

Phase stability of alloy-type lithium storage anode materials

Subproject 9.2

Subproject members:

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The global goals of our subproject 9.2 is development of a quantitative thermodynamic description of the complete quaternary Li-Si-Sn-C alloy system and the impact of oxygen in the Li-Si-O-C system in the bulk state. This includes the heterogeneous phase equilibria and the driving forces for phase reactions and phase transformations. These thermodynamic and constitutional alloy properties, as well as the concentration dependent chemical potential of Li, will be derived from consistent and experimentally supported Calphad-type modeling with the capability to predict these quantities in pertinent subsystems and multicomponent alloy systems and for a wide range of temperatures. Moreover, application and advancement of the coulometric titration (CT) technique in key samples of the above mentioned multicomponent alloy systems, selected by thermodynamic calculations from preliminary thermodynamic modeling. This will provide simultaneously data on the chemical potential and composition of Li in truly equilibrated states at higher temperatures, as opposed to the relatively rapid open circuit voltage (OCV) experiments. The CT technique will be advanced in close cooperation with several partners in the SPP.

The our group has specialized in a combination of experimental techniques with Calphad-type investigation of multicomponent, multiphase alloy systems for many years. As a result a range of state of the art laboratory equipment has been specially developed or modified for high precision measurement of thermodynamic and phase diagram data. This working method has already been successfully implemented in the investigation of the binary Li-C and Li-Si system. Here, new thermodynamic descriptions of the Li-C and Li-Si binary systems were developed based on new experimental phase diagram work performed in the framework of the priority program:

New Li-C phase diagram (Fig. 1). For the first time a Calphad-type assessment was performed for the Li-C system, covering all thermodynamic and phase equilibrium data. Key experiments were performed under well defined conditions and the thermodynamic stability of the compounds Li_2C_2 and LiC_6 was elucidated. The stable Li-C phase diagram was determined (for bulk, or coarse grained alloys), and it differs drastically from the two diagrams proposed in the literature. The reported very low solubility values of C in liquid Li (with low nitrogen contamination) are found to be supported by thermodynamic considerations. It is experimentally demonstrated that $\alpha/\beta\text{-Li}_2\text{C}_2$ is the only stable compound and that LiC_6 is a metastable compound. All of the enthalpy of formation data reported in the literature for LiC_6 are shown to be incompatible with this fact.

The Li-Si phase diagram from 0 K to liquidus temperatures (Fig. 2). Thermodynamic and constitutional data of the Li-Si system were critically reviewed and the importance of using original

experimental data is highlighted. An effective method to assess the reliability of solubility data in dilute solution was presented. The C_p -functions of all Li-Si compounds were experimentally determined by cooperation partners in SPP 1473 for 0-900 K and those for pure Li and Si from 0-298 K in our group. A consistent thermodynamic description of all solid phases in the Li-Si system from 0 K to high temperature is developed jointly with that for the liquid phase using the Calphad method. This is the first calculated and validated Li-Si phase diagram extending down to 0 K.

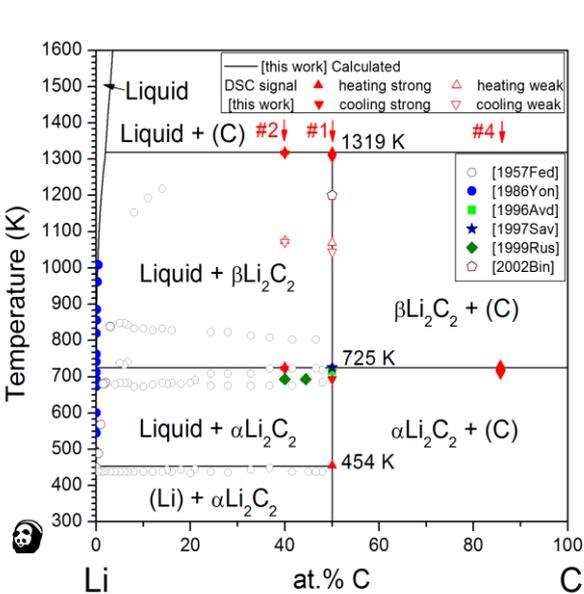


Fig. 1 Li-C phase diagram with experimental data superimposed; additional shorthand notation for references, indicating year and first author, is provided in brackets. Compositions of samples (#1, #2, #4) from present work are marked by red arrows.

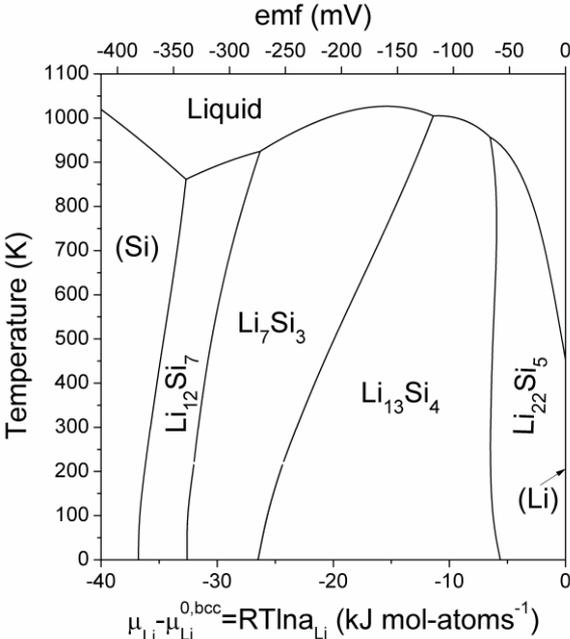


Fig. 2 Calculated section of the Li-Si phase diagram from 0 K to high temperature. The liquidus of (Si) approaches 1687 K for $a_{Li} \rightarrow 0$, outside the section. The reference for the chemical potential of Li is pure solid bcc-Li. The emf scale displays the voltage in an electrochemical cell between pure solid Li and Li-Si alloys.