# Analysis on the capacity degradation mechanism of a series lithium-ion power battery pack based on inconsistency of capacity*

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The lithium-ion battery has been widely used as an energy source. Charge rate, discharge rate, and operating temperature are very important factors for the capacity degradations of power batteries and battery packs. Firstly, in this paper we make use of an accelerated life test and a statistical analysis method to establish the capacity accelerated degradation model under three constant stress parameters according to the degradation data, which are charge rate, discharge rate, and operating temperature, and then we propose a capacity degradation model according to the current residual capacity of a Li-ion cell under dynamic stress parameters. Secondly, we analyze the charge and discharge process of a series power battery pack and interpret the correlation between the capacity degradations of the battery pack and its charge/discharge rate. According to this cycling condition, we establish a capacity degradation model of a series power battery pack under inconsistent capacity of cells, and analyze the degradation mechanism with capacity variance and operating temperature difference. The comparative analysis of test results shows that the inconsistent operating temperatures of cells in the series power battery pack are the main cause of its degradation; when the difference between inconsistent temperatures is narrowed by 5 °C, the cycle life can be improved by more than 50%. Therefore, it effectively improves the cycle life of the series battery pack to reasonably assemble the batteries according to their capacities and to narrow the differences in operating temperature among cells.

**Keywords:** lithium-ion battery pack, series, capacity degradation, dynamic stress

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## 1. Introduction

Lithium-ion battery packs have been widely used as energy sources. As one of the important types of connection, series has an important influence on the cycle performance and service life of power battery pack. The degradation mechanism of its capacity is an important foundation to study its cycle life. Therefore, scholars around the world have conducted a lot of research on the cycle life of cells and power battery packs.

The curing of cathode active ion and the growth of solid electrolyte interphase (SEI)[1–3] are the main factors of the performance degradation of lithium-ion power battery. The degradation of a lithium-ion power battery is related to both the stability of its internal electrochemical system[4–10] and the working conditions of the power battery pack, in particular, charge rate, discharge rate, and operating temperature. Some scholars have conducted in-depth study and analysis for the effect of temperature on the cycle life or shelf life[11,12] and described the effect by using the Alan Vilnius equation. In Refs. [13]–[15], the effect of discharge rate has been qualitatively analyzed on the cycle life of lithium-ion battery in chemical mechanism. Smith and Wang,[16] and Ni *et al.*[17] established the cycle life models of different discharge rates. Li *et al.*[18] have studied the capacity degradation of a lithium-ion power battery with operating temperature, charge–discharge voltage, charge rate, and discharge rate, and thus clarified the importance of discharge rate and charge cut-off voltage for its life.

In addition to the cell factors, the short-board effect caused by the inconsistency between cells is also a factor which influences the degradation of lithium-ion power battery packs. Wang *et al.*[19] studied the consistency and degradation of a lithium-ion power battery, and reached the conclusion that operating temperature had a significant effect on the degradation of its performance and the extension of performance differences was an important factor for the performance degradation of a power battery pack. Li *et al.*[20] analyzed the inconsistency of a series power battery pack in the charging process, and designed an equalizing charging system to improve the inconsistency and extend its cycle life. However, the quantitative study of degradation has not been considered so far.

Due to the diversification and intercoordination of influencing factors, there has been no deterministic function or precise model to establish the degradation process of power

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battery. It is an effective method to establish the degradation law of cell based on the results of experimental data, and correct the model parameters according to the differences in battery structure and materials. Wu *et al.*[21] predicted the cycle life with linear extrapolation and accelerated degradation curve extrapolation. Christophersen *et al.*[22] proposed a prediction model of power degradation for the second generation of lithium-ion battery with artificial neural network. This model can accurately predict the cycle life of such a battery after its power has degraded by 50% due to a low fitting error. Honkura *et al.*,[23] Ramadesigan *et al.*[24] and Roscher *et al.*[25] conducted predictive analysis for the capacity degradation of power battery by the charging and discharging curve. Such methods are used to carry out comparison and modeling based on the degradation data, so they provide a good foundation for the research of power battery pack.

In this paper we construct a degradation model under constant stress parameters on the basis of the degradation data, and then establish the degradation model under dynamic stress parameters according to the current residual capacity of a Li-ion cell. With the analyses of the charging and discharging process of series power battery pack, we establish a capacity degradation model under inconsistent capacity of cells, and conduct parameter sensitivity analysis and experimental comparison analysis.

## 2. Degradation model under dynamic stress for power battery

### 2.1. Capacity degradation model under constant stress parameters for a power battery

#### 2.1.1. Assumptions of the accelerated degradation model

The accelerated degradation test of a power battery investigates the degradation path, cycle life, and reliability index[26] under normal stress or at any other stress level using the degradation path under high stress such as high temperature, high charging rate, high discharging rate, and high depth of discharge. Then, we can conduct comparative analyses for the degradation under different stress intensity conditions, and calculate the degradation values of a certain stress at different levels.

The following assumptions are made for the accelerated degradation test of a power battery.

(i) The accelerated stress types and stress levels selected can only change the degradation speed of the power battery, without changing its failure mechanism;

(ii) The accelerated stress selected can regularly accelerate the degradation rate of the product.

In this paper, the operating temperature, charge rate, and discharge rate are selected as the accelerated stress of power battery. Meanwhile, in order to ensure that the failure modes and failure mechanisms of the battery do not change, the stress level selected meets the following requirement: $T \in (283\ \mathrm{K}, 323\ \mathrm{K})$, $R_\mathrm{c} \in (0.1\ \mathrm{C}, 2.0\ \mathrm{C})$, and $R_\mathrm{d} \in (0.2\ \mathrm{C}, 3.0\ \mathrm{C})$. In this paper, $T$ represents the operating temperature of battery, $R_\mathrm{c}$ the charge rate, $R_\mathrm{d}$ the discharge rate, $C_\mathrm{R}$ the rated capacity of battery, $t$ the cycle index of battery and it can also be treated in the manner of continuous time as a generalized time.

#### 2.1.2. Capacity degradation model under single stress parameters

According to the statistics of experimental degradation data sample, the capacity degradation of a power battery under stress conditions is of Gaussian degradation process, i.e., $x(s,n) \sim N\left(u(s,n), \sigma^2(n)\right)$.

After conducting curve fitting and degradation analysis for $\hat{u}(s,n)$ of experimental data, it can be seen that the capacity degradation of power battery can be represented by the following function:

$$u(s,t) = f_i(s) \cdot t^{h_i(s)}, \tag{1}$$

where $h_i(s)$ represents the constant obtained through curve fitting, $s$ the stress type. $T$ ($i = 1$, $h_1(T)$ a constant), $R_\mathrm{d}$ ($i = 2$, $h_2(R_\mathrm{d})$ is a constant) and $R_\mathrm{c}$ ($i = 3$, $h_3(R_\mathrm{d})$ is a constant), can be separately selected.

##### 2.1.2.1. Capacity degradation model under temperature stress parameters

Based on the Arrhenius model,[27] the relationship between degradation rates under operating temperature $T$ is as follows:

$$f_1(T) = k \exp(F/T).$$

Based on Eq. (1) and supposing $G = \ln k$, the capacity degradation model under stress parameter $T$ is given by

$$u(T,t) = f_1(T) \cdot t^{h_1(T)} = \exp(G + F/T) \cdot t^{h_1(T)}. \tag{2}$$

##### 2.1.2.2. Capacity degradation model under double stress parameters of charge rate and discharge rate

According to Tong *et al.*'s,[28] Zheng *et al.*'s,[29] and Omar *et al.*'s[30] reports on the Peukert equation in a lithium-ion battery, the Peukert equation can be used to study the capacity degradation of a lithium-ion battery. When taking charge rate and discharge rate as the accelerated stress, the coefficient and stress of degradation equation satisfy the following formula:

$$f_i(s) = D s^{c'} + E, \tag{3}$$

where $D$ and $c'$ are normal numbers; $E$ is a constant; when $i = 2, 3$, values of $s$ denote discharge rate $R_\mathrm{d}$ and charge rate $R_\mathrm{c}$, respectively.

Based on Eqs. (1) and (3), the capacity degradation model under the stress parameter of $R_\mathrm{d}$ is achieved as

$$u(R_\mathrm{d}, t) = \left(D_\mathrm{d} \cdot R_\mathrm{d}^{c'_\mathrm{d}} + E_\mathrm{d}\right) \cdot t^{h_2(R_\mathrm{d})}, \tag{4}$$

where $D_{\rm d}$, $c'_{\rm d}$, $E_{\rm d}$, and $h_2(R_{\rm d})$ are constants.

In a similar way, the capacity degradation model under the stress parameter of $R_{\rm c}$ can be given by

$$u(R_{\rm c},t)=\left(D_{\rm c}\cdot R_{\rm c}^{c'_{\rm c}}+E_{\rm c}\right)\cdot t^{h_3(R_{\rm c})}, \tag{5}$$

where $D_{\rm c}$, $c'_{\rm c}$, $E_{\rm c}$, and $h_3(R_{\rm c})$ are constants.

### 2.1.3. Capacity degradation model under stress parameters of $(T,R_{\rm c},R_{\rm d})$

The capacity degradation in the process of charging and discharging cycle of power battery is the accumulation of the slight degradation in each charging and discharging process. Assuming that the two kinds of degradations are independent of each other, the accumulations of degradation between in charging and discharging process have a linear relationship.

The degradation equation of battery capacity under the double stress conditions of $(T_0,R_{\rm c},R_{\rm d})$ can be calculated as

$$\begin{aligned}u(T_0,R_{\rm c},R_{\rm d}) &= u(T_0,R_{\rm c},R_{\rm d0})+u(T_0,R_{\rm c0},R_{\rm d})\\ &\quad -u(T_0,R_{\rm c0},R_{\rm d0})\\ &= u(R_{\rm c},t)+u(R_{\rm d},t)-u(T_0,t).\end{aligned}$$

Furthermore, we have

$$\begin{aligned}u(T_0,R_{\rm c},R_{\rm d}) &= \left(D_{\rm c}\cdot R_{\rm c}^{c'_{\rm c}}+E_{\rm c}\right)\cdot t^{h_3(R_{\rm c})}\\ &\quad +\left(D_{\rm d}\cdot R_{\rm d}^{c'_{\rm d}}+E_{\rm d}\right)\cdot t^{h_2(R_{\rm d})}\\ &\quad -\exp(G+F/T_0)\cdot t^{h_1(T)},\end{aligned} \tag{6}$$

where $T_0$, $R_{\rm c0}$, $R_{\rm d0}$ are the fixed values of conventional charge–discharge process in cycle life testing program. In this paper, $T_0=298$ K, $R_{\rm c0}=0.5$ C, and $R_{\rm d0}=0.5$ C.

The accelerated degradation factors of temperature stress are as follows:

$$\begin{aligned}\xi^2_{T2,T1}(t) &= x_{T1}(t)/x_{T2}(t)=\frac{\exp(G+F/T_1)\cdot t^{h_1(T)}}{\exp(G+F/T_2)\cdot t^{h_1(T)}}\\ &= \exp\left[F\cdot(T_1^{-1}-T_2^{-1})\right].\end{aligned} \tag{7}$$

Substituting $T_1=T_0$ and $T_2=T$ in the temperatures of degradation factors into Eq. (7), and assuming that charge and discharge rates and temperature have independent effects on the degradation rate of battery, the degradation equation of battery capacity under the three stress conditions of $(T,R_{\rm c},R_{\rm d})$ is as follows:

$$u(T,R_{\rm c},R_{\rm d})=\exp\left[F\cdot(T_1^{-1}-T_2^{-1})\right]\cdot u(T_0,R_{\rm c},R_{\rm d}). \tag{8}$$

Based on the fitting curve of experimental data of single stress, $h_1(T)=h_2(R_{\rm d})=h_3(R_{\rm d})=h(s)$ is a constant. After simplifying formula (8), the degradation equation of battery capacity under three stress conditions of $(T,R_{\rm c},R_{\rm d})$ is as follows:

$$u(T,R_{\rm c},R_{\rm d})=J(T,R_{\rm c},R_{\rm d})\cdot t^{h(s)}, \tag{9}$$

where

$$\begin{aligned}&J(T,R_{\rm c},R_{\rm d})\\ &= \exp\left[F\cdot(T_0^{-1}-T^{-1})\right]\\ &\quad\cdot\left[D_{\rm c}\cdot R_{\rm c}^{c'_{\rm c}}+D_{\rm d}\cdot R_{\rm d}^{c'_{\rm d}}+E_{\rm c}+E_{\rm d}-\exp(G+F/T_0)\right].\end{aligned} \tag{10}$$

It is the capacity degradation equation of power battery under $(T,R_{\rm c},R_{\rm d})$, which describes the speed of power battery under $(T,R_{\rm c},R_{\rm d})$.

### 2.1.4. Capacity degradation model of cell under dynamic stress

$u_t(T,R_{\rm c},R_{\rm d})$ is the capacity degradation at the time of $t$, and the following formula can be established:

$$\begin{aligned}&\begin{cases}u_t(T,R_{\rm c},R_{\rm d})=J(T,R_{\rm c},R_{\rm d})\cdot t^{h(s)}\\ u_{t+1}(T,R_{\rm c},R_{\rm d})=J(T,R_{\rm c},R_{\rm d})\cdot(t+1)^{h(s)}\end{cases}\\ &\Rightarrow u_{t+1}(T,R_{\rm c},R_{\rm d})\\ &= \left\{u_t(T,R_{\rm c},R_{\rm d})^{1/h(s)}+J(T,R_{\rm c},R_{\rm d})^{1/h(s)}\right\}^{h(s)}.\end{aligned} \tag{11}$$

In the above formula, $u_{t+1}(T,R_{\rm c},R_{\rm d})$ represents the amount of the previous degradation, which is the total amount of degradation after one degradation under the stress level of $(T,R_{\rm c},R_{\rm d})$. Thus, $u_t(T,R_{\rm c},R_{\rm d})$ can be regarded as a degradation state occurring, and it is related to the degradation amount and the stress in the previous cycle but unrelated to the stress $(T,R_{\rm c},R_{\rm d})$ in this cycle. The stresses in the $i$-th cycle are respectively recorded as $T_i$, $R_{{\rm c},i}$ and $R_{{\rm d},i}$. Formula (11) can be transformed into the following formula:

$$\begin{aligned}&u_{t+1}(T_{t+1},R_{{\rm c},t+1},R_{{\rm d},t+1})\\ &= \{u_t(T_t,R_{{\rm c},t},R_{{\rm d},t})^{1/h(s)}\\ &\quad +J_{t+1}(T_{t+1},R_{{\rm c},t+1},R_{{\rm d},t+1})^{1/h(s)}\}^{h(s)}.\end{aligned} \tag{12}$$

Formula (12) describes the relationship between the degradation amount $u_{t+1}(T_{t+1},R_{{\rm c},t+1},R_{{\rm d},t+1})$ at the time of $t+1$ under stress $(T_{t+1},R_{{\rm c},t+1},R_{{\rm d},t+1})$ and the degradation amount $u_t(T_t,R_{{\rm c},t},R_{{\rm d},t})$ of the previous moment. If this cycle begins from a new battery, $u_0(T_0,R_{{\rm c},0},R_{{\rm d},0})=0$.

The degradation amount after $t'$ times of cycle can be obtained after conducting deformation processing for Eq. (12), that is, the cell capacity degradation model under the dynamic stress of the degradation amount is as follows:

$$\begin{aligned}&u_{t+t'}(T_{t+t'},R_{{\rm c},t+t'},R_{{\rm d},t+t'})\\ &= \left[u_t(T_t,R_{{\rm c},t},R_{{\rm d},t})^{1/h(s)}\right.\\ &\quad \left.+\sum_{i=1}^{t'}J_{t+i}(T_{t+i},R_{{\rm c},t+i},R_{{\rm d},t+i})^{1/h(s)}\right]^{h(s)}.\end{aligned} \tag{13}$$

## 3. Capacity degradation model of a series power battery pack based on inconsistency

### 3.1. Analyses on charging and discharging process of series power battery pack

To better analyze the charging and discharging process of the series battery pack, the power battery is simplified into a resistance model and the series power battery pack model is established as shown in Fig. 1. $U_{\mathrm{OCV}(i)}$ represents the open-circuit voltage of the $i$-th cell of power battery pack, $R_{(i)}$ the resistance of the cell (the sum of DC resistance and polarization resistance), $U_{(i)}$ the terminal voltage of the cell, $C_{(i)}$ the residual capacity of the cell, $C_i$ the initial capacity of each cell, $C_{\max(i)}$ and $u_{(i)}$ denote the maximum available capacity and the capacity degradation of the cells respectively, $U^{\mathrm{B}}$ refres to the terminal voltage of the power battery pack, $U_{\max}$ the cut-off voltage for charging of the cell, and subscript $_{(i,t)}$ describes that this parameter is of the state of the $i$-th cell in the $t$-th cycle.

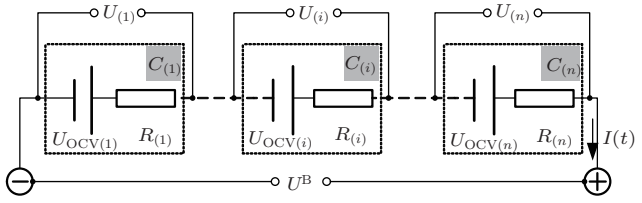



**Fig. 1.** Series power battery pack model.

#### 3.1.1. Residual capacity and maximum available capacity of a power battery pack

To guarantee the safety and cycle life of the power battery, the state of charge (SOC) of the battery is normally controlled within a range from 20% to 100% of the full load, and the charging and discharging process are controlled by extreme voltages of cells. For a series power battery pack, charge–discharge current $I(t)$ is a function of time $t$, and the charge–discharge capacity of battery is $C = \int_0^t I(t)\,\mathrm{d}t$. Therefore, the charge–discharge capacities of each cell in the series power battery pack in each cycle are the same.

At the beginning of the $t$-th cycle, the maximum available capacity of the $t$-th cell is $C$, its degradation capacity is $u_{(i,t-1)}$. A formula can be established as follows:

$$C_{\max(i,t)} = C_i - u_{i,t-1}. \tag{14}$$

When the capacity of a cell is released to the cut-off voltage for discharging, although the other cells with good performance and capacity retain some values of electric quantity, the electric quantity of the power battery pack is still deemed to be fully released. Therefore, the maximum available capacity of power battery pack is as follows:

$$C^{\mathrm{B}}_{\max(t)} = \min\{C_{(1,t)}, \ldots, C_{(i,t)}, \ldots, C_{(n,t)}\}. \tag{15}$$

The capacity degradation may be caused to some extent by the cell during the cycle. The rechargeable capacity of cell can be reduced. Recording the degradation amount in the $t$-th cycle as $\Delta u_{(i,t)} = u_{(i,t)} - u_{(i,t-1)}$, and the residual rechargeable capacity as $\Delta C_{(i,t)} = C_{\max(i,t)} - C_{(i,t)}$, the rechargeable capacity of each battery is as follows:

$$C_{\mathrm{ch}(i,t)} = C^{\mathrm{B}}_{\max(t)} + \Delta C_{(i,t)} - \Delta u_{(i,t)}. \tag{16}$$

Similar to the discharge process, in order to protect the safety of charging, when the capacity of a cell is full, the series power battery pack stops charging. Thus, the rechargeable capacity of the series power battery pack is as follows:

$$\begin{aligned} C^{\mathrm{B}}_{\mathrm{ch}(t)} &= \min\left\{C_{\mathrm{ch}(1,\mathrm{t})}, \ldots, C_{\mathrm{ch}(i,t)}, \ldots, C_{\mathrm{ch}(n,t)}\right\} \\ &= C^{\mathrm{B}}_{\max(t)} - \min\{\Delta C_{(1,t)} - \Delta u_{(1,t)}, \ldots, \Delta C_{(i,t)} \\ &\quad - \Delta u_{(i,t)}, \ldots, \Delta C_{(n,t)} - \Delta u_{(n,t)}\}. \end{aligned} \tag{17}$$

At the beginning of the $(t+1)$-th cycle, the $t$-th charge–discharge cycle of series power battery pack occurs, and the capacities of cells meet the following formula:

$$\begin{aligned} C_{(i,t+1)} &= C_{(i,t)} - C^{\mathrm{B}}_{\max(t)} + C^{\mathrm{B}}_{\mathrm{ch}(t)} \\ &= C_{(i,t)} - \min\{\Delta C_{(1,t)} - \Delta u_{(1,t)}, \ldots, \Delta C_{(i,t)} \\ &\quad - \Delta u_{(i,t)}, \ldots, \Delta C_{(n,t)} - \Delta u_{(n,t)}\}. \end{aligned} \tag{18}$$

It can be seen that the available capacity of the cell is related to not only its own capacity degradation, but also the capacity degradation of the battery pack. The capacity reduced in each cycle is the maximum degradation amount of cell, and the degradation rate of power battery pack is larger than that of the cell. Due to the poor operating conditions of part of the cells, especially temperature conditions, the charge–discharge capacities of other cells can be reduced sharply and the cycle life of the power battery pack can be affected.

#### 3.1.2. Discharge current of power battery pack

The SOC of each cell is as follows:

$$\mathrm{SOC}_{(i,t+1)} = C_{(i,t+1)}/C_{\max(i,t+1)}. \tag{19}$$

Because $U_{\mathrm{OCV}}$ is a monotonic nonlinear function[31,32] of the SOC of the cell, in order to simplify the calculation, the following assumptions are made in the subsequent calculation: the initial open-circuit voltages of all cells in the power battery pack are consistent; under the same SOC, the values of $U_{\mathrm{OCV}}$ are the same, the same type of batteries have the same $U_{\mathrm{OCV}} - \mathrm{SOC}$ relation, that is,

$$U_{\mathrm{OCV}(i,t+1)} = U(\mathrm{SOC}_{(i,t+1)}). \tag{20}$$

Based on the power battery pack model in Fig. 1, the relation can be established as follows:

$$U_{(i,t+1)} = U_{\mathrm{OCV}(i,t+1)} - I(t)\cdot R_{(i,t+1)}, \tag{21}$$

$$U^{\mathrm{B}} = \sum_{i=1}^{n} U_{(i)}. \tag{22}$$

Regarding the power demand of the power supply as the orientation principle, the output current of power battery pack should satisfy the following formula:

$$I(t) = P/U^{\mathrm{B}} = P\Big/\sum_{i=1}^{n}\left[U_{\mathrm{OCV}(i,t+1)} - I(t)\cdot R_{(i,t+1)}\right]$$
$$\Rightarrow I(t) = \frac{\sum_{i=1}^{n} U(\mathrm{SOC}_{(i,t+1)}) - \sqrt{\left[\sum_{i=1}^{n} U(\mathrm{SOC}_{(i,t+1)})\right]^2 - 4\cdot P\cdot \sum_{i=1}^{n} R_{(i,t+1)}}}{2\cdot \sum_{i=1}^{n} R_{(i,t+1)}}. \quad (23)$$

### 3.2. Capacity degradation model of a series power battery pack

Under the constant temperature and charge rate, the degradation coefficient of the cycle can be determined, and therefore the degradation amount of cell can be calculated. The available capacity of the power battery pack can be measured according to formula

$$C^{\mathrm{B}}_{\max(t)} = \min\left\{C_{(1,t)},\ldots,C_{(i,t)},\ldots,C_{(n,t)}\right\}.$$

Because the charging of a series power battery pack is completed when the cell with the smallest capacity is full and the power of the cell with the discharging of the cell with the smallest capacity is fully discharged when the discharging is completed, based on different degradation quantities and available capacities of all cells, the available capacity of each cell in the cycle can be expressed as follows:

$$C_{(i,t+1)} = C_{(i,t)} - \min\{\Delta C_{(1,t)} - \Delta u_{(1,t)},\ldots,\Delta C_{(i,t)} - \Delta u_{(i,t)},\ldots,\Delta C_{(n,t)} - \Delta u_{(n,t)}\}. \quad (24)$$

In the initial cycle, i.e., the $t$-th cycle, the degradation amount of cell is $u_{(i,t)}$, the capacity is $C$, in the $(t+t')$-th cycle, the maximum available capacity of cell $C$ and the state of charge $\mathrm{SOC}_{(i,t+t')}$ are respectively as follows:

$$C_{\max(i,t+t')} = C_i - u_{(i,t+t'-1)},$$
$$\mathrm{SOC}_{(i,t+t')} = C_{(i,t+t')}/C_{\max(i,t+t')}. \quad (25)$$

The currents of series power battery pack in the charging and discharging process are the same, and the battery is charged by means of constant rate. The charge rate of each cell is $R_{\mathrm{c},t+1}$, and the operation is generally conducted when its maximal value is $1/3C$.

In the $(t+t')$-th cycle, the discharge rate of power battery pack is

$$R_{\mathrm{d}(t+t')} = \frac{I(t)}{C_{(i,1)}} = \frac{\sum_{i=1}^{n} U(\mathrm{SOC}_{(i,t+t')}) - \sqrt{\left[\sum_{i=1}^{n} U(\mathrm{SOC}_{(i,t+t')})\right]^2 - 4\cdot P\cdot \sum_{i=1}^{n} R_{(i,t+t')}}}{C_{(i,1)}\cdot \sum_{i=1}^{n} R_{(i,t+t')}}. \quad (26)$$

At that time, the degradation coefficient of cell is

$$J_{t+t'}(T_{(t+t')}, R_{\mathrm{c}(t+t')}, R_{\mathrm{d}(t+t')}) = [D_{\mathrm{c}}\cdot R_{\mathrm{c}(t+t')}^{c'_{\mathrm{c}}} + D_{\mathrm{d}}\cdot R_{\mathrm{d}(t+t')}^{c'_{\mathrm{d}}} + E_{\mathrm{c}} + E_{\mathrm{d}} - \exp(G + F/T_0)]\cdot\exp[F\cdot(T_0^{-1} - T_{(t+t')}^{-1})]. \quad (27)$$

It can be seen from cell degradation formula (14) under dynamic stress that the degradation model of cell in series power battery pack is

$$u_{(i,t+t')}(T_{(i,t+t')}, R_{\mathrm{c}(i,t+t')}, R_{\mathrm{d}(i,t+t')}) = \left[u_{(i,t)}(T_{(i,t)}, R_{\mathrm{c}(i,t)}, R_{\mathrm{d}(i,t)})^{1/h(s)} + \sum_{j=1}^{t'} J_{i,t+j}(T_{(i,t+j)}, R_{\mathrm{c}(i,t+j)}, R_{\mathrm{d}(i,t+j)})^{1/h(s)}\right]^{h(s)}. \quad (28)$$

According to the charge–discharge stress conditions of a power battery pack in Eqs. (26) and (27), the degradation of each cell is calculated and analyzed based on Eq. (28), and the total degradation amount of power battery pack is

$$u_{t+t'} = \max\{u_{(1,t+t')}(T_{(1,t+t')}, R_{\mathrm{c}(1,t+t')}, R_{\mathrm{d}(1,t+t')}), u_{(i,t+t')}(T_{(i,t+t')}, R_{\mathrm{c}(i,t+t')}, R_{\mathrm{d}(i,t+t')}),\ldots, u_{(n,t+t')}(T_{(n,t+t')}, R_{\mathrm{c}(n,t+t')}, R_{\mathrm{d}(n,t+t')})\}. \quad (29)$$

## 4. Prediction and experimental analysis of cycle life for a series power battery pack

### 4.1. Prediction of cycle life and analysis of influencing factors for a series power battery pack

There are some inconsistencies in the individual batteries in series, and their capacities follow a normal distribution $N(\mu,\sigma^2)$.[19] In this paper, the object of analysis is a battery pack composed of 8 cells with a rated capacity of $1.5\times10^4$ mA·h, that is, $\mu = 1.5\times10^4$. The following analysis describes the inconsistencies of capacity of cells in power bat-

tery pack using different capacity variances based on the capacity mean. We conduct predictive analysis using the random normality capacity vector $\boldsymbol{C} = [\,C_1\ C_2\ C_3\ C_4\ C_5\ C_6\ C_7\ C_8\,]$.

The open-circuit voltage $U_{\mathrm{OCV}}$ of the cell is a function of its SOC. After measuring the open-circuit of a cell and conducting polynomial curve fitting, the fitting curve is established as shown in Fig. 2.

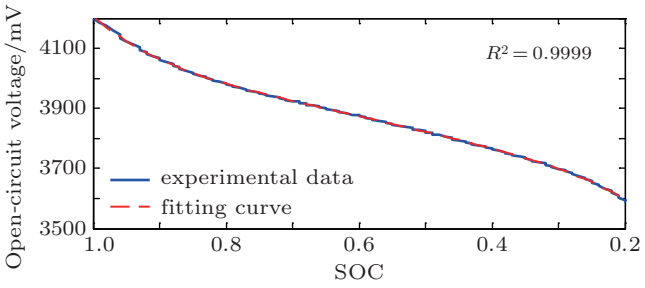



**Fig. 2.** (color online) Fitting curve of open-circuit voltage of a power battery with a capacity of $1.5\times10^4$ mA·h. $U_{\mathrm{OCV}} = 7169\times\mathrm{SOC}^5 - 20170\times\mathrm{SOC}^4 + 23019\times\mathrm{SOC}^3 - 13389\times\mathrm{SOC}^2 + 4499\times\mathrm{SOC} + 3078$.

It can be seen that the fitting function of the open-circuit voltage is

$$U_{\mathrm{OCV}} = 7.169\cdot\mathrm{SOC}^5 - 20.170\cdot\mathrm{SOC}^4 + 23.019\cdot\mathrm{SOC}^3 - 13.389\cdot\mathrm{SOC}^2 + 4.499\cdot\mathrm{SOC} + 3.078.$$

To facilitate the calculation, assuming that the internal resistance of the power battery pack is a constant, obtaining a mean based on the actual measurement values, and setting the internal resistance of each cell to be 5 mΩ, the internal resistance of the battery pack is $\sum R_{(i,t+1)} = 40$ mΩ.

If the power output of the power battery pack is 0.5 C of its initial condition, the following formula can be established:

$$P = 0.5\ \mathrm{C}\times 15\ \mathrm{A\cdot h}\times 4.2\ \mathrm{V}\times 8 = 25.2\ \mathrm{W}.$$

Based on the open-circuit voltage, internal resistance and power value above, the discharge rate $R_{\mathrm{d}(t+t')}$ can be calculated from Eq. (26).

Taking $C^{\mathrm{B}}_{\max(t)} = \min\{C_{(1,t)},\ldots,C_{(i,t)},\ldots,C_{(n,t)}\}$ as the evaluation point of cycle life, the cycle life of series power battery pack is

$$C^{\mathrm{B}}_{\max(t)} = 80\%\cdot C^{\mathrm{B}}_{\max(1)} = 12064\cdot R^{-0.37}_{\mathrm{d}(t+t')}.$$

For the series power battery pack, the charge rate and the discharge rate conditions are the same, and the temperature difference is the main source of different degradation coefficients in the degradation parameter conditions. Due to the difference in the position and ventilation conditions in the battery box of cells, on the basis of the environmental conditions, the temperature difference matrix is introduced. Due to different cooling and heating modes, the control range of temperature difference varies. For a power battery box with a cell temperature difference controlling range of 10 °C, the matrix of large temperature difference conditions is set to be $\Delta\boldsymbol{T}_1 = [2\ 3\ 6\ 9\ 10\ 6\ 3\ 1]$; for the power battery box with a cell temperature difference controlling range of 5 °C, the matrix under small temperature difference is set to be $\Delta\boldsymbol{T_2} = [2\ 3\ 3\ 4\ 5\ 3\ 3\ 1]$, and the values respectively represent the difference values between the operating temperature of each of the cells and atmospheric temperature.

The degradation factor of a power battery is an average statistic, so it cannot thoroughly or accurately describe the degradation rate of each battery. Meanwhile, if all power batteries are described with the same statistics, the degradation difference of cell caused by production variance can be neglected. From the point of view of probability statistics, the degradation amount of cells are independent of each other; the difference follows a normal distribution. When predicting the cycle life, an initial random degradation coordinating factor is added to the degradation factor of each battery, which is, $\Delta\boldsymbol{F_J} = [\,F_1\ F_2\ F_3\ F_4\ F_5\ F_6\ F_7\ F_8\,]$. The factor follows a normal distribution, and the value can be fitted into $N(2, 0.36)$ according to the experimental data.

When the capacity distribution parameters are $\mu = 1.5\times10^4$, $\sigma = 10^3$, and the temperature difference vector is $\Delta\boldsymbol{T}_1$, the data can be obtained as shown in Fig. 3 and Table 1.

**Table 1.** Degradation prediction values of a series power battery pack when the capacity standard deviation is $\sigma = 10^3$ under large temperature difference.

| | | Capacity of cell when $\sigma = 10^3$ (mA·h) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Cell1 | Cell 2 | Cell 3 | Cell 4 | Cell 5 | Cell 6 | Cell 7 | Cell 8 |
| Initial capacity | | 13442 | 14889 | 13784 | 15612 | 14375 | 15666 | 15256 | 15384 |
| At the termination of cycle life | Residual capacity | 11124 | 12571 | 11466 | 13294 | 12050 | 13349 | 12938 | 13066 |
| | Maximum available capacity | 11866 | 13203 | 11873 | 13373 | 12050 | 13740 | 13503 | 13854 |
| | Degradation capacity | 1576 | 1686 | 1911 | 2239 | 2325 | 1926 | 1753 | 1530 |
| | Maximum SOC value | 93.7% | 95.2% | 96.6% | 99.4% | 100.0% | 97.2% | 95.8% | 94.3% |

The degradation curves of the batteries with maximum degradation and minimum degradation are as shown in Fig. 3. Table 1 shows that due to the difference in working state parameter, the maximum difference in capacity degradation of each cell reaches 795 mA·h, which is 34.19% of the maximum degradation amount. The cycle life of the series power battery pack is 188 times, and the difference in maximum available capacity of cell at the termination of cycle life can reach 1988 mA·h. Moreover, due to the capacity characteristics of the series system in the process of discharging, except for Cell 5, the residual capacities of other cells are all lower than their maximum available capacities. This fact means that if equalization charging is conducted for the power battery pack, the residual capacity of the power battery pack will be further improved.

Under the control of different values of standard deviation $\sigma$, the consistency of cell changes, and thus its capacity and cycle life data are obtained as shown in Table 2. With the same capacity mean, the smaller the standard deviation, the better the consistency of power battery and the longer its cycle life is. On condition that $\sigma = 10^3$ and $\sigma = 100$, the cycle life is extended by nearly 30%. Therefore, it can effectively improve the cycle life of power battery by controlling the capacity standard deviation.

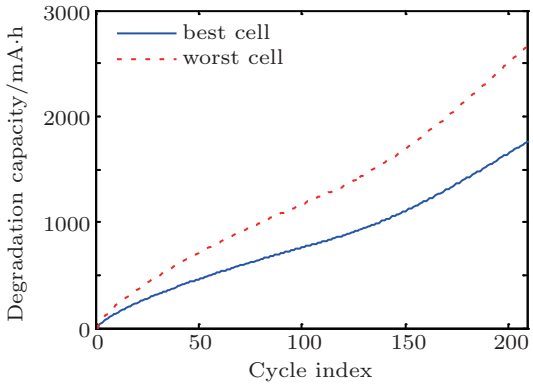



**Fig. 3.** (color online) Degradation prediction curves of cell when the capacity standard deviation is $\sigma = 10^3$ under a large temperature difference.

**Table 2.** Cycle life prediction values of series power battery pack with different capacity variances under large temperature difference.

| Standard deviation of capacity | Capacity of cell/mA·h | | | | | | | | Cycle life |
|---|---|---|---|---|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 3 | Cell 4 | Cell 5 | Cell 6 | Cell 7 | Cell 8 | |
| $\sigma = 1000$ | 16016 | 15682 | 14824 | 15043 | 14380 | 15490 | 13809 | 16426 | 210 |
| $\sigma = 500$ | 14455 | 15699 | 14882 | 15349 | 15236 | 14269 | 14660 | 14632 | 233 |
| $\sigma = 300$ | 15457 | 15250 | 15497 | 14830 | 14671 | 15421 | 14694 | 15265 | 261 |
| $\sigma = 100$ | 14959 | 14895 | 15066 | 15140 | 14874 | 14964 | 14974 | 15020 | 282 |
| $\sigma = 0$ | 15000 | 15000 | 15000 | 15000 | 15000 | 15000 | 15000 | 15000 | 292 |

When the temperature difference vector is $\Delta \boldsymbol{T}_2$ and the capacity is normally distributed with standard deviation $\sigma = 100$ and $\sigma = 500$, we can obtain the data in Table 3. Table 3 shows that the difference in cycle life reaches 20%. By comparison with the data in Table 2, there is an obvious gap between values of the cycle life, and the cycle life is increased by nearly 70% due to the improvement of temperature conditions. Therefore, from the point of view of improving the cycle life of series power battery pack, the control of temperature difference plays a great role in extending the cycle life.

**Table 3.** Cycle life prediction values of series power battery pack under small temperature difference and different capacity standard deviations.

| Capacity standard deviation | Capacity of cell/mA·h | | | | | | | | Cycle life |
|---|---|---|---|---|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 3 | Cell 4 | Cell 5 | Cell 6 | Cell 7 | Cell 8 | |
| $\sigma = 100$ | 14990 | 15045 | 15029 | 15123 | 15045 | 15211 | 15084 | 15048 | 479 |
| $\sigma = 500$ | 14872 | 15363 | 14597 | 15089 | 15476 | 14865 | 15063 | 14822 | 398 |

Under different temperature differences and capacities, SOCs after 1000 times of degradation are respectively recorded, and the data are obtained and shown in Table 4.

**Table 4.** SOCs of a cell under different temperature differences and capacity standard deviations.

| | SOC of cell | | | | | | | | Cycle life |
|---|---|---|---|---|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 3 | Cell 4 | Cell 5 | Cell 6 | Cell 7 | Cell 8 | |
| $\sigma = 500, \Delta \boldsymbol{T}_1$ | 70.7% | 69.6% | 82.0% | 91.9% | 100.0% | 80.8% | 67.1% | 62.5% | 222 |
| $\sigma = 100, \Delta \boldsymbol{T}_2$ | 90.0% | 90.9% | 91.8% | 95.4% | 100.0% | 93.5% | 91.6% | 85.6% | 472 |

It can be seen from Table 4 that after several cycles, the difference in SOC between cells becomes large, the lowest difference in the first pack is 62.5%, and the lowest difference in the second pack is 85.6%. Because the consistency of the second pack is relatively good, its life service is twice that of the first pack, and the SOC difference is small. This shows that in charge–discharge cycle, the available capacity of each cell in series power battery pack is limited by the minimum capacity; the greater the capacity difference, the greater the SOC difference is, which leads to reduction in open-circuit voltage of each cell. In the case of a certain power, the discharge rate of the battery pack will be increased, and therefore the cycle life of the power battery is shortened.

## 4.2. Experimental analysis of cycle life of series power battery pack

### 4.2.1. Methods of data test

To conduct comparative analysis for the prediction data, an accelerated life test is carried out for the power battery pack consisting of 8 cells in series.

(I) Type of battery to be tested

The power battery used in this paper is polymer manganese lithium-ion power battery. The cathode material is spinel lithium manganese oxide, and the anode material is natural graphite, the diaphragm is PP/PE/PP, electrolyte solvent is a mixture of DC, EC, and EMC (1:1: 1), and the solute is $LiPF_6$ (1 mol/L). The nominal capacity of the battery is 15 A·h. The nominal voltage is 3.7 V. The cut-off voltage for charging is 4.2 V. The cut-off voltage for discharging is 3.0 V.

(II) Program for cycle test

In the process of charge–discharge cycles, the stress condition is a constant temperature of 40 °C and a charge–discharge rate of 1 C. The program for cycle life test is as follows:

1) static: 10 min;

2) charging: to charge the battery with a constant current of 1 C, charge it with a constant voltage after the voltage reaches 4.2 V, and complete the charging process after the current has reduced to 0.05 C;

3) static: 10 min;

4) discharging: to discharge the battery with a constant current of 1 C, and complete the discharging process after the voltage has reached a cut-off voltage of 3.0 V;

5) repeat Steps 1) to 4) for 93 times.

### 4.2.2. Results of data test

From our investigation, due to the high stress conditions of the battery pack, in the 50th cycle, the available capacity of power battery pack can be reduced to 10211 mA·h, and the minimum capacity of cell is 10792 mA·h, but the capacities of part of the cells are relatively high. We test and adjust the power battery, replace the two cells with low capacity and form a new pack after conducting supplementary charging. The performance of the power battery pack can go back to normal. In the initial charge–discharge cycle, the charging and discharging conditions are the same as those of previous 50 time tests. At the end of 43-th cycle, the available capacity of the power battery pack can reduce to 10182 mA·h, and the minimum capacity of the cell is 10264 mA·h. The prediction data and test data of the power battery pack are shown in Table 5.

**Table 5.** Values of test and predicted cell capacity in the power battery pack consisting of 8 batteries in series.

| | | Capacity of cell/mA·h | | | | | | | | Available capacity of power battery pack/mA·h |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Cell 1 | Cell 2 | Cell 3 | Cell 4 | Cell 5 | Cell 6 | Cell 7 | Cell 8 | |
| Previous 50 times | Initial capacity | 15230 | 14364 | 14560 | 12520 | 14401 | 14568 | 13314 | 14963 | 12520 |
| | Capacity at the terminal of test | 13170 | 13274 | 13080 | 10792 | 12204 | 12629 | 11196 | 12689 | 10211 |
| | Capacity at the terminal of prediction | 12983 | 12117 | 12313 | 10383 | 12154 | 12321 | 11067 | 12716 | 10273 |
| | SOC at the terminal of prediction | 99.08% | 99.62% | 99.73% | 99.03% | 99.97% | 99.89% | 100.00% | 98.08% | 98.94% |
| Later 43 times | Initial capacity | 13170 | 13274 | 13080 | 14930 | 12204 | 12629 | 15010 | 12689 | 12204 |
| | Capacity at the terminal of test | 11521 | 11850 | 11745 | 12626 | 10264 | 10935 | 11698 | 11435 | 10182 |
| | Capacity at the terminal of prediction | 11156 | 11260 | 11066 | 12916 | 10190 | 10615 | 11996 | 10675 | 10090 |
| | SOC at the terminal of prediction | 97.62% | 98.14% | 98.19% | 100.00% | 98.26% | 98.25% | 99.97% | 96.63% | 99.02% |

It can be seen from Table 5 that due to the differences between the cells in the power battery pack, not all SOCs of the cells can reach 100% at the same time after the charge–discharge cycle. Specifically, because of the existence of this difference, the available capacity of the power battery pack is not equal to the maximum available capacity of the cell in the pack, and it is lower than the available capacity when fully charged. It can be seen from the prediction values at the termi-

nation of the previous 50 charge–discharge cycles, the maximum value of maximum available capacities of the cells in the pack is 12863 mA·h, and the minimum value is 10282 mA·h, but the available capacity of the battery pack is 10273 mA·h. This fact shows that the available capacity of power battery pack is related to not only the degradation of the cells in the pack, but also the inconsistency in SOC among the cells, and the maximum available capacity cannot be fully released due to the cut-off voltage in the cycle. This result is the same as that of the charge–discharge cycle after replacing the disadvantaged cell.

The degradation path and prediction data curves of the battery pack are shown in Fig. 4. Figure 4 shows that the degradation paths of test data and prediction data are equivalent to each other, that the maximum difference in available capacity between the two power battery packs is 194 mA·h, a percentage of 1.733% equivalently, and that the correlation coefficient of the two data is $R^2 = 0.996$, indicating that degradation model can depict the degradation and cycle life of power battery to some extent.

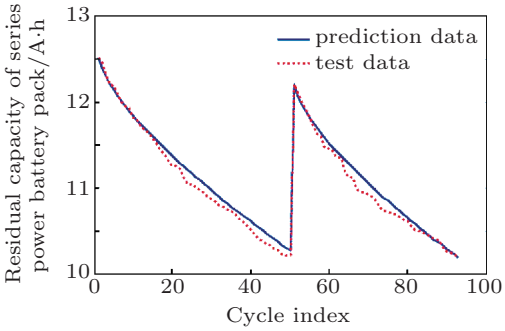



**Fig. 4.** (color online) Degradation path and prediction data of a power battery pack consisting of 8 batteries in series.

From the results and analyses mentioned above it follows that for a series power battery pack, there are inconsistencies in the degradation of cell in the pack due to stress difference; on the basis of inconsistent initial capacity, the available capacity of a series power battery pack is greatly affected by the batteries with low capacities, and the short-board effect of power battery pack is obvious. Therefore, to achieve the maximum capacity, good consistency should be kept for each cell when designing and assembling a series power battery pack.

## 5. Conclusions

I) The degradation process of a series power battery is a process of continuing deterioration and aggravating cycle. On the one hand, the discharge rate of a series power battery pack will gradually rise with the increase in the number of charge–discharge cycles, which will exacerbate the degradation of cell and thus result in increased degradation of the power battery pack; on the other hand, the intensified degradation of a power battery pack will improve the increase in discharge rate, and thus further accelerate the degradation rate of the power battery pack.

II) The available capacity of a series power battery pack mainly depends on the cell with the minimum capacity. The results of degradation analysis show that the smaller the capacity variance of the power battery pack, the longer its cycle life is; the reasonable assembling of the cells can give play to the performance of cells and improve the overall performance and cycle life of the power battery pack.

III) In the process of charge–discharge cycles, the charge rate and the discharge rate of the cells in a series power battery pack are always the same, and the temperature difference is the main factor affecting the inconsistency in capacity degradation of the power battery pack. When the temperature difference is narrowed by 5 °C, the cycle life will be increased by more than 50%. It can greatly increase the cycle life of a series power battery pack to assemble the cells based on their capacities and narrow the operating temperature difference among the cells.

IV) The experimental results show that this model can effectively describe the degradation characteristics of a series power battery pack. When the increase of heat productivity caused by the increase of internal resistance after the degradation of cell is taken into account, the degradation speed will be faster than the analysis result, and the capacity degradation process of the series power battery pack can also be described accurately.

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