Fast screening of capacity and internal resistance for cascade utilization of the retired power lithium-ion batteries

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Abstract: The residual capacity and internal resistance of lithium-ion batteries are important indicators for evaluating the retired batteries, and they are also prerequisites for the cascade utilization of retired batteries. Screening of capacity and internal resistance of retired batteries was studied in this paper. In terms of battery residual capacity, the battery charging system is used to obtain the battery charging curves from which IC characteristics are extracted and screened. The relationship between the IC characteristics and the battery capacity is obtained using a neural network algorithm to achieve capacity estimation. In terms of internal resistance, the charge and discharge strategies of batteries connected in series was first studied, and then a screening method for battery internal resistance was designed based on such charge and discharge strategies. The overall results of this paper provided the basis for the selection of retired power batteries.

1. Introduction
In recent years, promoted by governmental policies, the new energy vehicle industry has developed rapidly. In 2018, 1.2575 million new energy vehicles were produced and 1.247 million were sold, up 60.9% and 62% compared with the same period last year. The overall industrial development trend is heading for the goal of "the production capacity of pure electric vehicles and plug-in hybrid electric vehicles to reach 2 million and the cumulative production and sales volume to exceed 5 million by 2020" in the development plan for energy conservation and new energy industry (2012-2020) [1-2]. When the capacity of lithium-ion batteries in electric cars drops to 70-80% of their rated capacity, they are no longer suitable for a continued use in electric vehicles and need to be retired [3]. Although these batteries can’t meet the standards of electric vehicles, they can be used in the secondary situation such as the stationary battery storage [4]. But, the retired batteries should be sorted and regrouped based on their current state of health (SOH) before they can be utilized in other application areas. Thus, how to achieve
rapid and accurate screening is an important task for cascading use of battery, and is also a key issue of echelon utilization [5].

At present, the main research on cascading battery applications includes the study on the attenuation mechanism of lithium-ion batteries, the health state estimation of retired batteries, the detection of internal resistance, the detection of self-discharge and the safety assessment [6]. ZHANG et. al. conducted the electrochemical impedance spectroscopy (EIS) test for the lithium ion batteries, identified the equivalent circuit model through EIS, and found that the positive SEI membrane was the leading factor for impedance increase and power performance deterioration [7]. Based on the characteristics of terminal voltage response of lithium ion battery under current pulse test, MENG et. al. proposed a new method for accurate estimation of battery state-of-health (SOH) based on support vector machine technology [8]. Xu Jing et. al. studied the three testing principles and methods of internal resistance, and proposed the optimal sampling point (discharge drop edge, charging rise edge) and sampling time for testing internal resistance of lithium ion batteries in echelon. The electrochemical impedance model was established, and the influence of polarization on internal resistance was reduced [9].

In this paper, the decommissioned automotive battery was taken as the research object, and the decommissioned battery was rapidly evaluated by the experimental research and screening method of capacity and internal resistance. The IC analysis method is applied to the capacity screening of retired batteries to increase the speed of capacity screening; an internal resistance screening and grouping method is proposed to improve the consistency between the cells in the battery module. The separation evaluation of retired batteries can be realized. The method is simple, efficient and scientific, which can greatly improve usability of the battery separation.

2. Method
The method and steps for screening capacity and internal resistance are shown in Figure 1.
Capacity: ① The IC curve is obtained from the charging curve of the battery. ② Extract the characteristic factor of IC curve. ③ Feature factors are input into the neural network model to train the model. ④ Estimate the capacity.

Internal resistance: ① Analyze the voltage difference curve to get the consistency characteristics of the battery. ② Analyze the correspondence relationship between battery charge-discharge cut-off voltage and capacity from battery consistency characteristics. ③ Formulate battery charging and discharging strategies. ④ Formulation of resistance screening parameters.

The following describes the important methods used in the experiment.

Incremental capacity analysis (ICA) method firstly obtains voltage-capacity (V-Q) curve through current integration through constant current charge-discharge curve, and then derives incremental capacity (IC) curve by using voltage-capacity curve to derive voltage. The intercalation and deintercalation reactions of lithium ions on the positive and negative electrodes during the charging and discharging of lithium-ion batteries. At this time, the two-phase transition process of the electrode material corresponds to the peak on the IC curve. By analyzing the peak spacing or peak area of the curve, the amount of electricity participating in the phase transition process of the material can be obtained, thereby obtaining the battery capacity attenuation [10-11]. To obtain a high-quality IC curve, you need to use a small current rate (such as 1/25C) to charge and discharge test, but in order to shorten the test time, you often use a higher current rate to test (such as 1/3C or 1/2C). The actual test proves that the use of higher current rate can also obtain the status of health (SOH) of the battery.

Convert the battery charge-discharge voltage curve to the capacity increment curve $V$-$t$ curve (when the current increment curve $V$-$t$ curve is converted to $dQ/dV$ curve): during the constant current charging process, the charging current is $I$, and the charging capacity $Q = It$. Then $dQ = I \cdot dt$, namely formula (1).

$$dQ/dV = I \cdot dt/dV$$  \hspace{1cm} (1)

Where, $Q$ is the capacity of the battery, $V$ is the battery terminal voltage, $I$ is the charging and discharging current, and $t$ is the time.


Figure 1. Screening methods and steps

During the constant current charging process, there will be a voltage platform. At this time, the battery charging capacity continues to increase and the battery voltage does not change significantly. That is, when the \(dQ\) changes, the corresponding \(dV\) is small, indicating that the \(dQ/dV\) value is large. The flatter the battery voltage platform, the larger the peak value of the capacity increment curve, and the change in the peak value of the capacity increment curve can reflect the change of the voltage platform. This converts the voltage platform that is not easy to analyze into an IC curve that is easy to observe and analyze. The sensitivity of the battery analysis method is improved by calculating the capacity increment curve. Voltage platform reaction the electrochemical reaction inside the cell reaches equilibrium, which is the description of the process of electrode ion disembedding. The voltage platform contains the inside information of the battery, and the capacity increment curve can be analyzed to show not only the reaction rate of the electrode, but also the multiple voltage platforms formed by the separation of lithium ions on the graphite cathode. The peak value and peak potential in the capacity increment curve contain the information of lithium ions involved in electrochemical reactions in different aging states of the battery, which is a way to conduct electrochemical model analysis without damaging the battery.

3. Experiment

3.1 Capacity experiment

3.1.1 Draw IC curve experiment

The object of the experiment is the 2.2Ah NCM power batteries retired from the pure electric vehicle. The battery test system is the CT6001 series battery tester of Wuhan LANDIAN Company. All battery tests are conducted at room temperature. The experiment and analysis are as follows:

1. 0.2C constant current charge to charge cut-off voltage (4.2V);
2. constant voltage charge until current drop to 0.01C;
3. 0.2C constant current discharge to the lower cut-off voltage (2.7V) (the discharged capacity is regarded as The remaining capacity of the battery);
4. The data sampling period is set to 10s to get the data of battery capacity Q changing with voltage V.
The numerical derivation of the $Q$-$V$ curve results in the IC curve, as shown in Figure 2 (a). Due to the interference of the noise signal in the battery test system, the curve is not easy to observe and analyze. Therefore, it is necessary to smooth the curve. The filtering adopted in this paper is moving average filtering and wavelet filtering. The filtering effect is shown in Figure 2 (b). Compared with the original signal filtering, the signal is smooth and the distortion is small, which greatly reduces the difficulty of analysis.

3.1.2 Extract feature parameters
It can be seen from Figure 2 (b) that the curve has two distinct peaks. These two peaks are the result of the phase transition of the positive and negative electrodes of the battery. It is known from literature that the curve should have 5 peaks, and this experiment only has two peaks. The reason is that it requires a very small charge rate to observe the 5 peaks (such as 1/20C, 1/30C). The peaks appear in the battery electrode phase transition process. Only at a small magnification can the phase change of the two electrodes of the battery be fully reflected. At a higher magnification, the phase transition of the electrode is too late to react, so that some peaks are not prominent or even disappear. In order to improve the test efficiency, the experiment cannot be performed with too small a magnification, so the curve cannot reflect the entire phase transition process of the electrode, but there are also two obvious peaks. We can also use these two peaks for analysis.

The characteristic parameters of the curve are extracted, and the curve is divided into two peaks, peak I and peak II respectively, and the lowest point between the two peaks is the peak valley. The vertical coordinate of peak I is $I_C^1$, the horizontal coordinate of peak I is $V_1$, and the peak I corresponds to battery capacity $Q_1$; the vertical coordinate of peak II is $I_C^2$, the horizontal coordinate of peak II is $V_2$, and the peak II corresponds to the battery capacity of $Q_2$; peak I and peak II The vertical coordinate of the peaks and valleys is $I_C^3$, the horizontal coordinate is $V_3$, and the corresponding battery capacity of the valley is $Q_3$; the right slope of the peak I is $k_1$; the left slope of peak II is $k_2$; the correlation (correlation coefficient) of curves between different batteries, as shown in equation (2).

$$r_{YS} = \frac{\sum_{i=1}^{n} (y_i - \bar{Y})(s_i - \bar{S})}{\sqrt{\sum_{i=1}^{n} (y_i - \bar{Y})^2} \sqrt{\sum_{i=1}^{n} (s_i - \bar{S})^2}}$$

(2)

Where, $y_i$ represents the i-th dimension (i-th data point) of the IC feature vector of the battery, $n$ represents the dimension of the vector (the number of selected IC data points), and $\bar{Y}$ the average value of the IC feature vector of the battery, $s_i$ represents the i-th dimension of the IC feature vector of the standard battery, and $\bar{S}$ represents the average value of the IC feature vector of the standard battery (No. 1 battery as the standard battery).

The correlation coefficient with the static capacity is calculated, of which the right slope $k_1$ of peak I and the capacity correlation coefficient is -0.7776, the right slope $k_2$ of peak II and the capacity correlation coefficient is -0.4131, the curve correlation and capacity correlation coefficient is 0.8876, and other parameters The correlation coefficient with capacity is shown in Table 1.

| Table 1 Correlation coefficient between characteristic parameters and capacity |
|-----------------|-----|-----|-----|
| Parameter       | Q   | V   | IC  |
| PeakI           | 0.8454 | -0.8859 | 0.8089 |
| PeakII          | 0.6997 | -0.8789 | 0.6702 |
| peak valley     | 0.4560 | -0.8183 | -0.5024 |
Considering that the curves $V_1$, $V_2$, and $V_3$ have a strong correlation, only the peak I corresponds to the voltage $V_1$. Other health factors are $Q_1$, $C_1$, $k_1$, $r_{VS}$ with high correlation coefficient. Most of the parameters of the curve are related to the peak I, so only some data of the charging curve is needed.

The correlation coefficient between the selected parameters and the capacity is calculated, of which the right slope $k_1$ of peak I and the capacity correlation coefficient is -0.7776, the right slope $k_2$ of peak II and the capacity correlation coefficient is -0.4131, the curve correlation and capacity correlation coefficient is 0.8876, and the correlation coefficients of other parameters are shown in Table 1. Considering that there is a strong correlation between curves $V_1$, $V_2$, and $V_3$, only $V_1$ is taken as the health factor. Other health factors are $Q_1$, $C_1$, $k_1$, $r_{VS}$ with high correlation coefficient. Most parameters of the curve are related to peak I, so only part of the curve data is needed.

![Battery charging IC curve](image1)

(a) Original curve;

(b) Filtered curve

Figure 2. Battery charging IC curve

### 3.1.3 Neural network capacity estimation

There are many health factors, and there may be a non-linear relationship between health factors and capacity, which will affect the accuracy of capacity estimation. Neural network is a commonly used data fusion method, which has the advantages of self-learning, self-adaption and simulation of arbitrary nonlinearity. In this paper, RBF neural network is selected.

There are 69 batteries in total, the first 60 batteries are used as training objects, and the last 9 batteries are used as prediction estimates. The health factor with a high correlation coefficient is selected as the
input of the RBF neural network, including \((Q_1, V_1, C_1, k_1, r_\gamma S)\), and the output is the residual capacity. This creates a 5-input, 1-output RBF neural network.

A total of 69 battery data, the first 60 are taken as training objects, and the last 9 batteries are used as prediction estimates. Iterate and train the model, and the comparison between the model prediction results and the real values is shown in Figure 3. The model can estimate the residual capacity of the battery more accurately, and the error is within 3%. Most parameters of the curve are related to peak I, so only part of the data of the charging curve is needed. After establishing the incremental feature database of retired battery capacity, the residual capacity can be estimated relatively quickly.

![Figure 3. The predicted results of the model are compared with the actual results](image)

### 3.2 Internal resistance experiment

#### 3.2.1 Influence of voltage difference experiment

For parallel and series battery modules. Parallel connection enables charging and discharging of the cells in the group without the interference of the current size. The different capacities are charged or discharged at the same time, and the voltages across the cells are equal. The series connection means that the cells in the group are charged and discharged under the same current condition, and the same capacity is charged or discharged at the same time, and there may be a voltage difference between the single cells. The consistency of the cells in series is mainly reflected by the voltage difference between the battery cells in the group during charging and discharging. The smaller the voltage difference between the cells, the better the consistency between the cells and the more stable the performance of the battery module.

In order to study the effect of voltage difference between the cells of the series batteries, charge and discharge experiments were carried out on a 2S module composed of two cells. The capacity of the cell is 2050.31mAh and 2049.15mAh respectively, which are connected in series to form a module. The experimental circuit diagram is shown in Figure 4 and the experimental steps are as follows:

1. 0.2C constant current charge to charge cut-off voltage 8.4V;
2. Constant voltage charge until current drop to 0.01C;
3. 0.2C constant current discharge to the lower cut-off voltage 6.4V;
4. Record module voltage and two cells voltages;
5. Make a difference between the two cell voltages and record.

The cycle capacity of the 2S module is 1981.691 mAh, accounting for 96.71% of the battery capacity before series connection. The voltage difference curve is shown in Figure 5. (Figure 5(a) is the charging voltage difference curve, and Figure 5(b) is the discharge voltage difference curve). The maximum voltage difference appears in the SOC region between the high and low ends.
As shown in Figure 3, the voltage difference between the two cells is relatively stable in the middle-SOC region, but the voltage difference between the two cells changes greatly and the voltage difference increases in the initial and final stages of charging and discharging.

The main reason is that in the process of battery charging and discharging, there will be a large polarization resistance in the low-SOC region and the high-SOC region. If the polarization of one battery is different from that of the other, the voltage difference will increase.

Since the voltages of the two cells in the high-SOC and low-SOC regions will show great differences, the discharge cut-off voltage of the battery module can be appropriately increased and the charging cut-off voltage can be appropriately reduced, which can not only reduce the voltage difference between the two cells, but also increase the number of module cycles. But this shortens the voltage range of the module cycles, which will cause the battery's cycle capacity to decrease.

For a battery module, on the premise of satisfying the capacity demand, it plays a positive role in reducing the voltage difference between cells by appropriately reducing the voltage range of the module charging and discharging cycles. However, a quantitative analysis of the relationship between cut-off voltage and capacity is required to determine the optimal voltage interval.

3.2.2 Cut-off voltage and capacity experiment
In order to study the influence of the cut-off voltage on the cycle capacity, a quantitative experiment was carried out on the relationship between the charge cut-off voltage (up cut-off voltage) and discharge cut-off voltage (low cut-off voltage) of the series module 2S and the cycle capacity. The experimental steps are as follows:
(1) The fixed low cut-off voltage is unchanged at 5.98V, and the cycle capacity when the up cut-off voltage is 8.4, 8.3, 8.25, 8.2, 8.1, 8.05, 8.00, 7.95, and 7.9V is tested respectively;

(2) The fixed up cut-off voltage is unchanged at 8.4V, and the cycle capacity at the low cut-off voltages of 5.8, 5.9, 6.0, 6.1, 6.2, 6.3, 6.4, 6.6, and 6.8V is tested respectively;

(3) Record and plot the data of cut-off voltage and corresponding capacity.

The results are shown in figure 6. The low cut-off voltage slope is far less than the up cut-off voltage slope. That is, the low cut-off voltage is not sensitive to the capacity. If the discharge low cut-off voltage is increased within a certain range, the cycle capacity will be reduced, but the reduction ratio is small. On the contrary, the up cut-off voltage of charging is very sensitive to the circulating capacity of the batteries.

Therefore, the low cut-off voltage can be appropriately increased to achieve the purpose of reducing the voltage difference. The up cut-off voltage is very sensitive to capacity, and a slight change will have a large impact on the capacity, so the upper cut-off voltage should be increased as much as possible.

Based on the fact that the lower cut-off voltage is insensitive to capacity, indicators for charging and discharging strategies and batteries screening can be formulated. That is to appropriately increase the lower cut-off voltage of charge and discharge to achieve the purpose of reducing the pressure difference, and the upper cut-off voltage should be as high as possible under the premise of meeting the consistency requirements.

The internal resistance of the battery cells in series (including the ohmic resistance and the polarization resistance) largely determines the pressure difference between the two cells.

Since the value of the polarization resistance increases at both ends of the SOC (low SOC and high SOC), the method of increasing the low cut-off voltage for the low SOC region is used to reduce the voltage difference. On the other hand, the up cut-off voltage is very sensitive to the capacity and cannot be greatly reduced. Therefore, when screening the battery's internal resistance, focus on the internal resistance in the high SOC region. In other words, the internal resistance at the upper cut-off voltage (including ohmic resistance and polarization resistance) is used as the screening standard. In this way, the internal resistance of the battery can be quickly screened (that is, the batteries are charged to the up cut-off voltage to measure its internal resistance).

![Figure 6. Battery cut-off voltage and cycle capacity](image-url)

4. Results and discussion

Due to the influence of measurement noise, the IC curve of the cell cannot be directly obtained by numerical derivative. The IC curve is processed by moving average filtering and wavelet filtering to obtain a smooth and easy to analyze curve.

The reaction process of the positive electrode is mainly nickel ions converted from divalent ions ($\text{Ni}^{2+}$) to trivalent ions ($\text{Ni}^{3+}$), and trivalent ions ($\text{Ni}^{3+}$) into tetravalent ions ($\text{Ni}^{4+}$). The negative electrode reaction process is four phase transitions among the five states of graphite ($C_6$, $C_{12}$, $C_{18}$, $C_{36}$, $C_{60}$).
The appearance of multiple voltage platforms in Figure 2 (b) is the result of the different reactions of the cell's positive and negative electrodes superimposed on each other.

Figure 3 shows the comparison between the output of the neural network prediction model and the true capacity of the single battery. The relative error is within 3%, and to a certain extent, the capacity and trend of the battery can be predicted more accurately.

The IC curve analysis method requires only part of the region of the battery charging curve, and does not need to fully charge and then discharge the battery. Under the current test of the same rate, the test time will be about 50% shorter than the traditional test method.

The voltage difference is relatively stable in the middle region of the SOC, and there is a large difference between the two ends, which is mainly caused by the inconsistency of the polarization resistance. Although the ohmic resistances of the two cells are similar, the polarization resistances of the two cells are significantly different.

It can be seen from the results in Figure 6 that in the low SOC region, appropriately increasing the low cut-off voltage will not cause a relatively large loss to the capacity discharged by the module. When the cells are working, try to avoid the cells working in the low SOC area. In the high SOC area, the consistency of the cells should be improved as much as possible. That is, the internal resistance of the two battery cells should be the same, and the voltage difference of the cells in the module can be reduced.

5. Conclusions

In this paper, the residual capacity and internal resistance of retired batteries are studied respectively. Firstly, in terms of capacity, the IC curve analysis method is introduced into the screening of retired batteries, combined with the neural network algorithm, a good capacity estimation effect is achieved, and the relative error is within 3%. Under the premise of establishing a battery capacity increment database, it is 50% faster than the traditional test method at the same rate. Secondly, the influence of voltage difference of battery series modules is studied, and it is found that the high voltage difference occurs in the low and high SOC regions of the battery. The main reason is that the battery has a large polarization resistance in the SOC regions at both ends, which makes the single voltage inconsistent. Finally, according to the insensitivity of low SOC region voltage to capacity, the screening strategy of battery internal resistance is developed, which can realize the rapid screening of battery internal resistance.

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References

[1] TANG Baojun, WANG Xiangyu, WANG Bin, et al. Analysis and Prospect of China's New Energy Vehicles Industry Development Level[J]. Journal of Beijing Institute of Technology (Social Sciences Edition), 2019,21 (02): 12-17.
[2] DAI Xiaoxia, CAO Huili, XU Yangyang. Problems and countermeasures of large-scale development of power battery echelon utilization in China[N]. China computer Daily, 2018-10-29 (014).
[3] Saxena S, Le Floch C, MacDonald J, et al. Quantifying EV battery end-of-life through analysis of travel needs with vehicle powertrain models[J]. Journal of Power Sources, 2015, 282: 265-276.
[4] WANG Gang, ZHAO Guangjin, WU Wenlong, et al. Cascade utilization and recycling of power lithium battery[M]. Beijing: China Power Press, 2014
[5] SUN Dong. Research on Key Technologies for Lithium-ion Battery Second Use[D]. Shanghai: Shanghai University, 2016.
[6] Ding Li, Li Fan, Cai Wenjia, et al. Analysis on aging characteristics of lithium-ion batteries[J].
[7] Zhang X, Grube R, Shin K K, et al. Automotive battery state-of-health monitoring: a parity relation based approach[J]. IFAC Proceedings Volumes, 2009, 42(8): 552-557.

[8] Meng J, Cai L, Luo G, et al. Lithium-ion battery state of health estimation with short-term current pulse test and support vector machine[J]. Microelectronics Reliability, 2018, 88: 1216-1220.

[9] Xu Jing, Zhang Caiping, Wang Guoxiu, et al. Research on testing method of ohmic resistance for Li-ion batteries in techonology[J]. Power supply Technology, 2015, 39(2): 252-256.

[10] Guo Qipei, Zhang Caiping, Gao Yang, et al. Incremental Capacity Curve Based State of Health Estimation for LNMCO Lithium-ion Batteries[J]. Global Energy Internet, 2018 (2): 12.

[11] Ma Zeyu, Jiang Jiuchun, Wang Zhanguo, et al. A Research on SOC Estimation for LiFePO4 Battery with Graphite Negative Electrode Based on Incremental Capacity Analysis[J]. Automotive engineering, 2014, 36 (12): 1439-1444.