A Fitting Method to Characterize the Gaseous Venting Behavior of Lithium–Ion Batteries in a Sealed Chamber during Thermal Runaway

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Abstract: The venting event of thermal runaway has attracted public attention due to safety issues aroused by frequent fire accidents of new energy vehicles. However, the quantitative description of venting behavior is incomplete for tests in a sealed chamber due to the initial violent injection. In this study, nine types of batteries covering 28 cases in total were employed to investigate the influence of energy density, ambient temperature, pressure, and SOC on the venting behavior, characterized by normalized gas amount; maximum gas releasing rate; and venting durations $t_{50}$, $t_{90}$, $t_{95}$, and $t_{99}$. Then, a ‘two-point’ fitting method was proposed to modify outcomes concerning real-time gas amounts. The results show that at 100% SOC, the normalized gas amount ranges within 0.075–0.105 mol/Ah for NCM batteries and 0.025–0.035 mol/L for LFP batteries, while the maximum gas releasing rate presents a strongly positive correlation with the capacity of NCM batteries (0.04–0.31 mol/s) and a slight increase for LFP batteries (0.02–0.06 mol/s). Eventually, the three venting patterns were summarized and advanced according to the energy density and SOC of the targeted battery. This research can provide a reference for risk evaluations of the venting process and safety design for structure and pressure relief in battery systems.

Keywords: lithium–ion battery; thermal runaway; normalized gas amount; gas releasing rate; venting duration; venting pattern; venting system design; safety evaluation

1. Introduction

Lithium–ion batteries are widely employed in the field of new energy vehicles for their advantages such as high specific energy density and long life cycles [1–3]. However, safety issues such as frequent fire accidents mainly resulting from thermal runaways [4–6] have attracted public attention recently. The release of gases produced inside the batteries as a consequence of thermal runaway has become a crucial process that contributes greatly to combustion or an explosion [7,8].

Lithium–ion batteries, suffering from abuse conditions including mechanical abuse, thermal abuse, or electrical abuse, may be involved in a series of exothermic reactions among various materials such as cathode, anode, and electrolyte, which are always accompanied by gas production [9–11]. The accumulated gases inside the battery will increase rapidly with respect to time as well as battery temperature, leading to a necessary process called the venting event or venting process [12–15]. In the venting process, other solid materials and the remaining electrolytes are ejected out along with the vented gases [16], resulting in a complicated problem in understanding the temporal variation of the physical properties of emissions.
The overall characteristics of a venting event between the initial state and the final state have been investigated well by many researchers, for example, the total amount of gases and the composition and proportion of ejections. In a sealed chamber filled with nitrogen, the total gas amount was about 0.03 mol/Ah for a lithium iron phosphate (LFP) battery and 0.08 mol/Ah for a ternary nickel–cobalt–aluminum (NCA) battery at a fully-charged state [17], while the results of a ternary nickel–cobalt–manganese (NCM) battery were summarized from 51 samples to exhibit a linear dependency on the battery capacity, with a slope around 0.09 mol/Ah [18]. Nevertheless, the capacity of batteries involved in the above research was limited, especially for the LFP and NCA cases below 10 Ah. Additionally, the identification of emissions has been implemented in various thermal runaway tests. The main gas components were identified to be CO₂, CO, H₂, and short-chain hydrocarbons such as CH₄ and C₂H₄ if detected at normal temperatures [13,17–19]. At elevated temperatures, electrolyte vapors might become the primary component of LFP batteries, while more substances with a relatively high boiling temperature were able to be detected, such as hydrocarbons with large carbon numbers [16]. Moreover, over 30 elements were discovered in the solid ejections called vented particles, most of which were composed of elements mainly from cathode active materials, anode active materials, and current collectors, such as Ni, Co, Mn, Li, Al, Cu, C, H, and O [20].

To deeply explore the venting process, a few efforts have been made in experiments and simulations. Relevant experiments were carried out in a sealed chamber filled with nitrogen to achieve thermodynamic parameters, namely, average temperature and pressure in the vessel, in order to calculate the total gas amount and collect ejections [21,22], and the Schlieren and high-speed photography were introduced to gain morphological venting characteristics, especially for initially uneven venting [23,24]. Both the temperature and pressure showed a sudden rising trend once the venting event appeared in the sealed chamber. However, both temperature and pressure in the chamber are awfully susceptible to test conditions and vary under diverse conditions, even for an identical battery, failing to reflect the actual situation. Simulations were also introduced to describe the venting process. Some researchers attempted to throw light onto the motivation of the venting process inside the battery, implying that the internal pressure of the battery was influenced by thermal expansion of the original gases, generated gases, vaporized electrolytes, and battery shell deformation [12,15,25]. Other researchers emphasized jet behaviors such as velocity, appearance, and ignition in an open environment using a coupled conjugate heat transfer and computational fluid dynamics model [26,27]. Unfortunately, few studies focus on the venting intensity from the perspective of the real-time amount of released gases.

Although there is abundant research on the venting process during thermal runaway, it is imperative to develop a valid and effective method for calculating the real-time amount of vented gases and evaluating venting behaviors, which exert a significant influence on pressure relief system design for the battery system as well as the evaluation of physical hazards induced by venting impact.

In this study, sealed chambers with a volume of 230 L and 1000 L were arranged to conduct thermal runaway tests in an inert atmosphere. NCM and LFP batteries with a specific energy density ranging from 165 Wh/kg to 289 Wh/kg were prepared to explore the gaseous venting behaviors based on a ‘two-point’ fitting method developed in Section 2.3. Characteristic parameters containing normalized amounts of the total released gases, maximum gas releasing rate, and venting duration were utilized to analyze the correlations with specific energy density, ambient temperature, ambient pressure, and state of charges (SOCs). Eventually, three typical venting patterns were proposed and verified in order to qualitatively interpret and characterize the venting process. This research can provide a standard methodology for the analysis of venting processes tested in a sealed chamber and will benefit safety design for the pressure relief and physical structure of battery systems.
2. Experiments

2.1. Experimental Setup

In order to investigate the gaseous venting behavior, a gas-tight and horizontal container, called the sealed chamber, as shown in Figure 1, was designed to carry out thermal runaway experiments to measure thermodynamic parameters during a process of a venting event for lithium–ion batteries. It mainly consisted of a chamber covered with an insulation layer, a heater, a fixed plate, an exhaust port, thermocouples, pressure sensors, and two valves. In the chamber, the adjustment of ambient temperature or pressure before the venting event was performed by turning on the heater, vacuuming, or adding the inert gas.

Figure 1. The sealed chamber. (a) A diagrammatic sketch to display the main components of the testing system. (b) Physical image. Ambient pressure and temperature were measured separately by several pressure sensors fixed to the container and thermocouples placed randomly and uniformly. It depended on each case whether the heater worked or not. The sealed chamber used in this study had two sizes: 230 L and 1000 L.

All experiments were conducted as the following procedures. Firstly, a tested battery was charged to 100% SOC using a constant current-constant voltage mode and discharged to the given SOC if required. Then, the tested battery was placed on the fixed plate covered with a layer of insulation. Two to four K-type thermocouples were configured to calculate the average ambient temperature in the chamber. The pressure sensors were suitable for measuring an absolute pressure ranging from 0 to 1.6 MPa with a full-scale error of 0.5%. Next, the vitally important step was the process of gas exchange, namely, extraction and inflation. After locking the chamber, we utilized a vacuum pump to remove the air slowly until the vacuum degree reached 0.8 and immediately filled the chamber with fresh nitrogen to the given pressure—mostly atmospheric pressure—and repeated this twice to control the oxygen concentration below 1%. By establishing a nearly pure nitrogen atmosphere, the venting process would be rarely affected by reactions with oxygen, and the safety of the thermal runaway test was promoted. If experiments were carried out under different pressures or temperatures, the vacuum pump, nitrogen cylinder, and heater were operated as required. The batteries in this study were heated to thermal runaway by a lateral heating plate (400–1000 W) or the heater (5000 W) near the wall of the chamber directly. Signals of ambient temperature and pressure were monitored and recorded by a data acquisition instrument for the whole process. The average values of the above thermodynamic parameters were eventually adopted to explore the gaseous venting behavior.
2.2. Tested Samples

In order to obtain the comprehensive results, a total of 9 types of sample batteries were employed, including lithium iron phosphate (LFP) batteries with different capacities and ternary Li(Ni_{x}Co_{y}Mn_{z})O_{2} (NCMxyz) batteries with ratios x:y:z of 5:2:3, 6:2:2, and 8:1:1. By weighing and measuring the physical outline of all tested batteries prior to each test, the specific energy density as well as volumetric energy density was compared in Figure 2. The specific energy density of the sample batteries ranged from 165 Wh/kg to 289 Wh/kg, showing a linear correlation with volumetric energy density because of the similar battery density as the dashed line in Figure 2. The slope of the fitted line is 2.39, close to 2.38 of Koch’s result [18], and ranging between 2 [28] and 2.7 [29].

![Energy density of the tested batteries. The dashed line is a linear fit passing through zero point.](image)

In this study, 28 cases in total were involved and divided into four groups according to the test conditions, which are listed in Table 1. For group A, thermal runaway tests began at normal temperature and pressure for fully charged batteries to figure out how the specific energy density affected gaseous venting behaviors; for group B, only NCM811 prismatic batteries were adopted to study the effect of ambient temperature; for group C, batteries with medium nickel contents and relatively low SOCs were selected to analyze the venting characteristics under different pressures; for group D, three SOCs, 0%, 50%, and 100%, were taken into account. Considering each condition respectively, the influence of energy density, temperature, pressure, and SOC on venting behaviors could be revealed.

**Table 1. Test conditions. Four groups A, B, C, and D represent four test conditions: (A) at room temperature for 100% SOC; (B) at high temperature over 150 degrees Celsius; (C) under different pressures; (D) at different SOCs.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Cathode</th>
<th>Capacity (Ah)</th>
<th>Battery Type</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NCM811</td>
<td>117</td>
<td>Prismatic</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>2</td>
<td>NCM811</td>
<td>71</td>
<td>Pouch</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>3</td>
<td>NCM622</td>
<td>50</td>
<td>Prismatic</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>NCM523</td>
<td>153</td>
<td>Prismatic</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>NCM523</td>
<td>50</td>
<td>Prismatic</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>LFP</td>
<td>150</td>
<td>Prismatic</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>7</td>
<td>LFP</td>
<td>304</td>
<td>Prismatic</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>LFP</td>
<td>280</td>
<td>Prismatic</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>LFP</td>
<td>304 1</td>
<td>Prismatic</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

1 The battery size was different from no. 7.
2.3. ‘Two-Point’ Fitting Method

Although test conditions were varied, the temporal variations of average temperature and pressure acquired from each test were able to reflect the gaseous venting behavior. Actually, the molar amounts of vented gases decided by the above two thermodynamic parameters is a preferable variable to describe the whole venting event. The amount of gas \( n \) ejected out of the examined battery was calculated by applying the ideal gas law \([13,16]\) as follows:

\[
n(t) = \frac{P_{avg}(t)V}{RT_{avg}(t)} - n_0
\]

where \( n \) denotes the gas amount released from the tested battery as a variable of time (in mol); \( P_{avg} \) is the average value of the recorded pressure in the chamber at time \( t \) (in Pa); \( V = 0.23 \) or \( 1 \) m\(^3\), the volume of the sealed chamber; \( R \) is the ideal gas constant, 8.314 J/K/mol; \( T_{avg} \) is the average temperature inside the chamber (in K); and \( n_0 \) is the initial amount of gases inside the chamber before the venting process.

Before the process of the venting event, the interior of the chamber was regarded as in an equilibrium state; hence, the initial gas amount \( n_0 \) from the ideal gas law was approximately precise and convincing. Similarly, at the end of the venting event, the releasing rate of gases produced inside the battery gradually decreased; therefore, it was reasonable and tolerable to introduce the ideal gas law, assuming that the internal gases were in a quasi-equilibrium state. However, there was a non-equilibrium stage due to extremely uneven temperature fields caused by the violent ejections, where the ideal gas law was not applicable, as shown in Figure 3. This stage was unpredictable because of the complex variations in the ejections. Though an assumption of uniform ejection can complete the unpredictable stage for simplification, the maximum rate of gas release would obviously be lower than the correct value, leading to an underestimation of the intensity of the venting event. The uniform ejection assumption cannot interpret the fact that the venting process gradually weakens, resulting in a discontinuity point at the end. In general, \((t_0, n_0)\) and \((t_f, n_f)\) can be decided by the ideal gas law \([25]\) in the quasi-equilibrium stage, and \((t_1, n_1)\) and \(n_{total} \) are easily obtained from Equation (1), where \( n_2 \) is the slope of linear fit locally at \( t_1 \), almost varying within 0.01–0.1 mol/s. Usually, the rising rate of gas amounts after the point has a trend of approximately monotonic decrease.

![Figure 3](#)

**Figure 3.** A ‘two-point’ fitting method to determine \( n(t) \) for the whole process. The solid line (black) and dotted line (black) are results calculated by the ideal gas law. The dashed line (purple) is the fit.

The ‘two-point’ fitting method was applied in the non-equilibrium stage as a better approximation instead of a linear fit, where gas amounts determined by the ideal gas law seemed to deviate from the actual curve for inaccurate temperature and pressure. When \((t_0, n_0)\),
where $n(t)$ is the total amount of released gases, equal to the total gas amount in the chamber minus the initial gas amount before venting, and the coefficients $a$ and $b$ are given in Equations (3) and (4). $b$ denotes the maximum gas releasing rate when $a$ is greater than zero in popular cases. The fitting curve from Equation (2) combined with the curve in the quasi-equilibrium stage can describe the whole venting process. If more points after $t = t_1$ are adopted to establish a cubic or higher polynomial function, the fit may be distorted because no additional information is provided effectively. It should also be noted that although the ‘two-point’ fitting method provides a concise description of complicated venting processes at the initial stage, it is an approximation method for evaluation.

In addition to the maximum gas releasing rate, another valuable parameter was achieved by employing the above fitting method, that is, venting duration. The derivative value of gas amounts with respect to time approached zero at the end of the venting event, resulting in a significant sensitivity of the duration. Equivalent parameters $t_{50}$, $t_{90}$, $t_{95}$, and $t_{99}$, were developed to evaluate the completeness of the venting process, defined as the length of the interval between the start point of the venting event and the point where the amount of released gases reached 50%, 90%, 95%, and 99% of the total amount, respectively.

3. Results and Discussion

3.1. A Case Study on the Application of the ‘Two-Point’ Fitting Method

To better understand the aforementioned ‘two-point’ fitting method, a typical case of a 100% SOC 153 Ah battery with an NCM523 cathode was taken as an example to illustrate the data processing and analysis processes, shown in Figure 4. The battery was laterally heated to thermal runaway at a normal temperature and pressure in the 1000 L chamber filled with nitrogen initially.

![Figure 4](image-url)

Figure 4. A typical case of 100% SOC 153 Ah NCM523 battery for the application of ‘two-point’ fitting method. (a) The thermodynamic behavior in the sealed chamber. The gray, red, and blue points are the average temperature, pressure, and gas amount without modification during thermal runaway in the chamber. (b) The modified results. Venting durations are obtained from the figure.
Figure 4a presents the gas amount and average temperature and pressure in the chamber with respect to time. Before the venting event, the interior of the chamber was in equilibrium, where the temperature and pressure were almost maintained unchanged, with 40.88 moles of gases. Once the safety valve opened, the gases certainly suffered from an unstable period in terms of the venting intensity, in which the ideal gas law was not applicable and the average temperature was difficult to measure accurately. After a few seconds, gas flow disturbance inside the chamber was improved, as evident from the diminished peaks. By computing the rising rate of released gases, the hypothesis was approximately held in this study if the derivative of the gas amount was lower than 0.1 mol/s and declined in a continuously monotonous trend.

As a consequence, \((t_0, n_0), (t_1, n_1), \text{ and } (t_1, n_1')\) in the fitting method chosen as \((0, 40.88), (60, 52.09), \text{ and } (60, 0.0667)\) were substituted into Equations (2)–(4), modifying the inappropriate curve of gas amount redrawn in Figure 4b. The modified gas amount expressed as net gas production varied inversely with the modified gas releasing rate. The total gas amount generated in the whole process reached 13.05 mol. In consideration of the convenient comparison with results from other studies, the unit L/s, L/Ah, or L under the standardized test conditions (298.15 K and 100 kPa) is displayed in the brackets following the values in mol/s, mol/Ah, and mol, separately. The maximum gas releasing rate for the tested battery appeared at the beginning of the venting event, with a value of 0.31 mol/s (6.94 L/s). In the middle of the venting process, \(t_{50}\) was obtained as 26 s (0.203 mol/s, 4.55 L/s), when the vented gases reached up to half of the total gas production. In the same way, \(t_{90}, t_{95}, \text{ and } t_{99}\) could be achieved as 68 s, 86 s, and 136 s, meaning that only one or two minutes were required to release all the gases. Because the derivative of gas amounts approached zero, a minor measurement error may have resulted in a huge difference at \(t_{99}\), leading to a weak reference value.

It should be noted that not all cases showed the same venting behavior due to the complicated process in the non-equilibrium stage, but could be handled by a similar method. Furthermore, several cases such as batteries with 0% SOC were not necessary to address because of gentle venting intensity or relatively small disturbance in the thermodynamic state.

### 3.2. The Influence of Energy Density

Application scenarios depend on the energy density of batteries to a degree, accounting for safety as well as durability. For instance, LFP batteries are widely used in battery energy storage systems, while NCM batteries are commonly adopted in new energy vehicles for their excellent volumetric energy density. Therefore, disparate strategies for pressure relief systems should be proposed for various situations according to the specific venting intensity. Batteries are taken into consideration with a specific energy density ranging within 165–289 Wh/kg and a capacity within 50–304 Ah, almost satisfying most application scenarios.

Normalized gas amounts as well as maximum gas releasing rates represent the ability to generate gases from thermal runaway reactions, directly resulting in overpressure and a strong impact on the structure in various degrees. Figure 5 illustrates the gaseous venting behaviors of fully charged LFP and NCM batteries at normal temperatures and pressures regarding total gas amount and maximum gas releasing rate with respect to specific energy density and capacity. As evident from Figure 5a, the range of normalized gas amounts, defined as gas production per unit capacity, is significantly different with cathodes, while there is a weak positive correlation between normalized gas amount and specific energy density, considering LFP or NCM separately. In regard to NCM batteries, the normalized gas amount varies within 0.075–0.105 mol/Ah (1.68–2.35 L/Ah), consistent with 0.09 mol/Ah [18] and 0.08 mol/Ah [17] to a certain degree, while that for LFP batteries is only 0.025–0.035 mol/L (0.56–0.78 L/Ah), close to 0.03 mol/Ah, found in previous work [17], implying that NCM batteries generate more than around 1–3 times the gases in moles compared to LFP batteries. It is noteworthy that for batteries with LFP cathodes or low SOCs, more substances such as the liquid electrolyte uninvolved in exothermic
It should be noted that not all cases showed the same venting behavior due to the influence of Ambient Temperature. Venting duration is another parameter to describe the evolution of venting events. Combined with \( t_{50}, t_{90}, t_{95}, \) and \( t_{99}, \) the evolution of a venting process is roughly sketched, as shown in Figure 6 where the y-axis ranges within 0–1, corresponding to the subscripts of the above variables. Without a doubt, the venting process of NCM batteries is terminated much earlier than that of LFP batteries. Generally, the venting event disappears in only 2 or 3 min for NCM batteries, while several or tens of minutes are necessary for all gases to be ejected out of LFP batteries, suggesting a longer period to deal with the exhaust. Interestingly, venting durations seem close to each other for NCM batteries, allowing similar strategies to be applied to the battery system.

**Figure 5.** Gaseous venting characteristics. (a) The total gas amount versus specific energy density. (b) The predicted maximum gas releasing rate versus battery capacity. The slope of the linear fit is 0.0023 and the intercept is −0.0482.

**Figure 6.** Venting durations for batteries with different cathodes.
3.3. The Influence of Ambient Temperature

Ambient temperature not only accelerates the evaporation of electrolytes ejected out of the tested battery but also increases the proportion of gaseous components with a large molecular weight [16]. Figure 7 shows a comparison of predicted maximum gas releasing rates under different temperatures for 117 Ah prismatic NCM811 batteries, and only the cases of 50% SOC and 100% SOC make sense. A venting event occurring at elevated temperatures tends to erupt more violently and increase by double, compared to either 0.374 mol/s under 160–250 degrees Celsius with 0.185 mol/s at room temperature for 50% SOC or 0.481 mol/s under 160–250 degrees Celsius with 0.219 mol/s at room temperature for 100% SOC.

![Figure 7](image)

Figure 7. Comparison of predicted gas releasing rates under different temperatures; 117 Ah prismatic NCM811 batteries with 0%, 50%, and 100% SOC were examined. Thermal runaway test under room temperature for 0% SOC is absent in view of detection precision.

Table 2 lists the rest parameters for venting characteristics under different ambient temperatures. The gas production of both the 50% SOC case and the 100% SOC case grew around 10% at elevated temperatures, and the characteristic durations reduced to half the results at normal temperatures. However, the 50% SOC battery seemed to finish the venting event slightly earlier against the recognition of a more significant severity for higher SOCs. On the one hand, the total gas amount released from the 50% SOC battery was approximately 71% of the 100% SOC battery, leading to a smaller gas amount corresponding to each venting duration. On the other hand, the electrolytes in the lithium-ion batteries, mainly composed of Dimethyl Carbonate (DMC), Ethyl Carbonate (EC), and Diethyl Carbonate (DEC), possessed a boiling point below 130 degrees Celsius, except EC (248 degrees Celsius) [30,31], implying a great tendency to vaporize at elevated temperatures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>n (mol)</th>
<th>$t_{50}$ (s)</th>
<th>$t_{90}$ (s)</th>
<th>$t_{95}$ (s)</th>
<th>$t_{99}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% SOC</td>
<td>7.93 (0.78)</td>
<td>26 (–13)</td>
<td>68 (–36)</td>
<td>80 (–41)</td>
<td>109 (–58)</td>
</tr>
<tr>
<td>100% SOC</td>
<td>11.13 (1.09)</td>
<td>30 (–14)</td>
<td>71 (–34)</td>
<td>88 (–44)</td>
<td>126 (–70)</td>
</tr>
</tbody>
</table>

3.4. The Influence of Ambient Pressure

The burst pressure of the safety valve installed on battery shells is around 1.2 MPa for cylindrical batteries and roughly 0.5 MPa for prismatic batteries [22,32]. If the internal
pressure of the battery minus the external pressure is over the burst pressure, a venting event could happen. When the battery works under a higher or lower operating pressure, the occurrence of a venting event may change with ambient pressure, contributing to different venting behaviors.

Table 3 declares the characteristic parameters under different pressures for NCM622 batteries at 60% SOC and NCM523 batteries at 75% SOC. Venting events occurring under a relatively high pressure give off more gases, except with the NCM622 battery at 0.1 MPa, which could be mainly influenced by internal reactions. Both NCM523 and NCM622 batteries ejected more violently at the lowest pressure level in this study. In addition, venting durations, despite the obtainable data, were absent from the venting processes, including an obvious pilot injection, because it remains uncertain what would happen before the second injection during a process of thermal runaway. The valid data on venting durations for NCM622 illustrate a strong injection at first but a weak injection after 

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pressure 1 (MPa)</th>
<th>n (mol)</th>
<th>Max(dn/dt) (mol/s)</th>
<th>$t_{50}$ (s)</th>
<th>$t_{90}$ (s)</th>
<th>$t_{95}$ (s)</th>
<th>$t_{99}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCM622</td>
<td>0.1</td>
<td>1.73</td>
<td>0.033</td>
<td>33</td>
<td>94</td>
<td>118</td>
<td>163</td>
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<tr>
<td></td>
<td>0.18</td>
<td>1.29</td>
<td>0.012</td>
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<tr>
<td></td>
<td>0.26</td>
<td>1.43</td>
<td>0.013</td>
<td>59</td>
<td>109</td>
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</tr>
<tr>
<td>NCM523</td>
<td>0.02</td>
<td>2.16</td>
<td>0.062</td>
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<td>N/A</td>
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<tr>
<td></td>
<td>0.1</td>
<td>2.43</td>
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<tr>
<td></td>
<td>0.26</td>
<td>2.63</td>
<td>0.048</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

1 Absolute pressure. 2 Venting process including an obvious pilot injection will not be discussed here.

3.5. The Influence of SOC

The SOC of batteries will vary within 0–1 due to charging or discharging; hence, the venting process can appear at any SOC. Although higher SOC signifies more dangerous circumstances, the unique characteristics at low SOCs are worthy of study. Figure 8 calculates the modified gas amounts at 0%, 50%, and 100% SOC for both NCM811 prismatic batteries and 280 Ah LFP prismatic batteries. For 100% SOC, the ejection is violent and of short duration, producing a large amount of gases over 0% SOC and 50% SOC. For 0% SOC and 50% SOC, thermal runaway is not triggered when the safety valve opens, leading to a long period to release generated gases and vaporize electrolytes. However, batteries with 50% SOC will enter into thermal runaway after a few minutes, and the second injection appears. This common phenomenon for both NCM and LFP batteries should be noted for hazard suppression regarding fire accidents.

More specifically, the detailed parameters are listed in Table 4. A positive correlation of total gas amount and maximum gas releasing rate with SOC was satisfied for both LFP and NCM811 batteries. The above parameters had a prominent difference between 0% SOC and 50% SOC for NCM811 batteries compared with LFP batteries as a result of the extremely high energy density of NCM811 over LFP. With regard to the four parameters for venting durations, LFP batteries showed a prominent trend where all parameters decreased monotonously with SOC. By contrast, for NCM811 batteries, if we take account of the start time $t = 428$ s of the second injection, all durations became smaller for 50% SOC than those for 100% SOC, which may be explained by the lower gas production and roughly comparative intensity of thermal runaway. The similarity of venting patterns for LFP and NCM811 will be discussed in Section 3.6.
3.6. Discussion

Although energy density, ambient temperature, ambient pressure, and SOC were taken into consideration to determine gaseous venting behavior as mentioned above and various results of characteristic parameters, three typical venting patterns, namely, the evolution of the venting process, are summarized to represent universal relevance in Figure 9a.

**Figure 9.** Venting patterns. (a) Three typical venting patterns summarized in this study. (b) A schematic diagram for the evolution of internal pressure of the tested battery during the process of thermal runaway.
The venting event was strongly correlated with the evolution of pressure inside the battery as well as the burst pressure of the safety valve. Figure 4b proposes schematically the contributions of chemical reactions, thermal expansion of the original gases, and evaporation of electrolytes into the internal pressure without venting and shell deformations [12, 15, 22, 25, 33]. Once a battery is chosen, the burst pressure of the safety valve should vary within a small range, leading to a similar temperature on average corresponding to the venting event. When the battery temperature reaches around that value, whether thermal runaway is triggered or not determines different venting patterns. The three venting patterns are summarized as follows:

- **Pattern 1** \( (T_v \geq T_{TR}) \): venting events mainly induced by thermal runaway, which are generally found for batteries with high energy density or SOCs. The ‘two-point’ fitting method is considered to apply broadly in such cases.
- **Pattern 2** \( (T_v < T_{TR}) \): venting events mainly induced by the vaporized electrolytes and subsequent thermal runaway reactions, which are common in medium SOCs. The ‘two-point’ fitting method is suitable for the second injection caused by thermal runaway.
- **Pattern 3** \( (T_{TR} \) does not exist\): venting events mainly induced by the vaporized electrolytes only, which are universal for relatively low SOCs. Usually, no thermal runaway will occur; in other words, the energy release is not remarkable.

On the whole, Pattern 1 is characterized by one injection and a rapid venting process, Pattern 2 is characterized by two injections with a relatively strong injection after thermal runaway, and Pattern 3 shows no thermal runaway but a long venting duration.

### 4. Conclusions

In order to figure out the characteristics of gaseous venting behaviors, the present study carried out thermal runaway experiments for LFP and NCM batteries in sealed chambers filled with a nitrogen atmosphere with volumes of 230 L and 1000 L. These tested batteries had a specific density ranging within 165–289 Wh/kg and a capacity between 50 Ah and 304 Ah. Modified by a ‘two-point’ fitting method, the influence of energy density, ambient temperature, ambient pressure, and SOC were investigated on the characteristic parameters, including normalized gas amount, maximum gas releasing rate, and four venting durations, \( t_{50} \), \( t_{90} \), \( t_{95} \), and \( t_{99} \). Ultimately, three typical venting patterns are proposed to summarize most venting behaviors. The main conclusions are as follows:

- Energy density, ambient temperature, ambient pressure, and SOC are found to greatly affect the venting behaviors of NCM and LFP batteries. The intensity of the venting process seems weaker for lower energy density, temperature, and SOC and higher pressure.
- The normalized gas amount ranges within 0.075–0.105 mol/Ah (1.68–2.35 L/Ah) for 100% SOC NCM batteries and 0.025–0.035 mol/L (0.56–0.78 L/Ah) for 100% SOC LFP batteries.
- In a sealed chamber filled with nitrogen, the maximum gas releasing rate shows a strongly positive and linear correlation with the capacity of NCM batteries and a weakly positive trend for LFP batteries. Moreover, it also increases with ambient temperature and SOC significantly.
- Venting durations \( t_{50} \), \( t_{90} \), \( t_{95} \), and \( t_{99} \) reflect the evolution of the venting process, demonstrating a considerable difference between LFP and NCM batteries, for which the durations are close. In general, venting durations reduce with elevated temperature and SOC.
- Nearly all venting events obey the three typical venting patterns advanced in this study according to the energy density and SOC of the targeted battery.

This work provides a method and procedure to evaluate the risk of venting processes and will benefit safety design for battery systems in terms of physical structure and pressure relief strategies. Furthermore, it inevitably remains to be settled how the mechanism of gas generation will be satisfied with the results from the sealed chambers and improved to predict venting behaviors in consideration of the effects of ejected particles.
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