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Linking of model and commercial active materials for lithium ion batteries by in-situ determination of thermodynamic and kinetic data

Introduction

Essential requirements for the development of high-performance lithium ion batteries include the knowledge of kinetic limitations and of the thermodynamic stability. The systematic studies envisaged here are based on a new technique to determine temperature and enthalpy of phase transformations as function of composition of the active materials while the lithium content is controlled in-situ. Thereby, piezoelectric transducers are used as thin film calorimeters. Those devices enable the depostition of thin films of interest and the simultaneous application of further methods such as X-ray diffraction and impedance spectroscopy. Microgravimetry and stable tracers with subsequent mass spectrometry are applied to investigate the kinetics and the routes of the transport. Materials of interest include conventional oxides of the system $Li(Co,Ni,M)O_2$ (M = Mn, Al) and new TiO_2/Si and MoS_2 compounds showing distinct microstructures due to preparation processes such as anodic oxidation. Based on the identification of the limiting transport step for lithium ions, modifications of the active surfaces or reduction of the diffusion lengths by tailoring the microstructure are intended. Further, the applicability of ionic liquids as electrolytes in combination with the above electrode materials is investigated.

Those data and, in particular, the microstructure of the electrodes form the basis to develop transport, defect chemical and thermodynamic models. Simultaneously, the data will be provided to the collaborators performing thermodynamic calculations.

The descriptions below shall give you a brief overview of the projects progress (January 2012), sorted by fields of work.

Langasite ($La_3Ga_5SiO_{14}$) microbalances as high temperature calorimeter for thin films

Piezoelectric transducer have been widely used as resonating sensors. The material of choice usually is quartz since it is cheap and easy to fabricate. But quartz crystals undergo a phase change at a temperature of 573 °C which leads to a loss of the piezoelectric properties. In langasite there is no such phase change. This material keeps its good piezoelectric properties up to a temperature of 1470 °C at which the crystal starts to melt. The wide range of temperature makes langasite an interesting candidate for calorimetric applications at high temperatures. Therefore the piezoelectric transducer, coated with the material of interest, is heated in a furnace, while the change of the resonance frequency is monitored. Langasite also enables the deposition of complete thin film batteries since thermal annealing of the layers (e.g. solid electrolyte) won´t destroy the piezoelectric crystal.

The system is successfully tested on several phase transitions (solid-solid, solid-liquid) of elements such as aluminium, tin, zink and silver. As an example Figure 1 shows the solid-liquid phase transition of aluminum. The next step is to extend the setup for complete processing in inert atmosphere. This extended setup is currently being tested and further developed.

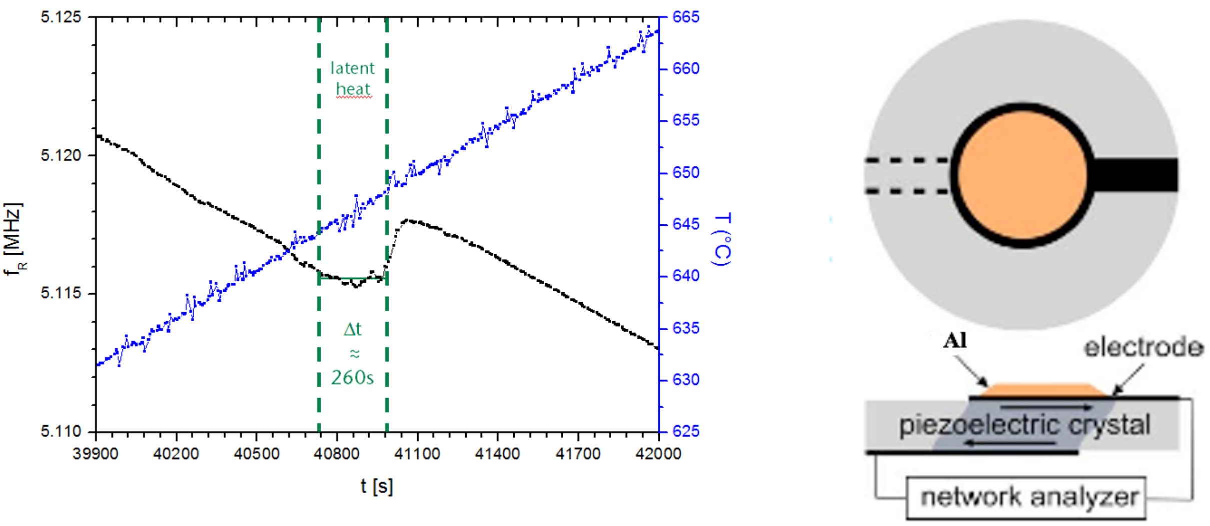

Fig.1 Calorimetric data of the solid-liquid phase transition of aluminum (left); schematic illustration of the setup (right)

Nano-crystalline molybdenum disulfide (MoS_2) as a high capacity anode material

MoS_2 has been investigated as an active electrochemical material for several years [10]. Like graphite MoS_2 is a layered compound, with sheets consisting of molybdenum atoms placed between two layers of sulfur atoms. The Van-der-Waals interactions between those sheets are, similar to graphite, very weak. This makes MoS_2 feasible as a solid lubricant and as an intercalation compound for lithium ions. As anode in lithium ion batteries MoS_2 has a theoretical capacity of over 1100 mAh/g (cf. graphite: 372 mAh/g). Besides the high capacity a key feature of molybdenum sulfide is the variability of morphologies. It can be prepared as bulk material, several nano crystalline powder variations and like graphite also nano-tubular depending on the synthesis route. These different morphologies allow to study the effect of size and form on the electrochemical (kinetic) as well as on the thermodynamic behavior without changing the material composition.

We have already tested several synthesis routes for the preparation of nano-crystalline MoS_2, characterized the materials (XRD, REM see figure 2) and started with the first cycling experiments (against metallic lithium). The next step is to collect electrochemical as well as thermodynamic data of several different MoS_2 systems for evaluation and analysis.

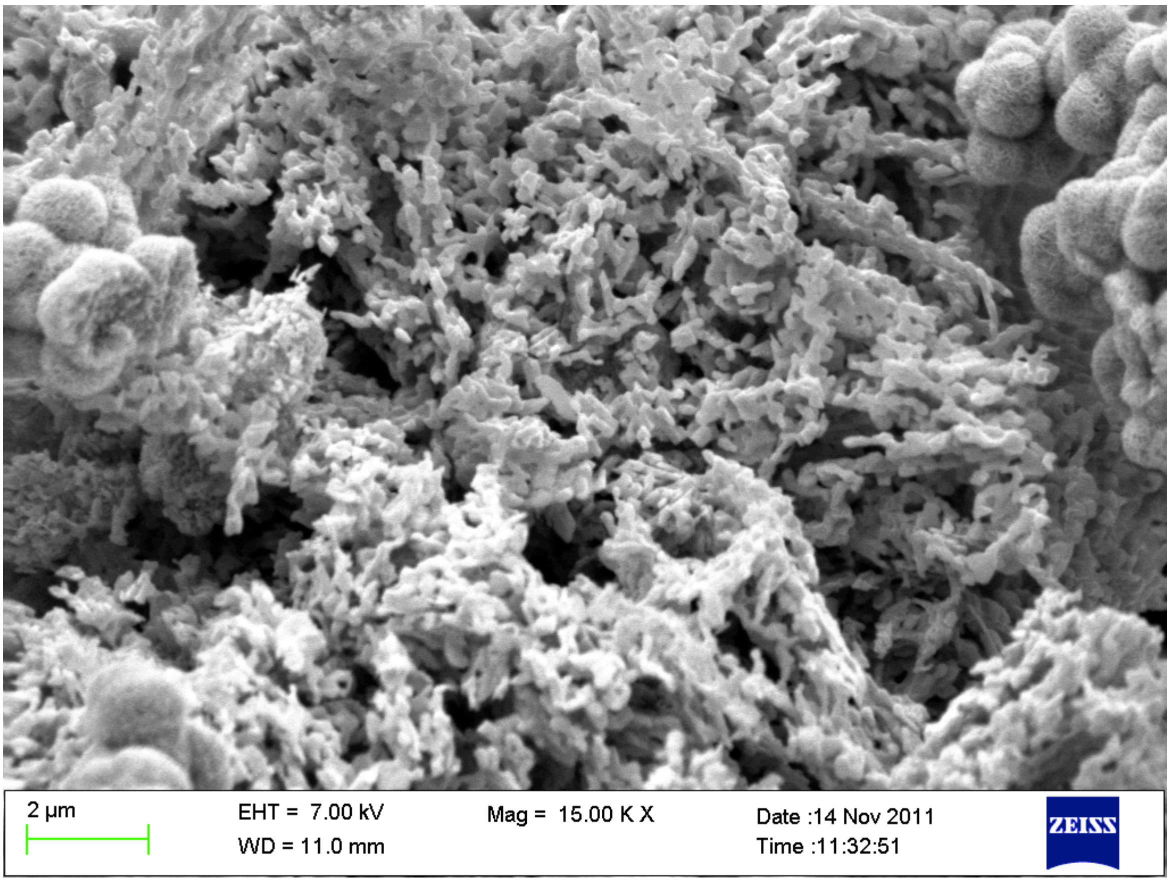

Fig. 2 SEM Image of nano-crystalline MoS2 Sample