Study on Combustibility of Key Components of LiFePO4/C Battery with prelithiation technology

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Abstract. Prelithiation technology has greatly improved the service life of LiFePO4/C battery, but its influence on the combustibility of the battery is still unclear. In this paper, the combustibility of the key components (positive electrode, negative electrode and separator) of LiFePO4/C battery with prelithiation technology and conventional LiFePO4/C battery are compared, and the differences in combustion parameters (effective combustion heat, total heat release, heat release rate) and smoke parameters (total smoke production, CO yield, CO2 yield, and specific extinction area) between the two types of batteries are analyzed. The results show that the combustibility of the two types of batteries is basically similar, and there is no significant difference. With the decrease of the capacity retention rate, the combustibility and smoke generation of the battery show a downward trend.

1. Introduction
In recent years, there have been many fire accidents in Li-ion batteries, which have aroused widespread concern. Li-ion battery fire has multiple attributes of gas, solid and liquid fire. Understanding the particularity of Li-ion battery fire is helpful to the fire prevention design of Li-ion battery system and the configuration of matching fire extinguishing system.

In terms of combustion characteristics of lithium-ion batteries, a large number of experimental studies have been carried out. For example, Huang's team carried out the fire extinguishing test of LiFePO4/C battery by nail penetration test [1], and found that LiFePO4/C battery has a longer combustion time and a weaker flame intensity, while ternary lithium battery has a shorter combustion time and a higher flame intensity. Deng et al. studied the combustion characteristics of LiFePO4/C battery pack [2]. Their research showed that the thermal runaway temperature of LiFePO4/C battery pack was about 200 ~ 300℃, and the gas flame temperature could reach 1100℃. Zhang et al. studied the thermal runaway combustion characteristics of Li-ion batteries [3]. Their research showed that the evolution of the combustion of Li-ion batteries can be divided into three stages. First, the external abuse conditions triggered the self-acceleration process of the chemical reaction inside the Li-ion battery. Second, the pressure relief valve is opened and the gas and heat inside the battery release. Third, the released gas and battery itself begin to fire.

Above studies focused on conventional LiFePO4/C battery (C-battery). The new LiFePO4/C battery with prelithiation technology (P-battery) has shown greater application value due to the significantly
longer service life, however there is no relevant research on the combustibility of the P-battery, and the impact of prelithiation technology on the combustibility of batteries is still unclear. Therefore, this paper makes a comparative study on the combustibility of P-battery and C-battery, analyses the differences in combustion parameters and smoke parameters between the two types of battery components.

2. Research program

2.1. Battery accelerated life test
In order to obtain battery samples with different capacity retention rates (CRRs), the batteries (P-batteries and C-batteries) with rated capacity (24Ah) were accelerated in aging under 1C rate charge/discharge cycle at 45℃. Every 500 cycles are a cycle. After each cycle, the capacity calibration was carried out. The procedure of capacity calibration is as follows: first, adjust the temperature of the test chamber to 25 ℃, then charge the battery with 0.5C (12A) rate to 3.65V, and then discharge to 2.5V with 0.5C(12A) rate after standing for 2h, and take the final discharge capacity as the actual capacity of the battery. The battery samples with capacity retention ratio (CRR) of 100%, 77.8%, and 65.3% were obtained after different cycles.

2.2. Battery components fire test
Batteries were adjusted to the fully charged state, then they were disassembled in a glove box(inert atmosphere, H₂O<0.1ppm, O₂<0.1ppm), the battery key components (the positive electrode, negative electrode and separator) were taken out, which were assembled to the small-sized cell according to the size requirements of the cone calorimeter. All samples were placed in the glove box and were packed in the aluminum-plastic film bag.

In this paper, the R-S/FTT0007 cone calorimeter produced by British FTT company is used. The test procedure is based on ISO5660-1 standard. The exhaust flow rate is 24 L/s, the irradiation intensity is 50 kW/m², the test environment temperature is 25.8℃, and the relative humidity is 30%. Samples were tested five times repeatedly, and the average value of five times test are taken as the result to ensure the accuracy. The test equipment and test process are shown in Figure 1. The following combustion parameters of the sample are obtained by testing: ignition time, heat release rate, total released heat, effective combustion heat, mass loss rate, CO and CO₂ output and specific extinction area.

Figure 1. Test scene diagram of cone calorimeter
3. Discussion and analysis

3.1. Battery component fire parameters analysis

During the test, it was observed that the test samples were curled and deformed, which may result in the fluctuation of data and the impact on the combustion efficiency of battery components. Figure 2 shows the results of five times test. From the data results of multiple tests, it can be clearly seen that there is no difference between the components of P-battery and C-battery in terms of the effective combustion heat and total released heat, especially the test data of the negative electrodes of P-battery and C-battery are basically equivalent. For batteries with different CRRs, the effective combustion and total heat release of negative electrode are greater than those of positive electrode and separator, and with the decrease of CRR, these two parameters are in a downward trend. The effective combustion heat and total released calorific values of the negative electrode of P-battery with 100%CRR are in the range of 6-10 MJ/kg and 3.5-5.5 MJ/m² respectively, but when the CRR drops to 65.3%, its effective combustion calorific value is lower than 4 MJ/kg. As the effective combustion heat reflects the combustion degree of volatile gas in gas flame, the effective combustion heat of negative electrode decreases with the decrease of CRR, which indicates that the amount of combustible gas in negative electrode may decrease with the decrease of CRR. It may be related to the gradual decomposition and consumption of electrolyte inside the battery after long-term use (such as side reactions inside the battery and the formation of SEI film).
Figure 3. Combustion heat release rate curve of battery components, (a) positive electrode, (b) negative electrode, (c) separator, (d) cell

Figure 3 shows the combustion heat release rate curve of battery components. From Figure 3, it can be seen that the change trend of heat release rate of P-battery negative electrode is consistent with that of C-battery negative electrode, and the peak value of heat release rate of P-battery negative electrode is slightly higher than that of C-battery negative electrode, which may be due to the relatively high lithium content of P-battery negative electrode and it releases more heat during combustion reaction. And due to the same reason, the combustion heat release rate of P-battery cell is relatively higher than that of C-battery cell, which is shown in Figure 3(d). On the other hand, the heat release rate of negative electrode combustion is obviously higher than that of positive electrode and separator. With the decrease of the CRR, the combustion heat release rate of battery components gradually decreases.

3.2. Battery component smoke parameters analysis
Figure 4 is the total smoke production curve of key components of P-battery and C-battery. It can be seen that the total smoke generation trend of P-battery negative electrode is consistent with C-battery negative electrode. The difference between P-battery negative electrode and C-battery negative electrode is that the lithium content varies, but the main components of flue gas are carbonaceous compounds and carbonaceous particles, so there is no difference between P-battery negative electrode and C-battery negative electrode in smoke generation. Similarly, there is no obvious difference between P-battery cell and C-battery cell in smoke generation. On the other hand, with the decrease of the CRR, the smoke generation of battery components gradually decreases. 

The yield of CO, CO$_2$ and the specific extinction area are shown in Table 1. The data in the table is the average of five times test data. From table 1, it can be seen that the smoke generation parameters of P-batteries are no different from those of C-batteries.

| Samples         | CO yield / (kg/kg) | CO$_2$ yield / (kg/kg) | Specific extinction area / (m$^2$/kg) |
|-----------------|--------------------|------------------------|-------------------------------------|
| 100% CRR C-battery |                   |                        |                                     |
| Positive electrode       | 0.50               | 16.81                  | 68.27                              |
| Negative electrode      | 0.16               | 26.19                  | 73.87                              |
| Separator             | 0.39               | 75.54                  | 387.28                             |
| 100% CRR P-battery     |                   |                        |                                     |
| Positive electrode       | 0.43               | 25.33                  | 71.73                              |
| Negative electrode      | 0.20               | 25.55                  | 67.95                              |
| Separator             | 0.58               | 79.12                  | 398.43                             |
| 82.78% CRR P-battery   |                   |                        |                                     |
| Positive electrode       | 0.31               | 9.46                   | 62.67                              |
| Negative electrode      | 0.15               | 24.43                  | 59.95                              |
| Separator             | 0.01               | 0.12                   | 213.48                             |
| 65.30% CRR P-battery   |                   |                        |                                     |
| Positive electrode       | 0.11               | 3.13                   | 54.22                              |
| Negative electrode      | 0.04               | 8.43                   | 50.17                              |
| Separator             | 0.01               | 0.11                   | 211.63                             |
The specific extinction area reflects the capability of generating smoke when the sample burns in the combustion process. From table 1, it can be seen that the specific extinction area of the separator is much larger than that of the positive electrode and negative electrode, which means the separator (immersed with electrolyte) is the main source of flue gas from battery combustion. The CO and CO$_2$ yields and specific extinction area values of batteries with 100%CRR are higher than those of batteries with 82.78%CRR and 65.30%CRR. This may be due to the fact that the electrolyte inside the battery gradually decomposes and consumes because of participating in the side reaction and the formation of SEI film, which leads to the reduction of the amount of electrolyte and the reduction of smoke generation.

4. Conclusion

(1) There is no difference between P-battery and C-battery in terms of effective combustion heat and total released heat, and the test data of P-battery negative electrode is basically equivalent to that of C-battery negative electrode. The effective combustion heat and total released heat of the negative electrode are both greater than those of the positive electrode and separator, and show a downward trend with the decrease of CRR.

(2) The heat release rate of P-battery negative electrode is consistent with that of C-battery with combustion time, and the peak value of heat release rate of P-battery negative electrode is slightly higher than that of C-battery negative electrode, which may be due to the relatively high lithium content of negative electrode and it releases more heat during combustion reaction.

(3) The trend of the total smoke generation of P-battery negative electrode with time is consistent with that of C-battery negative electrode. And there is no obvious difference in smoke generation between P-battery and C-battery. With the decrease of the CRR, the smoke generation amount of the battery decreases gradually.

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