Study on electrochemical impedance spectrum of C-LiFePO$_4$ power battery

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Abstract. Electrochemical impedance spectroscopy (EIS) can provide the change of ohmic resistance (Rs), charge transfer impedance (Rct) and diffusion impedance (Zw) in the different charging/discharging states, which is a powerful tool to evaluate the application state of the battery. This paper tested EIS of 60 Ah C/LiFePO$_4$ power battery in different SOC and SOH states, and analyzed the variation tendency of Rs, Rct and Zw with the change of SOC and SOH states. The experimental results showed that Rs value keeps stable while values of Rct and Zw increase apparently at both ends of SOC (0~25% and 75~100%) at different SOC states. For different SOH states, the values of Rs, Rct and Zw keep stable in the range of 100~95% SOH. But when SOH decreases to 90%, it is found that the capacity of 60 Ah battery decreases while the resistant value increases obviously. Therefore, EIS parameters can reflect partially the polarization state of the internal battery, so as to predict the degradation state of the storage lithium-ion battery.

1. Introduction
Li-ion batteries are widely used in large energy storage systems such as electric vehicles and energy storage power stations due to their advantages of high specific energy, high specific power, long cycle life and high charge-discharge efficiency. The battery's SOC state and the battery's health state (SOH) are important performance parameters in the process of battery use, representing the battery's remaining capacity and remaining life respectively. A reasonable and accurate estimation of battery SOH is conducive to mastering the aging degree of batteries, providing reliable information for the maintenance and screening of battery groups, and extending the service life of batteries. More importantly, it can lay a foundation for accurate estimation of the SOC of each aging stage of the battery, prevent over-charge or over-discharge, and ensure the safe use of the battery. As early as 1998, F. Huet[1] reviewed the studies on SOC and SOH estimation of lead-acid and nickel-cadmium battery systems by means of ac impedance spectroscopy in a number of scientific journals, which provided a strong reference value for the application of ac impedance method in lithium ion battery SOC and SOH.
2. Experiment
The graphite/LiFePO4 power battery produced by avic lithium battery was selected in the experiment. The voltage of the monomer battery was 3.25v and the nominal capacity was 60 Ah.

The intelligent single-battery tester was used to conduct the full charge and full discharge cycle experiment. The charging process of the battery is firstly charged at A current of 1C (1C = 60 A) to 3.65 V, and then the constant voltage is charged until the current drops to 0.1c. The discharge process USES 1 C times of constant discharge to 2.5 V.

When the battery cycle was carried out to 1, 100, 200, 400, 600, 800 weeks, electrochemical ac impedance test (EIS) was performed on the battery in different SOC states in the same cycle using the us P4000 electrochemical workstation. In the test process, the battery voltage of 2.5v corresponds to SOC ~ 0, 3.65v corresponds to SOC ~1 as the standard, and the charging and discharging capacity of 0.5c is used as the basis for the selection of different SOC. The SOC range is 0~100% and the interval is 25%. Before each test EIS batteries let stand for 2 h, to ensure that the battery voltage is in stable state, the whole experiment process under 23.5 ℃.

The constant potential EIS test was used in the experiment, and the potential value was set as the open circuit voltage, the sinusoidal voltage amplitude was 4 mV, and the scanning frequency range was 10 k Hz ~50 m Hz. Zsimpwin software in electrochemical workstation was used for impedance spectrum data fitting and related EIS parameters were recorded.

3. Results and discussion
3.1. battery cycle performance
In order to investigate the changes in LiFePO4 power battery's ac impedance (EIS) with SOC and (SOH), we conducted a 1C full charge and full discharge cycle test on the battery and analyzed the charge-discharge performance and capacity attenuation at different cycle times, as shown in figure 1.

![Figure 1. Capacity retention rate-cycle number curves and charging-discharging curves(inset) of LiFePO4 power batteries](image)

According to the figure, the capacity retention rate of LiFePO4 power battery after 800 weeks of full-charge and full-discharge cycle under 1C ratio is 91.6%, and the battery capacity decreases slowly with the increase of cycle number during the whole cycle. FIG. 1 illustrates the typical charging and discharging curve of the battery. The initial stage (low SOC state) and the end stage (high SOC state) in the figure show large voltage changes, and the voltage platform in the middle part is relatively flat. During the 800 cycle, the charging and discharging curves of the battery are similar, indicating that the battery is in a stable circulation state, which provides a basis for testing the impedance spectrum of the battery in different states.
Battery health (SOH) is a relative quantity, which refers to the ratio of the capacity released by the power battery from the full state discharge to the cut-off voltage to the nominal capacity of the new battery [2]. As the constant current full charge and full discharge circulation system is adopted in the experiment, SOH of the corresponding cycle of the battery can be calculated according to the definition of SOH, that is, the capacity retention rate of the battery. As can be seen from figure 1, the battery SOH gradually decreases with the increase of cycle times. In order to facilitate the analysis of the change of EIS with SOH in different weeks, we have sorted out the experimental data, as shown in table 1.

| Cycling Number | 1   | 100 | 200 | 400 | 600 | 800 |
|---------------|-----|-----|-----|-----|-----|-----|
| SOH%          | 100 | 99.8| 98.3| 95.0| 92.4| 91.6|

3.2. definition method

Battery ac impedance performance and equivalent circuit

Electrochemical impedance spectroscopy (EIS) measures the impedance variations of each part of the system with small amplitude sine wave potential or current as the perturbation signal [3]. FIG. 2 shows the Nyquist plots of ac impedance measured by the experimental power battery in the state of SOC~25%.

![Figure 2. Electrochemical impedance spectroscopy (EIS) curves of LiFePO4 power battery at 25% SOC](image)

Among them, the high-frequency EIS is a straight line in the 4th quadrant, and the slope is approximately 1, which is a reflection of the inductive performance of the power battery. This process is mainly caused by the porosity of the electrode, the non-uniformity of the surface, and the connection of leads [4], which can be represented by an inductance L. Since battery impedance is only affected by temperature in the high frequency region of > 30hz and has nothing to do with SOC [5], this paper does not analyze the change of EIS in high frequency region with SOC and SOH. The junction point of high and medium frequency area, namely the intersection point of curve and horizontal axis, is ohmic impedance Rs, reflecting the sum of impedance of electrolyte, diaphragm, collector fluid and collector fluid and the interface between positive and negative poles [3]. The arc part of the intermediate frequency EIS is caused by the charge transfer impedance of Li+ at the interface between the electrode and the electrolyte, which is usually represented by a parallel circuit of charge transfer internal resistance Rct and dual-layer capacitor Cdl. Since the arc part in the figure is a flattened semicircle, indicating that the double-layer capacitance is not pure capacitance, Cdl can be replaced by the electric double-layer element Q [6]. It should be noted here that the charge transfer impedance in the intermediate frequency should actually include the reaction impedance of the positive electrode and the negative electrode. Since the response frequency reflected by the two is the same in the power battery system, they can be
combined together, only considering the total impedance. However, if one electrode performance attenuation occurs, different spectral forms may appear. Low frequency area EIS is with Li + electrode active material in the solid state diffusion impedance related a slash, 45 ° slope in theory, but due to the porous electrode and Li + diffusion in solid phase, and the influence of embedded capacitor appeared deviation. This diffusion process is generally represented by Warburg impedance $Z_w$.

**Figure 3.** Equivalent circuit of LiFePO$_4$ power battery

Based on the above analysis, it can be seen that the equivalent electrochemical impedance model includes four parts: inductance $L$, ohmic resistance $R_s$, charge transfer resistance $R_{ct}$/ electric double-layer element $Q$ parallel composite element, and diffusion resistance $Z_w$. Compared with the classic Randles equivalent circuit elements, the high-frequency inductance is increased. Therefore, the modified Randles model [1] is adopted in this study, as shown in figure 3. In order to accurately study the variation law of impedance of each part of the battery with SOC and SOH, we used Zsimpwin electrochemical analysis software to fit the impedance spectrum according to the equivalent circuit, so as to obtain the EIS parameter values. The fitting results are shown in table 2. It can be seen that the error of the test data and fitting data of other parameters is about 2% except for the electrical double-layer element $Q$, which indicates that the equivalent circuit model can meet the accuracy requirements of the fitting analysis. In this study, the variation of ohm impedance $R_s$, charge transfer impedance $R_{ct}$ and diffusion impedance $Z_w$ with the SOC and SOH of the battery was investigated.

| Index | Fixed | Symbol | Start       | End       | %error |
|-------|-------|--------|-------------|-----------|--------|
| 1     | 0     | L      | 3.568E-7    | 3.568E-7  | 1.243  |
| 2     | 0     | Rs     | 0.0004589   | 0.0004589 | 0.9424 |
| 3     | 0     | Q      | 30          | 30        | 9.2    |
| 4     | 0     | n      | 0.8621      | 0.8621    | 3.355  |
| 5     | 0     | Rct    | 0.0003759   | 0.0003759 | 1.192  |
| 6     | 0     | W      | 4733        | 4733      | 2.176  |

Note: the value of the symbol "W" is admittance, inversely related to diffusion impedance

### 3.3. The impedance variations of EIS in different SOC states

In order to comprehensively study the change law of battery EIS with SOC, we tested the electrochemical impedance of different SOC at different cycle times. Figure 4 shows the curve of EIS spectrum at week 1, 200, 400 and 800 of battery cycle with SOC. It can be seen from the figure that under four different cycle cycles, the change law of EIS with SOC is almost the same, the curve of high frequency area is almost coincident, and the curve of low and medium frequency area is relatively dispersed. When SOC=0, the curve radius of arc curvature in EIS intermediate frequency region is the largest, while when SOC~25%, the radius of arc curvature is obviously reduced. When SOC increases to 50%, the radius of arc curvature is still decreasing, but the variation is smaller and smaller. However, the low-frequency diagonal lines in different SOC states are almost parallel, indicating that the diffusion behavior of total ions in the electrode remains unchanged under different SOC states. In summary, when
SOC < 50%, the EIS map of the battery is greatly affected by SOC, especially the change of charge transfer impedance represented by the arc part on the curve with SOC is obvious. However, when SOC > is 50%, EIS atlas changes little.

Figure 4. EIS morphology changes with SOC at different cycle numbers

In order to further analyze the relationship between the impedance behavior of each part of the battery and SOC, we used the equivalent circuit in 2.2 to fit the impedance spectrum data in different states, and obtained the variation curves of ohm impedance Rs, charge transfer impedance Rct, and diffusion impedance Zw with SOC state, as shown in figure 5.

As shown in figure 5 (a), the battery ohm impedance Rs hardly changes with cycle times and SOC, which indicates that the battery ohm impedance remains consistent under different SOC within 800 weeks, and the contact of each part of the battery does not change significantly. In figure 5 (b), as SOC increases, the charge transfer internal resistance Rct decreases first and then increases. In the SOC interval of 0~25%, the charge transfer impedance Rct is reduced, and then tends to be stable. In the range of 75%~100% SOC, Rct shows an increasing trend. This can be interpreted as that in low and high SOC regions, the electrode is close to full charge and full discharge, and no obvious electrode reaction occurs, resulting in increased charge transfer impedance. Under 400 weeks, the charge transfer impedance basically remains the same, but after 800 weeks, the charge transfer impedance increases significantly, which is obviously caused by the gradual deterioration of the electrode performance and the increase of Rct as the number of cycles increases. As shown in figure 5 (c), diffusion impedance Zw is affected by SOC in the same way as Rct. This is due to the full or empty state of the electrode at the end of the charge-discharge phase, making it more difficult for Li+ to embed or detach from the active material, resulting in increased diffusion impedance.
3.4. The impedance variations of EIS in different SOH states

In order to investigate the changes of battery EIS with SOH state, electrochemical ac impedance spectra of the same SOC with different SOH state were summarized. The EIS curves in figure 6 are the EIS curves when SOC is 0, 25%, 50%, 100%. It can be seen from the figure that under all SOC states, the change law of battery EIS with SOH state is basically consistent, part of the high frequency curve is concentrated, while the low and medium frequency curve is relatively dispersed. When the battery SOH is in the range of 100%~95%, the curvature radius of the curve arc section in the intermediate frequency area increases first and then decreases, but the range of variation is small in this process. When SOH decreases below 92.4%, the curvature radius of EIS circular arc increases significantly. This shows that when the battery SOH is between 100% and 95%, the battery EIS does not change much with SOH. With the further decrease of SOH, the battery gradually ages and the performance decays accordingly, leading to significant changes in the electrochemical impedance spectrum.
4. Conclusion
In this paper, the electrochemical alternating current impedance of the 60Ah LiFePO$_4$ power battery under the state of SOC and SOH was studied in the full charging and discharging cycle. The equivalent circuit model was used to fit the impedance spectrum data, and the EIS parameters representing the impedance behavior of each part of the battery were obtained.

Based on different SOC and SOH ohmic resistance Rs, charge transfer impedance Rct and diffusion impedance Zw EIS parameters such as the analysis of the results show that in the condition of different SOC, Rs is almost constant, Rct and Zw along with the increase of SOC shows the tendency of increase with the decrease of the first, on both ends of 0 ~ 25% and 75% ~ 25% range is especially significant changes, in both ends of the SOC range with the reduction in electrochemical reaction degree, electrochemical polarization and diffusion polarization all showed a trend of increase; Under different SOH states, Rs does not change much, and Rct and Zw are basically stable within the range of 100%~95% SOH, indicating that the battery is still in good working condition within at least 800 weeks of circulation. Although the parameters of electrochemical impedance spectrum do not show a certain dependence with SOH when the battery performance does not decline significantly, it can reflect the working state of the battery through impedance information when the battery performance declines significantly. Therefore, the study in this paper can provide a qualitative judgment basis for the state of the power battery SOC and SOH. With the deepening of the experiment, it is possible to establish the correlation between EIS parameters and SOH, so as to achieve the purpose of predicting battery health.

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