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
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Information to the research work in the
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General purpose of the project

A crucial task of this priority program is the generation of thermodynamic and kinetic data of relevant material systems. Up to now the mainly used materials for LIB anodes are graphite and graphite-like materials. This has a lot of benefits, but also some disadvantages, like limited lithium ion storage capacity and energy density. One idea is to substitute the graphite by metals like eutectic alloys systems. In the first funding period of the priority program 1473 "WeNDeLIB", the research was focused on the ternary system Cu-Li-Sn[1] and the binary constituent systems[2-5] .

Based on the fruitful co-operations between the project partners Hans Flandorfer from the Department of Inorganic Chemistry / Materials Chemistry, University of Vienna, Damian Cupid (KIT Karlsruhe) and Torsten Markus (Research Center Jülich) within the first funding period, a new project for the second funding period of DFG SPP 1473[6] was proposed. It is aimed at the investigation of relevant Sb- and Li- containing intermetallic ternary systems as well as on Li-Si and Li-O-Si.

Since the Department of Inorganic Chemistry / Materials Chemistry has a long time experience in the experimental determination of thermodynamic data of metallic systems, the main object is to perform phase diagram investigations and thermochemical measurements on Cu-Li-Sb, Li-Sb-Sn and its constituent binaries Li-Sb and Sb-Sn, which are promising alloy systems for this class of materials.

State of the art

The binary systems Cu-Sb, Sb-Sn, Li-Sb, Li-Sn and Cu-Li

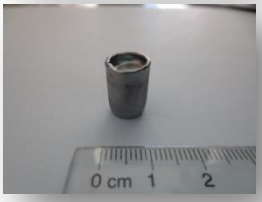
The binary system Cu-Sb[7] has been investigated experimentally already some years ago within the COST MP0602 action[8] on lead-free high temperature solders. The system Li-Sn has been verified experimentally within the first funding period, all available literature data and the new experimental results have been merged into a new CALPHAD-optimization[4]. In the system Cu-Li also some new experiments were performed by the Viennese and the Jülich groups, which will be the fundament for a new critical optimization done by our project partners in Karlsruhe.

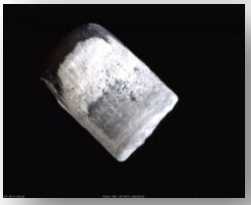
For Li-Sb a few[9] data are available. The assessed data are compiled in Massalski's handbook[10]. For this system, a critical reinvestigation with modern methods would be appreciable, because especially the high-temperature regions seem to be quite tentatively. The system Sb-Sn is seemingly quite well known. However, several contradictory experimental works can be found in primary literature. The number of phases and their phase equilibria are differently described. Especially occurrence, stability range and crystal structure of the phase Sb_2Sn_3[11], as well as the crystal structure of Sb_xSn_{1-x}[12-15] are of interest and worth to be reinvestigated.

The ternary systems Cu-Li-Sb and Li-Sb-Sn

For Cu-Li-Sb only one ternary compound was hitherto reported which has the composition $CuLi_2Sb$[16]. It crystalizes in an ordered Zintl-type cubic structure which can be derived from the binary BiF_3-type. Electronic structure calculations have been performed by Reshak and Kamarudin [17]. Matsuno et al. [18] made XRD, coulometric titration and various calculations, e.g. DFT first–principle calculations. They claimed the existence of a CuLiSb to $CuLi_{1.5}Sb$ solid solution phase exhibiting Heusler-type structure. Finally, the authors give a tentative ternary phase diagram which, however, is not based on a detailed experimental investigation of alloy samples but on calculations. In addition it does not correspond to the Cu-Sb constituent as accepted in literature. Further experimental investigations based on XRD and thermal analysis similar to those performed on Cu-Li-Sn within the first project have to be carried out. Although in Li-Sb-Sn there are a few works available on electrochemical performance and lithium insertion mechanisms into SbSn[19-24], only scarce information (one ternary compound Li_2SbSn[25]) is presented regarding the phase diagram.

Phase diagram investigation

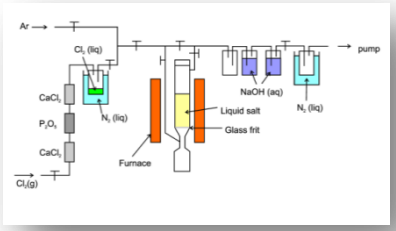




Generally, working with Li metal is challenging because of its high oxidation potential and vapor pressure, low melting point and creeping of liquid phases. Special methods, working devices and materials, e.g. sample preparation in the glove box and the use of Ta crucibles were applied. Although there is equipment and experience for the handling of such materials available in the department, working with Li metal is not a routine procedure. Thus, the re-investigation of the well-established Li-Sb binary system was the start of our work. Samples at selected compositions were produced to validate our experimental setup operating with Li-containing alloys. At temperatures above 500 °C and higher Li-contents (≥ 60 at%) the Li-vapor is able to penetrate the Ta-crucible. In addition, at temperatures above 500°C during presence of solid or liquid (Sb), the Sb reacts with the Ta-crucible and forms intermetallic Sb-Ta-phases[26-28]. Therefore elaborated combined crucible solutions for higher temperatures have to be found.

For sample preparation calculated amounts of initial materials were taken according to the desired composition. Alloying and annealing was carried out in resistance and induction furnaces. Characterization of the obtained alloys was done by powder X-ray diffraction (XRD) and single crystal XRD. Powder XRD was used as a standard method for phase analysis. Lattice parameters were refined by Rietveld method implemented in TOPAS software, which serves to fit the obtained X-ray diffraction pattern. Thermal effects caused by phase transformation on heating and cooling were recorded by DTA (Differential Thermal Analyses). DTA measurements were carried out in closed Ta crucibles in inert gas atmosphere. Such information is necessary for the construction of binary phase diagrams and isopleths (vertical sections) of ternary alloy systems. For samples without Li (Cu-Sb and Sb-Sn), EDX and EPMA are the methods of choice to find out the composition of the phases present in the obtained alloys. These data give valuable information on phase equilibria and solidification processes. However, Li is not accessible to those techniques due to its low rate of X-ray emission. This is indeed a problem, which could be overcome by the use of coulometric titration technique and EMF-measurements.

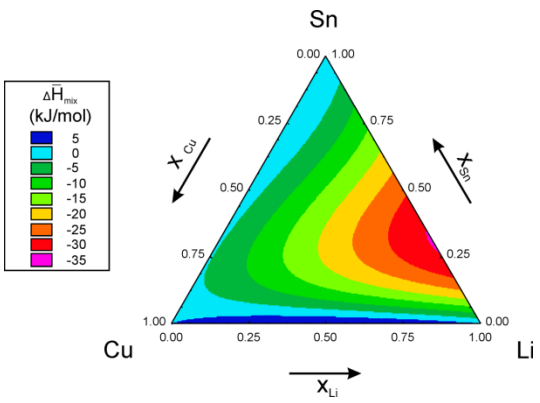
Thermochemical measurements



EMF (Electro-Motoric Force) measurements are powerful experimental techniques to determine chemical potentials of the components in alloy systems. EMF methods for both solid and liquid electrolytes are available at our department. Doing measurements at various temperatures leads to the partial enthalpies and entropies. By Gibbs-Duhem integration, the integral values can be obtained. Titrating lithium into a binary sample and simultaneously monitoring the EMF-values results in a concentration vs. potential plot, which allows an estimation of the phase relations an indirect an assumption of the solubility ranges of binary and ternary phases.

The enthalpy of formation of liquid and solid alloys is measured by drop calorimetric methods using two high temperature Calvet-type micro-calorimeters. All the experiments are carried out in high purity Ar atmosphere to avoid oxidation. Crucible materials, e.g. molybdenum or boron nitride have to be chosen according to the experimental conditions.

Due to relatively high vapor pressure of Li, isopiestic vapor pressure methods can be employed in order to determine the activity of Li in Li-alloys. Furthermore, this method provides phase diagram information and can be used for sample preparation.



Thermodynamic calculations

The goal of the project is to provide valuable experimental data for calculation and simulation of materials properties for the design of new LIBs. The very well established CALPHAD (**CAL**culation of **PHA**se **D**iagrams) method will be used to prove the consistency of our experimental data. Our project partners in the group of Dr. Damian Cupid, well experienced in using CALPHAD, have done thermodynamic optimization of Cu-Sn and Li-Sn and will continue with Cu-Li and the ternary Cu-Li-Sn system. As soon as concise new experimental data are available for the Sb-containing systems further optimization work can start.

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