

**Project 12: Thermodynamics and Kinetics for Stabilization of Conversion-Type Electrodes for LIB
 Based on Nano 3d Transition Metal Oxides**

**Sub-Project 3 „Thermodynamic Description of Stabilization of Nano-Materials in Conversion Type
 Electrodes in LIB”**

Electrodes based on the conversion mechanism for the electrochemical storage of lithium are promising for next-generation lithium ion batteries since they exhibit a high theoretical specific capacity (more than 700 mAh/g) and charge density compared to the commonly used and well-established intercalation-type electrodes^{1,2,3}. The difference between the mechanisms associated with conversion and intercalation-type electrodes is that for conversion-type electrodes, lithium ions react with the transition metal oxide at the cathode to form nano-particles of lithium oxide and the pure transition metal as shown in Figure 1, whereas during the intercalation process, lithium ions are incorporated into the host structure of the cathode material. Via the conversion mechanism, described by the following formula



where M is a transition metal and X is an anion (O, N, F, S, P), more than one unit charge per mole of lithium ions can be transferred during charge/discharge processes, which leads to a large theoretical capacity.

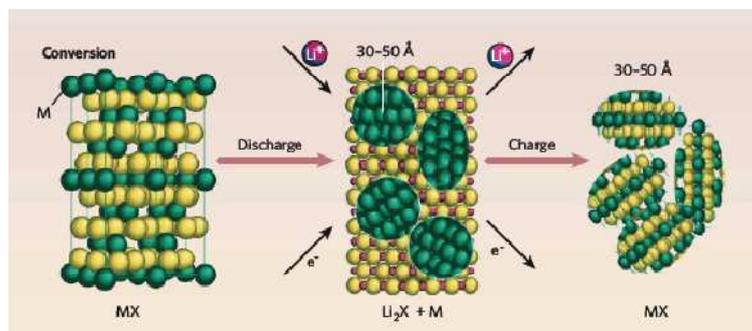


Figure 1: Schematic of the conversion reaction during discharge and charge of a lithium ion battery⁴.

The sub-project focuses on the thermodynamic description of the stabilization of nano-materials in conversion-type electrodes in lithium ion batteries. A battery relevant thermodynamic investigation of the Li-Cu-Fe-O conversion system should be performed. Experimentally determined thermodynamic data which is incorporated into the CALPHAD thermodynamic modeling of the system is used. The theoretical calculation of the open circuit voltage and chemical potential of lithium in the cathode materials should be validated using electrochemical measurements of self-assembled coin-cells.

¹ S. Grugéon, S. Laruelle, R. Herrera-Urbina, L. Dupont, P. Poizot and J-M. Tarascon, „Particle Size Effects on the Electrochemical Performance of Copper Oxides toward Lithium”, *Journal of The Electrochemical Society*, 2001, **148**, 285-292

² C. Chen, N. Ding, L. Wang, Y. Yu and I. Lieberwirth, „Some new facts on electrochemical reaction mechanism for transition metal oxide electrodes”, *Journal of Power Sources*, 2009, **189**, 552-557

³ J. Cabana, L. Monconduit, D. Larcher, M. R. Palacin, “Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reaction Through Conversion Reactions”, *Advanced Materials*, 2010, **22**, E170-E192

⁴ M. Armand, J.-M. Tarascon, „Building Better Batteries”, *Nature*, 2008, **451**:652-657

As a first step the ternary system Cu-Fe-O has been modeled using thermodynamic optimization. The dataset describes the system from 923 K to 1273 K. A calculated isothermal section is shown in Figure 2, which shows good agreement with experimental data from Yund and Kullerud⁵. Additionally, experiments were conducted to get insight into lower temperature transformations using DTA. The results were recently published⁶.

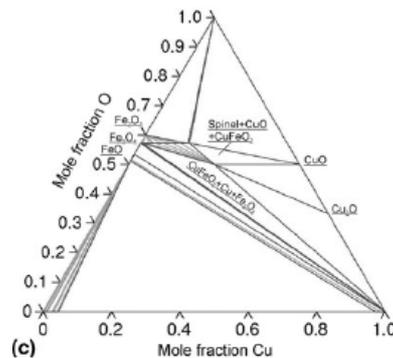


Figure 2: Calculated isothermal section at 1273 K and a total pressure of 1 atm.⁶

For calorimetric experiments (drop-in calorimeter and DSC) as well as battery tests, stoichiometric CuFe_2O_4 samples were prepared via sol-gel self combustion method^{7,8} and solid state reaction. The obtained powder from the sol-gel method has a crystallite size in the nm range (approx. 70 nm after an annealing treatment for 5 h at 400 °C) and is very porous. In collaboration with WG Gruner/Ehrenberg (sub-project 1) further stoichiometric nano-sized powder will be prepared with self-combustion and inverse emulsion reaction to determine thermodynamic differences of nano- and micro-sized materials.

Furthermore, critical literature evaluation of the missing binary and ternary systems of the Li-Cu-Fe-O system is done to set up datasets for assessment of these systems with the CALPHAD technique using the software THERMO-CALC.

⁵ R. A. Yund and G. Kullerud, "Stable Mineral Assemblages of Anhydrous Copper and Iron Oxides", *American Mineralogist*, 1964, **49**: 689-696

⁶ A. Khvan, O. Fabrichnaya, G. Savinykh, R. Adam and H. J. Seifert, "Thermodynamic Assessment of the Cu-Fe-O System", *Journal of Phase Equilibria and Diffusion*, 2011, **32**:498-511

⁷ M. Bomio, P. Lavela and J.L. Tirado, "Electrochemical Evaluation of CuFe_2O_4 samples obtained by Sol-Gel Methods Used as Anodes in Lithium Batteries", *Journal of Solid State Electrochemistry*, 2008, **12**:729-737

⁸ W. Gruner, J. Thomas, L. Giebeler, H. Ehrenberg and D. Wadewitz, "Interactions of Copper and Iron in Conversion Reactions of Nano- sized Oxides with Large Variations in Iron Copper Ratio", *Journal of The Electrochemical Society*, 2011, **158**: A1383-1392