Study on the Flammability Limits of Lithium-Ion Battery Vent Gas under Different Initial Conditions

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ABSTRACT: In this paper, the flammability limit of the battery thermal runaway vent gas (BVG) is studied numerically by using the CHEMKIN 2.0 code. The research content mainly includes the change of flammability limit with the state of charge, initial temperature, and initial pressure. The chemical reaction kinetics at the flammability limit is also analyzed. The results show that the flammability limit obtained by numerical simulation is in good agreement with that calculated by Le Chatelier’s mixing rule. The lean and rich limits increase with the increase of the initial pressure, and the increasing trend gradually slows down. As for the change of initial temperature, higher the temperature is, wider the limits are. In addition, according to the simulation results, the fitting formula of the flammability limit changing with the initial conditions is given. Furthermore, in order to reveal the important elementary reactions controlling the flammability limit, the sensitivity analysis with respect to the flame speed and heat release rate analysis of the elementary reactions are carried out at the flammability limit. Finally, the effect of CO₂ and H₂ content on the flammability limit of BVG is discussed.

1. INTRODUCTION

In recent years, lithium-ion batteries (LIBs) have been extensively used in an increasing variety of electronic devices. With the increasingly stringent emission regulations, particularly LIBs have become more acceptable as a power source for vehicles due to their “zero” emission characteristics, high energy density, and long cycle life. Nonetheless, safety concern is always a big obstacle for LIBs to be widely applied. When the cells experience abnormal conditions, such as serious overheating or internal short circuits, thermal runaway will happen and may lead to an explosion, which is very dangerous to human life and public property. Feng et al. provided a comprehensive review of the thermal runaway mechanism of LIBs for electric vehicles. Many scholars have carried out a lot of research on the thermal runaway phenomenon of batteries, including the experimental study on fire behaviors, emission measurement during thermal runaway, the simulation of thermal runaway propagation process, and so forth. During the process of thermal runaway, the temperature of the battery increases sharply and a lot of battery vent gas (BVG) is released. BVG is one of the important sources of hazards in the process of thermal runaway because it consists of several types of combustible gases. Some experimental results reported that the composition and amount of the batteries’ exhaust gas were largely affected by the cathode materials. Nevertheless, the main components of the gases produced by the batteries including CO₂, CO, H₂, CH₄, C₂H₆, and C₂H₄ were almost unchanged. Furthermore, CO₂ and CO account for a large portion at any state of charge (SOC), and as the SOC increased, the CO₂ concentration decreased, the CO and CH₄ concentration increased, and total hydrocarbons varied between 20 and 30%.

When the battery is in a thermal runaway condition, the temperature may exceed the acceptable range, and the active substances will decompose or react with each other to produce flammable gas. The following series of chemical reactions will be triggered at high temperature: the decomposition of the solid electrolyte interphase (SEI) layer, the reaction between the anode material and electrolyte, the reaction between the cathode material and electrolyte, the electrolyte decomposition, and the reaction between the anode and the binder. For the gases with a high proportion in BVG, the breakdown of the SEI layer can produce CO₂:

\[
(\text{CH}_2\text{OCO}_2\text{Li})_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 + \text{CO}_2 + 1/2\text{O}_2
\]

The reduction of CO₂ with intercalated Li at the anode can release CO:

\[
2\text{CO}_2 + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_2\text{CO}_3 + \text{CO}
\]
H₂ can come from the reactions between Li and the binders. In the presence of H₂, CH₄ can be formed by the reduction of the electrolyte to lithium carbonate. Other hydrocarbons, such as C₃H₆, can be generated by the reactions of Li and the solvent. The detailed mechanism of gas production can be referred to in ref 18.

The production of BVG will increase the internal pressure of the battery. If the pressure exceeds the capacity that the safety valve can withstand, the safety valve will open and these gases will be ejected from the battery. Once the flammable gas mixture is emitted, it may accumulate in or around the car and can be ignited by the hot battery itself or other unexpected activities, such as electric sparks.

Although BVG contains a large amount of inert gases, such as CO₂, the combustion phenomena frequently occurred when BVG was released from the batteries. Therefore, it is important to study the flammability of BVG under different conditions. The critical composition delineating the flammable and nonflammable mixture is called the flammability limit, which includes the lean (lower) flammability limit (LFL) and the rich (upper) flammability limit (UFL). The flammability limit is of great significance in gas production and fire safety. On the research of BVG, Karp experimentally measured the LFL and the UFL of BVG at 100% SOC. The results showed that the LFL was about 7.88%, and the UFL was about 37.14%. In addition, it was verified that the flammability limits of the BVG can be well estimated by applying Le Chatelier’s (L-C) mixing rule. As shown in the following equation

\[
(FL)_{\text{mix}} = \left( \sum_{i=1}^{n} \frac{X_i}{(FL)_i} \right)^{-1},
\]

where (FL)₂ is the flammability limit of the mixture, Xᵢ is the volume fraction of the fuel i, (FL)ᵢ is its flammability limit, and n is the total number of fuel components.

Somandepalli et al. also studied the composition and flammability limits of the released gas when a LIB pack fails and goes into thermal runaway in an enclosed space. Guo et al. calculated the flammability limits of BVG by using the L-C mixing rule and found that the flammable range was extended with the increase of SOC. Li et al. studied the flammability of the BVG released from 18,650 LIBs by the L-C mixing rule, and the effect of CO₂ addition was also investigated. However, most of the previous work was carried out under ambient temperature and pressure conditions. The actual thermal runaway process of LIBs occurs at higher temperatures and pressures. The main combustibles in BVG are H₂ and CO. Li et al. investigated the LFL of syngas (H₂/CO) at different preheating temperatures and different levels of inert gas dilution. It was found that the effect of inert dilution on the LFL is more significant than that of the unburned gas temperature. Mendiburu et al. proposed a method to determine the LFL and UFL of pure compounds including CH₄, H₂, and CO in air at atmospheric pressure and different initial temperatures.

The objectives of the current work are the following. Most research studies on flammability limit are based on the L-C mixing rule. However, the derivation of the “L-C” formula assumes that the product of fuel volume fraction and fuel calorific value in the mixture at the flammability limit is a fixed value. At the same time, only the thermal effect of the dilution gas is considered, and the chemical effect of dilution gas is ignored. If the volume fraction of H₂ or CO₂ is too large, the predicted value may deviate from the actual value. Furthermore, the composition of BVG is very complex, and there are usually more than five types of components that account for a relatively large proportion. Therefore, the calculation of the chemical reactions using detailed kinetics is needed to evaluate the flammability limit accurately. Moreover, the gas eruption process of a battery mainly occurs at high temperature and high pressure conditions, so it is necessary to study the flammability limit of BVG under high temperature and high pressure conditions.

Therefore, in this study, the investigation of the flammability limit of BVG under different SOCs was performed by using one-dimensional (1-D) laminar flame calculations coupled with the detailed kinetic mechanism. Then, a typical five-component BVG mixture was proposed based on the experimental data under different SOCs. After that, the variation trend of the LFLs and UFLs under different initial temperature and pressure conditions was analyzed. Furthermore, a fitting formula of the flammability limit changing with the initial conditions was given. In addition, the sensitivity analysis with respect to the laminar flame speed and the heat release rate analysis at the flammability limit were performed, and the dominant reactions controlling flammability limits were discovered.

### 2. RESULTS AND DISCUSSIONS

The detailed components data of BVG is shown in Table 1, which is obtained from ref 16. For NCA cells, the main components are H₂, CO₂, and CO. Moreover, when the value of SOC is greater than 75%, the proportion of each component changes slightly.

According to the experimental results in ref 16, when the battery emits gas, the temperature of BVG is higher than 150 °C. In addition, the pressure that a safety valve of LIB can bear is usually several atmospheres. In order to meet the actual situation and be convenient for comparative analysis, the initial pressure of the study is set as 1–5 atm and the initial

| no. | SOC (%) | H₂ (%) | CO₂ (%) | CO (%) | CH₄ (%) | C₂H₆ (%) | C₃H₈ (%) |
|-----|---------|--------|---------|--------|---------|---------|---------|
| 1   | 0       | 1.7    | 94.6    | 1.6    | 1.6     | 0.3      | 0       |
| 2   | 25      | 15.5   | 62.7    | 5.5    | 8.7     | 0.3      | 0       |
| 3   | 50      | 17.5   | 33.8    | 39.9   | 5.2     | 3.2      | 0.4     |
| 4   | 75      | 24.2   | 20.8    | 43.7   | 7.5     | 3.3      | 0.5     |
| 5   | 100     | 22.6   | 19.7    | 48.9   | 6.6     | 2.4      | 0       |
| 6   | 120     | 23.5   | 20.8    | 48.7   | 5.4     | 1.6      | 0       |
| 7   | 127     | 28.8   | 16.2    | 46.6   | 6.4     | 1.3      | 0.3     |
| 8   | 132     | 25.8   | 18.9    | 49.2   | 4.7     | 1.4      | 0       |
| 9   | 143     | 26.2   | 22      | 43.3   | 6.9     | 1.5      | 0       |
temperatures are determined as 298, 450, and 600 K in accordance with the ambient temperature, gas eruption temperature, and short-circuit temperature, respectively.

2.1. Verification of the Simulation Model. Figure 1 shows the simulation and experimental results of the laminar flame speed of CO/H₂/CH₄/CO₂−air mixtures, where the numerical simulation results are represented as lines and the experimental results are given by symbols. The components of different mixtures can be found in Table 2. Figure 1a shows the results at ambition temperature and pressure. The radiative-heat loss conditions are described by the optically thin (OPT) model and statistical narrow band (SNB) model in this figure. Generally, the trend and values of the simulation results agree well with the experimental data. The radiation model has little effect on the flame speed, and the prediction results of SNB model are closer to the experimental values than those of adiabatic and OPT model. In adiabatic conditions, no turning point occurs, which means that it is difficult to determine the flammability limit. However, when the radiation-heat loss model is used to estimate the heat loss, the LFL and UFL turning points appear. Therefore, it is necessary to include the radiation model when conducting the simulation study of the flammability limit, and the SNB model can accurately predict the laminar flame speed of the mixture. Figure 1b verifies the prediction ability of laminar flame speed at elevated temperature and pressure conditions. Considering the range of initial condition in this paper (temperature 298–600 K, pressure 1−5 atm), the laminar flame speed of the mixtures at \( T_u = 450 \) K, \( P = 1 \) atm and \( T_u = 303 \) K, \( P = 3 \) atm are verified. The results show that the trend and values of the simulation results are in good agreement with the experimental data. From the above analysis, it can be concluded that the simulation model can accurately predict the laminar flame speed of the multi-component gas under different initial conditions.

Moreover, in order to further verify the accuracy of the simulation model, the flammability limits of BVG under several SOCs are calculated through the 1-D laminar premix flame simulation and compared with the experimental data calculated by the L-C mixing rule. As mentioned above, the L-C mixing rule has been proved to be accurate in predicting the flammability limit of BVG. The components of BVG are taken from Table 1, and the calculation method of the L-C mixing rule can be found in ref 24.

| label | CO (%) | H₂ (%) | CH₄ (%) | CO₂ (%) |
|-------|--------|--------|---------|---------|
| G1    | 40     | 40     | 0       | 20      |
| G2    | 40     | 40     | 20      | 0       |
| G3    | 40     | 40     | 0       | 20      |

Figure 2. Flammability limits of BVG with different SOC values. (a) Laminar flame speed and (b) values of flammability limit.
The laminar flame speed of BVG was calculated by gradually increasing or decreasing the equivalence ratio of the mixture. It can be seen from Figure 2a that when the volume fraction of the fuel is too low or too high, a turning point will appear in the laminar flame speed curve. These two turning points are called the LFL point and UFL point, respectively. When the volume fraction of the mixture is between these two limit points, the mixture can be ignited, otherwise the flame cannot spread.

The values of the fuel volume fraction at the turning point are extracted and compared with the L-C calculation results. As shown in Figure 2b, the 1-D flame calculation results of LFL and UFL are consistent with those of L-C. The maximum absolute deviation of LFL is less than 2.5% and that of UFL is less than 3.5%. Therefore, the 1-D numerical simulation model can accurately predict the flammability limit of the target mixture.

2.2. Flammability Limit of BVG under Different SOCs.

Figure 3 shows the flammability limits of the BVG under different SOCs and different initial temperature and pressure. When the initial conditions are ambient temperature and pressure, UFL is increased with the increase of SOC, and the maximum value is about 62% when SOC is 132%. With further increase of the SOCs, the UFL is decreased. However, the LFL is basically kept constant when SOC is greater than 75%, which is because the change of the vent gas composition is too small and it has little effect on the flammability limit. The lowest LFL is around 10% when SOC reaches 75 or 100%, which means that the vent gas is flammable when its volume fraction in the air is larger than 10%.

As shown in Figure 3a, when the initial pressure (P) increases from 1 to 5 atm, both the UFLs and LFLs increase. The increase extent of UFL is significantly higher than that of LFL, which are around 10 and 1%, respectively. This means that as the pressure increases, the reactivity of the rich mixture increases significantly, while the reactivity of the lean mixture decreases slightly. When the initial temperature (T_u) is increased from 298 to 600 K, the UFL still shows a clearly increasing trend, while the LFL is decreased slightly. More specifically, the LFL is reduced by nearly 4%, and the UFL is increased by about 10%. This behavior is because with the increase of T_u the total energy of the mixture is increased by the additional enthalpy, which results in a more flammable mixture under both rich and lean conditions, and the flammable range is expanded.

Figure 4 shows the flammable range of BVG under different SOCs and initial conditions. The flammable range is defined as the volume fraction range between the UFL and LFL (i.e., UFL minus the LFL). In general, an increase in initial temperature or pressure can both extend the flammable range. At ambient temperature and pressure conditions (T_u = 298 K, P = 1 atm), the battery with higher SOC has a larger flammable range than that under lower SOC conditions. When the initial temperature and pressure change from ambient condition to high temperature and pressure condition (T_u = 600 K, P = 5 atm), the flammable range can be significantly increased from less than 50 to 70% or above, thus increasing the risk of catching fire. This is why the emitted gas is easily ignited when the LIB is in a thermal runaway state.

It is clear that when the SOC is greater than 75%, the LFL, UFL, and flammable range of the BVG are only changed a little. In addition, the fire risk of the BVG is larger at a higher SOC. Therefore, the BVG with typical components under high SOC conditions is used in the following study. According to the experimental data, the typical mixture of the BVG under high SOC is chosen as 48% CO + 25% H₂ + 5% CH₄ + 2% C₂H₄ + 20% CO₂ (mole fractions). In the following sections, the components of BVG will not be changed.

Figure 3. Flammability limits of BVG with different SOC values under different initial conditions. (a) Change in initial pressure and (b) change in initial temperature.

Figure 4. Flammable range of BVG under different SOCs.
2.3. Influence of the Initial Temperature and Pressure.

For the typical BVG, the relationship between laminar flame speed and volume fraction in the air under different initial temperatures and pressures is shown in Figure 5a,b. The calculation conditions are $P = 1$ atm, $T_u = 298$, $450$, $600$ K and $T_u = 298$ K, $P = 1$, $2$, $3$, $4$, $5$ atm, respectively.

The results show that when the volume fraction of fuel is the same, the laminar flame speed increases with the increase of temperature, while the peak flame speed is always at the volume fraction of $35\%$, that is, the equivalent ratio is about $1.4$. The peak flame speed has doubled when the initial temperature increases from $298$ to $450$ K, and when the initial temperature continues to raise to $600$ K, the flame speed further increases by about $70\%$. When the initial temperature keeps constant, the laminar flame speed decreases with the increase of pressure. However, the peak flame speed still occurs
at the fuel volume fraction of 35%. When the pressure increases from 1 to 3 atm, the peak flame speed reduces by 30%. Furthermore, when the initial pressure increases from 3 to 5 atm, the peak flame speed is decreased by about 16%.

Figures 6 and 7 show the variation of the flammability limit at different initial temperature and pressure conditions. Generally, there is a linear relationship between the flammability limit and the initial temperature. Specifically, for every 150 K increase in temperature, the LFL decreases by about 1.8%, while UFL shows an opposite trend. When $T_u$ increases from 298 to 450 K, the UFL is increased by about 5%; when $T_u$ continues to increase to 600 K, the UFL is further increased by about 7%. This phenomenon is consistent with the flammability limit of CO/H₂/CH₄ mixture measured by Wierzba and Wang.31

When the initial temperature remains unchanged, the lean and rich limits increase with the increase of pressure, and the increasing trend gradually slows down at higher pressure condition, as shown in Figure 7. Moreover, the increase proportion of the UFL is significantly higher than that of LFL with the increase of pressure, thus expanding the flammable range and indicating potentially greater danger of catching fire and explosion.

It can be seen from Figures 6 and 7 that in the current calculation range, the flammability limit values have a certain linear relationship with the initial temperature and a certain quadratic function relationship with the initial pressure. So, the relationship between flammability limit and initial temperature and pressure can be represented by a second-order polynomial

$$LFL = L_{298} - 0.012 \times (T - 298) + 0.75 \times (P - 1) - 0.01 \times (P - 1)^2$$  \hspace{1cm} (2)

$$UFL = U_{298} + 0.0034 \times (T - 298) + 4.5 \times (P - 1) - 0.45 \times (P - 1)^2$$  \hspace{1cm} (3)

where $L_{298}$ and $U_{298}$ are the LFL and UFL, respectively, at $T_u = 298$ K, $P = 1$ atm.

Comparing the results calculated by this formula and the results of the simulation, it is found that the maximum absolute error and the maximum relative error of the LFL are 0.19 and 2.1%, respectively. For UFL, the maximum absolute error and the maximum relative error are 1.46 and 2.27%, respectively.

Furthermore, in order to verify the applicability of this formula, the flammability limits of the BVG calculated by these two methods are compared when $T_u$ is 500 K, and the values of SOC are 25 and 50%. The detailed results are presented in Table 3. It is found that when SOC is 50%, the maximum relative error of the LFL and UFL between simulation and formula calculated results is less than 4.8%. However, when SOC is 25% and the pressure is greater than 1 atm, the maximum absolute error between the simulation results and calculation results is around 10%. This may be due to the high content of CO₂ in the BVG.

Therefore, the fitting formula can be used to predict the flammability limit of BVG when the SOC value of the battery is greater than 25% under different initial temperature and pressure conditions. $T_u$ ranges from 298 to 600 K, and $P$ ranges from 1 to 5 atm.

2.4. Sensitivity Analysis. In order to figure out the most important elementary reactions affecting the flammability limit under different conditions, the normalized sensitivity coefficients for each reaction with respect to the laminar flame speed at the flammability limit are calculated. Figure 8 highlights the 10 elementary reactions that exhibit the largest

| SOC = 50%, 1 atm | fitting formula (%) | simulation (%) | absolute error (%) | relative error (%) |
|------------------|---------------------|----------------|--------------------|-------------------|
| 9.98/62.84       | 9.86/61.19          | 0.12/1.65      | 1.65/2.69          |
| 11.08/70.04      | 10.77/70.34         | 0.31/0.3       | 0.3/0.43           |
| 11.38/73.64      | 11.09/77.35         | 0.29/3.71      | 3.71/4.80          |
| 12.04/52.86      | 11.72/51.86         | 0.31/1.00      | 2.66/1.92          |
| 13.14/60.06      | 12.11/67.74         | 1.02/7.68      | 8.42/11.33         |
| 13.44/63.66      | 11.87/73.45         | 1.57/9.79      | 13.19/13.32        |

Figure 8. Normalized sensitivity coefficients of the laminar flame speed at LFLs. (a) Change in initial temperature and (b) change in initial pressure.
normalized sensitivity coefficient on the laminar flame speed at LFL, where Figure 8a has fixed $P = 1$ atm, and Figure 8b has fixed $T_u = 450$ K.

As shown in Figure 8a, the reactions R1 and R9 exhibit the highest positive and negative sensitivities at these three initial temperature conditions, respectively. Reaction R1 is the main chain-branching reaction producing the OH and O radicals, which can significantly promote the laminar flame speed. On the other hand, reaction R9 is the chain-termination reaction, which transforms the active H radical into a stable HO2 radical. It can reduce the concentrations of active radicals and inhibit the flame propagation. Thus, the LFLs of the mixtures are mostly determined by the competition between reactions R1 and R9.

With the increase of the initial pressure, the chain-propagation reaction R3

$$\text{OH} + \text{H}_2 \Leftrightarrow \text{H} + \text{H}_2\text{O} \quad \text{(R3)}$$

becomes more and more important. When $P = 5$ atm, the sensitivity coefficient of reaction R3 is comparable to that of reaction R1. The consumption of OH radical in reaction R3 produces H radical, which promotes the forward progression of reaction R1. In this case, these two reactions play an important role in improving the flame speed.

As for reactions with negative sensitivities, reaction R9 still appears to have higher priority in reducing the flame speed. Furthermore, another chain-termination reaction R13

$$\text{HO}_2 + \text{OH} \Leftrightarrow \text{H}_2\text{O} + \text{O}_2 \quad \text{(R13)}$$

becomes more and more important with the increase of initial pressure, from which two stable species will be produced. Under the combined effect of reactions R13 and R9, the concentrations of active OH and H radicals are eliminated effectively. Therefore, the flame speed can be reduced, and the flame propagation is inhibited.

Figure 9 shows the main reactions with the highest sensitivity coefficients at UFL. As Figure 9a illustrates, the chain-branching reaction R1 is the main reaction with positive sensitivity under the temperature of 298 K. While when $T_u$ rises to 600 K, the H2O2 decomposition reaction R16

$$\text{H}_2\text{O}_2(+) \Leftrightarrow 2\text{HO}(+) \quad \text{(R16)}$$

becomes more and gradually becomes the dominant reaction. On the other hand, the polymerization reaction of CH4 and H, and the CO oxidation reactions R98 and R24

$$\text{CH}_4 + \text{H}(+) \Leftrightarrow \text{CH}_3(+) \quad \text{(R98)}$$

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have the highest negative sensitivity coefficients. These two reactions will consume H and OH radicals to generate the relatively stable CH₄ and CO₂ molecules, thus inhibiting the chain propagation process.

When \( T_u \) is fixed, the sensitivity coefficient of reaction R16 increases with the increase of pressure and finally becomes the dominant reaction when the initial pressure is greater than 3 atm. On the other hand, the HO₂-related chain terminal reaction R110 become the largest negative coefficient reaction as the initial pressure increase to 3 bar. It is interesting to find that when initial pressure is greater than 3 atm, the sensitivity of reaction R9 changes from negative to positive. This is because reaction R9 can consume active H radical and produce HO₂. With the increase of pressure, reaction R47 gradually becomes more and more important, which can consume HO₂ to generate H₂O₂. The generated H₂O₂ can promote reaction R16 to go forward, and R16 appears to have highest priority for increasing flame speed. Therefore, as the pressure increases, reaction R9 first suppresses and then promotes the laminar flame speed.

With the increase of both initial temperature and pressure, there is an obvious increase in the normalized sensitivity coefficients of the major reactions, which means these reactions become more important for the increase and decrease of the flame speed.

### 2.5. Heat Release Rate Analysis

In order to further study the chemical reaction kinetics at the flammability limit, the heat release rates of each reaction are calculated and the reactions with higher exothermic and endothermic rate were extracted. Figure 10a indicates that the main chain-branching reaction R1 is the main endothermic reaction, and the main chain-termination reaction R9 has the highest exothermic rate at LFL when \( T_u = 298 \text{ K, } P = 1 \text{ atm.} \) As for the UFL, reaction R16 is also the main endothermic reaction, and the exothermic process is dominated by the polymerization reactions related to CH₃ including reactions R98 and R151. It should be noted that reaction R98 has the highest negative sensitivity coefficient to laminar flame speed at UFL.

Figure 11 shows the heat release rate of the main reactions under higher temperature and pressure conditions. As illustrated in Figure 11a, the reaction dominating the exothermic process at LFL is the same as that under ambient temperature and pressure. This means that the change of initial conditions has little effect on the heat release rate of reactions around LFL. In terms of UFL, the main endothermic reaction changes from reactions R1 to R16. Compared with sensitivity analysis, reaction R16 has the largest positive sensitivity.
coefficients under higher pressure conditions. As for the exothermic reactions, reaction R9 still plays a leading role, and reaction R163 also shows a considerable exothermic rate at UFL.

2.6. Effect of CO2 and H2. As the major components of the BVG, the influence of H2 and CO2 on the flammability limit is studied in this section. The proportion of H2 and CO2 are increased or decreased on the basis of the original typical mixture (48% CO + 25% H2 + 5% CH4 + 2% C2H4 + 20% CO2). These are chosen as 5, 25, and 45% for H2 and 0, 20, and 40% for CO2. The other compositions are changed according to their initial proportions.

Figure 12a shows that the variation of the laminar flame speed versus volume fraction when varying the content of CO2 and H2. With the increase of the hydrogen mole fraction, the flame speed is increased significantly, while the flame speed is decreased obviously with the addition of CO2. This is expected.

Figure 12b shows the flammability limits of different mixtures. In general, the CO2 content has little effect on the UFL. However, the LFL is increased with the increase of CO2. With the increase of H2 mole fractions, the LFL is reduced, while the UFL is increased. Specifically, the LFL is increased by about 22% when the content of CO2 increases from 0 to 20% (typical). In addition, when the content of CO2 increases from 20% (typical) to 40%, the relative increase proportion of LFL is about 36%. However, the change rate of UFL is relatively small, which is less than 2.5%. When the content of H2 is increased from 5 to 25% (typical), the LFL is decreased by 6% and UFL is increased by 9.2%. Furthermore, when the content of H2 is increased from 25% (typical) to 45%, these two values become 7.3 and 8.3%, respectively.

Considering that the change of CO2 has great influence on the LFL, the sensitivity analysis of reaction rates with respect to the laminar flame speed at LFL is carried out. As Figure 13 shows that variation in CO2 content did not change the main reactions which has great influence on the flame speed. The main chain-branching reaction R1 and the main chain-termination reaction R9 exhibit the highest positive and negative sensitivities at these three CO2 concentrations, which is similar to the previous section.

### 3. CONCLUSIONS

The influence of initial temperature and pressure on the flammability limits of LIB vent gas (BVG) was investigated by the numerical method. The main results are summarized as follows:

When the SOC of the battery is large, BVG has lower LFL, higher UFL, and larger flammable range. When SOC is more than 75%, LFL changes slightly and UFL basically expands with the increase of SOC value.

In the current calculation range (temperature 298–600 K, pressure 1–5 atm), the LFL of BVG decreases linearly with the increase of initial temperature, while UFL shows an opposite trend. With the increase of initial pressure, both the LFL and UFL increase. According to its changing trend, a polynomial fitting formula between the flammability limit value and the initial temperature and pressure is proposed. It has been verified that this formula can be used to calculate the flammability limit of the battery thermal runaway vent gas.

Sensitivity analysis and heat release rate analysis results show that LFL is mainly determined by the competition between the chain-branching reaction: H + O2 ⇄ O + OH and the chain-termination reaction: H + O2(+M) ⇄ HO2(+M), while UFL is also affected by the oxidation reaction of CH3 and CO. Besides, with the increase of initial pressure, the chain-termination reaction of HO2 and the decomposition reaction of H2O2 have more and more influence on flame propagation. In addition, at the LFL, the reaction with higher negative sensitivity coefficient to flame speed usually dominates the exothermic process; on the contrary, the reaction with higher positive sensitivity coefficient usually dominates the endothermic process.

Finally, the content of CO2 has a greater impact on LFL, and the content of H2 has an impact on both LFL and UFL.

### 4. NUMERICAL APPROACH

The 1-D laminar premixed flame was calculated by the PREMIX code,32 combined with the gas-phase CHEMKIN II33 and TRANSPORT34 software packages for processing the chemical reaction mechanism and for calculating the transport properties. Transport property formulations include the option of using multicomponent or mixture-averaged formulas for molecular diffusion. The convective terms and the diffusive terms were calculated by the windward difference and central difference, respectively. The final grid number was over 250 to ensure a fully converged flame speed prediction. The beginning of the computational boundary was set at x = −2.0 cm and the end point was x = 10 cm. All calculations were carried out within the detailed mechanism of Curran (C1–C2),35 which consists of 79 components and 412 elementary reactions.

Radiant heat loss plays an important role in the flammability limit, so the calculation of radiant heat loss should take into consideration the main asymmetric molecules with high radiation absorption capacity, such as CO2, CO, and H2O. Here, the radiation-heat loss term is added to the energy equation as a source term.
\[ m \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left( \frac{dT}{dx} \right) + \frac{1}{T} \sum_{i=1}^{k} \rho Y_i \frac{dK}{dx} - \frac{1}{T} \sum_{i=1}^{k} \rho Y_i \frac{dK}{dx} = 0 \]  

(4)

where \( m \) is the mass burning rate, \( T \) is the temperature, \( x \) is the spatial coordinate, \( c_p \) is the heat capacity at constant pressure, \( \lambda \) is the thermal conductivity, \( K \) is the total number of species, \( Y_i \) is the mass fraction of \( i \)th species, \( \rho \) is the mass density, \( \rho Y_i \) and \( w_i \) are the production rate, enthalpy, and molecular weight of \( i \)th species, respectively. \( q(x) \) is the radiation-heat flux, with \( x \) representing spatial coordinate.

For the OPT (optically thin) model,\(^37\) the volumetric rate of radiation-heat loss can be written as

\[ \frac{dq(x)}{dx} = 4k_{pl} \sigma (T^4 - T^4) \]  

(5)

where \( k_{pl} \) is the Planck mean absorption coefficient of the gases, \( k_p = \sum P_i \). \( P_i \) is the subscipt \( i \) is the \( i \)th species, \( P_i \) is the local partial pressure of the specific species, \( \sigma = 5.669 \times 10^{-8} \) W/m\(^2\) K\(^4\). \( K^4 \) is the Stefan–Boltzmann constant. \( k_i \) is the Planck mean absorption coefficient of the \( i \)th species as a function of temperature, and its value can be obtained from ref \(^38\).

The SNB model is a random model with an \( S^{-1} \) exponential tailed distribution of line intensities and is employed to estimate the radiation-heat loss of CO, CO\(_2\), and H\(_2\)O.\(^30\) The 1-D wave number averaged radiation-heat transfer equation (RTE) is

\[ \mu \frac{dI}{dx} = -k_x I_x + k_y I_y \]  

(6)

Assuming that the radiation intensity of boundary spectral \( I_w \), on the left and right sides are diffusive walls

\[ I_w = \varepsilon_w I_{w0} + \left( 1 - \varepsilon_w \right) \int_0^1 \mu' I_{v, v'} d\mu' \]  

(7)

where \( \mu \) and \( \mu' \) are the direction radiation cosine. \( I_x \) and \( I_y \) are the averaged spectral radiation intensity and spectral blackbody radiation intensity over a bandwidth \( \Delta v \), respectively. \( k_x \) and \( \varepsilon_w \) are the average absorption coefficient and the wall emissivity, respectively. The superscript \( ' \) and subscript \( w \) represent the incoming direction and quantities at the wall, respectively. The RTE can be made discrete using the method of Kim and Lee\(^39\) and solved using the discrete ordinate method. Detailed methods are available in ref \(^40\). Finally, the total net radiation-heat loss \( q(x) \) is obtained by integrating the spectral radiation intensity over the whole range of wave numbers and solid angles.

\[ q(x) = \frac{d}{dx} \left( \int_0^\infty \int_{-1}^1 \mu I_{v, n_d} d\mu dv \right) = \sum_{\Delta v} \left( \sum_{n=1}^{N} \mu I_{v, n_d} \omega_n \right) \Delta v \]  

(8)

where \( N \) is the total direction number and \( \omega_n \) is the weight function in direction \( n \). For more detailed calculation methods and formulas, we can refer to the research by Ruan et al.\(^40\)

Ruan et al. numerically calculated the flammability limits of premixed CH\(_4\)/O\(_2\)/CO\(_2\) flames by SNB model and OPT model. Results showed that the SNB model can predict flammability limits more accurately, and the OPT model loses effectiveness for higher CO\(_2\) dilution rates and lower equivalence ratios. The prediction ability of the two radiation models for laminar flame speed is verified, and the SNB model is finally selected in this study. The equivalence ratio \( (\varphi) \) is defined by the following formula\(^41\)

\[ \varphi = \frac{(F/A)_i}{(F/A)_e} \]  

(9)

where the \( F/A \) is the ratio of the mass of fuel to the mass of air in the mixture. The subscript “st” denotes the stoichiometric state. Thus \( \varphi < 1, \varphi = 1, \) and \( \varphi > 1, \) respectively, correspond to lean combustion, stoichiometric combustion, and rich combustion.

In addition, the PREMIX code must be modified to include the ability to solve the singular Jacobian matrix at the turning point of the flammability limits. Here, the one-point temperature-controlling continuation method was used to capture the turning point.\(^36\) The method is based on using an existing solution close to it as the initial estimation and the response curve is subsequently produced by adding a new point near the edge of the existing curve and hence lengthening it. The basic concept is to exchange the functions of control parameters and response parameters by introducing an “internal condition”

\[ x = x^*; T = T^*; x = x^* \]  

By fixing \( x^* \) and incrementing the value of \( T^* \), the continuous mapping between flame response and control parameters is realized. Here, \( x^* \) and \( T^* \) are generally chosen among the existing grid points of an existing solution, and there is no particular restriction except that \( x^* \) should exist in relatively steep temperature gradient regions. Therefore, by first determining the appropriate values of \( T \) and \( x \) in the existing solution and then continuing to solve to the next point under the internal conditions, the response curve can be generated from the existing solution.

Sensitivity analysis is a quantitative study of how a model’s solution depends on the parameters. In this study, the normalized sensitivity coefficient of the logarithmic form is expressed as

\[ F_{sen} = \frac{A \frac{dX}{X} \frac{dA}{A}}{10} \]  

(10)

where \( A \) is the pre-exponential factor of the reaction rate coefficients, \( X \) is the laminar flame speed or species mole concentration.

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Notes
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