German Research Foundation, Priority Programmme 1473, Materials with New Design for Improved Lithium Ion Batteries - WeNDeLIB

Werkstoffe mit neuem Design für verbesserte Lithium-Ionen-Batterien - WeNDeLIB

GTT Users´ Meeting
June 30, 2017; Herzogenrath

Hans Jürgen Seifert

INSTITUT FÜR ANGWANDTE MATERIALIEN – ANGEWANDTE WERKSTOFFPHYSIK (IAM-AWP)

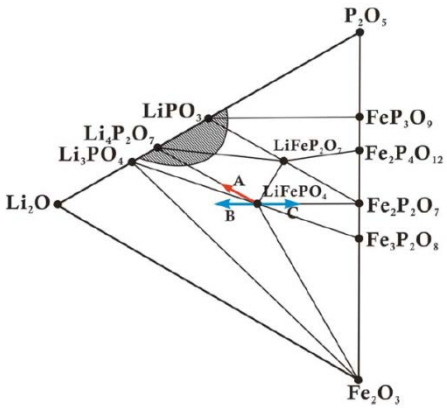
1st funding period: 09/2010 - 08/2013
2nd funding period: 09/2013 - 08/2016

Programme Commission:

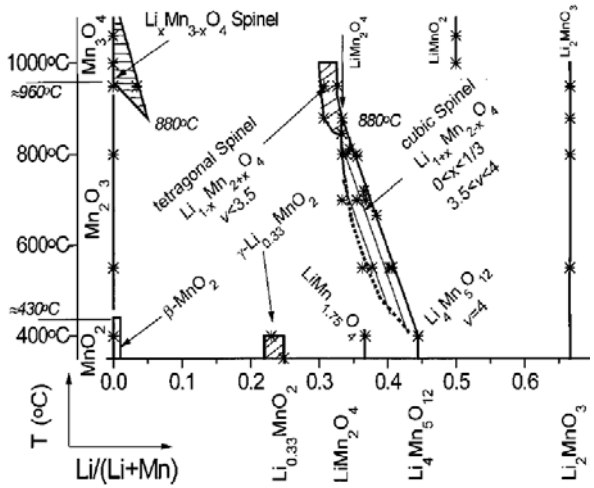
Prof. Dr. Hans J. Seifert	• Karlsruhe Institute of Technology, KIT • Coordinator
Prof. Dr.-Ing. R. Schmid-Fetzer	• TU Clausthal • 1st repr. coordinator
Prof. Dr. Martin Winter	• University of Münster • 2nd repr. coordinator
Dr. Andreas Gutsch	• Karlsruhe Institute of Technology, KIT
Prof. Dr. Torsten Markus	• University of Applied Science Mannheim
Prof. Dr.-Ing. Ingo Steinbach	• RUB, ICAMS, Bochum
Prof. Dr. Alexandra Navrotsky	• University of California, Davis

- Scientific Focus -

Interdisciplinary Work – Correlation of:



Materials
- **Thermodynamics,**
- **Constitution,**
- **Kinetics**

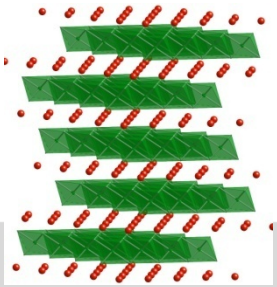


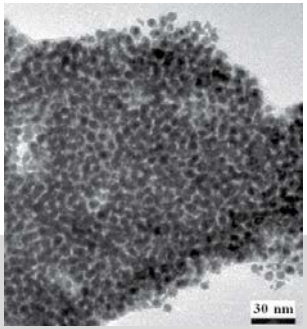
Modelling, Simulation

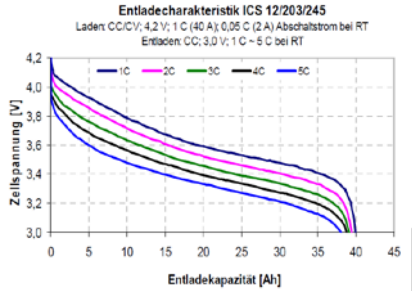
Crystal chemistry, Microstructure,

Innovative Materials Synthesis

Electrochemical performance and thermal behaviour of cells / batteries







2nd Funding Period
Funded Joint Projects

Schneider (RWTH Aachen), Seifert (KIT)
Design of an all solid state thin film lithium ion battery and their electrochemical-thermodynamic modeling and evaluation (JP 3)

Cupid (KIT), Flandorfer (Univ. Wien), Markus (Hochschule Mannheim)
Experimental thermodynamics and phase relations of new electrode materials for Li-ion batteries studies in the systems Li-Sb-Sn, Cu-Li-Sb, Li-Si, and Li-Si-O (JP 4)

Fritze (TU Clausthal / Goslar)
Linking of model and commercial active materials for lithium ion batteries by in-situ determination of thermodynamic and kinetic data (JP 6)

Albe (TU Darmstadt), Graczyk-Zajak (TU Darmstadt), Seifert (KIT)
Nanocomposites as anode materials for lithium ion batteries: Synthesis, thermodynamic characterization and modeling of nanoparticular silicon dispersed in SiCN(O) and SiCO-based matrices (JP 8)

2nd Funding Period
Funded Projects

Rettenmayr (Univ. Jena), Schmid-Fetzer (TU Clausthal), Song (TU Peking)
Phase stability of alloy-type lithium storage anode materials (JP 9)

Kortus (TU Freiberg), Mertens (TU Freiberg)
Rational tuning and thermodynamic characterization of Lithium silicides and lithium iron phosphate as electrode materials for lithium ion batteries - Calorimetric, kinetic and theoretical investigations of the relations between reactivity, morphology and size effects (JP 10)

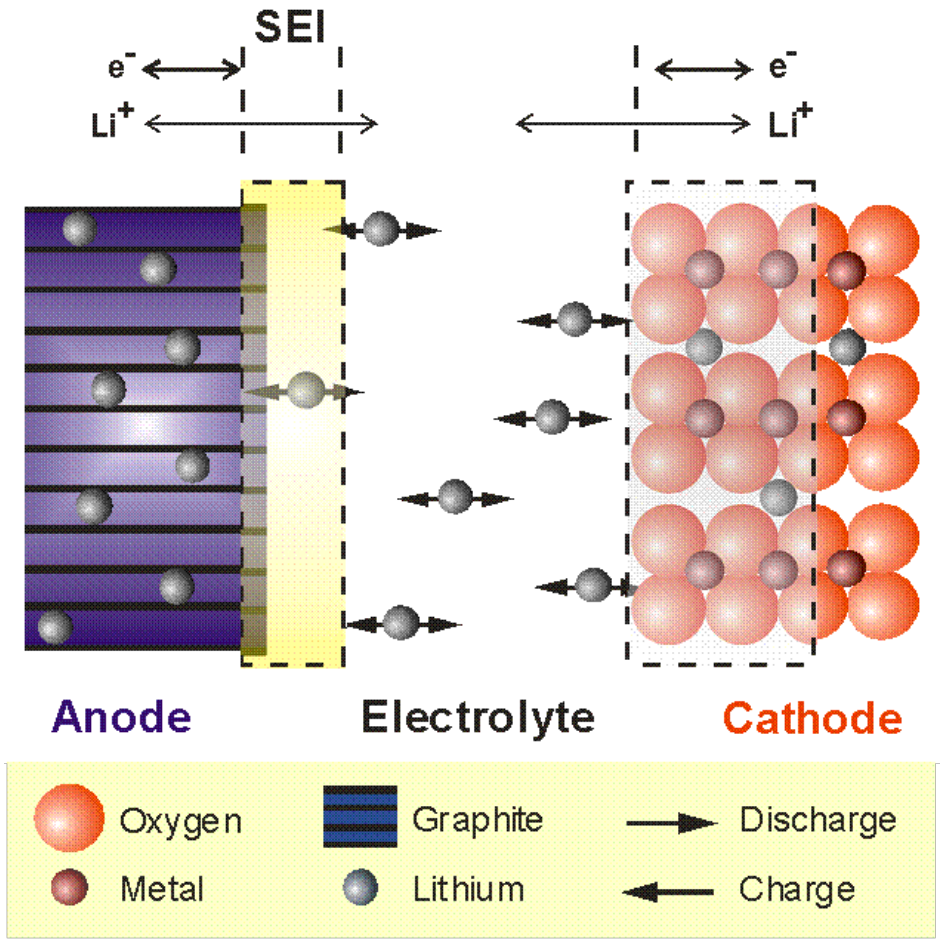
Ehrenberg (KIT), Rafaja (TU Freiberg), Seifert (KIT), Winter (Univ. Münster)
Thermodynamics and kinetics for stabilization of conversion-type electrodes for LIB based on nano 3d transition metal oxide composites (JP 12)

Seifert (KIT)
Coordination Funds (JP 1)

Conferences, meetings, workshops over the whole funding period (09/2010 - 08/2016)

- 7 topic workshops on electrochemical thermodynamics (Ringberg workshops)
- 6 Workshops for scientific discussions of the joint projects (organized in collaboration with DGM)
- 5 Summer/Spring/Fall schools on selected electrochemical, thermodynamics and battery issues
- Countless individual joint project meetings
- 7 Conference Symposia
- Gender equality workshops

Lithium ion cell; Intercalation mechanisms

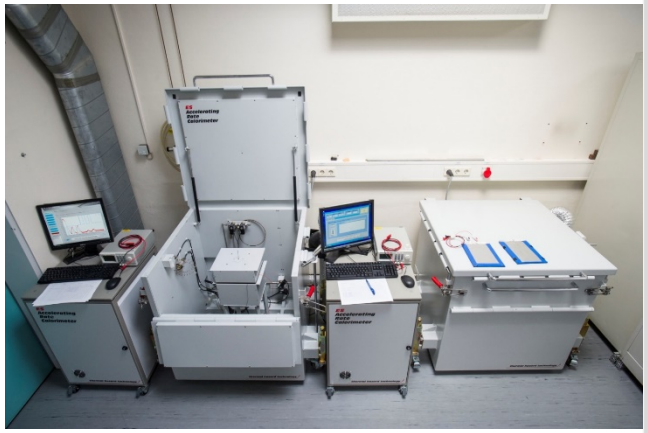


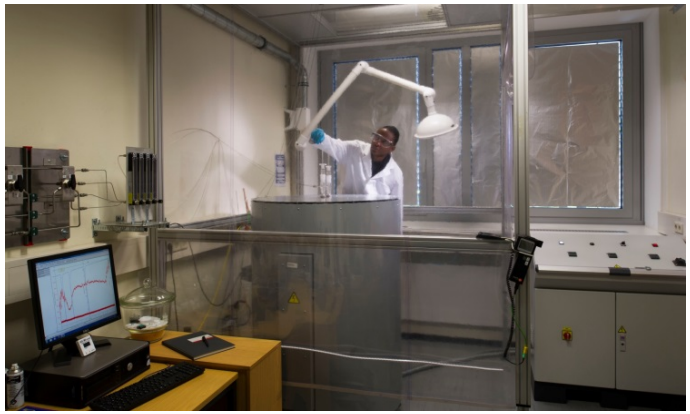
$$Li_x AN + CA \xrightarrow{\text{discharge}} AN + Li_x CA$$

2nd Funding Period – Focus Group on Calorimetry Coordination: Dr. Damian Cupid

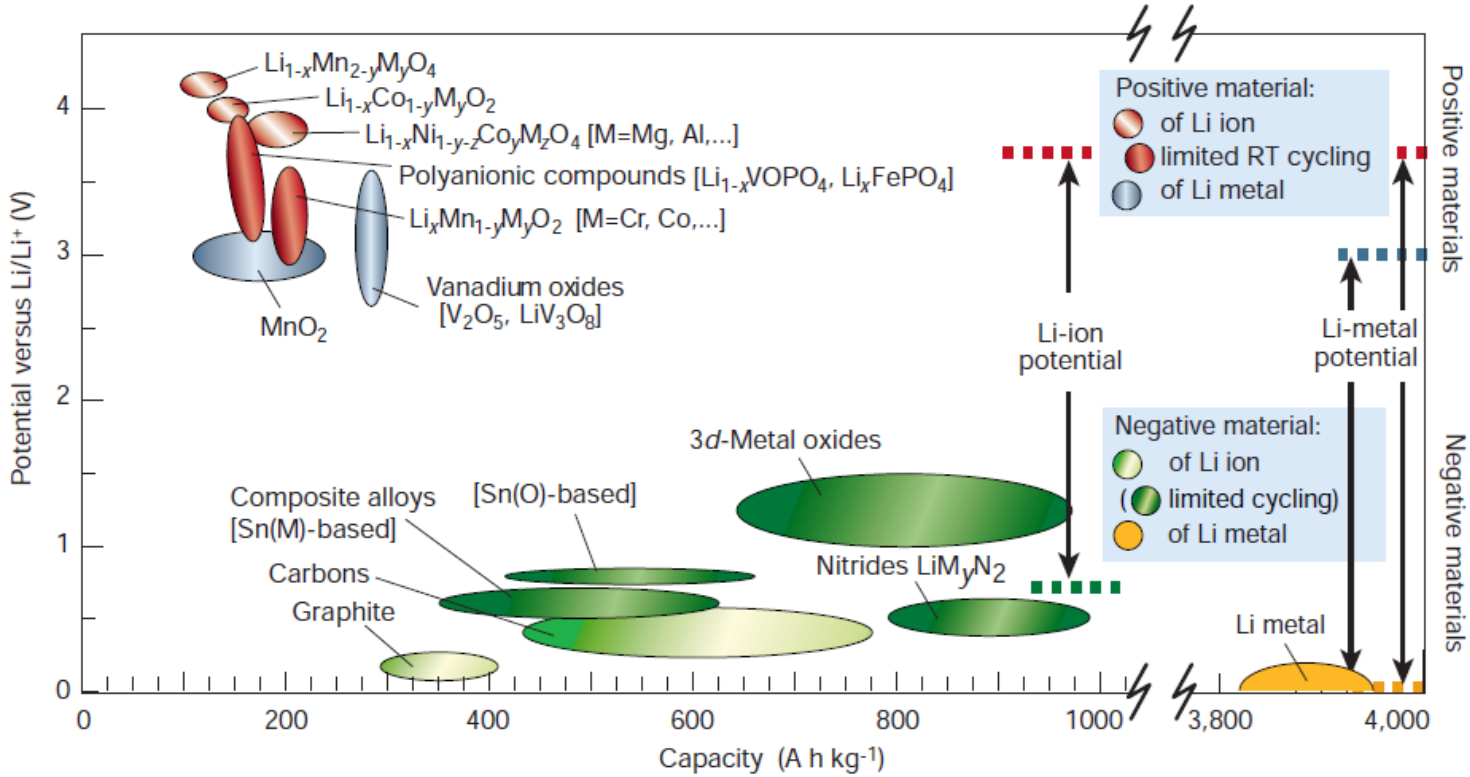
Improve visibility of important methods of analysis. Exchange of methodological experiences. Discussion of scientific results.

- Differential Scanning Calorimetry (DSC)
- Thin film calorimetry
- High temperature drop (solution) calorimetry
- Accelerating Rate Calorimetry (ARC)
- Isothermal Battery Calorimetry (IBC)





Electrode Materials for LIB



J.M. Tarascon et al., Nature, 2001, 414:359-367

- Commercial electrode materials
  - Intercalation-type
  - Graphite
    - Specific capacity 372 mAh/g
- New electrode materials
  - Conversion-type
  - Metal oxides
    - Specific capacity > 400 mAh/g

Relationships Thermodynamics and Electrochemistry

Full lithium ion cell discharge reaction

$$Li_xAN + CA \xrightarrow{\text{discharge}} AN + Li_xCA$$

Free energy of the full reaction is:

$$\Delta G(x,T) = -n \cdot F \cdot E_0(x,T)$$

Free energy of the full reaction can be written:

$$\Delta G(x,T) = -\Delta H(x,T) - T\Delta S(x,T)$$

Neglecting T-dependence:

$$\Delta G_0(x,T) = -\Delta H(x) - T\Delta S(x)$$

Combining equations:

$$\Delta S(x) = F\left(\left.\frac{\partial E_0(x,T)}{\partial T}\right|_x\right) \quad \Delta H(x) = F\left(-E_0(x,T) + T\left.\frac{\partial E_0(x,T)}{\partial T}\right|_x\right)$$

$E_0(x,T)$	**Open circuit voltage**
n	**Charge number (n=1 for Li^+)**
F	**Faraday constant**
ΔH, ΔS	**Heat and entropy of reaction**
$\left.\frac{\partial E_0(x,T)}{\partial T}\right\|_x$	**Temperature slope of $E_0(x,T)$**

Thermodynamic functions of active materials are needed

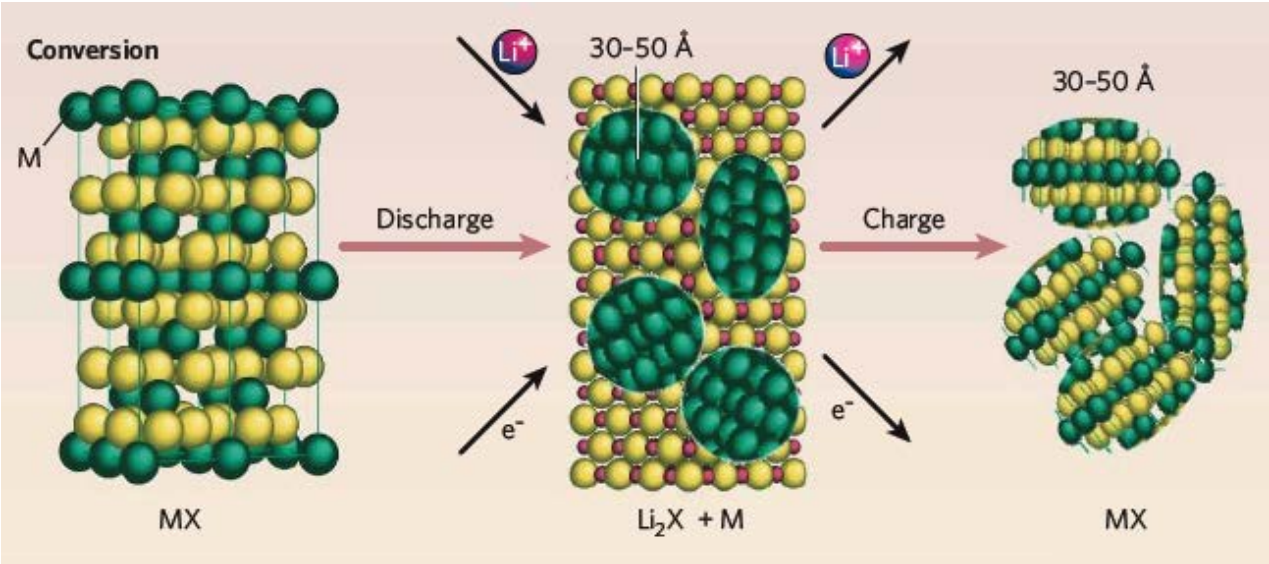
Electrochemical conversion mechanism

X = O, N, F, S, P

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

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}



M. Armand et al., Nature, 2008, 451:652-657

$$CuO + 2\cdot e^- + 2\cdot Li^+ \longleftrightarrow Cu^0 + Li_2O$$

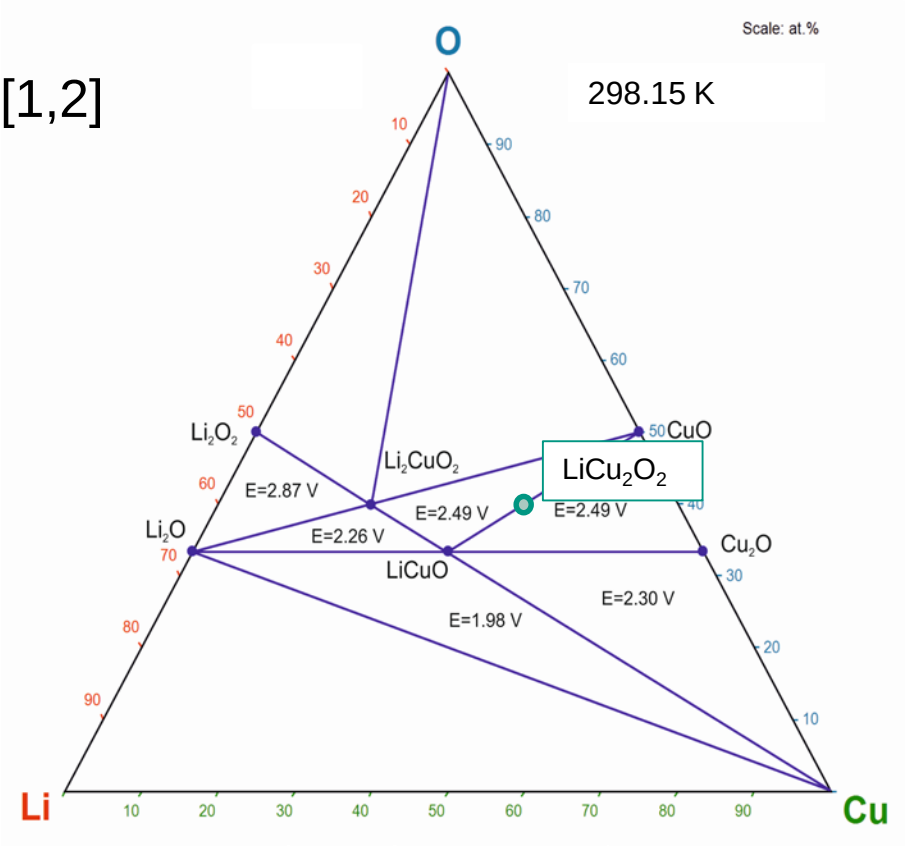
- Cu-Fe-O electrodes for LIB exhibit
  - Fe-oxides: high theoretical capacity
  - Cu-oxides: cycling stability

Literature Review

- Thermodynamic stable phases
- Gibbs energy of formation data from EMF measurements [1]
- Enthalpy of formation data [2]
- Two isothermal sections at 298 K [1,2]

Phase	Temperature stability range
LiCuO	< 980 °C
Li_2CuO_2	< 1020 °C
$LiCu_2O_2$	890 – 1050 °C in air
	stable in argon, polymorphic
	transition around 720 °C
$LiCu_3O_3$	> 800 °C in air
$LiCuO_2$**	
Li_3CuO_3	
$Li_3Cu_2O_4$	250 – 330 °C in oxygen

**can be only synthesized via delithiation of Li_2CuO_2



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

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

Thermodynamic Modeling

Stochiometric phase (AB)

$$G(AB) = H_A^{SER} + H_B^{SER} + a + bT + cT\ln T + \ldots$$

Description via the reaction from the binary oxides

$$m\mathrm{Li_2O} + n\mathrm{Cu_2O} + p\mathrm{CuO} \leftrightarrow \mathrm{Li}_{2m}\mathrm{Cu}_{2n+p}\mathrm{O}_{m+n+p}$$

Gibbs energy of reaction at 25 °C

Patat et al.

$$\Delta_r G_{\mathrm{Li}_{2m}\mathrm{Cu}_{2n+p}\mathrm{O}_{m+n+p}} = \Delta_r H_{\mathrm{Li}_{2m}\mathrm{Cu}_{2n+p}\mathrm{O}_{m+n+p}} - T\Delta_r S_{\mathrm{Li}_{2m}\mathrm{Cu}_{2n+p}\mathrm{O}_{m+n+p}}$$

$$= \Delta_f G^o_{\mathrm{Li}_{2m}\mathrm{Cu}_{2n+p}\mathrm{O}_{m+n+p}} - \underbrace{m\Delta_f G^o_{\mathrm{Li_2O}} - n\Delta_f G^o_{\mathrm{Cu_2O}} - p\Delta_f G^o_{\mathrm{CuO}}}_{\text{Binary descriptions}}$$

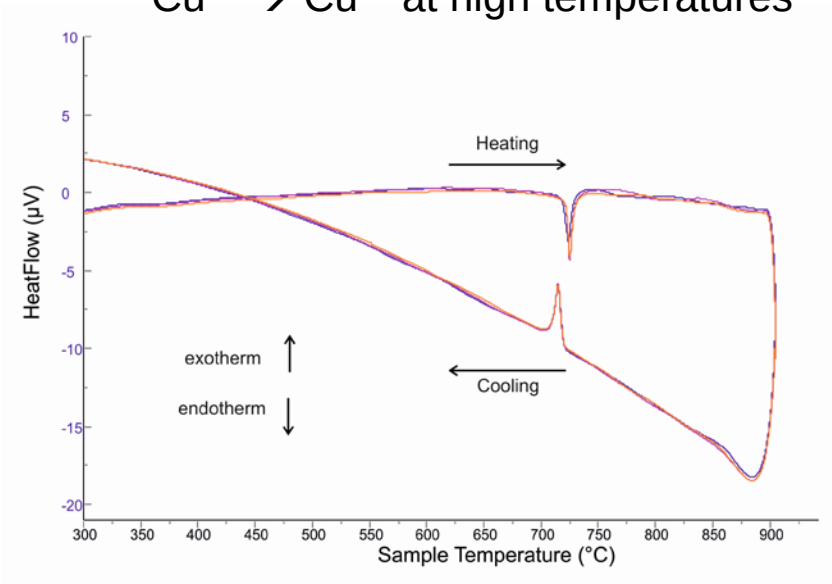
Godshall

N.A. Godshall, Solid State Ionics 1986, 18&19:788-793 S. Patat et al., Solid State Ionics 1991, 46:325-329

a) Phase Stability of $LiCu_2O_2$

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

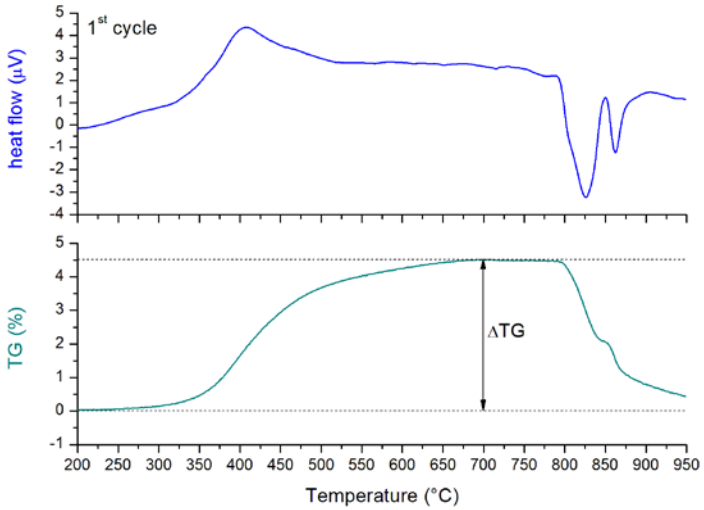
- In argon
  - Reversible phase transformation at 715 ± 2 °C
  - Slight mass loss due to reduction of $Cu^{+2} \rightarrow Cu^{+1}$ at high temperatures



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

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

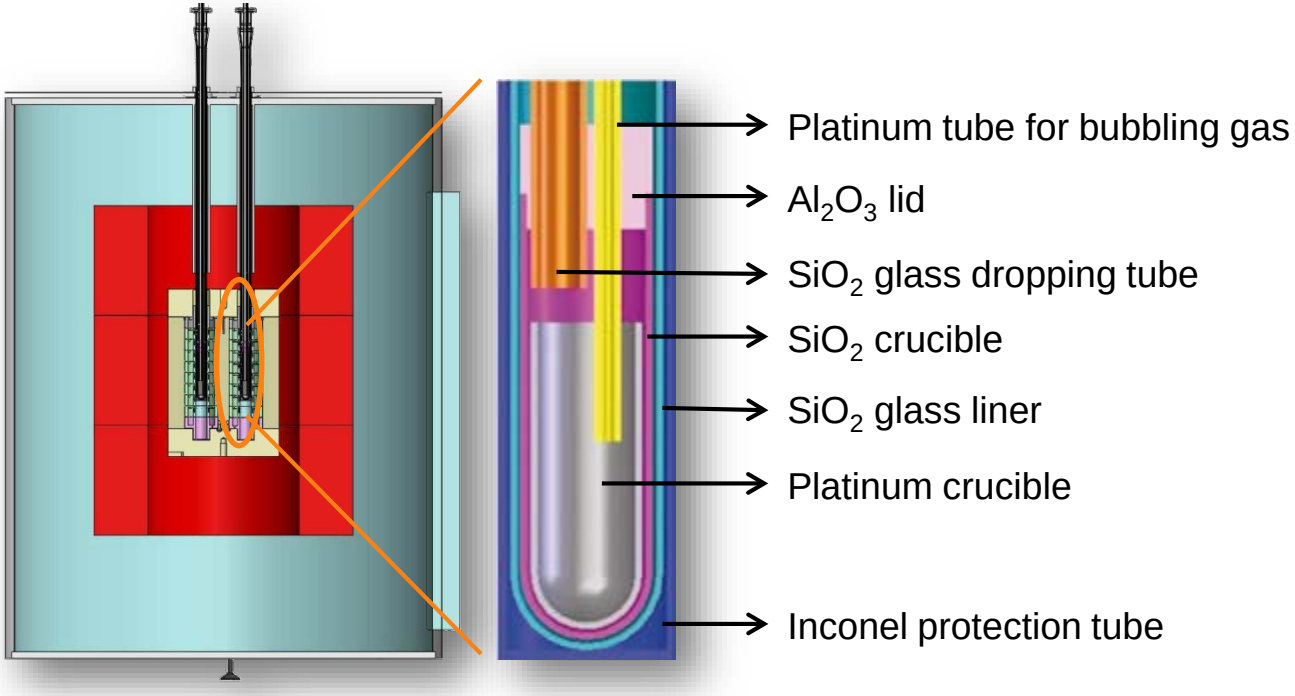
  - 2 reversible reactions at 780 °C and 850 °C: Formation of $LiCu_3O_3$ and $LiCu_2O_2$



M. Lepple et al., J. Mater. Sci. 2013, 48:5818-5826, S. A. Ivanov et al., ArXiv e-prints, Nov. 2012 A.A. Bush et al., Inorganic Materials, 2004, 40:44-49

High Temperature Oxide Solution Calorimetry – Enthalpies of Formation

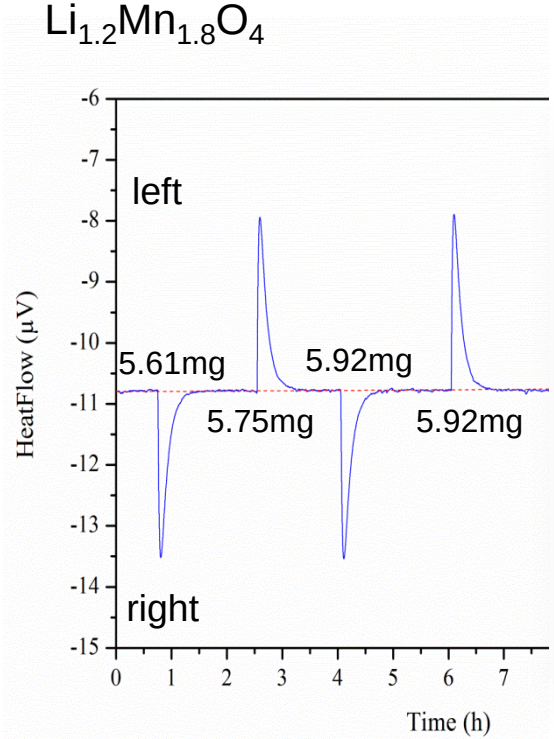
- Drop Solution Calorimeter (Alexsys 1000, Setaram)
  - Twin-Calvet-Type
  - Sodium molybdate ($3Na_2O{\cdot}4MoO_3$) solvent
  - Solution calorimetry performed at 700 °C

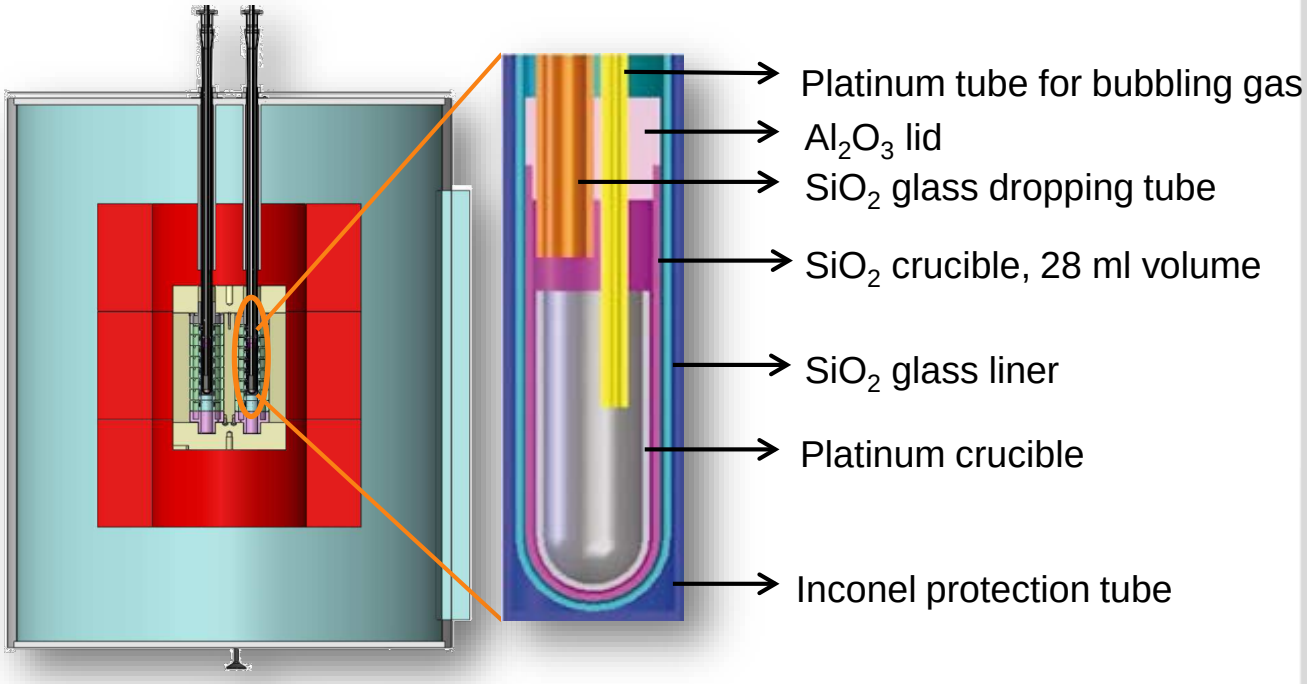


b) High Temperature Calorimetry

- Solution Calorimetry
  - Twin Calvet-Calorimeter (AlexSys, SETARAM)
  - Sodium molybdate ($3Na_2O{\cdot}4MoO_3$) solvent used for solution calorimetry
  - Solution calorimetry performed at 700°C (800°C at UC Davis)

$Li_{1.2}Mn_{1.8}O_4$





b) Enthalpies of dissolution

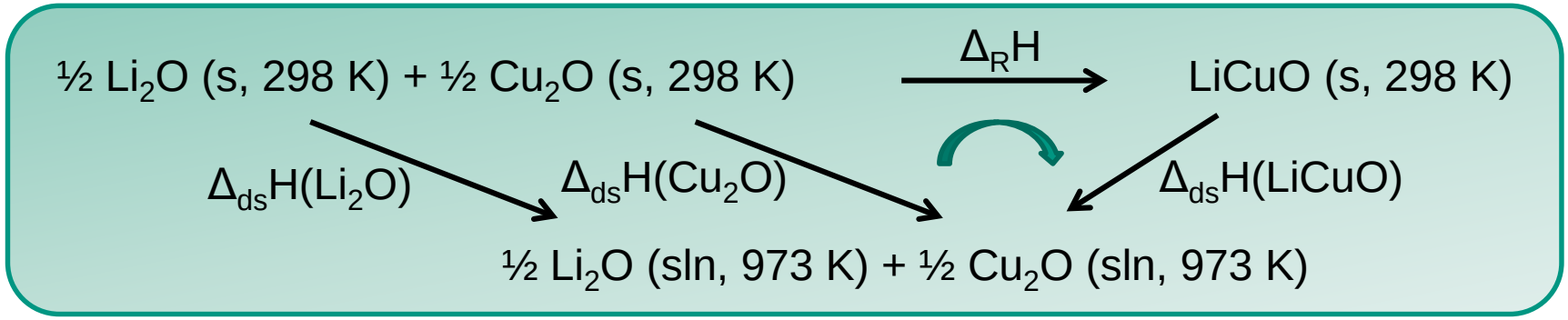
- Binary oxides

	700°C	800°C	Literature (700°C)
Li_2O	-	-84 ± 2 kJ/mol	-93 ± 2.3 kJ/mol [1]
CuO	44 ± 1 kJ/mol	53 ± 2 kJ/mol	44.2 ± 0.4 kJ/mol [2]
Cu_2O	-71 ± 1 kJ/mol	-19 ± 2 kJ/mol	-

- Ternary oxides

LiCuO	-71 ± 2 kJ/mol	-	
Li_2CuO_2	-27 ± 2 kJ/mol	1.2 ± 0.8 kJ/mol	

- Thermodynamic cycle → enthalpies of formation from oxides



[1] M. Wang, A. Navrotsky, Solid State Ion. 166 (2004) , [2] S.-N. Le, A. Navrotsky, V. Pralong, Solid State Sciences 10 (2008)

b) Enthalpies of formation

- Enthalpies of formation from the oxides at 25 °C

	700°C	800°C	Patat et al.
LiCuO	-11 ± 2 kJ/mol	-	-6.7 ± 2.27 kJ/mol
Li_2CuO_2	-23 ± 4 kJ/mol	-31 ± 4 kJ/mol	-26.65 ± 5.23 kJ/mol

- Enthalpies of formation from the elements at 25 °C

	700°C	800°C	Patat et al.
LiCuO	-395 ± 5 kJ/mol	-	-391 ± 7 kJ/mol*
Li_2CuO_2	-777 ± 10 kJ/mol	-786 ± 10 kJ/mol	-781 ± 15 kJ/mol*

* Expanded uncertainties (k=2, 95% confidence interval) calculated from reported uncertainties

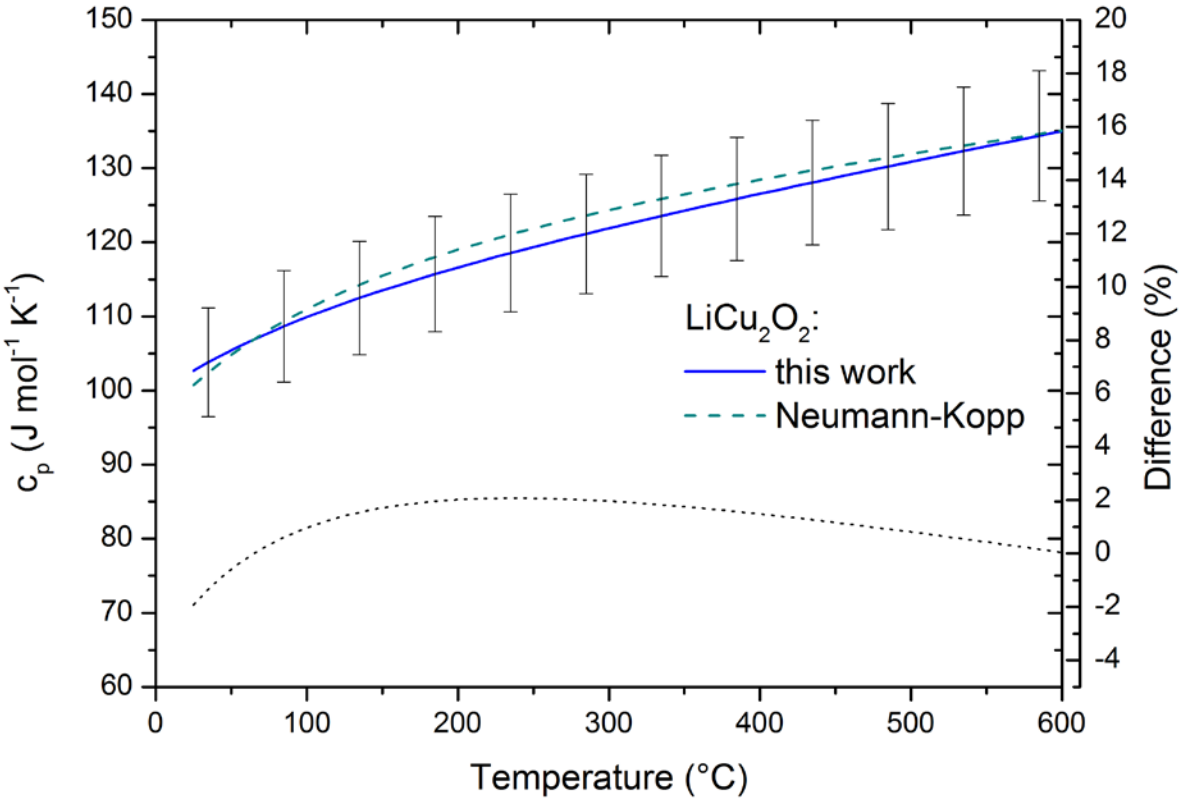
S. Patat et al., Solid State Ionics 1991, 46:325-329

c) Specific heat capacity of $LiCu_2O_2$

- Proof of applicability of Neumann-Kopp-Rule

$$c_p(\mathrm{LiCu_2O_2}) = c_p(\mathrm{CuO}) + {}^1/_2\, c_p(\mathrm{Cu_2O}) + {}^1/_2\, c_p(\mathrm{Li_2O})$$

- DSC 404 F1 (Netzsch)
  - 50-500 °C



M. Lepple et al., JPED 2014, 35: 650-657

d) Thermodynamic Modeling

Stochiometric phase (AB)

$$G(AB) = H_A^{SER} + H_B^{SER} + a + bT + cT\ln T + \ldots$$

Description via the reaction from the binary oxides

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Gibbs energy of reaction at 25 °C

Patat et al.

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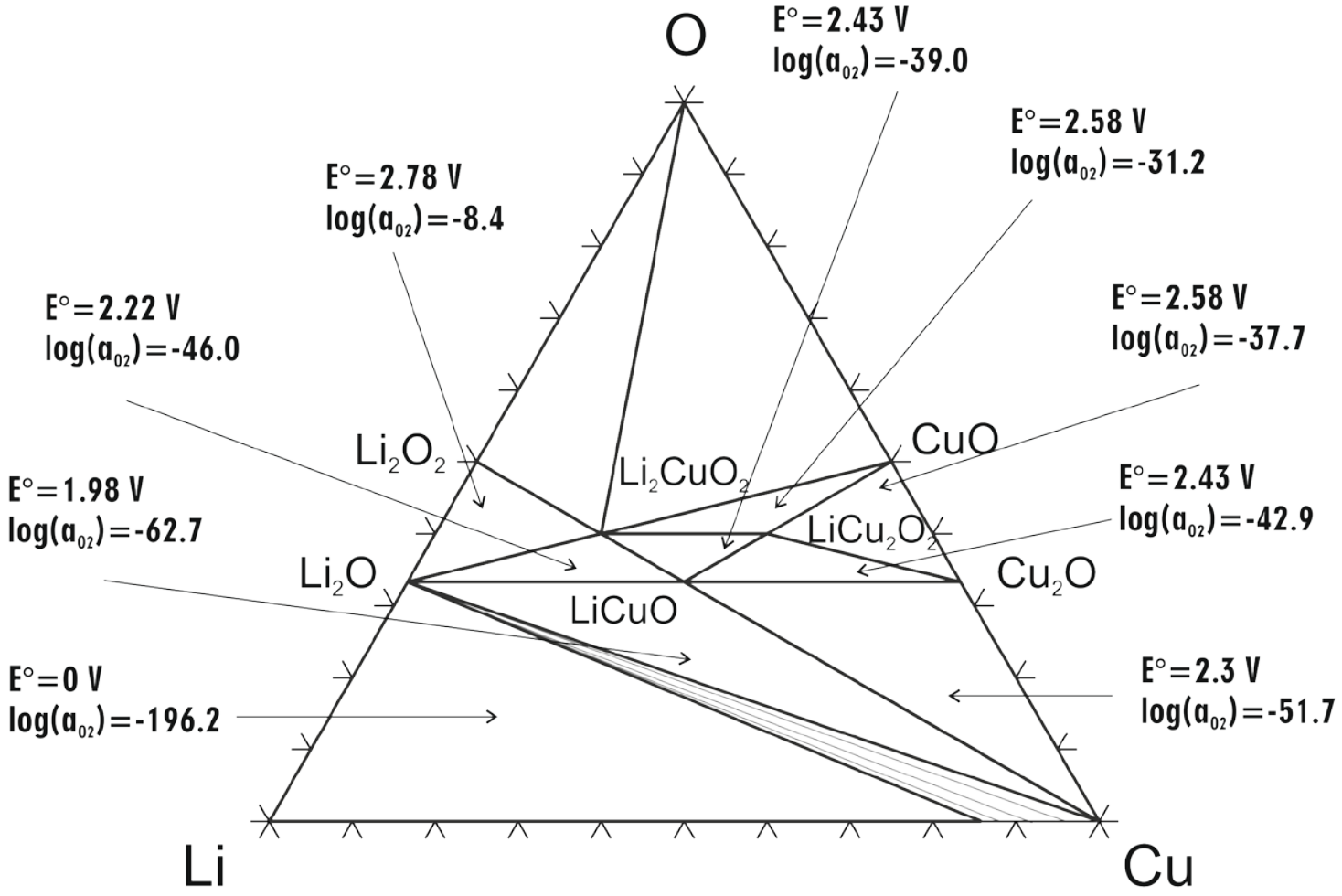
$$= \Delta_f G^o_{\mathrm{Li}_{2m}\mathrm{Cu}_{2n+p}\mathrm{O}_{m+n+p}} - \underbrace{m\Delta_f G^o_{\mathrm{Li_2O}} - n\Delta_f G^o_{\mathrm{Cu_2O}} - p\Delta_f G^o_{\mathrm{CuO}}}_{\text{Binary descriptions}}$$

Godshall

N.A. Godshall, Solid State Ionics 1986, 18&19:788-793 S. Patat et al., Solid State Ionics 1991, 46:325-329

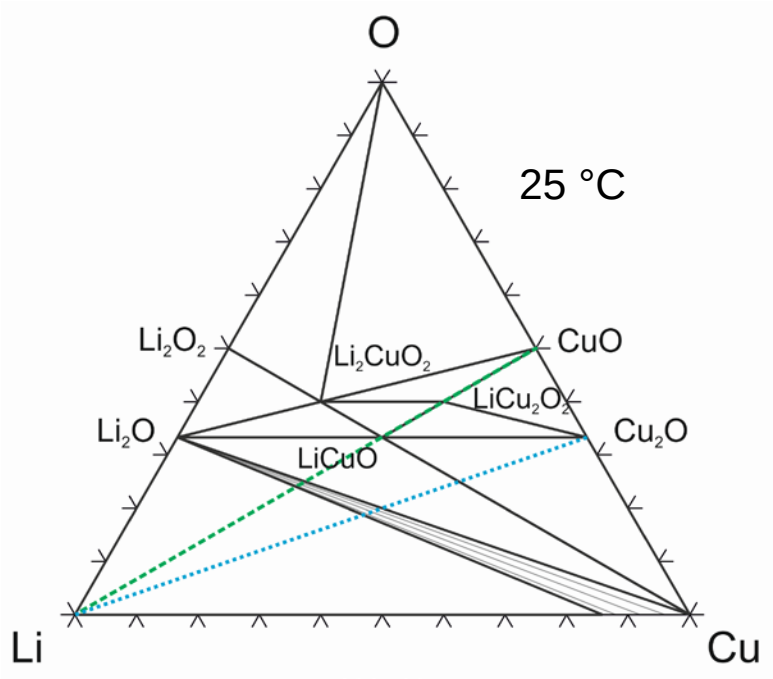
Calculated Li-Cu-O Diagram at RT

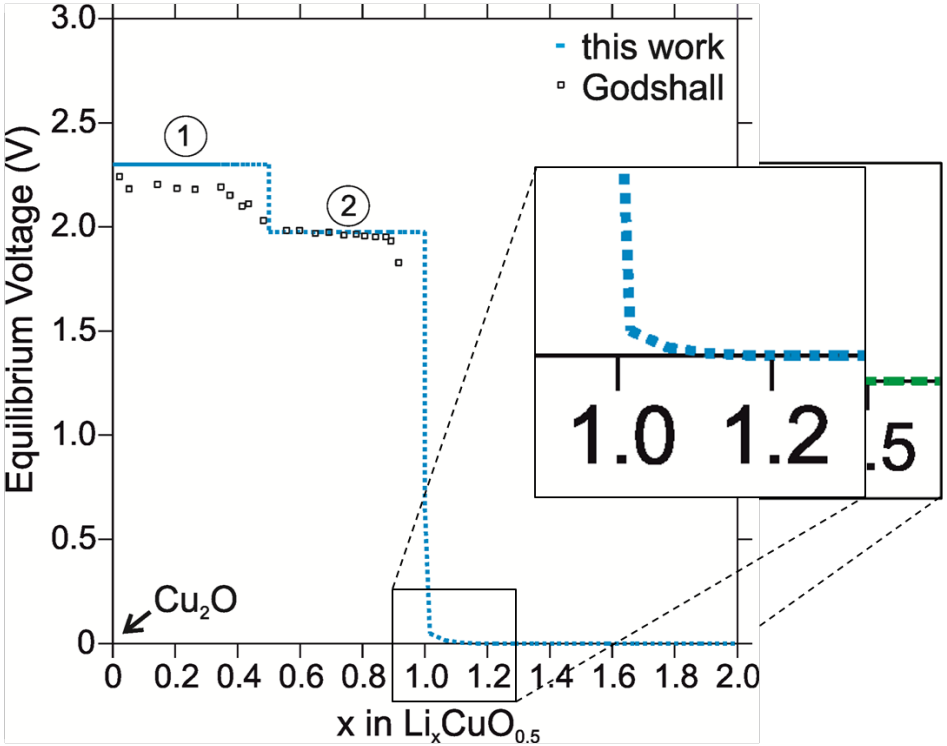


Titration Curve at RT

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

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





Conclusions

- High temperature solution calorimetry was used for getting enthalpy of formation data
- Calorimetric studies as base for Calphad-type work
- Calculations of Li-Mn-O and Li-Cu-O systems
- Calculation of coulometric titration curves
- Use of calculated data as input for thermal modelling of batteries

- Helmholtz Association, Portfolio and Alliance Programmes;
- BMBF STROM2

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

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