Article

Impact of Lithium Salts on the Combustion Characteristics of Electrolyte under Diverse Pressures

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Abstract: The electrolyte is one of the components that releases the most heat during the thermal runaway (TR) and combustion process of lithium-ion batteries (LIBs). Therefore, the thermal hazard of the electrolyte has a significant impact on the safety of LIBs. In this paper, the combustion characteristics of the electrolyte such as parameters of heat release rate (HRR), mass loss rate (MLR) and total heat release (THR) have been investigated and analyzed. In order to meet the current demand of plateau sections with low-pressure and low-oxygen areas on LIBs, an electrolyte with the most commonly used lithium salts, LiPF₆, was chosen as the experimental sample. Due to the superior low-temperature performance, an electrolyte containing LiBF₄ was also selected to be compared with the LiPF₆ sample. Combustion experiments were conducted for electrolyte pool fire under various altitudes. According to the experimental results, both the average and peak values of MLR in the stable combustion stage of the electrolyte pool fire had positive exponential relations with the atmospheric pressure. At the relatively higher altitude, there was less THR, and the average and peak values of HRR decreased significantly, while the combustion duration increased remarkably when compared with that at the lower altitude. The average HRR of the electrolyte with LiBF₄ was obviously lower than that of solution containing LiPF₆ under low atmospheric pressure, which was slightly higher for LiBF₄ electrolyte at standard atmospheric pressure. Because of the low molecular weight (MW) of LiBF₄, the THR of the corresponding electrolyte was larger, so the addition of LiBF₄ could not effectively improve the safety of the electrolyte. Moreover, the decrease of pressure tended to increase the production of harmful hydrogen fluoride (HF) gas.

Keywords: Lithium-ion battery; electrolyte; combustion characteristic; cone calorimeter; low pressure

1. Introduction

Thermal runaway (TR) is mainly caused by the sharp temperature rise inside lithium-ion batteries (LIBs), which could be induced by abuse or other reasons such as short-circuit, overcharge, high-rate charge/discharge. TR is also related to the cathode material and release of oxygen. In addition, TR would eventually lead to the combustion or explosion of the battery. The electrolyte is one of the main combustibles in LIBs. During TR processing, the electrolyte inside LIBs would cause an injection of gases and flammable liquids. The combustion of the electrolyte could release a lot of heat, accelerate the spread speed of the fire, and produce toxic and harmful gas such as hydrogen fluoride (HF). Electrolyte containing carbonate and carboxylate solution is a kind of combustible liquid, recently it has been the focus for intensive studies on the combustion characteristics of it. Moreover,
investigating the combustion behavior of the electrolyte could be beneficial for developing safer LIB materials and their range of application.

The electrolyte exhibits complex fire behaviors during the whole combustion process of LIB due to its high content in LIBs and properties such as flowing easily as a liquid. According to previous research, the onset thermal decomposition temperature of a typical electrolyte from the lithium salts and the interactions between the salts and the solvents is about 70 °C [1–3]. Once thermally decomposed, it is extremely easy for this to lead to battery leakage due to the generated numerous heat and gases. Furthermore, with higher temperature, the electrolyte would react with anode and cathode materials [4], while the simultaneously leaking electrolyte would form a combustible liquid pool. Once ignited, it could cause an enormously dangerous pool fire. If the internal temperature of the battery is relatively higher, it could grow into a jet fire then speed up fire spread greatly. In January 2013, the fuselage of a Boeing 787 belonging to All Nippon Airways was damaged severely due to the pool fire in the auxiliary power unit caused by the leakage of electrolyte from LIBs.

Given the flammability and the resulting serious consequences, the pyrolysis and combustion characteristics of the electrolyte have received an extensive attention from scholars around world in recent years. Currently, in most commercial electrolyte, the commonly used and added lithium salt is LiPF6 or LiBF4. In order to comprehensively understand the reactions and mechanisms during the combustion process of the electrolyte with these two types of lithium salt, a comparative analysis of the chemical reactions of LiPF6 in ethylene carbonate/dimethyl carbonate (EC/DMC) electrolyte and PF5 with EC/DMC was conducted. The results indicated that the two samples generated almost the same products [2,3,5]. Thus, Gachot et al. further explored the chemical reactions of LiPF6 in EC/ethyl methyl carbonate (EC/EMC) and put forward the high-temperature thermal decomposition mechanisms containing LiPF6 as follows [2,3,5–9],

1. Lithium was thermal decomposed to produce PF5: LiPF6 (s) ↔ LiF (s) + PF5 (g);
2. PF5 reacted with water to produce HF: PF5 + H2O → PF3O +2HF;
3. PF5 could also react with carbonate or carboxylate solution to produce substances such as C2H3F. For example, C2H3OCOOC2H5 + PH5 → C2H3OCOOPH4 + HF + CH2 = CH2; C2H3OCOOC2H5 + PH5 → C2H5OCOOPH4 + C2H3F.

Except for LiPF6, as for the other kinds of lithium salts it is generally recognized that LiBF4 is superior to LiPF6 in many aspects such as high temperature properties, reaction characteristics with water and qualitative chemical stability [10,11]. However, LiBF4 has the small volume of anions, so it is easy to combine with lithium-ion in solution resulting in its weak ion transport capacity [12,13]. This is even though, because of the low electrical conductivity, the electrolyte containing LiBF4 has not been used for large-scale application, while under a low-temperature environment, there are some advantages for electrolyte with LiBF4. Zhang et al. [14] prepared electrolyte with 1 M LiBF4 and lithium difluoro(oxalate)borate (LiODFB) dissolved in EC/propylene carbonate (PC)/EMC (1:1:3, volume ratio). The investigation indicated that LiBF4 with LiODFB could improve the electrochemical performance for cells over a relatively wide temperature range. The results showed that the synergistic effects between LiBF4 and LiODFB made LiBF4 become one of the alternative wide-temperature electrolyte salts for LIBs.

During the electrolyte combustion process, the lithium salt play an important role. Moreover, the carbonate and carboxylate solutions as solvents also have their own properties. Materials with low viscosity and high dielectric constant are suitable for LIB electrolytes, while in most instances the substances with high viscosity, high dielectric constant such as EC and the solution with low dielectric constant, low viscosity such as diethyl carbonate (DEC) were frequently selected to be mixed as electrolyte solvents. In addition, the solvents with low flash points and ignition temperatures could evaporate quickly at low temperature and be oxidized with Lewis acid PF5 produced by the decomposition of lithium salts, and PF5 would not play a significant role during the electrolyte combustion processing due to its strong reactivity and low concentration. Heat release rate (HRR)
is one of the most important parameters during the combustion process and has gained extensive attention. Fu et al. conducted cone calorimeter experiments for electrolyte containing EC/EMC/DMC with LiPF$_6$ to study the combustion characteristics of the corresponding pool fire. The results indicated that being inflammable, the electrolyte showed some unique combustion characteristics similar to gasoline and other traditional hydrocarbons with properties such as low C content, high gasification heat, and low combustion heat [15]. In order to investigate the applicability of cone calorimeter to obtain the HRR of electrolyte, two kinds of HRR calculation methods were compared by Zhang et al. [16]. The results showed that the oxygen consumption (OC) calorimetry by using cone calorimeter and the thermochemistry (TC) theory were both applicable to calculate the HRR of the electrolyte [16].

However, all the above research and experiments were conducted under normal ordinary atmospheric pressure, while LIBs were applied in many cases under low pressure, especially the application of power batteries in the plateau area. At present, there is insufficient comprehension of the quantitative safety and combustion characteristics of LIBs and the electrolyte, and the thermal property parameters such as HRR under low pressure are almost absent. As for the conventional fuels like ethanol and n-heptane, there are a lot of scholars studying the effect of pressure on their combustion behavior from several aspects such as the mass loss rate (MLR), flame height, fire plume temperature to illustrate the influence mechanism of pressure [17–22]. The electrolyte is essentially a kind of liquid fuel, but it is different from the traditional conventional fuels, so it is necessary to analyze the burning behavior and various parameters of its pool fire under low pressure. Therefore, two kinds of electrolyte with different lithium salt LiPF$_6$ or LiBF$_4$ were selected in this paper to conduct pool fire combustion experiments in Hefei with the atmospheric pressure of 100.09 kPa, Lhasa with the atmospheric pressure of 65.23 kPa, and Lijiang with the atmospheric pressure of 76.11 kPa, respectively, among which the HRR data were obtained in Hefei and Lhasa. The HRR data could not be acquired in Lijiang due to equipment limitation, so only the mass loss could be estimated in all three experimental locations. In the prior studies, the type of lithium salt was also essential to the thermal safety of the electrolyte [23]. Hence, two different lithium salts LiPF$_6$ and LiBF$_4$ were chosen to study the combustion behaviors of their electrolyte.

2. Experimental Section

2.1. Samples and Materials

The electrolytes used in this paper were EC/DMC/DEC/ethyl acetate (EC/DMC/DEC/EA) with a volume ratio of 1:1:1:1, while 0.75 mol/L LiPF$_6$ or LiBF$_4$ was dissolved in the solvent, respectively. In the blends, EA was the solvent additive. Except for the combustion experiments conducted under standard atmospheric pressure in Hefei City, Anhui Province, they were also carried out in low pressure environments in Lhasa City, Tibet Province and Lijiang City, Yunnan Province to investigate the effects of air pressure and different lithium salts on the combustion characteristics of electrolyte. Lhasa is a plateau area with low pressure, low oxygen and low temperature, while the low-temperature performance of LiBF$_4$-based electrolyte is superior than that of LiPF$_6$. Considering the influence of environmental temperature and according to Smart et al. [24], the concentration of lithium salt in solution was chosen as 0.75 mol/L.

The specific composition of the carbonate and carboxylate solution and the corresponding physicochemical property parameters used in this paper are listed in Tables 1 and 2, respectively. The percentage of water and HF in all materials is less than 0.002%. All electrolytes were prepared in an inert gas atmosphere environment by Tianjin Jinniu Co., Ltd. (Tianjin, China).
Table 1. List of carbonate and carboxylate used for electrolyte thermal safety study in this paper.

| Name             | Chemical Formula | Formation Heat (kJ/mol) | Combustion Heat (kJ/g) | Flash Point (°C) | Density (g/cm³) |
|------------------|------------------|-------------------------|------------------------|------------------|-----------------|
| ethylene carbonate (EC) | C₃H₄O₃         | −535.6                  | 13.2                   | 145              | 1.3             |
| dimethyl carbonate (DMC) | C₃H₆O₃         | −582.6                  | 14.4                   | 17               | 1.1             |
| diethyl carbonate (DEC) | C₅H₁₀O₃       | −644.3                  | 20.9                   | 25               | 1.0             |
| ethyl acetate (EA)    | C₄H₈O₂         | −463.2                  | 25.5                   | −4               | 0.9             |

Table 2. Composition and parameters of the two kinds of electrolyte in this study.

| Sample Number | Composition                                                                 | Conductivity (25 °C, mS/cm) | Specific Gravity (20 °C, g/cm³) |
|---------------|-----------------------------------------------------------------------------|------------------------------|---------------------------------|
| 1             | 0.75 mol/L of LiPF₆ dissolved in EC/DMC/DEC/EA with a volume ratio of 1:1:1:1. | 10.36                        | 1.153                           |
| 2             | 0.75 mol/L of LiBF₄ dissolved in EC/DMC/DEC/EA with a volume ratio of 1:1:1:1. | 3.73                         | 1.158                           |

2.2. Apparatus

HRR is a parameter that could quantitatively reflect the fire risk of materials, so it is widely focused upon. The history of measuring HRR could be traced back to the 1980s. Researchers in the National Building and Fire Research Lab developed the first generation of a cone calorimeter on the basis of the OC calorimetry principle, which could simulate a real fire by presetting radiation power, then measured parameters such as HRR and the time to ignition (TTI) during the whole combustion including igniting, fire development and extinguishing for the materials. After years of continuous development and improvement, the cone calorimeter was extensively used in building materials combustion performance testing and evaluation, consequently became one of the most important instruments in the fire science field [25,26].

The basic principle of OC calorimetry can be expressed in Equation (1):

\[
\dot{q}(t) = \frac{\Delta h_c}{r_0} (1.10) C \sqrt{\frac{\Delta p}{T_e}} \frac{X_0^0 - X_{O_2}}{1.105 - 1.5X_{O_2}}
\]

where \(\dot{q}(t)\) is the HRR of the measured material, and \((\Delta h_c/r_0)\) is an empirical value. According to a large amount of experimental data, about \(13.1 \times 10^3\) kJ heat would be released for every 1 kg oxygen consumed during the combustion process of most building materials.

- C is the calibration coefficient of the orifice flowmeter.
- \(\Delta p\) is the pressure difference of the orifice flowmeter.
- \(T_e\) is the absolute temperature of the gas at the orifice flowmeter.
- \(X_0^0\) is the oxygen concentration in the environment measured by the gas analyzer during the initial 1-min baseline testing.
- \(X_{O_2}\) is the oxygen concentration measured by the gas analyzer in the exhaust pipe. The structure of cone calorimeter is as shown in Figure 1.
2.3. Procedures

In this paper, a Shimazu UW/UX series Tray Electronic Balance was used for mass measurement. The measuring accuracy was 0.01 g and the maximum measurement range was from 0 to 6.4 kg. A circular oil pan with a diameter of 10 cm was utilized in the experiments, and electrolyte with volume of 25 mL was added for each cone calorimeter experimental measurement. In order to ensure the consistency of experimental conditions at the three areas, Hefei, Lijiang and Lhasa, no external radiation heat flow was applied in this paper, and the electrolyte was directly ignited by an ignition source. The flame temperature data were measured by K-type thermocouples and a model 7018 temperature collection module. Positions of thermocouples and radiation heatflowmeter in Lhasa and Lijiang were as shown in Figure 2. There were only 2 thermocouples in the cone calorimeter experimental platform in Hefei due to the limited space above the sample pan. During the combustion process, HF content was measured by a portable gas analyzer (SGA-600 produced by Shenzhen Singoan Electronic Technology Co., Ltd., Shenzhen, China) with a measuring range from 0 to 20 ppm.

![Structure diagram of cone calorimeter.](image)

**Figure 1.** Structure diagram of cone calorimeter.

A series of experiments were conducted in accordance with the standards for the measurement of the open cup flash point for electrolyte without pre-treatment at the low atmospheric pressure of 66.5 kPa.
in Lhasa. Since the flash points of two samples were lower than the then environmental temperature, the definite values were not obtained. Details are described in the supplementary materials.

3. Results and Discussion

3.1. Combustion Process and Phenomena

Figure 3 indicates the combustion processes of the two samples in Hefei and Lhasa. The whole combustion process could be divided into four stages as ignition, stable combustion, boiling combustion and extinguishment. The boiling combustion stage was similar to the stable one except for the flame height, so the stable combustion stage was selected as shown in Figure 3, and the definition of it was referred from the previous research [19]. In this study, the method to ensure the stable combustion stage was observing the experimental videos and selecting the stage roughly, then fitting the MLR curve to obtain the accurate stable combustion stage. There were two main differences between the two electrolytes. Firstly, the flaming degree of the electrolyte with LiPF$_6$ was more intense than that of the electrolyte with LiBF$_4$ and the blue part of the flame occupied a smaller percentage in Figure 3a,g. Secondly, there was dense smoke in the extinguishment stage for electrolyte with LiPF$_6$ in Figure 3c,i which indicated that an incomplete combustion occurred. When the environmental pressure decreased, there was more blue area in the flame, which was because the lower pressure would lead to less production of carbon black (CB) and more production of polycyclic aromatic hydrocarbons (PAHs) which could radiate blue light [17].

HF content of the two samples in Hefei and Lijiang could not be detected by the cone calorimeter instrument due to the limited detection types of gas analyzer, so a portable off-line gas analyzer was applied to measure it. The peak value of HF content of the electrolyte with LiPF$_6$ in Lhasa was beyond the range of the instrument (>20 ppm) while the peak value of electrolyte with LiBF$_4$ in Lhasa was 19 ppm, which indicated that the combustion at lower pressure would produce more HF for both the
two samples and LiPF$_6$ might increase the production of the gas. More details about the HF content were described in the supplementary materials.

3.2. Temperature and Radiation Power

Figure 4 gives the average flame temperature and radiation power of the two samples at different pressures during the stable combustion stage. Obviously from the bar graph, the temperatures rose as the pressure decreased, which was mainly because the flame radiative heat loss significantly reduced at low pressures [17,19,27]. The radiation power results also proved the explanation. In addition, there was less cool air for the flame to entrain to cool itself at lower pressures. With different pressures, the flame temperatures of the two samples were similar to the corresponding values of fuels such as n-heptane when compared to those in a previous study, which indicated that the flame temperature was an uncorrelated parameter to the fuel variety [19].

![Figure 4. The average flame temperature and radiation power of the two samples at different pressures during the stable combustion stage.](image)

The average fire centerline temperature values at different heights of the two samples under different pressures during the stable combustion stage are shown in Figure 5. On the whole, the gap between the two samples was small while the temperature values of LiPF$_6$ were slightly higher than those of LiBF$_4$, mainly because of the shorter combustion duration. Thus, with a similar total heat release (THR), the shorter the combustion duration, the higher the flame temperature. From the effect of pressure on the temperature values, the decreasing trend of temperature values obtained by thermocouples at different positions in Lijiang was more obvious than that in Lhasa during the height range of 0.05 m to 0.21 m, while it was gentler during 0.21 m to 0.31 m, which was mainly because the flame height in Lhasa was slightly higher than that in Lijiang. During the combustion process, the electrolyte was gasified, and the combustible gas would rise up under the heat flows, entraining the air to complete the combustion process. While there was less air to be entrained at low pressure, a longer entraining time was necessary to complete the combustion process, resulting in a thinner, higher and
longer flame shape [28]. Thus, with the same height range between 0.05 to 0.21 m, the decreasing speed of flame temperature was faster in Lhasa.

![Figure 5](image_url)  
**Figure 5.** The average fire centerline temperatures at different heights of the two samples under different pressures during the stable combustion stage.

To further analyze the temperatures of the electrolyte fire plumes, a characteristic length, $z^*$, was induced to describe the fire size which was defined as [28,29]:

$$z^* = \left(\frac{Q}{\rho_\infty c_p T_\infty \sqrt{g}}\right)^{2/3}$$  \hspace{1cm} (2)

where $Q$ is the HRR, $\rho_\infty$, $c_p$, $T_\infty$ and $g$ are the density, specific heat capacity of air, ambient temperature and gravity acceleration, respectively. The HRR in Lijiang could be calculated by the MLR and the combustion heat, which in Lhasa could be obtained by the cone calorimeter directly. From Table 1, the combustion heat of the mixture could be calculated, and the value was 19.21 kJ/g for the carbonate and carboxylate blend EC/DMC/DEC/EA. According to the HRR results in Hefei and Lhasa, the combustion efficiency in Lijiang could be obtained as about 0.71. Then $z^*$ could be calculated as the results shown in Figure 6. Based on $z/z^*$, the stretch effect of the flame at low pressure could be eliminated, where $z$ is the height from the pool surface with a unit of m. The temperature increment at different dimensionless heights is shown in Figure 6. McMaffrey divided the fire plume to three regions as the flame zone, intermittent flame zone and plume zone [30]. However, for the electrolyte combustion, the intermittent flame zone trended to merge together with the other two zones, which was similar to the results in the previous study [31]. Through the recorded experimental videos in this study, the flame pulsation frequency of the electrolyte could be observed and calculated. By comparing the experimental phenomena with n-heptane from observation of the videos, the fluctuation frequency of the electrolyte fire was lower, which indicated that the electrolyte combustion was more stable [19]. Thus, the area of intermittent flame zone decreased to a quite small degree, and the bound between flame zone and plume zone was more distinct and stable, resulting in the disappearance of the intermittent flame zone, as shown in Figure 6.
Figure 6. The average fire centerline temperatures with different heights of the two samples under different pressures during the stable combustion stage.

3.3. Mass Loss Rate (MLR)

The changing mass and MLR curves of the electrolyte with LiPF$_6$ at different conditions are shown in Figure 7. The results excluded that with the increase of altitude, the sample with the same mass burned longer and the MLR decreased. The mass data were differentiated to obtain the MLR. The whole combustion stage was divided into four stages as ignition, stable combustion, boiling combustion, and extinguishing. This was done by observing the MLR curves of the electrolyte and the recorded experimental videos, selecting a relative stable stage and linearly fitting it, then choosing the range between the two tangents with the longest distance on the fitting line and the MLR curve, respectively, which could be determined as the stable combustion stage, as shown in Figure 7. One of the aims in this study is to analyze the relevant parameters of the stable combustion. Thus, the MLR could be obtained by fitting the data of this stage (liner fitting in Figure 7).

Figure 7. Changing mass and mass loss rate (MLR) curves of the electrolyte with LiPF$_6$ at different altitudes: mass in Hefei (black square), mass in Lijiang (yellow circle), mass in Lhasa (blue triangle), linear fitting mass of Hefei (red dotted line), MLR in Hefei (black line), MLR in Lijiang (yellow line) and MLR in Lhasa (blue line).
To contrast Figure 7 with Figure 8, the residue mass of burnt electrolyte with LiBF$_4$ was lower than that with LiPF$_6$ due to the smaller molecular weight (MW) of LiBF$_4$. From the perspective of combustion, peak MLRs of two types of electrolyte were almost the same, but what was worth noting was that the burning time increased at all altitudes, and what was reflected in the curve was that the stable combustion stage shrank significantly, and the extinguishing stage increased clearly, which could be elucidated that fire hazard of the electrolyte with LiBF$_4$ was superior to another sample.

Figure 7. Changing mass and mass loss rate (MLR) curves of the electrolyte with LiPF$_6$ at different altitudes: mass in Hefei (black square), mass in Lijiang (yellow circle), mass in Lhasa (blue triangle), linear fitting mass of Hefei (red dotted line), MLR in Hefei (black line), MLR in Lijiang (yellow line) and MLR in Lhasa (blue line).

Figure 8. Mass and MLR changing curves of the electrolyte with LiBF$_4$ at different altitudes: mass in Hefei (black square), mass in Lijiang (yellow circle), mass in Lhasa (blue triangle), MLR in Hefei (black line), MLR in Lijiang (yellow line) and MLR in Lhasa (blue line).

The changes of MLR and MLR per unit area of two electrolytes with the variety of pressure were as shown in Figure 8, while the changes of both peak and average values with the pressure satisfied the following formula:

\[ m'' \propto A \cdot P^\beta \]  \hspace{1cm} (3)

The coefficients were plotted in the diagram. As stated in Figure 9, peaks of the two samples had the same trend with the variety of pressure, but the pressure had a greater and more obvious influence on peak values with the addition of LiBF$_4$. Peak MLRs of two different kinds of electrolyte were affected by pressure equally in stable combustion. Numerically, the exponential coefficients of several fuels were as listed: 1.3 for n-heptane, 1.0 for diesel, 0.9 for gasoline and 0.7 for methanol, respectively. Therefore, the exponential coefficient of the electrolyte were close to that of diesel [32]. The coefficient was increased with the increase of carbon atom mass percentage. The calculated percentage of carbon atom mass in methanol is 0.4375, and the percentage of it in the electrolyte solution was 0.4584, which was slightly higher than that of methanol. Thus, the results of this paper were consistent with prior studies. Some scholars concluded that the pressure index coefficient of EC/EMC/DMC electrolyte was 0.56, which was much less than that of the conventional fuels [31]. The discrepancies between these studies could be explained by the influence of experimental environment. In previous studies, researchers conducted experiments in an experiment module with limited closed space, low pressure and low oxygen concentration. Therefore, the results would be more sensitive to the gas concentration or lithium salts variety in the module, resulting in the different results in this study.
Figure 8. Mass and MLR changing curves of the electrolyte with LiBF$_4$ at different altitudes: mass in Hefei (black square), mass in Lijiang (yellow circle), mass in Lhasa (blue triangle), MLR in Hefei (black line), MLR in Lijiang (yellow line) and MLR in Lhasa (blue line).

The changes of MLR and MLR per unit area of two electrolytes with the variety of pressure were as shown in Figure 8, while the changes of both peak and average values with the pressure satisfied the following formula:

$$m_{\text{MLR}} \propto A \cdot P^{-u}$$

Figure 9. Peak and average values of MLR in stable combustion stage with the change of pressure: peak value for sample with LiPF$_6$ (black), average value for sample with LiPF$_6$ (red), peak value for sample with LiBF$_4$ (blue), average value for sample with LiBF$_4$ (green).

3.4. Heat Release Rate (HRR)

In this paper, OC calorimetry was adopted to test the HRR in Lhasa and Hefei, and pressure had a significant impact on the volume flow in the exhaust pipe during the calculation. According to a previous study, the volume flow of the gas in the exhaust pipe in Lhasa can be calculated as follows [33]:

$$\dot{V}_{298} = 17.8 \left( AK_t / K_p \right) \left( \Delta P / T_s \right)^{0.5}$$

while that in Hefei was calculated as follows:

$$\dot{V}_{298} = 22.4 \left( AK_t / K_p \right) \left( \Delta P / T_s \right)^{0.5}$$

In this paper, based on the above two formulas, the experimental results of HRR in Lhasa and Hefei were as shown in Figures 10 and 11.

From Figure 10, the peak value of HRR (pHRR) in Lhasa had an obvious difference with that in Hefei for electrolyte with LiBF$_4$, which reduced considerably under low pressure. The average HRR from the stable combustion stage in Lhasa is 94.7 kW/m$^2$, which is 52.7% of that in Hefei (179.6 kW/m$^2$). Remarkably, THR in Lhasa was almost the same as that in Hefei, reduced by only 5.8% (46.8/44.1 MJ/m$^2$). In Figure 11, the HRR curves of the electrolyte with LiPF$_6$ had the similar overall trend with the curves in Figure 10. For electrolyte with LiPF$_6$, an electrolyte pool fire would release less heat at high altitude, and pHRR fell considerably due to the lower combustion efficiency. These conclusions were consistent with prior studies of LIBs and some other research on solid fuels [31,33,34].
3.4. Heat Release Rate (HRR)

In this paper, OC calorimetry was adopted to test the HRR in Lhasa and Hefei, and pressure had a significant impact on the volume flow in the exhaust pipe during the calculation. According to a previous study, the volume flow of the gas in the exhaust pipe in Lhasa can be calculated as follows:

\[
V_{\text{Lhasa}} = 17.8 \frac{A_K}{K_1 K_4} \left( \frac{\Delta P}{T_0} \right)^{0.9} \tag{4}
\]

while that in Hefei was calculated as follows:

\[
V_{\text{Hefei}} = 22.4 \frac{A_K}{K_1 K_4} \left( \frac{\Delta P}{T_0} \right)^{0.9} \tag{5}
\]

In this paper, based on the above two formulas, the experimental results of HRR in Lhasa and Hefei were as shown in Figures 10 and 11.

Figure 10. Heat release rate (HRR) curves of electrolyte with LiBF₄ in Hefei (black) and Lhasa (red).

Figure 11. HRR curves of electrolyte with LiPF₆ in Hefei (black) and Lhasa (red).

As for the two different types of lithium salts, HRR of electrolyte with LiBF₄ was a little higher than that of the electrolyte with LiPF₆ in Hefei. But under relative lower pressure, the average HRR was substantially lower, which indicated that pressure had a greater influence on the HRR of electrolyte with LiBF₄.
There was a significant gap between the combustion duration of the two electrolytes. The combustion of electrolyte with the addition of LiBF₄ lasted about 1.6 times longer than that of electrolyte with LiPF₆, and the reasons were as follows: firstly, when the same amount of lithium salt added into carbonate and carboxylate solution, the electrolyte with LiBF₄ had more flammable carbonate and carboxylate solution due to the smaller MW of LiBF₄, so it had a higher THR and a longer combustion time. Secondly, according to the previous study, LiBF₄ could suppress the generation of C=O in some liquid hydrocarbons like lubricants at 120 °C, signifying that the generation of CO₂ was suppressed in the liquid samples in this paper [35]. There were two ways for CO₂ production. One was from the reactions of carbonate and carboxylate in liquid and the other was from the evaporation, thermal decomposition and combustion of electrolytes [15,16]. Thus, the degradation of the carbonate and carboxylate was suppressed, and more samples were evaporated to participate the combustion and lead to more heat release and longer combustion time. Figure 12 shows the production of CO and CO₂ of the two electrolytes in Hefei. The production of CO rose rapidly at the end of the combustion process with the addition of LiPF₆, which was corresponding with the large amount of smoke released as shown in Figure 3c. Furthermore, from Table 2, the conductivity of the electrolyte with LiBF₄ was lower, which indicated that the addition of LiBF₄ would neither improve the safety nor reduce the electrochemical performance of the electrolyte.

![Figure 12. CO and CO₂ production of electrolyte with LiPF₆ or LiBF₄ in Hefei.](image)

4. Conclusions

The combustion characteristics of the electrolyte containing EC/DMC/DEC/EA carbonate and carboxylate solution and different lithium salts LiPF₆ or LiBF₄ were elucidated, and the effect of pressure on the combustion properties of the electrolyte was investigated in this paper:

1. The decrease of pressure would increase the production of HF for both electrolytes while the HF content released by the electrolyte with LiPF₆ was higher. The flame temperatures at low air pressure were higher and the radiation power was lower. According to the temperature distribution from the fire plume center line, there were only a flame zone and plume zone for electrolyte combustion, which were different from those regions of traditional fuels with an extra intermittent flame zone.

2. There was a positive exponential relationship between average MLR, peak MLR and pressure in the stable combustion stage of the electrolyte pool fire. All conclusions were consistent with the variation trend of hydride index coefficient obtained by predecessors.

3. In the high-altitude environment, due to the decrease of combustion efficiency, the electrolyte pool fire would release less heat. Meanwhile, the peak and average values of HRR would decrease...
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