A Strategy for the Characterization of Lithium Containing Materials Based on Hydrogenation Reactions and Low Temperature Calorimetry

Franziska Taubert, Daniel Thomas, Jürgen Seidel, Regina Hüttl,

Klaus Bohmhammel, Florian Mertens

Institut für Physikalische Chemie, TU Bergakademie Freiberg, Leipziger Str.29,

09596 Freiberg, Germany

florian.mertens@chemie.tu-freiberg.de

With the dominance of lithium based materials in many battery storage applications a strong interest in the precise thermodynamic characterization of very different lithium containing materials has gained importance. Such new materials encompass developments in all areas, i.e. materials for anodes, cathodes and even electrolytes. Among these developments the ones for conversion electrodes and solid state electrolytes cathode materials are the most promising ones for further improvements in respect to storage capacity. In the current presentation we demonstrate a general procedure that significantly improves the determination of the heat of formation for lithium containing materials. The procedure is based on a combination of low temperature calorimetry and hydrogenation reactions. The particular applicability to lithium systems is rooted in the high stability of lithium hydride and the high diffusivity of the small lithium ion. The method will be demonstrated on the systems Li_x-Si_y and Li_xSn_y. Both systems are of interest as potential conversion electrode materials for anodes. A critical review of the thermodynamic characterization of the various phases revealed a significant lack in the availability of thermodynamic data such as heat capacities, absolute entropies and heats of formation. In addition, beside structural ambiguities, new phases were recently discovered. The work to be presented will mainly be a synopsis of the calorimetric measurements recently performed by our and other groups in the temperature range from 2 to 873K. In addition, aspects of the materials synthesis, crystal structure, and phase boundaries of will be discussed and a comparison with thermodynamic data obtained from hydrogenation PCI measurements will be given. The largely extended data base of the Li.Si system has already been used in the literature for a reevaluation of the phase diagram by CALPHAD simulations and served as a reference a for finite temperature density functional calculations, which lead to an excellent agreement between theory and experiment. The same strategy was also applied to the system Li-Sn.

- F. Taubert, J. Seidel, R. Huettl, M. Bobnar, R. Gumeniuk, F. Mertens
  The heat capacity and entropy of the four lithium stannides $Li_{17}Sn_4$, Li_7Sn_2 , $Li_{13}Sn_5$ and Li_7Sn_3 in the temperature range (2 to 865) K
  Journal of Chemical Thermodynamics **2019**, 130, 119-128

- D. Thomas, N. Bette, F. Taubert, R. Huettl, j. Seidel, F. Mertens
  Experimental determination of the enthalpies of formation of the lithium silicides Li_7Si_3 and $Li_{12}Si_7$ based on hydrogen sorption measurements
  Journal of Alloys and Compounds **2017**, 704, 398-405