The thermodynamic investigation of ternary (Co,Cu,Ni)-Li-Sn systems for new LIB anode materials

Joint DFG Project
within
WeNDeLIB priority program

Conducted by
Dr. Damian Cupid, KIT, Karlsruhe
AO.Prof. Dr. Hans Flandorfer, University of Vienna
Doz. Dr. Torsten Markus, FZ-Jülich

Information to the research work in the
Dep. of Inorganic Chemistry / Materials Chemistry
at the University of Vienna

Local project manager: AO.Prof. Dr. Hans Flandorfer
Project co-worker: Mag. Siegfried Fürtauer, PhD Student

1 The part of the project operated in Austria is administrated by the FWF according to the DACH regulations
General purpose of the project

The construction of electric vehicles for the automotive market is a hot topic in industrial and public research. Thus many research programs and actions are currently running in this field, also with the aim of the development and the design of new Li-ion batteries. The “Deutsche Forschungsgemeinschaft” (DFG) approved the priority program 1473 “Materials with New Design for Improved Lithium Ion Batteries – WeNDeLIB” with the aim to provide a database for the tailored development (design) of high performance LIBs (LIB = lithium ion battery).

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. Hans Flandorfer from the Department of Inorganic Chemistry / Materials Chemistry, University of Vienna has lanced a join proposal together with Torsten Markus (Research Center Jülich) and Damian Cupid (KIT Karlsruhe) with the topic “Thermodynamics of new LIB-electrode materials”. 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 (Co,Cu,Ni)-Li-Sn and its constituent binaries, which are promising alloy systems for this class of materials.

2 actual an accumulator
State of the art

The binary system Ni-Sn has been newly investigated in detail in our group and Cu-Sn was object of elaborate high-temperature PXRD in order to clarify the complex phase relations in the Cu-rich part of the phase diagram. An improved version of Co-Sn showing a hitherto unknown intermetallic compound CoSn$_3$ was published by Lang and Jeitschko. Calorimetric measurements at many different temperatures have been performed on Cu-Sn and Ni-Sn and such work was done as well for Co-Sn.

Phase diagram studies and recent thermodynamic assessments as well as calorimetric and EMF measurements for the system Li-Sn are available in literature. The remaining three binary systems are Co-Li, Cu-Li and Ni-Li. The information on phase relations and thermochemistry of the three systems is generally poor, especially for Co-Li and Ni-Li. Preliminary phase diagrams for all three systems are available in Massalski’s handbook. Thermodynamic investigations of the binary system have been published. These three binary systems are aim of some additional investigations. To our best knowledge, no phase diagrams are available for the three ternary systems (Co,Cu,Ni)-Li-Sn. However, some information regarding ternary compounds was published for Cu-Li-Sn and Li-Ni-Sn. For no one of the three ternary systems thermodynamic data have been published yet.
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-Sn 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.

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 metallographic techniques. 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. EDX and EPMA are very important to find out the composition of the phases present in the obtained alloys, which gives valuable information to phase equilibria and solidification processes. However, Li is not accessible to those techniques due to its low rate of X-ray emission, therefore only the atomic ratio of the heavier elements could be determined. 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.
Thermochemical measurements

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. 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.

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 (CALculation of PHAs e Diag rams) method will be used to prove the consistency of our experimental data. A further application will be the extrapolation of binary data to the ternary systems for optimizing the experimental setup. Dr. Damian Cupid, well experienced in using CALPHAD, has started with the thermodynamic optimization of Cu-Sn and will continue with Cu-Li and Li-Sn and the ternary Cu-Li-Sn system.

**References**

(3) Fürtauer, S.; Flandorfer, H., University of Vienna, 2010.