Overcharge experiment analysis of the LiFePO$_4$/C battery with prelithiation technology

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Abstract. Prelithiation technology can improve the service life of batteries, but whether it will affect the safety of batteries has not been studied. In this paper, the temperature differences between LiFePO$_4$/C batteries with prelithiation technology and conventional LiFePO$_4$/C batteries in overcharge test are analysed, the shell deformation values of these two types of batteries are compared, and the influence of battery capacity retention rate on overcharge safety of batteries is discussed. The analysis shows that there is no obvious difference in overcharge safety between two types of batteries, and batteries with prelithiation technology are similar to conventional batteries in terms of shell deformation value, the highest temperature of shell and the temperature fluctuation of flue gas escaping from pressure relief valve.

1. Introduction
LiFePO$_4$/C battery is one of the main energy storage batteries in the field of electric energy storage in China, which has the advantages of high charge/discharge efficiency, relatively low cost and small self-discharge rate. In order to further enhance the application value of LiFePO4/C battery, there are many technical routes at present, such as developing the surface coating [1-2], ion doping [3-4] and material nanocrystallization [5] technologies of lithium iron phosphate materials to improve the battery rate performance, using phosphate materials such as lithium ferric pyrophosphate [6] and lithium vanadium phosphate [7] on high voltage platform to improve the energy density of battery, using prelithiation technology to compensate the active lithium consumed by the battery [8] and improve the capacity retention rate of the battery.

In these technical schemes, the life of LiFePO$_4$/C battery using prelithiation technology (P-battery) can reach 10,000 times, which has significant life advantage compared with conventional LiFePO$_4$/C battery (C-battery) and is one of the relatively promising technologies. However, this new type of LiFePO$_4$/C battery may affect the safety of the battery because the lithium content in the battery is increased by prelithiation technology. At present, there is no research on the safety difference between P-battery and C-battery. In this paper, the overcharge tests of P-battery and C-battery are studied, and the differences between two types of batteries in overcharge tests are compared and analysed, and the influence of battery capacity retention rate (CRR) on overcharge safety of battery is analysed.
2. Research program

2.1. Accelerated aging test
The research objects of this paper are C- and P-battery, with rated capacity of 24Ah and working voltage of 2.65V-3.6V. Battery degradation is accelerated under 1.0C rate charge/discharge cycle at a constant temperature of 45℃. Every 500 cycles are a cycle. After each cycle, the capacity calibration is 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%, 80%, 70% were obtained after different cycles.

2.2. Battery overcharging test
Before the overcharge test, the charge states of batteries were adjusted to the full charge state. The charging procedure is as follows: first, charge the battery to 3.65V with a constant current of 0.5C(12A), then switch to 3.65V constant voltage charging until the current is less than 0.05C(1.2A), and then stop charging. After standing for 12 hours, overcharge tests were carried out at the rates of 0.5C(12A) and 1C(24A), respectively, then stop charging until the battery voltage dropped to 0V. During the overcharging test, the changes of battery voltage and temperature with time were recorded.

3. Discussion and analysis

3.1. Overcharging test analysis between P-Battery and C-battery

| Battery type | CRR  | Overcharging rate | Shell thickness before test | Shell thickness after test | Shell deformation |
|--------------|------|-------------------|-----------------------------|---------------------------|------------------|
| C-battery    | 100% | 2C                | 27.2                        | 52.3                      | 25.1             |
|              |      | 1C                | 27.3                        | 52.4                      | 25.1             |
|              |      | 0.5C              | 27.3                        | 52.5                      | 25.2             |
| P-battery    | 100% | 2C                | 27.1                        | 52.3                      | 25.2             |
|              |      | 1C                | 27.1                        | 52.2                      | 25.1             |
|              |      | 0.5C              | 27.2                        | 52.5                      | 25.3             |
| P-battery    | 90%  | 1C                | 30.2                        | 52.3                      | 22.1             |
|              |      | 0.5C              | 30.8                        | 51.8                      | 21.0             |
| P-battery    | 80%  | 1C                | 32.0                        | 52.2                      | 20.2             |
|              |      | 0.5C              | 31.4                        | 52.7                      | 21.3             |

Table 1 shows the change of battery shell thickness before and after overcharging test for P-battery and C-battery. During overcharge, batteries undergo complex electrochemical reactions, resulting in gas-phase by-products and rising internal temperature, resulting in continuous increase of battery internal pressure. When the critical pressure of pressure relief valve is reached, the battery shell will swell. It can be seen that both P-battery and C-battery have swelled after overcharging test, and the shell deformation of P-battery is basically the same as that of C-battery, indicating that the pressure inside C-battery and P-battery due to overcharge side reaction is basically the same under the condition that the battery capacity, volume and critical pressure of the pressure relief valve are similar. The deformation of P-batteries with different CRRs varied. When the CRR of P-battery decreases, the
deformation of P-battery also decreases, indicating that the destructive power caused by overcharging also decreases.

Figure 1 is temperature data of C-battery and P-battery at the 0.5C and 1.0C rate overcharging test. It can be seen that the temperature at 1cm above the pressure relief valve rises rapidly after the battery is short-circuited, and the rate exceeds 1℃/s, which is caused by the escape of gas inside the battery. The temperatures of different parts (positive electrode, negative electrode, side center and surface center) of C-battery and P-battery are gradually rising during the overcharging process, but the rising rate does not reach 1℃/s. Even when the voltage suddenly drops to 0V, that is, the battery is short-circuited, the temperature does not show rapid growth. According to the national standard (GB/T 36276-2018), there were not thermal runaway for both C-battery and P-battery. On the other hand, the maximum temperature of batteries is about 100℃, and the maximum temperature of the flue gas escaping after the pressure relief valve is broken does not exceed 70℃, while the maximum temperature of thermal runaway of general lithium ion batteries can reach 500-600℃. From this point of view, neither P-battery nor C-battery has thermal runaway reaction.

The temperatures at 1cm above the pressure relief valve of C-battery and P-battery fluctuate obviously for many times in the overcharging process, and there is no obvious difference. This indicates that even if the battery is no longer overcharged, the exothermic side reaction will continue to occur for a period of time, but due to the lack of external forced energy input, this exothermic side reaction gradually terminates automatically, showing that the temperature at this place gradually drops after obvious fluctuations. In addition, it can be seen that the short-circuit time is shortened at high rate overcharge, the internal temperature of the battery is slightly reduced, for example, the temperature...
above the pressure relief valve reaches 60-70℃ during 0.5C rate overcharge, and the temperature at 1C rate is about 50℃ during 1C rate overcharge.

3.2. Overcharging test analysis of P-batteries with different CRRs

Figure 2 is temperature data of P-batteries with 100% CRR, 90% CRR, and 80% CRR at 0.5C rate overcharging test. It can be seen that the temperature rise of batteries with declining capacity is lower than that of new batteries. The maximum surface temperature of new batteries is about 100℃ at the negative pole, while that of batteries with declining capacity is about 90℃, which is consistent with the analysis conclusion in Table1.

In addition, it can also be found from figure 2 that when the CRRs of batteries decays from 100% to 80%, the interval between the occurrence of internal short circuit and the rupture of the pressure relief valve is prolonged (from 90s to 156s), and the interval between the two peaks of the temperature 1cm above the pressure relief valve is correspondingly prolonged (from 497s to 714s), which also corresponds to the above conclusion, which means after the battery capacity declines, the internal thermal effect of the battery weakens, and it takes a longer time to reach the critical pressure of the pressure relief valve, and the speed of exothermic reaction in the battery is delayed.

4. Conclusion

(1) Both P-battery and C-battery have experienced shell bulging in overcharging test, and the shell deformation is basically the same. When the CRR decreases, the deformation decreases
correspondingly, which indicates that the decline of CRR leads to the reduction of the scale of side reaction in the battery, so the destructive power caused by overcharge also decreases correspondingly.

(2) According to the threshold of thermal runaway of national standard, neither P-battery nor C-battery has thermal runaway reaction in overcharging test. The temperature at 1cm above the pressure relief valve of the two types of batteries fluctuated obviously for many times after the overcharge was terminated, and there was no significant difference. After the overcharge is stopped, the exothermic side reaction continues to occur in the battery for a while, but due to the lack of external forced energy input, this exothermic side reaction gradually terminates automatically.

(3) With the decrease of the CRR, the maximum temperature value decreased, and the interval between internal short circuit and pressure relief valve rupture and the interval between two peaks of temperature at 1cm above pressure relief valve were prolonged.

In summary, there is no obvious difference in overcharge safety between P-battery and C-battery. The deformation of the shell, the highest temperature of the shell and the temperature fluctuation of flue gas escaping after the pressure relief valve is broken are all close between P-battery and C-battery.

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