Detection of battery capacity degradation based on morphological structure

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Abstract. Owing to the fact that the existing battery capacity degradation detection method ignores the changes of battery internal morphological structure as the cycle number increases, it is hard to predict the rapid capacity degradation of the battery during the cycle process, which leads to errors of the battery capacity degradation detection result. This paper analyzes the changes in the morphological structure of the battery under different cycle numbers by means of tomographic images. At the same time, through the method of numerical analysis, the impact that the battery internal morphological structure change exerts on the battery capacity degradation is quantitatively analyzed, which provides a new way for detecting the capacity degradation of lithium ion battery.

1. Introduction

Owing to the advantages of high energy density, no memory effect, small self-discharge rate and long cycle life, lithium ion batteries have been widely used in electric vehicles [1-2]. When the electric vehicle is running, the battery capacity will degrade gradually with the deepening of using degree [3]. Detection of lithium battery capacity degradation can realize the real-time monitoring of the working state of the battery and provide decision support for fault prevention, which is of great significance [4]. At present, when detecting the battery capacity degradation based on electrochemical performance, battery capacity degradation rate is widely used to indicate the degree of lithium ion battery capacity degradation. And the value of battery capacity degradation rate can be obtained by cyclic charging and discharging experiments or by establishing a theoretical model [5-6]. The expression of the battery capacity degradation rate is:

\[ \Delta Q = \frac{Q_{\text{loss}}}{Q} = \frac{\Delta Q}{Q} \]  

(1)

In Equation (1), \( Q \) represents the initial battery capacity, \( Q \) represents the battery capacity after several cycles, \( \Delta Q \) represents the capacity degradation of the battery after several cycles. At present, the commonly used battery capacity degradation rate prediction model considers battery capacity degradation rate as function of the battery discharging temperature \( T \), the battery discharging rate \( C_{\text{rate}} \), the battery discharging depth \( DoD \), and the battery cycle number \( N \) [6]. And its expression is:

\[ \Delta Q = f(T, C_{\text{rate}}, DoD, N) \]
\[ Q_{\text{loss}} = B \cdot \exp \left( \frac{-31700 + 370.3 \times C_{\text{rate}}}{RT} \right) \cdot \left( N \times \text{DoD} \times Q_{\text{full}} \right)^{0.55} \]  

(2)

In Equation (2), B represents the pre-factor, R represents the ideal gas constant, \( Q_{\text{full}} \) is lithium power battery nominal capacity.

However, when the lithium-ion batteries are being used, there may be a sharp decline in capacity. As shown in Figure 1, a certain type of lithium iron phosphate power battery is subjected to periodic charging and discharging experiments according to technical specification (\( T=298K \), \( \text{Crate}=3 \) and \( \text{DoD}=100\% \)), and the relationship between lithium iron phosphate battery discharging capacity \( Q(N) \) and the cycles number \( N \) is shown in Figure 1 [7].

![Figure 1](image_url)

**Figure 1.** Discharging capacity as a function of cycles number.

As shown in Figure 1, the battery has a small capacity degradation rate during the first 41 cycles. When the cycles number is 42, the battery capacity shows a sharp degradation. If the capacity degradation of the battery is evaluated by the decrease of the discharging capacity of the previous 41 cycles, the battery capacity degradation condition cannot be fully and truthfully reflected.

During the cycles of charging and discharging, in addition to changes of electrochemical performance parameters (current, voltage, impedance, operating temperature), the internal morphological structure of the battery will also change, such as the loss of active material, formation of solid electrolyte interface (SEI) film on electrode surface [8]. The capacity degradation detection method based on electrochemical performance ignores the change of the internal morphological structure of the battery during the charging and discharging process of the battery, which makes it hard to detect the capacity degradation of the battery accurately. This will directly affect the power, economy and safety of electric vehicles, and restrict the further promotion and application of electric vehicles.

Aiming at the problem that the current battery capacity degradation detection method based on electrochemical performance cannot detect the capacity degradation of lithium-ion battery in electric vehicle accurately, a capacity degradation detection method based on battery morphological structure is proposed. Taking a certain type of lithium iron phosphate battery as the experimental object, the electrochemical experiment was first carried out to obtain the relationship between the capacity degradation rate of the lithium ion battery and the cycles number. Subsequently, the internal morphological structure of the battery was detected by X-ray by means of a tomographic image test system. On this basis, the correspondence between the capacity degradation rate of the battery and the
internal morphological structure of the battery is analyzed, thereby laying a solid foundation for detecting battery capacity degradation accurately based on morphological structure.

2. Detection method of battery capacity degradation based on morphological structure

Known from the existing research, the capacity of the battery is determined by the positive electrode structure, the negative electrode capacity, and the amount of lithium ions available [9-10]. According to Faraday's law, the amount of reactive material on the electrode is proportional to the amount of electricity passing [11]. Therefore, lithium battery capacity \( Q \) can be expressed as:

\[
Q = x_p \cdot Q_p + x_n \cdot Q_n = x_p \cdot zF \cdot \frac{m_p}{M_p} + x_n \cdot zF \cdot \frac{m_n}{M_n}
\]  

(3)

In Equation (3), \( x_p \) and \( x_n \), which indicate the lithium ion ratio of the positive and negative electrode, depends on the battery structure. The subscripts \( p \) and \( n \) represent the positive and negative electrodes of the power battery, respectively, \( z \) is the electrons number during the reaction period, \( F \) represents the Faraday constant, \( M \) represents the molar mass of the reaction materials, and \( m \) is the quality of the battery active materials participating in the reaction.

According to the electrochemical principle, a plurality of pole piece units make up of a single cell [12], and a positive electrode, a diaphragm and a negative electrode make up of the pole piece unit. The positive and negative electrode active materials are uniformly mixed with a conductive agent and a binder to prepare a slurry, which is then applied to the surfaces of the positive and negative electrode. Therefore, battery capacity \( Q \) can be further expressed as:

\[
Q = x_p \cdot Q_p + x_n \cdot Q_n = x_p \cdot \frac{zF}{M_p} \sum_{j=1}^{j} \varepsilon_j p_i \rho_{p,i} s_{p,i} h_{p,i} + x_n \cdot \frac{zF}{M_n} \sum_{j=1}^{j} \varepsilon_j n_j \rho_{n,j} s_{n,j} h_{n,j}
\]

(4)

In Equation (4), \( \rho_{p,i} \), \( \rho_{n,j} \), \( s_{p,i} \), \( h_{p,i} \), \( s_{n,j} \), \( h_{n,j} \) are the battery morphological structure parameters, and they denotes the \( jth \) order density of the positive and negative electrode active materials and its corresponding activity coefficient, coating area and coating thickness, respectively.

According to Equation (4), it can be seen that battery capacity \( Q \) is defined by battery structural morphology parameters. As the number of lithium ion cycles increases, electrochemical reactions including lithium ion intercalation and deintercalation will occur, and not only will the lithium battery internal resistance, operating current and voltage be changed, but also the structure and parameters of the active materials will be altered accordingly. As cycles number changes from \( \lambda \) to \( \lambda' \), changes of active materials coating thickness, coating area and density will happen. Therefore, the amount of change in the capacity of the battery can be expressed as:

\[
\Delta Q = Q^{\lambda'} - Q^{\lambda} = x_p \cdot \frac{zF}{M_p} \sum_{j=1}^{j} \varepsilon_j p_i \left( \left( \rho_{p,i}^{\lambda'} + \Delta \rho_{p,i}^{\lambda'} \right) \left( s_{p,i}^{\lambda'} + \Delta s_{p,i}^{\lambda'} \right) \left( h_{p,i}^{\lambda'} + \Delta h_{p,i}^{\lambda'} \right) - \rho_{p,i} \cdot s_{p,i} \cdot h_{p,i} \right) + x_n \cdot \frac{zF}{M_n} \sum_{j=1}^{j} \varepsilon_j n_j \left( \left( \rho_{n,j}^{\lambda'} + \Delta \rho_{n,j}^{\lambda'} \right) \left( s_{n,j}^{\lambda'} + \Delta s_{n,j}^{\lambda'} \right) \left( h_{n,j}^{\lambda'} + \Delta h_{n,j}^{\lambda'} \right) - \rho_{n,j} \cdot s_{n,j} \cdot h_{n,j} \right) = x_p \cdot zF \cdot \Delta \psi_p^{\lambda'} + x_n \cdot zF \cdot \Delta \psi_n^{\lambda'}
\]

(5)

In Equation (5), \( \Delta \psi_p^{\lambda'} \) and \( \Delta \psi_n^{\lambda'} \) represent the equivalent positive and negative electrode active materials morphological structure change. And it can be deduced that the battery capacity degradation is mainly determined by \( \Delta \psi_p^{\lambda'} \) and \( \Delta \psi_n^{\lambda'} \). The commonly used battery capacity degradation detection method ignores the influence of the variation of the battery morphological structure on the battery capacity degradation, resulting in errors in battery capacity degradation detection.

\( \Delta \psi_p^{\lambda'} \) and \( \Delta \psi_n^{\lambda'} \) can be obtained by measuring the density, area, thickness, and area change of the positive and negative electrode active materials of the electrode unit. The experimental equipment includes a tomographic measurement system, an electrochemical characteristic measurement system, as shown in Figure 2.
Among them, the tomographic measurement system is mainly composed of an X-ray generator and a photodetector [13], and its task is to utilize the atomic interaction between the X-ray photon flow and lithium ion battery structure (positive and negative materials, separator and electrolyte, etc.) to measure the morphological changes of the positive and negative active materials in a non-destructive, real-time and graphical way. The density of the positive and negative active materials of the lithium ion battery can be obtained by the gray value of active materials on the tomographic image, and the area change value can be reflected by the amount of change in the active materials area on the tomographic image. The amount of change in the coating thickness of the active material is very small, so it is considered to be constant during the cycle of the battery; And the electrochemical characteristic measurement system obtains the electrochemical characteristic information such as the corresponding capacity degradation rate parameter by measuring the current and voltage corresponding to the charging and discharging process of the lithium ion battery.

3. Experimental setup
In order to analyze the effect of the change of the morphological structure of the internal active materials on the battery capacity degradation during the cycle process, square lithium iron phosphate power batteries labeled A0, A1, A2, A3 (referred to as lithium experimental batteries) for electric vehicles with a nominal capacity of 10 Ah in the same batch are used as the experimental objects. Through testing the working current and voltage of lithium experimental batteries in a certain working state, electrochemical property information such as capacity of the positive and negative materials, internal resistance of the battery, and cyclic volt-ampere performance of charging and discharging can be obtained. Tomography measurement system is used to measure the three-dimensional shape and structure of the battery. The system has a geometric spatial resolution of 1 μm and a density spatial resolution of 0.5%.

Before the experiment, results of the initial capacity test of the batteries show that the initial capacities of the four batteries are 11.2, 10.9, 11.1, and 10.9 Ah, respectively. It can be concluded from the results that the consistency of the battery is good. During the experiment, the ambient temperature is controlled at 25°C, the discharge rate is 3 C, and the discharge depth is controlled to be 100%. The numbers of cycles of A0, A1, A2, and A3 are controlled to be 2, 59, 120, and 164 respectively. The following experimental operations are performed to obtain relevant results:

1. Wiring and setting the temperature T of the electric blast drying oven, firstly charging at a constant current of 0.5C to a cut-off voltage of 3.65V, then carrying out constant voltage charging to an off current of 0.02C, and then setting aside for 30 minutes.
2. Discharging with a preset C_rate constant current until the preset DoD, and then set the battery aside for 30 minutes.
(3) Taking step 1-2 as a cycle, the static capacity is measured every 24 cycles. If the preset N is reached, the battery is charged with a 0.5 C constant current to the preset SOC, and the lithium battery image is measured. Repeat steps (1)–(3).

According to the experimental step (3), the tomographic images of the lithium experimental batteries A0, A1, A2 and A3 under different capacity degradation states are measured by the tomographic imaging measurement system, and the spatial coordinates of the tomographic images are shown in Figure 3.

4. Experimental results analysis
Through the electrical performance test, the curve of the discharging capacity of three batteries A1, A2 and A3 with the number of cycles can be obtained, as can been seen in Figure 4.

As is shown in Figure 4, it can be concluded that A1 has the fewest number of cycles among the three batteries, but the capacity degradation is the most serious. When the cycles number of the battery is 42, the capacity degradation rates of A1, A2 and A3 are 21.03%, 2.76% and 0.76% respectively. So as to further analyze the performance of the power battery's capacity degradation shown on the power battery's electrical performance parameters (terminal voltage, capacity), a constant current charging experiment is performed on the A0, A1, A2, and A3 batteries at a charging rate of 0.5C to obtain the charging capacity increment curve of the power battery. As shown in Figure 5.

As is shown in Figure 5, the cycle number 59 of the A1 battery is less than 120 and 164 of A2 and A3, but the voltage value corresponding to the peak value of the figure moves in the direction of high voltage, which means increases of the internal resistance of the battery. Compared with A2 and A3, the height of all peaks of A1 is significantly reduced, representing a reduction in the amount of active
materials and available lithium ions [9]. That is to say, the capacity degradation rate of the battery with a smaller cycles number is more serious than batteries with a larger cycles number. This is obviously contradictory to the general conclusion that "under the same experiment condition, the more the cycles number of the battery, the greater the capacity degradation rate". Therefore, it is necessary to analyze the battery internal morphological structure changes during the capacity degradation process in combination with the CT image.

![Figure 5](image)

**Figure 5.** Constant current charging capacity increment curve of experimental battery with different cycle times.

Taking y=2.34mm and y=4.45mm as examples, respectively, to obtain the tomographic image of the corresponding morphological structure of $G(x, 2.34, z, \rho_{x}^{2.34})$, $G(x, 4.45, z, \rho_{x}^{2.34})$, $G(x, 2.34, z, \rho_{x}^{4.45})$, $G(x, 4.45, z, \rho_{x}^{4.45})$, $G(x, 2.34, z, \rho_{x}^{2.120})$, $G(x, 4.45, z, \rho_{x}^{2.120})$, $G(x, 2.34, z, \rho_{x}^{164})$ and $G(x, 4.45, z, \rho_{x}^{164})$, as shown in Figure 6.

![Figure 6](image)

**Figure 6.** Battery tomography image: (A) A0 (y=2.34mm), (B) A1 (y=2.34mm), (C) A2 (y=2.34mm), (D) A3 (y=2.34mm), (E) A0 (y=4.45mm), (F) A1 (y=4.45mm), (G) A2 (y=4.45mm), (H) A3 (y=4.45mm).
In order to quantitatively analyze active materials content of the positive and negative electrode in the battery as the number of battery cycles changes, the image processing software image-pro plus is used to obtain the battery positive and negative active materials area on different cross-section images, as shown in Figures 7 and 8.

**Figure 7.** Statistical diagram of positive electrode active materials area on the cross section of the battery.

**Figure 8.** Statistical diagram of negative electrode active materials area on the cross section of the battery.

As can be seen from Figure 7 and Figure 8, a rapid capacity degradation phenomenon happens on A1, at the same time, compared with the A0, A2, and A3, the area of the positive electrode and the negative electrode active materials in different cross sections show a rapid decline. The size of the active materials area on the tomographic image indicates how much the battery active materials can be used. Therefore, in battery A1 the capacity of which shows a rapid decline, compared with A0, A2 and A3, the content of the positive and negative active materials inside the battery also show a rapid decline.

According to the principle of CT imaging, the density of materials and the gray scale have a one-to-one correspondence. The RMS values of the pixel values of the negative electrode active materials on different cross-section tomograms are counted to acquire Figure 9.

**Figure 9.** RMS graph of the pixel of the negative electrode active materials on the battery cross section.

As can be seen from Figure 9, for battery A1 in which a rapid capacity drop occurs, the RMS value of the negative electrode active materials pixel is much smaller than A0, A2, and A3 in different cross sections. Combined with the electrochemical principle of the battery, it is known that during
continuous charge and discharge process, the active lithium ions react on the surface of the negative electrode of the battery to form an SEI film [8]. As the SEI film becomes thicker, the loss of active lithium ions increases, and the battery capacity continues to degrade. After the SEI film is formed on the negative electrode surface, the proportion of the negative electrode active material content in the corresponding gray scale interval is reduced on the tomographic image, and the corresponding pixel is also reduced in the gray scale interval. As a result, in the same gray scale interval, the root mean square of the pixel value is reduced.

Table 1 and Figures 10, 11, and 12 can be obtained by superimposing the area of the positive and negative electrode active materials of each cross section of the battery and the root mean square value of the negative electrode active materials of each cross section. As can be seen from Figures 10, 11 and 12, there is a one-to-one correspondence between the total area of the positive and negative electrode active materials, the total number of negative electrode active materials root mean squares, and the battery capacity.

**Figure 10.** Battery capacity, positive electrode active materials area statistics.

**Figure 11.** Battery capacity, negative electrode active materials area statistics.

**Figure 12.** Statistical diagram of the RMS value of the negative electrode active materials pixels and battery capacity.
### Table 1. Battery parameter statistics.

|                         | battery | A0     | A1     | A2     | A3     |
|-------------------------|---------|--------|--------|--------|--------|
| capacity                |         | 10.9   | 7.8    | 10.4   | 10.6   |
| Total area of positive electrode active materials | 2507.3  | 1331.6 | 2568.1 | 2496.8 |
| Total area of negative electrode active materials | 1392.96 | 250.4  | 1023.4 | 1243.8 |
| RMS value               | 8644464 | 1421788| 6422672| 7576945|

Using the data in Table 1, correlation analysis is performed on the battery capacity, the area of the positive electrode active materials, the area of the negative electrode active materials, and the root mean square value of the negative electrode active materials pixels. The correlation coefficients among the battery capacity and the area of the positive and negative electrode active materials, and the root mean squares of the pixels are 0.9796, 0.9883, and 0.9916, respectively. With the help of the tomographic image, it is proved that the capacity degradation of the battery depends on the content of lithium ions and positive and negative electrode active materials through analyzing the change of the internal morphological structure of the battery. Moreover, the roles of loss of number of active lithium ions and the loss of the negative electrode active materials play have a greater impact on the battery capacity degradation than the loss of the positive electrode active materials content.

### 5. Conclusions

Based on the relationship between lithium-ion battery capacity degradation and its inner morphological structure, it is concluded that as the morphological structure change of lithium-ion battery caused by the electrochemical reaction is neglected, detecting lithium-ion battery capacity degradation rate based on electrochemical performance may cause error, which is harmful for further promotion and application of electric vehicles. With the help of tomographic images, battery capacity degradation is detected from the perspective of battery internal morphological structure changes. Theoretical analysis and experiments show that:

1. As the capacity of the lithium-ion battery degrades, the corresponding performance of the internal morphological structure of the battery is expressed as a decrease in the content of positive electrode active materials, negative electrode active materials, and active lithium ions.

2. The effect of the consumption of active lithium ions on the battery capacity degradation is greater than the negative electrode active materials consumption and the positive electrode active materials consumption on the battery capacity degradation. With the help of tomographic image, information on the internal morphological structure change of the battery during battery capacity degradation process can be obtained, which provides a new method for detecting battery capacity degradation.

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