Thermodynamic description of the Li-Si-System based on calorimetric and hydrogenation measurements

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The dominating anode material in Lithium-Ion-Batteries (LIB) is graphite with a specific capacity of 372 mAh g^{-1}. An attractive alternative in few of costs and capacity is silicon. The formation of $Li_{17}Si_4$ leads to a theoretical specific capacity of 4054 mAh g_{Si}^{-1} [1]. A basic understanding of the underlying phase and electrochemical equilibria based on reliable thermodynamic data in the Li-Si-system is essential for the battery development. For this reason, our group performed extensive experimental studies on lithium silicides using calorimetry and hydrogenation equilibrium measurements in the ternary system Li-Si-H.

Currently, five stable phases $Li_{17}Si_4$, $Li_{16.42}Si_4$, $Li_{13}Si_4$, Li_7Si_3 und $Li_{12}Si_7$ are discussed in literature, as well as the so-called high-pressure phase LiSi and the metastable phase $Li_{15}Si_4$. The heat capacities of the five stable phases [2,3] and the enthalpies of formation of Li_7Si_3 and $Li_{12}Si_7$ based on hydrogen sorption investigations have already been reported by our group [4].

The focus of this contribution is directed to the experimental determination of the heat capacities and entropies of LiSi and $Li_{15}Si_4$ and the determination of the enthalpies of formation of the stable phases by combining the heat capacity and entropy results with the hydrogenation equilibrium pressure data determined by recording pressure-composition-isotherms in a Sieverts type apparatus at 450°C, 475°C and 500°C. The heat capacities were measured using two different calorimeters: a Physical Properties Measurement System (Quantum Design) in the temperature range from 2 K to 300 K and a DSC111 (Setaram) in the temperature region from 300 K to 600 K. The measurements at low temperatures allow the calculation of the standard entropy of the lithium silicides. Applying the resulting new thermodynamic data set, completely based on experimental data, the phase diagram of the Li-Si-system has been calculated with excellent quality by the CALPHAD method.

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