SPP 1473 – WeNDeLIB

Design of cathode materials for improved capacity, stability and safety for lithium ion batteries based on the system LiMO_2 (M = Co, Mn, Ni)

Keke Chang, Bengt Hallstedt and Denis Music

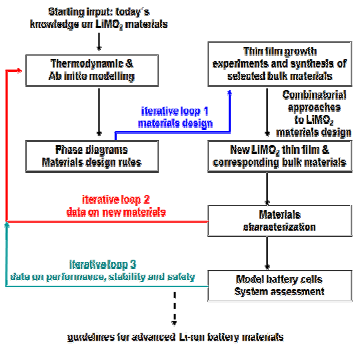
Materials Chemistry, RWTH Aachen University, D-52056 Aachen, Germany
E-mail: chang@mch.rwth-aachen.de

Abstract

The Li–O system has been investigated by means of the CALPHAD approach. The liquid phase and two stable lithium oxides, Li_2O and Li_2O_2, 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. The phase equilibria and thermodynamic data in the literature are satisfactorily accounted for by the present thermodynamic description.

The Li–Co–O and Li–Ni–O systems have been investigated by means of *ab initio* calculations and empirical methods. An approach based on *ab initio* calculations to obtain accurate enthalpies of formation for transition metal oxides is proposed. With the obtained enthalpies of formation and the empirical entropy data, the Gibbs energy functions of oxides in the Li–Co–O and Li–Ni–O systems are determined. To prove the accuracy of this thermodynamic model, we calculate the cell voltages of lithium ion batteries. 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.

Project strategy/Methods



➢ **We are on the first step.**

Modeling of the Li–O system: the CALPHAD method

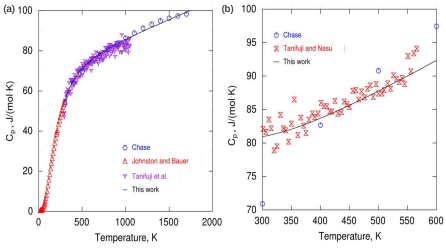


Fig. 1. Heat capacity data of (a) Li_2O and (b) Li_2O_2 from literature compared with the C_p function used in this work.

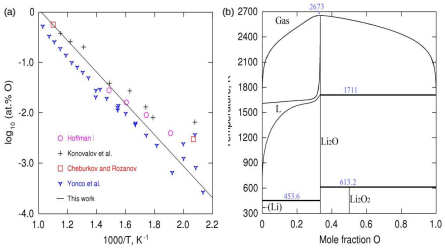
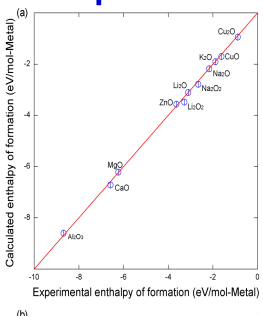
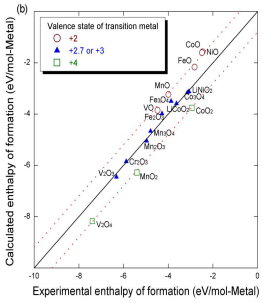


Fig. 2. (a) Calculated solubility of O in liquid compared with the experimental data;
(b) Calculated Li–O phase diagram including the gas phase at 1 bar total pressure.

Enthalpies of formation: *ab initio* calculations

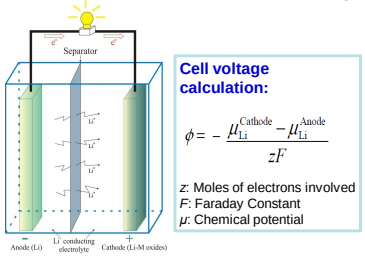




- **For the oxides of non-transition metals and transition metals with valence state +2.7 or +3, the calculated enthalpies of formation at 0 K agree well with available experimental data.**
- **For oxides of transition metals with valence state +2 and +4, the data are inconsistent.**
- **We propose that the accurate enthalpy of formation can be obtained by correcting the pristine GGA data with -0.8 and +0.8 eV shifts per metal atom for oxides of transition metals with valence state +2 and +4, respectively.**

Fig. 3. Calculated enthalpies of formation for (a) non-transition metal oxides and (b) transition metal oxides compared to the experimental results.

Predictions of cell voltages



Cell voltage calculation:

$$\phi = -\frac{\mu_{Li}^{Cathode} - \mu_{Li}^{Anode}}{zF}$$

z: Moles of electrons involved
F: Faraday Constant
μ: Chemical potential

Fig. 4. Schematic diagram of a lithium ion battery. The arrows show the discharging process, electron and Li^+ move at charging in reverse direction.

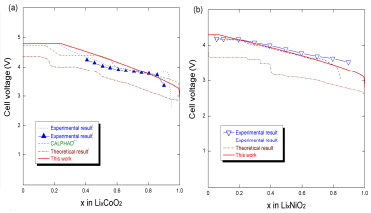


Fig. 5. Calculated cell voltages of Li/O3-Li_xMO_2 (M = Co, Ni; 0≤x≤1) at 300 K compared to the experimental data, CALPHAD calculation and the previous theoretical results: (a) Li/O3-Li_xCoO_2; (b) Li/O3-Li_xNiO_2.

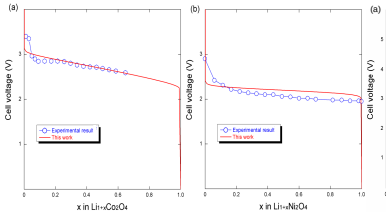


Fig. 6. Calculated cell voltages of Li/$Li_xM_2O_4$ (M = Co, Ni; 1≤x≤2) at 300 K compared to the experimental results: (a) Li/$Li_xCo_2O_4$; (b) Li/$Li_xNi_2O_4$.

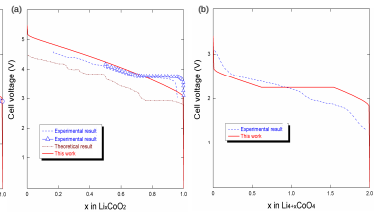


Fig. 7. Calculated cell voltages of (a) Li/O2-Li_xCoO_2 (0≤x≤1) and (b) Li/$Li_{4+x}CoO_2$ (0≤x≤2) at 300 K compared to the experiments and the previous theoretical results.

➢ **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.**

Conclusions

- ➢ **The Li–O phase diagram is established for the first time.**
- ➢ **A set of self-consistent thermodynamic parameters for the Li–O system is obtained.**
- ➢ **The calculated Li–O phase diagram and thermodynamic properties agree well with the literature data.**
  An approach to accurately calculate enthalpies of formation for transition metal-containing oxides is proposed.
- ➢ **The Gibbs energy functions of the binary and ternary oxides in the Li–Co–O and Li–Ni–O systems are obtained by the *ab initio* calculations and empirical predictions.**
- ➢ **The calculated cell voltages of lithium ion batteries are in good agreement with the experimental data.**

Acknowledgement

Financial support from the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

Summer School SPP1473 – WeNDeLIB (September 20-24, 2011)