Effect of Discharge Rate on Positive Active Material of Lead Carbon Battery for Energy Storage

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Abstract. Lead carbon battery has been widespread concern with its excellent performance of charge and discharge under High Rate Part State of Charge (HRPSoC) as well as its cycle performance. In this paper, the cycling performance of lead carbon battery for energy storage was tested by different discharge rate. The effects of different discharge rate on the composition and morphology of positive active materials in the cycle was studied by XRD and SEM. The effect of different discharge rate on the ohmic impedance of lead carbon battery was studied by testing Electrochemical Impedance Spectroscopy with different capacity retention rates. The results show that with the increase of the discharge rate, the content of PbO₂ in the positive active material increases, the active substance utilization and the particle size of PbO₂ crystal declines, and the ohmic impedance of the battery decreases.

1. Introduction
Long life, low cost and high security are the basic requirements of a power system for energy storage batteries. Lead-acid batteries are widely used as storage batteries currently because of their low cost, mature technology and high security. But their short cycle life¹ cannot meet the needs of the large-scale energy storage technology in the new energy field for long life batteries².

A lead carbon battery has some carbon material introduced into its negative electrode based on lead-acid batteries, and thus significantly improves its performance of rapid charge and discharge in the high rate part state of charge (HRPSoC) as well as its cycle performance. The negative carbon material can significantly improve the negative electrode sulfation of the lead carbon battery in the HRPSoC mode³⁴. With the progress of the research, the performance of the negative electrode is becoming better, the bottleneck of battery life transferred to the positive electrode, which fails mainly due to active material softening and directly affects the battery life⁵.

In order to further analyze the performance of the lead carbon battery in the field of energy storage, this paper probes into the cycle performance of the lead carbon battery tested at different discharge rates and analyzes the effect of different cycle conditions on the positive active materials.
2. Experimental Method

2.1. Experimental Battery
Tailor-made 2V/15Ah lead carbon batteries are used to cycle under different conditions for cycle performance test, electrochemical impedance spectroscopy (EIS) test, X-ray diffraction (XRD) test and scanning electron microscope (SEM) test.

2.2. Battery Charge and Discharge Cycle Test
The Digtron and Maccor battery testers are used to test the capacity and cycle performance of lead carbon batteries. A research is made through high-temperature accelerated experiments on the effect of different discharge rates on the positive active materials and its mechanism. A total of four batteries are employed, with one of them as reference not cycled. The reference battery is used to compare with the cycled batteries in composition and morphology. The C4 capacity is calibrated and the electrochemical impedance spectroscopy is tested after each cycle. Table 1 shows the initial C4 capacity and cycle conditions of each battery:

| Table 1. The working conditions of batteries |
|---------------------------------------------|
| Experimental Condition | #1 | #2 | #3 | #4 |
| C4 capacity         | 14.06 | 14.01 | 13.96 | 13.94 |
| Temperature         | \ | 40°C | 40°C | 40°C |
| Charge rate         | \ | 0.2C | 0.2C | 0.2C |
| Discharge rate      | \ | 0.5C | 1C | 2C |
| Depth of charge and discharge | \ | 30% SoC - 80% SoC |

2.3. EIS Test
PGSTAT 302N workstation made by Metrohm is used to test the electrochemical impedance spectroscopy of batteries. The batteries are set at 80% SoC, with the test amplitude at 3mV and the frequency range between 0.1Hz and 100kHz.

2.4. XRD and SEM Tests of Positive Plates
The batteries to be dismantled for positive active materials are set at 80% SoC (base on the latest C4 capacity calibration after cycle). D8 Advance X-ray diffractometer made by Bruker is used for XRD tests, with the test range between 20° and 80° and the scan speed at 0.2°/s. S4800 field emission scanning electron microscope made by Hitachi is used for SEM tests.

3. Results and Discussion
The C4 capacity is calibrated at 25 °C after cycle and compared with its value before the cycle, and the capacity retention rate of the battery is thus obtained.
Figure 1. The cycle number vs. capacity retention rate

Figure 1 shows the relations of cycle times with capacity retention rates of #2, #3 and #4 batteries at different discharge rates. The capacity retention rates of #2, #3 and #4 batteries drop to 78.29% (after 200 cycle times), 79.12% (after 450 cycle times) and 82.83% (after 600 cycle times) respectively. These three batteries almost have the same state of health at the end of the cycles.

3.1. Macroscopic Morphology of Positive Plates

Figure 2. The macroscopic features of positive plates and separator before and after cycles

Figure 2 shows the positive plates and diaphragms before and after cycles. The positive plate of #1 battery which is not cycled is compared with those of #2, #3 and #4 batteries which are cycled under different working conditions in macro-surface state, micro-surface morphology and composition. The black solid matter on the positive plates is PbO\(_2\), and the white solid matter is PbSO\(_4\) which is dense and hard. The black residue on the diaphragms is softening PbO\(_2\) powder.

3.2. Effect of Discharge Rate on Positive Active Material Composition

In figure 3, (a) shows the XRD patterns of the positive active materials of #1, #2, #3 and #4 batteries respectively. Since the dismantled batteries are set at 80% SoC, the four batteries contain both β-PbO\(_2\) and PbSO\(_4\). #1 battery is not cycled and therefore should theoretically contain some α-PbO\(_2\)\(^{[6]}\), but the XRD test does not show any α-PbO\(_2\). The reason is that most of the original α-PbO\(_2\) is consumed in the process of activation and calibration. α-PbO\(_2\) can only be produced under weak base conditions and no α-PbO\(_2\) is further produced in the battery. As a result, there is no α-PbO\(_2\) on the positive plate.
of #1 battery. In figure 3, (b) shows contents of the positive active materials calculated according to the K-value method. The $\beta$-PbO$_2$ content in #1 battery is greater than those in #2 and #3 batteries, probably because the reversible capacity of #1 battery has not been yet recovered before cycles and the utilization of the active materials is lower at 80% SoC. The capacity retention rates of #2, #3 and #4 batteries are similar to each other, and their $\beta$-PbO$_2$ contents directly reflect the utilization of active materials at 80% SoC. It can be seen from the data in the figures that the $\beta$-PbO$_2$ contents in the active materials increase along with the discharge rates after cycles. That is, the battery with high discharge current needs more active materials in the event of the same charge capacity. It means that high current discharge reduces the utilization of active materials. On the other hand, the PbSO$_4$ contents in the positive active materials decrease along with the increase in discharge current.

![Figure 3. (a) The XRD patterns of positive active materials of #1-#4 Batteries; (b) $\beta$-PbO$_2$ content on positive plates of #1-#4 batteries](image)

3.3. Effect of Discharge Rate on the Morphology of Positive Active Materials

In figure 4, (a), (b), (c) and (d) show the microscopic morphology patterns (magnified by 2000) of the positive active materials of #1-#4 batteries respectively. It's (a) shows that the initial positive active materials mainly consisting of homogeneously distributed fine $\beta$-PbO$_2$ particles and a small amount of PbSO$_4$ particles. (b), (c) and (d) in figure 4 show the positive active materials after cycles, with the particles significantly bigger. The particles of positive active materials become bigger after cycles. The positive active materials of the three batteries after cycles have the similar particle adhesion, which is less than that of the initial positive active materials. Therefore, the charge and discharge cycles of the batteries can gradually change the $\beta$-PbO$_2$ in the active materials from small dense particles to large loose ones. It is known from figure 4 that (b), (c) and (d) that the $\beta$-PbO$_2$ particles in the active materials become smaller with the increase in the discharge rate. A high discharge rate causes more electrochemical activity points on the plate in the process of discharge, and thus produces more PbSO$_4$ particles per unit time. However, the PbSO$_4$ particles are smaller due to the short discharge time. Small PbSO$_4$ particles could change into small $\beta$-PbO$_2$ particles in the process of charge at the same rate. It is more
likely for the particles to come off from the plate due to the loose structure of the small particles.

Figure 4. (a), (b), (c) and (d) The SEM patterns of positive active materials of #1-#4 batteries

3.4. Effect of Discharge Rate on Electrochemical Impedance Spectroscopy of Battery

![Graphs](image)

Figure 5. (a), (b) and (c) The EIS patterns of #2-#4 batteries at 80% SoC (d) The EIS pattern of #2-#4 batteries at 80% SoC before and after Cycles
In figure 5, (a), (b) and (c) show the EIS patterns of #2, #3 and #4 batteries at 80% SoC at different capacity retention rates. It can be seen from figure 5 that the batteries have the higher ohmic impedance before cycles. The ohmic impedance decreases gradually with the decrease in capacity retention rate, because the positive plates are covered with PbSO$_4$ at 80% SoC before cycles and the batteries have a higher ohmic impedance. The irreversible dense PbSO$_4$ on the positive plates is gradually converted into more dispersed reversible PbSO$_4$. As a result, the active materials are more conductive, with electrons more easily reaching inside the active materials, so the ohmic impedance decreases. (d) shows that the ohmic impedance of #2, #3 and #4 batteries increasingly decreases with the decrease in capacity retention rate. It means that a higher discharge rate can decrease the ohmic impedance greatly when the batteries have the same capacity retention rate. It is evidenced that a higher discharge rate could decrease the PbSO$_4$ content on the positive plate, and thus reduce the plate resistance.

4. Conclusions
The electrochemical performance of lead carbon batteries and the composition and morphology of the active materials are obtained by means of testing the electrochemical impedance spectroscopy of lead carbon batteries at different discharge rates during cycles and the XRD and SEM of the positive active materials after cycles. The results show that:

1) When lead carbon batteries are used at higher discharge rate, the discharge rate directly affects the size of PbO$_2$ particles in the positive active material. The higher the discharge rate, the smaller the PbO$_2$ particles.

2) The discharge rate directly affects the utilization rate of PbO$_2$ during cycles. The utilization rate of PbO$_2$ decreases with the increase in discharge rate.

3) The PbSO$_4$ near the tab is converted into the active material PbO$_2$ during cycles, and the internal resistance of battery decreases. The higher discharge rate, the lower ohmic impedance.

5. References
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