Phase stability of alloy-type lithium storage anode materials, Priority Program SPP1473

In the present joint project the quaternary alloy system Li-Si-Sn-C with the respective subsystems Li-Si, Li-Sn, Li-Si-C and Li-Sn-C is investigated. The Calphad method is used for describing the equilibrium thermodynamics. Since nanostructuring is generally accepted as a strategy to achieve an increased cycling stability in Li batteries, the contribution of grain and phase boundaries to the phase stability in the alloy systems is modeled on the basis of excess free energies as a function of the structural length scales.

A description of sub project 9.1:

Due to the high sensitivity of Li against oxygen, nitrogen and humidity, alloy production, handling and characterization of Li-alloys are challenging. Synthesis of alloys of the quaternary system Li-Si-Sn-C is carried out in a glove box under argon atmosphere in an oxygen and water free environment (oxygen and water concentration below 1 ppm). Starting point are binary Li-C alloys (Li2C2 and LiC6 phases). that are characterized by X-ray diffraction (XRD) in air tight capsules.

Fig.1 Experimental setup inside the glove box

The thermodynamic properties of these alloys are characterized at TU Clausthal, measured data act as input data for the assessment of the phase diagrams using the Calphad methodology (sub project 9.2).

Nanostructuring is carried out by high energy ball-milling and subsequent sintering by Spark Plasma Sinteriung (SPS) at Beijing UT (sub project 9.3).

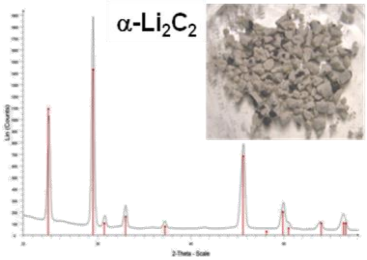

Fig.2 XRD 2θ scan of Li_2C_2

The nanostructured material is characterized by Transmission Electron Microscopy (TEM) at FSU Jena. As a consequence of the high sensitivity of Li alloys to influences from the surrounding, TEM lamella are prepared in high vacuum by Focused Ion Beam (FIB). Additionally, a transfer system under Ar atmosphere is established that avoids contamination/oxidation of the samples during transfer to the TEM.

The nanoscale microstructures are characterized in detail by means of high resolution TEM (HRTEM) and nano beam electron diffraction (NBED). The aim is to determine grain size distribution, phase distribution and the orientation relationships between neighbouring nanograins. For this, current TEM analysis methods have been further developed and extended to ultra fine grain sizes.

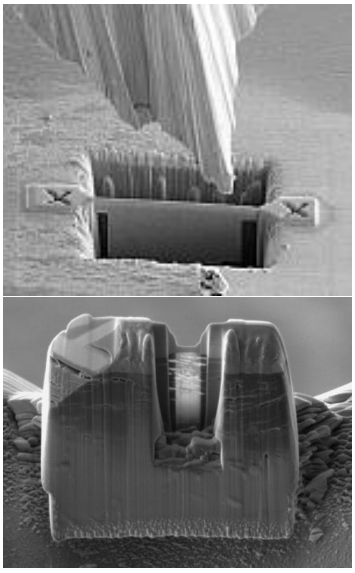

Fig.3 FIB sample preparation

Based on the measurements of the parameters of the nanostructure, thermodynamic models that describe the thermal stability of nanograins and the structure stability of some prominent phases in the Li-Si-Sn-C systems will be developed (sub project 9.3).

With the phase diagrams, the comprehensive thermodynamic description and the tools developed in this project, an estimation of cycling stability and the prediction of Li storage capacity will be possible for a large range of compositions in the above mentioned alloy system, and promising materials for Li battery alloys will be identified.