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Research Paper

Effects of rest time after Li plating on safety behavior—ARC tests with commercial high-energy 18650 Li-ion cells

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ABSTRACT

During charging at low temperatures, metallic Lithium can be deposited on the surface of graphite anodes of Li-ion cells. This Li plating does not only lead to fast capacity fade, it can also impair the safety behavior. The present study observes the effect of rest periods between Li plating and subsequent accelerated rate calorimetry (ARC) tests. As an example, commercial 3.25 Ah 18650-type cells with graphite anodes and NCA cathodes are cycled at 0 °C to provoke Li plating. It is found that the rest period at 25 °C between Li plating and the ARC tests has a significant influence on the onset temperature of exothermic reactions (T_{SH}), the onset temperature of thermal runaway (T_{TR}), the maximum temperature, the self-heating rate, and on damage patterns of 18650 cells. The results are discussed in terms of chemical intercalation of Li plating into adjacent graphite particles during the rest period. The exponential increase of capacity recovery and T_{SH} as a function of time suggests a reaction of 1st order for the relaxation process.

1. Introduction

Today Li-ion technology is used for energy storage in a variety of applications such as smartphones, smartwatches, tablet/laptop computers, mp3 players, power tools, stationary energy storage, human spaceflight, unmanned aerial vehicles (UAV), light electric vehicles (LEV), as well as electric cars (EV, HEV, PHEV). During the whole life of a battery, the safety is most important.

Unfortunately, the life-time of state-of-the art Li-ion cells is limited by aging mechanisms on the material level [1–6]. One critical aging mechanism under investigation is Li plating on graphite anodes [5–20]. The reason for Li plating are negative anode potentials vs. Li/Li^+, which can be determined in full cells with an additional reference electrode [5,7,9,17,18]. During charging of a cell, the anode potential gets lower and the cathode potential increases. The difference between anode and cathode potential is the cell voltage [17,18].

The tendency of lower anode potentials is favored by low temperatures [5–7,17–19,21], high charging C-rates [6,9,18], and high SOC [7,9,18]. The combination of these parameters determines if Li plating happens or not [18].

An overview on possible processes (i-v) on the anode surface involving Li is shown in Fig. 1. During charging under Li plating conditions, there is a rivalry between intercalation of Li^+ ions from the electrolyte into graphite (ii) and deposition of metallic Li on the surface of the graphite anode (iv) [10,14,22]. This rivalry can be regarded as parallel reactions. During discharging with Li plating present on the graphite surface, metallic Li is stripped (iii) [14,21] and intercalated Li is de-intercalated (i). During a rest period, metallic Li can also chemically intercalated into adjacent graphite particles (v) [11,23].

The dendritic growth of metallic Li is often discussed as a main safety concern regarding Li plating [24–27]. The reason is that Li dendrites lead to internal short circuits between anode and cathode and could cause thermal runaway. We would like to stress that dendrite growth is not the only problem, since massive Li plating on anodes – which had not necessarily grown dendritically – leads to stronger exothermic reactions with electrolyte in differential scanning calorimetry (DSC) experiments [13].

On the cell level, a measure for cell safety is the onset temperature of exothermic reactions T_{SH} in accelerated rate calorimetry (ARC) tests [13,28–32]. In ARC tests, cells are heated step-by-step under quasi-adiabatic conditions until exothermic reactions are detected (heat-wait-seek experiment) [13,29,30,33]. In particular, a recent study on commercial cells with Li plating in our lab[13] showed

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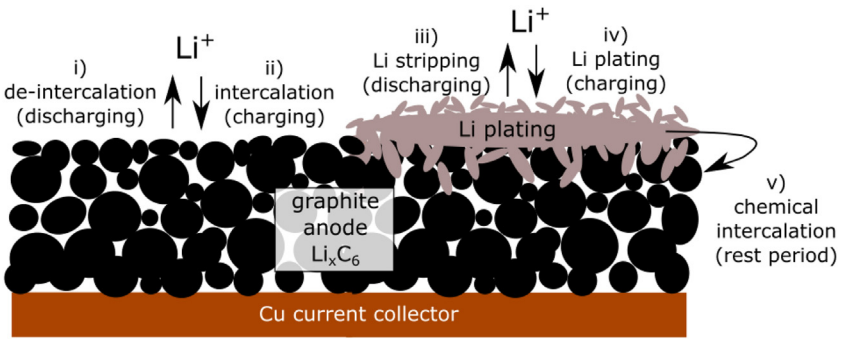

Fig. 1. Overview on possible processes on a graphite anode surface involving Li: Li intercalation into graphite (ii) and Li deposition on the anode surface (iv) during charging, Li de-intercalation from lithiated graphite (i) and stripping of deposited metallic Li (iii) during discharging. During a rest period, metallic Li can chemically intercalate into graphite if it is in direct contact (v).

(i) a stronger exothermic reaction of graphite anodes in DSC experiments,
(ii) a stronger degree of destruction after thermal runaway (ejection of jelly roll),
(iii) a low onset temperature in the range of 30–53 °C leading to thermal runaway under the quasi-adiabatic conditions in ARC tests.

One effect on safety behavior that has to best of our knowledge not been investigated so far is a rest period after Li plating. Mandeltort and Yates measured the intercalation kinetics of adsorbed Li submonolayers into graphite single crystals (HOPG) under ultra-high vacuum conditions [23]. Their measurements showed that Li moves from the graphite surface into the graphite with a comparably low activation barrier of 0.16 ± 0.02 eV [23]. Fan and Tan found by analysis of voltage curves that Li plating produced during charging at −20 °C diffuses into the graphite anode within 10 h at room temperature [8]. Dilation measurements by Bauer et al. showed a decrease of the thickness of pouch cells after charging at −5 °C [20]. Zinth et al. investigated the relaxation of lattice constants of commercial graphite/NMC cells with Li plating by neutron diffraction [11]. The authors found that during a rest period of 17–20 h, LiC_{12} is transformed into LiC_6 indicating the chemical intercalation of metallic Li into graphite [11].

Since Li in its metallic form is the cause for decreased safety behavior [13], it can be expected that chemical intercalation of Li plating into adjacent graphite and the results of thermal runaway tests are correlated. Since there is a dearth of knowledge on this is topic, this is investigated in the present study. Furthermore, damage patterns of the cells after thermal runaway are evaluated for cells with and without Li plating.

2. Experimental

All electrochemical tests were performed by a Basytec CTS system in combination with climate chambers (Vötsch). The high-energy 18650 cells under investigation include NCA cathodes, they have a specified minimum capacity of 3.25 Ah, a cell voltage range of 2.5–4.2 V, and a nominal voltage of 3.6 V. The cell weight with external tabs and without plastic shell is 46.0 g.

From previous investigations in our lab it is known that this cell type reaches ∼80% of the initial capacity after 18 cycles at 0 °C when charged and discharged at 0.5C (CC-CV charging to end-of charge voltage/cut-off current: 0.165A and CC discharging to end-of-discharge voltage) [9]. Therefore these conditions were used to provoke Li plating. The rest period between charging and discharging was 10s. Cycling started with the cell at 3.6 V and ended with a charged cell. Consequently, the ARC tests were performed with the cells charged to 4.2 V (CC-CV) at the cycling temperature of 0 °C and at 25 °C for the fresh cells.

The cells with Li plating were subject to ARC tests after rest periods of 1.5 h and 8d after cycling. For comparison, fresh cells were charged with a rate of 0.2C at 25 °C, which is known not to lead to Li plating for this cell type [9]. In order to exclude any effects of low cell temperature in combination with the ARC temperature control loop, additional fresh cells were cooled down to 0 °C for 2 h, before they were heated to 25 °C for 1.5 h similar to the cells with Li plating. These cells showed a very similar behavior to the fresh cells handled at 25 °C only and therefore effects of the cell

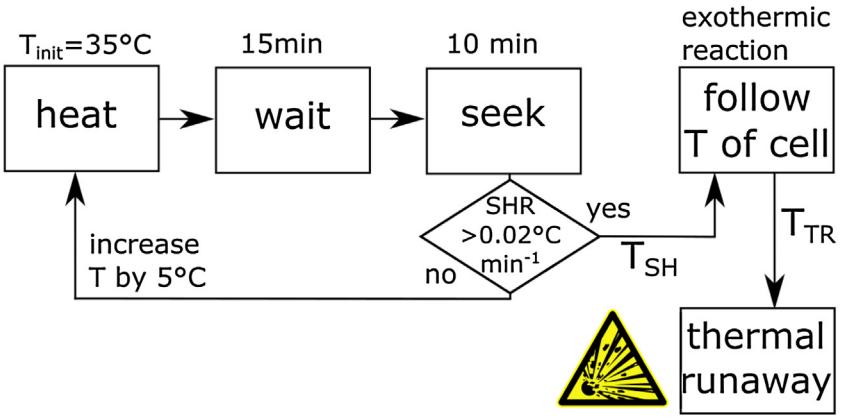

Fig. 2. Heat-wait-seek algorithm used to force the cells into thermal runaway.