Experimental Thermodynamics and Phase Relations of New Electrode Materials for Li-Ion-Batteries

Studies in the systems Li-Sb-Sn, Cu-Li-Sb and the constituent binary systems Li-Sb and Sb-Sn

Joint DFG Project

within

WeNDeLIB priority program

Conducted by

Dr. Damian Cupid, KIT, Karlsruhe

AO.Prof. Dr. Hans Flandorfer, University of Vienna

Priv.-Doz. Dr. Torsten Markus, FZ-Jülich

Information to the research work in the

Forschungszentrum Jülich GmbH

Local project manager: Priv.-Doz. Dr.-Ing. Dr. Torsten Markus
Project co-worker: Dipl.-Ing. David Henriques
Dipl.-Ing. Dieter Kath

Li-Ion batteries are well recognized as a possible and efficient way to store electric energy. For use in mobile applications, however, these batteries have to meet several design criteria, such as number of charge/discharge cycles, energy density and safety. The latter is one of the crucial requirements that have so far prevented the wide spread use of these batteries, since for instance moisture will lead to explosions (thermal runaway).

However the knowledge of basic thermodynamic data concerning the battery relevant systems is very weak. This knowledge is a necessary precondition for advanced materials design based on thermodynamic modeling. This comprises also the design of new and advanced materials for achieving higher performances of the devices.

In order to be able to understand the behavior of different materials and the corresponding material interactions, it is important to understand the thermochemical functionality of the whole assembly. Due to the high amount of components present in these systems, their thermodynamic modeling is desirable. The CALPHAD method, which is highly accepted, is a semi empirical method that requires thermodynamic data as an input. The need for thermo chemical data is required not only in the research and development phase but also throughout the product life cycle. To overcome some of the problems encountered in the development of new and advanced battery materials it is necessary not only to have an understanding of the fundamental science but also the physical and chemical interactions of the various components within the device. These interactions have a large influence on the characteristics and performance of the devices because of the high temperatures and longtime scales involved.

Thermodynamic key data can be measured with the method of Knudsen effusion Mass Spectrometry (KEMS). This method is very well suited for the determination of Gibbs Energies as well as Enthalpies and Entropies of mixing, thermodynamic activities and chemical potentials of mixtures.

The potential of the Knudsen effusion mass spectrometric technique for the use in the course of high temperature chemistry can be summarized as follows:

- Identification of the equilibrium forming gaseous species of the vapor in the Knudsen cell
- Partial pressure determination of the equilibrium species generally in the range between 10-5 Pa and 10 Pa and up to temperatures of more than 2500 K
- Computation of thermodynamic properties by using the determined temperature dependence as for example enthalpies and entropies of vaporization, dissociation and

formation or the temperature dependence of equilibrium constants of chemical reactions.

The systems under investigation will be the ternary systems Li-Sb-Sn as well as their corresponding subsystems as feasible anode materials and $LiSiO_2$ as cathode material. The investigations include at the experimental evaluation of phase relations by means of XRD, thermal analysis and metallography as well as vapor pressure measurements using Knudsen Effusion Mass Spectrometry and also electrochemical investigations.

The specific sample compositions will be defined according to a literature review which will be made in the first stage of the project. Measurements will be most likely done at each 10 at% for the binary systems and in accordance with the identified phase fields in the phase diagram. Sample preparation will be performed according to the procedures developed in the first project phase in Vienna.