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

A description of sub project 9.3:

It is generally accepted that nanostructured materials have the potential to overcome the detrimental volume changes of the anode materials and kinetic difficulties in the diffusion of lithium ions during charge/discharge cycling. The present study is to obtain a quantitative understanding of the stability of phases in the nanostructured Li-Si-Sn-C alloy systems, which are promising to be developed as candidates as suitable anode materials for lithium storage in Li-ion batteries.

Combined with the relevant phase diagrams and thermodynamic descriptions of the coarse grained Li-Si-Sn-C alloys (**research work in sub project 9.2**), the excess thermodynamic properties due to the high density of grain boundaries in the nanostructured counterparts will be assessed. A model describing the excess volume in the nanocrystalline alloys as a function of the grain size has been developed for the binary (Li-C, Li-Si and Li-Sn) system, and will be extended to the ternary systems (Li-Si-C and Li-Sn-C). The model calculations may provide deterministic correlation between the nanostructure characteristics and the volume changes of the Li-Si-Sn-C systems during charge/discharge cycling.

On the experimental side, a unique oxygen-free in-situ synthesis system is used to prepare fully nanostructured alloys. In this completely closed system, the alloy ingots were firstly synthesized in the chamber of the spark plasma sintering (SPS) equipment. Then the ingots were crushed and ball-milled to make the amorphous alloy powders. The powders were sintered by SPS, in which the crystallization and densification took place concurrently, and alloy bulks with ultrafine nanograin structures were obtained. At present, the nanocrystalline Li-C (Li_2C_2, LiC_6 as representative), Li-Si (Li_7Si_3, $Li_{22}Si_5$) and Li-Sn (Li_7Sn_2, $Li_{13}Sn_5$) alloy bulks have been prepared. It has been confirmed that the unexpected phases or impurities were not introduced during the experimental procedures. Due to the fact that the Li-C, Li-Si and Li-Sn alloys react with water, the TEM samples of those alloys will be prepared by the FIB technique. The nanoscale microstructures will be characterized in detail by means of HRTEM and nano beam electron diffraction at FSU-Jena (**research work in sub project 9.1**). Based on the experimental measurements on the grain size distribution, nanograin boundary crystallographic parameters and the orientation relationships between neighbouring nanograins, thermodynamic models that describe the thermal stability of nanograins and the structure stability of some dominant phases in the Li-Si-Sn-C systems will be developed.

In the present project, three project partners (**sub projects 9.1-9.3**) combine theoretical competences in the Calphad method, the thermodynamics of nanomaterials and the combination of thermodynamics and kinetics during phase transformations, as well as experimental competences in the measurement of thermodynamic properties, production of nanomaterials and characterization of nanoscaled structures.