



Research Paper

Comparison analysis on the thermal runaway of lithium-ion battery under two heating modes



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HIGHLIGHTS

- The joint experimental methods of internal materials and full cell are presented.
- The voltage drop of test cell is influenced by consumption of cathode and separator.
- Thermal runaway induced by high temperature can be divided into three stages.
- Thermal runaway can be avoided by heat dissipation before temperature beyond 150 °C.

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ABSTRACT

The thermal stability evaluation of materials in a soft-pack commercial cell is tested using C80 calorimeter, including anode, cathode, separator and full cell (mixing of the three materials including additional electrolyte). Thermal runaway characteristic of the commercial cell is tested on the accelerating rate calorimeter (ARC) with two heating modes, including internal heating mode and external heating mode. The results show that the thermal stability of internal material for tested cell follows the below order: anode < separator < cathode. The voltage drop is influenced by the consumption of cathode and separator, while the effect of anode consumption on the voltage can be negligible. Both onset temperature and critical temperature in external heating mode are larger than that in internal heating mode. Thermal runaway induced by high temperature of the tested cell can be divided into three stages: 1) the cell can work under normal mode and all the internal exothermal reaction can be ignorable, 2) the exothermal of anode which can be detected and the thermal runaway can be stopped by effective heat dissipation, and 3) the cathode reaction and separator melting which cause the cell voltage drop and thermal runaway of the cell is inevitable in this stage.

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1. Introduction

The use of lithium ion batteries becomes more and more widely, from small electronic products such as music players, laptops, computers, to large energy power devices such as electric vehicles (EVs) and energy storage power stations. However, the security risk lithium ion batteries is with us all the time. Lots of accidents including fires and explosions relevant to lithium ion batteries have been reported since 1991. Tens of thousands of mobile phone fires or explosions have been reported since 2006. Especially in 2016, there were many explosion accidents for Samsung Galaxy Note 7 mobile phones, which were finally recalled all around the world. The safety issue becomes the bottleneck of lithium ion battery using

as power battery. As we know that fire, over-heating, overcharging, short circuit including external and internal, or crushing can trigger the battery to failure or thermal runaway with fire and explosion. Many researchers [1–21] paid their attentions to the safety issue of lithium ion battery. Balakrishnan et al. [1] summarized possible scenarios that can trigger thermal runaway and also discussed the safety mechanisms of the cell. The detail reactions of different internal materials were also reviewed in reference [1]. The relationship between temperature and internal reactions during thermal runaway had been summarized [2,3]. When the temperature reaches 90–120 °C, the solid electrolyte interface (SEI) film starts exothermic decomposition [4–6]. The SEI film in some electrolyte systems decomposes at a lower temperature of about 69 °C [7]. When the temperature exceeds 120 °C [6], the SEI film after decomposition is unable to protect negative carbon electrode from side reactions with organic electrolyte and combustible gases are produced [8]. When the temperature is about 130 °C, the separator will start melt-

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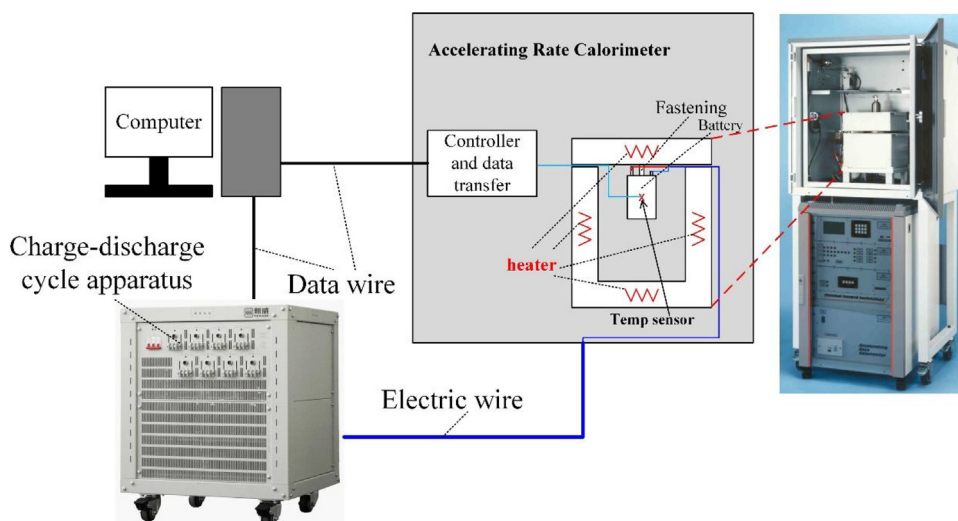


Fig. 1. Schematic of two heating experimental designs.

ing and shutting the cell down. When the temperature becomes higher, the positive material will start decomposition (LiCoO_2 at 150°C [9], $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ at 160°C [10,11], $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ at 210°C [10], LiMnO_2 at 265°C [4], LiFePO_4 at 310°C [9]) and oxygen will be produced. When temperature is above 200°C , the electrolyte will decompose and produce combustible gases [6], and it will have violent reaction with the oxygen produced by the decomposition of positive electrode [11] which will trigger the battery to thermal runaway and may cause fire in some serious situations. Maleki et al. [12] conducted ARC tests and found that thermal runaway of lithium ion battery is close to the decomposition temperature range of the unwashed positive electrode. Ping et al. [13] analyzed side reactions of $\text{Li}_x\text{CoO}_2/\text{Li}_x\text{C}_6$ during thermal runaway stage, and the analysis showed that the reactions during thermal runaway of $\text{Li}_x\text{CoO}_2/\text{Li}_x\text{C}_6$ including SEI film decomposition, separator melt, which caused the short circuit of positive and negative materials, and followed by the decomposition of internal materials including electrolyte, anode, cathode and the side reactions between internal materials as the temperature increasing. Ye et al. [14] analyzed the thermal runaway characteristic under overcharge. Feng et al. [15] investigated the thermal runaway by using experimental and numerical simulation methods. Larsson et al. [16] investigated the thermal runaway characteristics of lithium ion battery caused by fire. The thermal runaway of working materials in lithium ion battery system was studied with common used battery materials, and the no return temperature T_{NR} is 75°C and the self-accelerating decomposition temperature (SADT) is 66.5°C [17]. The thermal decomposition of electrolyte, anode and cathode were carried out during thermal runaway stage [18,19]. The main fuel in lithium ion battery is electrolyte, which is a solution consists of organic solvent and inorganic salt [17]. Recently, Feng et al. [20] reviewed the thermal runaway mechanism of power lithium ion battery.

Different abuse conditions cause same result that the self-heating of battery is triggered. In order to prevent cell/battery from thermal runaway, it is necessary to find the detail induced mechanism of thermal runaway for lithium ion battery. Temperature is a significant factor which is critical to the internal reaction during thermal runaway. The intent of this work is to investigate the effect of high temperature on the thermal runaway characteristic of a commercial package cell with active material of $\text{LiCoO}_2/\text{graphite}$. In this paper, thermal stability of internal materials is tested by C80 calorimeter firstly, and then two different heating modes are tested, including internal heating mode and external heating mode.

Finally, the thermal stability of internal materials is used to explain the detail reaction during the internal and external heating modes.

2. Experimental

The test cell is a commercial soft-pack cell with capacity of 950 mAh, and the cathode and anode electrode are lithium cobalt oxide (LiCoO_2) and graphite, respectively. The operating range of voltage is from 2.75 V to 4.2 V. The C80 micro calorimeter was used to test the thermal stability of internal materials, while the thermal runaway characteristic of cells under two different heating modes was tested by the ARC. A 3.82 V battery was disassembled during the thermal stability evaluation test. The anode, cathode, separator were separated into three different sealed bags. Four different thermal stability tests were taken including anode, cathode, separator and full cell. The samples of anode and cathode were powdery scraped from the current collectors, and the sample of separator was film, while the sample of full cell just mixed anode, cathode and separator with an additional of 1 M LiPF_6 in EC + DEC (1:1 w/w) electrolyte. The thermal stability test was heated from 30°C to 300°C with temperature rise rate of $0.2^\circ\text{C}/\text{min}$.

Two different heating modes are provided by ARC which can provide an adiabatic environment condition. The external heating mode was provided with the heating mode of ARC, under which the battery was heated with the temperature rise rate of $1^\circ\text{C}/\text{min}$ from room temperature to 150°C . The cells for external heating mode experiments were preconditioned to state of charge (SOC) range of 0%–100% with 25% interval. The internal heating mode was provided with the adiabatic mode of ARC, under which the heat generation of battery during charge and discharge stage was all absorbed by the battery itself. The cells for internal heating mode experiments were preconditioned to 100% SOC and the heat absorbed during discharging stage was used to simulate the internal heat influence on the thermal runaway, and the discharging currents were set from 0.5 A to 2.5 A with 0.5 A interval. Fig. 1 shows the experimental schematic for external and internal heating modes, and the thermocouple was pasted at the surface center of the battery with high-temperature adhesive tape, which means that the detected temperature is lower than the core temperature during internal heating mode, while larger than the core temperature during external heating mode. The cell was hugged at the top side of the ARC cavity. The collecting line between charge/discharge cyler and the cell is electric wire.

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