Computational Thermodynamics for Material Design of Energy Storage Materials

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Abstract

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

In order to be able to understand the behavior of the interplay 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 associated but also the physical and chemical interactions of the various components within the device.

The knowledge of basic thermodynamic data concerning battery relevant systems is very weak. This knowledge would be a necessary pre condition for advanced materials design based on thermodynamic modeling. This promotes the design of new and advanced materials for achieving higher performances of the devices. The capacity, voltage, rates, and energy densities of these systems, are determined by the cathode material. Nowadays, Li-ion batteries contain $LiCoO_2$ as the cathode material, whose RedOx potential is around 4 V (potential against a Li/Li+ anode), with a capacity of ~140 mAh/g[1]. This material is reactive with the solution components and undergoes exothermic reactions at elevated temperatures. Thus, it is mandatory to understand these processes and the relevant thermodynamic interactions.

The research on such anode materials for Li-ion batteries is currently a hot topic. Although nano-crystalline and thin film materials will certainly be an important issue, the basic properties of the bulk materials must be the starting point for all further considerations. A systematic development and design of such materials applying thermodynamic and kinetic modeling requires basic thermodynamic data in terms of stability and phase relations along with additional information. The creation of a suitable thermodynamic data base for relevant alloy systems is thus a crucial issue. Beside this technological aspect the thermodynamic investigation of such alloy systems will significantly broaden and improve the basic knowledge of their phase relations and thermochemistry. Furthermore valuable contributions to the theory of alloying processes in the solid and liquid state can be expected.

The contribution at hand will focus on the method of advanced materials design combining experimental techniques with computer based thermochemical modeling using thermodynamic databases which have been accomplished using the CALPHAD type approach. For the determination of phase stabilities in dependence of the Li content and the cycling number, also first principle calculations have been performed. Results of this fundamental approach will be discussed and compared with experimental results.

[1] K. Mizushima; P. C. Jones; P. J. Wiseman; J. B. Goodenough, Materials Research Bulletin 1980, 15, (6), 783-789