Study of the factors affecting a lithium battery's aging behavior

Hongwei Wang [1, a], Xingzhou Guo [1, b], Jinyu Ma [1, c], Tiantian Huang [1, d],
Ziqiang Tao [1, e] and Guangcheng Xi [1, f]

[1] Key Laboratory of Consumer Product Quality Safety Inspection and Risk Assessment, State Administration for Market Regulation, Chinese Academy of Inspection and Quarantine, Beijing 100176, China.

[a] wanghw@caiq.org.cn, [b] guoxz@caiq.org.cn, [c] majy@caiq.org.cn, [d] huangtt@caiq.org.cn,
[e] taozq@caiq.org.cn, [f] xigc@caiq.org.cn

Abstract. It is the precondition and basis for ensuring the reasonable use of a battery to accurately calculate and predict the battery's aging state. However, there are a lot of difficulties in accurately calculating the aging state of a battery. For example, there are a variety of stresses that have an impact on the aging of the battery, such as, temperature, charging and discharging currents, end of charge/discharge voltages. A battery's aging behavior under a multi-stress effect has posed a tough challenge to experimental processes. Moreover, the way a different stress affects the aging of a battery is difficult to determine, and the coupling relations and coupling strength between different factors are not clear. Therefore, in this paper, the statistic method of analyzing major effects is used to have analyzed the degrees of the effect that the four stresses have on the battery's aging. The results indicate that, as ranked in order of from more primary factors to more secondary factors, the four stresses are: i1> V1> i2> T (constant charging current > end-of-charge voltage > constant discharge current > ambient temperature), and all these four stresses have a significant effect on the battery's capacity attenuation rate.

Keywords: lithium-ion battery; charge and discharge; the factors affecting; aging behavior.

1. Introduction

Throughout the service life of a battery, the pattern in its capacity attenuation and internal resistance increase will change. When the battery has aged to a certain degree, its capacity will decrease rapidly, namely, the "capacity plunge" phenomenon. In addition, when a "capacity plunge" happens to a battery, the battery is usually close to the end of its service life, and after the plunge, the pattern of aging behavior in the battery is more complicated and diversified. Therefore, this paper will discuss the battery's aging behavior before the occurrence of "capacity plunge", i.e. the pattern in a battery's capacity attenuation at the early stages of aging. During the use of a battery, the stresses affecting its electric performance parameters are many in varieties, including ambient temperature, humidity, mechanical pressure, electric current, electric voltage, and SOC range. It can be learnt from early investigation and research that, among many factors, the major stresses affecting a battery's electric performance are ambient temperature and the electric stress during its use [1-5]. In this study, 4 stresses, ambient temperature, constant charging current, end-of-charge current, and constant discharging current, are chosen and studied, so as to find out how the four stresses rank in order of from primary to secondary factors in a battery's electric performance attenuation.

2. Experiment

The experiments on Samsung ICR 18650-22P batteries (Li NixCoyMnzO2) in cyclic aging processes have been carried out under different conditions (including: ambient temperature (T), constant charging current (i1), end-of-charge voltage (V1), constant discharging current (i2), and 3 representative cases chosen for each operating mode), and 9 sets of cyclic aging experiments in different operating modes have been devised with the orthogonal table L9(3). The Fig.1 shows a picture of the experiment.

Fig. 1 Aging experiment

3. Analysis of the results

3.1 Results from analyzing main effects

Because the interactions between factors are evenly distributed among all the columns in the L9(34) table, the effects of the interactions between other stresses can be ignored when discussing the major causes of the stresses in every column. In this study, the effects of four stresses on the aging of a battery are taken into account all together, and the method of study the main effect of four stresses is similar to the case of a single stress. With the third column (T) taken as an example, the process of analyzing the main effect of factors in a multi-stress operating mode is described in the followings.

In this study, the response is to DF, and the formula for calculating the main effect of the temperature (T) at level 1(0°C) is (1), with the calculation result being 1.60. If a similar formula is used, it can be calculated that the main effects of T at levels 2 and 3 are 1.35 and 1.37, respectively.

$$\mathrm{E}_{\mathrm{T}(0°\mathrm{C})} = \frac{1}{\mathrm{m}} \times \frac{1}{\mathrm{n}} \times \left(\sum\nolimits_{\mathrm{T}=0°\mathrm{C}} \mathrm{DF}_{\mathrm{i}}\right) = \frac{1}{2} \times \frac{1}{3} \times \left(\sum\nolimits_{\mathrm{i}=1}^{3} \mathrm{DF}_{\mathrm{i}}\right) \tag{1}$$

$$\mathrm{E}_{\mathrm{T}(25°\mathrm{C})} = \frac{1}{\mathrm{m}} \times \frac{1}{\mathrm{n}} \times \left(\sum\nolimits_{\mathrm{T}=0°\mathrm{C}} \mathrm{DF}_{\mathrm{i}}\right) = \frac{1}{2} \times \frac{1}{3} \times \left(\sum\nolimits_{\mathrm{i}=4}^{6} \mathrm{DF}_{\mathrm{i}}\right) \tag{2}$$

$$\mathrm{E}_{\mathrm{T}(55°\mathrm{C})} = \frac{1}{\mathrm{m}} \times \frac{1}{\mathrm{n}} \times \left(\sum\nolimits_{\mathrm{T}=0°\mathrm{C}} \mathrm{DF}_{\mathrm{i}}\right) = \frac{1}{2} \times \frac{1}{3} \times \left(\sum\nolimits_{\mathrm{i}=7}^{9} \mathrm{DF}_{\mathrm{i}}\right) \tag{3}$$

In the formula (1), m is the number of identical sample batteries in each operating mode, and n is the number of the operating modes under the experimental conditions.

The main effect of the temperature reaches its strongest at level 1, and becomes the weakest at level 3. Therefore, the formula is (2) for calculating its main effect in response to DF, with the result being 0.25. See the Table 1.

$$\mathrm{F}_{\mathrm{T}} = \mathrm{Max}\left(\mathrm{E}_{\mathrm{T(i)}}\right) - \mathrm{Min}\left(\mathrm{E}_{\mathrm{T(i)}}\right) = \mathrm{E}_{\mathrm{T}(0°\mathrm{C})} - \mathrm{E}_{\mathrm{T}(25°\mathrm{C})} \tag{4}$$

The main effects of all four stresses in response to DF at different levels can be calculated using a similar method, as shown in the Fig. 2. Based on the definition of DF, it can be known that, the stronger the effect of the stresses is at a certain level, the faster the battery ages when it is cycled at this level of the stresses. Therefore, by analyzing the Fig.2, the effects of each stress at different levels on the aging of the battery can be obtained. By comparing the conclusions drawn with the orthogonal experimental method and those in existing literature using the method of controlling variables, the correctness of the orthogonal experimental method can be explained to a certain extent in analyzing the major causes of the effects on the aging of a battery.

Table 1. Main effect

Experimental conditions	Main effect
Ambient temperature T/°C	0.25
Constant charging current i1/C	1.09
End-of-charge voltage V1/V	1.08
Constant discharging current i2/C	0.84

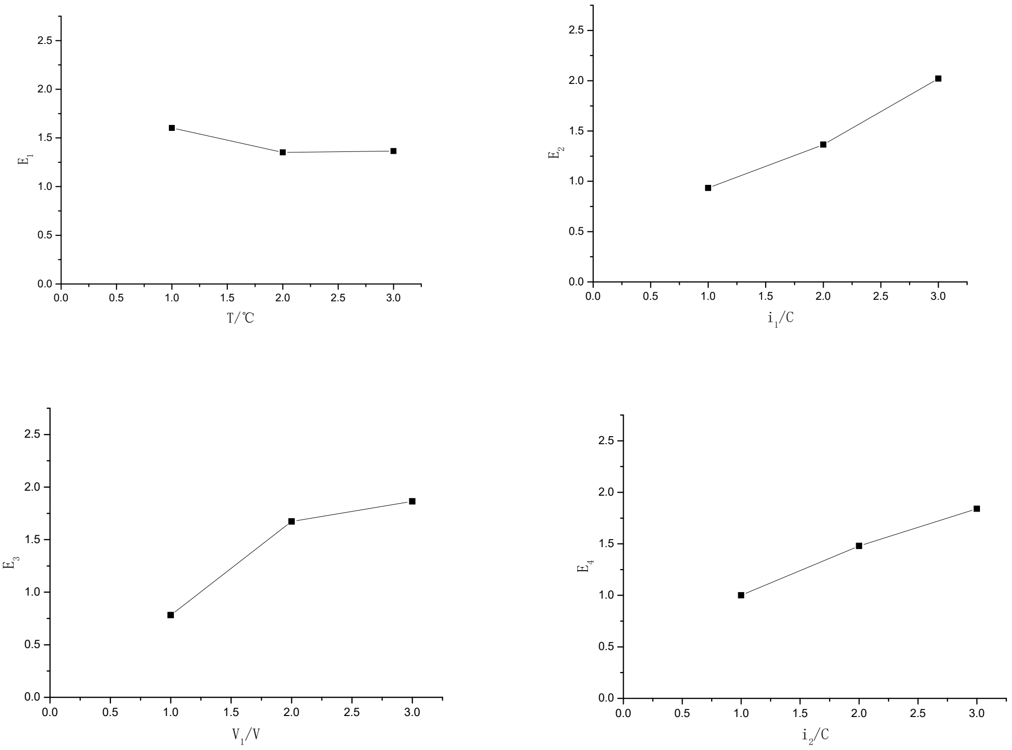

Fig. 2 The main effects of the four stresses at different levels in response to DF

3.2 Temperature

In the experiment, the three levels selected for the temperature are 0°C, 25°C and 55°C, respectively. The results in the Fig.2 indicate that, the value of DF for the aging of the battery reaches its highest at 0°C, which means the battery's capacity attenuates the fastest in this case. The results from existing studies indicate, the effect of temperature on a battery's capacity attenuation complies with the Arrhenius relation, that is, a battery's capacity attenuation rate increases with the rise in ambient temperature. However, when a battery is cycled at a lower temperature, it is easy for lithium extract to appear on the surface of its cathode, resulting in its total lithium ions being consumed somewhat, and speeding up the aging of the battery. Therefore, the effect of temperature stress on a battery's aging can be described with the formula (3). When the temperature is relatively low, EA,p mainly controls the battery's capacity attenuation rate (EA,p<0). When the temperature is relative high, EA,s mainly controls the battery's capacity attenuation rate (EA,s>0). Therefore, both high and low temperatures will speed up a battery's capacity attenuation rate, and this conclusion is consistent with that drawn from the orthogonal experiment.

$$r = A_P \cdot \exp\left\{-\frac{E_{A,\ p}}{K_B \cdot T}\right\} + A_s \cdot \exp\left\{-\frac{E_{A,\ s}}{K_B \cdot T}\right\} \tag{5}$$

3.3 Charging current

In the experiment, the three levels for the charging current are 0.2C, 0.5C and 1C, respectively. The results in the Fig.2 indicate, the value of DF for the aging of the battery increases as the charging current goes up, which means the battery's capacity attenuation rate positively correlates the charging current. It is proposed in the papers published by Zhang et al. that a higher charging current will help the uneven distribution of lithium ions on the surfaces of active particles, leading to locally too high concentrations of lithium ions, and resulting in higher over-potential, so as to induce lithium to be separated out. In addition, charging at a higher current will accelerate the rate of lithium ions going into and coming out of active particles, increasing the rate of active particles colliding and contracting, possibly inducing the active particles to break up, so as to result in the loss of active substances. Therefore, the conclusion drawn from the orthogonal experiment with charging current stress can be explained with the above theories, which indicates the credibility of the conclusions drawn from the orthogonal experiment.

3.4 End-of-charge voltage

In the experiment, 4.1 V, 4.2 V and 4.3 V are taken respectively as the end-of-charge voltage. The results in the Fig.2 indicate, the value of DF for the aging of the battery decreases as the end-of-charge voltage goes up, which means there is a positive correlation between the battery's capacity attenuation rate and the end-of-charge voltage. This conclusion is consistent with the research results that are already published so far, and can be comprehended through the aging mechanism of a battery. A high voltage during charge will cause the anode's voltage to rise, and the cathode's voltage to fall, so as to more easily induce the electrolyte to have a reduction reaction in the anode, and an oxidizing reaction in the cathode. Therefore, the conclusion drawn from the orthogonal experiment is trustworthy concerning the effect of an end-of-charge voltage on the aging of a battery.

3.5 Discharging current

In the experiment, 0.2C, 0.5C and 1C are taken respectively as the discharging current. The results in the Fig.2 indicate, the value of DF for the aging of the battery increases as the discharging current goes up, which means there is a positive correlation between the battery's capacity attenuation rate and the discharging current. This conclusion is consistent with the research results that are currently already published. Choi et al. have used the method of controlling variables to compare a battery's capacity attenuation rates at the discharging rates of 1C,1.2C and 1.4C, and found that the capacity attenuation speeds up as the discharging rate goes up. In addition, the conclusion drawn from the orthogonal experiment is trustworthy concerning the effect of a discharging current on the aging of a battery.

The above analytical results indicate the credibility of the orthogonal experimental method in studying the aging of a battery. In addition, the main effects of different stresses on the value of DF can be calculated, as shown in the Fig. 3 and Table 2. The results from calculating the main effect of every stress in the figure actually include three components: (1) the effect of the stress on the response; (2) the partly interaction between the four stresses; (3) experimental errors. The interaction between stresses is evenly distributed among all the columns in the L9(34) orthogonal table, and the value of each stress item's experimental error can be considered to be the same. The results in the Fig.3 indicate, these stresses have an obvious effect on the battery's aging. Moreover, the degree at which a stress affects a battery's capacity attenuation rate positively correlates the main effect of the stress. Therefore, in the order of from primary to secondary factors in the aging of a battery, the four stresses studied this time are: i1> V1> i2> T.

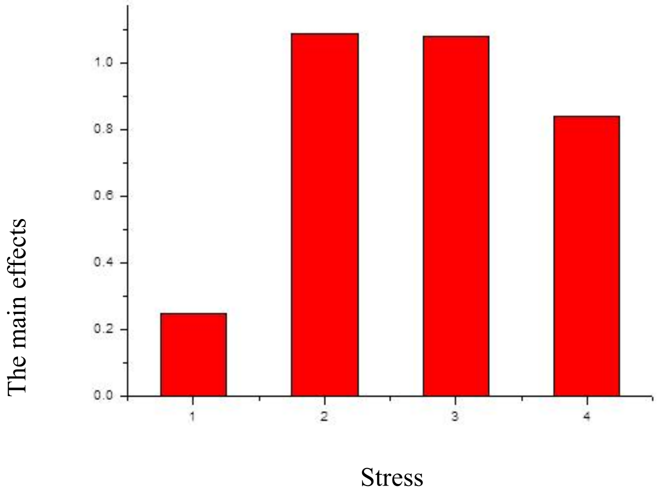

Fig. 3 The main effects of different stresses on the aging of a battery

Table 2. The main effects of different stresses on the aging of a battery

Stress	Experimental conditions
1	Ambient temperature T/°C
2	Constant charging current i_1/C
3	End-of-charge voltage V_1/V
4	Constant discharging current i_2/C

4. Summary

The degrees at which four stresses affect the aging of a battery have been studied with the statistical method of analyzing main effects, and the results indicate that, in the order of from primary to secondary factors in the aging of the battery, the four stresses are ranked as: i1> V1> i2> T (constant charging current > end-of-charge voltage > constant discharging current > ambient temperature), and all these four stresses have an significant effect on the battery's capacity attenuation rate. In the process of analyzing main effects, this paper has compared the results from orthogonal experiments with those in existing published literature that are obtained by studying the effects of different stresses on the aging of a battery using the method of controlling variables, indicating somehow the correctness of the conclusion from orthogonal experiments.

It needs to be noted that, although the relations in terms of prominence between different stresses compared in this study relates to the range within which each stress level is chosen in the experimental design, the stress levels in this study are selected by reference to the descriptions about a particular battery in its handbook, and the range is as extensive as possible so as to cover all the possible levels that each stress may reach during the use of the battery. Therefore, the conclusion drawn from that is capable of providing guidance on how to choose stresses in follow-up studies.

5. Acknowledgements

The work was supported in part by NQI project: National key R & D program of China (2024YFF0619700).

References

[1] Su Laisuo, Study of Energy Type Lithium-ion Cell Degradation Behavior under Multiple Stresses. Beijing: Tsinghua University, 2016.

[2] Wang Caijuan, Su Laisuo, Song Yang, Zhang Jianbo. Aging analysis of Li-ion battery based on relation of resistance-capacity. Battery Bimonthly, 2016, 46(6):317-320.

[3] Su L, Zhang J, Wang C, et al. ldentifying main factors of capacity fading in lithium ion cells using orthogonal design ofexperiments: Applied Energy, 2016, 163, 201-210.

[4] Yan Shengrui, Sun Xiaohan, Wang Dan, Liu Xiaolei. The Aging Behavior Analysis of Lithium-ion Batteries Using Different Charging Strategy. Automobile Technology & Material, 2021, 11: 42-46.

[5] Xiang Yue, Jiang Bo, Dai Haifeng. Deep Learning Hybrid Model for Lithium-Ion Battery Aging Estimation and Prediction. Journal of Tongji University (Natural Science Edition). 2024, 52(S1): 215-222.