Study on Thermal Runaway Process of LiFePO4/C Batteries

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Abstract. The LiFePO4/C battery has been widely used in many fields, and its safety problems are gradually attracting widespread concern. In this paper, two kinds of LiFePO4/C batteries with 25 Ah and 200 Ah were taken as research objects. The thermal runaway phenomena of two batteries were analyzed, and the difference of thermal runaway phenomena between two batteries were compared. The results show that the safety valve of the 200 Ah battery ruptures earlier and the thermal runaway occurs earlier under the same overcharge rate. The work provides a reference for the protection design of LiFePO4/C batteries.

Key words: LiFePO4; thermal runaway; overcharge; capacity.

1. Introduction

At present, the LiFePO4/C battery is widely used in portable power supply, mobile phone, notebook, electric vehicle and other fields. Compared with other types of Lithium ion batteries (LiCoO2/C, LiMn2O4/C, LiNiCoAlO2/C), its safety is generally considered relatively good. However, there have been several fire accidents of the LiFePO4/C battery in recent years, which has attracted widespread attention.

A lot of research work has been carried out on the safety of the LiFePO4/C battery. GUO Pengyu et al. [1] analyzed a fire accident in the prefabricated compartment of the LiFePO4/C battery in an energy storage power station, the results show that the cause of the fire is the overcharge caused by the reverse connection of the battery. Li Yu et al. [2] studied the internal structure and thermogenesis mechanism of cylindrical LiFePO4/C battery after nail penetration, which indicates that the damage of nail penetration to the LiFePO4/C battery is devastating and causes thermal runaway. Wang Xiong et al. [3] discussed the fire risk and control of Lithium ion battery in Electric Vehicle, and summarized the gas composition of Lithium ion battery in the process of thermal runaway. Peter J.Bugryniec et al. [4] compared the safety of LiFePO4/C battery and LiCoO2/C battery, the results show that the thermal runaway of the LiFePO4/C battery occurs when heated to 180°C.

The above research work plays an important role in understanding the safety mechanism of LiFePO4/C batteries. However, there are relatively few researches on the process of thermal runaway of LiFePO4/C batteries, especially the analysis of the phenomenon of thermal runaway. In this paper, the
thermal runaway phenomena of LiFePO$_4$/C batteries with 25 Ah and 200 Ah were analyzed, and the difference of thermal runaway phenomena between two batteries were compared.

2. Experiment

2.1. Battery Parameter
Two kinds of LiFePO$_4$/C batteries with 25 Ah and 200 Ah were taken as research objects, which came from the same manufacturer. The battery parameters are shown in Table 1.

| Battery parameters | 25Ah | 200Ah |
|--------------------|------|-------|
| Type               | Square Shell | Square Shell |
| Size/mm            | 173×19×110 | 384×145×57 |
| Normal voltage/V   | 3.2   | 3.2   |
| +/- electrode material | LiFePO4/C | LiFePO4/C |
| Electrolyte        | PC/DC/DEC | PC/DC/DEC |
| Packaging materials | Aluminium | Aluminium |

2.2. Experiment Device
As shown in Figure 1, the entire overcharge test system consists of a programmable high-power DC charger, a video recorder and a data recorder.

![Experiment device](image)

Figure 1. Experiment device

Before the test, all batteries were charged to full charge at 1C rate. The overcharge test was conducted in an open environment. The constant current overcharge test was conducted at 1C rate. The highest voltage of the charger was set to 35V. When the charger voltage reached 35V, it automatically switched to constant voltage charging. The charge stopped until the thermal runaway of batteries occurred.

3. Analysis
Figure 2 and Figure 3 show the phenomenon of each stage in the process of thermal runaway of batteries under overcharge condition. Table 2 shows the start time and end time of each stage corresponding to 25 Ah and 200 Ah batteries. For 25 Ah battery, in 0-1111s, the side reaction caused by overcharge continuously generates flue gas, which made the internal pressure of the battery increase, and the battery gradually expanded and deformed. When the battery was charged to the 1112 s, the internal pressure of the battery reached the opening pressure of the safety valve, then the safety valve was broken, and a small amount of flue gas was ejected from the safety valve. When the battery was charged to the 1162 s, the amount of flue gas increased significantly, lasting about 180 s. From the 1553 s, the flue gas was ejected violently and the temperature increased rapidly, which indicated that the thermal runaway occurred. After 10s, the battery exploded.

Compared with 25 Ah battery, the thermal runaway process of 200 Ah battery experienced the first four stages: (1) battery case expansion, (2) the safety valve rupture and small amount of flue gas
emission, (3) slow flue gas emission, and (4) quick flue gas emission. But the 200 Ah battery did not explode.

![Image of battery thermal runaway phenomena](image)

**Figure 2.** The phenomenon of 25 Ah battery thermal runaway, (a) battery case expansion, (b) the safety valve rupture and small amount of flue gas emission, (c) slow flue gas emission, (d) quick flue gas emission, and (e) explosion

![Image of battery thermal runaway phenomena](image)

**Figure 3.** The phenomenon of 200 Ah battery thermal runaway, (a) battery case expansion and safety valve rupture, (b) small amount of flue gas emission, (c) slow flue gas emission, (d) quick flue gas emission

| Phenomenon                                | Time (s) | 25 Ah battery | 200 Ah battery |
|-------------------------------------------|----------|---------------|----------------|
| Expansion                                 |          | 0-1111        | 0-497          |
| Safety valve rupture, small amount of flue gas emission | 1112-1161 | 498-895       |
| Slow flue gas emission                    |          | 1162-1552     | 896-1076       |
| Quick flue gas emission                   |          | 1553-1563     | 1077-1257      |
| Explosion                                 |          | 1564          | /              |

**Table 2.** The thermal runaway evolution time of batteries

In Table 2, it can be seen that the starting time of each stage in the process of the 200 Ah battery thermal runaway was earlier than that of the 25 Ah battery, and the safety valve broke when the 200 Ah battery was charged to the 498 s, which took less than half of the time of the 25 Ah battery. This may be because the battery thermal runaway is the result of the imbalance between the internal thermal accumulation and the external thermal dissipation. When the battery capacity is increased, the surface area that can be used for heat dissipation corresponding to the unit capacity of the battery is reduced.
For example, the surface area / capacity ratio of the 200 Ah battery is 8.58 cm²/Ah, while that of the 25 Ah battery is 19.53 cm²/Ah, which results in the heat dissipation effect of the 200 Ah battery is obviously weaker than that of the 25 Ah battery. It means the internal temperature of large capacity battery may be higher under the same overcharge condition, therefore accelerates the side reactions and causes the safety valve to break earlierly. In addition, the volume of the 200 Ah battery is larger, and its expansion deformation effect on internal pressure release is better than that of the 25 Ah battery, maybe that is why the 200 Ah did not explode.

4. Conclusion
In this paper, the thermal runaway tests of the 25 Ah and 200 Ah LiFePO₄/C batteries were carried out. The results show that the safety valve of the 200 Ah battery ruptured earlier and the thermal runaway occurred earlier under the same overcharge rate. The 200 Ah battery exploded, while the 20 Ah battery did not explode. This is because the surface area corresponding to the unit capacity of the 200 Ah battery is smaller and the heat dissipation effect is weaker than that of the 25 Ah battery, which makes the internal thermal accumulation speed of the 200 Ah battery faster. The work in this paper will contribute to the safety design of LiFePO₄/C battery system.

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