Electrochemical Impedance Analysis of C/LiFePO₄ Batteries in Cycling Process

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Abstract. In this paper, the cycle performance and capacity fading of commercial C/LiFePO₄ batteries were studied at different rate. The electrochemical impedance spectroscopy (EIS) of the battery was tested and analyzed in different charge-discharge cycles. The morphologies of anode and cathode at different cycle numbers were also characterized by scanning electron microscope (SEM). The experimental results show that the capacity fading of the batteries become faster at higher rate cycling. The SEM images of the cycled electrodes exhibit that capacity fading of the batteries is possibly attributed to the degradation of the anode structure. When the performance of the battery deteriorates sharply, there is a new semicircular arc appearing in the low-mid frequency region in the relative EIS, indicats that the change of EIS can correlate with the state of the battery performance degradation. Therefore, the performance characteristics of battery can be evaluated according to electrochemical impedance spectroscopy. It could also provide scientific and technical support for the fast evaluation system of battery on the cycling performance.

1. Introduction

At present, lithium ion batteries are widely used in large energy storage systems such as electric vehicles and energy storage power stations. However, there are differences in the performance of the individual battery groups. Continuous charging and discharging cycle will accelerate the capacity of the battery pack and attenuate, leading to premature deterioration of some batteries and affecting the normal operation of the energy storage system [1,2]. Therefore, it is necessary to be able to predict and identify the health status of batteries in advance, conduct rapid evaluation and grading screening on in-service batteries, eliminate or grade the batteries with different degradation degrees, avoid the security risks of battery system and improve operation efficiency. More and more studies have been conducted to judge the battery health by internal resistance at home and abroad [3,4]. As the capacity attenuation mechanism of lithium battery is very complex, after long-term use, the positive and negative electrode impedance increases significantly, electrolyte decomposition occurs, and electrode material structure is damaged or detached, which are the reasons that affect the deterioration of battery health [5].

Based on the research of lithium ion battery capacity attenuation situation of under different charging and discharging system, test capacity attenuation in the process of the corresponding electrochemical
impedance spectroscopy, ac impedance spectroscopy analysis and each part of the impedance changing with the cell cycle, and ac impedance spectra and the corresponding relationship between the state of the battery performance deterioration to judge the health status of the battery and the establishment of pilot using battery fast evaluation system to provide the technical support.

2. Experiment

2.1. Battery cycle life test
The test object in this paper is commercial no. 5 graphite/ferric phosphate lithium battery, the standard voltage range is 2.0-3.65v, and the nominal capacity is 550 mAh.

Put battery being measured at 25 °C constant temperature box, the Wuhan Blue Electrical T2001 test system for different ratio of battery charging and discharging cycle life experiments, using constant current constant voltage charging process, adopts the way of constant current discharge process. The charging and discharging system is as follows: the charging process of the first group of batteries is firstly charged to 3.65v with a current of 1C (1C = 550 mA), and then charged at constant voltage until the current drops to 0.1c. In the discharge process, the same 1C multiplier was used to permanently transport the electricity to 2.0v. The second battery group USES a 2C multiplier cycle, other conditions are the same as one group.

2.2. Battery ac impedance test
The cell cycle under 1C and 2C rate was selected. When the battery cycle was completed to 0, 50, 100, 200, 400, 800 cycles, American VersaSTAT 3 electrochemical workstation was used to conduct the ac impedance test (EIS) on the battery, and the battery was in the discharge state. The test adopted the constant potential EIS test method, and the potential value was set as the open circuit voltage, the sinusoidal voltage amplitude was set as 10 mV, and the scanning frequency was 10 k~10 m Hz. The ac impedance spectrum of the battery with different cycle weeks was tested, and the corresponding equivalent circuit was established for fitting analysis, and the variation law of the impedance of each component of the battery with cycle weeks was obtained.

2.3. Morphology of the electrodes
The electrode morphology at different stages of the battery cycle was characterized by scanning electron microscopy (SEM, FEI Sirion 2000) at the beginning and end of the cycle.

3. Results and discussion

3.1. Analysis of the capacity attenuation of the battery under different power ratios

![Figure 1. Capacity retention rate-cycle number curves of C/LiFePO₄ batteries at 1C and 2C rate](image)
Figure 1 shows the capacity-cycle relation curve of lithium iron phosphate battery under the ratio of 1 c to 2C. The capacity retention rate of the battery after 800 weeks of circulation under 1C ratio is 81.10%, and the battery capacity decreases slowly with the increase of cycle number during the whole cycle. The capacity of the battery decreases sharply after 50 weeks of cycle under 2C, and the capacity retention rate after 200 weeks is only 58.59%. Therefore, under the condition of full charge and discharge, high rate charging and discharging will lead to rapid deterioration of battery performance. After 800 weeks of battery with 1C cycle, the battery performance remains good and can still work normally. The batteries with a 2C multiplier cycle deteriorated 50 weeks later and deteriorated more severely in subsequent cycles.

3.2. Analysis of battery ac impedance spectrum

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 C/LiFePO\textsubscript{4} battery at 1C rate under different cycle numbers](image)

In order to investigate the changes of the impedance of each part of the battery in the circulation process, the electrochemical impedance of the battery in different cycles was studied. Figure 2 shows the ac impedance spectrum of the battery at 1C times in different cycles. As can be seen from the figure, all EIS are composed of arcs in the high frequency region and slashes in the low frequency region, representing the impedance information of charge transfer process and diffusion process respectively [6]. During the first 100 weeks of cycle, the radius of curvature of arc decreases. During the cycle from 100 to 800 weeks, the radius of curvature of arc remains basically stable, indicating that the battery is in the activation stage at the earlier stage of cycle and the charge transfer process remains stable after that. In order to better analyze the impedance behavior of each part in the cycle, the equivalent circuit (FIG. 3) is adopted to fit the impedance spectrum data, where Re is the ohm internal resistance, including the impedance of electrolyte, diaphragm, collector fluid and the interface between collector fluid and positive and negative pole. Rct is the electrochemical impedance of the charge transfer process, including the reaction impedance of positive and negative poles. Q is a constant phase Angle element, representing the interfacial capacitance of electrochemical reaction. W is Warburg impedance of reaction diffusion and mass transfer process [6].
According to the equivalent circuit simulation, the impedance variations of each part of the battery with different cycle times in 1C are shown in figure 4. At the beginning of the cycle, the ohm internal resistance (Re) of the battery decreases rapidly and becomes stable after 100 weeks. And after 400 weeks it starts getting bigger again. The results show that there is a process of adjusting the internal components of a battery at the beginning of the cycle, including the infiltration of electrolyte inside the electrode, the distribution of electrode materials and the compact relation of electrode structure, which will lead to the reduction of ohm impedance. After a certain cycle, the irreversible reaction of the electrolyte increases, resulting in the electrolyte "drying up", or the electrode structure becomes loose due to repeated charging and discharging of the electrode materials, resulting in the increase of ohmic impedance. Electrochemical impedance (Rct) decreases rapidly at the beginning of the battery cycle and becomes stable after 100 weeks. This phenomenon is similar to the variation trend of the ohm internal resistance of the battery. With the initial charging and discharging activation of the battery, the electrode and material structure are more suitable for lithium ions to detach, and the electrochemical reaction of the anode and cathode is easier to carry out. The diffusion impedance (WR) of the battery increases first, then decreases, and finally becomes stable. This indicates that during the activation process at the beginning of the cycle, the solid diffusion of lithium ions in the material gradually improved, making the diffusion impedance (WR) gradually reduced. It can be seen from the whole cycle process that the above parameters (Re, Rct and WR) do not change much. After 800 cycles of 1C cycle, the battery is still in a healthy cycle process, and the battery performance change is a normal attenuation process.
Figure 5 shows the ac impedance curve of the battery with different cycle cycles at the 2C ratio. As can be seen from the figure, the initial EIS of the battery is also composed of a circular arc in the high frequency area and a diagonal line in the low frequency area. When the battery cycle reaches 50 weeks, some changes gradually occur at the straight line of the low-frequency area, that is, a distinct arc appears at the beginning of the straight line, and then the half-circle radius of the high frequency area gradually decreases, so that the entire EIS curve becomes composed of two irregular arcs and a diagonal line. Corresponding to the battery 2C cycle life curve (figure 1), the battery capacity decreased sharply after 50 weeks. Thus, when the battery performance is seriously deteriorated, a new arc will appear at the beginning of the line in the middle and low frequency area of the EIS spectrogram of the battery. In order to better fit the changing impedance spectrum, the equivalent circuit (FIG. 6) was used for data fitting. Relative to the 1C multiplier equivalent circuit (FIG. 3), the 2C multiplier equivalent circuit adds a RC element representing another charge transfer process, namely $R_{ct2}$ and $Q2$.

**Figure 6.** Equivalent circuit of C/LiFePO$_4$ battery at 2C rate

**Figure 7.** Impedance changes with cycle numbers at 2C rate
Through the simulation of equivalent circuit, the impedance variations of each part of the battery with different cycle times under the 2C ratio are shown in figure 7. The impedance variation trend of each part under the 1C power ratio was compared (figure 4). In the process of the whole cycle, ohmic resistance \((R_e)\) are around 0.1 Ω, little change; For electrochemical impedance \((R_{ct1})\) and diffusion impedance \((W_R)\), the change is especially significant. The electrochemical impedance \((R_{ct1})\) in high frequency area decreases rapidly at the beginning of the cycle and then increases. Diffusion impedance \((W_R)\) increases rapidly after the 50-week cycle. These changes are consistent with the 2C multiplier capacity cycle curve in fig.1, suggesting that the reason for the sharp attenuation of capacity after 50 weeks may be closely related to the changes of electrochemical impedance \((R_{ct1})\) and diffusion impedance \((W_R)\), but not much related to the changes of ohm impedance \((R_e)\). As can be seen from the impedance spectrum (figure 5), a circular arc gradually appeared at the low and medium frequencies after the battery was circulated for 100 weeks, suggesting the generation of new electrochemical reactions, which is also the reason for the reduction of the high frequency semicircle \((R_{ct1})\).

3.3. Electrode morphology analysis
In order to find out the change of electrode morphology in the cell cycle, we conducted SEM experiments of positive and negative electrodes with different cycles.

Figure 9 is the SEM photo of the lithium iron phosphate anode and graphite anode at different cycle times under the battery 2C ratio. As can be seen from the SEM photograph of the positive electrode of lithium iron phosphate (figure 9a), after the 50-week cycle, the electrode surface material is evenly distributed, the particle size is uniform, and the electrode structure is complete. After 200 cycle (FIG. 9b), the surface morphology of lithium iron phosphate positive electrode did not change significantly, indicating that the morphology and structure of the positive electrode did not change significantly after 200 cycle under 2C ratio. As can be seen from the SEM photo of graphite anode (FIG. 9c), the material on the electrode surface has begun to accumulate. When the electrode circulates for 200 weeks (FIG. 9d), the graphite electrode surface accumulates more seriously, the electrode structure shows obvious cracks, and the electrode structure is seriously damaged. It can be seen from this that the battery circulates under 2C, and the structure of lithium iron phosphate positive electrode hardly changes, but it has a great influence on the structure of negative electrode.

4. Conclusion
This article through to the lithium ion battery capacity attenuation under different ratio of research, combining with ac impedance spectroscopy and across the chip morphology changing with the cyclic time, battery capacity attenuation and impedance spectroscopy were analyzed, the correlation of electrode shape, results show that the high rate of circulation make cathode structure produces more severe damage, when the battery performance seriously deteriorated, impedance spectrum in the low frequency area will appear a new circular arc, corresponds to the slower the cathode electrochemical reaction. Therefore, the capacitance attenuation state of the battery can be judged by the characteristic change of electrochemical ac impedance spectrum. This discrimination rule is particularly important for the grading and screening of echelon utilization batteries. For example, among many batteries, if the EIS curve of some batteries is found to have a new arc at the line in the low and medium frequency region, it can be seen that these batteries have entered a serious deterioration stage and need to be removed and replaced. Therefore, this method can provide technical support for the establishment of screening principles and the rapid evaluation system of cascade utilization battery.

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