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Thermal runaway analysis and model of nickel-rich lithium-ion batteries in different overcharging states

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***Abstract*—Lithium-ion power batteries are favored for their light mass, high energy density and low pollution, but repeated thermal runaway accidents have prevented the large-scale use of lithium-ion power batteries. The thermal safety of lithium-ion batteries is also receiving increasing attention. In this paper, the thermal runaway characteristics of 18650 nickel-rich lithium-ion batteries triggered by heating in different overcharge states are investigated using an extended volume accelerated calorimeter (EV+-ARC). And the voltage data is collected. The battery's self-heating temperature was examined based on the experimental findings. The time required for the lithium-ion battery from safety valve opening to complete thermal runaway is compared. A thermal reaction kinetics TR model of the thermal runaway of Lithium-ion batteries is developed, and the model curves are in high agreement with the experimental curves.**

Keywords—Lithium-ion battery, state of charge, overcharge, thermal runaway

I. Introduction

The lithium-ion battery market has grown quickly in recent years. Due to their high charging efficiency, fast charging and discharging speed, high energy density and low self-discharge, the creation and use of lithium-ion batteries have drawn an increasing amount of interest. Lithium-ion batteries are core components of electric vehicles and energy storage devices, which can reduce carbon emission and protect the environment [1]. However, Lithium-ion batteries also have major drawbacks: when the temperature is too low, the internal resistance of the battery increases and the capacity decreases, which has an impact on the travel and acceleration of the car [2-3]; when the temperature is too high or there are other physical reasons, such as overcharge, over-discharge, puncture, internal short circuit and triggered thermal runaway [4], then the result is a terrible combustion and explosion, which brings great potential danger to people's life and property safety [5]. The temperature of the battery not only changes with the environment, but the battery itself will also heat up and change its own temperature in the working condition. At present, the structure of the battery has been optimized to its limits and only by using new materials is it possible to increase the capacity of the battery and maintain its stability [6].

It is well known that research on cathode materials and electrolytes does nothing to help increase the capacity of the battery and that the capacity of lithium-ion batteries mostly depends on the cathode material of the battery. Therefore, increasing the specific capacity of the cathode material is the most efficient method for producing lithium batteries with high energy density. However, the cathode specific energy density of commercial lithium batteries commonly available in the market today cannot meet the demand for higher usage, such as $LiCoO_2$,$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$,$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, spinel $LiMn_2O_4$, olivine $LiFePO_4$. It is this property that limits the application of lithium batteries in new energy vehicles and energy storage plants [7].

It is true that boosting the energy density of the positive electrode in lithium-ion batteries can enhance their performance. However, when the energy density rises, the thermal stability of lithium-ion batteries will become less and less stable, especially under fast charging [8]. The battery will also decompose oxygen and flammable gases such as CH_4, CO, C_2H_4, etc. at high temperature [9]. Although this oxygen is not enough to mix with flammable gases to cause violent combustion, it will react with materials such as electrolyte and generate a lot of heat in the battery. When the heat of the battery is not released and its own temperature rises higher and higher, thermal runaway will occur, posing a serious threat to people's production life. Consequently, more study is required into the thermal runaway of nickel-rich lithium-ion batteries.

The fire at the Beijing Dahongmen energy storage plant has renewed interest in the thermal runaway problem of lithium batteries, and many researchers at home and abroad have conducted a number of studies on this problem. Can-Yong Jhu et al. studied the thermal runaway performance of $LiCoO_2$ lithium batteries from different manufacturers using VSP2 to investigate the thermal stability of the batteries and the thermal runaway characteristics during adiabatic heating [10]. Feng et al. built a coupled electrochemical-overcharge-thermal model to model and analyze key parameters in order to expect to find a solution to the overcharge problem of lithium batteries [11]. Wang et al. studied the thermal stability of lithium batteries using C80 micro calorimeter and the extended volume accelerated calorimeter (EV+-ARC) and investigated the internal short circuit problem under different conditions by pinning experiments [12-13].

Although these excellent studies provide a good reference for the study of thermal runaway of lithium-ion batteries, less research has been done on the thermal runaway of Ni-rich lithium-ion batteries in the overcharge state.

This study looked into the 18650 nickel-rich lithium-ion battery's thermal runaway characteristics under conditions of coupled overcharging and heating brought on by EV+-ARC. In order to evaluate the thermal runaway characteristics, characteristic parameters such as cell voltage, surface temperature and temperature rise rate were acquired from the experiments to analyze the thermal runaway behaviors.

II. Experimental

A. Battery type and test method

The battery used in this experiment was a $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ (NCM811) 18650 lithium-ion battery (LG INR18650MJ1). The cell has a diameter of 18 mm and a height of 65.0 mm. It is a new type of high-capacity nickel-rich lithium-ion battery. The anode material is silicon graphite and the electrolyte is a $LiPF_6$ based solution. The battery sample has a nominal capacity of 3350 mAh. The nominal voltage is 3.7V. The weight is 47 grams. The operating voltage range is 2.5V to 4.2V. The parameters of the battery sample are shown in Table I.

TABLE I. THE PARAMETERS OF THE BATTERY SAMPLE

Items	Parameters
Length	65.1 mm
Diameter	18.5 mm
Surface area	0.0043 mm^2
Volume	1.75×10^{-5} mm^3
Mass	46.8 g
Nominal capacity	3350 mAh
Nominal voltage	3.635 V
Charge and discharge cut-off voltage	2.4-4.2 V

The lithium-ion battery charging platform is depicted in Fig.1. and includes three major components: the charging equipment is made up of the NBT5V10AC16-T, a single battery testing system platform produced by Ningbo Bite Measurement & Control Co. The battery storage equipment is made up of MEF1510-003 temperature chamber produced by Suzhou Jufu Instruments Co. Firstly, the battery capacity test is carried out using the experimental platform, including constant current and constant voltage charging and discharging. The current size for constant current charging and discharging is 1/3C, where 1C indicates that the current is equal to the nominal capacity value. The battery is then charged to 4.2V and awaits subsequent experiments.

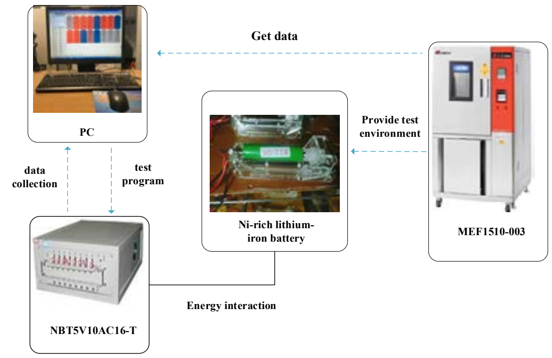
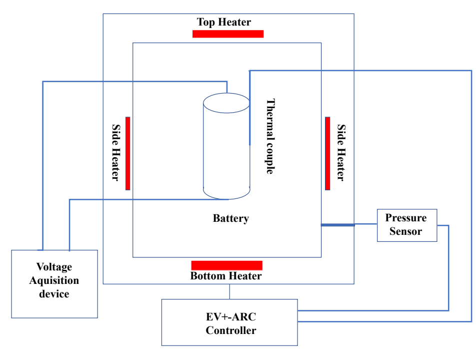


Fig.1. The experimental platform for charging and discharging

B. Thermal runaway experiments

In this study, all thermal experiments were carried out in an EV+-ARC manufactured by THT in the UK, as shown in Fig.2(a). The schematic diagram of thermal runaway is displayed in Fig.2(b). The EV+-ARC works on the same principle as the commonly used EV-ARC and standard ARC, and also follows the heat-wait-search (HWS) method for detecting the exothermic reaction of the sample. The difference is that the EV+-ARC is equipped with a much larger volumetric calorimeter than the standard ARC and EV-ARC, designed for battery research. the internal dimensions of the EV+-ARC calorimeter are 40 cm in diameter and 44 cm in depth . The EV+-ARC can therefore be most appropriately used for stability and abuse testing, and is also suitable for management studies.

(a)



(b)

Fig.2. (a) The experiment platform of TR test. (b) The schematic diagram of TR experiment.

In the thermal runaway (TR) studies of lithium-ion battery, the TNT equivalent is often used to represent the battery energy, which in turn can be related to the temperature rise by the heat capacity, as shown in equation (1).

$$\Delta Q = MC_p \Delta T \tag{1}$$

The thermal capacity of a battery can be measured prior to the thermal runaway test. As shown in Fig. 3, three batteries with similar characteristics are selected, a suitably sized polyimide heating sheet is glued to the surface of one battery, and they are then bundled together. The bundle is made using aluminum foil tape, which prevents the battery from exchanging heat with the outside world. As the heating sheet is in the center of the three cells, the inner surface temperature of the cell is regarded as core temperature. The results of specific heat capacity test are shown in Fig.4.

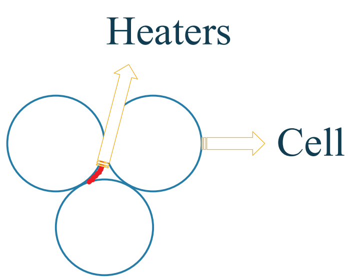


Fig.3. Schematic diagram of specific heat capacity experiment

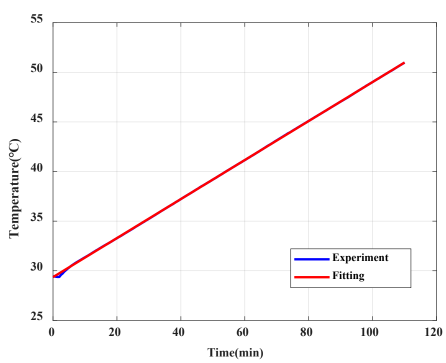


Fig.4. The test results of specific heat capacity

The specific heat capacity of battery cell is calculated as shown in equation (2), which gives a specific heat capacity of 1020J/Kg/K.

$$C_p = \frac{p}{m} \times \frac{1}{dT/dt} \tag{2}$$

The experimental platform for overcharging and thermal runaway of the battery is shown in Fig.4. The overcharging process of the battery is carried out in the EV+-ARC chamber. The fully charged battery is connected to the (instrument) made by MKL and a current of 1/6C is used to break the battery voltage of 4.2V. To overcome the effect of the polarization voltage, the voltage at the end of the charge is 0.05V above the target voltage. And the whole chamber is left open in order to reduce the effect of temperature changes on the battery at this time.

When the overcharge of the battery is complete, a heating-induced thermal runaway experiment is carried out. At this point the heating chamber is closed and the EV+-ARC is put into a heat-wait-search mode until the battery starts to generate its own heat. At this point the adiabatic mode is entered and the battery is allowed to warm up on its own until thermal runaway occurs. At the same time the upper computer receives the recorded voltage signal.

III. Experimental Results and Discussion

A. *Results of TR experiment*

The temperature and voltage variation curves of the batteries in different overcharge states during the thermal runaway experiment are shown in Fig.5. The whole process of TR can be divided into four stages, which is described as follows.

1) The EV+-ARC operates in the heat-wait-search mode, when the entire chamber heats the battery and no heat is generated by the battery itself. The self-heating rate of the battery is below the set value of 0.02°C /min. The voltage of the battery remains essentially unchanged.

2) The EV+-ARC detects that the battery is starting to generate its own heat and enters adiabatic mode and tracks the change in battery temperature. T_1 is the temperature at which the lithium battery generates its own heat, as determined by the temperature rate sensitivity setting. During this phase, the battery voltage drops rapidly to around 0V. The temperature of the cell does not rise quickly, the increase is mainly due to the destruction of the solid electrolyte interface (SEI) film and the anode, which has lost the protection of the SEI film, begins to react with the electrolyte, giving off heat. The temperature as the voltage drops to 0V is indicated by Tvd, as shown in Fig.5.

3) As the temperature of the battery rises, large amounts of gases such as O_2, CO_2, CH_4 etc. will appear inside the battery. The accumulation of large amounts of gas will cause the pressure inside the battery to rise and the safety vents will pop open to release the pressure. The temperature at which the safety vent pops open is noted as T_2. As the gases are released, the temperature of the lithium battery drops slightly. However, as the chemical reactions of other materials inside the cell continue, such as the decomposition of the SEI film, the decomposition of the cathode and the reaction between the anode and the electrolyte, the temperature of the cell rises further.

4) T_3 is the temperature at which the battery triggers thermal runaway. During this phase, the temperature rise of the battery is greater than 1°C/min. Violent chemical reactions take place inside the battery, such as the decomposition of the electrolyte, the decomposition of the cathode and the reaction between the anode and the electrolyte. This leads to a large amount of heat production and the temperature of the battery rises sharply to several hundred degrees Celsius in a very short period of time.

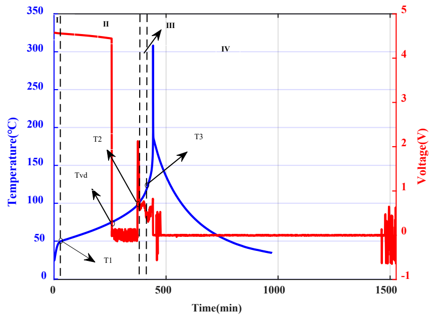


Fig.5. Voltage and temperature curves of TR experiment

B. *Effect of different overcharging states on thermal runaway of batteries*

The temperature rise rate and temperature curve of the battery when the SOC is 100 are shown in Fig.6. The temperature rise rate and temperature curve of the battery in different overcharging states are shown in Fig.7.

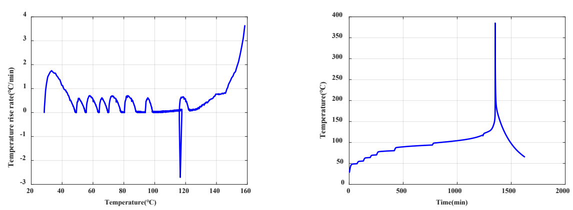
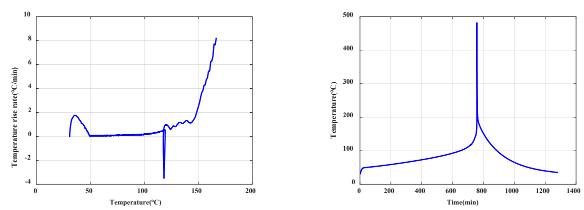
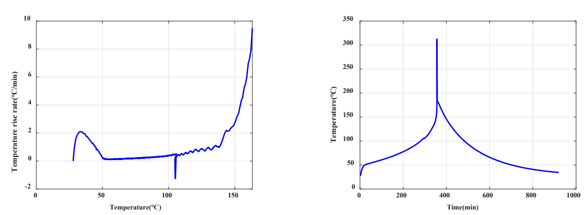


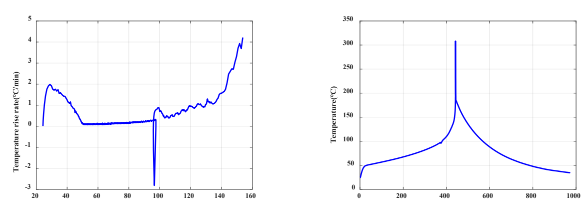
Fig.6. The temperature rise rate and the temperature curve when the SOC of the battery is 100



(a)



(b)



(c)

Fig.7. The temperature rise rate and the temperature curve when the battery voltage is (a) 4.4V (b) 4.6V (c) 4.8V

It is important to keep in mind that when the lithium battery is charged and the battery voltage is above 4.4V, the battery will not be allowed to stand for a while but will be heated to 50 degrees. EV+-ARC will detect that the battery has self-generated heat. Then the system will go directly into the adiabatic state. This means that while the battery is charged to 4.4V, the internal chemical structure is very unstable. The trigger temperature of self-generated heat is lower. In the working state, there is no standing time, which also leads to a great increase in the degree of danger.

Fortunately, by observing the above images, it can be found that in the case of thermal runaway with a battery voltage of 4.2V, the time from the opening of the battery safety valve to the thermal runaway of the battery is about 120 minutes. When the battery is in the state of 4.4V or above, the time from the safety valve opening to the complete thermal runaway of the battery is shortened, but it does not decrease linearly. The overall time is about 30 minutes. This means that even if thermal runaway occurs under working conditions, once we detect the sound signal or gas signal, we still have 30 minutes to take measures to avoid complete thermal runaway of the battery.

The comparison between batteries after the experiment and the original battery is shown in Fig.8.

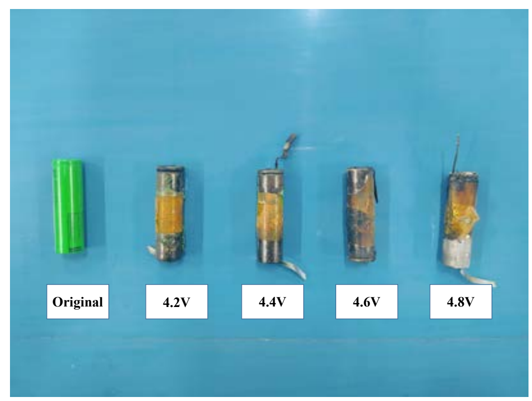


Fig.8. The photographs of sample battery before and after TR experiment.

The structure of jelly roll inside the last three batteries was seriously damaged. All batteries were severely carbonized. The mass of four batteries after thermal runaway is 9.1g, 11.6g, 11.6g and 10.5g respectively.

IV. Li-ion Battery Thermal Runaway Modelling

There are many chemical materials in lithium-ion batteries. The existence of SEI film limits the reaction between many materials. When the SEI film is damaged, the chemical reaction inside the battery will become violent. Therefore, it is very difficult to model the battery. Many scholars try to simplify the reaction process of the battery. Kun Jiang established a thermal runaway model of lithium-ion battery with less parameters [14]. This paper establishes a segmental thermal reaction kinetics TR model based on the data of Jiang. All of the work is based on Simulink.

The change in the lithium battery with time is shown in equation (3).

$$T(t) = T_{init} + \int \frac{dT(t)}{dt} \tag{3}$$

where T_{init} denotes the initial temperature of the battery with a value of 20°C and $\frac{dT(t)}{dt}$ is the temperature rise rate of the lithium battery, defined by the net heat generation of the battery, $Q_{net}(t)$. An energy conservation relationship exists between them as shown in equation (4).

$$MC_p \frac{dT(t)}{dt} = Q_{net}(t) \tag{4}$$

Where M stands for the mass of the battery, which is 46.8 g. C_p denotes the specific heat capacity of the battery, which is 1020 J/Kg/K, and can be obtained from the specific heat capacity experiment mentioned above.

The net heat generation can be obtained from equation (5).

$$Q_{net}(t) = Q_{heat}(t) + Q_{gen}(t) - Q_{conv}(t) \tag{5}$$

where $Q_{heat}(t)$ represents the amount of external heating provided before the EV+-ARC detects the self-generation of heat by the battery. $Q_{gen}(t)$ represents the amount of heat generated that the battery produces on its own, which contains a large number of complex chemical and electro-chemical reactions. $Q_{conv}(t)$ represents how much convective heat exchange occurs between the surroundings and the battery.

As the EV+-ARC only provides heat at the beginning, it ceases to provide heat after detecting the battery's own heat production. It also enters adiabatic mode.We can assume that the battery is supposed to have a constant internal temperature and to heat itself entirely using the energy it produces. There is no energy loss from the entire chamber until the cooling system is activated. Thus, equation (5) can be simplified to equation (6).

$$MC_p \frac{dT(t)}{dt} = Q_{net}(t) = Q_{gen}(t) = \Delta H \frac{d\alpha}{dt} \tag{6}$$

where ΔH is the enthalpy of the chemical reaction and can be defined by equation (7).

$$\Delta H = MC_p \Delta T_a \tag{7}$$

where ΔT_a is the adiabatic temperature rise rate parameter as shown in equation (8) and is equivalent to $T(t_1)$ minus $T(t_0)$. $T(t_0)$ represents the temperature at the start of adiabatic heating and $T(t_1)$ represents the temperature at the end of adiabatic heating.

$$\Delta T_a = T(t_1) - T(t_0) \tag{8}$$

α represents the conversion ratio (0< α <1). α can be defined by equation (9).

$$\alpha = \frac{T(t) - T(t_0)}{\Delta T_a} \tag{9}$$

The rate of reaction of a lithium battery can be obtained by derivation of the Arrhenius equation as shown in equations (10) and (11). Calculations for chemical reactions in relation to temperature have frequently been derived using this.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{Ea}{RT(t)}\right) f(\alpha) \tag{10}$$

$$f(\alpha) = \alpha^{n1} \left[1-\alpha\right]^{n2} \left[-\ln(1-\alpha)\right]^{n3} \tag{11}$$

where A denotes the frequency factor. Ea denotes the activation energy. r denotes the ideal gas constant of 8.314 J/mol/K. $f(\alpha)$ denotes the reaction mechanism, and n1, n2, n3 are the order of the reactions respectively. In modelling calculations of thermally runaway reactions, the common cases are n1=0, n3=0.

In the initial stage, since the heating of the cell comes mainly from external heating, the consumption of internal reactants is almost zero. Therefore, it can be assumed that n2 = 0, so that equation (11) can be simplified to equation (12).

$$f(\alpha) = 1 - \alpha \tag{12}$$

Combining the above equations (7), (8), (9), (10) and (12) can transform the conservation of energy equation (7) into equation (13).

$$\frac{dT(t)}{dt} = A \exp\left(-\frac{Ea}{RT(t)}\right)\left(T(t_1) - T(t)\right) \tag{13}$$

Equation (14) is obtained after taking the logarithm of equation (13).

$$\ln\left(\frac{dT(t)/dt}{T(t_1) - T(t)}\right) = \ln A - \frac{Ea}{R}\frac{1}{T} \tag{14}$$

The kinetic parameters can be defined by the linearly fitted adiabatic self-heating rates listed in equation (14).

Ultimately, the energy release from a lithium battery during thermal runaway can be expressed by equation (15).

$$Q_{gen}(t) = \frac{1}{\Delta t}\left(\Delta H - \int Q(\tau) d\tau\right) \tag{15}$$

where ΔH represents the total energy released by the lithium battery during the thermal runaway phase with a value of $4.882e^4$J and Δt represents the average time to release energy, set at 10s.

When the cooling system is activated, the convective heat exchange between the battery and the environment can be expressed computationally by equation (16).

$$Q_{conv}(t) = hS\left(T(t) - T_{amb}\right) \tag{16}$$

where h is the convective heat transfer coefficient with a value of 20W/m^2/K, S is the surface area of the lithium battery with a value of 0.0849 m^2 and T_{amb} represents the initial ambient temperature.

The comparison between simulation results and experimental values is shown in Fig.9.

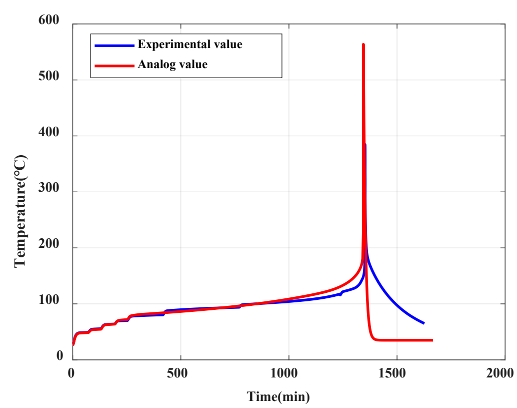


Fig.9. Thermal reactions kinetics TR model simulation results

V. Conclusion

In this paper, EV+-ARC was used to study the thermal runaway characteristics of $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ (NCM811) 18650 lithium-ion batteries at different overcharge stages. The voltage data of thermal runaway batteries is collected and compared with the temperature curve. Four stages of battery thermal runaway are analyzed. While lithium-ion batteries are overcharged under working conditions, the temperature point of self-generated heat is greatly reduced. By comparing the time from the opening of the safety valve of lithium-ion battery to the complete thermal runaway under different states, it is found that the time is not inversely proportional to the battery energy. If we can further study the law of time interval, we can formulate an industry standard to control the time of thermal runaway treatment of lithium batteries. At last, the thermal runaway of the lithium-ion batterie during overcharging is modelled using segmental thermal reaction kinetics TR, and the model curves and actual curves show excellent agreement.

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