DFG Priority Programme SPP 1473, WeNDeLIB
Thermodynamics and kinetics for stabilization of conversion-type electrodes for LIB based on nano 3d transition metal oxide composites

Thermodynamics of Copper Oxide Conversion Type Electrodes for Lithium-ion Batteries

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Introduction and Motivation

Electrodes based on materials in the Cu-Fe-O system are promising for next-generation lithium ion batteries as they exhibit a very high theoretical specific capacity and charge density. Thermodynamic and electrochemical investigations of the Li-Cu-O sub-system of the Li-Cu-Fe-O system combined with a CALPHAD-based assessment are important since the open circuit voltage of an electrochemical cell is determined by the standard Gibbs free energy of the cell reaction.

To investigate the Li-Cu-O sub-system, the ternary compounds Li_2CuO_2 and $LiCu_2O_2$ were prepared using the solid state reaction method. Phase transformations were studied using thermal analysis and the heat capacities were measured using differential scanning calorimetry. In addition, a thermodynamic description of the system at 25 °C was developed based on literature data.

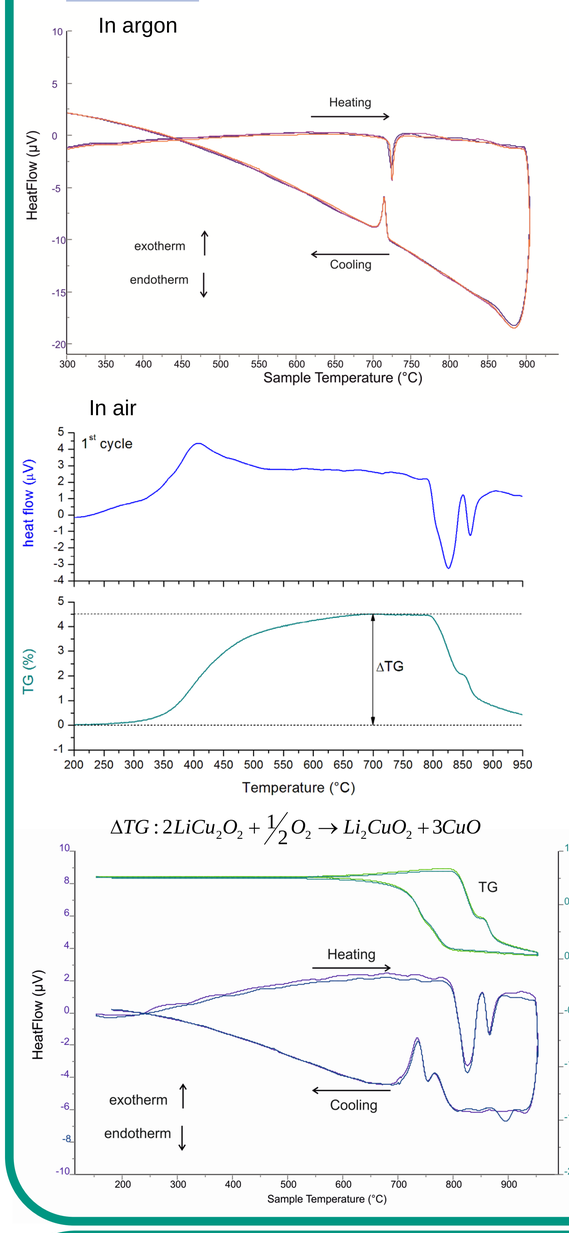
CuO was used as active material for the electrode and coin cells were assembled. First galvanostatic cycling tests at different charging rates were conducted.

Thermodynamics

Experimental Investigations

a) Phase stability of $LiCu_2O_2$

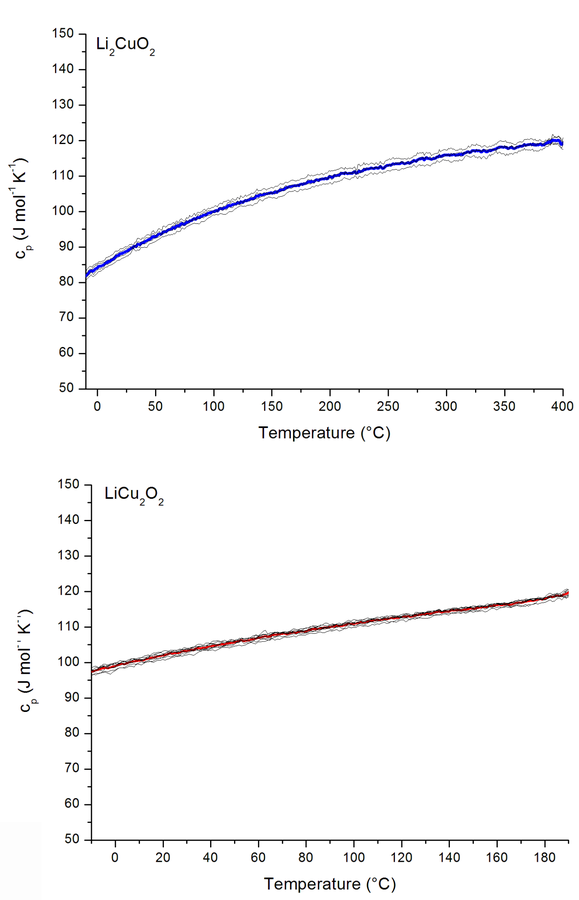
DTA/TG



$$\Delta TG: 2LiCu_2O_2 + \tfrac{1}{2}O_2 \rightarrow Li_2CuO_2 + 3CuO$$

b) Specific heat capacity

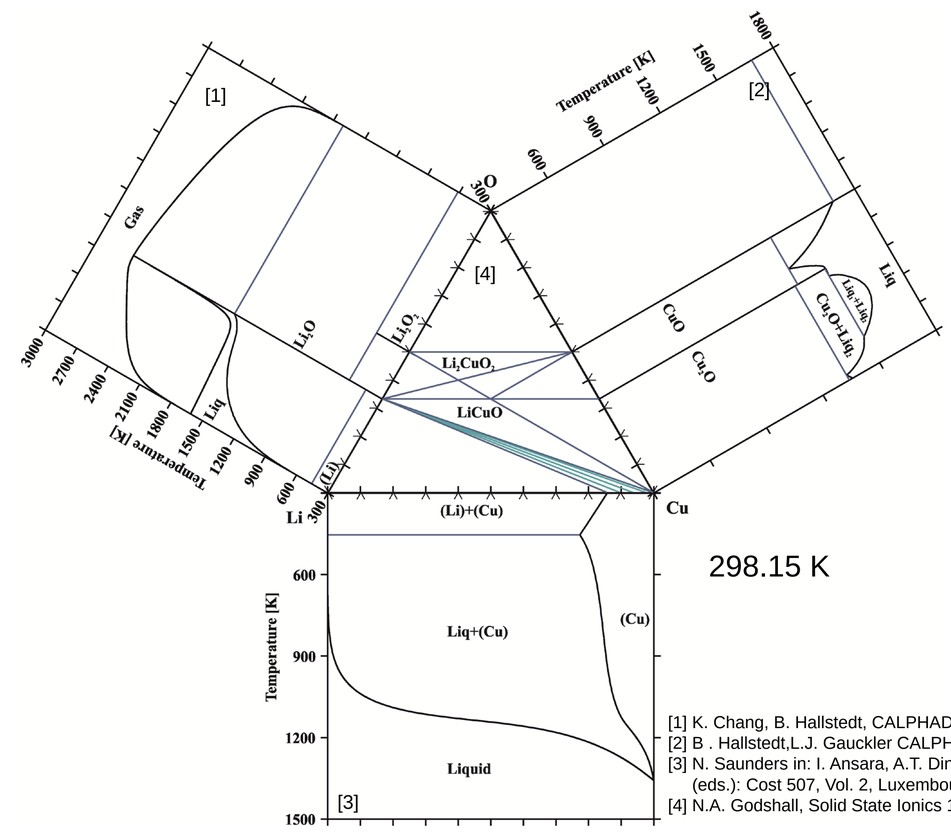
DSC



The results of these investigations will be used as input experimental data for the thermodynamic optimization of the multi-component system using the CALPHAD-method.

CALPHAD (Computer coupling of thermochemistry and phase diagram)

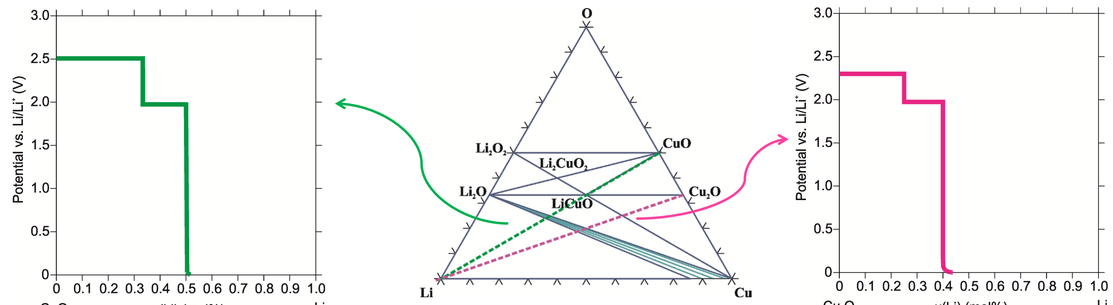
Thermodynamic description of the Li-Cu-O system at 298.15 K based on literature data for the binary systems [1, 2, 3] and the stoichiometric ternary compounds [4].



[1] K. Chang, B. Hallstedt, CALPHAD, 2011, 35:160-164
[2] B . Hallstedt,L.J. Gauckler CALPHAD, 2003, 27:177-191
[3] N. Saunders in: I. Ansara, A.T. Dinsdale, M.H. Rand (eds.): Cost 507, Vol. 2, Luxembourg,1998,168–169
[4] N.A. Godshall, Solid State Ionics 1986, 18&19:788-793

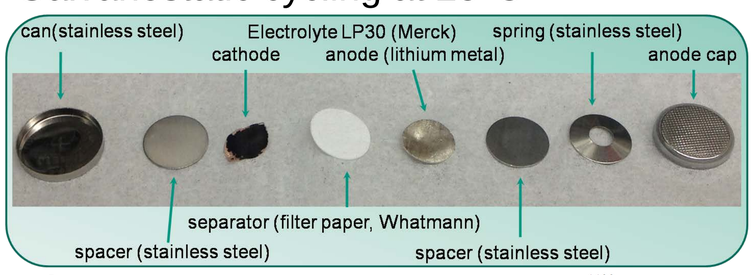
Calculated titration curves:

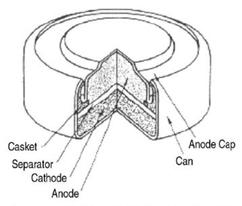
$$E = -\frac{\mu^{cathode}_{Lithium} - \mu^{0}_{Lithium}}{z \cdot F}$$



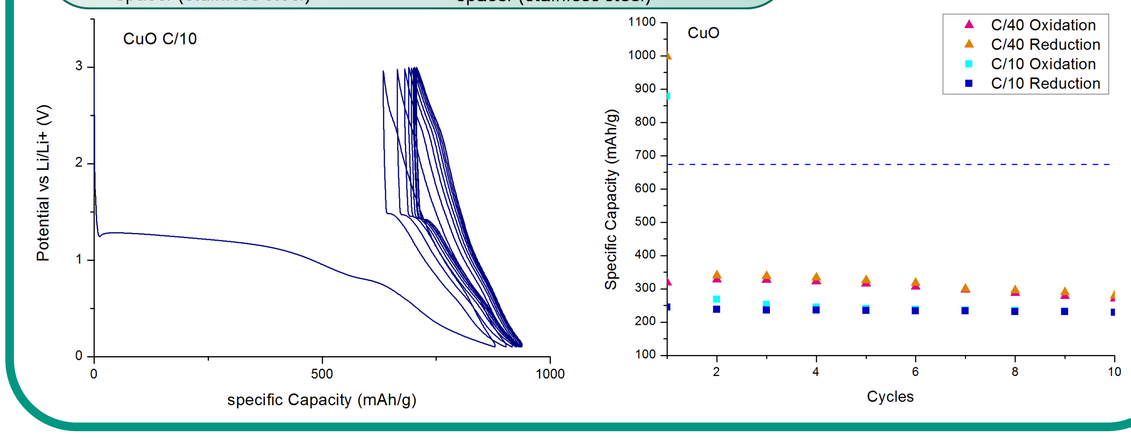
Electrochemical Investigations

Galvanostatic cycling at 25°C





C. Daniel, JOM, 2008, 60 (9):43-48



Summary

- Li_2CuO_2 and $LiCu_2O_2$ were synthesized in oxygen and argon atmosphere, respectively, at 700°C using the solid state method.
- The stability of $LiCu_2O_2$ was investigated using simultaneous DTA/TG. $LiCu_2O_2$ is stable in argon up to 705°C. However, in air $LiCu_2O_2$ reacts with oxygen in the atmosphere on heating.
- C_p data for the compounds Li_2CuO_2 and $LiCu_2O_2$ were measured.
- A dataset of the Li-Cu-O system valid at 298.15 K based on literature data has been developed.
- Theoretical electrochemical titration curves were calculated using the database.
- Copper-oxides were used as active materials for conversion type electrodes and coin cells were assembled.
- Galvanostatic tests with different C-Rates were performed.

Acknowledgements

This work is supported by the priority programme SPP 1473 WeNDeLIB of the German Science Foundation (DFG) in the project SE 647/14-1.