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 Oxides

WeNDeLIB SPP 1473 DFG

IAM Institute for Applied Materials

Thermodynamic Description of the Li-Cu-O System for Conversion Type Electrode Materials for Lithium Ion Batteries

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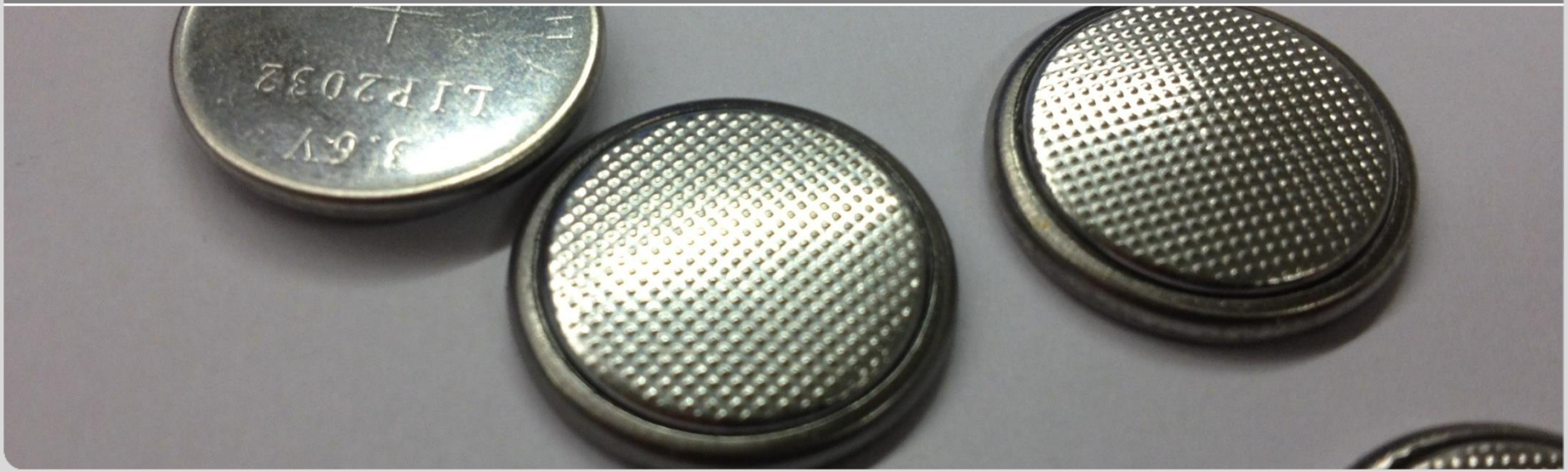
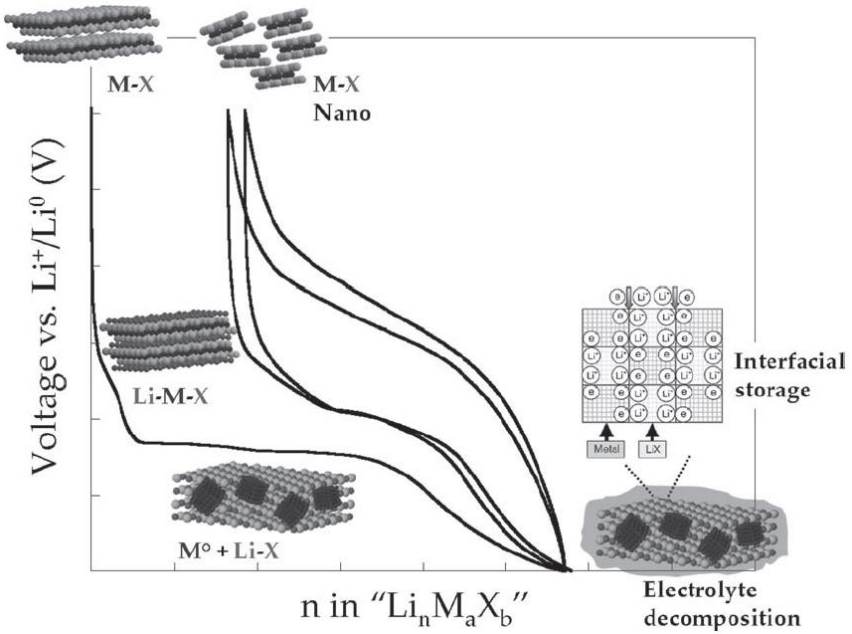


Electrochemical Conversion Mechanism

- Electrochemical conversion mechanism

$$MX_m + ne^- + nLi^+ \leftrightarrow M^0 + Li_nX_m$$

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



- More than 1 Faraday charge per mole can be transferred

⟶ High theoretical capacity

- Conversion mechanism does not need a stable crystallographic structure

⟶ freedom in material selection

- Bad cycling stability

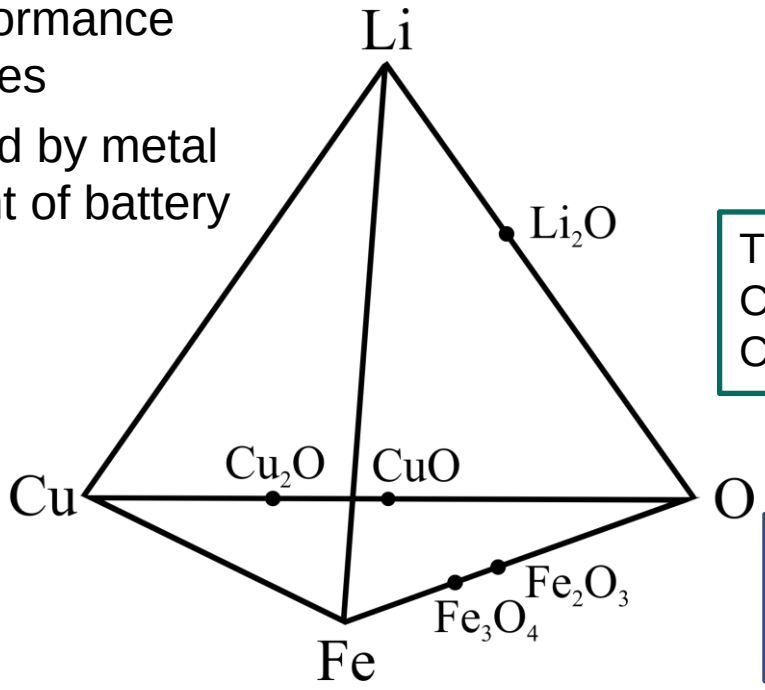
J. Cabana, et al. *Adv. Mater.* **22**, E170-E192 (2010).

Material System: Li-Cu-Fe-O

- Fe-oxides
  - High theoretical capacity
- Cu-oxides
  - Cycling stability
- Mixed transition metal compounds
  - Show an overall performance similar to simple oxides
  - Potential is dominated by metal content → adjustment of battery performance

$$CuFe_2O_4 + 8e^- + 8Li^+ \leftrightarrow Cu^0 + 2Fe^0 + 4Li_2O$$

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



Theoretical capacity:
CuO: 674 mAh g^{-1}
Cu_2O: 375 mAh g^{-1}

Theoretical capacity:
Fe_2O_3: 1007 mAh g^{-1}
Fe_3O_4: 926 mAh g^{-1}

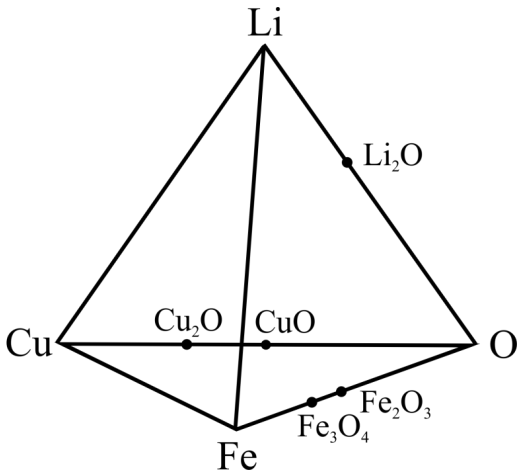
Motivation for Thermodynamic Descriptions

- Overall driving force across a electrochemical cell is determined by the change in the standard Gibbs free energy

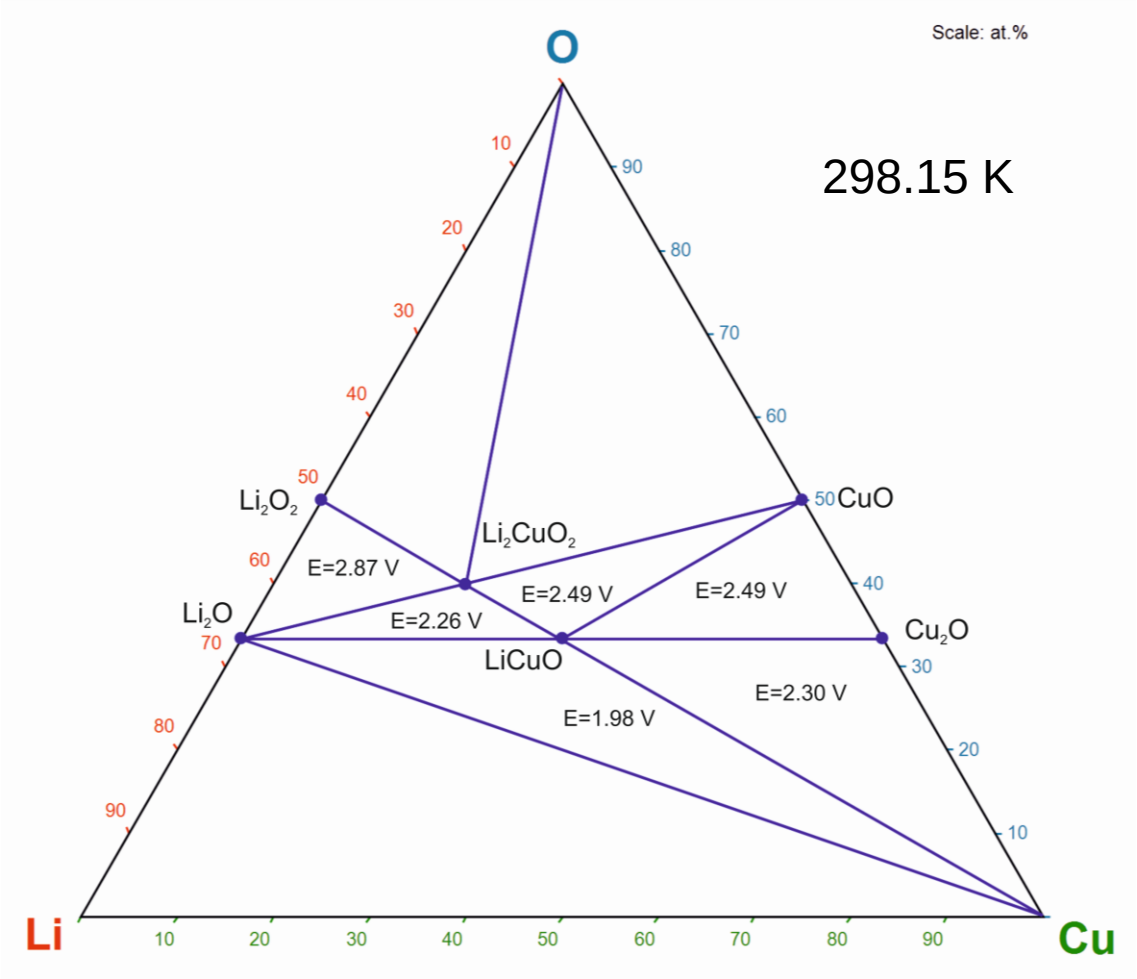
$$\Delta G = -z \cdot F \int_{n=0}^{n} E^0(n)dn$$

- Thermodynamic calculations based on the CALPHAD method (Coupling of thermochemistry and phase diagram)
  - Predict battery performance (OCV, capacity)

- Database development for the Li-Cu-Fe-O System:
  - The Cu-Fe-O ternary system assessed by Khvan et al., Journal of Phase Equilibria and Diffusion, 2011, 32:498-511
  - First calculated phase diagrams in the Li-Cu-O system addressed in present work



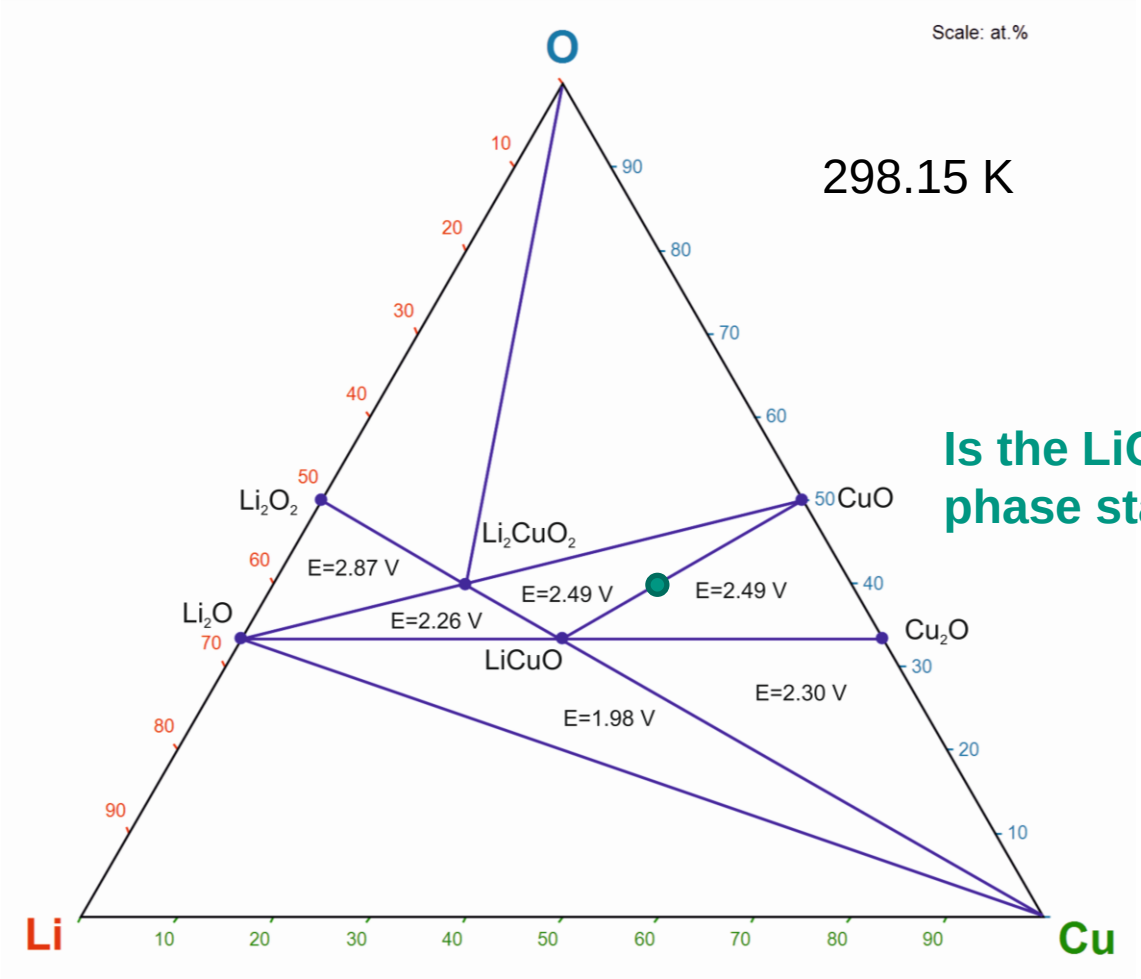
Li-Cu-O System at 298.15 K



Investigated by coulometric titration

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

Li-Cu-O System at 298.15 K

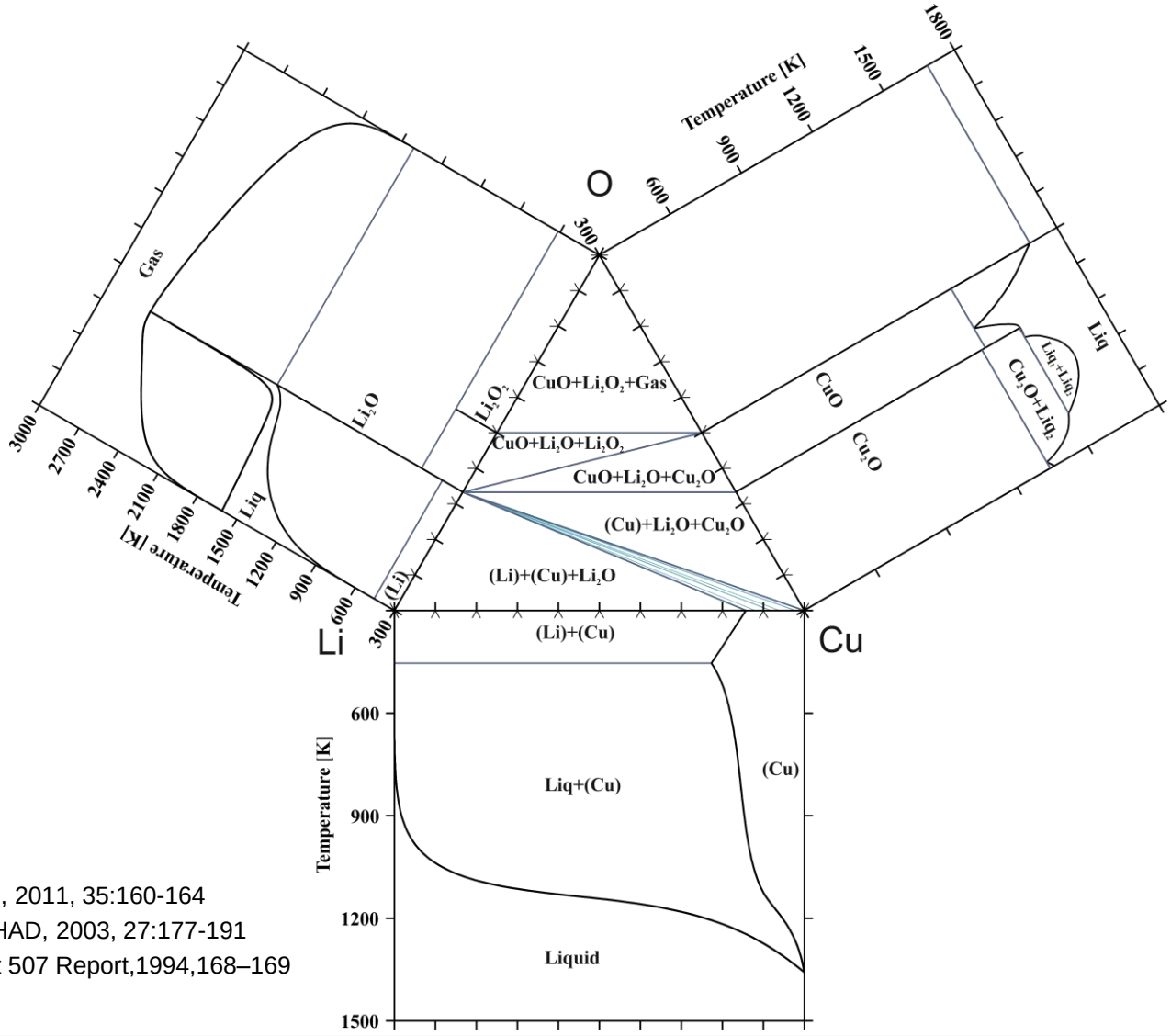


Is the $LiCu_2O_2$ phase stable?

S. Patat et al., Solid State Ionics 1991, 46:325-329

Database Developement Li-Cu-O System

Extrapolation from binary assessments



Li-O: K. Chang, B. Hallstedt, CALPHAD, 2011, 35:160-164
Cu-O: B. Hallstedt, L.J. Gauckler CALPHAD, 2003, 27:177-191
Li-Cu: N. Saunders, I. Ansara (Ed), Cost 507 Report,1994,168–169

Database Development Li-Cu-O System

1. Formation based on the compounds in the three-phase field
2. All phases in the three-phase equilibrium are considered as pure substances

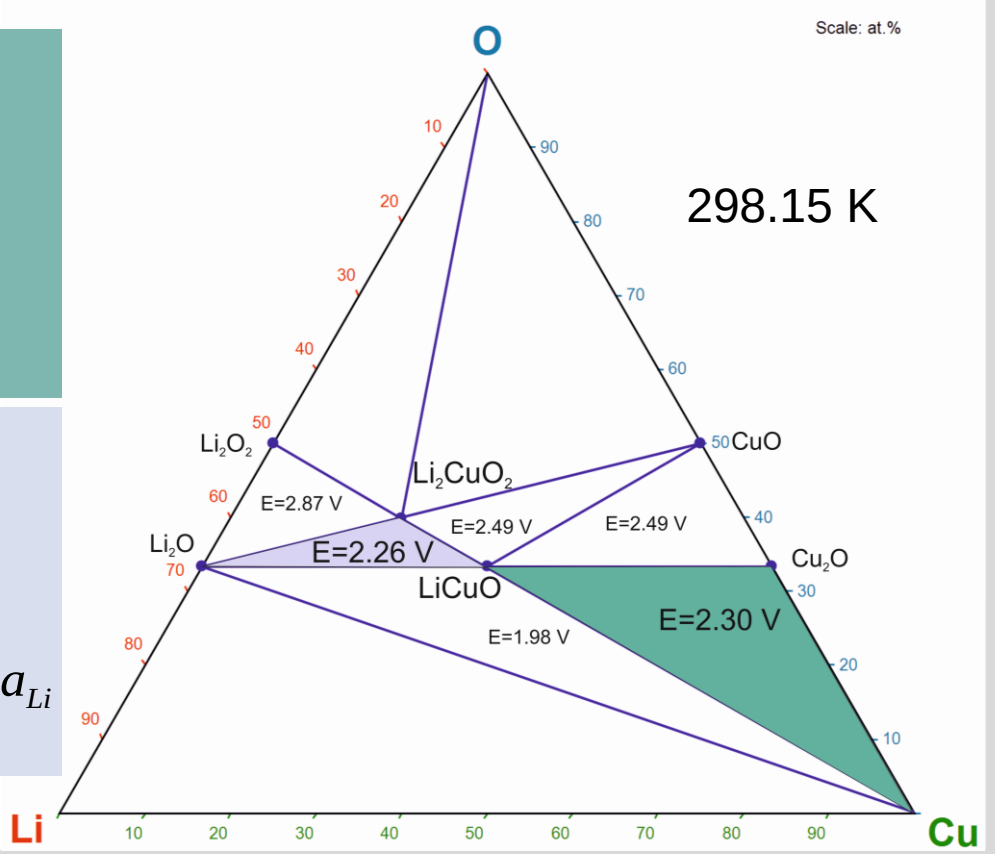
$$E = -\frac{\mu_{Li} - \mu_{Li}^0}{z \cdot F} = -\frac{RT \ln a_{Li}}{z \cdot F}$$

LiCuO:

1. $Cu_2O + Li \rightarrow LiCuO + Cu$
2. $\Delta_f G^0_{LiCuO} = \Delta_f G_{Cu_2O} + RT \ln a_{Li}$

Li_2CuO_2:

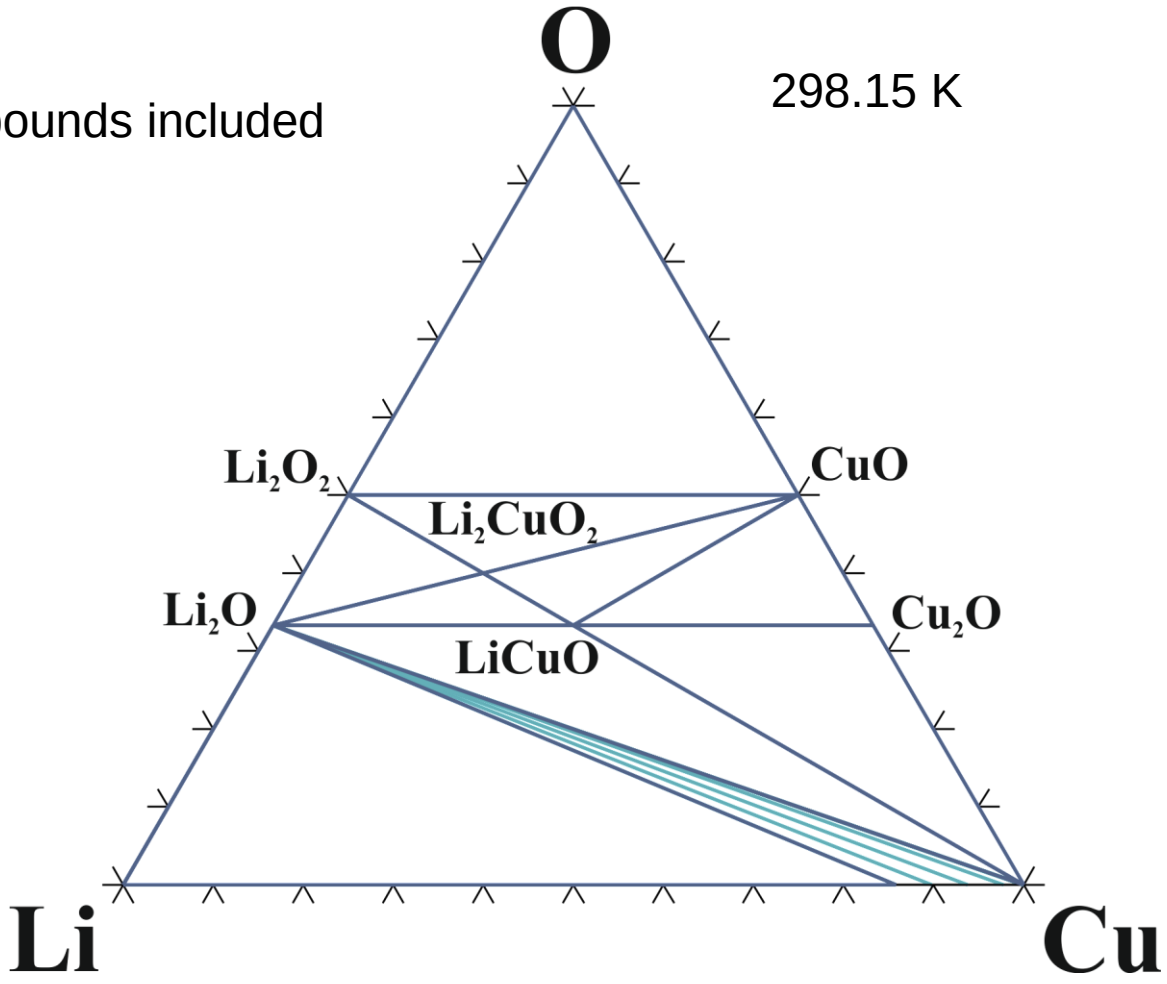
1. $LiCuO + Li_2O \rightarrow Li_2CuO_2 + Li$
2. $\Delta_f G^0_{Li_2CuO_2} = \Delta_f G^0_{LiCuO} + \Delta_f G^0_{Li_2O} - RT \ln a_{Li}$



Database Development Li-Cu-O System

Ternary compounds included

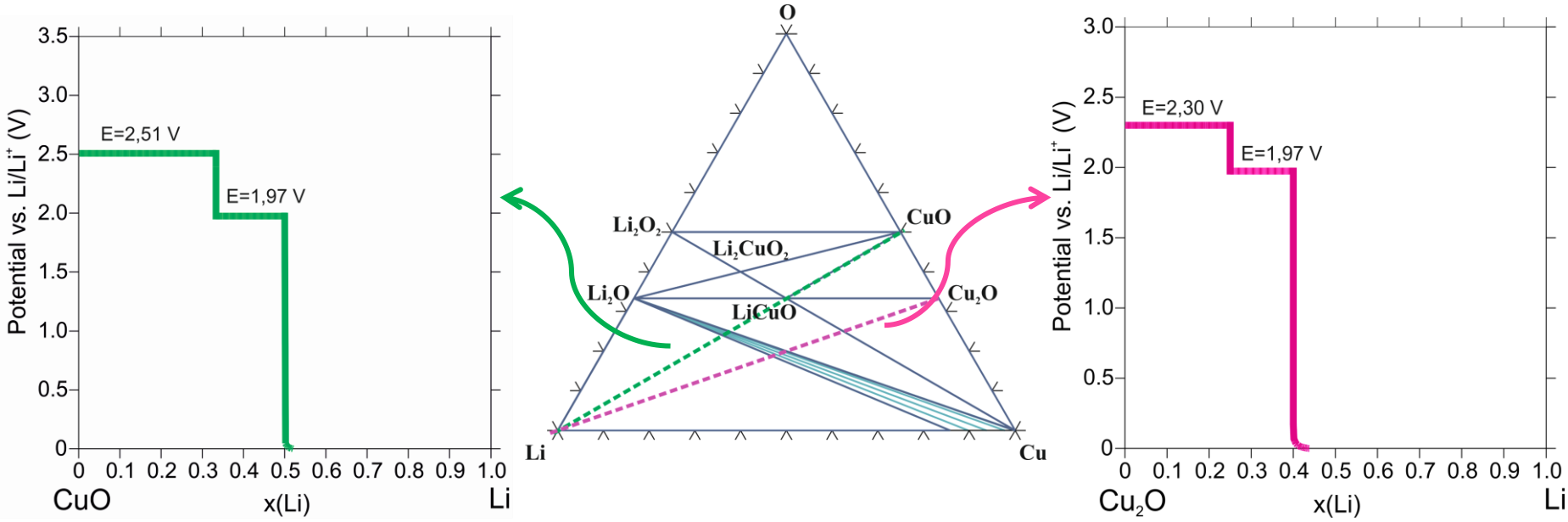
298.15 K



Titration Curves

- Equilibrium cell voltage as a function of lithium content at the cathode along selected composition paths

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



Description of Temperature Dependence

- Stoichiometric phase (AB)

$$G(AB) = GHSER_A + GHSER_B + a + bT + cT\ln T + \ldots$$

  - *a, c* → solution calorimetry, c_p measurements
  - *b,c* → low T c_p measurements (0 – 298.15 K), ab initio
  - *c* → c_p measurements

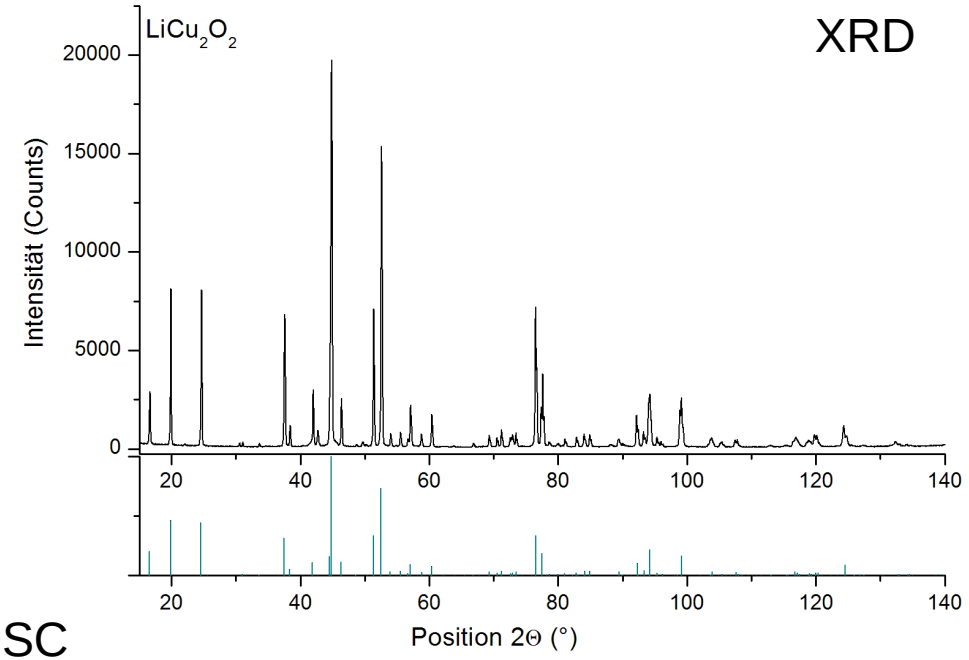
- Phase stability
  - DTA/TGA

$GHSER_A$: Gibbs free energy of component A with reference to the standard enthalpy of the element at 298.15 K

a, b, c,…: Variables

Experimental Investigations

- Sample preparation via solid state reaction
  - Li_2CuO_2
  - $LiCu_2O_2$
- Sample characterization
  - XRD

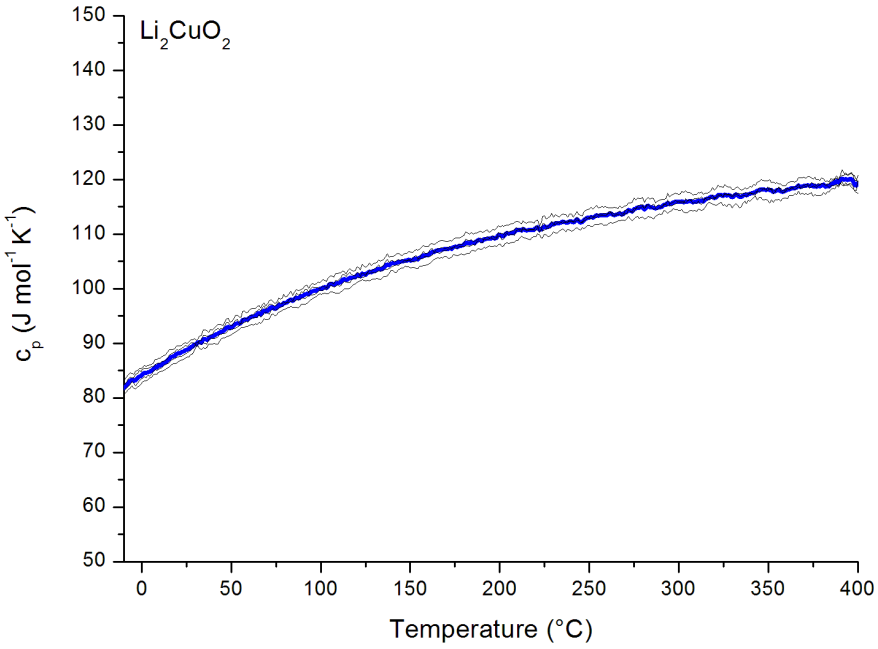


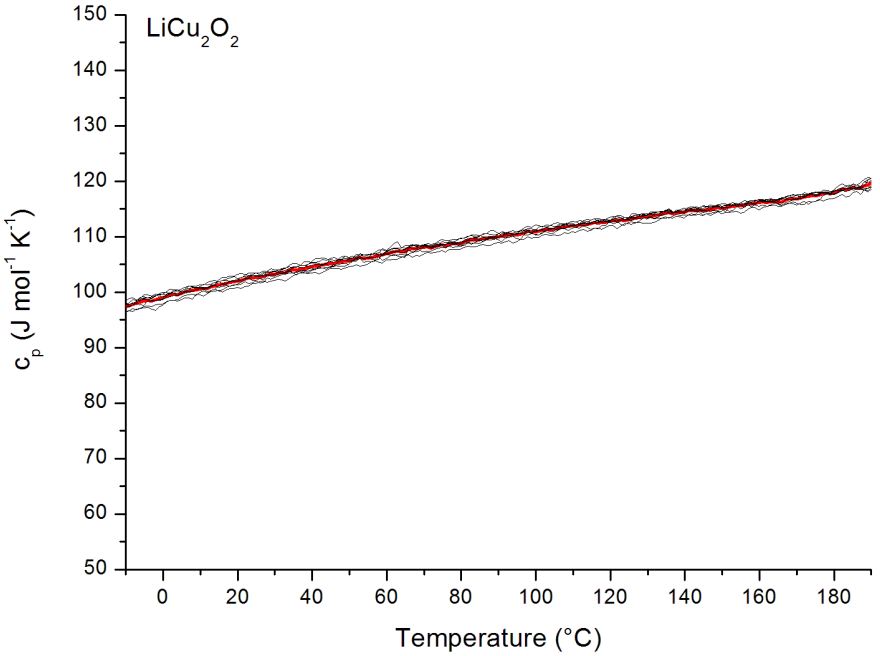
- Thermal analysis
  - Specific heat capacity with DSC
  - Phase stability of $LiCu_2O_2$ in argon and air with simultaneous DTA/TGA

➡ Include results in database

Heat Capacity

- Li_2CuO_2:
  - -10 – 400°C, HR=10 K/min
- $LiCu_2O_2$:
  - -10 – 200°C, HR=10 K/min

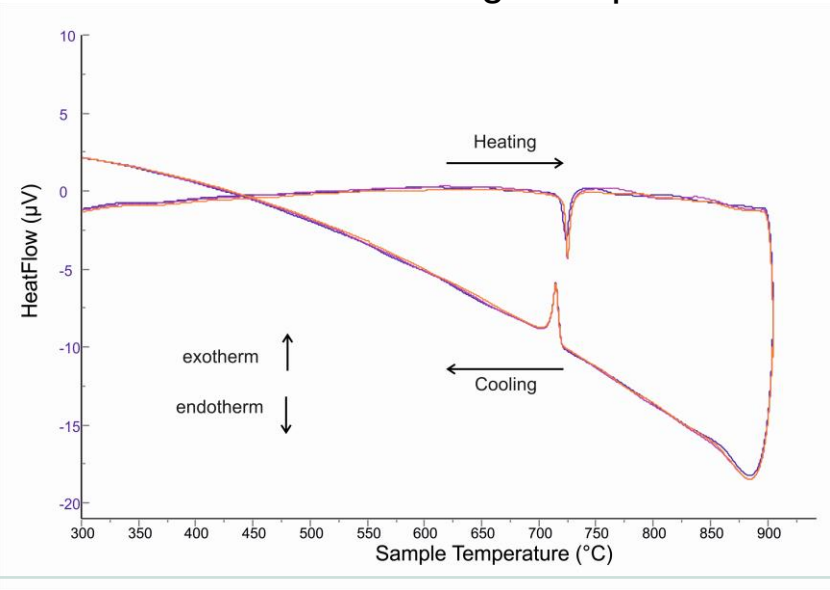




Phase Stability of $LiCu_2O_2$

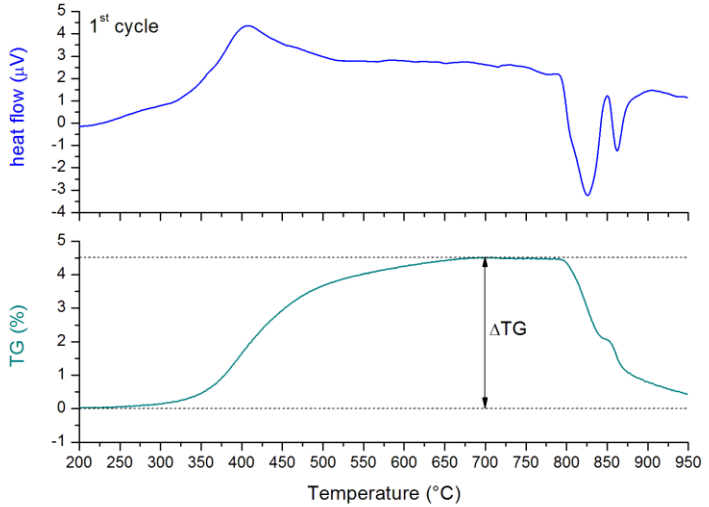
- Simultaneous DTA/TG (Setaram)
- 200-900°C, HR=10 K/min, 3 cycles

- In argon
  - Reversible phase transformation at 705 °C
  - Slight mass loss due to reduction of $Cu^{+2} \rightarrow Cu^{+1}$ at high temperatures



- In air
  - Irreversible phase transformation accompanied with mass gain ΔTG during 1st cycle

$$2LiCu_2O_2 + \frac{1}{2}O_2 \rightarrow Li_2CuO_2 + 3CuO$$



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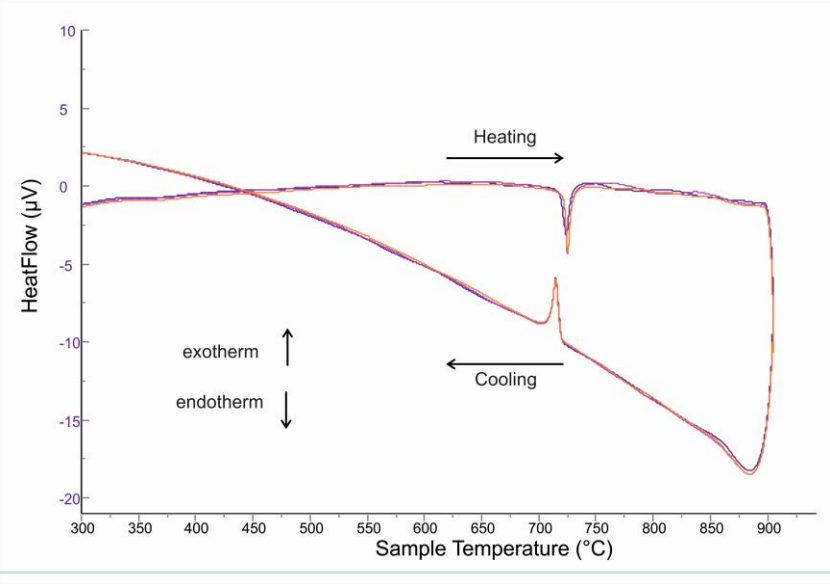
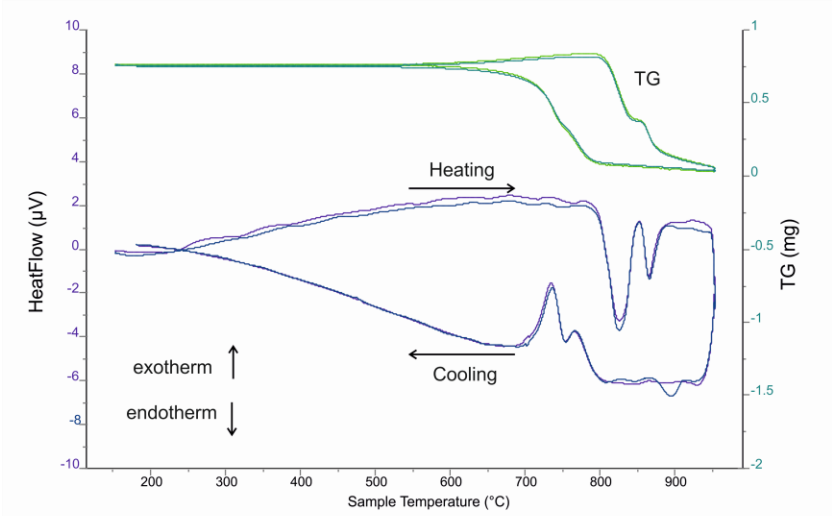


- In air
  - Irreversible phase transformation accompanied with mass gain ΔTG during 1st cycle

$$2LiCu_2O_2 + \frac{1}{2}O_2 \rightarrow Li_2CuO_2 + 3CuO$$

  - Reversible phase transformations in 2nd and 3rd cycles



Conclusions and Outlook

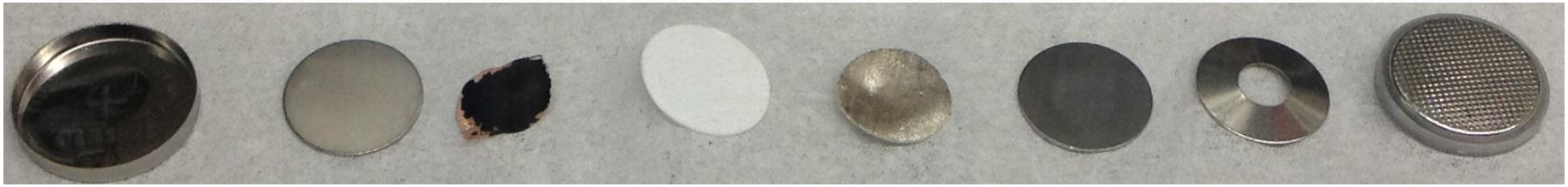
A thermodynamic description of the Li-Cu-O system at 298.15 K was developed

- Experimental data have to be incorporated to describe the temperature dependence

First measurements on the thermodynamic behavior of ternary Li-Cu-O compounds were conducted

- Further experiments are necessary
  - Quench experiments
  - High temperature XRD
- Solution calorimetry: $\Delta_f H$

Electrochemical investigations



Acknowledgment

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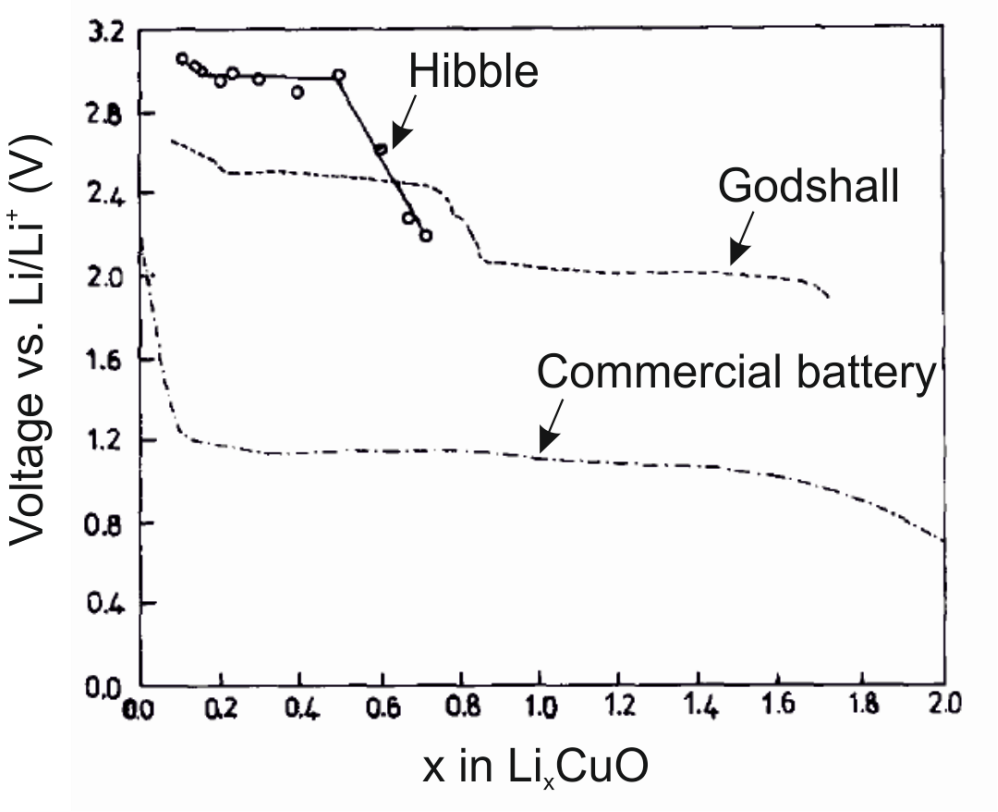
- Thanks to Robert Adam (TU Freiberg)

Thank you for your kind attention!

OCV vs. Experimental Results



Potential plateau of CuO and Cu_2O: ~1.4 V

S.J. Hibble, Solid State Ionics 1990, 39:289-295