Analysis of the thermal stability of a battery under over-charge and over-discharge

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Abstract. The results indicate that, when a battery is over-charged, the battery’s surface temperature increases first because of ohmic heat, and after that, internal short-circuit occurs, resulting in the battery experiencing thermal runaway. However, in the case of over-discharge, the battery’s surface temperature rise is limited. Therefore, during actual use, attention needs to be paid so as to prevent a battery from over-charge.

1. Introduce
Since its birth in 1991, because of its advantages such as high voltage, high energy density, and high specific power, a lithium-ion battery has been widely favored, currently widely used in various portable electronic devices. As the world is increasingly more pressed for energy, and the oil price keeps increasing continuously worldwide, battery electric vehicles and hybrid power vehicles will become an important means of transportation in future, and as an alternative power source, lithium-ion batteries will attract more attentions. In comparison with lithium batteries, lithium-ion batteries use graphite to replace metallic lithium as cathodes, largely improving their safety. However, in the cases of mechanical impact, high temperature, over-charge etc., lithium-ion batteries are still likely to explode and burn, and especially, high-capacity batteries are more prone to these problems. Therefore, the issue about safety or thermal stability has become a major problem for enlarging the sizes of lithium-ion batteries. Over-charge is one of the safety problems that may arise from the use of lithium-ion batteries, especially from the operation of lithium-ion battery packs. In addition, when a lithium-ion battery is wrongly used or abused, it will also likely to be overcharged. At the time of overcharge, a lot of gas has produced inside a battery, causing a hidden danger of explosion. Overcharge has a relatively big effect on a battery’s safety, and a battery’s inherent ability to endure overcharge is necessary for the commercialization of lithium-ion power batteries. At present, the methods of protecting lithium-ion batteries from overcharge mainly include physical and chemical ones. The physical methods are mainly through combining PTC elements, using external monitoring devices, and installing safety valves, while the chemical ones are mainly by means of the improvement on the
substances inside batteries[1-6]. Therefore, this paper has studied the thermal stability of the batteries under over-charge and over-discharge.

2. Experiment
Experimental samples: Samsung ICR 18650-22P batteries, which are as shown in the Fig.1. and should be counted.

![Fig.1. Experiment sample.](image1)

Experimental instruments: an acceleration rate calorimeter (Es-ARC) and a cyclic charge and discharge instrument (Neware).

Experimental procedure is as follows:
(1) Over-charge and over-discharge the sample battery separately at a rate of 0.2 C according to test requirements, with the end-of-charge voltage at 10V, and the end-of-discharge voltage at 0.1V;
(2) Place the sample battery inside the cavity of the calorimeter. Place the calorimeter’s tracking thermocouple in the centre on the battery’s surface. Fix it with high-temperature glue, and reinforce its outer part with metal wire, so as to prevent the thermocouple from coming off during test. Connect the battery’s anode and cathode separately to the cyclic charge and discharge instrument using a high-temperature-endurable cable (using an electric welding machine to fix a nickel strap about 3 cm in length onto the anode for connection with a wire). Fix the sample battery at the bottom of the calorimeter’s upper cover using high-temperature glue, in the meanwhile, and make sure the sample battery will not be in direct contact with the inner wall of the heat-measuring cavity during the test. Detailed arrangements are as shown in the Fig.2.

![Fig.2. The arrangement of the sample battery.](image2)

(3) Put the calorimeter’s upper cover in place after the battery is positioned. Close the explosion-proof box, and activate the Es-ARC. Charge and discharge the battery at a designed rate when the temperature inside the cavity reaches about 25°C. The parameters for the Es-ARC are as shown in the Conclusion.
Table 1. The settings for the parameters of the acceleration rate calorimeter.

| No. | Parameters                                | Value        |
|-----|-------------------------------------------|--------------|
| 1   | Initial temperature of the experiment     | 25 ℃         |
| 2   | Temperature at the end of experiment      | 500 ℃        |
| 3   | Increment in temperature rise             | 0 ℃          |
| 4   | Sensitivity to temperature rise           | 0.001 ℃/min  |
| 5   | Waiting time                              | 30 min       |
| 6   | Calculated temperature increment          | 0.2 ℃/min    |
| 7   | Cooling temperature                       | 25 ℃         |
| 8   | Safe pressure                             | 200 bar      |

3. Analysis of experimental results

The Fig.3 shows how the battery’s surface temperature and voltage have changed over time, when the battery is over-charged. At the time of test, the battery is charged at a rate of 0.2C until it has directly reached 10V. It can be seen from the figure that, the battery’s voltage is initially at 4.09V and reaches 4.96V after about 109min into the test, when the battery’s surface temperature rising rate increases, and after that, the voltage of the battery has dropped slightly to 4.88V, after which, the battery’s voltage rises to 8.66V suddenly, and 1s after that, the battery’s voltage reaches 10V, and the charging process is stopped, with the battery’s surface temperature at 48℃ at that time. After that, the battery’s surface temperature has continued increasing, finally causing thermal runaway. The initial temperature of thermal runaway is 202.61℃, and the peak temperature is 464.19℃. In comparison with the operating modes of 1C and 1.5C in the section 4.1 where thermal runaway has occurred, in the over-charge experiment, the initial temperature of thermal runaway is relatively low, and the peak temperature is also lower, but this sample battery’s mass loss is the greatest, reaching 25.28g. The reason for the lower peak temperature may be because that the battery has spouted out a lot of substances, which take away too much of heat.

The Fig.4 shows how the battery’s surface temperature and voltage have changed over time, when the battery is over-discharged. At the time of test, the battery is discharged at a rate of 0.2C until it has directly reached 0.1V. It can be seen from the figure that, the battery’s voltage is initially at 4.18V, and as the discharging process continues, the battery’s surface temperature has risen somewhat, but by a small margin. After about 278.9min into the test, the battery’s surface temperature reaches 34℃ while the voltage drops to 3.31V, after which, the battery has experience a sharp drop in voltage, while the battery’s surface rising rate has increased somewhat. After 297.26min into the test, the battery’s voltage has dropped to the set value of 0.1V, when the battery’s surface temperature has increased to 37.22℃, and after that, the battery’s surface temperature has seen an obvious sharp rise, rapidly reaching up to 44.32℃. It needs to be noted that, after the experiment has come to an end, the battery is restored to a voltage of about 3.85V, and the battery’s casing remains in its integrity, without liquid leakage or deformation, but no charge and discharge tests have been carried out on that sample battery since then.
Fig. 3. The changes in the battery’s surface temperature and voltage over time during the over-charge process.

Fig. 4. The changes in the battery’s surface temperature and voltage over time during the over-discharge process.

4. Conclusion

(1) When a battery is over-charged, the battery’s surface temperature increases first because of ohmic heat, and after that, internal short-circuit occurs, resulting in the battery experiencing thermal runaway. However, in the case of over-discharge, the battery’s surface temperature rise is limited.

(2) If a battery is over-charged, it will affect its thermal stability, and even trigger thermal runaway at worst. Therefore, during actual use, attention needs to be paid so as to prevent a battery from over-charge.

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References
[1] MA Yu-lin, YIN Ge-ping, XU Yu-hong et al. Progress of overcharge performance improvement for Li-ion batteries. Power technology, 2011.35(1) : 97-101(2011)
[2] MACNEIL D D, LU Z H, CHEN Z H, et al. A comparison of the electrode/electrolyte reaction at elevated temperatures for various Li-ion battery cathodes [J]. J Power Sources, 2002, 108: 8-14. (2002)

[3] PARK B C, KIM H B, MYUNG S T, et al. Improvement of structural and electrochemical properties of AlF3-coated Li [Ni1/3Co1/3-Mn1/3]O2 cathode materials on high voltage region [J]. J Power Sources, 2008, 178: 826-831. (2008)

[4] MIAO Dongmei, CHEN G Xinjun, SUN Changliang et al. Effects of overcharging on safety performance of Li2ion battery for electric bicycle. BATTERY BIMONTHLY, 2009.39(2): 77-79(2009)

[5] Funabiki A, Inaba M, Ogumi Z, A1c1 impedance analysis of electrochemical lithium intercalation into highly oriented pyrolytic graphite[J]1J Power Sources ,1997 ,68 (2) :227 – 2311(1997)

[6] CHEN G Y, RICHARDSON T J. Overcharge protection for rechargeable lithium batteries using electroactive polymers [J]. Electrochem Solid-State Lett, 2004, 7(2): A 23-A 26(2004)