CHARACTERISTICS OF THE THERMAL RUNAWAY
Work Package 1.4

ALBERO Project

Institut für Sicherheitstechnik/Schiffssicherheit e.V.

Behaviour of Lithium-Ion-Batteries in hazardous situations

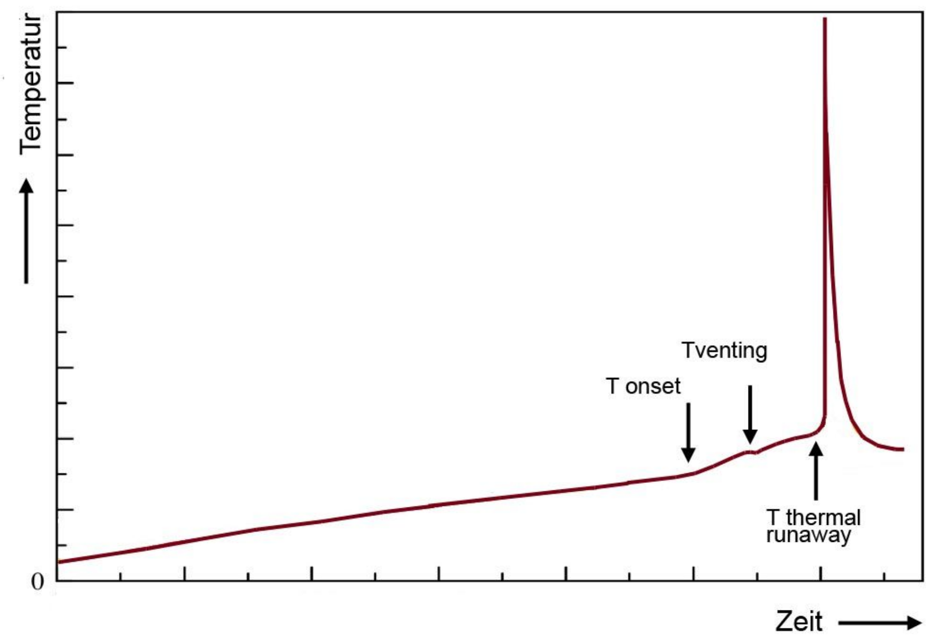
Institut für Sicherheitstechnik / Schiffssicherheit e.V.

Car batteries can overheat due to internal processes (electrical malfunctions, overcharging, uncontrolled chemical reactions) and external processes (solar radiation, fire in the environment, hot surfaces in the vicinity). Hence a thermal runaway can occur.

What is meant by thermal runaway?

A **Themal Runaway** refers to the overheating of an exothermic chemical reaction or technical apparatus due to a self-reinforcing heat-producing process. [1].

In recent years, calorimetric studies on the behavior of Li-Ion batteries under thermal load have been carried out in many working groups around the world. As a rule, 18650 single cells were analyzed in a heatable calorimeter. Over the years, the investigations have become more and more detailed, and distinctions have been made between cell chemistry, state of charge, aging, and so on. More recent investigations also deal with the thermal runaway during charging/discharging. The classic curve of such an experiment looks as follows:



A distinction is made between the onset temperature, i.e. the approach at which the heat development deviates from the constant heating rate, and the thermal runaway temperature, at which the chemical reactions in the cell continue to accelerate themselves and therefore a very sudden very sharp rise in temperature is recorded. The definition of the temperature varies at which thermal runaway is said to occur. For example, some define a temperature change of at least 4°C/s [2], others 100°C/min. [3].

[1] https://de.wikipedia.org/wiki/Thermisches_Durchgehen
[2] https://ec.europa.eu/jrc/sites/jrcsh/files/initializing-of-thermal-runaway-for-lithium-ion-cells.pdf
[3] Melcher, A.; Ziebert, C.; Rohde, M.; Seifert, H.J. Modeling and Simulation of the Thermal Runaway Behavior of Cylindrical Li-Ion Cells—Computing of Critical Parameters. *Energies* **2016**, *9*, 292.

Occasionally, the temperature is explicitly stated too at which the cell bursts and gases are released (T venting). This is usually between the onset temperature and the runaway temperature.

At what temperatures does thermal runaway occur?

A comprehensive literature research has been performed on scientific papers that dealing with the determination of the thermal runaway temperature. The table lists the cells tested and roughly the experimental conditions as well as the results found. The overview covers only a section of the research carried out, but gives a representative impression regarding the results.

battery details	**how heated?**	**thermal runaway TR at [°C]**	**source**
Sony (US18650) 4.06V open circuit voltage (OCV)	heated in calorimeter	104	Al Hallaj, S.; Maleki, H.; Hong, J.; Selman, J. Thermal modeling and design considerations of lithium-ion batteries. *J. Power Sources* **1999**, 83, 1–8.
Sony (US18650) 3.0V, open circuit voltage (OCV)		109	
Sony (US18650) 2.8 V open circuit voltage (OCV)		144	
18650 Li-NMC ($Li(Ni_{0.45}Mn_{0.45}Co_{0.10})O_2$)	heatable reactor with thermos elements	TR at 220, cell breakup at 160	Andrey W. Golubkov et. al : Termal runaway experiments on consumer Li-ion batteries with metal-oxide and olivon-type cathodes, *RSC Adv.*, **2014**(4), 3633 - 3642
18650 LCO/NMC $LiCoO_2$ and $Li(Ni_{0.50}Mn_{0.25}Co_{0.25})O_2$.		TR at 208	
$Li(NiCoAl)O_2$ nominal capacity of 3350 mAh at a nominal voltage of 3.60 V	heatable steel reactor with thermos elements	TR at 173, cell breakup at 130	Alexander Königseder: Investigation of the Thermal Runaway in Lithium Ion batteries, *Masterarbeit*, Technische Universität Graz, März **2017**
$Li(NiMnCo)O_2$, 3200 mAh at a nominal voltage of 3.75 V		TR at 166, venting 129	
$Li(NiMnCo)O_2$, 3500 mAh and a nominal voltage of 3.64 V		TR at 150, venting 122	
$Li(Ni0.8Co0.15Al0.05)O_2$ 3500 mAh and a nominal voltage of 3.60 V		TR at 166, venting 129	
$Li(NiCoAl)O_2$, 3300 mAh at a nominal voltage of 3.60 V		TR at 156	
$Li(NiMnCo)O_2$, 2500 mAh and a nominal voltage of 3.60 V		TR at 196, venting 117	
$Li(NiMnCo)O_2$,2600 mAh at a nominal voltage of 3.7 V		TR at 153, venting 147	
18650 cylindrical or prismatic $LiCoO_2$ batteries, spiral winding, differences in the connection of the individual cells (S-type or M-type)	malfunction of the center cell in a 9-cell pack with heating element, monitoring of the temperature	TR of the trigger cell in different tests: 204, 186, 119, 200, 157, 151	Carlos F. Lopez, Judith A. Jeevarajan, Partha P. Mukherjee: Experimental Analysis of Thermal Runaway and Propagationin Lithium-Ion Battery Modules, *Journal of The Electrochemical Society*,162(9) A1905-A1915, **2015**

	directly at the trigger cell and at surrounding cells		
18650 $LiFePO_4$	heated in calorimeter	T onset at 200	Wen, CY., Jhu, CY., Wang, YW. et al.: Thermal runaway features of 18650 lithium-ion batteries for LiFePO4 cathode material by DSC and VSP2 J Therm Anal Calorim (**2012**) 109: 1297. https://doi.org/10.1007/s10973-012-2573-2
Li-Ion, 2200 mAh, 3,7 V	no details	To at 92 TR at ca. 150	https://www.netzsch-thermal-analysis.com/de/materialien-applikationen/batterien/lithium-ion-cells-thermal-runaway/
$LiFePO_4$, 1200 mAh, 3,3 V		To at 80 TR at ca. 170	
$LiFePO_4$, 1100 mAh, 3,2 V		To at 116 TR at ca. 165	
18650 LCO, 2600 mAh	heated in calorimeter	To at 131	Jhu, C.Y.;Wang, Y.W.;Wen, C.Y.; Shu, C.M. Thermal runaway potential of $LiCoO_2$ and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ batteries determined with adiabatic calorimetry methodology. Appl. Energy **2012**, 100, 127–131.
18650 NMC, 2000 mAh		To at 175	
18650 LCO / Graphite, 2600 mAh, 30% charged	heated in calorimeter	To at 175	Chen, W.C.; Wang, Y.W.; Shu, C.M. Adiabatic calorimetry test of the reaction kinetics and self-heating model for 18650 Li-ion cells in various states of charge. J. Power Sources **2016**, 318, 200–209.
50% charged		To at 174	
80% charged		To at 140	
100 % charged		To at 122	
18650 LCO / Graphite, 800mAh, 0% charged	heated in calorimeter at different charge states	To at 165	Mendoza-Hernandez, O.; Ishikawa, H.; Nishikawa, Y.; Maruyama, Y.; Umeda, M. Cathode material comparison of thermal runaway behavior of Li-ion cells at different state of charges including over charge. J. Power Sources **2015**, 280, 499–504.
25% charged		To at 160	
50% charged		To at 155	
75% charged		To at 140	
100% charged		To at 125	
120 % charged		To at 116	
18650 $LiMn_2O_4$ / Graphite, 720 mAh, 0% charged	heated in calorimeter at different charge states	-	
25% charged		To at 110	
50% charged		To at 105	
75% charged		To at 105	
100% charged		To at 105	
120 % charged		To at 100	
$LiFePO_4$ cylindric, 2600 mAh	heated in calorimeter	To at 175	Orendorff, C.; Lamb, J.; Steele, L.A.; Spangler, S.W.; Langendorf, J.: Quantification of Lithium-Ion Cell Thermal Runaway Energetics; SAND2016-0486; Sandia National Laboratories: Albuquerque, NM, USA, **2016**
$Li(NiCoAl)O_2$ cylindric 3400 mAh		To at 160	

18650 $LiMn_2O_4$, 1650 mAh,	heated in calorimeter	To at 91	B. Lei, W. Zhao *, C. Ziebert, N. Uhlmann, M. Rohde, H. J. Seifert: Experimental Analysis of Thermal Runaway in 18650 Cylindrical Li-Ion Cells Using an Accelerating Rate Calorimeter, Batteries **2017**, 3, 14;
18650 $LiFePO_4$, 1100 mAh		To at 90	
18650 $Li(NiMnCo)O_2$ 2200 mAh		To at 91	
18650 $LiCoO_2$ / Graphite, 20%	heated in calorimeter at different charge states	TR at 231	Liu, J.; Wang, Z.; Gong, J.; Liu, K.; Wang, H.; Guo, L. Experimental Study of Thermal Runaway Process of 18650 Lithium-Ion Battery. *Materials* **2017**, *10*, 230.
40% charged		TR at 226	
60 % charged		TR at 220	
80 % charged		TR at 204	
100% charged		TR at 198	
18650 $LiCoO_2$ / Graphite, charging current 2,6 A	measurement during charging with different current levels	TR at 226	
charging current 5,2 A		TR at 217	
charging current 7,8 A		TR at 140	
charging current 10,4 A		TR at 133	
charging current 13 A		TR at 123	
pack of 3 from Li-Ion-batteries, charging current 5 A, discharging current 15 A	measurement in an adiabatic calorimeter, the heat is generated by continuous charging and discharging	To at 118 TR at 150	https://www.hazards.co//articles/pdf/b64cb47866ba2a84/Application%20Note%20-%20Runaway%20Li-on%20Battery%20Explosion%20latest%20**2012**.pdf
18650 Lix(Ni0.80Co0.15Al0.05)O_2, 0% charged	heating in calorimeter at different (over)-charge conditions	To at 160	A. W. Golubkov, S. Scheikl, R. Planteu, G. Voitic, H. Wiltsche, C. Stangl, G. Fauler, A. Thaler, V. Hacker: Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge, RSC Adv., **2015**, 5, 57171
25% charged		To at 150	
50% charged		To at 140	
75% charged		To at 140	
100% charged		To at 138	
112% charged		To at 144	
120% charged		To at 80	
127% charged		To at 80	
132% charged		To at 80	
143% charged		To at 65	
Lix$FePO_4$, 25% charged	heating in calorimeter at different (over)-charge conditions	To at 195	
50% charged		To at 130	
75% charged		To at 149	
100% charged		To at 140	
115% charged		To at 155	
130% charged		To at 80	

bicycle battery, manufacturer Phylion, 100% charged, but typically about 50% capacity due to cell aging.	electric heating, One-sided, 150 W		test results ALBERO May 2019, Trauen
prismatic cells (attempt A1)		TR at > 150°C 45min	Note: The temperature measurement takes place outside the cell, facing away from the heating source. Therefore, the cell temperature is higher than the temperature of the measuring point.
round cells (attempt A2)		TR at > 60°C 17 min, jet of flame	
pouch cells (attempt A3)		TR at ca. >120°C, 22 min	
pouch cells (attempt A4)		TR at ca. >120°C, 17 min	

table 1: literature research on test results on the thermal runaway of Li-Ion-batteries

Depending on the heating conditions, the measured events occurred after approx. 40 min at the earliest after the start of heating from room temperature, with the exception of experiment A2 and the pouch cells in the ALBERO experiments.

Summary in relation to ALBERO

All measured values listed in the table above were summarized in a graph. No distinction was made between cell chemistry, state of charge, etc.. Only the distinction between thermal runaway temperature, onset temperature or venting temperature or temperature of the runaway during charging was illustrated by different colors. As mentioned above, the definitions for the events "onset" and "thermal runaway" are not uniform. In the first publications on the subject around the year 2000, this distinction was not made at all. Measurements of the onset of thermal runaway in overcharged batteries are shown in gray. However, since it is assumed that all car batteries have functioning overcharge protection, these values are considered with a lower priority. With regard to the ALBERO project, the graphic illustrates the following basic statement:

Dangerous processes (incipient thermal runaway, bursting of the cell, release of gases, thermal runaway) must be expected from approx. 80 °C! In case of danger detection by temperature monitoring, the alarm thresholds must be set accordingly. In the event of a fire or hot surfaces in the environment, it must be assessed whether temperatures of more than 80°C can occur on the car battery over a longer period of time (at least 30 min).

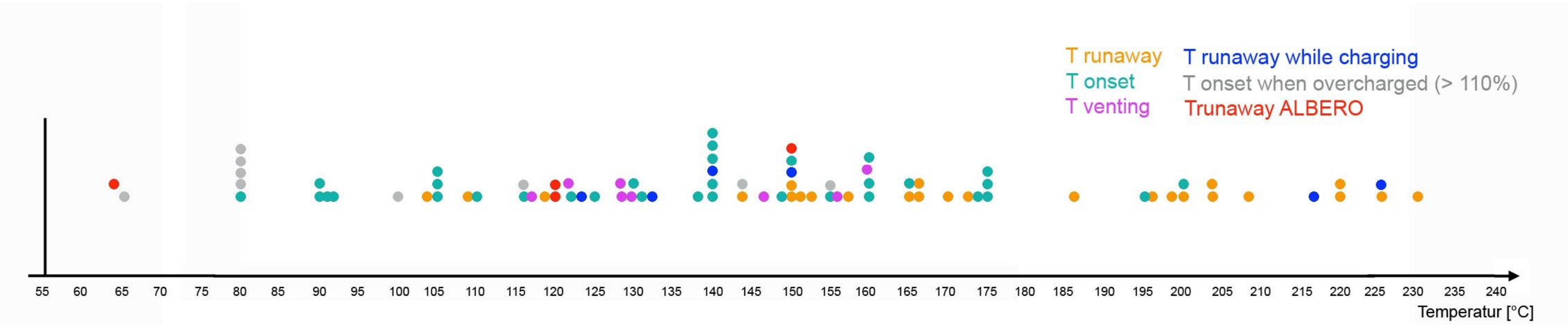


Figure: Summary of measurement results from Table 1 - event temperatures during heating of Li-Ion-batteries, events: incipient thermal runaway (T onset), bursting of the cell and release of gases (T venting), thermal runaway (T runaway).