Thermal runaway model of high-nickel large format lithium-ion battery under thermal abuse conditions

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Abstract. Battery safe necessitates preventing thermal runaway and its propagation. Aiming at the thermal runaway problem of pure electric vehicle lithium-ion power battery, a thermal runaway model for large-capacity lithium-ion prismatic batteries is developed. Two thermal abuse conditions: hot box and single-side heating are considered in the simulation. Corresponding experiments are conducted to verify the accuracy of the model. The results show that the gas generated by the decomposition of the solid electrolyte interface (SEI) membrane and the anode-solvent reaction triggered the pressure relief valve. The thermal runaway process of single-side heating has a temperature difference of more than 200°C, and thermal runaway may have occurred when the local temperature of the battery is normal. This lays a foundation for subsequent research and system development.

1. Introduction
Lithium-ion batteries (LIBs) are regarded as the privileged choice for solving energy and environmental issues and are widely used in electric vehicles. However, with the increase in the use of high nickel cathode and high energy density batteries, electric vehicle fire accidents caused by battery thermal runaway have emerged one after another. Therefore, researches on the mechanism and model of thermal runaway of LIBs have attracted extensive attention.

The causes of thermal runaway of lithium-ion batteries are divided into thermal abuse, mechanical abuse, and electrical abuse. Generally, mechanical abuse and electrical abuse are accompanied by thermal abuse, and the propagation of thermal runaway in the battery pack is also carried out by thermal abuse. Therefore, research on battery thermal abuse is of great significance to battery safety and thermal runaway protection.

Feng[4] used EV-ARC to test the thermal runaway characteristics of a 25Ah graphite/LiNiₓCoₓMn₁₋ₓO₂ prismatic battery. The study showed that the temperature distribution during thermal runaway of large-format batteries is quite different. It is meaningful to study the temperature distribution inside and outside the battery. Wang[5] used an electric furnace and a cylindrical heater to heat a fully charged 50Ah graphite/LiNiₓCoₓMn₁₋ₓO₂ battery, and compared the effects of different heating methods, positions, area and power. The study found that the risk of thermal abuse increased with the increase of heating power and heating area.
Many numerical models are used to study thermal runaway behaviors. Kim [6] established a three-dimensional cylindrical graphite/LiCoO$_2$ thermal runaway model, and simulated the thermal runaway behavior of the battery under different heating conditions. They found that smaller batteries dissipate heat faster than larger batteries, so thermal runaway is less likely to occur. They also obtained the propagation process of the abuse reaction triggered by local heating in the battery. Kong [7] studied the thermal runaway behavior of 18650 batteries of different materials under different heating conditions by simulating, and found the poor thermal stability of the battery with high nickel positive electrode, and the heating of the bottom of the battery can trigger thermal runaway faster.

At present, there are few related researches on the thermal runaway model of large format LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ prismatic batteries under thermal abuse conditions. In this paper, a large format LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ prismatic battery thermal runaway 3D model is established based on the thermal abuse experiments, and the thermal runaway behavior of the battery during the hot box and single-side heating process are simulated. The results have a significant guidance for the safety design of high nickel battery packs.

2. Thermal abuse experiment design

A prismatic battery for thermal abuse experiments is used in this study, and the capacity of battery is about 130-150 Ah. The anode material of the battery is graphite, and the cathode material is LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$. The heat abuse experiment is carried out in two ways: a hot box experiment and a single-side heating experiment. The initial temperature in the hot box experiment is 45°C, and the temperature rises slowly to 132°C in a stepped shape and then remains unchanged. The single-side heating experiment uses a ceramic heater with a power of 300W to heat the center of the large surface of the battery. Before the experiment, the battery is fully charged, and a thermocouple is used to obtain the temperature variation of the battery surface. In the hot box experiment, we tested the temperature of the center of the large surface of the battery; in the single-side heating experiment, we tested the temperature of the center of the heating surface and its opposite surface. The experiment setups are shown in Figure 1.

3. Thermal runaway model

3.1 Three-dimensional heat transfer model

The structure of the prismatic battery in this article is shown in Figure 2. The battery is composed of a metal shell and two closely-fitting jellyrolls. There is an air gap between the battery casing and the jellyrolls. In Figure 2, 1 is the thermal resistance of the battery shell $R_{shell}$, 2 is the thermal resistance of the air gap $R_{air}$, 4 is the thermal resistance of the contact between two jellyrolls $R_{jr}$, and 3and 5 are the thermal resistances of the jellyrolls $R_{jr}$. The inside of the battery exchanges heat with the outside through these thermal resistances.
The main heat generation that causes the battery temperature rising in the early stage of the experiment is the heat exchange with the hot box and the heating plate. When the battery temperature reaches a certain height, it will cause a series of exothermic side reactions inside the jellyrolls, and the battery self-heating will begin. The heat abuse experiment of the battery is an unstable heat conduction process, and the battery is the internal heat source of the system. The heat transfer process of the entire three-dimensional model conforms to the three-dimensional heat conduction equation as equation (1).

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} (k_x \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y} (k_y \frac{\partial T}{\partial y}) + \frac{\partial}{\partial z} (k_z \frac{\partial T}{\partial z}) + Q_t$$  (1)

$$R_i = \frac{\delta_i}{k_i}$$  (2)

Where $\rho$ represents the density of the battery; $c$ represents the specific heat capacity of the battery; $k_x$, $k_y$, and $k_z$ refer to the thermal conductivities in the x, y, and z directions; $T$ represents the temperature; $t$ is the time; $Q_t$ is the internal heating power of the battery. The relationship between thermal conductivity and thermal resistance is shown in Equation (2). Where $\delta_i$ is thermal resistance layer thickness.

The initial conditions of the model are denoted as:

$$T(x,y,z,0) = T_0$$  (3)

The battery exchanges heat with the external environment through thermal radiation and convection heat transfer, and the process is controlled by equation (4) and equation (5) respectively.

$$-k \frac{\partial T}{\partial n} = \varepsilon \sigma (T^4 - T_{amb}^4)$$  (4)

$$-k \frac{\partial T}{\partial n} = h(T - T_{amb})$$  (5)

Where $\varepsilon$ is thermal radiant emissivity; $\sigma$ is the Stefan-Boltzmann constant of the battery heat radiation; $k$ is the thermal conductivity of the battery; $h$ is convective heat transfer coefficient; $T_{amb}$ is the ambient temperature.

As shown in the enlarged view in Figure 2, the jellyrolls are composed of multiple layers of materials. In the three-dimensional thermal model, the jellyroll is assumed as anisotropic material with the same thermal conductivity in the x and y directions but different thermal conductivity in the z direction. The thermal conductivity of the jellyroll in the length x and width y directions is calculated by parallel thermal resistance, and the thermal conductivity in the thickness z direction is: 

![Figure 2. Diagram of battery thermal resistance of prismatic battery](image-url)
is calculated by series thermal resistance. Where \( L_i \) refers to the thickness of each layer in the jellyroll, \( k_i \) is the thermal conductivity of each layer.

\[
k_{x, jr} = k_{y, jr} = \frac{\sum L_j k_j}{\sum L_j} \tag{6}
\]

\[
k_{z, jr} = \frac{\sum L_j}{\sum \frac{L_j}{k_j}} \tag{7}
\]

### Table 1. The thermophysical parameters\(^{[8, 9]}\)

| Parameters     | Descriptions                          | unit   | Values  |
|----------------|---------------------------------------|--------|---------|
| \( \rho_{jr} \) | density of the jellyrolls             | Kg/m\(^3\) | 2055.2  |
| \( c \)       | specific heat capacity of the jellyrolls | J/(kg \cdot K) | 1399.1 |
| \( K_{x, jr} \) | thermal conductivities in the x direction of the jellyrolls | W/(m \cdot K) | 29.557  |
| \( K_{y, jr} \) | thermal conductivities in the y direction of the jellyrolls | W/(m \cdot K) | 29.557  |
| \( K_{z, jr} \) | thermal conductivities in the z direction of the jellyrolls | W/(m \cdot K) | 0.89724 |
| \( \varepsilon \) | thermal radiant emissivity             | 1      | 0.04    |
| \( h \)       | convective heat transfer coefficient   | W/(m\(^2\) \cdot K) | 12      |
| \( k_{shell} \) | the thermal conductivity of the battery shell | W/(m·K) | 238     |
| \( k_{air} \)  | the thermal conductivity of the air gap | W/(m·K) | 0.0321  |
| \( R_{ap} \)   | the thermal resistance of the contact between two jellyrolls | K \cdot m\(^2\)/W | 0.005   |

### 3.2 Battery heat generation model

The total heat generation of the battery consists of three parts: side reaction heat \( Q_{side} \), internal short circuit heat \( Q_{short} \) and pressure relief valve heat dissipation \( Q_{vent} \).

\[
Q_T = Q_{side} + Q_{short} + Q_{vent} \tag{8}
\]

In the hot box experiment, when the surface temperature of the battery reached about 132°C, the pressure relief valve was triggered and caused the battery temperature to drop in a short time. A constant power heat dissipation lasting ten seconds is used to define \( Q_{vent} \) in the paper as Equation 2. According to the results of the experiment, \( W_{vent} \) is 1600 W. However, in the single-side heating experiment, the effect of \( Q_{vent} \) is very small, and it hardly changes the trend of battery temperature changes.

\[
Q_{vent} = -W_{vent}(T > 132^\circ C, \Delta t = 10 \text{s})
\]

\[
Q_{side} = Q_{sei} + Q_{neg} + Q_{pos} + Q_{ele} + Q_{sep} \tag{9}
\]

\( Q_{side} \) is composed by five parts: the SEI film decomposition reaction heat \( Q_{sei} \) the anode-solvent reaction heat \( Q_{neg} \), the cathode decomposition reaction heat \( Q_{pos} \), the electrolyte decomposition reaction heat \( Q_{ele} \) and the separator decomposition reaction heat \( Q_{sep} \). 

\( Q_{sei} \) can be expressed in equation (10)-(12). Where \( R_{sei} \) is the rate reaction; \( c_{sei} \) is the dimensionless amount of lithium-containing meta-stable species in the SEI; \( R=8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \).

\[
R_{sei} = A_{sei} \exp \left[ -\frac{E_a_{sei}}{RT} \right] c_{sei} \tag{10}
\]
\[ \frac{dc_{sei}}{dt} = -R_{sei} \]  
(11)

\[ Q_{sei} = H_{sei}W_{C}R_{sei} \]  
(12)

\( Q_{neg} \) can be expressed in equation (13)-(15). Where \( R_{neg} \) is the reaction rate; \( c_{neg} \) is the dimensionless amount of lithium intercalated into the carbon; \( t_{sei} \) is a dimensionless measure of the thickness of the SEI layer thickness.

\[ R_{neg} = A_{neg}\exp \left[ -\frac{E_{a,neg}}{RT} \right] \exp \left[ \frac{t_{sei}}{t_{sei,0}} \right] c_{neg} \]  
(13)

\[ \frac{dc_{neg}}{dt} = -R_{neg} \]  
(14)

\[ Q_{neg} = H_{neg}W_{C}R_{neg} \]  
(15)

\( Q_{pos} \) can be expressed in equation (16)-(18). Where \( R_{pos} \) is the reaction rate; \( \alpha_{pos} \) is the degree of conversion.

\[ R_{pos} = A_{pos}\exp \left[ -\frac{E_{a,pos}}{RT} \right] \alpha_{pos}(1 - \alpha_{pos}) \]  
(16)

\[ \frac{d\alpha_{pos}}{dt} = -R_{pos} \]  
(17)

\[ Q_{pos} = H_{pos}W_{pos}R_{pos} \]  
(18)

\( Q_{ele} \) can be expressed in equation (19)-(21). Where \( R_{ele} \) is the reaction rate; \( c_{ele} \) is the dimensionless amount of electrolyte concentration.

\[ R_{ele} = A_{ele}\exp \left[ -\frac{E_{a,ele}}{RT} \right] c_{ele} \]  
(19)

\[ \frac{dc_{ele}}{dt} = -R_{ele} \]  
(20)

\[ Q_{ele} = H_{ele}W_{ele}R_{ele} \]  
(21)

\( Q_{sep} \) can be expressed in equation (22)-(24). Where \( R_{sep} \) is the reaction rate; \( c_{sep} \) is the dimensionless amount of separator concentration.

\[ R_{sep} = A_{sep}\exp \left[ -\frac{E_{a,sep}}{RT} \right] c_{sep} \]  
(22)

\[ \frac{dc_{sep}}{dt} = -R_{sep} \]  
(23)

\[ Q_{sep} = H_{sep}W_{sep}R_{sep} \]  
(24)

The heat generated during the breakdown of the separator is simulated using the energy released by the first-order RC circuit. Electrochemical energy is stored by a capacitor, and Joule heat is generated when current flows through the resistor. The voltage changes and heat release at both ends of the capacitor are shown in the following equations. \( R_{\Omega} \) is the short-circuit internal resistance, here is 0.04 \( \Omega \); \( C \) is the battery equivalent capacitance, here is 15000 F. \( V_{n} \) is short-circuit voltage, the initial value is 4.1 V.

\[ \frac{dV_{tr}}{dt} = -\frac{V_{tr}}{R_{\Omega}C} \]  
(25)

\[ Q_{short} = \frac{V_{tr}^2}{R_{\Omega}} \]  
(26)
Other parameters in the model are shown in Table 3.

**Table 2. Details of model parameters** [7, 11, 12]

| Parameters     | Descriptions                          | unit | Values         |
|----------------|---------------------------------------|------|----------------|
| $A_{sei}$      | frequency factor of SEI film          | s$^{-1}$ | $1.667 \times 10^{15}$ |
| $E_{a,sei}$    | activation energy of SEI film         | J/mol | $1.3508 \times 10^{5}$ |
| $H_{sei}$      | unit weight heat generation rate of SEI| J/kg  | $2.57 \times 10^{5}$ |
| $A_{neg}$      | frequency factor of anode-solvent     | s$^{-1}$ | $2.5 \times 10^{13}$ |
| $E_{a,neg}$    | activation energy of anode-solvent    | J/mol | $1.3508 \times 10^{5}$ |
| $H_{neg}$      | unit weight heat generation rate of anode-solvent | J/kg | $1.714 \times 10^{6}$ |
| $A_{pos}$      | frequency factor of cathode           | s$^{-1}$ | $7.25 \times 10^{16}$ |
| $E_{a,pos}$    | activation energy of cathode          | J/mol | $2.18 \times 10^{5}$ |
| $H_{pos}$      | unit weight heat generation rate of cathode | J/kg  | $6 \times 10^{5}$ |
| $A_{ele}$      | frequency factor of electrolyte       | s$^{-1}$ | $3 \times 10^{15}$ |
| $E_{a,ele}$    | activation energy of electrolyte      | J/mol | $1.74 \times 10^{5}$ |
| $H_{ele}$      | unit weight heat generation rate of electrolyte | J/kg  | $6.5 \times 10^{5}$ |
| $A_{sep}$      | frequency factor of separator         | s$^{-1}$ | $1.5 \times 10^{50}$ |
| $E_{a,sep}$    | activation energy of separator        | J/mol | $4.2 \times 10^{5}$ |
| $H_{sep}$      | unit weight heat generation rate of separator | J/kg | $2.33 \times 10^{5}$ |
| $W_c$          | the volume-specific carbon content in | g/m$^3$ | $2.8 \times 10^{5}$ |
| $W_{pos}$      | the volume-specific, positive-active  | g/m$^3$ | $1.221 \times 10^{6}$ |
| $W_{ele}$      | the volume-specific electrolyte content in | g/m$^3$ | $6.104 \times 10^{5}$ |
| $W_{sep}$      | the volume-specific separator content in | g/m$^3$ | $1 \times 10^{5}$ |
| $c_{sei0}$     | SEI film decomposition reaction initial value | l  | 0.15 |
| $\alpha_0$    | cathode decomposition reaction initial value | l  | 0.04 |
| $c_{neg0}$     | anode-solvent reaction initial value | l  | 0.75 |
| $c_{ele0}$     | electrolyte decomposition reaction initial value | l  | 0.75 |
| $c_{sep0}$     | separator decomposition reaction initial value | l  | 1 |
4. Result and discussion

4.1 Simulation and experimental results of the hot box test

![Temperature curve](image_a)

![Temperature curve enlargement](image_b)

![Temperature rise rate curve](image_c)

![Heat generation by side reactions](image_d)

Figure 3. Experimental and simulation results of the hot box experiment (a) Temperature curve. (b) Partial enlargement of temperature curve. (c) Temperature rise rate curve. (d) Heat generation by side reactions calculated from the model.

From Figure 3(a) and Figure 3(b), it can be seen that the battery temperature rises evenly with the heating of the heating box in the early stage. At 100°C, the temperature difference between the battery and the heating box begins to decrease, indicating that the battery generates self-heating. The temperature and surface temperature of the battery exceeds the ambient temperature after 800s of heat preservation; when the surface temperature of the battery reaches 135°C, the battery pressure relief valve begins to release gas. The process of releasing gas brings a strong heat dissipation, and the battery temperature is temporarily reduced. Combined with Figure 3(d) and the experimental process, although the decomposition of the SEI film produces less heat, the gas generated will cause the battery to expand. As the subsequent anode-solvent reaction accelerates, more gas is produced. The gas causes the battery pressure relief valve to begin to release gas. The anode-solvent reaction accelerates the temperature rise and causes the separator to decompose. As the separator decomposition reaction finished, internal short-circuit occurs and the battery temperature rises sharply. Figure 3(d) shows that the heat after a short-circuit in the battery mainly comes from the decomposition of the positive electrode and the heat generated by the internal short-circuit, which is the direct cause of the greater...
harm of high nickel thermal runaway. Comparing the results of experiments and simulations, the thermal runaway model based on chemical reaction kinetics can accurately describe the thermal behavior of the battery during thermal runaway. Usually, the temperature rise rate exceeds 1°C/s as the standard to judge the occurrence of thermal runaway. The thermal runaway trigger temperature calculated by the model is 147°C, which is close to the experimentally measured 149°C; After the internal short circuit occurs, the instantaneous temperature rise rate of the battery surface obtained by the simulation is one order of magnitude lower than the actual measured rate. The reason is that the battery will burst and catch fire after a short circuit inside the battery, which affects the thermal resistance between the battery core and the outer shell and may cause inaccurate testing.

4.2 Simulation and experimental results of the single-side heating test

![Simulation and experimental results of the single-side heating test](image-url)
Figure 4. Battery temperature distribution at different times

Figure 5. (a) Experimental and model comparison of the center temperature of T1 and T2. (b) Comparison of experiment and model of temperature rise rate of T2.

It can be seen from Figure 4(b) that when the heating lasts for 533.7 seconds, the battery has an internal short circuit at the center of the heating surface and causes a sharp temperature rise, and then the thermal runaway gradually spreads to the full battery. After about 7s, the entire battery core has already experienced thermal runaway. After that, the heat gradually spreads to the shell of the non-heated surface. In Figure 5(a), T1 represents the temperature at the center of the surface where the heating plate is located, and T2 represents the temperature at the center of the opposite surface of the heating surface. It can be seen from Figure 5(a) that the simulation results of the entire thermal runaway propagation process are similar to the experimental results. The instantaneous temperature of the heating surface of the battery measured in the experiment is up to 1200°C, which may be caused by the direct contact between the thermocouple and the flame during the flame spraying process of the battery. The abnormal drop in temperature measured on the non-heated surface may be caused by poor thermocouple contact due to severe deformation of the battery. According to the simulation result in Figure 5(b), when the thermal runaway spreads to the center of the upper surface of the battery, its temperature is only 67.5°C, which is close to the experimental measurement 64.3°C. This shows that the model can accurately simulate the propagation process of thermal runaway inside the battery.

The temperature cloud diagram of the simulation results in Figure 4 shows that the maximum internal temperature of the battery can reach 1000°C during the thermal runaway process. It is difficult to measure the internal temperature of the battery during the experiment. This model provides the possibility for the calculation of the internal temperature of the battery. The results of experiments and simulations show that when a prismatic battery is heated by an abnormal heat source, due to the multi-layer thermal resistance of the shell, gap and interfaces, the temperature difference at different points on the battery surface may exceed 200°C before thermal runaway occurs. When thermal runaway occurs, the temperature of some areas may still be within the normal working range of the battery. This indicates that for a large-capacity prismatic battery, monitoring the battery temperature by only one temperature measurement point cannot guarantee the safety of the battery and predict the occurrence of thermal runaway.

5. Conclusion

This paper establishes a three-dimensional thermal runaway model for a large format LiNi0.8Co0.1Mn0.1O2 prismatic lithium-ion battery under thermal abuse conditions, and verifies the accuracy of the model through corresponding thermal abuse experiments, revealing the internal reaction mechanism and thermal runaway of thermal runaway under thermal abuse conditions and the propagation process of thermal runaway from the local to the full battery.
Through the hot box experiment and simulation, it is found that the triggering of the battery pressure relief valve is mainly caused by the gas produced from the decomposition of the SEI film and the anode-solvent reaction. Through the experiments and simulation of single-side heating, it is found that the local temperature of the battery may still be in the normal operating range when the local heating causes thermal runaway. The results show that relying on single-point temperature measurement data cannot avoid the occurrence of thermal runaway in time, which provides suggestions for the safe design of battery packs. Subsequent research will be based on this model to carry out more complex working conditions and battery pack thermal runaway simulations.

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