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Study on Evaluation Method of Aging Degree of Lithium-ion Batteries

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Summary

Traditional, the main basis for evaluating the aging degree of batteries is the capacity decline and the increase of internal resistance. However, this evaluation method can not accurately reflect the real capability of batteries. For example, a battery may not be low in capacity, but in fact its performance is so poor that it can not meet the load requirements. Therefore, we create different battery aging paths through aging cycle experiments.Taking one hundreds of charging and discharging cycles as one cycle, Capacity calibration and power characteristic test of the test battery are carried out.The experiment shows that it is not imperfection to evaluate the aging degree only according to the capacity fading of the battery. It should also be comprehensively evaluated from the perspective of battery power. So this paper proposes a method to evaluate the aging degree of battery by using the maximum power of battery. At the same time, a Thevenin RC circuit is used as the equivalent circuit and the parameters are identified. It provides a basis for comprehensively evaluating the aging degree of power lithium-ion batteries. The correlation between ohmic resistance and polarization internal resistance of battery and battery power was also found.

Key Words: *Lithium-ion battery, Aging degree, Power characteristics*

1 Introduction

As a time-varying non-linear electrochemical system, the aging process of power batteries is affected by random factors such as working conditions and environment in the applications of electric vehicles and new energy rail transit vehicles. The degradation mechanism of power batteries is very complicated.

During the aging process of the battery, the capacity decline and the increase of internal resistance are accompanied by the occurrence. We found that the power loss of batteries under different aging paths was different when the same capacity was lost. Therefore, it is imperfect to evaluate the aging condition only according to the decline of battery capacity, and the change of battery power should be considered.

Based on the aging degree of lithium-ion batteries for new energy vehicles, this paper studies the influencing factors and testing methods of battery cycle life, and studies the life of single battery and series battery from the point of view of battery fading mechanism and actual battery management.Through the equivalent circuit parameter identification, it provides a basis for comprehensively evaluating the aging degree of power lithium-ion batteries. At the same time, based on a large number of battery life test data, this paper focuses on the cycle degradation process and degradation mechanism of power lithium-ion batteries under different test conditions. It is of great practical significance to popularize the application technology of power lithium-ion batteries and their groups in electric vehicles and smart grid energy storage technology.

2 Aging mechanism analysis

In view of the specific application environment of batteries, determining the aging mechanism is one of the most important and challenging tasks and goals for battery applications. Lithium-ion batteries are actually lithium-ion concentration cell, with positive and negative electrodes made up of two different lithium-ion intercalation compounds.

When charging lithium-ion batteries, Li^+ are detached from the positive electrode and embedded into the negative electrode by electrolyte. At this time, the negative electrode is in the lithium-rich state and the positive electrode is in the lithium-poor state. On the contrary, Li + is detached from the negative electrode and embedded into the positive electrode by electrolyte. The positive electrode is in the lithium-rich state and the negative electrode is in the lithium-poor state. During charge-discharge cycles, Li^+ reacts "embedding-de-embedding" on the positive and negative electrodes respectively, and Li^+ moves back and forth between the positive and negative electrodes.

The aging process of batteries is very complicated because of the coupling effect of working environment and operating mode on the aging process of batteries. Therefore, the aging phenomena such as capacity decline and impedance increase do not depend on the same factors. The origin of cell aging mechanism can be chemical or mechanical, and it is strongly dependent on the composition of active materials of positive and negative electrodes.

We mainly evaluate the aging degree of lithium ion battery from two aspects: external characteristics and internal characteristics.

2.1 External characteristics of battery

The main external characteristics of battery aging are capacity fading and internal resistance increasing. The electrochemical reasons for this phenomenon are different. They have different origins and nonlinear dependence.

2.2 Battery internal characteristics

The internal characteristics of the battery are mainly manifested in three aspects: the change of SEI film, the loss of active material and lithium ion. SEI film is formed naturally when the battery is first charged. It is a natural barrier between the negative material and electrolyte of the battery. It is used to prevent the loss of active material and the reduction of electrolyte caused by the corrosion of the negative electrode by electrolyte. Continuous formation, dissolution and regeneration of SEI film will lead to lithium ion loss.

The loss of active material on the surface of the electrode will increase the impedance of the electrode. The potential difference between electrode surface and electrolyte caused by high SOC, overcharge and overdischarge will accelerate this phenomenon. High temperature will lead to poor permeability of SEI membrane to lithium ions, thus increasing the impedance of the negative electrode. Low temperature can cause lithium metal to precipitate and deposit on the surface of the negative electrode.

3 Experimental design and analysis data

In this chapter, the different aging paths of power lithium-ion batteries are analyzed. In order to establish the relationship between the key working characteristics of lithium-ion batteries under different operating modes and their internal aging mechanism, a large number of systematic tests are carried out.

3.1 Aging cycle test

Experimental subject : Three lithium-iron phosphate battery with capacity of 60Ah.

Experimental purposes: Make No. 1 battery in overcharge state, No. 2 battery in full discharge state (benchmark), No. 3 battery in overcharge and overdischarge state.

Experimental steps:

(1) Three batteries were discharged to 2.8V cut-off, and the No. 1 battery was charged with 1% capacity (0.6Ah), and the No. 3 battery was discharged with 1% capacity.

(2) The 3 batteries are connected in series and charged with CCCV at 1C multiplying current, Standing for 0.5 hours, discharging the No. 2 battery with 1 C rate current crosswise to 2.8 V, standing for 10 minutes, then discharging the No. 2 battery with C/3 rate current to 2.8 V. Stand for 0.5 hours.

(3) Cycle step (2), No. 1 battery is always in the overcharge state, No. 3 battery is always in the overcharge and overdischarge state (small initial capacity). In the process of aging cycle, capacity calibration and HPPC test are carried out respectively in a hundred cycles.

3.1.1 Capacity calibration

The power battery was charged with standard CCCV at C/3 current, and then discharged to the cut-off voltage at the same current. The discharge capacity is taken as the maximum available capacity of the current battery. Battery capacity under different aging paths can be obtained.

Six nodes, 0, 50, 100, 200, 300 and 400 cycles, were selected to measure the maximum available capacity of the three batteries for six times respectively.The numerical value is shown in Table 1, and the broken line diagram is drawn to get Figure 1.

3.1.2 HPPC

According to the FreedomCAR battery experiment manual, the composite pulse power test is adopted(HPPC test). The purpose of the test is to identify the parameters of the battery models under different charging conditions and calculate the 10s power.

Experimental steps: (1) In the discharge stage, the SOC of the battery group was reduced from 0.9 to 0.2, and eight HPPC experiments were carried out (180A constant current discharge for 10 seconds, 40 seconds at rest, 135A charge for 10 seconds). (2) During the charging stage, the SOC of the battery group was increased from 0.1 to 0.8, and eight HPPC experiments were carried out (180A constant current charging for 10 seconds; static charging for 40 seconds; 135A discharging for 10 seconds).

Data processing: Calculate the power of charging for 10 seconds and discharging for 10 seconds, respectively.The formula is as follows:

$$P_{DCH} = \frac{V_{MIN}\,(OCV_{DCH} - V_{MIN})}{R_{DCH}}, \qquad R_{DCH} = \frac{OCV_{DCH} - V_{10s}}{I_{DCH}} \tag{1}$$

$$P_{CH} = \frac{V_{MAX}\,(V_{MAX} - OCV_{CH})}{R_{CH}}, \qquad R_{CH} = \frac{V_{10s} - OCV_{CH}}{I_{CH}} \tag{2}$$

Through data processing, the power characteristics of three batteries on six nodes can be obtained. As shown in Table 2, and draw its broken line diagram to get Figure 2.

3.2 Analysis of experimental results

As can be seen from Table 1, the attenuation rate of No. 1 battery capacity is 2.61%, that of No. 2 battery capacity is 1.68%, and that of No. 3 battery capacity is 1.69%.Table 2 shows the results of battery power test under different aging paths.

Table1. Test results of battery capacity under different aging paths

	1	2	3
0	57.636	57.271	56.001
50	57.816	57.601	56.365
100	57.517	57.376	56.078
200	56.965	56.96	55.712
300	56.629	56.638	55.396
400	56.131	56.308	55.055
Attenuation rate	2.61%	1.68%	1.69%

Table2. Test results of battery power under different aging paths

	1	2	3
0	1218.7636	1039.6235	1148.0000
50	1183.4009	1066.6988	1246.0000
100	1051.6535	1225.0000	1170.8646
200	1043.4375	1209.6000	1162.9091
300	1017.5817	1204.1267	1143.1149
400	1006.1124	1188.8072	1128.2008

As you can see from Figures 1 and 2, battery capacity and battery power have experienced a process of first rising and then falling.To personify batteries is like the ability of a man to be the best in his youth.Therefore, when evaluating the aging degree of batteries, we should look for the maximum capacity and power of batteries as the starting point.

Figure. 1 and 2 are normalized to get Fig. 3. It can be seen that the power loss under different aging paths is different when the same battery capacity is lost.

Therefore, it can be concluded that it is imperfect to evaluate battery life only by residual capacity. It also needs comprehensive evaluation from the power point of view.

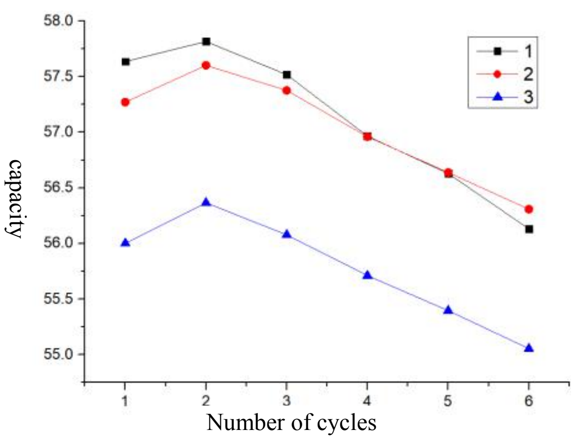


Fig.1 Changes of capacity decline under different aging paths

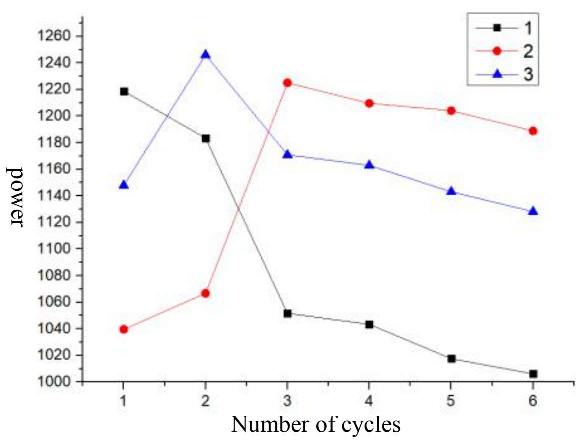


Fig.2 power degradation under different aging paths

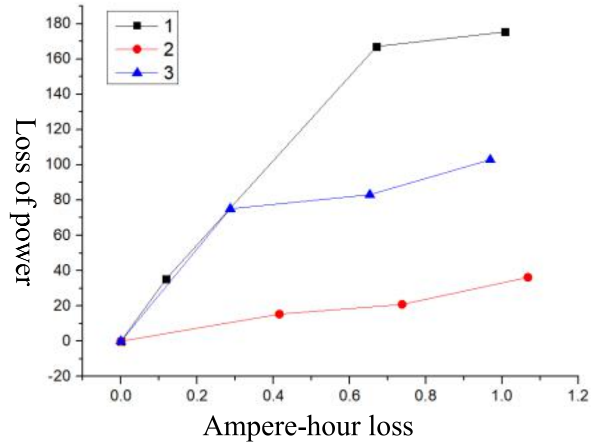


Fig.3 Variation of power loss and ampere-hour loss under different aging paths

3.3 Parameter identification

3.3.1 Model selection

The first order RC circuit structure of the Thevenin model is chosen to describe the internal resistance and polarization characteristics of the battery.

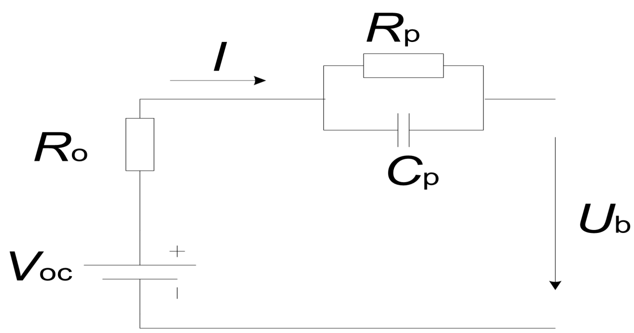


Fig. 4 first order RC circuit structure

Model input： I

Model output： $U=-U_b+V_{oc}$

Model equation： $V_{oc}=U_b+IR_o+U_p \qquad \dot{U}_p=-\frac{U_p}{C_pR_p}+\frac{I}{C_p}$

The difference equations of the system are as follows：

$$U(k)=-\alpha_1 U(k-1)+\beta_0 I(k)+\beta_1 I(k-1) \tag{3}$$

The least squares recursive algorithm is used to identify the parameters of the system. This method has strong correction. Whenever the data is input at the new time, it will correct the previous estimate and get a new estimate.

$$R_0 = \frac{\beta_0 - \beta_1}{1-\alpha_1} \quad (4) \qquad R_P = \frac{2(\beta_1 - \alpha_1\beta_0)}{1-\alpha_1^2} \quad (5) \qquad C_P = \frac{T(1-\alpha_1)^2}{4(\beta_1 - \alpha_1\beta_0)} \quad (6)$$

3.3.2 Data analysis

1) The curves of internal resistance R0 at each SOC point and the curve of power at each SOC point are compared：

Battery No. 1

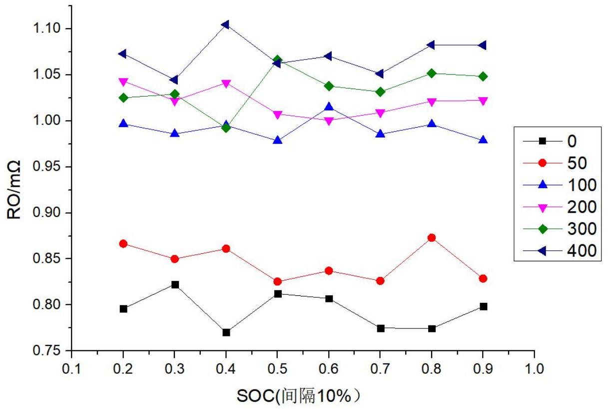


Figure.5 Changes of internal resistance under different aging degrees

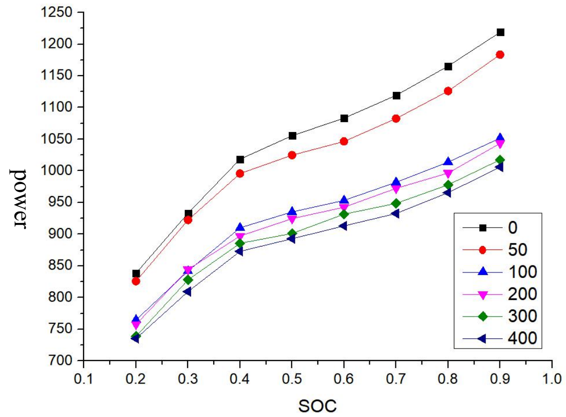


Figure.6 Power Variation under different aging degrees

Battery No. 2

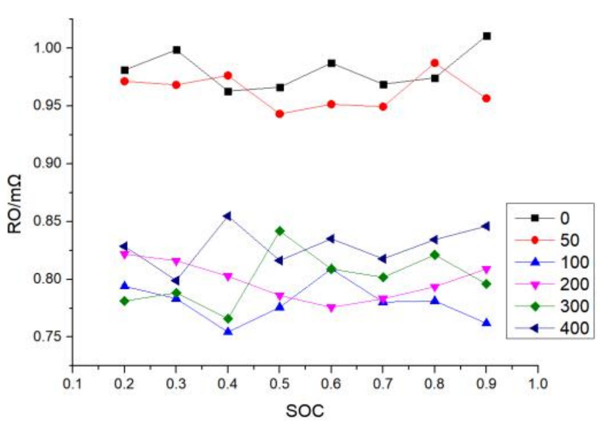


Figure.7 Changes of internal resistance under different aging degrees

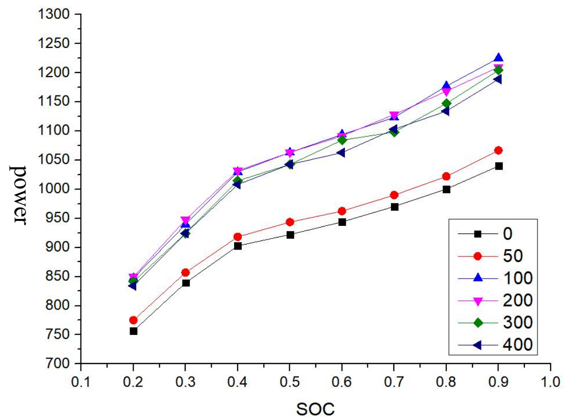


Figure.8 Power Variation under different aging degrees

Battery No. 3

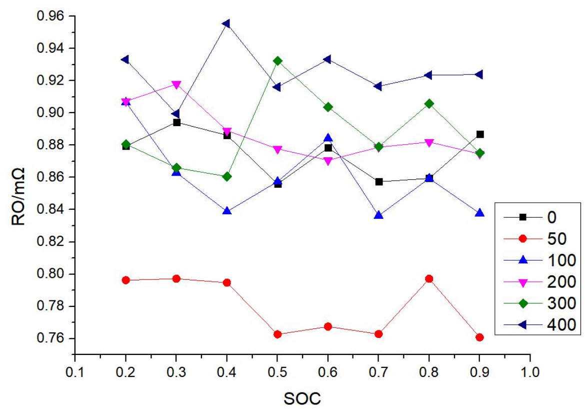


Figure.9 Changes of internal resistance under different aging degrees

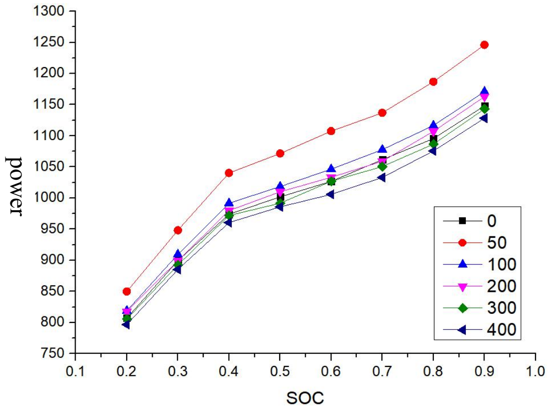
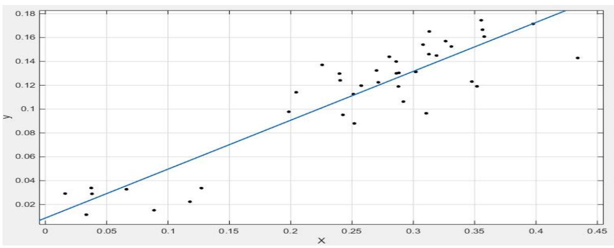


Figure.10 Power Variation under different aging degrees

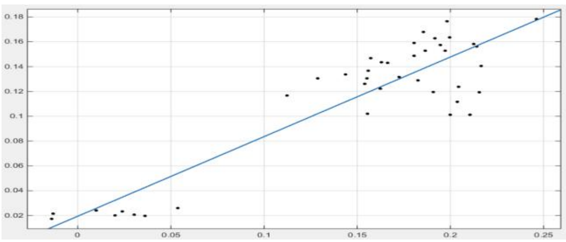
2) Integrate the above two group drawings. The scatter plots of the power decline rate, the increase rate of internal resistance and the increase rate of polarization internal resistance of the three monolithic batteries are shown in the figure.

Battery No. 1



R^2=0.8275

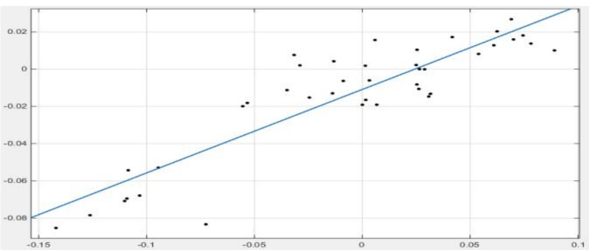
Fig. 11 Scatter distribution of power decay rate and internal resistance increase rate



R^2= 0.8111

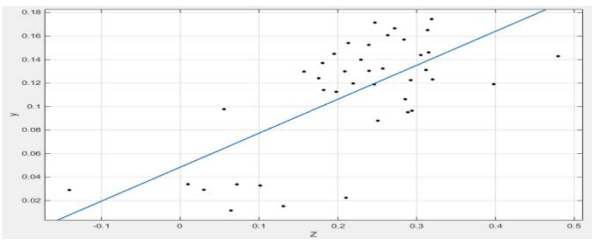
Fig. 12 Power dissipation rate and polarization internal resistance increase rate distribution

Battery No. 2



R^2= 0.7969

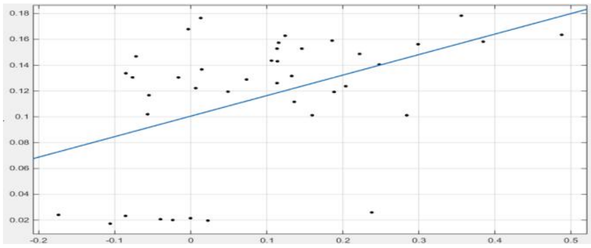
Fig. 13 Scatter distribution of power decay rate and internal resistance increase rate



R^2=0.4651

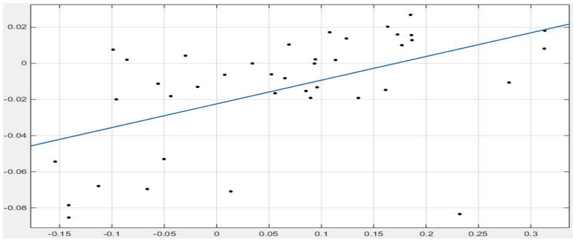
Fig. 14 Power dissipation rate and polarization internal resistance increase rate distribution

Battery No. 3



R^2= 0.2115

Fig. 15 Scatter distribution of power decay rate and internal resistance increase rate



R^2= 0.277

Fig. 16 Power dissipation rate and polarization internal resistance increase rate distribution

4 Conclusion and Prospect

Different aging paths are created through aging cycle experiments. It is found that the traditional method of evaluating battery aging based on the decline of battery capacity is not perfect, and it should be evaluated comprehensively from the perspective of battery power. From the scatter plots of power fading rate, internal resistance increasing rate and polarization internal resistance increasing rate, it can be seen that the distribution of scatter points has a general trend. The scatter distribution map is linearly fitted by MATLAB, and the fitting accuracy is obtained. From the fitting accuracy, the ohmic resistance and polarization resistance of the battery have an impact on the power, and the ohmic resistance has a greater impact on the battery power.

At the same time, we can also see that the correlation between internal resistance and polarization resistance for power is different when the battery experiences different aging paths, which indicates that the internal resistance has reached different aging state.Therefore, the reliability of evaluating the aging degree of batteries based on the maximum power of batteries is proved.

In the follow-up work, in order to explore the relationship between the internal state of batteries and SOP, and get the model of evaluating battery aging with SOP. Therefore, ICA test should be carried out in every 100 cycles of batteries to analyze the data of internal changes, so as to establish a SOP-based battery aging evaluation method.

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