Fading Mechanism Analysis of NCM Lithium-Ion Battery Under Different Degrees of Overcharge

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Abstract

Power batteries are always misused and abused due to the fault or failure of battery management system (BMS), resulting the overcharge and over-discharge. In this study, NCM lithium-ion battery is used as the research object. Cyclic experiments of different overcharge degrees under voltage and capacity as cut-off conditions are performed, respectively. The evolution of the basic performance parameters under different conditions are observed. As the overcharge deepens, it will lead to accelerated degradation of capacity and deterioration of kinetic performance. In addition, overcharge with capacity has worse performance and is accompanied by a sharp rise in battery cut-off voltage. In-situ analysis method is used to describe the battery fading mechanism. The phase change reaction at 4.4V consumes the cathode material used for the normal charging process. The side reactions after charging to 4.7V generate a large amount of heat. Inventory lithium ions are lost and the electrode reaction uniformity is deteriorated as the cycle process. Ultimately, the battery has different tolerances under different overcharge strategies. Overcharge with capacity has faster decay rate, while overcharge with voltage has worse security.

Keywords: lithium-ion battery, overcharge, character parameters change, fading mechanism, in-situ analysis

1. Introduction

With the emergence of energy and environmental issues, electric vehicles have made great strides. However, due to the fault or failure of the BMS, the power battery will be misused and abused. When the battery is seriously abused, the battery may fail in an abuse event, and even cause safety problems such as thermal runaway [1]. However, in most cases, the battery does not exhibit severe external performance such as thermal runaway during the abuse process, but causes some internal structural changes. These changes accumulate inside the battery, causing the battery to be rapidly degraded during subsequent use process. The probability of safety hazards and failures is greatly increased, and it is easy to cause thermal runaway. It is therefore necessary to investigate the performance change and attenuation mechanism of power battery under the abuse condition for battery fault diagnosis and electric vehicle safety [2-4].

At present, the evolution process and failure mechanism of battery after abuse have been studied. Overcharge is one of the most harmful types of battery abuse. Due to the intercalation of excess lithium ions, lithium dendrites grow on the surface of the anode. In addition, the cathode material generates a large amount of heat and releases oxygen due to excessive deintercalation of lithium, resulting in the structural instability [5, 6]. By measuring the external parameters of the battery, the changes in model parameters, such as open circuit voltage, ohmic internal resistance, polarization internal resistance, and polarization capacitance, are analyzed from the perspective of the circuit. Ref. [7] compared the electrochemical impedance spectra of the battery before and after overcharging. The electrochemical impedance spectroscopy is extremely sensitive to battery overcharge. After overcharging, the battery voltage returns to normal, but the magnitude of the electrochemical impedance spectrum is still very large. Ref. [8] studied the overcharge decay behavior of composite electrode batteries, and combined the capacity increment analysis (ICA) method to divide the overcharge process into four stages. Refs. [9-11] paid more attention to the thermal runaway caused by overcharge. The behavior of heat production during battery overcharging is quantified.

In addition to in situ analysis, the evolution of the battery material structure, such as lithium dendrite growth, current collector dissolution, electrode or
electrolyte decomposition, electrode porosity deterioration, gas generation, diaphragm shrinkage or partial closure, and the like, is observed through ex-situ analysis method. In Refs. [12, 13], it was observed that intragranular cracks occurred in the electrode material after the battery was overcharged at room temperature by scanning microscopy, which may be the dominant factor causing the structural change of the material. In Ref. [14], the overcharge study was carried out especially in low temperature environments. The electron/Li+ migration ability and electrolyte diffusion/transfer efficiency were reduced due to crystal structure damage. In Ref. [15], the structural transformation of the battery cathode material after overcharging was also found at 55 °C. Ref. [16] studied the decomposition of electrolyte caused by overcharging at different charging rates. Ref. [17] compared the effects of overcharge on NCM424 and NCM333. The generation of oxygen at high voltages is the dominant factor in subsequent structural changes. Ref. [18] studied the phenomenon of lithium deposition during overcharge of graphite and hard carbon anode materials. The lithium dendritic activity formed varies with the nature of the negative electrode.

The tolerance of NCM lithium-ion batteries of different overcharge degrees under distinct overcharge strategies has rarely been studied. Taking the charging voltage or charging capacity as overcharge cut-off conditions are two different overcharging strategies. With the charging voltage and capacity as the overcharge cut-off conditions, the charging capacity and voltage will vary with the number of cycles. Different charging strategies will result in different decay rates. Studying the battery's tolerance under different overcharge degrees has important guiding significance for battery-optimized design of battery manufacturers and users' mastery of battery health. In the second part, two overcharge experiments are carried out for NCM lithium-ion batteries with charging voltage and charging capacity as overcharge cut-off conditions. In the third part, the change of NCM lithium-ion batteries performance parameters are studied. After that, the fading mechanism is analyzed by ICA and differential voltage analysis (DVA) method. Finally, the viewpoints of this paper are summarized and the future work is prospected.

2. Experimental program

The battery used in the experiment was a commercial NCM lithium-ion battery with a nominal capacity of 37 Ah. The test equipment was American Arbin LBT21014 Battery Testing System. The experimental batteries were placed in a high and low temperature test chamber at 25 °C. To ensure the safety of the experiment, the batteries were tested with splints. The appearance of the experimental battery is shown in Fig. 1.

![Fig. 1 The appearance of the experimental battery](image)

The test scheme was divided into two parts: basic battery performance test and cyclic overcharge test. The experimental battery was first subjected to capacity calibration by constant current-constant voltage (CC-CV) charge and CC discharge. The charge and discharge rate of the CC stage is selected to be 1C. The charge cut-off voltage is 4.2V and the discharge cut-off voltage is 2.8V. The initial capacity is recorded as Q0. After that, the battery was discharged to 2.8 V at 0.05 C, and a charge and discharge test at 0.05 C was performed to observe the change in the maximum usable capacity of the battery. Finally, at 10% SOC interval, constant current charging was continued for 10 s at 2 C rate, and allowed to stand for 40 s. The constant current discharge was continued for 10 s at 2 C rate, and the open circuit voltage (OCV), internal resistance and polarization voltage of the battery were measured. Cyclic overcharge tests of two different strategies were performed after the basic performance test. With the charging voltage as the overcharge cut-off condition, the battery was charged to 4.2V, 4.3V, 4.5V and 4.7V at a constant current of 1C. After standing for 0.5 h, it was discharged at a constant current of 1 C to 2.8 V, and then allowed to stand for 0.5 h. Correspondingly, the battery was charged at a constant current of 1C to 100% Q0, 110% Q0, and 120% Q0 with the charging capacity as the overcharge cut-off condition. This paper aims to study the effects of different overcharge degrees. 4.2V and 100% Q0 are only used as a reference for normal batteries. Therefore, they will be considered as the same situation. During the experiment process, the basic performance test was performed after multiple cycles of the overcharge test. In order to avoid the contingency of the experiment, two batteries were tested at the same time under each condition.

3. Results and Discussion

3.1 Evolution of battery character parameters

When the battery is overcharged by two different strategies, the first overcharge shutdown voltage of the battery charged to 110% Q0 and 120% Q0 is about 4.3V and 4.5V, which is almost the same as the overcharge strategy with the charging voltage as the cut-off condition. Then, as the number of cycles increases, the
performance parameters of the NCM lithium-ion battery change greatly. The end-of-charge voltage of the battery charged 120% Q₀ increased from 4.5V to 4.7V. As the degree of overcharge is deepened, the charge termination voltage rises sharply, which is significantly different from the overcharge strategy with the charging voltage as the cut-off condition.

Battery capacity is one of the performance parameters we are most concerned about. In the case of the electric vehicle, it is generally considered that when the battery capacity declines to 70%-80% of the initial rated capacity or the internal resistance increases to 160%-200% of the initial value, the termination condition of the battery life is reached. However, the specific values depend on the battery type. The battery capacity decay rates for different charging voltages and different charging capacities are shown in Fig. 2(a-b). Under two different overcharge strategies, the battery capacity decay rate gradually increases as the overcharge degree deepens. The capacity decay rate is less than 0.1% for the overcharge voltage is 4.3V and 4.5V. But it suddenly rises to 1.15% as the overcharge voltage reaches 4.7V. The decay rate under the capacity overcharge condition did not exceed 0.13%, the 110% Q₀ and 120% Q₀ battery decay rates were both higher than 4.3V and 4.5V. Although the two strategies have similar performance when they are overcharged for the first time. As the overcharge continues, the overcharge strategy with the charge capacity as the cut-off charging condition has a faster capacity decay rate, accompanied by a continuous increase in the battery voltage. During the charging process of the electric vehicle, overcharge of a single battery in the battery pack always occurs. The faster decay of its capacity and the rapid rise in voltage will cause a significant drop in the energy efficiency of the battery pack.

**Fig. 2** Battery capacity decay rate for (a) different charging voltages and (b) different charging capacities

Capacity degradation of the battery is always accompanied by a decline in dynamic performance. Destruction of the lattice structure and decomposition of the electrolyte will hinder the migration of lithium ions between the solid phase and the liquid phase. Response on the circuit is the change of the internal resistance and the polarization voltage. Fig. 3(a-b) and Fig. 4(a-b) respectively show the variation of the 1s DC internal resistance and the 10s polarization voltage. As the degree of charge is deepened, both the internal resistance and the polarization voltage increase rapidly. The damage to the battery according to the capacity overcharge is still higher than the overcharge according to the voltage, which shows similar characteristics with the capacity decay. The kinetic performance rapidly deteriorates after overcharging, resulting in poor consistency of the battery pack. In particular, the deep overcharge has a huge impact, which seriously jeopardizes battery safety.

**Fig. 3** Battery resistance increase rate for (a) different charging voltages and (b) different charging capacities

**Fig. 4** Battery polarization voltage increase rate for (a) different charging voltages and (b) different charging capacities

In addition, a more striking thing is that as the degree of overcharging deepens, the 1C discharge capacity of the battery is closer to the 0.05C discharge capacity. For batteries charged 110% and 120% Q₀, the actual capacity before overcharging are 92.6% of the maximum available capacity. After overcharging, the actual capacity is 96.9% and 99.0% of the maximum available capacity. To explain this phenomenon, Fig. 5(a-b) and Fig. 6(a-b) show the OCV-SOC and Vp-SOC curve of overcharge battery.

**Fig. 5** (a) Charged 110% Q₀ and (b) Charged 120% Q₀ battery OCV-SOC curve
Vp = V - OCV  

In equation (1), V is the terminal voltage, OCV is the open circuit voltage. Vp reflects the internal resistance and the polarization voltage. After the battery is charged to 110% and 120% Q0, the OCV-SOC curve hardly changes. The charging Vp-SOC curve is shifted upwards. The discharge curve is shifted downward significantly in the interval below 10%. It indicates that the internal resistance and polarization voltage increase slightly during the charging and high SOC interval discharge. On the contrary, they decrease significantly at the low SOC interval during discharge, resulting in a lower discharge termination SOC. According to the battery OCV-SOC curve, the discharge termination SOC of the battery charged 110% and 120% Q0 was decreased by 3.7% and 4.3%, respectively. It can be concluded that the overcharge will lead to deeper discharge of the battery, behaving positive feedback effect, which does greater damage to battery performance.

3.2 Fading mechanism analysis

ICA and DVA are two effective methods for analyzing the battery fading mechanism [19-22]. There is a new behavior on the IC curve in the overcharge process, as the cut-off voltage increases. The 1C IC curve of first cycle under different charge cut-off voltages is shown in Fig. 7. When the voltage is lower than 4.5V, only peak ① and ② are revealed in the charging IC curve. Meanwhile, the discharge IC curve has only peak ①. The improvement of current rate leads to a reduction in the number of observed peaks compared to 0.05C in Fig. 9. However, when the charging voltage reaches 4.5V or even 4.7V, the charging IC curve shows an additional peak ③ around 4.4V, peak ② correspondingly appears in the discharge IC curve. In the case of Li4CoO2, various hexagonal and monoclinic phases are observed at the similar voltage [5].

It is worth noting that during the second cycle of overcharge, the battery charged 4.7V showed a voltage platform around 4.08V and the battery temperature rose sharply, which is displayed in Fig. 8(a). It is possible that the charging current is consumed by other reactions inside the battery. When the battery is overcharged to 4.7V at the first cycle, the cathode material generates a large amount of heat and releases oxygen due to the higher voltage and excessive lithium deintercalation. The internal pressure of the battery increases and the structure is destroyed. The electrolyte begins to oxidize and decompose, and other side reactions occur. In this case, when the voltage of the battery reaches 4V during the second cycle of overcharge, Li2MnO3 starts to undergo other phase change reactions [5]. The temperature begins to rise, which in turn promotes the occurrence of other side reactions, as indicated by the significant peak ④ on the IC curve shown in Fig. 8(b). In addition, the height of peak ② suddenly drops during the second cycle of overcharge. The generation of the peak ③ depletes the cathode material which is used to carry out the phase change reaction at the peak ②. Subsequently, the battery capacity commenced decline, and the peak ③ gradually disappeared.

Material loss of different modes are mainly divided into 6 cases: The loss of lithiated cathode/anode material, the loss of lithium ion, the loss of delithiated cathode/anode material and the increase of internal resistance [20]. The degradation mode can be identified by the characteristic change of IC curve. The 0.05C IC curve before and after overcharging for batteries charged 110% and 120% Q0 are shown in Fig. 9(a-b).
The lithium ion battery graphite anode has five platforms throughout the discharge process, corresponding to the states of intercalating lithium ion content. In Fig. 9(a), the heights of the characteristic peak ① and ② slightly decrease, indicating that the inventory lithium ion is lost. In Fig. 9(b), the heights of the peak ① and ② are significantly decreased, and the peak ④ is shifted to the right. All characteristic peaks during the charging process are shifted to the right. It indicates that the charged 120% $Q_0$ battery also occurs inventory lithium ion loss, and the internal resistance of charging increases. In the low SOC interval, the battery internal resistance of discharging decreases. The results of IC curve analysis are consistent with the Vp-SOC curve.

**Fig. 9** 0.05C IC curve for battery (a) charged 110% $Q_0$ and (b) charged 120% $Q_0$

DV curve has the ability to explain the change of the negative electrode lithium insertion amount and the uniformity of the electrode reaction during the decay process [21]. Fig. 10(a-b) shows the evolution of DV curve before and after overcharging. The shape of the characteristic peak ① during the discharge process characterizes the content of lithium ions in the battery negative active material. The offset of peak ① and ② signifies the degree of electrode reaction uniformity of the battery. The shapes of the characteristic peak ① became sharper, indicating that lithium ion loss occurred during the degradation of the charged 110%, 120% $Q_0$ battery, which is consistent with the analysis of the IC curve. Both the characteristic peak ① and ② are shifted to the left. The electrode reaction uniformity of the battery is deteriorated. It is verified that overcharge may result in damage to the structure of the battery material.

**Fig. 10** 0.05C DV curve for battery (a) charged 110% $Q_0$ and (b) charged 120% $Q_0$

The fading mechanism of the battery after overcharging has new properties. Different overcharge degrees have different effects on the battery under different overcharge strategies. When the battery voltage reaches 4.5V or even 4.7V, part of the cathode material reacted at the peak ② is used to form the peak ③. At the second charge of 4.7V, some complex side reactions produced a very prominent peak ④. With the charging capacity as a cut-off condition, when the battery voltage was increased to 4.7 V, the formation of the peak ④, severe side reaction, and the sudden rise in temperature were not observed. Obviously, under normal circumstances, there is a certain limitation to determine the tolerance of the overcharge and the health status of the battery according to the voltage. The battery has different tolerance levels under different overcharge strategies. Overcharge with capacity will have a faster decay rate, while overcharge with voltage has worse security.

4. Conclusion

NCM lithium-ion batteries have new features in battery performance parameters and fading mechanisms under different overcharge degrees. We can summarize that with the deepening of the overcharge, it will lead to accelerated degradation of capacity and intensified deterioration of kinetic performance. In addition, overcharge with capacity has worse performance, and it is accompanied by a sharp rise in battery cut-off voltage. The phase change reaction at 4.4V consumes the cathode material used for the normal charging process. The side reactions after charging to 4.7V generate a large amount of heat. Inventory lithium ions are lost and the electrode reaction uniformity is deteriorated as the cycle process. All of these phenomena will cause damage to the battery and increase the risk of a battery safety accident. Finally, the battery has different tolerance levels under different overcharge strategies. It is therefore insufficient to describe the battery tolerance to overcharge depending on single affecting index. Following will combine the battery performance variation law and fading mechanism to extract typical parameters that characterize the degree and times of battery overcharge, providing the foundation for battery fault diagnosis.

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