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Experimental Investigation of the Overcharge Effects on Commercial Li-Ion Batteries with Two Different Anode Materials

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Lithium-ion batteries are now a widespread technology in automotive applications. Together with the life of the batteries and their performance, safety plays a fundamental role in ensuring the spread of electromobility in our society. Overcharge is one of the most severe safety problems for the large-scale application of lithium-ion batteries. In this work the results of the overcharge tests performed on Lithium Ion cells with different anode materials are presented: a comparison was made between graphite-based anode Li-ion batteries and Lithium Titanate Oxide (LTO)-based anode Li-ion batteries. Experimental tests were performed with different current intensities: it was thus possible to analyze the effects of an overcharge as the current supplied varies.
The graphite-based anode Li-Ion batteries are equipped with protection devices which act by blocking the passage of current in the cell and avoiding venting and/or explosion phenomena; on the other hand, LTO-based anode Li-Ion Batteries, although considered intrinsically safer batteries, experienced thermal runaway during the overcharge tests. Increasing the overcharge current, the effects of the electrical abuse are more destructive.

1. Introduction

In recent years, the automotive industry has been investing in increasingly advanced technologies, useful for achieving the continuous reduction of CO_2 emissions. Lithium-Ion Batteries (LIBs) have been considered to be the most competitive power source of Electric Vehicles (EV), Hybrid Electric Vehicles (HEV), Plug-in Hybrid Electric Vehicles (PHEV), because of their high-energy density (100-265 Wh/kg or 250-670 Wh/L) and good performance. Besides those advantages, this technology still presents several unsolved issues that may arise under abnormal abuse conditions. Overcharge is one of the most important safety issues for the state-of-the-art Lithium-Ion Batteries. Overcharge can lead to thermal runaway and ultimately to fire or explosion of the batteries. Therefore, it is necessary to understanding the real mechanism of LIBs under overcharge conditions to prevent it efficiently.
There are numerous works in the literature on the behavior of lithium-ion batteries during overcharging (Ruiz et al., 2018; Zhu et al., 2019; Ouyang et al., 2015; Zheng, 2018). Leising et al., 2001a,b, performed tests on prismatic lithium ion batteries with $LiCoO_2$ cathode (LCO) and graphite anode to clarify the mechanism of the overcharging reaction. Ohsaki et al., 2005, studied the overcharge reactions in detail and divided the process into 4 stages according to the characteristics of the Thermal runaway. Ohsaki et al.,2005, concluded that the thermal runaway is mainly due to a violent reaction, at high temperatures, between the deposited lithium and the electrolyte: this consideration is also in agreement with the studies of Arora et al.,1999 and the results of the simulations of Spotnitz et al., 2003.

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In the current literature all experimental tests were performed on graphite-based anode Li-ion cells: in this paper graphite-based anode batteries were compared with LTO-based anode batteries, considered intrinsically safer. The cells were tested at different charge rates by monitoring the State Of Charge (SOC%) and the surface temperatures.

2. Experimental set up

The overcharge tests were performed in a dedicated test field: the FARO plant (Figure 1), located in the C.R. Casaccia, was created with the aim of safely allowing the execution of abuse tests on cells and battery packs. It develops on an area of about 900 m^2 and is equipped with: facilities for the management of abuse tests, control room and warehouses.

(a) (b)

Figure 1: (a) FARO plant and (b) cell (type NCR18650B) under test

The cells are tested inside a bulletproof box and monitoring is performed with:

- a thermal infrared camera: Flir S60 model, T_{max}: 1500°C, Thermal sensitivity: <0.1°C, Accuracy: ±2°C o ±2%;
- 3 calibrated thermocouples, type K (accuracy of ±0.1°C) located on each tested cell;
- a fast camera: Redlake MotionPro Y3S1-M model, velocity 3000 fps @ 1280 x 1024;
- a National Instruments "CompactDAQ" chassis with a thermocouple module (24 bit ADC, 16 channels) and one voltage input module (16 bit ADC, 32 channels);
- a data acquisition system designed by using LabVIEW.

Each tested cell was subjected to preliminary standard charge/discharge cycles with the Eltra E-8094 cycler, (nominal voltage 3.6 ÷ 6V, current 0 ÷ 280A) while the abuse tests were performed with the portable cycler Eltra E-8325 (voltage 0 ÷ 18V, maximum charge current 80A and maximum discharge current 150A). Using the cycler it was possible to acquire the data relating to the state of the battery and to identify the maximum SOC% reached at the end of the overcharge. Two types of Li-ion batteries were selected in order to compare two different anodic chemistry: graphite-based anode Li-ion cells (NCR18650B) and LTO-based anode cells (LTO40120). The main characteristics of the cells are shown in Table 1.

Table 1 Characteristics of the tested cells.

	LTO40120	NCR18650B
Rated Capacity	10000 mAh	3200 mAh
Nominal Voltage	2.4V	3.6 V
Max. Charge Voltage	2.8 V	4.2 V
Standard Charge	5000 mA (0.5C)	1625 mA (0.5C)
Charge Temp. Range	-20 °C to +50℃	0 °C to +45°C
Dimensions (DxH)	40 mm x 120 mm	18.5 mm x 65.3 mm
Weight	280±10 g	46.5 g

Three standard cycles were performed on each cell before abuse tests (100% SOC).
The following cells were overcharged as described below:

- 5 NCR18650B cells:
    - 1 cell with an overcharge current of 1.6 A (0.5 C) until the cell is fully charged;

- 1 cell with an overcharge current of 3.2 A (1 C) according to the standard SAE J2464:2009;
- 3 cells with an overcharge current of 9 A (3 C): since in the datasheet provided by the manufacturer there are no indications on the maximum current, a charge current of 3C is used for the test, as indicated in the standard SAE J2464:2009.

• 3 LTO40120 cells:
  - 1 cell with an overcharge current of 10 A (1 C) according to the standard SAE J2464:2009;
  - 1 cell with an overcharge current of 40 A (4C), i.e. the maximum current indicated by the manufacturer (according to SAE J2464:2009);
  - 1 cell with an overcharge current of 80 A (8C). In this case, the worst abuse condition is obtained by following the indications of the UN38.3:2015, IEC 62281:2016 RLV standards, i.e. using a charging current equal to 2 times the maximum current indicated by the manufacturer.

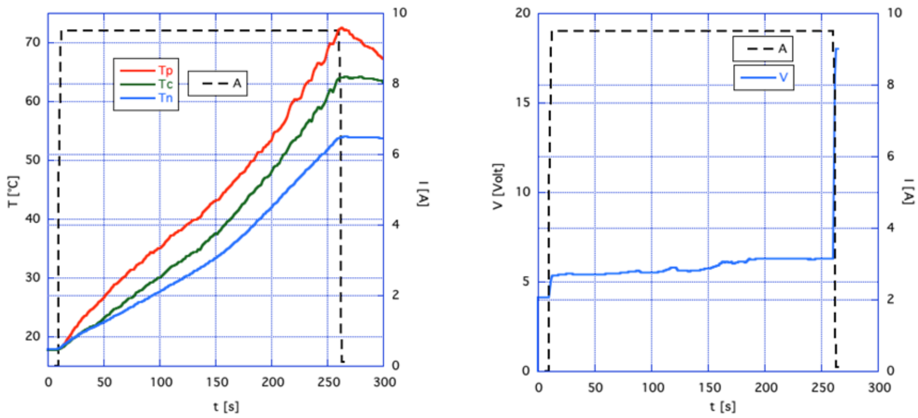
3. Results and discussion

The Table 2 summarizes the results obtained in the overcharge tests performed on NCR18650B cells. In all the tests, the cells did not show any safety problems: no venting phenomena, nor fire and/or explosion occurred. These cells, defined unprotected by the manufacture, are actually equipped with a current interrupt device (CID), a device that cuts off the electrical circuit permanently when triggered by excessive cell pressure. The tested cells showed a gradual increase in temperature during overcharging until the intervention of the CID, which disconnected the circuit in all cases in correspondence with a sudden increase in voltage (Figure 2).

Table 2 Summary of the results obtained from the overcharge tests on graphite-based anode Li-Ion cells.

n. cell	Overcharge current	Duration of the overcharge	Initial temperature (T_0)	Maximum temperature (T_{max})	$\Delta T = T_{max} - T_0$	SOC%
1	9.6 A	251 s	17.9 °C	72.4 °C	54.5 °C	120.7
2	9.6 A	252 s	17.3 °C	66.8 °C	49.5 °C	120.7
3	9.6 A	271 s	22.5 °C	63.2 °C	40.7 °C	122.3
4	3.2 A	781 s	19.3 °C	42 °C	22.7 °C	120.9
5	1.6 A	1931 s	18.3 °C	37 °C	18.7 °C	124.9

For the three tests performed at the highest current (9.6 A), the T_{max} reached varies considerably: between the first and the third test there was a difference of about 9°C. This demonstrates that in the same abuse conditions, the cells can give rise to behaviors that are sometimes not repeatable.



(a) (b)

Figure 2 Overcharge with a current of 9.6 A, cell n.1: a) temperatures close to: the cell positive terminal (Tp), the cell centre (Tc), the cell negative terminal (Tn), b) voltage and current.

When the overcharge current decreases, the maximum temperature reached tends to drop significantly. With a current of 1.6 A (1C) a maximum temperature of 37°C is reached; with a current of 9.6 A (3C), 60°C is

always exceeded. The SOC% achieved, before the intervention of the CID, is very similar in the different tests: even when the current varies, no significant variations of SOC% are recorded.
In all the overcharge tests there is evidence of a higher temperature reached close to the positive terminal: the passive protection devices are located here. The temperature rise could be connected to the increase in resistance to the passage of current due to the presence of such devices (Figure 2a and Figure 3).

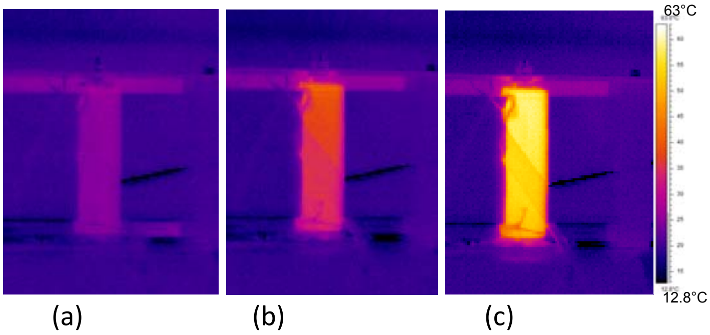


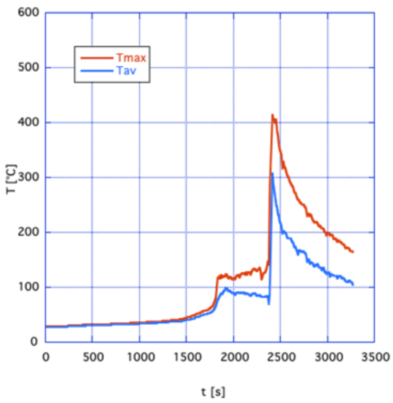
Figure 3 Thermal image of the cell n.1 after: a) t=27 s, b) 149 s, c) 230 s.

The behavior of the cells with the LTO anode subjected to overcharge was completely different: all the cells underwent a copious release of gas and, with high discharge currents, a real explosion of the cell occurred. Table 3 summarizes the results obtained in the overcharge tests on the LTO40120 cells. The SOC% of thermal runaway reached, tends to increase as the overcharge current decreases: with low charge currents a SOC% of about 150% has been reached.

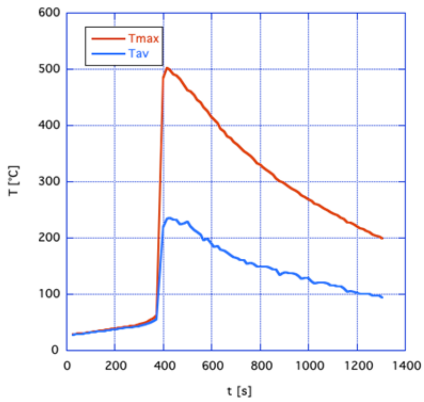
Table 3 Summary of the results obtained from the overcharge tests on LTO-based anode cells.

n. cell	Overcharge current [A]	Duration of the overcharge [s]	Initial temperature (T_0) [°C]	Maximum temperature (T_{max}) [°C]	$\Delta T = T_{max} - T_0$ [°C]	SOC%
1	80	231	26.3	550 °C	523.7	136.8
2	40	373	25	500 °C	475	141.3
3	10	1816	24.7	414 °C	389.3	149.9

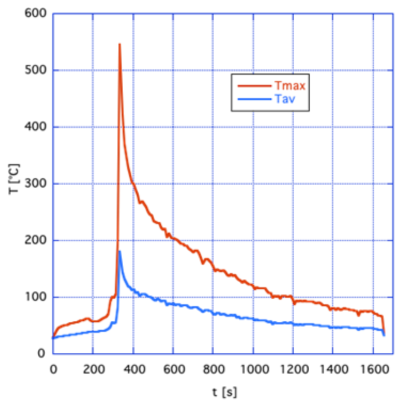
Cell n°3, subjected to a 1C rate of overcharge, had a behavior during the abuse test that saw the succession of 3 phases (Figure 4a):
- Phase 1: from 0 to 1816 s. The cell underwent a gradual increase in temperature until reaching 82°C in 1816 s, at this time there was a sudden increase in voltage and the overcharge ended. At the same time, the expulsion of the outer casing of the cell took place, while the central body remained on the support (Figure 5). The external case flew 3 meters away from the support where the cell was allocated for the test.
- Phase 2: from 1816 s to 2380 s. The temperature of the central body on the support, increased until it reached a T_{max} of about 120°C and began to oscillate around this value. This phase lasted for about 10 minutes.
- Phase 3: 2380 s to 2410 s. The central body of the battery at the end of phase 2 underwent a sudden increase in temperature with the simultaneous release of gas. In this phase, a maximum temperature peak of 414°C was recorded. After the gas was released, the cell gradually began to cool down.
Cell n°2, subjected to a 4C rate of overcharge, had a behavior during the abuse test that saw the succession of 2 phases (Figure 4b):
- Phase 1: from 0 to 373 s. The cell underwent a gradual increase in temperature until it reached about 71 ° C in 376 s, at this time there was a sudden increase in voltage. At the same time, the cell released a considerable quantity of gas from the lower part and, due to the effect of the back pressure, it detached from the support.
- Phase 2: from about 376 s to 420 s the cell underwent a sudden increase in temperature and reached a maximum peak of 500°C, recorded with the thermal infrared camera, in the area where the venting took place.
Cell n°1 subjected to a 8C rate of overcharge, after about 230 s from the beginning of the test, underwent a sudden increase in temperature reaching about 550°C in few seconds (Figure 3c).
The cell exploded: a large amount of gas was released and flames were generated. The explosion of the cell was preceded by a moderate venting.



(a)



(b)



(c)

Figure 4 Maximum (Tmax) and average (Tav) Temperatures recorded during the overcharge test with a current of: a) 10A, b) 40A, c) 80 A.

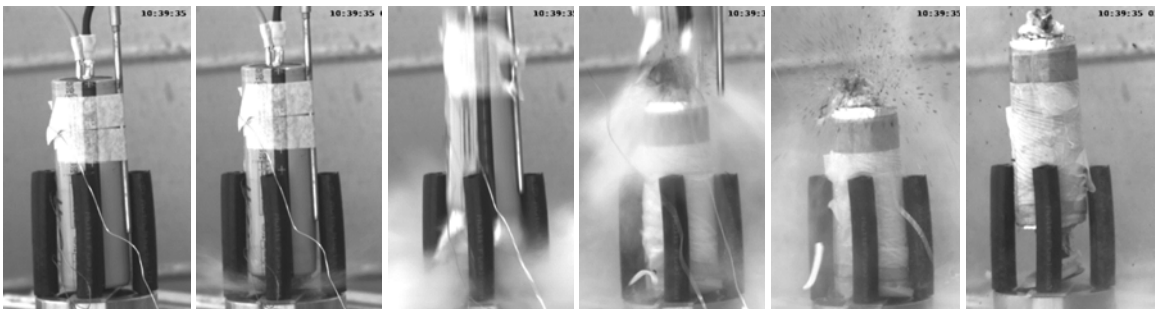
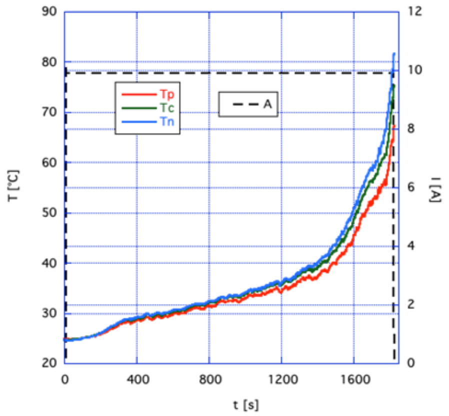
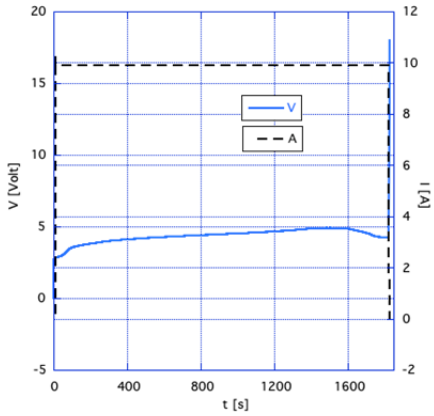


Figure 5 Venting of the cell subjected to a 1C rate of overcharge: expulsion of the external case during the phase 1

As the overcharge current increases, the maximum temperature reached increases and the energy was released from the cell more abruptly and violently. In all the tests, the sudden temperature rise occurred in correspondence with a sudden increase in the cell voltage, as evident in Figure 6.



(a)



(b)

Figure 6 Overcharge with a current of 10 A, cell n.1, phase 1: a) Temperatures recorded with the thermocouples b) Voltage and current.

4. Conclusions

In this work a comparison was made between Li-ion cells with different anode materials (graphite and LTO) subjected to overcharge abuse tests. The tests were performed with different current intensities to analyze the effects as the current supplied varies. LTO-based anode Li-Ion Batteries, although considered intrinsically safer batteries, experienced thermal runaway during the overcharge tests. On the contrary, the intervention of the CID in the graphite-based anode Li-ion cells avoided the fire/explosion and even venting of the overcharged cells. For high overcharge currents (3C) the temperature exceeded 60°C before the CID tripped, while for lower currents the temperature slightly exceeded 40 °C. The presence of the protection devices at the positive terminal causes an increase in resistance to the passage of current, with a consequent localized temperature rise. For the LTO cells the results showed that the thermal runaway SOC% increases as the supplied current decreases: contrarily the maximum surface temperature increases with the increase of the C-rate, although more energy is injected into the cells for the overcharge tests with lower C-rates. For the LTO-based anode cells there was also evidence of the fact that, as the overcharge current increases, the thermal runaway led to a more violent and sudden release of energy with the generation of flames.

Acknowledgments

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References

Arora P., Doyle M., White R.E., 1999, Mathematical modeling of the lithium deposition overcharge reaction in lithium-ion batteries using carbon-based negative electrodes, J. Electrochem Soc, 146(10), 3543-53.

Leising R.A., Palazzo M.J., Takeuchi E.S., Takeuchi K.J., 2001, Abuse testing of lithium-ion batteries: characterization of the overcharge reaction of LiCoO2/graphite cells, J. Electrochem. Soc., 148, A838-44.

Leising R.A., Palazzo M.J., Takeuchi E.S., Takeuchi K.J., 2001, A study of the overcharge reaction of lithium-ion batteries, J. Power Sources, 97, 681-3.

Ohsaki T., Kishi T., Kuboki T., Takami N., Shimura N., Sato Y., Sekino M., Satoh A., 2005, Overcharge reaction of lithium-ion batteries, J.Power Sources, 146(1-2), 97-100.

Ouyang M., Ren D., Lu L., Li J., Feng X., Han X., Liu G., 2015, Overcharge-induced capacity fading analysis for large format lithium-ion batteries with LiyNi1/3Co1/3Mn1/3O2 + LiyMn2O4 composite cathode, J.Power Source, 279:626-35.

Ruiz V., Pfrang A., Kriston A., Omar N., Van den Bossche P., Boon-Brett L., 2018, A review of international abuse testing standards and regulations for lithium ion batteries in electric and hybrid electric vehicles, Renewable and Sustainable Energy Reviews, 81, 1427–1452.

Spotnitz R., Franklin J., 2003, Abuse behavior of high-power, lithium-ion cells, J. Power Sources, 113:81-100.

Zheng, 2018, Fault Diagnosis of Overcharge and Overdischarge of Lithium Ion Batteries, CET, 71, 1453-1478.

Zhu X., Wang Z., Wang Y., Wang H., Wang C., Tong L., Yi M., 2019, Overcharge investigation of large format lithium-ion pouch cells with Li(Ni0.6Co0.2Mn0.2)O2 cathode for electric vehicles: Thermal runaway features and safety management method, Energy, 169, 868-880.