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Mechanisms of $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$/graphite battery degradation caused by overcharging cycling at low temperatures

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ABSTRACT

In a battery application, overcharging may occur due to possible inconsistency among the batteries, or failure of the battery management system, thereby accelerating the degradation of the batteries. At low temperatures, the overcharging is more likely to occur, because the charging cut-off voltage is more easily exceeded due to the stronger polarization effect. In this paper, the characteristics and mechanisms of $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$/graphite battery degradation caused by overcharging to 4.4-4.8 V at 0.2-1C currents at -10 ℃ were experimentally investigated. The results show that there are two modes of battery degradation, linear fading at 0.2C charging, and two-stage linear fading with turning points at 0.5C and 1C charging. According to the incremental capacity analysis curve, the loss of active material is the main mechanism leading to battery degradation, followed by the loss of lithium ions, and the conductivity loss is the least.

Keywords: Lithium-ion battery; Low temperature; Overcharge; Degradation

1. INTRODUCTION

In recent years, due to environmental and energy problems, lithium-ion batteries (LIBs), as a renewable energy storage technology, have been widely used in fields such as electric vehicles and large-scale energy storage systems. Among LIBs, $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$ (NCM) battery has become the main development direction of LIBs in the future due to its high energy density.

LIBs have problems with overcharging in practical applications. Overcharging causes capacity degradation and increases in internal resistance, and it is more likely to occur at low temperatures. On the one hand, in practical application, LIBs are attached in series and parallel into battery packs. The cut-off voltage may be exceeded because of the inconsistency of the capacity and internal resistance between the batteries or the failure of the battery management system, resulting in overcharging limitedly [1]. On the other hand, during low-temperature charging, the charge transfer rate and lithium ions diffusion rate reduce, and the polarization increases significantly [2]. The internal resistance under low-temperature conditions is significantly higher than that under room temperature conditions, thus it is easier for charging to reach the charging cut-off voltage and then overcharging.

Studies on limited overcharging mainly focus on the overcharging characteristics and degradation mechanisms at room temperature. Liu et al. overcharged the NCM battery to 4.5 V and cycled, and found that the loss of the positive electrode active material is the main degradation factor [3]. Juarez-Robles et al. studied the impact of different overcharging voltages on lithium cobalt oxide (LCO) batteries at ambient temperature and found that when the voltage was higher than 4.5 V, the electrolyte decomposition and Lithium plating dominate the degradation of the battery [4]. When batteries are overcharged at room temperature, the degradation mechanisms of the battery mainly include thickening of SEI, the change of positive and negative electrode structure, electrolyte decomposition, and lithium plating, leading to the decrease of battery capacity and the increase of internal resistance. At the same time, thermal safety decreases, and thermal runaway is more likely to occur.

At present, there are limited studies when the ambient temperature is not room temperature. Ouyang et al. studied the battery degradation behavior during

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overcharging cycles at different ambient temperatures, and found that the 5 V overcharged battery is more sensitive to ambient temperature than the 4.5 V overcharged battery [5]. Su et al. studied the NCA battery degradation behavior by orthogonal method and found that the degradation is mainly caused by the loss of lithium ions when charging to 4.3 V at 0°C [6]. It can be found that the overcharging characteristics and degradation mechanisms of batteries are different at different temperatures. Therefore, the degradation mechanisms of overcharging at low temperatures need to be further studied.

Based on the above analysis, the life tests of NCM batteries at the low temperature (-10°C) were carried out. The purpose of the present work is to identify and quantify the degradation mechanisms of overcharging batteries at the low temperature with different charging currents and charging cut-off voltages. The degradation mechanisms of batteries were quantitatively analyzed by using the incremental capacity analysis curve.

2. EXPERIMENT

2.1 Lithium-ion batteries and test equipment

The 18650 $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$/graphite lithium-ion cells with nominal capacities of 2.6 Ah were used in this paper. A multi-channel battery test system (NEWARE CT-4008, 5V-6A) was used to conduct charge-discharge experiments in an environmental chamber (GUANGDONG BELL BTH-150TC). The accuracies of the voltage and current of the battery test system are both ±0.05% FS (Full Scale), and the maximum deviation of the temperature in the environmental chamber is ±1°C. The experimental devices are shown in Figure 1.

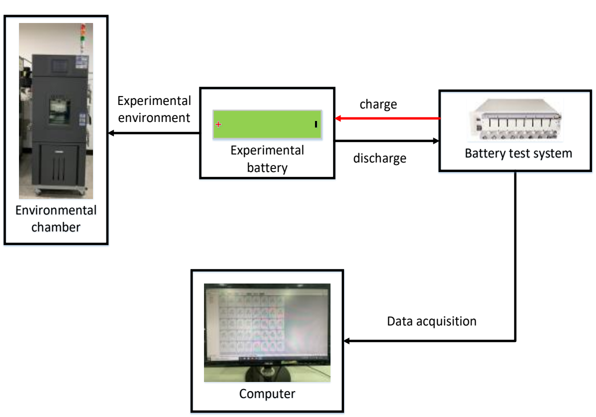


Figure 1 Schematic of the experimental setup

2.2 Reference performance test

A reference performance test (RPT) includes capacity tests and a low current rate (0.05C) charge-discharge test, and the purpose is to evaluate the basic performance of the battery.

The actual capacity after the low-temperature overcharging cycles is measured by two charge-discharge cycles. The current rate of the two charge-discharge cycles is 0.5C at 1 h rest between cycles. The discharge capacity of the second charge-discharge cycle is the actual capacity after the low-temperature overcharging cycles. The low current test with 0.05C is used to obtain the incremental capacity (IC) curve, which is an important method for non-destructive analysis of the battery degradation mechanisms.

In an RPT, two capacities are firstly tested, followed by the 0.05C rate charge and discharge test. Such an RPT can evaluate the basic performance of the battery.

2.3 Overcharging cycle tests at low temperatures

There were 12 cells tested under different conditions at -10 °C. Before the test, the cells were firstly put in the environmental chamber at -10°C for 3 h to ensure the heat balance of internal and external of the cell. Different test conditions are shown in Table 1.

Table 1 Overcharging test conditions at the low temperature

Cell number	Charging rate(C)	Charging cut-off voltage(V)
1	0.2	4.2
2	0.2	4.4
3	0.2	4.6
4	0.2	4.8
5	0.5	4.2
6	0.5	4.4
7	0.5	4.6
8	0.5	4.8
9	1	4.2
10	1	4.4
11	1	4.6
12	1	4.8

In Table 1, No. 1, 5, and 9 cells are blank control groups with the standard charging cut-off voltage. In addition to the experimental conditions in the table, the constant current-constant voltage (CC-CV) protocol is adopted for charging, the constant voltage cut-off current is 0.05C. At the same time, the discharge current is 0.5C. The tests were stopped after 50 low-temperature cycles or when the actual cell capacity measured by RPT was less than 10% of the initial capacity. The RPT is performed every 5 low-temperature cycles.

2.4 Initial battery characteristics

As there are 12 cells used in this paper, the cells need to be selected to ensure consistency. Before the experiment, all cells were activated with three charge-discharge cycles of 0.5C-0.5C current at 25 °C. The direct current internal resistance of the NCM battery changes little at 50% depth of discharge (DOD), thus the direct current (DC) internal resistance of 50% DOD was selected as the basis for selecting.

The average value of the capacity selected is 2.5298Ah, and the range is 0.81%. The average value of the DC internal resistance is 0.06817Ω, and the range is 1.58%. Therefore, it is considered that the cells with different experimental conditions could be compared.

3. RESULTS AND DISCUSSION

3.1 Capacity fade

The state of Health (SOH) index is usually used to compare the capacity fading. SOH is defined as the ratio of discharge capacity of the degradation battery to the initial capacity. Figure 2 shows the fading of battery capacity under the experimental conditions in this paper.

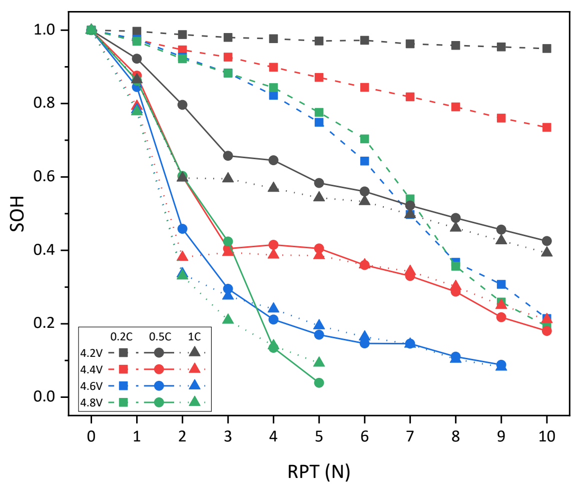


Figure 2 SOH changes with RPT

As can be seen from Figure 2, cell capacity fading is mainly divided into two modes. Mode 1 is linear fading in the whole experimental period, and mode 2 is two-stage linear fading with a turning point. The fading rate decreases after the turning point. Table 2 shows the fading modes of different cells.

Table 2 Fading modes of cells

	0.2C	0.5C	1C
4.2 V	mode 1	mode 2	mode 2
4.4 V	mode 1	mode 2	mode 2
4.6 V	mode 1	mode 2	mode 2
4.8 V	mode 1	mode 1	mode 2

It can be seen that the fading mode of 0.2C charged cells is mode 1, while there is a turning point for 0.5C and 1C charged cells, except the 4.8 V charged cell at 0.5C. The turning point of 0.5C charged cells is the 3rd RPT, and that of 1C charged cells is the 2nd RPT. As the capacity fading is linear, the capacity fading rates before the turning points were calculated, and the 0.2C charged cells without turning points can be considered to be also before the turning points. The results are shown in Figure 3.

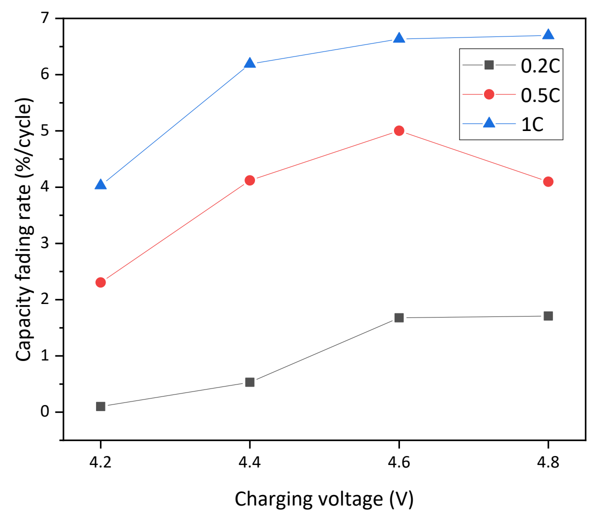


Figure 3 Cell capacity fading rate before the turning point

It can be seen from Figure 3 that before the turning point, the impact of the charging current on capacity is greater than the charging voltage. The battery fading rate increases with increasing charging current. When the cells were charged at 0.5C, the capacity fading rate of the 4.8 V charged cell is reduced compared with the 4.6 V charged cell. The reduction ratio of the capacity fading rate after the turning point is shown in Figure 4.

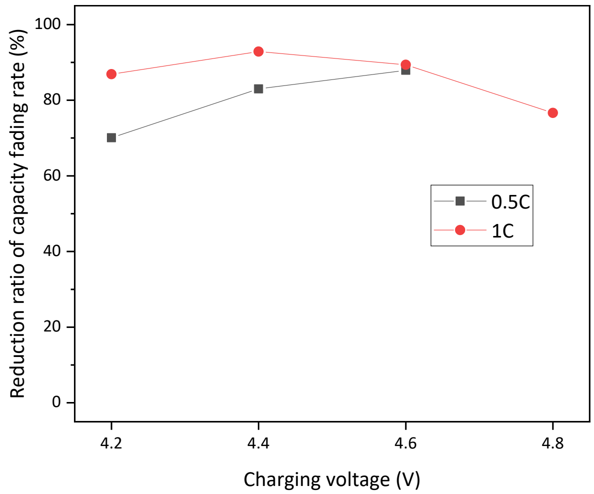


Figure 4 The reduction ratio of capacity fading rate after the turning point

The cells of fading mode 1 do not have the reduction ratio, and the reduction ratio of fading mode 2 after the turning point is more than 70%. It can be seen that the cell capacity fading rate varies greatly after the turning point, which is caused by the changes in the degradation mechanisms.

3.2 *Degradation mechanism analysis*

Generally speaking, the degradation mechanisms of LIBs include the loss of active material (LAM), the loss of lithium ion (LLI), and the conductivity loss (CL) [7]. Under the condition of low current charge and discharge, the battery works in an approximate equilibrium state, and the IC curve can highlight the changes of voltage platform in the Q-V curve. According to the IC curve, the degradation mechanisms of the battery can be identified [11]. Figure 5 shows the degradation mechanisms represented by the IC curve measured by the 1st RPT of 0.2C charged cells.

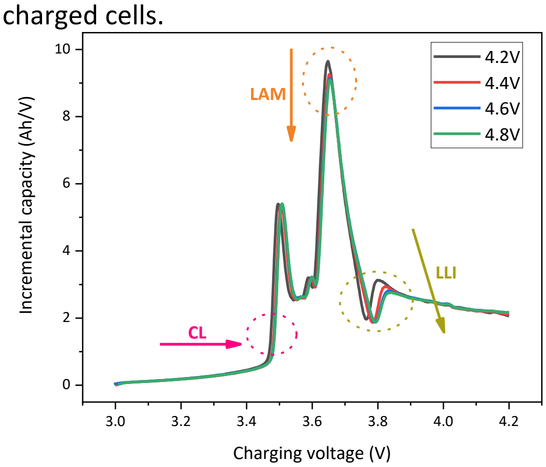


Figure 5 Degradation mechanisms represented by IC curve of the 1st RPT of the 0.2C charged cells

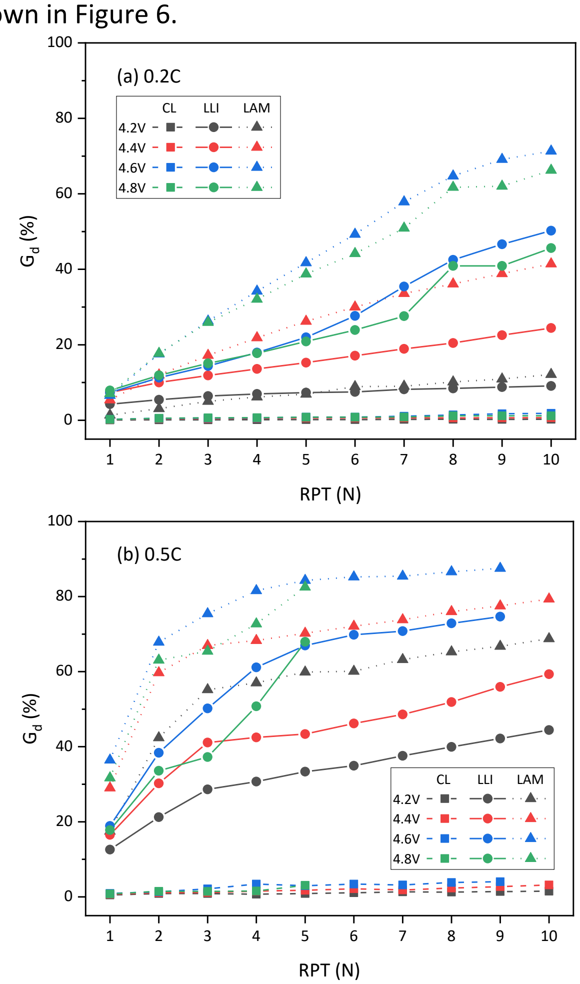
According to the literature, LAM and LLI can be quantified [8]. The growth G_d of each degradation mode can be calculated according to the IC curve. The specific calculation equations are shown in Equations (1)-(3).

$$G_{d,LAM,N}(\%) = \frac{abs(\max(\frac{\Delta Q}{\Delta V}))_1 - abs(\max(\frac{\Delta Q}{\Delta V}))_N}{abs(\max(\frac{\Delta Q}{\Delta V}))_1} \times 100 \quad (1)$$

$$G_{d,LLI,N}(\%) = \frac{abs(\max(Q))_1 - abs(\max(Q))_N}{abs(\max(Q))_1} \times 100 \quad (2)$$

$$G_{d,CL,N}(\%) = \frac{abs(\max(V))_1 - abs(\max(V))_N}{abs(\max(V))_1} \times 100 \quad (3)$$

From Equations (1)-(3), it can be seen that LAM can be obtained from the changes of the height of the peak, LLI can be obtained from the area of the peak, and CL can be obtained from the left-right translation of the IC curve. According to the calculation equations, the changes of battery degradation modes with RPT are shown in Figure 6.



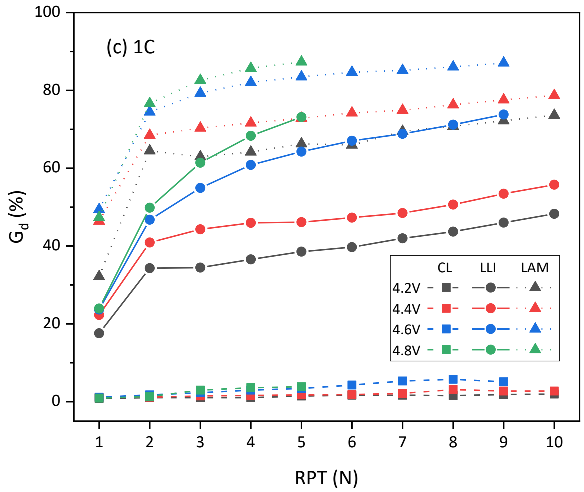


Figure 6 Changes of cell degradation modes with RPT
(a) 0.2C (b) 0.5C (c) 1C

It can be seen from Figure 6 that CL grows a little, and LAM grows fastest, followed by LLI. When the cells were charged at 0.2C, LLI and LAM increase linearly. When the cells were charged at 0.5C, LLI and LAM of the 4.2 V and 4.4 V charged cells show a turning point of the growth of G_d at 3rd RPT, and then the growth of G_d slow down. When the cells were charged at 1C, LLI and LAM have a turning point at 2nd RPT. It's worth noting that LLI and LAM are less than the 4.6 V charged cell when the cell was charged to 4.8 V at 0.5C, which is consistent with the capacity fading rate shown in Figure 3.

Overall, the trend of LLI and LAM is consistent with two modes of battery fading. There are no turning points of the cell charged to 4.6 V and 4.8 V at 0.5C. It can be considered that the turning point of cell capacity fading is caused by the changes of LLI and LAM. From 0.2C to 0.5C, the turning point of LLI and LAM will appear, and it will appear in advance from 0.5C to 1C.

In order to better explain the different fading modes of the battery capacity under the same RPT, the IC curve of the 5th RPT was calculated, which is no cells whose SOH have dropped below 10%, leading to the early end of the experiment. Figure 7 shows the results of CL, LLI, and LAM.

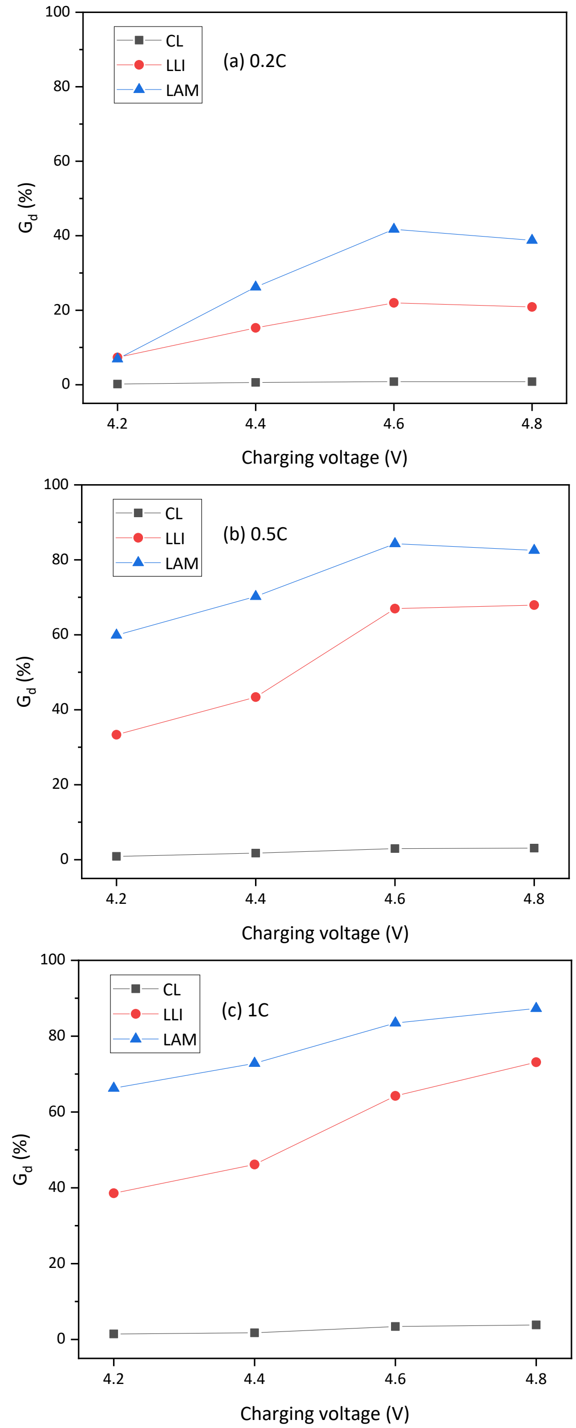


Figure 7 Calculation results of CL, LLI, and LAM of 5th RPT
(a) 0.2C (b) 0.5C (c) 1C

It can be seen from Figure 7 that at the 5th RPT, LAM has a significant contribution, followed by LLI, and CL is almost 0. When the cells were charged at 1C, LLI and LAM are slightly higher than that of 0.5C charged cells, and both of which are significantly higher than those of the 0.2C charged cells. It can be seen that the increase of LLI and LAM of the 0.2C and 0.5C charged cells slow down or even decrease when the cells were charged to 4.8 V.

However, when the cells were charged at 1C, LLI and LAM increase with increasing charging voltages.

Since CL has little effect on degradation, in order to better quantify the relative relationship between LAM and LLI, the calculated results of LAM/(LAM+LLI) at the 5th RPT are shown in Figure 8.

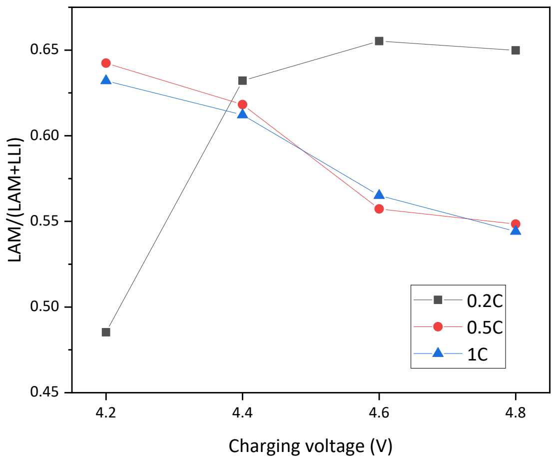


Figure 8 LAM/(LAM+LLI) results of 5th RPT

It can be seen from Figure 8 that when the cells were charged at 0.2C, the ratio of LAM first rises and then decreases with increasing charging voltage. When the cells were charged at 0.5C and 1C, the ratio of LAM decreases with increasing charging voltage, and the extent of both 0.5C and 1C charged cells is relatively consistent.

4. CONCLUSIONS

In this paper, the charging cycle tests of the NCM battery at -10°C were carried out. The degradation characteristics of overcharged cells at the low temperature were studied. The main conclusions are as follows:

1. There are two modes of battery capacity fading, one is linear fading (Mode 1) and the other is two-stage linear fading with a turning point (Mode 2). In fading mode 1, the effect of charging current on battery fading is greater than that of charging voltage, which is the same as the cells in fading mode 2 before the turning point. After the turning point, the reduction ratio of battery capacity of fading mode 2 is more than 70%.

2. Under the condition of overcharging at -10°C, the degradation mechanisms of NCM batteries are mainly LAM, LLI is the second, and CL is the least. The changing trend of LLI and LAM determines two modes of capacity fading. When the cells were charged at 0.2C, the proportion of LAM in LAM+LLI increases first and then decreases with increasing charging voltage, while which of the 0.5C and 1C charged cells decreases with increasing charging voltage.

For further industrial application, the results of this paper show that it is necessary to ensure cells consistency, otherwise, it will lead to rapid battery degradation. If cells were overcharged, they could only be allowed to withstand overcharging with smaller currents.

ACKNOWLEDGEMENT

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REFERENCES

[1] Yang N, Zhang X, Shang B, Li G. Unbalanced discharging and aging due to temperature differences among the cells in a lithium-ion battery pack with parallel combination. Journal of Power Sources 2016;306:733–41.

[2] Waldmann T, Hogg B-I, Wohlfahrt-Mehrens M. Li plating as unwanted side reaction in commercial Li-ion cells – A review. Journal of Power Sources 2018;384:107–24.

[3] Liu J, Duan Q, Ma M, Zhao C, Sun J, Wang Q. Aging mechanisms and thermal stability of aged commercial 18650 lithium-ion battery induced by slight overcharging cycling. Journal of Power Sources 2020;445:227263.

[4] Juarez-Robles D, Vyas AA, Fear C, Jeevarajan JA, Mukherjee PP. Overcharge and Aging Analytics of Li-Ion Cells. J. Electrochem. Soc. 2020;167(9):90547.

[5] Ouyang D, Chen M, Weng J, Wang J. A comparative study on the degradation behaviors of overcharged lithium - ion batteries under different ambient temperatures. Int J Energy Res 2020;44(2):1078 - 88.

[6] Su L, Zhang J, Wang C, Zhang Y, Li Z, Song Y et al. Identifying main factors of capacity fading in lithium-ion cells using orthogonal design of experiments. Applied Energy 2016;163:201–10.

[7] Han X, Ouyang M, Lu L, Li J, Zheng Y, Li Z. A comparative study of commercial lithium-ion battery cycle life in electrical vehicle: Aging mechanism identification. Journal of Power Sources 2014;251:38–54.

[8] Pastor-Fernández C, Uddin K, Chouchelamane GH, Widanage WD, Marco J. A Comparison between Electrochemical Impedance Spectroscopy and Incremental Capacity-Differential Voltage as Li-ion Diagnostic Techniques to Identify and Quantify the Effects of Degradation Modes within Battery Management Systems. Journal of Power Sources 2017;360:301–18.