

## **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 deposition 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  $\text{Li}(\text{Co},\text{Ni},\text{M})\text{O}_2$  ( $\text{M} = \text{Mn}, \text{Al}$ ) and new [TiO<sub>2</sub>/Si](#) and [MoS<sub>2</sub>](#) 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 ( $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ ) 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  $573\text{ }^\circ\text{C}$  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  $1470\text{ }^\circ\text{C}$  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.

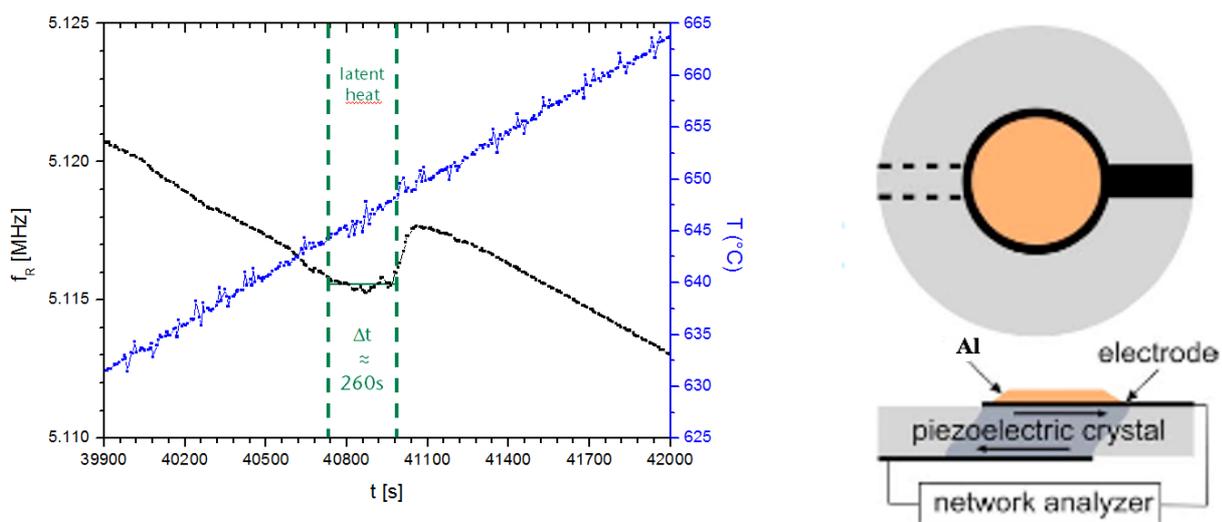


Fig.1 Calorimetric data of the solid-liquid phase transition of aluminum (left); schematic illustration of the setup (right)

## Nano-crystalline molybdenum disulfide (MoS<sub>2</sub>) as a high capacity anode material

MoS<sub>2</sub> has been investigated as an active electrochemical material for several years [10]. Like graphite MoS<sub>2</sub> 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<sub>2</sub> feasible as a solid lubricant and as an intercalation compound for lithium ions. As anode in lithium ion batteries MoS<sub>2</sub> 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<sub>2</sub>, 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<sub>2</sub> systems for evaluation and analysis.

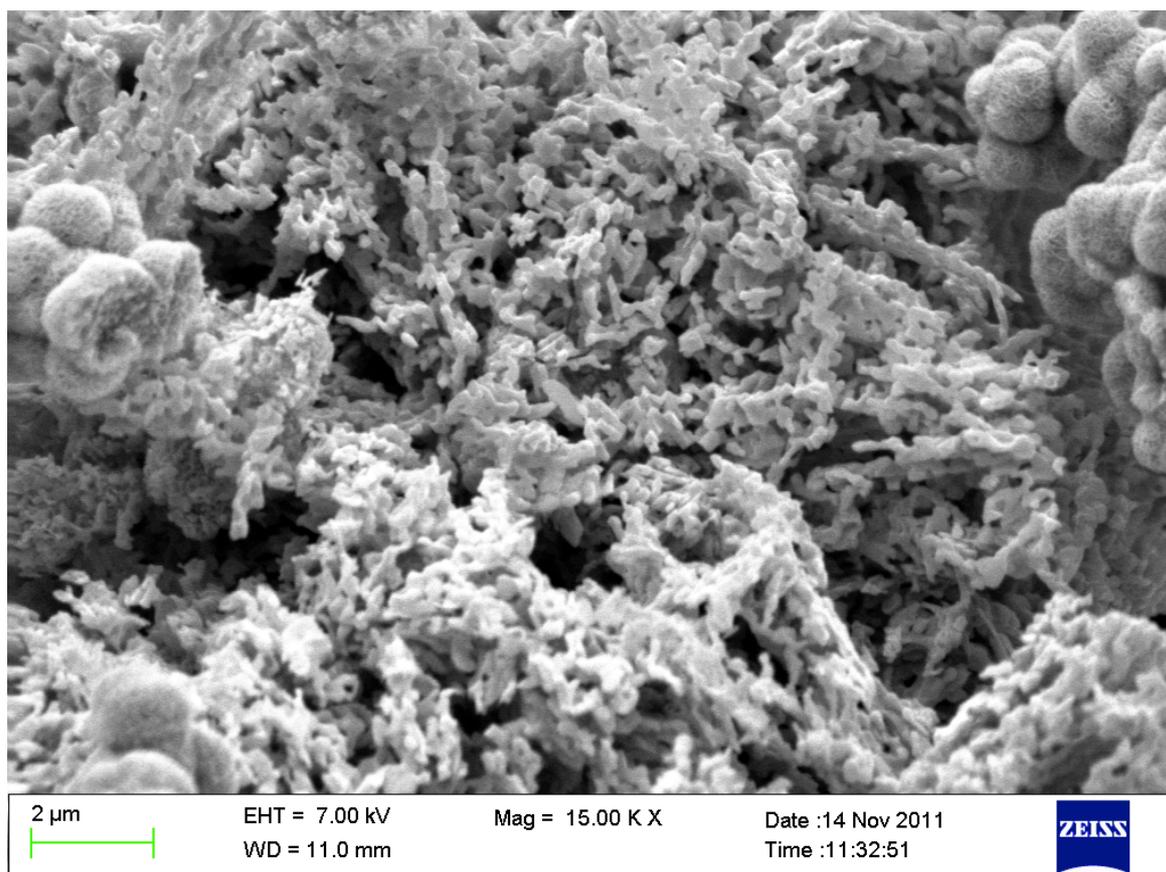


Fig. 2 SEM Image of nano-crystalline MoS<sub>2</sub> Sample

# TiO<sub>2</sub> – Amorphous Silicon Nano-porous Structures as Novel Anode Materials for Energy Storage Applications

## Research motivation and literature overview

Titania (TiO<sub>2</sub>) has been intensely investigated as a potential anode material for lithium-ion batteries. It has been concluded that because of its good electrochemical stability and high operating voltage TiO<sub>2</sub> has a promising future in Li-ion battery technology.

The high working potential of materials like LiMn<sub>2</sub>O<sub>4</sub>, olivine, LiM<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (M= Ni, Co) and LiCoPO<sub>4</sub> makes possible a combination with a high voltage anode material, such as TiO<sub>2</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> [1] By introducing high voltage anode materials like TiO<sub>2</sub> the risk of battery overcharging is reduced, avoiding the growth of metallic Li dendrites during the Li ion insertion and corresponding thermal runaway of the battery [1]. A cell built according to this concept belongs to the category of third generation Li-ion batteries. An additional advantage of TiO<sub>2</sub> is that it is non-toxic, low-cost and is easily available in various modifications.

It is known that the basic disadvantage of TiO<sub>2</sub> is its comparatively low capacity for lithium ion insertion – an essential parameter needed for a good battery performance. Similarly to many other materials TiO<sub>2</sub> modifications such as anatase, rutile, hollandite, and TiO<sub>2</sub>-B, would be more attractive anodes if, in nanoparticulate form, they could accommodate lithium reversibly and rapidly.

The properties of TiO<sub>2</sub> electrodes may improve dramatically when the material is porous because of a large surface area and open structure. A number of different approaches have been applied in order to obtain nano-porous TiO<sub>2</sub>. One is Ti anodization, performed in fluoride containing media [2-4]. By this method the obtained TiO<sub>2</sub> layer consists of self-organized nano-tubes with adjustable length and diameter and large active surface. Besides the large surface area the advantages of the TiO<sub>2</sub> nanoporous structure are that the TiO<sub>2</sub> thickness and amount can be regulated by the duration of the anodization process; the Ti/TiO<sub>2</sub> system combines a current collector (Ti) and the active material (TiO<sub>2</sub>) with no binders and additives necessary. One additional positive side effect is that TiO<sub>2</sub> nano-pores obtained by anodization are amorphous. It is known that amorphous TiO<sub>2</sub> in many experimental cases has a higher capacity than the crystalline one. If needed it can be transformed to a crystalline form (anatase or rutile) by annealing [4].

In order to obtain a material having better performance many active materials, including TiO<sub>2</sub> are applied in a form of nano-composites together with other active materials [5]. One of the possibilities for TiO<sub>2</sub> modification is Si. Si is a potentially promising anode material for Li-ion batteries, having very high capacity 4200 mAhg<sup>-1</sup> for the formation of the Li-Si alloy [6, 7]. Its main drawback is the volume expansion resulting from the mechanical stress accompanying Li alloying. This structural change during the electrochemical cycling in Li<sup>+</sup> is usually resulting in rapid capacity fade and mechanical decomposition of the structure [6].

In the current research we suggest a new approach combining the good stability, high surface area and electrochemical properties of TiO<sub>2</sub> with the high capacity of the amorphous silicon. By this approach we believe that Si clusters deposited in the stable TiO<sub>2</sub> nanoporous matrix could improve the electrochemical stability and increase the material capacity.

The Li ion insertion- extraction from/out of the Si modified and non-modified samples was studied in Li ion containing ionic liquid - butyl-methyl-pyrrolidinium bis(trifluoro)sulfonylimide (BMP<sup>+</sup>TFSI<sup>-</sup>) as a non-flammable and non-volatile organic electrolyte.

## Synthesis of TiO<sub>2</sub> nanoporous structures

Prior to the synthesis the Ti substrates were washed with distilled water, afterwards in acetone and treated in an ultrasonic bath in acetone. The electrochemical synthesis of TiO<sub>2</sub> ordered nano-structures was carried out in a two electrode electrochemical cell. The layers were produced by anodic oxidation in glycol or glycerol based solutions containing 0.5 % NH<sub>4</sub>F at 20 and 40 V. The duration of the process was from 1 to 5 hours. After the completion of the anodization the layers were washed with water, dried at 60 °C for 5 h, dried at 120 °C at vacuum for another 5h and transferred in a glove-box (Argon atmosphere with less than 1 ppm water and oxygen). During the constant voltage anodization the current was registered by a multimeter device. The surface morphology of the obtained layers was studied by scanning electron microscopy (SEM) (Fig. 3)

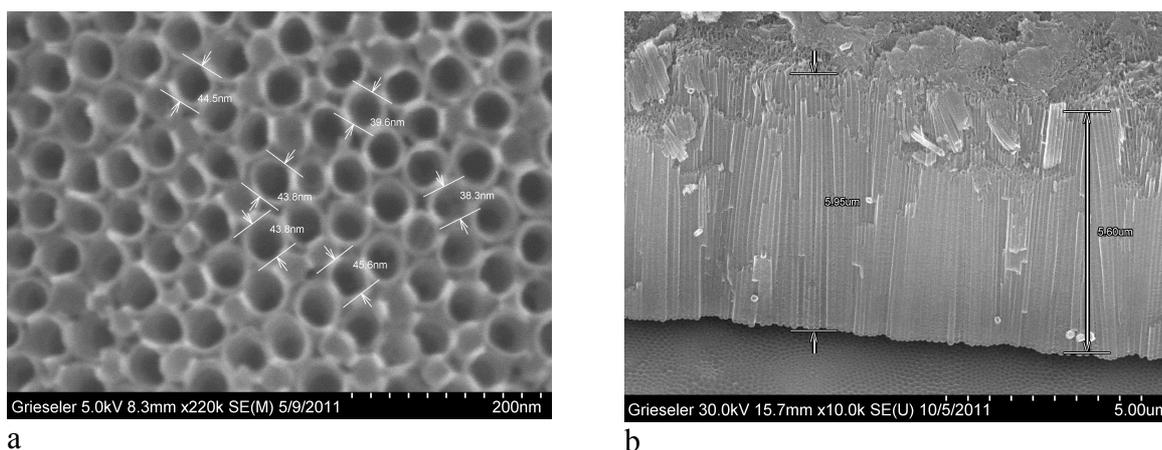


Fig 3. SEM images of anodized Ti foil. (a) top view, (b) cross section.

From the SEM micrographs it is seen that the pore diameter can be influenced by the applied voltage and electrolyte composition. The results from the SEM imaging are summarized in the following table.

Table 1

Electrolyte composition	Voltage / V	Pore diameter / nm
Glycol	20	40 - 50
Glycol	40	70 - 80
Glycerol	20	60 - 70
Glycerol	40	100

In the case of glycerol based electrolytes the pore diameter varies from 60 to 100 nm and for glycol 40 – 80 nm. The pore diameter can be as well influenced by regulating of the applied voltage. With increasing anodization voltage the pore diameter increases. The length of the nanopores depends on the duration of the process. With the help of SEM analysis a pore growth rate of 1 µm per hour of anodization was estimated for glycol solution at 40 V. The latter finding makes possible the estimation of the approximate amount of TiO<sub>2</sub>, knowing the nanopore diameter, their number and the layer thickness. The data about nanopore dimensions and TiO<sub>2</sub> amount are in a process of evaluation.

### Electrochemical properties of TiO<sub>2</sub> nanoporous structures in Li ion containing BMP, TFSI

After the synthesis and drying procedures the TiO<sub>2</sub> layers were electrochemically cycled in Li ion containing [BMP][TFSI] at different scan rates (50 – 500)  $\mu\text{V s}^{-1}$  (Fig. 4). The cyclic voltammetry shows a well-shaped quasi-reversible electrochemical couple that can be associated as the Li insertion – de-insertion into the TiO<sub>2</sub> nanostructure.

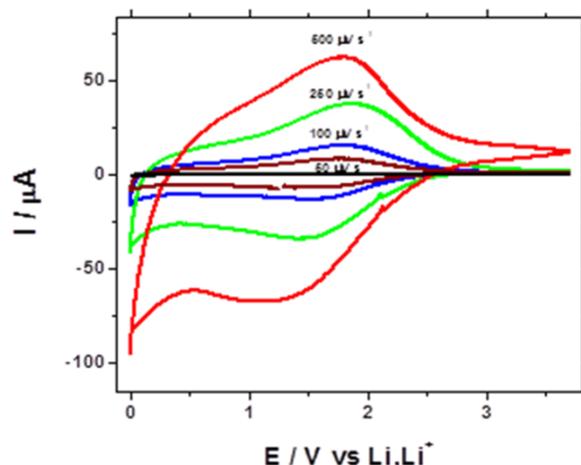


Fig. 4 CVs of Ti/TiO<sub>2</sub> nanoporous layer at different scan rates in 1M Li<sup>+</sup>TFSI, [BMP] [TFSI]

The curves underpin the good electrochemical stability of the material during continuous cycling. As a next step the layers were galvanostatically cycled at 100  $\mu\text{A}\cdot\text{cm}^{-2}$  (Fig.5). In order to minimize the effect of SEI formation the further performed electrochemical measurements were limited to cathodic potentials of 1 V. The result for multiple constant current cycling showed a good electrochemical stability, no plateau region (typical for amorphous TiO<sub>2</sub>). Furthermore, by prolonging the time of the anodization process the capacity of the material can be increased. The latter observation suggests that the growing structure of TiO<sub>2</sub> is active for Li-ion intercalation and the capacity can be controlled by the anodization period.

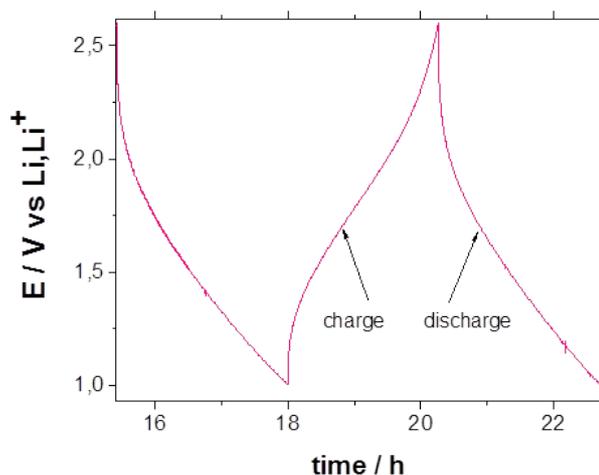


Fig. 5 Typical subsequent galvanostatic charge – discharge curves of Ti/TiO<sub>2</sub> nanoporous structure, recorded in 1M Li<sup>+</sup>TFSI, [BMP][TFSI]

The discharge rate capability of Ti/TiO<sub>2</sub> nanoporous structure was studied as a function of cycle number. At low rate of discharge (C/20 – C/5) the TiO<sub>2</sub> material displays capacity values in the range of 150 – 200 mAh g<sup>-1</sup>, close to the theoretical one 168 mAh g<sup>-1</sup>. A noticeable decrease of capacity was observed at C rates above C/5. A possible reason for the capacity drop at high C rate could be a slow Li ion diffusion in the TiO<sub>2</sub> nanopores due to kinetic limitations related to the high viscosity of the ionic liquid.

### Si modification of TiO<sub>2</sub> nanoporous structures

The TiO<sub>2</sub> nanostructures were modified by Si electro-deposition from ionic liquid. The electro-reduction was performed using 0.1 and 1M SiCl<sub>4</sub> [BMP][TFSI] solutions. The procedure for Si electrodeposition from ionic liquid has been described in more detail by Endres et coll. [8,9]. As seen on the cyclic voltammetric curves the potential of Si reduction depends on the Si concentration (Fig. 6). The substrates were firstly activated in SiCl<sub>4</sub> [BMP][TFSI] by one cathodic potential sweep and then Si was deposited potentiostatically at different potentials (-2.5 - -3.5 V).

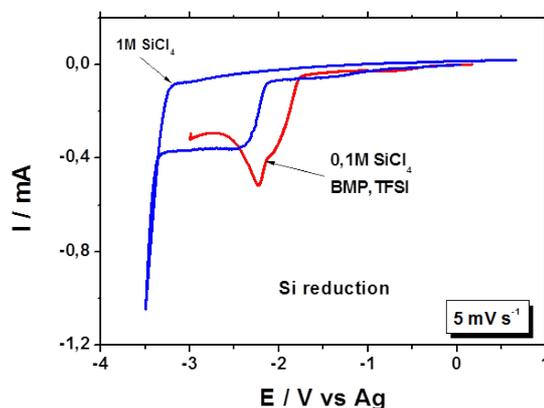


Fig. 6 Cathodic CV sweeps of TiO<sub>2</sub> nanoporous structure in 0.1M and 1M SiCl<sub>4</sub>, [BMP] [TFSI]

In order to understand in much more details the process of Si deposition on Ti/TiO<sub>2</sub> substrate the electroreduction of Si was performed by in situ micro-gravimetry using quartz crystal microbalance. After the activation by cyclic voltammetry potentiostatic Si deposition at -2.5 V was performed. The results show almost constant current (-0.1 mA) and close to linear frequency drop for about 60 min due to Si deposition. For times longer than 1 h the process was inhibited and no further mass change was observed.

In order to characterize the composition of the deposits we performed SEM imaging followed by EDX elemental analysis. The SEM results showed non-homogeneous structures covering the surface of TiO<sub>2</sub> nano-pores. The elemental analysis showed about 5 % Si, mainly distributed on the surface of the layer.

The Si modified TiO<sub>2</sub> nanostructure was studied by cyclic voltammetry in 1 M Li<sup>+</sup>TFSI<sup>-</sup>, [BMP] [TFSI]. Besides the electrochemical couple at 1.7 V corresponding to Li ion exchange in TiO<sub>2</sub> structure, a new pair of voltammetric peaks at about 0.75 V appears after Si electrodeposition. In order to clarify the impact of different parameters on Si electrodeposition on/in TiO<sub>2</sub> nanostructure further experiments will be performed.

## Summary of the results

- Thin film calorimetry based on a high-temperature stable langasite crystals is successfully established and tested on several elements.
- Synthesis and characterization of molybdenum disulfide ( $\text{MoS}_2$ ) via several hydrothermal synthesis routes.
- Ti/TiO<sub>2</sub> nanoporous structures are designed as a current collector – anode material system for Li-ion batteries.
- Li<sup>+</sup> insertion-deinsertion in Ti/TiO<sub>2</sub> nanoporous structures was tested in [BMP][TFSI] as a non-flammable, non-volatile ionic liquid electrolyte. TiO<sub>2</sub> nanoporous structure has a good cyclability in Li containing [BMP][TFSI].
- Ti/TiO<sub>2</sub> - Si nanoporous composite was suggested as a potential anode material with high performance for Li-ion batteries application. The Ti/TiO<sub>2</sub> samples were modified by potentiostatic Si deposition. The electrochemical behavior of Ti/TiO<sub>2</sub> - Si was studied by cyclic voltammetry in 1M Li<sup>+</sup>TFSI<sup>-</sup>, [BMP] [TFSI].

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