project report for "Design of cathode materials for improved capacity, stability and safety for lithium ion batteries based on the system $LiMO_2$ (M = Co, Mn, Ni)"

Subproject members: Elke Schuster, Hans Jürgen Seifert

The goals of our subproject are:

(1) Analysis of lithium ion batteries (commercial and self-constructed) for understanding the thermodynamic factors of the electrochemistry and battery safety. All these measurement will be done with a Accelerating Rate Calorimeter (ARC).

(2) Preparation of electrode materials (bulk) in the Li-Mn-O, and characterization with methods of materials science like DTA, Calorimetry, SEM combined with EDX and X-ray diffraction. Measuring thermodynamic properties of battery materials (enthalpies, chemical potentials, heat capacities) for the thermodynamic description of battery relevant phases.

(1) Accelerating Rate Calorimetry (ARC)

Batteries show a heat generation during charge and discharge so it is important, especially with regard to safety (keyword: thermal runaway), to know the thermal behavior of them. For this the Accelerating Rate Calorimeter ARC provides an adiabatic environment in which a sample can be studied under conditions of negligible heat loss and it's also possible to measure under isothermal conditions. Two of these Accelerating Rate Calorimeter (ARC) were installed and first measurement were done, to learn how it works.

The ideal environment for batteries are isothermal conditions, for the batteries it's possible to cool down after heating during discharge and no thermal runaway goes on. But the real conditions under which they work are from adiabatic nature, so two different measurement routines were designed. All shown test following below were done with commercial 40Ah pouch cells, such as they are used for electrical vehicles. At first all batteries were measured under isothermal conditions. In this case it's easier to identify the exothermic and endothermic parts of the charging and discharging process (figure 1). You can see that both charging and discharging parts shows these behavior, but overall discharging shows exothermic behavior and charging shows endothermic behavior. All over all no significant heating of the battery can be recognized. In a second part the batteries were cycled under adiabatic conditions, prevailing in battery packs (typical you use 50-60 batteries in one pack, closely stacked), with no chance for heat loss in the environment. For this they show a complete other behavior. You can again see different endothermic and exothermic parts, but additionally you can see a temperature increasing in the battery. In our case it's nearly 20K over four halfcycles. This means the battery can come into a thermal runaway and destroyed. The total heat generated in the battery consist of three part, “reversible” heat, “irreversible” heat, heat generated by “side reactions”. To minimize the hazard of thermal runaway it's important to know the amout of irreversible heat and to minimize this part. With a adept measuring routine it's possible to estimate the different parts of the heat generation. This is the future work. To find out the influence of the

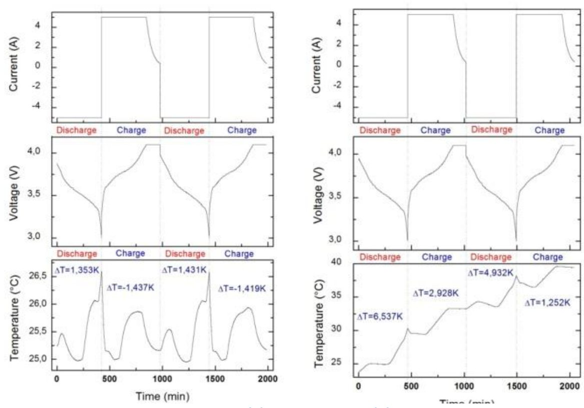

Figure 1: cycling under (a) isothermal and (b) adiabatic conditions

individual components of the battery (cathode, anode, separator) we started to build coin cells consisting of these individual components and also analyze their thermal behavior.

(2) Preparing bulk material to get thermodynamic parameters

To understand the correlation between electrochemical behavior and safety of batteries, it's important to understand the thermodynamic of materials inside the battery. But not very much thermodynamic parameters are available for the battery relevant systems like $LiMn_2O_4$. You can find two available phase diagrams but they show quiet different phase areas for $LiMn_2O_4$. So our work starts with preparing this spinell Li-Mn-O with different composition to fix the boundaries of the phase area (figure 2). Also we characterize our samples with SEM, XRD, ICP-OES and BET to get further information's. Next step will be measurements with an drop-in calorimeter to get thermodynamic parameters like enthalpy of formation and specific heat capacity of our samples for using this to create a thermodynamic database of the Li-Mn-O system. This already started with combine the thermodynamic descriptions of the binary systems Li-O and Mn-O taken from literature and project partners. Next step will be the description of the Li-Mn system an starting modeling the $LiMn_2O_4$ phase.

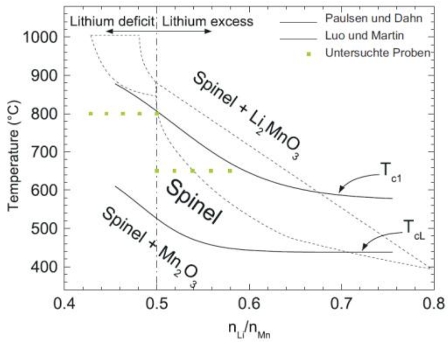

Figure 2: available phase diagram for the $LiMn_2O_4$-phase and compositions of our samples