Research on Cycle Aging Characteristics of Lithium Iron Phosphate Batteries

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Abstract. As for the BAK 18650 lithium iron phosphate battery, combining the standard GB/T31484-2015(China) and SAE J2288-1997(America), the lithium iron phosphate battery was subjected to 567 charge-discharge cycle experiments at room temperature of 25\textdegree C. The results show that the SOH of the battery is reduced to 80\% after 240 cycle experiments, which meets the requirements of aging and decommissioning. Calendar aging has a side effect on the experiment. As for the aging process of the battery, it provides experimental support for improving the service life of the battery.

1. Introduction
Lithium iron phosphate battery has the advantages of small volume and high energy density, which is widely used in New Energy Vehicle, Energy Storage Power Station and Micro Electronic Equipment Industry [1]. Lithium iron phosphate battery will be affected by the environment temperature, charge discharge cycles and other factors. Life prediction is very important to improve the safety of batteries. The model of life prediction is established through accelerated test process. The results show that calendar aging is the key factor leading to lithium-ion battery aging, but the experimental period is longer. The effects of charging ratio, the discharge ratio, the charging cutoff voltage, the discharge cutoff voltage and environmental temperature on the aging of the battery are studied. The results show that the service life of the battery can be extended at 30 ~ 35 \textdegree C, but the standard of comprehensive evaluation has not been established. The electrochemical impedance of lithium-ion batteries was studied by using different discharge depth, state of charge and discharge ratio. The results showed that the aging rate of lithium-ion battery was positively correlated with the resistance [4], but no evaluation criteria were given.

In this paper, the lithium iron phosphate battery was carried out cycle charge discharge test and calendar aging test. In the cycle aging experiment, the battery was charged and discharged test at room temperature of 25 \textdegree C. In the calendar aging experiment, the battery was placed in the outdoor environment. This experiment tests the characteristic data of lithium iron phosphate battery, such as voltage, current, charge capacity, discharge capacity, energy and resistance.

2. Experiment
2.1. experimental steps
In Figure 1, the experimental process is divided into five steps, such as standing, constant current...
charging, constant voltage charging, standing and constant current discharge. In Figure 2, this curve is the first charge discharge aging experiment of lithium iron phosphate battery after being put into static for 5 hours. ①: The 0.5c constant current charging stage, the current is maintained at 596mA, and the voltage increases from 2.5834v to 3.701v. ②: Constant voltage charging stage, the voltage is maintained at 3.6998v, and the current decreases from 513.4mA to 47.2mA, because under the action of constant electric field, the Li⁺ concentration polarization phenomenon gradually dissipates, and the moving speed of internal ions reflects the decrease of current. A fluctuates when the current drops, because with the end of constant current charging, the temperature of the battery changes, affecting the internal Li⁺ migration, and there is a temporary fluctuation. ③: The static stage, the voltage gradually tends to be stable at 3.4290v. ④: The 1C constant current discharge stage, the current remains at 1191.0mA, and the current drops from 3.3811v to 1.9882v. ⑤: The static stage, the voltage rises because of the voltage inside the battery There are Ohmic-Polarization and Concentration Polarization in the region.

Figure 1. Cycle aging test steps          Figure 2. Charge and discharge change of battery

2.2. experimental results and discussion
In Table 1, some data of this experiment, such as experiment serial number, test time, voltage, current, capacity, specific capacity, energy and state, are shown. The test is divided into 8 times, and the battery needs to be allowed to stand for 5 hours before the experiment.

| Number | Time    | Voltage/v | Current/mA | Capacity/mAh | Energy/mWh | Status |
|--------|---------|-----------|------------|--------------|------------|--------|
| 1      | 10:08:16| 3.3755    | 596        | 878.7        | 2894       | C CC   |
| 2      | 10:08:26| 3.3758    | 596        | 880.4        | 2899       | C CC   |
| 3      | 10:08:37| 3.3758    | 596        | 882.2        | 2905       | C CC   |
| 4      | 10:08:47| 3.3761    | 596        | 883.9        | 2911       | C CC   |
| 5      | 10:08:57| 3.3761    | 596        | 885.5        | 2916       | C CC   |
| 6      | 10:09:07| 3.3761    | 596        | 887.2        | 2922       | C CC   |
| 7      | 10:09:18| 3.3761    | 596.4      | 889          | 2928       | C CC   |
| 8      | 10:09:29| 3.3764    | 596        | 890.8        | 2934       | C CC   |
In Figure 3, the capacity change of battery after constant voltage charging showed a gradual downward trend. After 561 cycles of charge and discharge experiments, the capacity of battery decreased from 1193.3mAh to 727.2mAh. The SOH of the battery decreased from 100% to 60.94%. After the cycle aging and calendar aging experiments, battery status changed from new to scrap. In order to better consider the influence of calendar aging, the experiment was divided into eight times, with an interval of 360 hours. B shows that the capacity of the battery decreases in varying degrees after calendar aging. The experimental time is accumulated and the speed of calendar aging is accelerated. C: The charging capacity of the battery vibrates abnormally, because the SOH of the battery drops to 64.59%, the battery can't be used in echelon, and the Li+ concentration inside the battery changes, resulting in abnormal fluctuations. In Figure 4, lithium iron phosphate battery is discharged at a constant current of 1191.2ma, and the discharge stops when the voltage drops to 1.9882v. The discharge capacity of the battery decreased from 1190.9mah to 732mah, accounting for 61.47% of the total capacity.

In Figure 5, lithium iron phosphate battery aging experiment, the cumulative loss of battery capacity increased. When the SOH of the battery is 78.82%, the calendar aging loss capacity of the battery increases rapidly. In the fifth experiment, the available capacity of the battery was 770.8mAh, and the loss capacity was 20.9mAh, accounting for 2.17%. After that, the capacity loss of the battery was accelerated, and the battery entered into a very unstable state, which needed to be scrapped directly. In Figure 6, the percentage of capacity loss due to calendar aging of the battery increases rapidly after 1440 hours, with the maximum loss of 5.66%. The battery needs to be recycled.

In (a) of Figure 7, with the continuous charge and discharge experiments, the resistance of lithium iron phosphate battery increases from 44 mOhm to 116 mOhm. ①, ② and ③ SOH values are 94.16%,
87.46% and 77.90%. At this time, the batteries were in normal operation. ④ the resistance changed abnormally, and the SOH was 74.73% and 64.94% respectively. In (b) of Figure 7, after loess smoothing, the resistance change trend can be seen more clearly.

3. Conclusion

In this paper, it shows that calendar aging has a certain influence on the cycle-experiment. When the SOH of battery is 74.73%, the resistance of the battery fluctuates abnormally and the battery goes into aging state. When the SOH of battery is 64.94%, the battery is completely scrapped and needs to be disassembled. Therefore, it is of great significance to determine the decommissioning capacity of battery and study its echelon utilization.

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