Karlsruhe Institute of Technology

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

WeNDeLIB SPP 1473 DFG

IAM Institute for Applied Materials

Thermodynamic Aspects of the Li-Cu-Fe-O system used for conversion type electrode materials for Lithium Ion Batteries

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Electrodes based on materials in the 3d transition metal oxide system Cu-Fe-O are promising for next-generation lithium ion batteries as they exhibit a high theoretical specific capacity and charge density.

To investigate the Li-Cu-O sub-system, the ternary compound $LiCu_2O_2$ was prepared using the solid state reaction method. The phase purity was identified using X-ray diffraction. Thermal analysis was performed to check for phase transformations and differential scanning calorimetry was performed to measure the heat capacity. In addition, a thermodynamic description of the system at 25 ℃ was developed based on literature data.

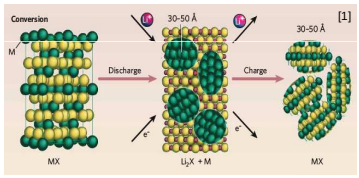
Active material for the electrode was synthesized via the sol-gel self combustion method and coin cells were assembled. First galvanostatic cycling tests at different charging rates were conducted.

Electrochemical Conversion Mechanism

$$M^{n+}X_m + n\cdot e^- + n\cdot Li^+ \leftrightarrow M^0 + n\cdot Li^+X_{m/n}$$

$$X = O, N, S, F, P$$

The reversible Li-driven electrochemical reduction of MX_m into a composite of metallic nanograins dispersed in a Li_2O matrix during discharge.



+ high theoretical capacity
+ high charge density
+ no need of a stable crystallographic structure, freedom in material selection

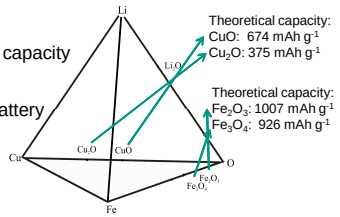
- bad cycling stability

Material System Li-Cu-Fe-O

$$CuFe_2O_4 + 8\cdot e^- + 8\cdot Li^+ \leftrightarrow Cu^0 + 2Fe^0 + 8\cdot Li^+O_{1/2}$$

Theoretical capacity: $CuFe_2O_4$: 896 mAh g^{-1}

- low toxicity
- low cost
- Fe-oxides ⟹ high theoretical capacity
- Cu-oxides ⟹ cycling stability
- Mixed oxides ⟹ adjustment of battery performance

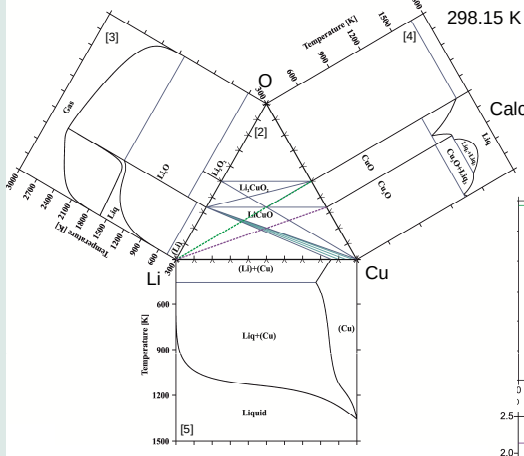


Thermodynamic calculations
- predict battery performance ⟹ equilibrium voltages (OCV)
⟹ plateau capacities

Thermodynamic examinations

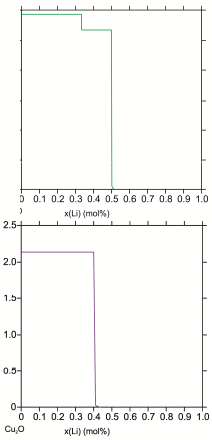
Thermodynamic calculations

based on the CALPHAD method (Coupling of thermochemistry and phase diagram)



Calculated titration curves:

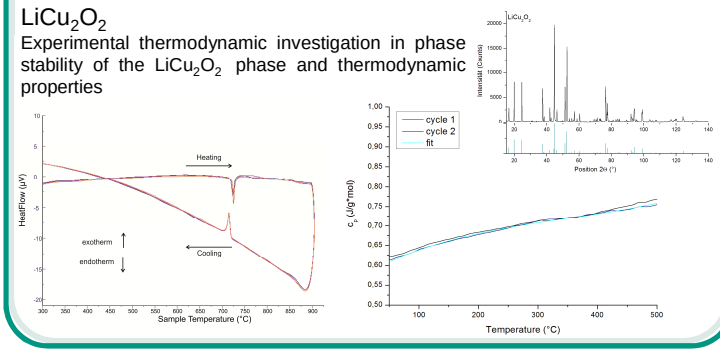
$$E = -\frac{\mu_{Lithium}^{cathode}}{z\cdot F}$$



A thermodynamic description of the Li-Cu-O system to calculate phase equilibria at 298.15 K was developed by using the binary descriptions from the literature [3, 4, 5] and including thermodynamic and electrochemical data [2] for the stoichiometric ternary compounds.

$LiCu_2O_2$

Experimental thermodynamic investigation in phase stability of the $LiCu_2O_2$ phase and thermodynamic properties

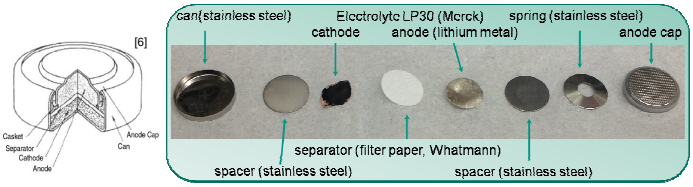


Electrochemical investigations

Sol-gel self combustion

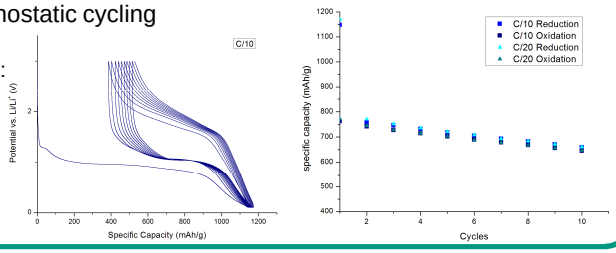
Synthesis of nano-crystalline powders with homogeneous distribution of mixed metal oxides

Coin cell assembling



Galvanostatic cycling

At 25℃:



Conclusions

- A dataset of the Li-Cu-O system valid at 298.15 K based on literature data has been developed and titration curves were calculated.
- $LiCu_2O_2$ was synthesized in Ar atmopshere at 700℃ using the solid state method.
- The phase stability of $LiCu_2O_2$ in Ar atmosphere up to 900℃ wasexamined using DTA/TG. A reversible phase transformation was detected at 705℃.
- C_P data for the compound $LiCu_2O_2$ from 50-400℃ was measured.
- Copper-iron-oxides were used as active materials for conversion type electrodes.
- Galvanostatic tests with different C-Rates were performed which show a strong capacity decrease during the first 10 cycles.

Acknowledgements

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[2] N.A. Godshall, Solid State Ionics 1986, 18&19:788-793
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