

# Thermodynamic Investigations in the Cu-Co-O System

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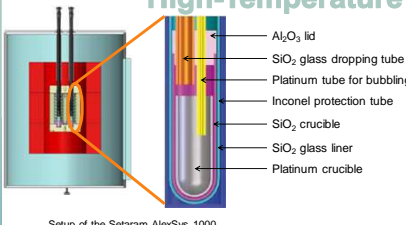
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Anode materials based on transition-metal oxides exhibiting the conversion mechanism are promising candidate electrodes for next generation lithium-ion batteries due to their high reversible capacities. In contrast to intercalation materials like  $\text{LiCoO}_2$ , the conversion mechanism is based on a complete phase transition of the participating materials  $\text{MX}_m + n \cdot e^- + n \cdot \text{Li}^+ \rightleftharpoons \text{M}^0 + n \cdot \text{LiX}_m$ , where M is a transition metal and X is O, N, F, S or P.

Electrochemical properties of lithium-ion batteries based on mixtures of  $\text{CuO}$  and  $\text{Co}_3\text{O}_4$  can be calculated and predicted using thermodynamic descriptions of the quaternary Li-Co-Cu-O material system<sup>(a)</sup>. Enthalpies of formation and heat capacities are important input data to develop thermodynamic descriptions of electrode material systems. In a first step, high-temperature calorimetry was used to determine the enthalpy of formation of  $\text{Co}_3\text{O}_4$  to clarify an existing contradiction in literature data. In a second step,  $C_p$ -measurements were performed using differential scanning calorimetry to confirm the  $C_p$ -data for  $\text{Co}_3\text{O}_4$ ,  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  in the literature.



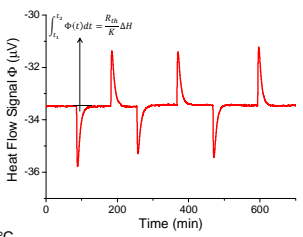
### High-Temperature Calorimetry



- Al<sub>2</sub>O<sub>3</sub> lid
- SiO<sub>2</sub> glass dropping tube
- Platinum tube for bubbling
- Inconel protection tube
- SiO<sub>2</sub> crucible
- SiO<sub>2</sub> glass liner
- Platinum crucible

Setup of the Setaram AlexSys 1000

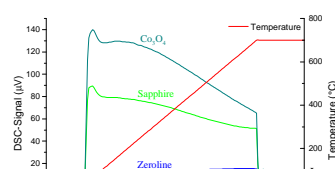
- AlexSys 1000 Calorimeter
- Isoperibolic Calvet Calorimeter operated at 700 °C
- Types of measurements performed:
  - Transposed Temperature Drop Calorimetry
  - No solvent
  - High-Temperature Oxide-melt Calorimetry
  - 3Na<sub>2</sub>O·4MoO<sub>3</sub> as solvent



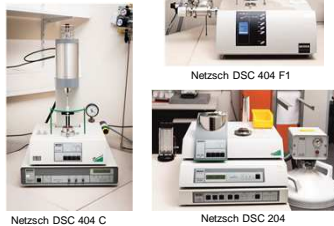
Drop solution measurement on AlexSys showing baseline and peaks. The peak area  $\int_{t_{\text{start}}}^{t_{\text{end}}} \Phi(t) dt$  is correlated to the enthalpy  $\Delta H$  by an experimentally determined calibration constant  $\frac{R_{\text{th}}}{K}$ .

### Differential Scanning Calorimetry

- Round robin heat capacity measurements using different calorimeters
- Evaluation of data following the 3 step method described by Gatta<sup>(b)</sup>
- Data fitting using the Maier-Kelley equation.



Measured curves for determining the heat capacity using the three step method.



Netsch DSC 404 F1  
Netsch DSC 404 C  
Netsch DSC 204

### Determination of Enthalpies of Formation

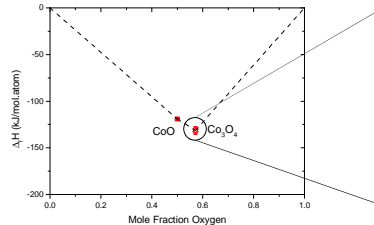
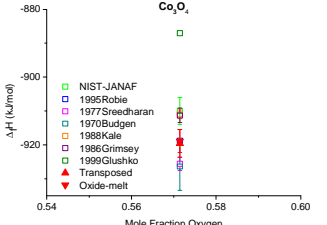
$$\frac{1}{2} \text{O}_2(g, 298.15\text{K}) + 3 \text{CoO}(s, 298.15\text{K}) \xrightarrow{\Delta_f H_{298.15\text{K}}} \text{Co}_3\text{O}_4(s, 298.15\text{K})$$

$$\Delta_f H(\text{CoO}) \quad \Delta_f H(\text{Co}_3\text{O}_4)$$

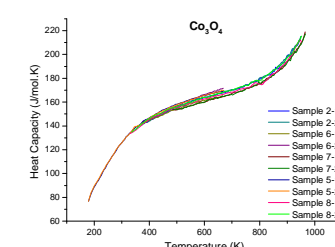
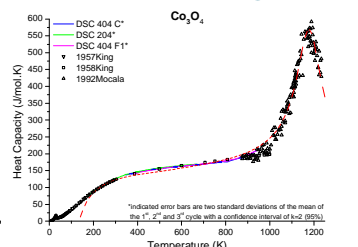
$$\frac{1}{2} \text{O}_2(g, 974.15\text{K}) + 3 \text{CoO}(s, 974.15\text{K}) \xrightarrow{\Delta_f H_{974.15\text{K}}} \text{Co}_3\text{O}_4(s, 974.15\text{K})$$

The enthalpy of oxidation of CoO and the enthalpy of formation of  $\text{Co}_3\text{O}_4$  were determined via thermodynamic cycles using transposed-temperature drop calorimetry and oxide-melt solution calorimetry. The values determined by the two different methods provide very similar results with a deviation of <0.5 %.

Results of the transposed-temperature drop measurements				Results of the oxide-melt solution calorimetry measurements			
$\Delta_f H(\text{CoO})$ (kJ/mol)	$\Delta_f H(\text{Co}_3\text{O}_4)$ (kJ/mol)	$\Delta_{\text{drop}} H$ (kJ/mol)	$\Delta_f H(\text{Co}_3\text{O}_4)$ (kJ/mol)	$\Delta_f H(\text{CoO})$ (kJ/mol)	$\Delta_f H(\text{Co}_3\text{O}_4)$ (kJ/mol)	$\Delta_{\text{drop}} H$ (kJ/mol)	$\Delta_f H(\text{Co}_3\text{O}_4)$ (kJ/mol)
-34.7 ± 1.2	112.1 ± 1.6	-205.3 ± 3.9	-919.6 ± 4.1	16.3 ± 0.7	264.7 ± 2.4	-204.7 ± 3.2	919.0 ± 3.4

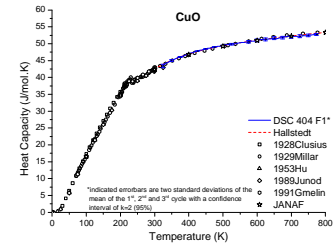
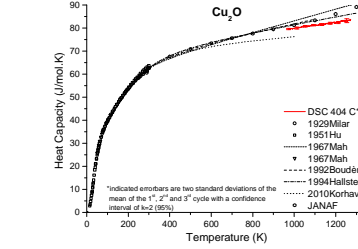



### Determination of the Heat Capacity

The heat capacity of  $\text{Co}_3\text{O}_4$  was measured from 173 K to 973 K. The data were averaged and fitted from 298 K to 750 K using the Maier-Kelley function  $C_p = A + BT + \frac{C}{T^2}$ . The data from 750 K to 973 K were fitted using a 5<sup>th</sup> order polynomial. The integrated heat increment  $H_{973\text{K}} - H_{298\text{K}} = 112.4 \frac{\text{kJ}}{\text{mol}}$  is in very good agreement with the data obtained from the transposed temperature drop measurements.

Resulting factors for the Maier-Kelley fits				
Compound	Temperature range (K)	A	B	C
$\text{Co}_3\text{O}_4$	298 K – 750 K	150.5 ± 1.3	0.0372 ± 0.002	-3.2 · 10 <sup>6</sup> ± 0.1 · 10 <sup>6</sup>
CuO	323 K – 773 K	51.27 ± 0.04	0.00385 ± 0.00006	-0.932 · 10 <sup>6</sup> ± 0.004 · 10 <sup>6</sup>
$\text{Cu}_2\text{O}$	973 K – 1273 K	66.26 ± 0.05	0.0116 ± 0.00004	-0.923 · 10 <sup>6</sup> ± 0.007 · 10 <sup>6</sup>

The heat capacity of  $\text{CuO}$  was measured<sup>(a)</sup> from 323 K to 773 K and the results are in very good agreement with literature. The heat capacity of  $\text{Cu}_2\text{O}$  from 973 K to 1273 K was directly measured<sup>(c)</sup> for the first time using DSC.

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<sup>(a)</sup>For thermodynamic modeling of conversion type electrodes see poster of M. Lepple et al. (Abstract Id. 1953, D3.3-P-TUE-P1-8).  
<sup>(b)</sup>G. della Gatta et al., Pure Appl. Chem. 78 (2006) 1455-1476.  
<sup>(c)</sup>M. Lepple et al., J. Phase Equilib. Diff. 35 (2014) 650-657.