Study on the influence factors of the cycle life of lead-acid battery in DC system

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Abstract. The high-current accelerated cycle test was used to detect and evaluate the lead-acid battery in the DC system. The results showed that at a temperature of 50 °C, a charge and discharge of 100A, a charge cut-off voltage of 2.4V, and a discharge cut-off voltage of 1.75V were used. The charging time is t₁ (t₁ is the charging time in the first cycle equal to the charging time when the capacity is discharged). The capacity retention rate is 93.31%, and the charging time is t₂ (t₂ is the charging capacity in the first cycle is 1.03 times the discharge capacity). The capacity retention rate is 74.72%. Overcharge can reduce the capacity retention rate; the slope during the charging and discharging stages has a good relationship with the capacity retention rate. The slope can be used to represent the capacity retention rate, so the capacity retention can be predicted in advance rate. The research results can realize the detection of DC batteries and provide a basis for battery quality evaluation.

1. Introduction

It is great significance that the battery is stable and has high capacity to provide for the load in the charge and discharge processes. The lead-acid battery in the substation is in a floating charge state for a long time to solve the battery self-discharge problem. But the method to detect battery performance by the charge and discharge at the ratio of 0.1c is very difficult to expose the hidden trouble of the battery. If the battery cannot discharge in the critical moment, it is very easy to occur safety accidents in the power grid. In order to effectively improve the reliability of DC power supply, State Grid Corporation of China has put forward higher requirements for special supervision of battery performance. The performance of the battery is declining gradually, and the degree of decline is difficult to quantify. The cycle life is closely related to the working environment temperature, charging and discharging depth, discharging times, maintenance and other factors. But these test methods used in the evaluation of cycle life, such as iso-energy measurement, discharge measurement, etc., have not give attentions to actual factors above. In this paper, the test method of high rate accelerated charge-discharge cycle is used to evaluate the lead-acid battery in dc system rapidly, which provides the basis for the quality evaluation of the battery.
2. The Test Part

2.1 Materials and Equipment
The test battery is 2V 600Ah valve controlled sealed lead-acid battery and model is GFMD-600C. The main part of the equipment as follows: An intelligent maintenance apparatus for single battery, which is used for battery charging and discharging and the model is DWY-12/100. A constant temperature water-bath, which is to provide the required test temperature and model is CH515. A paperless recorder is to record the current and voltage during battery charge and discharge processes, and its type is SIN-R2000. A battery internal resistance tester is used to test battery internal resistance and voltage, and its type is AT525D.

2.2 Battery Capacity Test
Before the capacity test, the batteries had been fully charged. In a constant temperature water bath at 25°C, the battery was considered to be fully charged when it is charged at a constant voltage of 2.4V/ single lattice to a stable current value of current-limiting I10A within 5h. A constant current discharge process was adopted at 60A, and the cut-off voltage was 1.8V. When the test stops, the tested capacity was the battery capacity.

2.3 The test process of high rate charge-discharge cycle
The fully charged battery was placed in a constant temperature water bath at 50°C. The cycle parameters were set as discharge current at 100A, discharge cut-off voltage at 1.75V, charging current at 100A, charging cut-off voltage at 2.4V, and the number of cycles was 15.

The values of cut-off charge time were recorded as t1 and t2, where t1 was the time of the charging capacity is equal to the discharging capacity in the first cycle, and t2 is the charging time of the charging capacity reaching to 1.03 times of the discharging capacity. The specific parameters of the equipment are shown in Table 1.

| Number | Temperature /°C | Discharge Current /A | Discharge Cut-off Voltage /V | Discharge Time/h | Charging Current /A | Charging Cut-off Voltage /V | Charge Time/h |
|--------|-----------------|----------------------|----------------------------|-----------------|---------------------|-----------------------------|--------------|
| 1      | 50              | 100                  | 1.75                       | 18              | 100                 | 2.40                        | t1           |
| 2      | 50              | 100                  | 1.75                       | 18              | 100                 | 2.40                        | t2           |

3. The Results and Discussion

3.1 Analysis of High Rate Accelerated Cycle Discharge Stage
For the high-rate accelerated charge and discharge cycle tests of 15 times of Number 2, the first, middle and last pair cycle discharge analysis in the cycle was shown in Fig. 1. It can be seen from Fig. 1 that the voltage drops rapidly in a very short period of time at the initial stage of discharge, and then decreases gently with the extension of discharge time. At the end of discharge, the voltage decline is accelerated. With the increase of the number of cycles, the rate of voltage drop increases, but the rate of voltage drop of the second cycle is lower than that of the first cycle. This may be because the time of the first cycle battery at 50 °C is not long, so the battery is not damaged. And battery is activated to improve its performance. Test 1 and 2 of the discharge voltage curve and its analysis are similar, but the voltage drop rate of Test 1 in the trend is slower than Test 2, that is, the battery performance in test 1 is superior to Test 2 [7]. The overcharging of Test 2 makes the battery charging process time is too long, accelerating cell aging. With the increasing of cycling times, for battery charging, the more cycling times, the faster battery performance decline. Therefore, the Test conditions and parameters for Test 2 have more serious damages to the battery performance than Test 1.
Fig. 2 shows the changes of capacity and energy in the discharge phase of Test 2 with the increase of the number of cycles. As can be seen from Fig. 2, with the increase of cycle times, the discharge capacity and energy of the battery decrease from 695.58Ah in the first cycle to 535.27Ah in the 15th cycle. And the energy decreases from 1.388kwh in the first cycle to 1.062kwh in the 15th cycle, indicating that the battery performance is damaged with the increase of cycle times. However, the output capacity and energy of the second cycle are both higher than that of the first cycle. It may be that the initial stage of the whole cycle (the first cycle) has activation effect on the battery, which makes the battery performance slightly improved. The relation curve of capacity, energy and cycle times in the discharge stage of Test 1 is similar to that of Test 2, but the decline trend of Test 1 is slightly slower than that of Test 2, indicating that the performance of the battery in Test 1 is superior to Test 2.

3.2 Analysis of High Rate Accelerated Cycle Charging Stage

The process of charging is as follows: firstly, battery voltage rises with charging in a constant current. When the voltage rises to 2.4V, the charging current drops. Then the process stops until the charging time reaches setting time. The parameters of Test 2 are set at the charging current of 100A, charging cut-off voltage of 2.4V and charging time of 8.66h. Fig. 3 shows that part of charging voltage curves in Test 2. As can be seen from Fig. 3, at the initial stage of charging, the voltage rises sharply, and then the rate of raising slows down. In the later stage of charging, the rate of voltage increasing increases until the voltage is 2.4V. With the increase of cycle times, the rate of voltage rise increases, indicating that the increase of cycle times leads to the deterioration of battery performance, making the battery more prone to saturation. However, the rising rate of voltage in the second cycle is slower than
that in the first cycle, indicating that the battery performance in the second cycle is better than that in the first cycle. This may be because the battery performance in the first cycle is not damaged, even it can be activated. The charging voltage curve of Test 1 is similar to that of Test 2. The rise rate of Test 1 is smaller than that of Test 2. With the increase of cycles, the difference between the rise rates of Test 1 and Test 2 becomes larger and larger. This indicates that the damaged condition of the battery in Test 1 is not as bad as that in Test 2, and the former still has a stronger electric capacity than Test 2.

![Voltage-Time Curve during Cycle Charging](image1)

**Figure 3. Voltage-Time Curve during Cycle Charging**

Fig. 4 shows the partial charging current curves of Test 2 after 15 cycles. The figure shows that in the stage of charging, the current is 100A at first, that can keep for some time. Then value of current decline, which rate of decline from fast to slow until the deadline, charging is over. With the increase of cycling times, constant current charging time is reduced. With the increase of cycling times, the time of current keeping at 100A is reduced gradually and the end current turn to lower and lower, which indicate that the battery has been overcharged, and with the increase of cycle times, the greater the overcharge, the greater the damage to the battery performance. But the second cycle, contrary to the above, the time for constant current time is longer than the first cycle. The declining rate of charging current at late stage is faster than the first cycle. The end current of second cycle is greater than the first. All above indicate the functions of the battery of second cycle has increased rather than destruction. The battery charging curves of current and time in Testing 1 is similar with Test 2. The constant-current charging time of Test 1 is longer than the Test 2. The decline rate of current at later stage and end current of Test 1 are higher than Test 2. For example, for the current end of the first cycle, in Test 1, is 37.36 A, while in Test 2, is 9.18 A. For the current end of the 15th cycle, former is 29.10 A, the later is 4.79 A. This indicates the overcharge of the battery in Test 1 is less than that in Test 2, and the damage degree to the battery in Test 1 is smaller.

![The Curve of Current - Time during Cycle Charging](image2)

**Figure 4. The Curve of Current - Time during Cycle Charging**

Fig. 5 shows the relationship curve between battery charging capacity, energy and cycle times in
Test 2. As can be seen from Fig. 5, with the increase of cycle times, both battery capacity and energy decrease, indicating that the increase of cycle times leads to damage of the battery and deterioration of its performance. The second cycle of battery capacity at a high level, may be the battery at the beginning of the cycle is not damaged, and the capacity and energy of the battery in the second cycle is higher than in the first cycle, which the battery is activated in the first cycle, so its performance is good performance. The curve of the relationship between battery charging capacity, energy and cycle times in Test 1 is roughly similar to that in Test 2. The biggest difference is that the decline trend of battery capacity and energy with the increase of cycle times in Test 1 is slower than that in Test 2, indicating that the performance of Test 1 in the charging stage is better than that in Test 2.

![Figure 5. Diagram of Charging Capacity, Energy of battery with Different Cycle Times](image)

3.3 Volumetric analysis

At 25 °C, for a fresh battery from a factory, before measuring its internal resistance and voltage, it should be kept one more hour after the battery is filled fully. The capacity test method of C10 is used in discharging and charging process. After the test, at 25 °C, the battery is kept for 1 h to measure internal resistance and voltage. Fig. 6 shows the curves of voltage-time during checking capacitance before and after the acceleration cyclic test with C10 of Test 2. It can be seen from Fig. 6 that in the initial stage of checking capacitor, the voltage drops obviously within a very short period of time. In the middle stage, the voltage drops gradually. In the later, the voltage declines at high speed. Compared with the two checking capacity tests, the voltage dropping rate before the accelerated test is slower than that after the accelerated test, and the time of checking capacity in former is longer than the later, indicating that the performance of the battery former is better than later. The battery is damaged after the accelerated test. The voltage-time curve of checking capacity in Test 1 is much flatter than that in Test 2, possibly because the damage of Test 2 to the battery is more than in Test 1.

![Figure 6. Quadratic Checking Capacitance Voltage Curve](image)
Table 2 shows the test data of the checking capacity before and after the battery acceleration in Test 2. It can be seen from Table 2 that the internal resistance of the battery of full charge is lower than that after discharge, the internal resistance before acceleration test is lower than that after acceleration test. The internal resistance of the diagonal positive and negative poles is higher than that of the adjacent positive and negative poles. Before the accelerated test, the battery capacity is 701.60Ah, and after the accelerated test, the battery capacity decreases to 524.22Ah, and the capacity retention rate is only 74.72%, indicating that the battery performance declines a lot after the Test 2. The capacity retention rate of Test 1 is 93.31%, indicating that overcharge has great damage to the battery and has great impact on the performance of the battery.

Table 2. Battery Parameters for the checking Capacity Stage

| Stage                        | The Battery Condition          | Internal resistance/mΩ | Capacity/Ah |
|------------------------------|--------------------------------|------------------------|-------------|
| Before the Battery Acceleration test | Keep 1h after fully charged   | Adjacent 0.313         | 701.60      |
|                              | Discharge to 1.80V and keep 1h| Adjacent 0.420         |             |
|                              |                                | Opposite 0.319         |             |
|                              |                                | Opposite 0.432         |             |
| After the Battery Acceleration test | Keep 1h after fully charged    | Adjacent 0.314         | 524.22      |
|                              | Discharge to 1.80V and keep 1h| Adjacent 0.510         |             |
|                              |                                | Opposite 0.326         |             |
|                              |                                | Opposite 0.526         |             |

3.4 Comprehensive Analysis of High Rate Accelerated Test of C10

Take the discharge and filling capacity of the first cycle as the base, and the ratio of the discharge and filling capacity of each cycle to the first cycle is denoted as n and m, respectively. The smaller n and m are, the worse the performance of the battery. Taking the number of cycles as the x-coordinate and n and m as the y-coordinate respectively, the relationship curve between capacity and the number of cycles is shown in Figure 7 and 8. The acceleration test for battery of No. 5 and No. 10 is at Test 2, and the acceleration test of other batteries is at Test 1. The figure 7, 8 shows that with the increase of cycles, n, m general downturn with occasional fluctuations. The downward trend of n, m for Test 2 is more obviously with the increase of cycling times, it means that condition of Test 2 has more huge damage to the battery. Therefore, available n, m can be used to represent the damage degree of the battery.

Figure 7. Curves of n and the number of cycles
The curves of \( m \) and the number of cycles is fitted linearly to obtain their slopes. The curve of the relationship between battery capacity retention rate and slope is shown in Fig.9, where the capacity retention rate is 74.72% for No. 10 battery and 75.96% for No. 5 battery. As can be seen from Fig. 9, with the increase of capacity retention rate, the absolute values of discharge slope and charging slope both show a decreasing trend. The slopes of No. 5 battery and No. 10 battery are significantly different from other batteries, and their capacity retention rate is also significantly different. The capacity retention rate is lower than 80%, the absolute slope is greater than 0.012, the capacity retention rate is higher than 85%, and the absolute slope is less than 0.008. Thus, the available slope can represent the capacity retention rate.

Figure 8. Curves of \( m \) and the number of cycles

Figure 9. The relation curve of battery capacity retention rate and slope

4. The Conclusion

The aging of the battery can be accelerated under extreme conditions such as high temperature, high ratio and overcharge. For rapid detection of battery life, all of accelerating the battery aging, high temperature, increasing rate of charging and discharging and overcharge time are effective means. In this paper, we use the following parameters: temperature is 50°C, discharging and charging currents are set at 100A, discharge cut-off voltage is of 1.75 V, charging by the voltage of 2.4 V, charging deadline is t1 and t2, respectively. The t2 is the charging time of the charging capacity reaching to 1.03 times of the discharging capacity. The battery performance degradation is accelerated by the overcharged. The curve slope between the ratio of each cycle discharge capacity to the first cycle discharge capacity can represent the degree of battery performance aging. According to the aging degree and different detection requirements, an appropriate charging time and cycle times can be selected to analyze and compare the battery life.
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