



Impact of cycling at low temperatures on the safety behavior of 18650-type lithium ion cells: Combined study of mechanical and thermal abuse testing accompanied by *post-mortem* analysis



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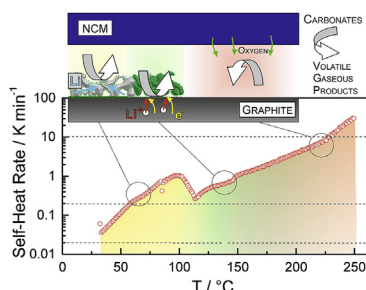
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HIGHLIGHTS

- High surface area (“dendritic”) lithium metal deposition on graphite anode promotes reduction of electrolyte.
- Increase of SOC generates more gaseous products in fresh cells.
- Strong exothermic reaction is observed in aged cells.
- SOC dependency of the exothermic reaction disappeared for aged cells.
- Risk of a thermal runaway is increased for aged cells.

GRAPHICAL ABSTRACT



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ABSTRACT

The impact of cycling at low temperatures on the thermal and mechanical abuse behavior of commercial 18650-type lithium ion cells was compared to fresh cells. *Post-mortem* analyses revealed a deposition of high surface area lithium (HSAL) metal on the graphite surface accompanied by severe electrolyte decomposition. Heat wait search (HWS) tests in an accelerating rate calorimeter (ARC) were performed to investigate the thermal abuse behavior of aged and fresh cells under quasi-adiabatic conditions, showing a strong shift of the onset temperature for exothermic reactions. HSAL deposition promotes the reduction of the carbonate based electrolyte due to the high reactivity of lithium metal with high surface area, leading to a thermally induced decomposition of the electrolyte to produce volatile gaseous products. Nail penetration tests showed a change in the thermal runaway (TR) behavior affected by the decomposition reaction. This study indicates a greater thermal hazard for LIB cells at higher SOC and experiencing aging at low temperature.

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1. Introduction

Due to their high energy density and, high power as well as their long life and Coulombic efficiency of nearly 100%, lithium ion

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batteries (LIBs) are the most promising electrochemical energy storage system for electric vehicles (xEVs), portable devices, smart electronics and stationary electricity storage [1]. Especially for automotive applications an excellent aging behavior (resulting in long cycle and calendar life) and a high safety are crucial and essential factors for the success of LIBs [2–5]. While safety [2–4,6,7] and aging [8–11] were investigated intensively in many studies. Combined studies were seldomly reported in the literature and showed mostly how the safety behavior could be influenced by aging parameters without clarifying the mechanisms and reasons behind [12–14].

The aging of LIBs is a complex interaction of chemical and physical mechanisms with inter-dependencies from nearly all active and inactive cell components. Amongst others, cell chemistry, state of charge (SOC) variation, charge/discharge cut-off voltages, temperature, applied current rate, manufacturing process and cell design were reported to influence the aging behavior [9–11,15–17].

By decreasing the temperature to below 0 °C, LIB performance suffers from capacity and voltage decrease, due to reduced mobility of lithium ions in the electrolyte, in the solid electrolyte interphase (SEI) [18,19] and in the graphitic particles [9,20–22]. Accordingly, charging at low temperatures leads to increased overpotentials which can lower the operation potential of graphite below 0 V vs. Li/Li⁺, hence lithium metal deposition on the anode surface, known as lithium plating, is facilitated. Lithium metal deposition is considered as one of the most critical aging mechanisms and an increased safety issue arises from short-circuit risks by the growth of high surface area lithium structures, known as dendritic [23], mossy or granular lithium, which is summarized as high surface area lithium (HSAL) [24,25].

With growing energy density and increasing battery pack sizes in xEVs the safety risks of using LIBs are increasing proportionately. Hence, the safety behavior of LIBs is a main concern for future development. To determine the cell safety, different abusive conditions for cells and materials were reported. The operated methodologies can be distinguished between thermal, mechanical or electrochemical/electrical abuse. Under thermal abuse conditions the cells undergo several consecutive reactions. Most of these temperature-activated reactions are exothermic and can drive the cell to undesirable situations, such as thermal runaway (TR). In this state the cell exceeds a certain temperature threshold value. The generated heat can no longer dissipate into the surrounding leading to further exothermic reactions, which will proceed until all reactive agents are involved and completely consumed or until the cell ruptures, accompanied by venting, flames, smoke or even explosions [3,26–28]. In general, the first exothermic reaction is the decomposition of the SEI layer (80–120 °C), followed by an electrolyte reduction in contact with Li from Li_xC₆ [3,28–30]. With increasing temperature the electrolyte starts to react with the cathode surface. The most severe exothermic reaction in case of layered oxide cathodes is usually the cathode decomposition accompanied with O₂ release and subsequent electrolyte decomposition [3,31]. Mechanical abuse methods, such as nail penetration tests, produce short-circuits leading to a release of electrochemical energy by rapid discharge, thus heating the cell by Joule-heating. The related release of thermal energy can be sufficient enough to trigger further thermal decomposition reaction resulting in a TR, as described above. Furthermore, the nail penetration test is used to simulate an internal short circuit [32]. To prevent such events a detailed understanding of the cell behavior under such abusive conditions is necessary.

In this work the influence of aging on the behavior under abusive conditions is studied on commercial state-of-the-art 18650-type cells. Since lithium metal deposition is considered as

one of the most critical aging mechanisms, low temperature cycling was chosen as the aging condition. The cells were cycled with 1C at 0 °C until 70% state of health (SOH) was reached. Typically an SOH between 70% and 80% is considered as the end of life (EOL) of a battery [33–35]. In order to reliably investigate the mechanisms mainly responsible for aging, comprehensive *post-mortem* studies of aged and fresh (100% SOH) cells were performed. Thermal behavior of the cells was studied under quasi-adiabatic conditions in an accelerating rate calorimeter (ARC). Mechanical abuse was determined with nail penetration tests. All abuse tests were performed on fresh and aged cells at a state of charge (SOC) of 0%, 50% or 100% to generate comprehensive insight into LIB cell behavior under abusive conditions.

2. Experimental

2.1. Cell selection, cycling conditions

In this study commercially available 18650-type lithium ion cells (2.2 Ah, Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O₂/Graphite) were investigated. This cell shows good and versatile characteristics with a state-of-the-art (2016) cathode material. The cells were cycled by a Maccor Series 4000 battery tester (Maccor, Inc., USA) in a Binder MK240 (BINDER GmbH, Germany) climate chamber to enable a constant surrounding temperature of 0 °C. The cycling protocol consists of a constant current/constant voltage (CC/CV) charge -procedure followed by a CC discharge in the full voltage window between 4.2 V and 2.75 V according to the Material Safety Data Sheets (MSDS/see supporting information Table S1). The CC step was performed with 1C (2.2 A) and the CV step until the current rate drops below C/20. The end of life (EOL) condition was defined as 70% SOH, which represents the capacity in comparison to the initial discharge capacity of the first cycle at 0 °C.

2.2. Cell opening and sample preparation

Cycled and fresh cells were fully discharged with a CC/CV protocol (equal to charging) prior to opening the cells, defined as state of charge (SOC) 0%. The cells were opened in a glove box (M. Braun Inertgas-Systeme GmbH, Germany) under argon (6.0 purity; Westfalen Gas) atmosphere (O₂ < 0.1 ppm, H₂O < 0.1 ppm) with a cutting tool from both sides. The jelly roll was removed from its case and the individual parts (outer separator, anode, inner separator, and cathode) were separated. Samples were taken with a punching tool and washed twice with 800 μL dimethyl carbonate (DMC, by Sigma-Aldrich anhydrous, ≥99%) from both sides to remove the conductive salt and other electrolyte residues. The samples were dried afterwards in the glove box. Electrolyte was extracted of the whole jelly-roll from additional cells by centrifugation (Sigma 3–16 P, Sigma Laborzentrifugen GmbH, Germany) at 4200 rpm for 30 min.

2.3. Scanning electron microscopy (SEM)

SEM was used to investigate the surface morphology of the electrodes. SEM images were obtained using a Carl Zeiss AURIGA CrossBeam workstation (Carl Zeiss SMT AG, Germany) with a 3 kV acceleration voltage at a working distance of 2 mm and a vacuum of 10⁻⁶ bar. The samples were transferred into the SEM using a self-built argon filled protection device, thus contact with oxygen and moisture can be excluded. The sample holder consists of an aluminum stage covered with an acrylic lid. Prior to the outward transfer from the glovebox, the sample holder is evacuated (≈0.5 bar). The negative pressure joins stage and lid until the higher vacuum of the SEM device opens the lid.

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