

Safety Investigations on the Negative Electrode of a Li-Ion Battery by Differential Scanning Calorimetry

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Introduction

Safety issues are a major task in modern energy storage systems. As a general rule, the more energy is stored, the more hazardous will the energy storage system potentially be. Therefore, beside many standard safety tests in the battery industry, safety analyses of single battery components are important to improve the safety of batteries [1,2]. The most difficult tests for fully charged Li-ion batteries are the nail penetration (local short circuit) and the heating test of fully charged batteries, which must not lead to an explosion or fire of the batteries. According to the literature [1], the positive electrode containing the highly oxidized compound LiCoO_2 , may evolve atomic oxygen above 493K, which will react with the organic solvent of the electrolyte solution. As a result, a large amount of energy is released, which heats up the cell.

Cycled carbon electrodes give off heat at temperatures of about 413K (Fig. 1). The effect is much smaller than that observed with the positive electrodes, but the heat evolved might bring the cell to temperatures of up to 493K, where the oxygen evolution occurs, which then may cause a thermal runaway of the cell. We must ask, therefore: "Can sufficient energy be set free from the negative electrode to cause a thermal runaway of the cell?"

Heat Evolution of Negative Electrodes

Differential scanning calorimetry (DSC) is well suited for studies of the heat evolution of electrodes. Generally, cycled carbon electrodes evolve heat within two temperature ranges (Fig. 1). A small heat evolution occurs at 393-423K [3], which is probably caused by the decomposition of the surface layer of the electrode. A larger heat evolution occurs at 543-573K, which is assigned to the decomposition of the binder. The heat evolution from fully charged electrodes is more pronounced than from cycled but discharged electrodes, which hardly contain any lithium and are called Li-free. Like positive electrodes, negative electrodes are more dangerous, when they are fully charged.

Another interesting question for battery manufacturers is the influence of the type of graphite on cell safety. We compared different types of carbon negative electrode materials. The DSC results are shown in Fig. 2 as a function of the irreversible charge loss of the corresponding negative electrodes. The heat evolution of a graphite with a high irreversible charge loss (TIMREX[®] KS6) is much more pronounced below 493K. Less heat is evolved using the highly crystalline graphite TIMREX[®] SLM44 or graphitized MCMB10-28, which shows a lower graphitization degree than the first two materials.

The properties of the electrochemical systems change during use. Therefore, we investigated an electrode of a cell, which was charged and discharged 1000 times with 100% of the available capacity. The cycling experiment lasted about 6 months. After these 1000 cycles the cell still had 63% of its initial capacity. Its carbon electrode

had a completely different DSC trace than the original material (SLM44) (Fig. 1). This indicates that the SEI layer has been changed during cycling.

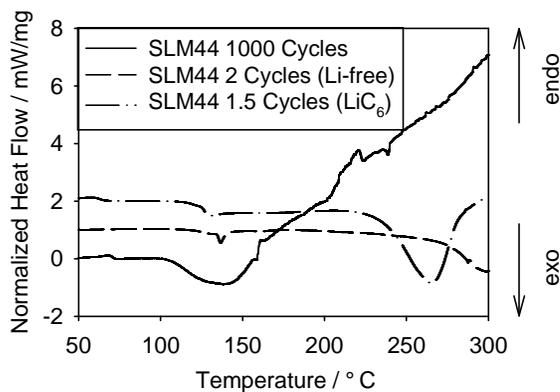


Fig. 1: The influence of cell history on heat evolution of a negative electrode containing the highly crystalline graphite TIMREX[®] SLM44.

Choice of Carbon Materials

The DSC traces of different carbon materials are not identical, but the amounts of heat evolved from low surface area material such as MCMB10-28, KS44 or SLM44 are approximately 200 J/g, whereas the high surface area material (KS6) displays a significantly higher heat evolution (~600 J/g). From these figures, we estimated the temperature increase in a cylindrical cell (18 x 65 mm). We assumed that this cell had a capacity of 1.4 Ah, weighed 39.4 g, which are typical values for a commercial lithium ion battery, and a specific heat of 0.92 J/g [4]. Using these estimates and assumptions we calculated that the temperature would increase about 30K for cells with MCMB10-28, KS44, and SLM44. The effect of slightly lower specific heat of MCMB10-28 is compensated by the 15% lower specific charge of this material. In contrast to the above materials, KS6 evolves much more heat and the estimated temperature increase is about 70K.

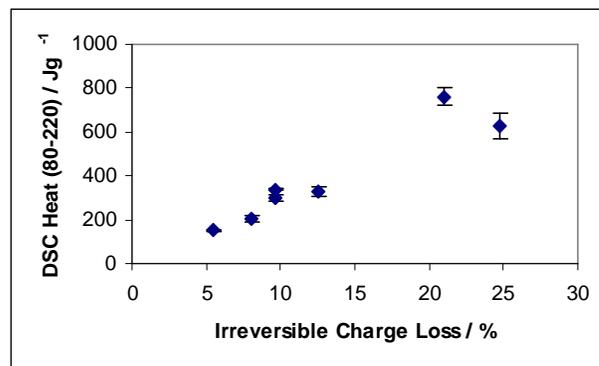


Fig. 2: Heat evolution of graphite negative electrodes resulting from DSC measurements in relation with their irreversible capacities in the first electrochemical Li^+ insertion cycle in 1M LiPF_6 EC/DMC 1:1 electrolyte.

References

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