Research Paper

Preventing Li-ion cell explosion during thermal runaway with reduced pressure

CrossMark

Andreas Hofmann [a,*], Nils Uhlmann [b], Carlos Ziebert [b], Olivia Wiegand [c], Alexander Schmidt [c], Thomas Hanemann [a,d]

[a] Karlsruher Institut für Technologie (KIT), Institut für Angewandte Materialien – Werkstoffkunde (IAM-WK), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[b] Karlsruher Institut für Technologie (KIT), Institut für Angewandte Materialien – Angewandte Werkstoffphysik (IAM-AWP), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[c] Karlsruher Institut für Technologie (KIT), Institut für Nanotechnologie – Projekt Competence-E (INT-PCE), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[d] Universität Freiburg, Institut für Mikrosystemtechnik, Georges-Köhler-Allee 102, 79110 Freiburg, Germany

HIGHLIGHTS

- Increase of Li-ion cell safety by reduced pressure.
- Li-ion cell thermal runaway without cell explosion.
- Reduced pressure via vacuum pump or suction unit.

ARTICLE INFO

ABSTRACT

Concerning Li-ion cells it is demonstrated by overcharging tests both on the shelf in a fume-hood and in an accelerating rate calorimeter that the application of reduced pressure in the moment of a thermal runaway accident can prevent a fire and in particular a cell explosion, caused by the electrolyte. Within the experiment, pouch-bag Li-ion cells (88 mAh and 264 mAh) composed of graphite and NMC ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) were overcharged by 10 C in order to induce a thermal runaway. In spite of a strong temperature increase, the cell remains tightly close during the thermal runaway without any fire or explosion in case of vacuum application.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Although considerable efforts were made to increase the cell safety of Li-ion based cells and battery packs due to fire accidents and high-energy materials, one of the main critical issues remains their abuse behaviour in terms of thermal runaway which usually results in cell explosions and fire accidents [1–3]. Additionally, toxic gases like HF and decomposition products are released to the environment during a cell opening [4]. Such an issue is very important when using large-scale battery packs or single cells with high energy content.

Large efforts were made on the material side so far by developing safer anode (e.g. lithium titanate [5,6]) or cathode materials (e.g. lithium iron phosphate [7–10]), electrolyte additives [11,12], electrolytes with reduced flammability [13–17], or the concept of solid electrolytes [18–23], gel-polymer electrolytes [24–28] and ceramic coated separators [29,30]. In multilayer separators, the resistance rises rapidly when the inner layer melts and blocks the lithium transport. Additional concepts on cell level are cell casing, overpressure valves which can release gases in a controlled manner and aerogel material [31] inside the cell which is able to absorb gaseous products. On battery level, heat absorbing material between single cells, battery pack casing and the cell relay including safety features are used to increase the safety of the Li-ion based cell packs. Nevertheless, state-of-the-art cell chemistry

* Corresponding author.
  E-mail address: andreas.hofmann2@kit.edu (A. Hofmann).

technology is still the use of highly flammable electrolytes, the use of polyolefine separators and electrode materials with a high content of combustible material (binder, carbon black and graphite). Thus, concepts are strongly needed which can increase the safety level of state-of-the-art Li-ion cells.

During a thermal runaway, the temperature inside the cell increases rapidly so that the electrolyte solvents start to boil and come into gaseous state [3,32]. This behaviour leads to a strong increase in pressure [33] and volume expand. As a consequence, a flexible cell-casing starts to blow up till the cell opens and highly flammable gaseous products are released to the environment. Usually, the temperature in this state already reached the auto-ignition temperature and the gaseous products start to burn or explode. An interrupt during this process can be obtained by a strong endothermic process. So it can be observed that during the endothermic boiling process of the solvent heat is absorbed. Nevertheless, there is a short delay which cannot set the cell back into a safe condition based on the solvent amount compared to the heat release during a thermal runaway. Additionally, the boiling temperature shifts to higher boiling temperatures at elevated pressure so much that the endothermic heat absorbance is attenuated compared to the boiling point temperature under standard conditions.

In order to remove some of the heat from the cell, it is possible to assemble the cell into a heat-absorbing material [31]. However, such prevention can work only outside of the cell and not intervene in the pressure increase directly. Another option to extract heat from the cell could be the use of reduced pressure. In this case, the boiling of the solvent is enabled at lower temperature. During this process, much more heat could be absorbed in a short period of time in dependence of the reduced pressure strength and gas flow characteristics. Additionally, the pressure inside the cell decreases rapidly and all gaseous and highly flammable products are removed from the cell.

In this paper the increase of cell safety level by using reduced pressure is introduced for the first time with the best of our knowledge and experimental evidence. The proof-of-concept is demonstrated in case of pouch-bag cells. Additionally, the method is discussed for use in larger pouch-bag cells and battery design.

2. Material and methods

The abuse tests were done with 44 mAh, 88 mAh and 264 mAh pouch bag cells with commercial available NMC cathode material ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$; 5.0 × 5.0 cm; 90 wt.% active material), graphite anodes (5.2 × 5.2 cm; 90 wt.% active material) and ceramic coated PET-based separator (5.5 × 5.5 cm). The cell characteristics are summarized in Table 1. The weight of the cell casing (coated aluminium bag and contact strips) is 5.50 ± 0.05 g for all cells.

An ethylene carbonate/dimethyl carbonate (EC: DMC = 50:50 wt.%) based electrolyte with 1 M $LiPF_6$ and 3 wt.% vinylene carbonate is used for all cells. The cell assembling was

performed in a dry room with dew point of <−70 °C. Before the abuse tests, all cells were cycled (100 cycles) at 2 C/3 C between 3 and 4.2 V to cause cell aging. The reference cells are used with no additional features. For adapting the reduced pressure unit, a small tube (Festo, PAN-6x1) was fixed inside the pouch cell with hot glue or super glue with temperature stability up to 160 °C. The cell opening, tube adaption and closing of the pouch-bag cell were put inside of an argon-filled glovebox (oxygen and water level <0.5 ppm). A manual valve enables the switch on of the reduced pressure in terms of a small vacuum pump (Pfeiffer, Duo 1.5 A, 1.5 m^3/h) or a suction device (Filtertrolley 2.1, ULT Jumbo, ACD). A laboratory DC power supply (Knürr-Heinzinger, LNG 50-4) is used for charging during the overcharge test (charging at current rate of 10 C up to 50 V; 88 mAh cells at $I = 0.90$ A; 264 mAh cells at $I = 2.70$ A; constant current). As the cell voltage rises to 15–25 V under strong cell swelling, the reduced pressure is engaged with the manual valve. The overcharging tests were performed both on the shelf in a fume hood and inside of an accelerating rate calorimeter (ARC, es-ARC, Thermal Hazard Technology); the reduced pressure was switched on at 15–20 V. The calorimeter chamber, with an inner diameter of 0.1 m and a height of 0.10 m, has one heater and one thermocouple located in the lid and bottom as well as two heaters and two thermocouples (all type N) in the side wall. The heaters adjust the required temperatures depending on the measurement conditions. The cell temperature is recorded by a main or so-called bomb thermocouple attached onto the surface of the cell by temperature-resistant (up to 250 °C) adhesive tape. This bomb thermocouple of type N is placed in the center of the region where the electrode sheets are located. In addition to the automated temperature recording from the calorimeter, the temperature was logged with the device Siemens Thermizet B4001. Standardly the temperature is measured at the front side; a control is done at the backside for individual cells with a second temperature sensor. The experimental flow chart is depicted in Fig. 1. Within this experimental set-up, the ARC was not used as a heating source for the cell. All heat was generated by the overcharging procedure.

In order to estimate the temperature of no return, a hot-box-test (5 °C·min^{-1} heating) was performed on ARC (es-ARC, Thermal Hazard Technology) calorimeter. The starting temperature was set to 50 °C. At the same time, the temperatures of the cell and the calorimeter (top/side/bottom) were recorded. The sensitivity rate of the calorimeter was set to 6 °C·min^{-1}. The cell voltage at the beginning of the test was 4.2 V. Within the test, no overcharging was applied.

3. Results and discussion

During preliminary tests it is proved that it is very difficult via overcharging at moderate current rates (5–10 C) to bring small pouch bag cells of 44 mAh nominal capacity to any kind of

Table 1
Cell characteristics of the pouch bag cells. The density d of the electrolyte is $d = 1.27$ g·cm^{-3}. A Teflon-based tube (0.51 ± 0.05 g) is installed in each pouch-bag cell for gathering gas which is built during cell formation. The contact strips are composed of Al (135 mg/sheet) and Cu (242 mg/sheet). A ceramic coated separator (135 mg/sheet) is used for all tests between both electrodes. Based on the composition of the cell, a C_p-value of 1.2 J·(K·g)$^{-1}$ was calculated for the 88 mAh cells according to literature methods at 60 °C assuming an additive contribution of the individual components to C_p [34,35].

Nominal cell capacity/mAh	Electrolyte amount/μl	Nominal voltage before over-charging/V	Electrode sheets (o = one side coated, t = two side coated)		Electrode material weight/mg (including inactive material, without aluminum or copper)		Mass of pouch-bag cell (total)/g
			NMC	C	NMC	C	
44	450 ± 3	4.2 ± 0.1	1 (o)	1 (o)	326 ± 1	256 ± 1	7.1 ± 0.3
88	900 ± 5	4.2 ± 0.1	1 (t)	2 (t)	652 ± 2	1024 ± 4	9.6 ± 0.3
264	2700 ± 20	4.2 ± 0.1	3 (t)	4 (t)	1956 ± 6	2048 ± 8	15.6 ± 0.3