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Effects of over-discharging cycling on battery degradation at low temperatures

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ABSTRACT

Over-discharging is easier to occur at low temperatures. In this paper, the degradation characteristics were investigated by discharging to 2.75-0 V at 0°C and discharging at constant voltage for 0 and 2 hours, respectively. The results show that capacity fades linearly except for the 0 V-2 h cell that fades at an accelerated rate. The fade rates increase with decreasing discharging voltage. Besides, both the longer time of constant voltage and the lower discharging voltage contribute to loss of lithium inventory, loss of active materials, and internal resistance increase.

Keywords: Lithium-ion battery; Over-discharge; Low temperature; Degradation

NONMENCLATURE

Abbreviations	
AC	Alternating Current
CC-CV	Constant Current-Constant Voltage
EIS	Electrochemical Impedance Spectroscopy
FS	Full Scale
IC	Incremental Capacity
LAM	Loss of Active Material
LIBs	Lithium-ion Batteries
LLI	Loss of Lithium Inventory
NCM	$LiNi_xCo_yMn_{1-x-y}O_2$
SEI	Solid Electrolyte Interface
SOC	State of Charge
SOH	State of Health
Symbols	
R	Resistance

1. INTRODUCTION

Lithium-ion batteries (LIBs) have high energy densities and high power densities, thus are the best choice for electric vehicle power battery systems so far [1]. Among the LIBs, $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM) batteries have great potential due to their high energy density and excellent cycling performance [2].

In practical applications, cells are connected in series in a battery pack, and their capacities are not identical. As the cells with higher capacities are fully discharged, those with lower capacities will probably be discharged beyond their rated capacities, leading their voltages lower than the standard cut-off voltage, namely over-discharging [3]. Over-discharging is more likely to happen at low temperatures because it is easier to drop below the discharging cut-off voltage due to the large polarization effect, that is, the difference between the electrode potential and the equilibrium potential under the experimental condition is large.

The effect of over-discharging on the battery at room temperatures has been studied by many researchers. Zheng et al. [4] over-discharged $LiFePO_4$ battery to 0.5 and 0.0 V and found that over-discharging would not only lead to serious capacity fades but also worsen cycle performance under subsequent normal working conditions [5]. Johannes et al. [6] used the three-electrode NCM/graphite battery to obtain the potential change during over-discharge at 20°C. They found that the cathode potential continued to decrease during the progress while the anode potential increased almost vertically at the initial stage of over-discharge, and then entered a stable state when it reached about 3.56 V (vs Li/Li^+). They believed that this potential platform was caused by the continuous oxidation of the anode copper collector. Therefore, over-discharge could induce some side effects when the anode reaches a certain high potential, which reduces the safety performance and cycle performance of the batteries.

In addition, continuous over-discharging cycles will accelerate the battery degradation manifested by capacity fades and internal resistance increase. Wang et al. [7] found that excessive deintercalation of lithium ions on the anode would lead to the decomposition of the solid electrolyte interface (SEI) after the over-discharging cycles of the $LiNi_xCo_yAl_{1-x-y}O_2$ battery at room temperatures. Secondary SEI generated on the anode in the subsequent charging process, leading to the resistance increase in the charge transfer process and loss of lithium inventory (LLI). Dan Doughty and E. Peter Roth [8] thought that if the battery is over-discharged and can be recovered (that is, it can be charged and recycled) with internal short circuit, it is more likely to lose control under a high state of charge (SOC), which brings great risk of thermal runaway. However, most investigations, including the above of the degradation characteristics during over-discharge have been conducted at room temperatures with few studies of low-temperature effects. Different time of constant voltage at a certain over-discharge voltage may affect the cell because of the large polarization [3], which should be studied further.

This paper focuses on the degradation characteristics of LIBs over-discharging to 2.75 V-0 V at low temperatures to ensure the recyclability of the cells. Meanwhile, the step of constant-voltage (CV) discharge is designed to decrease the polarization, so that the influence of instantaneous potential and the approximate equilibrium potential on the degradation of over-discharged batteries is studied. Charging-discharging cycle tests of NCM batteries at different discharging voltages (2.75 V, 2 V, 1.5 V, 1 V, 0.5 V, 0 V) were carried out at 0°C, and the degradation characteristics were investigated using incremental capacity (IC) curve and electrochemical impedance spectroscopy (EIS) analysis.

2. EXPERIMENT

2.1 Lithium-ion battery and the experimental system

In this paper, 18650 type $LiNi_5Co_2Mn_3O_2$/Graphite cells with the standard cut-off voltage of 2.75-4.2 V and the nominal capacity of 2.6 Ah were used. A battery test system (NEWARE CT-4008, 5V-6A) was used to perform the battery cycle tests, an environmental chamber (GUANGDONG BELL BTH-150TC) was used to control the ambient temperature, and an electrochemical workstation was used to measure cell alternating current (AC) impedance. The voltage and current accuracies of the test system are both ± 0.05% FS (Full Scale), and the maximum temperature deviation of the chamber is ± 1°C. Fig.1 is a schematic diagram of the experimental systems.

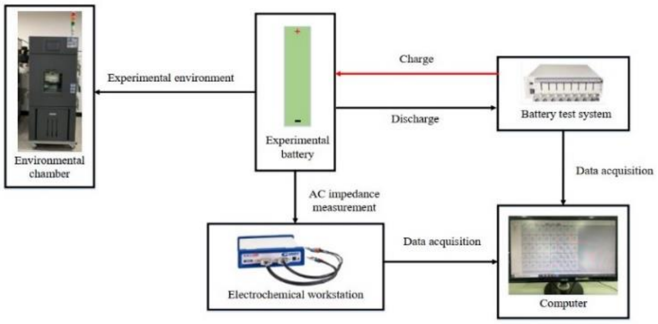

Figure 1 Schematic of the experimental setup

Cells were selected based on their capacities and internal resistance before the formal tests to ensure consistency. In the selection experiment, capacities were obtained as the discharging capacity of the last cycle of five standard charging-discharging cycles, that is, cells were charged with constant current-constant voltage (CC-CV) protocol and discharged with CC protocol. Besides, internal resistance was obtained by performing the hybrid pulse power characteristic test [9]. As a result, the capacity maximum deviation of cells used in this paper was less than 1%, and the maximum deviation of the direct current internal resistance was less than 2%.

2.2 Over-discharging cycles at low temperatures

The over-discharging cycles were carried out at the low temperature of 0°C, ten cycles as a group. There were 12 cells tested under different conditions, as shown in Table 1. They were firstly put in the environmental chamber before the test at 0°C for 3 h to ensure their heat balance.

Table 1 Over-discharging test conditions

Cell number	Discharging voltage	CV discharging time
1	2.75 V	0 h
2	2.75 V	2 h
3	2 V	0 h
4	2 V	2 h
5	1.5 V	0 h
6	1.5 V	2 h
7	1 V	0 h
8	1 V	2 h
9	0.5 V	0 h
10	0.5 V	2 h
11	0 V	0 h
12	0 V	2 h

The CC-CV protocol is adopted for the charging and discharging progress, and the current is 0.5 C in the CC stage of discharging progress. Besides, the charging current was set to 0.15 C to prevent the cells from lithium plating at low temperatures [10]. The CV cut-off current for charging is 0.05 C, while the CV stage for discharging is controlled by time. It can be seen from Table 1 that No. 1 and No. 2 cells are set as standard discharging cut-off voltage and compared with other over-discharged cells. Besides, the cells were left for 0.5 h between the discharging and charging process, and the tests were stopped after 100 low-temperature cycles.

2.3 Reference performance test

The reference performance test was designed to evaluate the basic performance of cells at 25°C after each group of the low-temperature cycling tests, consisting of a capacity test, a small current charging-discharging (0.05 C) test, and an AC internal resistance test.

(1) Capacity test

The capacity was measured by two charging-discharging cycles at 0.5 C-0.5 C with 1 h rest between the charging and discharging process, and the discharging capacity of the second cycle was considered as the actual capacity after the low-temperature cycles [11].

(2) Small current (0.1 C) charging-discharging test

After the capacity test and 1 h rest, cells were discharged and charged at 0.1 C-0.1 C to obtain the IC curve [12], which helped to monitor battery degradation online and analyze battery degradation characteristics [13]. The cells needed to be left for 1 h between the discharging and charging process.

(3) AC internal resistance test

After the small current test and 3 h rest, the EIS test was performed in the open-circuit state. The EIS test frequency range was 0.01 Hz-10 kHz, and the peak voltage amplitude was 5 mV.

3. RESULTS AND DISCUSSION

3.1 Capacity fades

The state of health (SOH), defined as the ratio of the discharging capacity to the initial capacity, is a major cell degradation index.

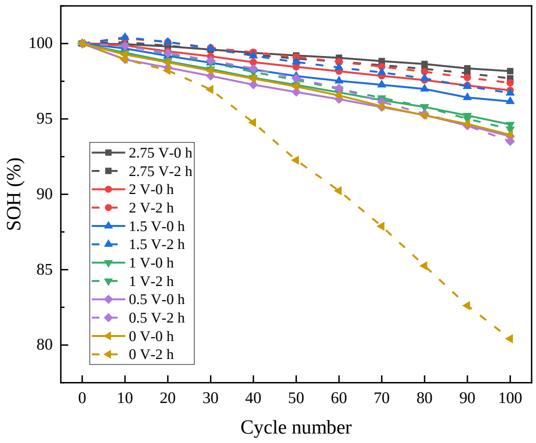

Figure 2 SOH changes with cycle numbers

Fig. 2 shows the SOH changes with increasing cycle number. It is seen that SOH fades linearly with increasing cycle number except for the 0 V-2 h cell. For comparison, the fade rates can be characterized by the slopes of SOH [14].

The fade rates characteristic of the cells with the same constant voltage discharging time and different discharging voltages are different. For the 0 h cells, the SOH fade rates increase with decreasing discharging voltage (2.75 V-0.5 V). However, the fade rate of the 0 V cell no longer increases, but decreases, compared with the 0.5 V cell. For the 2 h cells, the SOH fade fates increase with decreasing discharging voltage, in which the 0 V cell fade rate increases rapidly, and there is a turning point after 20 cycles. After the turning point, the fade rate of the 0 V-2 h cell increases significantly, and the SOH reaches 80.4% after 100 cycles, while the SOH of other cells is above 93%.

For cells with the same discharging voltage and different constant voltage discharging times, their characteristics can be divided into two categories. At standard discharging voltage (2.75 V) and 0 V, the fade rates of the 2 h cells are higher than that of the 0 h cells. However, for other over-discharging voltages (2 V-0.5 V), the fade rates of the 0 h cells are higher than those of the 2 h cells.

It can be seen that the degradation characteristics of over-discharged cells at low temperatures are different from those at room temperature. Juarez-Robles et al. [15] used $LiCoO_2$/Graphite cells and cycled them with 4 cut-off voltages: 2.7 V, 1.5 V, 0.0 V, and −0.5 V. They found that the SOH of cells decreases faster with decreasing discharging voltages. Zheng et al. [16]used $LiFePO_4$/Graphite cells and cycled them for 110 cycles with 2.0 V, 1.5 V, 1.0 V, 0.5 V, and 0 V. They found that the capacity of the cells with 1.5 V and 1.0 V decreased slightly, while those with 0.5 V and 0 V decreased seriously. For 0 V cell, its capacity retention rate is only 75.59%. It is found in the above literature that side reactions such as SEI growth and copper dissolution will gradually become serious, leading to faster capacity fades with decreasing discharging voltages. However, low temperatures inhibited the side reaction at 0 V-0 h cell, resulting in the capacity fade rate of the 0 V-0 h cell and the 0.5 V-0 h cell being similar. Surprisingly, the capacity fade rate of the 0 V-2 h cell decreased significantly. It may be because the polarization is greater when the voltage drops to 0 V under low-temperature conditions. Thus, after a long-time of constant voltage, the actual potential tends to the equilibrium potential, aggravating the side reaction.

3.2 Incremental capacity curve analysis

IC curves are an efficient way to identify the LIB degradation characteristics [17]. Generally speaking, the degradation modes of LIBs are mainly divided into loss of active materials (LAM), LLI, and internal resistance increase [18], and internal resistance increase would be described in Section 3.3. The IC curve peak represents the phase transition process of the positive electrode and negative electrode active materials, and the corresponding peak area represents the capacity involved in the phase change [18]. If LAM occurs, the height of the highest IC peak decreases at an approximately constant voltage; if LLI occurs, the peak area decreases, that is, the cell capacity decreases [19]. Therefore, the change of peak value and peak area can characterize battery degradation. In this paper, the IC curves of 0 h cells and 2 h cells after 100 cycles were characterized, and IC curve changes of the 0 V-0 h and the 0 V-2 h cell with increasing cycle number were also characterized, as shown in Fig. 3.

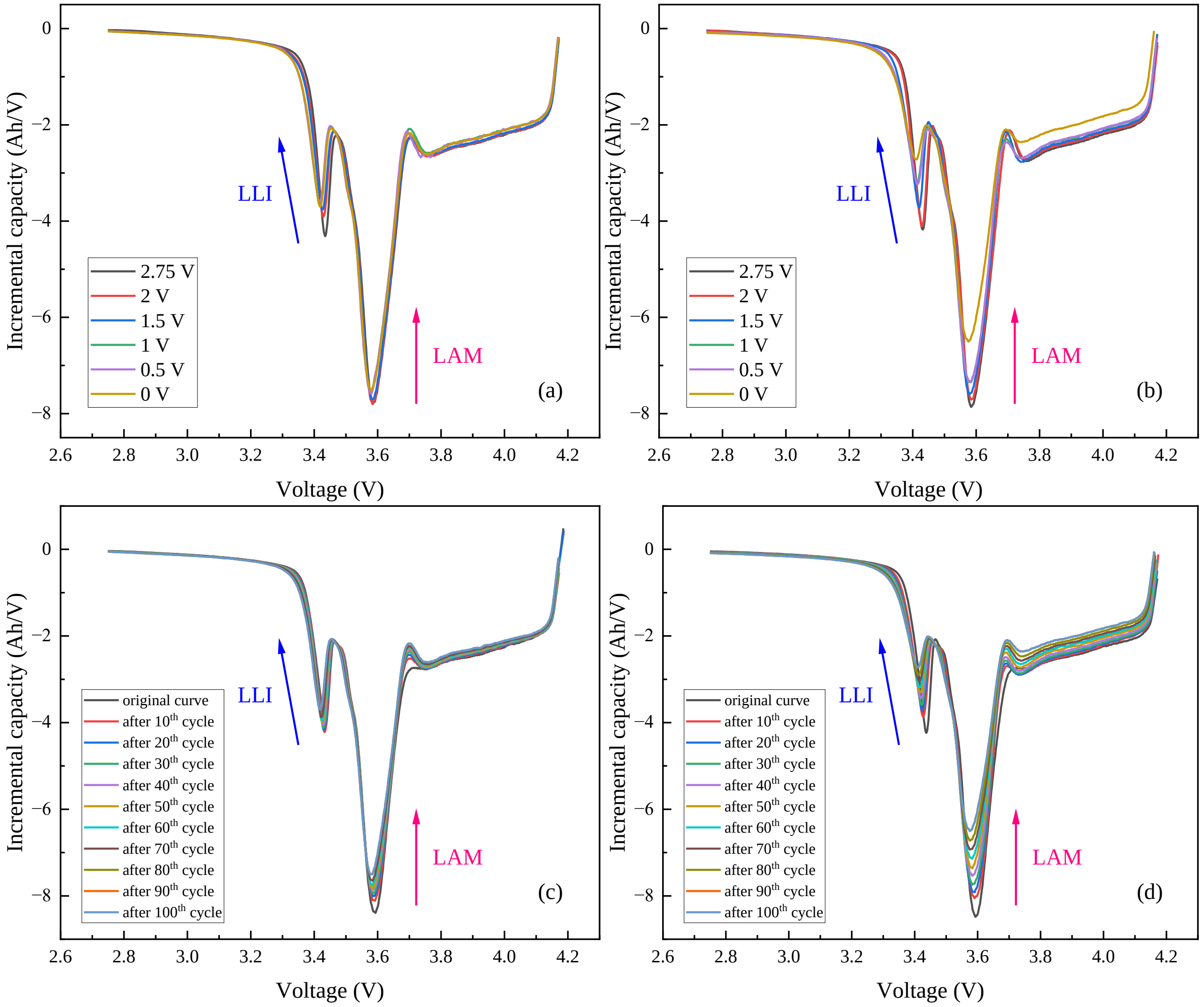

Fig. 3 IC curves (a) 0 h cells after 100th cycles (b) 2 h cells after 100th cycles (c) 0 V- 0 h cell (d) 0 V-2 h cell

It can be seen that the IC curves of NCM cells during discharge mainly present three peaks, of which the middle peak is the highest. From Fig. 3(a), it can be found that 0 h cell changes are small. The peak value of the highest peak decreases with decreasing discharging voltage, but the amplitude of change is very small, which means that though LAM occurs, it is not significant. Meanwhile, the peak area decreases rapidly from the standard discharging voltage (2.75 V) to over-discharging voltage cells, which means that the over-discharging leads to LLI. However, the slow growth of LLI in the 2 V-0 V range means that though over-discharging could cause LLI, the contribution of lower over-discharging voltage to LLI is limited. From Fig. 3(b), it can be seen that the highest peak value decreases faster compared with Fig. 3(a), especially for the 0 V cell, which means that the electrode material of the 0 V cell is seriously damaged. Besides, peak area decreases significantly with decreasing discharging voltage, which means that the long-time constant voltage contributes to LLI because the side reactions become serious.

From Fig. 3(c) and 3(d), it can be found that the highest peak value and peak area decreases with increasing cycle number, but the reduction speed of the 0 V-2 h cell is faster than that of 0 V-0 h cell. For these two cells, the highest peak value decreases fastest in the first 10 cycles, and decreases at an approximately equal rate in the subsequent 90 cycles. Therefore, it can be considered that the influence of over-discharging cycles at low temperatures on LAM does not change with increasing cycle number. Similarly, the reduction rate of peak area also changes little with increasing cycle number. This shows that the side reactions caused by over-discharging at low temperatures do not be more serious with increasing cycle number, and the growth rate of LLI and LAM does not change.

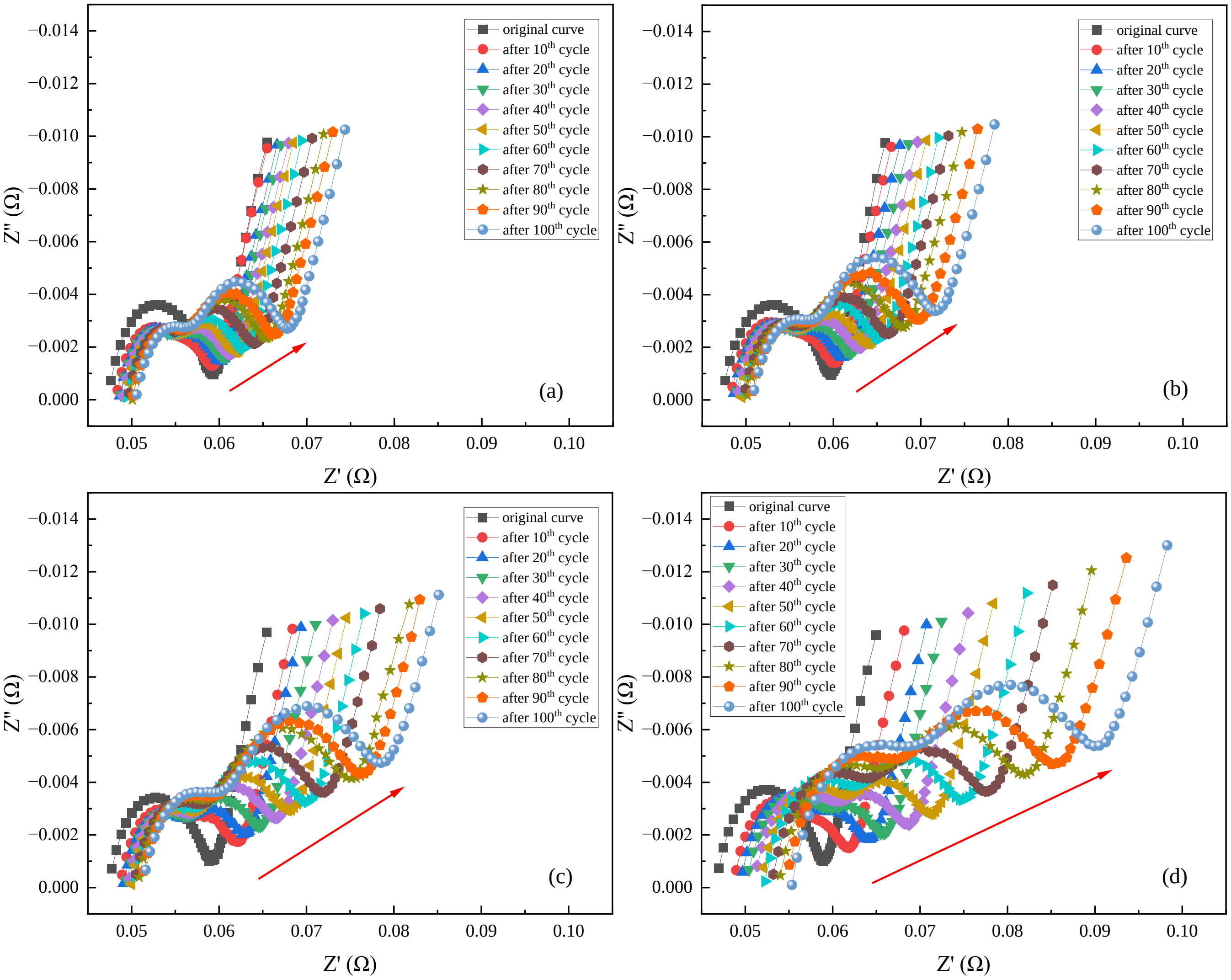

Fig. 4 Nyquist plots (a) 2.75 V-0 h cell (b) 2.75 V-2 h cell (c) 0 V- 0 h cell (d) 0 V-2 h cell

3.3 Electrochemical impedance spectroscopy analysis

EIS is a powerful tool for nondestructive analysis of internal changes of cells [20]. In this paper, EIS is used to analyze the AC impedance of degraded cells after cycling under different over-discharging conditions at low temperatures. There are four representative cells selected, namely the 2.75 V-0 h cell, the 2.75 V-2 h cell, the 0 V-0 h cell and the 0 V-0 h cell, as shown in Fig. 4.

From Fig. 4, it can be found that the curve shifts upward to the right as the number of cycles increases, which is caused by the increase of ohmic internal resistance R_{ohm} and polarization internal resistance R_{p} (including R_{SEI} and R_{ct}) [7]. When R_{ohm} increases, the Nyquist plot shifts to the right; besides, when R_{p} increases, the two semicircles (some have only one semicircle) expand, causing the Nyquist plot to shift to the upper right. Thus, the more R_{ohm} and R_p increase, the more the Nyquist curve shifts to the upper right.

From Fig. 4(a) and 4(b), it can be seen that the resistance of the 2.75 V-2 h cell grows faster than that of the 2.75 V-0 h cell, indicating that the 2.75 V-0 h cell degrades faster, which is consistent with capacity fades. Similarly, from Fig. 4(c) and 4(d), the resistance of the 0 V-2 h cell increases significantly faster than that of the 0 V- 0 h cell, indicating that 2 h constant voltage time has obvious influence on the cell impedance.

It can be seen that the ascending order of the amount of the Nyquist plot offset to the upper right is the 2.75 V-0 h cell, the 2.75 V-2 h cell, the 0 V-0 h cell and the 0 V-0 h cell. This is because that the lower discharging voltage and longer time make side reactions such as SEI growth and copper dissolution serious, leading to the resistance increase.

It is noted that the original cells only have one semicircle, and as the number of cycles increases, two semicircles begin to appear, and the boundary between the semicircles becomes obvious with increasing cycle number. This is because R_{ct} of the original cell is small and cannot be separated from R_{SEI}. As the battery degrades, R_{ct} gradually increases and becomes completely independent to form the second semicircle.

4. CONCLUSIONS

In this paper, the over-discharging cycle tests of the NCM battery at 0°C were carried out and the degradation characteristics of over-discharged cells at low temperatures were studied. The main conclusions are as follows:

(1) SOH fades linearly with increasing cycle number except for the 0 V-2 h cell, whose fade accelerates after the turning point. Meanwhile, SOH fade rates increase with decreasing discharging voltage except for the 0 V-0 h cell, whose fade rate is similar with 0.5 V-0 h cell. At 2.75 V and 0 V, the fade rates of the 2 h cells are higher than that of the 0 h cells. However, at 2 V-0.5 V, the fade rates of the 0 h cells are higher than those of the 2 h cells.

(2) Compared with the 0 V-2 h cell, LAM and LLI of the 0 V-0 h cell are not significant, which means that the long-time constant voltage contributes to LLI and LAM because the side reactions become serious. Meanwhile, the growth rate of LAM and LLI do not change with increasing cycle number.

(3) The more R_{ohm} and R_p increase, the more the Nyquist curve shifts to the upper right. Meanwhile, the lower discharging voltage and longer time make side reactions serious, leading to the ascending order of the amount of the Nyquist plot offset to the upper right is the 2.75 V-0 h cell, the 2.75 V-2 h cell, the 0 V-0 h cell and the 0 V-0 h cell.

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