Phase stability of alloy-type lithium storage anode materials

- Sub project 9.1 -

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<u>Planned actions in subproject 9.1:</u>

The quaternary alloy system Li-Si-Sn-C with the respective ternary subsystems Li-Si-C and Li-Sn-C will be investigated in the second part of the SPP. Due to the high sensitivity of Li with respect to humidity, oxygen, nitrogen, alloy production of quaternary Li-Si-Sn-C alloys will be carried out in a glove box under purified argon atmosphere. In the first part of the project, procedures with glove bags for maintaining a protective atmosphere during handling and characterization of alloys were developed, so that the transfer to the XRD device, optical and electron microscopes can be done without an accompanying deterioration of the samples.

Key samples of the ternary and quaternary alloy systems that are selected in discussion with the partners at TU Clausthal and Beijing UT are first produced at FSU Jena, employing the variety of alloy making technologies that were adapted in the past 2½ years for Li alloys. The phase composition of the resulting alloys is identified by X-ray diffraction (XRD) in air-tight capsules. Additionally, annealing experiments will be performed to evaluate phase stabilities.

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 Sintering (SPS) at Beijing UT (**sub project 9.3**).

The nanostructured material is characterized by Transmission Electron Microscopy (TEM) at FSU Jena. TEM foils will be made using the transfer system and a focused ion beam device with the parameters developed in the first part of the project. The microstructural features will be correlated with the thermodynamic model that describes the thermal stability of nanograins and the stability of prominent phases (**sub project 9.3**). It is expected that the phase stability as a function of grain size of model calculations and experiments can be correlated and that direct insight into phase transformation mechanisms can be gained. Phase stability is characterized by Nano Beam Electron Diffraction (NBED) in combination with high resolution imaging (HRTEM). Both grain orientation and phase determination via NBED will benefit from the algorithm that automates definite indexing of the NBED pattern from randomly oriented nanograins, developed in the first part of SPP1473. It is also planned to further extend the analysis capabilities of the method for complete grain boundary analysis of nanocrystalline materials.

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.

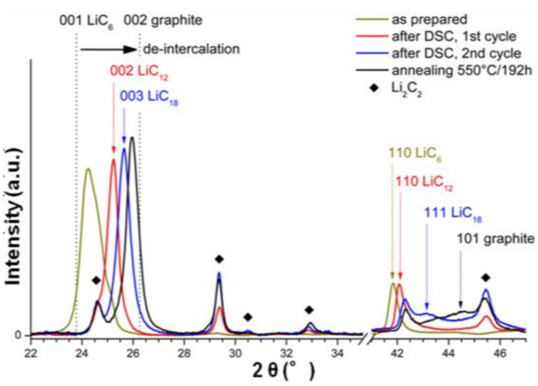

Fig.1: XRD patterns of LiC_6 after several DSC cycles and annealing experiments show gradual decomposition of LiC_6 into Li_2C_2 and C-richer phases

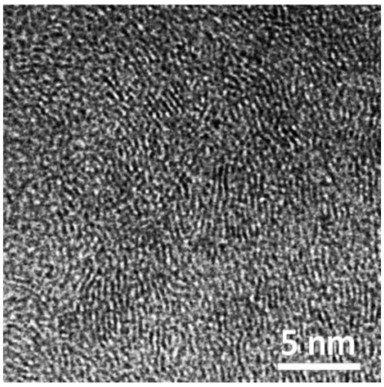

Fig.2: HRTEM image of nano-crystalline Li_2C_2

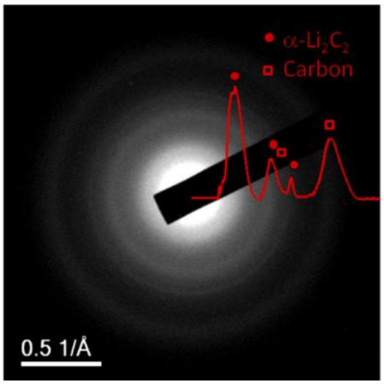

Fig.3: Electron diffraction pattern of nanocrystalline Li_2C_2