

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

*[Joint Project 6.2]*

## Summary

Precise knowledge of the thermodynamic and calorimetric properties of the active materials used in lithium ion batteries is a key issue for the improvement of the entire system, considering especially lifetime and safety aspects. Currently, the role of thin-film batteries becomes more and more important. Here, it is crucial that thin film-electrodes behave, in general, differently compared to bulk electrodes. Therefore, conventional calorimetric techniques suitable for thin films at high temperatures must be developed. Presently, calorimetry on thin films is subject of various research approaches, but in general limited to temperatures below 350 °C. The challenge is now to combine both aspects, i.e. the calorimetry on thin films and the investigations in the high-temperature range. The latter must be extended far beyond the common operation range of lithium ion batteries to determine calorimetric data up to the synthesis temperatures. By this, information is gathered about the applicable thermodynamic process conditions a material can stand during battery production.

To overcome this challenge, the measurement technique Thin-Film Calorimetry (TFC) was developed during first funding period of WeNDeLiB priority program. In second period, the system will be optimized. It is based on high-temperature stable piezoelectric langasite ( $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ ) resonators, which serve as planar temperature sensor. The material enables to extend the measurement range up to about 1000 °C. As far as we know, this is

the only system existing with which direct access to calorimetric data of thin films is granted up to this temperature. It enables investigation of thin films including battery layer sequences. Thereby, even in-situ measurements during (de-)lithiation of thin-film cells are doable.

The systematic studies performed here are mainly based on this technique. Temperature and enthalpy of phase transformations are determined as function of composition of the active materials while the lithium content is controlled in-situ. Thereby, thin films deposited on piezoelectric transducers will be used which enables not only TFC, but also the simultaneous application of further methods such as X-ray diffraction and impedance spectroscopy. Microgravimetry and stable tracers with subsequent mass spectrometry will be applied to investigate the kinetics and the routes of the transport. Materials of interest include conventional oxides of the system  $\text{Li}(\text{Co},\text{Ni},\text{M})\text{O}_2$  ( $\text{M} = \text{Mn}, \text{Al}$ ) and new materials like Molybdenum Disulfide ( $\text{MoS}_2$ ) compounds showing distinct microstructures due to preparation processes. 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.

Those data and, in particular, the microstructure of the electrodes will form the basis to develop transport, defect chemical and thermodynamic models. Simultaneously, the data will be provided to the collaborators performing thermodynamic calculations. In the field of thin-film material characterization numerous TFC based collaborations were agreed within and outside the priority program.

The descriptions below shall give you a brief overview of the projects progress in the first funding period and its further development as it is intended for the second period. The topics are sorted by fields of work.

# Thin-Film Calorimetry (TFC)

(based on a high-temperature stable piezoelectric resonators)

## Device development: High-temperature calorimeter for thin-film applications

The newly developed measurement method, Thin-Film Calorimetry (TFC), is based on high-temperature stable planar temperature sensors. For these, piezoelectric langasite ( $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ ) microbalances, vibrating in thickness shear mode, are used.

Piezoelectric transducers 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 transformation at a temperature of 573 °C which leads to a loss of the piezoelectric properties. In langasite there is no such phase change up to the melting point of 1473 °C. The material keeps its good piezoelectric properties up to at least 1100 °C when damping starts to reduce signal quality. The wide range of temperature makes langasite a promising candidate for calorimetric applications, even at high temperatures.

The method is based on the monotonous temperature dependence of the resonance frequency of langasite resonators which is e.g. -200 Hz/K at 600 °C. By monitoring the change of resonance frequency as function of temperature or time, any deviations of the signal can be addressed to the investigated materials. These disturbances in frequency are correlated with a certain temperature increase (decrease) generated by an exothermic (consumed by an endothermic) phase transformation and can further be calculated to an amount of heat (see figure 1). By running the resonator in the microbalance mode prior and after deposition of the film of interest, the exact mass of the film can be accessed by the TFCsystem itself via using the Sauerbrey equation. Using these information, the enthalpies of the phase transformations, occurring in the thin films, can be determined.

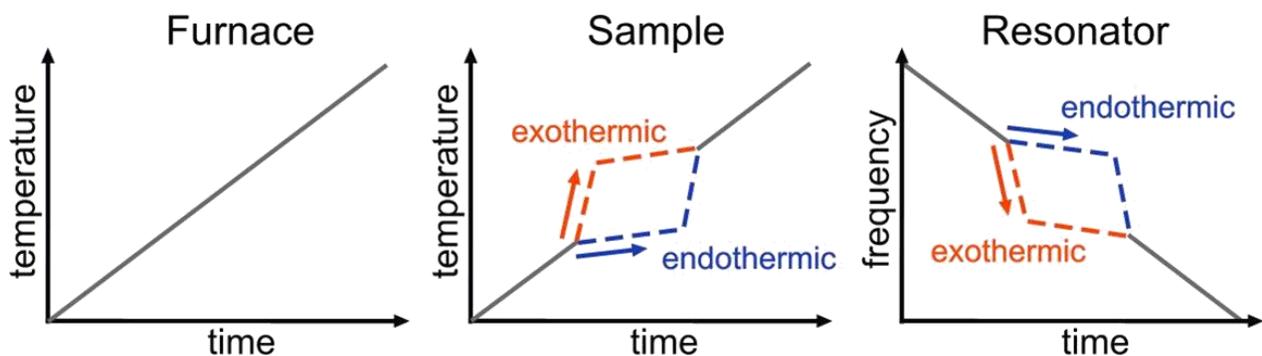


Fig. 1: Scheme of the TFC principle: Effect of a phase transformation during continuous heating of the furnace (left) and its effect on sample temperature (middle) and resonator's resonance frequency (right).

The resonators are provided with keyhole shaped platinum electrodes deposited via pulsed laser deposition (PLD). On top of these, the material of interest is deposited via varying routes (e.g. PLD, magnetron/ion beam sputtering ...). A scheme of the piezoelectric resonator is shown in figure 2. To get access to the calorimetric data, the piezoelectric transducer, coated with the material of interest, will be heated in a furnace, while the change of the resonance frequency is monitored.

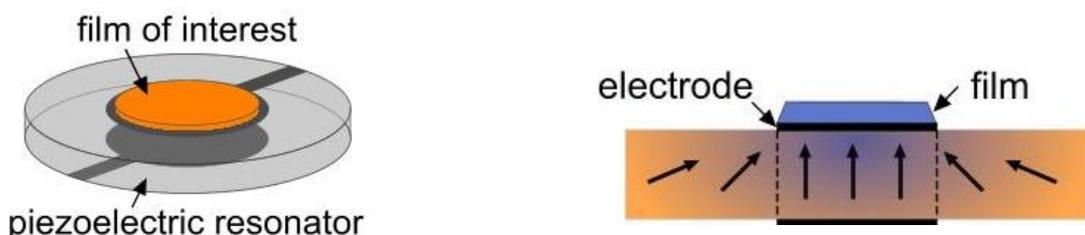


Fig. 2: (left) Scheme of the resonator coated with electrodes and the film of interest; (right) The heat flux inside a resonator is shown schematically. The active resonator volume between the metal electrodes is indicated by the dashed lines. For simplification, the scheme shows the film of interest on one side, only.

Battery materials require sample handling in inert atmospheres. In the first funding period, this is realized by constructing and developing systems for sample preparation (portable PLD chamber) and measurement (TFC setup) which are portable and gastight, so that they can be inserted into a glove box. For example, the targets for PLD are mounted to the holder inside a glove box. Subsequently, the deposition is performed under vacuum. The systems are shown in figure 3 and 4.

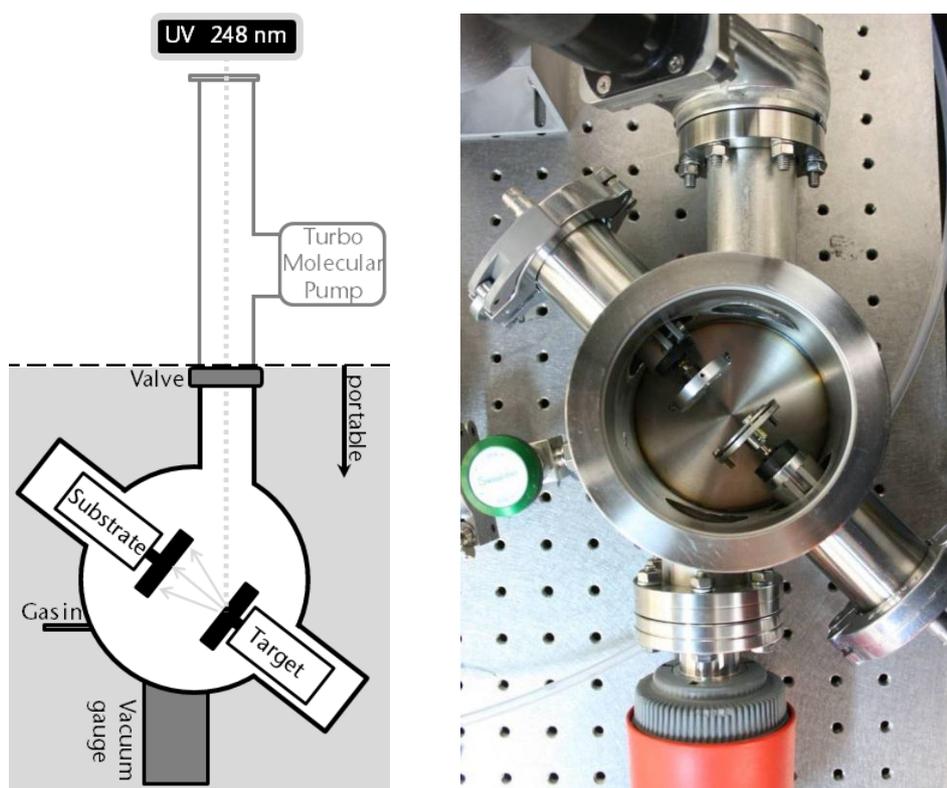


Fig. 3: Portable PLD chamber; (left) scheme; the gray shaded area is portable and can be transferred inside a glove box; (right) photograph of the portable part.

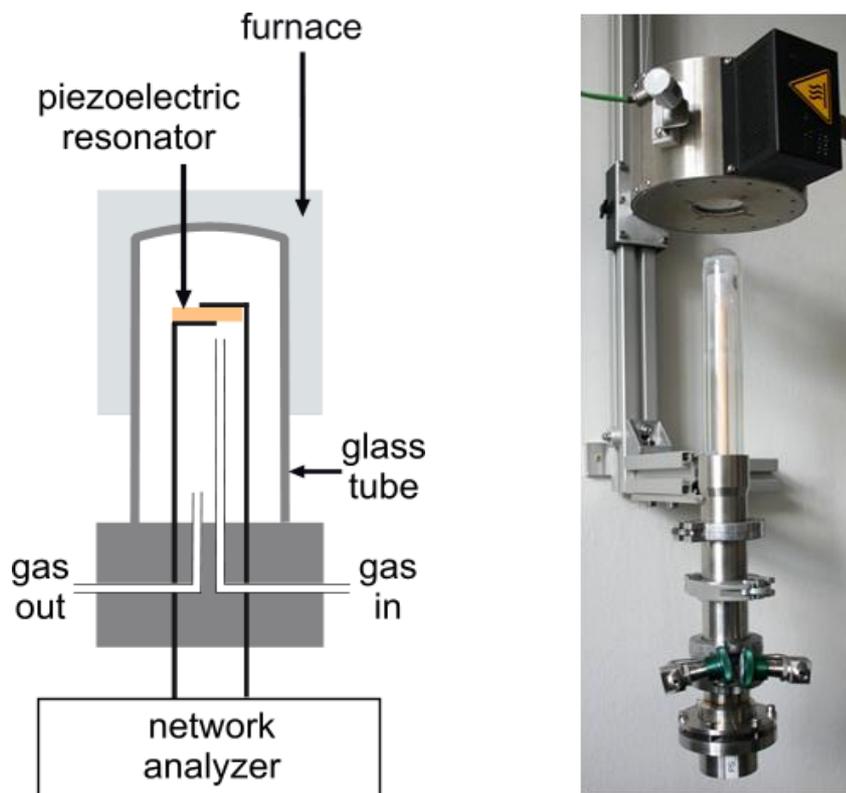


Fig. 4:  
TFC based on planar temperature sensors;  
(left) scheme;  
(right) photograph of the TFC system and vertical moveable tube furnace (up to 1000 °C).

The next step is to modify the setup to improve sensitivity. For example, the following modifications and improvements of the current TFC system are planned:

#### 1) Improved temperature control

Presently, the temperature control causes frequency fluctuations of the TFC resonators which correspond to an uncertainty in temperature determination of about  $\pm 0.2$  K. Further, a distinct period is found as visualized in figure 5. Those fluctuations disturb the data evaluation. In particular, it is difficult to determine the exact temperature where a phase transformation starts. In order to solve the problem and to minimize electromagnetic fields, a DC power supply with an improved control algorithm should be purchased and installed.

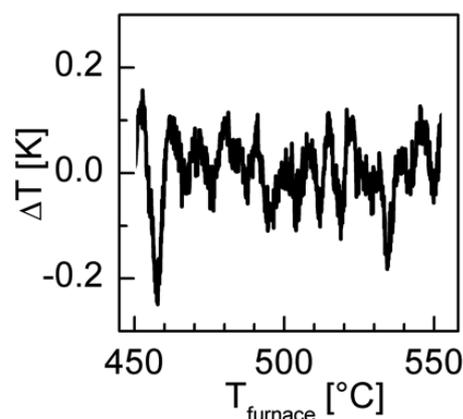


Fig. 5:  
Temperature fluctuations of the resonator while applying a constant heating rate of 1.2 K/min.

## 2) Calibration of the thermal capacity of the resonator/film arrangement

Quantitative determination of the enthalpy occurring during phase transformation requires a calibration of the resonator devices. Thereby, a heater structure deposited via mesh printing on the back side of a resonator should enable to apply well defined amounts of energy by electrical heating (I in figure 6). If this is done in the vicinity, but not at the phase transformation temperature, the impact of small amounts of heat on the resonance behaviour can be studied and compared with the effect caused by phase transformations.

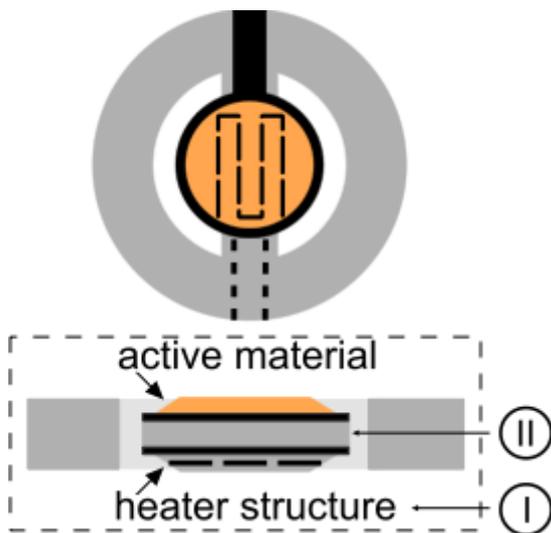


Fig. 6: Improved design of piezoelectric resonators to determine phase transformations.



Fig. 7: Freestanding resonator prepared by ultrasonic milling.

## 3) Improved resonator response

The application of thin freestanding resonators is planned (II in figure 6). They show higher resonance frequencies which goes along with higher temperature coefficients of the resonance frequency and lower the heat capacities. Both effects improve the ability to detect small enthalpies. Those resonators are machined using a CNC ultrasonic mill. Such a resonator is shown in figure 7.

## 4) Determination of the specific heat of langasite

Precise knowledge of the exact specific heat for each temperature is crucial for the exact determination of enthalpies. Therefore, precise characterization with the exact resonator material, used in this project, is intended via simultaneous thermogravimetric analysis (STA).

## Material characterization

The system was successfully tested on several phase transformations (solid-solid, solid-liquid) of well-known elements such as aluminum, tin, zinc and silver. As an example, figures 8 and 9 show the solid-liquid phase transformation of tin.

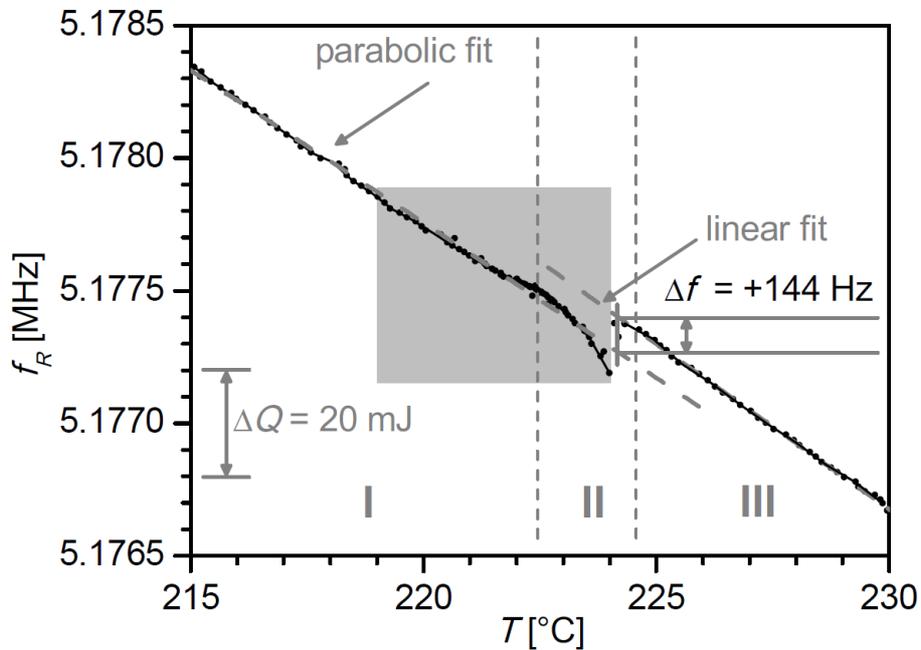


Fig. 8: TFC diagram in the vicinity of the melting point of tin. Section I: Parabolic decrease of the frequency due to external heating [in  $\gamma$ -phase]. Section II: Formation of the melt. Section III: Further frequency decrease after formation of liquid tin.

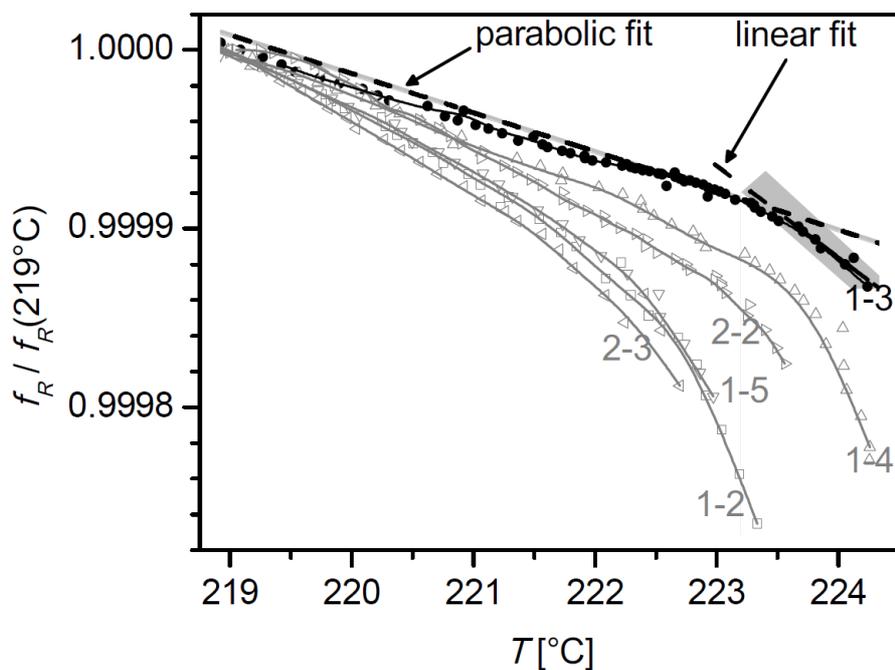


Fig. 9: TFC diagram in the vicinity of the melting point of tin for several measurements and samples. Here, the gray shaded area from figure 8 is enlarged.

Thin-Film Calorimetry on battery materials has been performed on several cathode materials (e.g. NCA, LMO), anode materials ( $\text{MoS}_2$ , Sn) and solid electrolytes (LVSO, LiPON). Other materials are going to be evaluated in the second funding period, mostly in close collaboration with partners of the WeNDeLIB priority program (see section “TFC based collaborations”). Especially noteworthy is the collaboration with Ulrich (Karlsruhe, JP 3.3) on lithium manganese oxide (see figure 10) which led to two joined publications [1,2].

Langasite resonators also enable the deposition of complete all-solid-state electrochemical thin-film cells since thermal annealing of the layers (e.g. for achieving crystallographic order in electrodes or solid electrolyte) does not destroy the piezoelectric crystal. Therefore, the next step is to build up an operational battery cell composed out of the materials mentioned above.

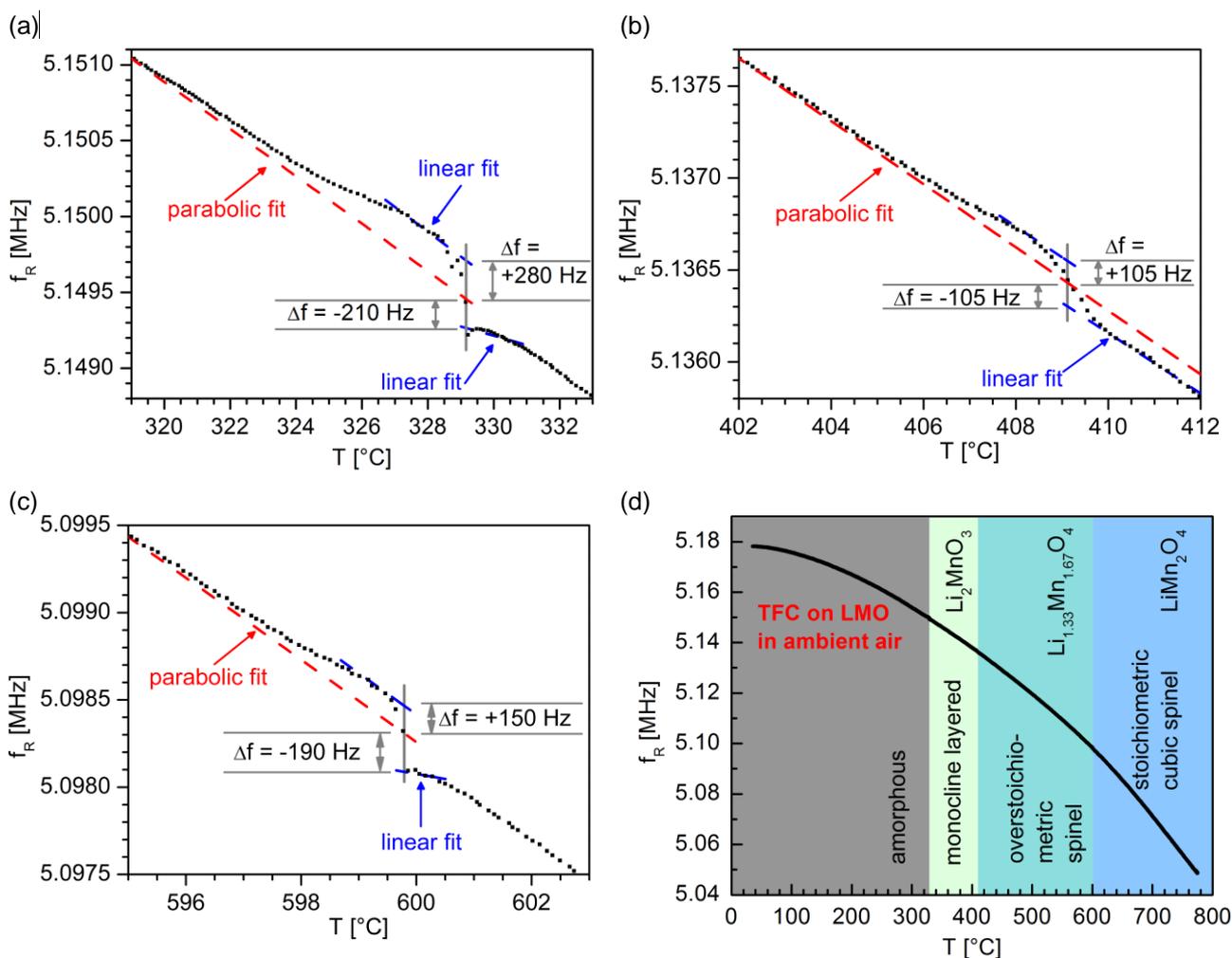


Fig. 10: TFC measurement of lithium manganese oxide (LMO), carried out in ambient air, shows three phase transformations. The according phase of crystallization is determined by X-ray diffraction and Raman spectroscopy. (a) TFC diagram in the vicinity of the crystallization point of LMO, crystallization in monocline layered  $\text{Li}_2\text{MnO}_3$ ; (b) TFC diagram of the phase transformation from monocline layered  $\text{Li}_2\text{MnO}_3$  (rock salt structure) to the overstoichiometric spinel  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ ; (c) TFC diagram of the phase transformation from overstoichiometric spinel  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  to the stoichiometric cubic spinel  $\text{LiMn}_2\text{O}_4$ ; (d) Phases of the LMO thin film. The structural changes and resonance frequency over temperature are given.

## TFC based collaborations

The newly developed TFC system attracted increasing interest within and outside the priority program and is the base for numerous collaborations. Since the current TFC capacity is limited, some of them could be initiated, only. In order to overcome that bottleneck, a second TFC system will be build at the beginning of the second funding period. The following list of collaborations was agreed:

- *Ulrich (Karlsruhe): Li-(Mn+Me)-Oxide, Me = Ni, Al, ... (JP 3.3)*  
Langasite resonators are coated with the active materials by magnetron sputtering in Karlsruhe and subsequently characterized in Clausthal by TFC in different atmospheres (ambient air, pure Ar, ...). In parallel, reference samples are investigated by XRD and Raman spectroscopy in Karlsruhe to identify the phases belonging to the phase transformations.
- *Cupid (Karlsruhe): Li-(Mn+Me)-Oxide, Me = Ni, Al, ... (JP 4.1)*  
The experimental results of the collaboration with Ulrich will be correlated with thermodynamic calculations performed by the Cupid group.
- *Seifert (Karlsruhe): Li-Cu-Fe-O (JP 12.3)*  
Different compositions of Li-Cu-Fe-O are synthesized via self-combustion in Karlsruhe. Subsequently, PLD targets are prepared and used to coat resonators in Clausthal. The TFC analysis is accompanied by structural characterizations in Clausthal and Karlsruhe to identify the phases.
- *Schmitz (Münster): LiPON, LFP–LiPON–Sn all-solid-state cell (JP 13.2)*  
Resonators, prepared in Clausthal, are coated with thin-film all-solid-state cells (LiFePO<sub>4</sub>-LiPON-Sn) via ion beam sputtering in Münster. TFC on these cells is performed at different temperatures. Cycling of these batteries is planned. Preliminary tests with the solid electrolyte LiPON are performed as well. The collaboration in this field will be intensified in the second period within the focus group Thin-film battery technology.
- *Mertens (Freiberg): Li<sub>1-x</sub>FePO<sub>4</sub> (JP 10.3)*  
Lithium iron phosphate in different lithiation states is synthesized at Freiberg. Using these powders several PLD targets are prepared. Thin films of these samples are investigated via TFC to identify the temperature of the two-phase formation (LiFePO<sub>4</sub> ↔ FePO<sub>4</sub>) as function of the Li content. Additionally, smooth Li<sub>1-x</sub>FePO<sub>4</sub> films will be deposited via PLD in Clausthal to perform contact angle measurements in Freiberg.

- Ludwig (Bochum):  $\text{LiFePO}_4$ ,  $\text{LiFe}_{1-x}(\text{Al/Ni/...})_x\text{PO}_4$  (JP 11.2)*

Langasite resonators are coated with the active materials by sputter deposition in Bochum and subsequently characterized in Clausthal by TFC in different atmospheres (ambient air, pure Ar, ...). It shall be studied, if the effect of two-phase formation is present only in  $\text{LiFePO}_4$ , or as well in the doped materials.
- Seifert, Rohde (Karlsruhe): HT-stable solid electrolytes*

Resonators are coated with solid electrolytes that are presumed to be high-temperature stable by magnetron sputtering in Karlsruhe. TFC is performed in Clausthal to investigate the operation limits. One of the materials chosen here is lithium vanadium silicon oxide (LVSO). In future tests other promising solid electrolytes will be chosen in Karlsruhe and investigated in Clausthal.
- Rettenmeyer (Jena):  $\text{LiC}_6$  and  $\text{Li}_2\text{C}_2$  (JP 9.1)*

$\text{LiC}_6$  and  $\text{Li}_2\text{C}_2$  are synthesized in Jena. Related PLD targets are prepared in Clausthal and Jena. The data obtained by TFC in Clausthal will be compared to DSC measurements performed in Jena.
- Bund (Ilmenau): NMC and NMCA (JP 6.1)*

Li-Ni-Mn-Co-O and Li-Ni-Mn-Co-Al-O powders of varying stoichiometry are synthesized via self-combustion in Ilmenau. Subsequently, TFC is performed to investigate the thermodynamic stability as function of the material composition.
- Pecquenard (Bordeaux, France): all-solid-state cells*

Preparation of thin-film batteries to be characterized by the TFC.

## Nano-crystalline molybdenum disulfide ( $\text{MoS}_2$ ) as high capacity anode material

$\text{MoS}_2$  has been investigated as an active electrochemical material for several years. Like graphite  $\text{MoS}_2$  is a layered compound, with sheets consisting of molybdenum atoms placed between two layers of sulfide atoms. The Van-der-Waals interactions between those sheets are, similar to graphite, very weak. This makes  $\text{MoS}_2$  feasible as a solid lubricant and as an intercalation compound for lithium ions. As anode in lithium ion batteries  $\text{MoS}_2$  has a theoretical capacity of over 1100 mAh/g (cf. graphite: 372 mAh/g). Besides the high capacity a key feature of molybdenum disulfide 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 effects of size and form on the electrochemical (kinetics) 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  $\text{MoS}_2$ , characterized the results (XRD, SEM see figure 11) 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  $\text{MoS}_2$  systems for evaluation and analysis.

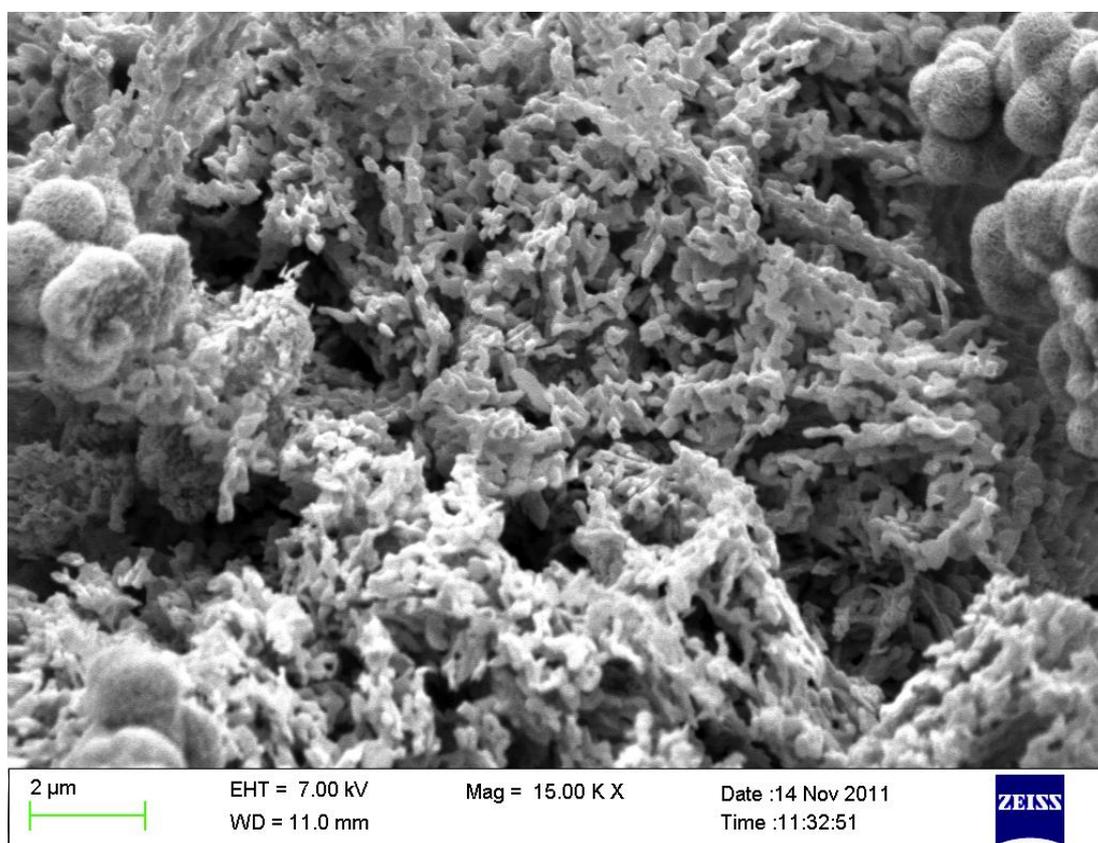


Fig. 11 SEM image of nano-crystalline  $\text{MoS}_2$  sample.

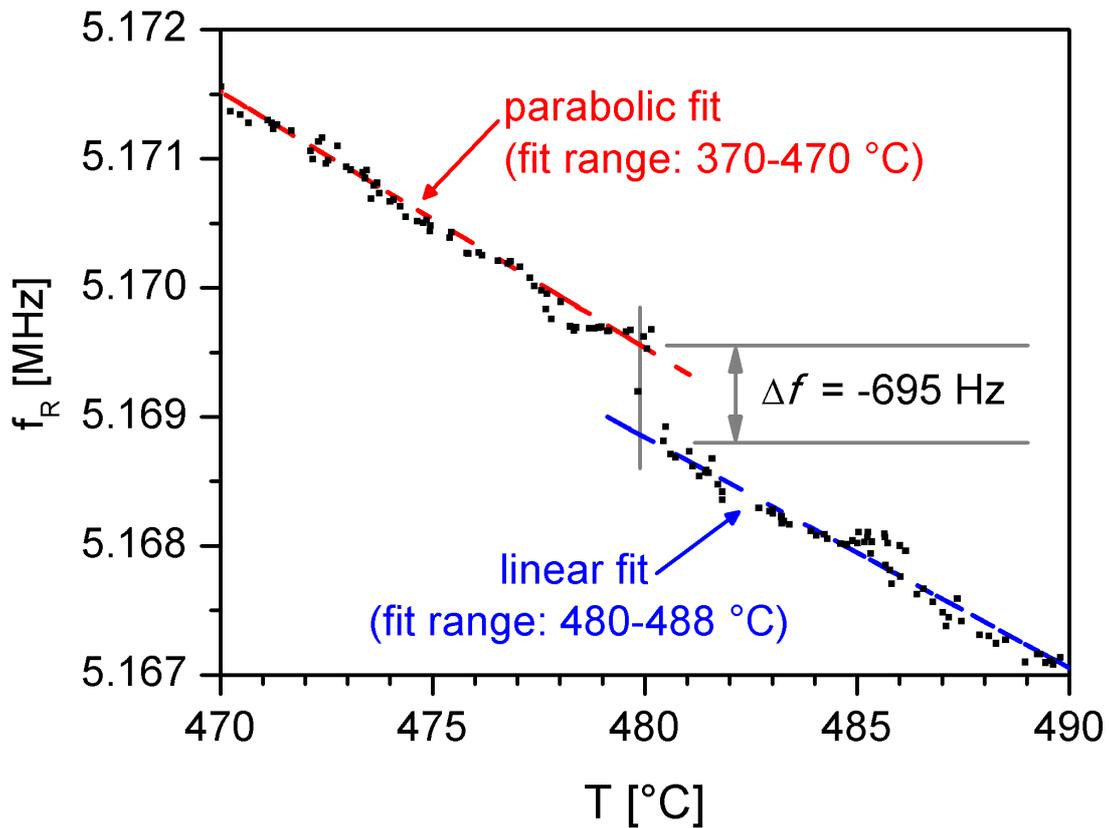


Fig. 12: TFC diagram of the partial crystallization of a thin  $\text{MoS}_2$  thin film, deposited via PLD.

### Molybdenum Disulfide/CNT composites as high capacity active material

Molybdenum disulfide ( $\text{MoS}_2$ ) nanostructures are potential candidates to replace graphite in the anodes of next generation lithium-ion batteries (LIB). This material exhibits two lithiation mechanisms. If a  $\text{MoS}_2$  containing half-cell is operated at potentials above 1 V vs.  $\text{Li/Li}^+$ , the material works as intercalation compound. If the potential is set to values below 1 V, a conversion reaction takes place resulting in a lithium-sulfur electrode with reversible capacities of over 1000 mAh/g. Like in most conversion type electrodes the major drawback of this operation mode is its bad cycling stability due to a loss of electrical contact during repeated cycling.

In this project we synthesized and tested different  $\text{MoS}_2/\text{CNT}$  composites as active materials to address these stability issues. The CNTs provide a mechanically stable conducting network, thereby minimizing the amount of “dead”, i.e. non-contacted active material. Furthermore the mechanical stability of the CNT network is supposed to tolerate the mechanical stress resulting during repeated cycling.

A hydrothermal route is chosen for the synthesis of the nanoparticles since it does not require neither high temperatures nor toxic or expensive reactants. Characterization is performed for three different weight ratios of CNT/MoS<sub>2</sub>: 1/10, 1/100 and 1/1000.

Electrical characterization of the material by impedance spectroscopy shows an increase in conductivity by several magnitudes of the powder mixtures with respect to MoS<sub>2</sub> even for low CNT additions. Electrochemical tests performed in lithium half-cells exhibit capacities of over 800 mAh/g, which is more than twice as much as the standard carbon anode. Cyclic voltammetry measurements confirm the multi step reaction mechanism during the first lithiation cycles. It can be derived from these measurements that the MoS<sub>2</sub> in the electrode almost completely reacts to Li<sub>2</sub>S and molybdenum within the first 5 cycles. In the following cycles the molybdenum is working as catalyst for the reversible lithium sulfur reaction.

## Project related publications

### Thin-Film Calorimetry

- [1] Hendrik Wulfmeier, Daniel Albrecht, Svetlozar Ivanov, Julian Fischer, Sven Ulrich, Andreas Bund, Holger Fritze, **High-Temperature Thin-Film Calorimetry – A Newly Developed Method Applied to Lithium Ion Battery Materials**, Journal of Materials Science 48 (2013) 6585-6596, DOI: 10.1007/s10853-013-7455-x
- [2] Hendrik Wulfmeier, Daniel Albrecht, Svetlozar Ivanov, Julian Fischer, Rolf Grieseler, Peter Schaaf, Sven Ulrich, Andreas Bund, Holger Fritze, **Thin Film Calorimetry - Device Development and Application to Lithium Ion Battery Materials**, Materials Research Society Symposium Proceedings Vol. 1496 (2013), DOI: 10.1557/opl.2013.104
- [3] Hendrik Wulfmeier, Daniel Albrecht, Holger Fritze, Svetlozar Ivanov, Andreas Bund, **Messsystem zur Bestimmung thermodynamischer Eigenschaften dünner Schichten bei hohen Temperaturen**, Proceedings 11. Dresdner Sensor Symposium, Dresden/Germany, 2013-12-09 – 2013-12-11 (2013) 34-39, DOI: 10.5162/11dss2013/2.2, ISBN: 978-3-9813484-5-3

### Molybdenum disulfide

- [4] Daniel Albrecht, Hendrik Wulfmeier, Svetlozar Ivanov, Andreas Bund, Holger Fritze, **Electrochemical Performance of Ionic Liquid - Molybdenum Disulfide Li-Ion Batteries**, Journal of Applied Electrochemistry 43 (2013) 559–565, DOI: 10.1007/s10800-013-0548-z
- [5] Daniel Albrecht, Hendrik Wulfmeier, Svetlozar Ivanov, Andreas Bund, Holger Fritze, **Synthesis of Different Molybdenum Disulfide Nanostructures and their Applicability in Lithium Ion Batteries with Ionic Liquid Electrolytes**, Materials Research Society Symposium Proceedings Vol. 1496 (2013), DOI: 10.1557/opl.2013.126