be found in Ref. [2].

[2] K. Chang, B. Hallstedt, D. Music, Thermodynamic and electrochemical properties of the Li–Co–O and Li–Ni–O systems, Chem. Mater., article in press.

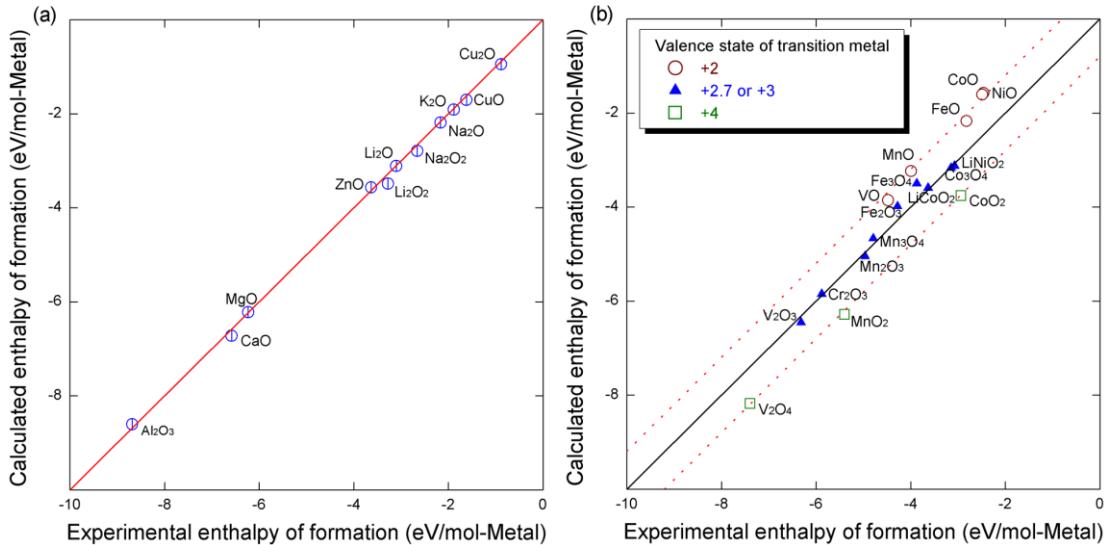


Fig 2. Calculated enthalpies of formation for: (a) non-transition metal oxides compared to the experimental results; (b) transition metal oxides compared to the experimental results.

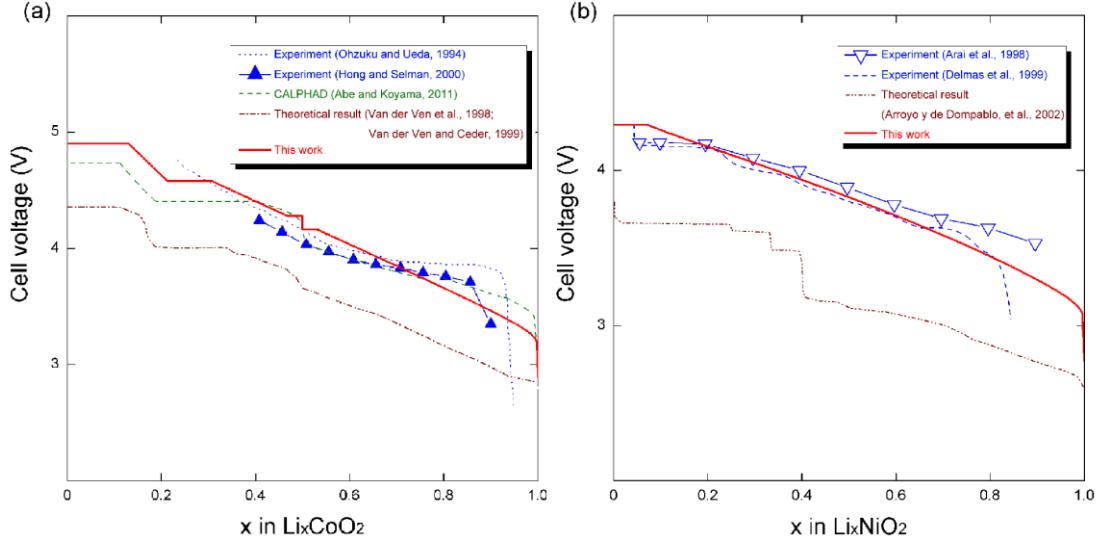


Fig 3. Calculated cell voltages of $\text{Li}/\text{O}_3\text{-Li}_x\text{MO}_2$ ($\text{M} = \text{Co}, \text{Ni}; 0 \leq x \leq 1$) at 300 K compared to the experimental data, CALPHAD calculation and the previous theoretical results (a) $\text{Li}/\text{O}_3\text{-Li}_x\text{CoO}_2$; (b) $\text{Li}/\text{O}_3\text{-Li}_x\text{NiO}_2$.

3. Thermodynamic description of the $\text{LiNiO}_2\text{-NiO}_2$ pseudo-binary system and extrapolation to the $\text{Li}(\text{Co,Ni})\text{O}_2\text{-(Co,Ni)}\text{O}_2$ system

The $\text{LiNiO}_2\text{-NiO}_2$ pseudo-binary system has been studied using the CALPHAD approach coupled with *ab initio* calculations. The O1 phase, the H1-3 phase, the ordered and disordered O3 phases, are thermodynamically described using sublattice models. Calculated phase diagrams of the $\text{LiNiO}_2\text{-NiO}_2$ pseudo-binary system are shown in Fig. 4. The calculation is in good agreement with the experimental data.

Based on the experimental information and present *ab initio* results, we consider the $\text{LiCoO}_2\text{-CoO}_2$ and $\text{LiNiO}_2\text{-NiO}_2$ systems to be ideally mixing. Using the extrapolated thermodynamic description of the $\text{Li}(\text{Co,Ni})\text{O}_2\text{-(Co,Ni)}\text{O}_2$ system, the cell voltages of $\text{Li}/\text{O}_3\text{-Li}(\text{Co,Ni})\text{O}_2$ cells are calculated and compared with experimental data, as shown in Fig. 5. The good agreement shows the viability of the present approach.

More detailed information can be found in Ref. [3].

[3] K. Chang, B. Hallstedt, D. Music, Thermodynamic description of the $\text{LiNiO}_2\text{--NiO}_2$ pseudo-binary system and extrapolation to the $\text{Li}(\text{Co},\text{Ni})\text{O}_2\text{--}(\text{Co},\text{Ni})\text{O}_2$ system, to be submitted.

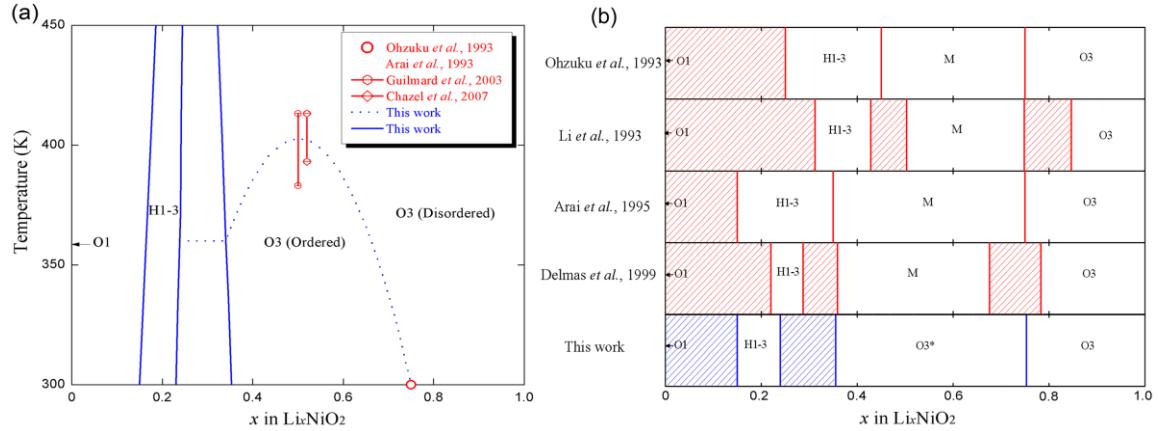


Fig. 4. Calculated phase diagram of the $\text{LiNiO}_2\text{--NiO}_2$ pseudo-binary system compared with the experimental data: (a) from 300 K to 450 K; (b) at 298 K.

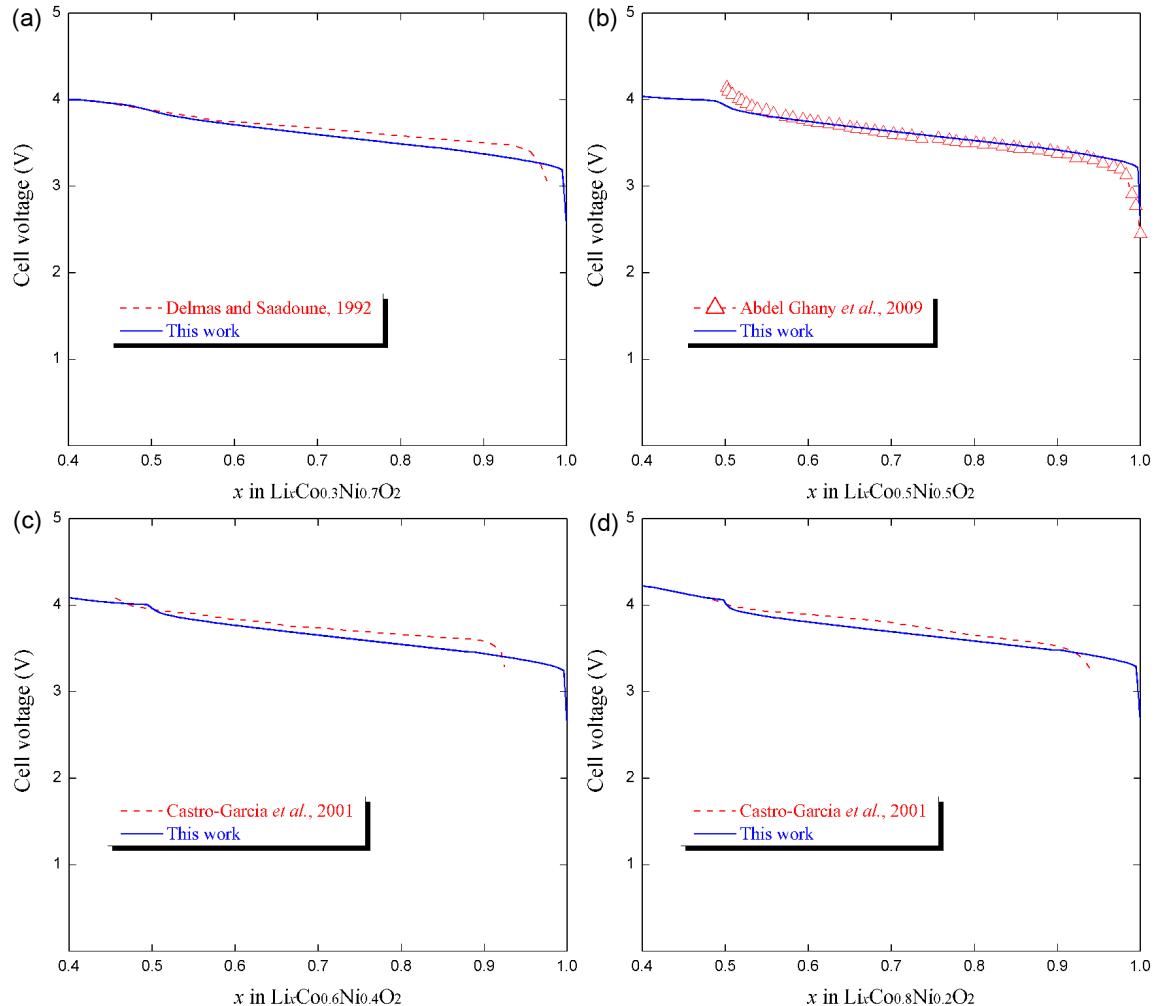


Fig. 5. Calculated cell voltages of $\text{Li}/\text{O}_3\text{--Li}_x\text{Co}_y\text{Ni}_{1-y}\text{O}_2$ ($0.4 \leq x \leq 1$) at 300 K compared to the experimental data: (a) $y = 0.3$; (b) $y = 0.5$; (c) $y = 0.6$; and (d) $y = 0.8$.