Influence of Cycling on the Electrochemical Impedance Spectroscopy for Lithium Iron Phosphate Batteries

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Abstract. Electrochemical impedance spectroscopy (EIS) is one of the most effective methods that can be used to study the cycling decay behavior of lithium ion batteries (LIBs) without destruction of the battery. In this paper, in order to understand and to analyse the impedance response of the Lithium iron phosphate (LFP) batteries during various cycling rates, an equivalent circuit model (ECM) is established to investigate the cycling influence on the ECM parameters of LIBs. The influence of the discharging process on the patterns of the ECM was also analysed. The results indicate that the sum ohmic resistance and the Li+ diffusion through the SEI layer resistance keep increasing and the charge transfer resistance drop during the cycling when the retention capacities are higher than 90%. While the LFP batteries cycle under 1 C, the charge transfer resistance of them drop at first and then increase significantly after around 200 cycles when the retention capacities are lower than 80%. The results also show that when the LFP batteries are discharged during one single cycle, the sum ohmic resistance, the Li+ diffusion through the SEI layer resistance and the charge transfer resistance keep increasing. The results in this study indicate that EIS is a useful tool to obtain information for monitoring the state of health of LIBs.

1. Introduction

Lithium ion batteries (LIBs), with high gravimetric and volumetric energy density, high operating voltage levels, low self-discharge and long cycle life, have been extensively used in the portable electronic devices, cellular phones and electric vehicles (EVs) etc. [1-2]. In order to operate the batteries in these systems effectively and safely, an understanding of the influence of state of health (SOH) and state of charge (SOC) on the batteries is very important [3]. Various models have been established to study the performance of lithium-ion batteries [4]. Electrochemical impedance spectroscopy (EIS) is one of the most useful tools can be used to investigate electrochemical behaviors of LIBs during cycling [5]. It has been proved in the published works that EIS combined with equivalent circuits can be used to study the EIS patterns of the LIBs. Various equivalent circuit models (ECM) have been established to obtain EIS parameters of lithium-ion battery during cycling. The typical models are composed of electrical components, such as inductor, resistor, capacitor, Warburg impedance, constant phase element, and their values are identified via EIS [4]. It is crucial to understand the electrochemical characteristics of LIBs at all relevant conditions [6]. The previous studies investigated the influence of ambient temperature, the cycling currents, the state of charge and the state of health, etc. on the ECM characteristics of LIBs [4-8]. In this work, the influence of cycling under three different currents on the...
ECM parameters of Lithium iron phosphate batteries were investigated, and the effects of SOC during cycling were also studied.

2. Materials and methods
The Lithium iron phosphate (LFP) (IR18650EH) cells were purchased from Tianjin Lishen Battery Joint-Stock Co., Ltd. Their nominal capacity was 1.6 Ah. Their cathode is Lithium iron phosphate, and their anode is graphite. The LFP cells were divided into three groups, and they were charged and discharged under 0.32, 0.8 and 1.6 A, respectively. The cycling processes were carried out by the MACCOR SERIES 4200 Battery test system. The charge-discharge process was done as the following steps. The LFP cells were charged at the current of 0.32 or 0.8 or 1.6 A until the voltage reached 3.65 V. Then they were charged at 3.65 V until the current dropped to 80 mA. In the final step, they were discharged at the current of 0.32 or 0.8 or 1.6 A until their voltage reached 2.5 V. Electrochemical impedance spectroscopy (EIS) measurements were obtained by Zahner Zennium machine. The testing ambient temperature was 25°C. The frequencies were ranging from 1 kHz to 10 mHz, and the perturbation signal was 10 mV. The ECM models and parameters were enabled by Zahner Analysis software. The EIS patterns of the batteries at various SOC were also discussed.

3. Results and discussion

3.1. The capacities fade of the LFP batteries during cycling

![Graph showing retention capacity of LFP batteries during cycling]

Figure 1. The retention capacity of the LFP batteries during cycling. All the retention capacities were normalized to the fresh cells, whose retention capacities were set as 100%. The cycling currents of the group a, b and c LFP cells were 0.32, 0.8 and 1.6 A, respectively.

It is illustrated in Figure 1 that the capacities of the LFP batteries cycling under 0.32 and 0.8 A showed similar fading trends, while the capacities of the LFP batteries cycling under 1 A decreased much faster. The retention capacities of the LFP batteries cycling under 0.32 and 0.8 A are still higher than 90% after 600 cycles. The retention capacities of the LFP batteries cycling under 1.6 A decreased to 90% after around 150 cycles, and dropped to 80% after around 200 cycles, at last sharply declined after 300 cycles.

3.2. The equivalent circuit models for LFP batteries
A number of ECMs for LIBs have been established by numerous reports [4-13]. It was described in the literature that the EIS of the LIBs could be divided into various ranges [11]. In the very high frequency,
such as 1 kHz, an inductive behavior can be identified in the impedance spectrum. This behavior is mainly caused by the determination setup such as the connecting lines and the type of cable wiring \cite{11}. The purely ohmic resistance at abscissa zero crossing for the imaginary part of the impedance, which is dominated by the internal conductivity of the LIBs, is the only ECM parameter could be directly measured. In the middle high frequency ranges, the processes are caused by the charge-transport processes and are represented in the impedance spectrum in the form of semicircular arches. In the low-frequency range diffusion processes dominate in the anode and cathode. The course of the impedance spectrum corresponds to a 45º rising line in the Nyquist plot \cite{11, 14}. In this paper, it was proved that the equivalent circuit model showed in Figure 2 could be used to simulate the measured EIS spectra of the batteries. The simulated spectra matched the measured spectra very well (Figure 3). As it was noted in the literature \cite{5}, L is dominated by the high-frequency inductance. The Rs denotes the sum internal ohmic resistance of the LIBs. The R1 in parallel with C1 simulates the resistance of Li⁺ diffusion through the SEI layer. The R2 in parallel with CPE (constant phase element, CPE) simulates the charge transfer reaction at the electrode/electrolyte interface. W impedance is dominated by the Li⁺ diffusion process in the porous active materials. The C_{int} describes the Li-ion accumulation effect in intercalation/de-intercalation electrodes for low-frequency perturbations.

![Figure 2](image.png)

**Figure 2.** The equivalent circuit model for LFP batteries.

![Figure 3](image.png)

**Figure 3.** The measured and simulated Nyquist spectra for LFP batteries. The cycling current of the LFP cells was 0.8 A.

3.3. **The influence of cycling on the parameters of equivalent circuit models for LFP batteries**

The simulated parameters Rs, R1 and R2 of the LFP batteries are showed in Figure 4, 5 and 6, respectively. The Rs and R1 values of the LFP batteries cycling under 0.32 and 0.8 A showed similar trends which increased slightly during cycling. The R2 values of the LFP batteries cycling under 0.32 and 0.8 A also showed similar trends which decreased during the first 600 cycling. The Rs, R1 and R2 values of the LFP batteries cycling under 1.6 A during the first 100 cycles showed the similar trends.
with those of the LFP batteries cycling under 0.32 and 0.8 A, while the $R_s$, $R_1$ and $R_2$ values of the LFP batteries cycling under 1.6 A increased dramatically after 100 cycles. It was showed in figure 1 that the retention capacities of the 1.6 A current cycling batteries were higher than 90% during the first 100 cycles and rapidly decreased after 150 cycles. It can be concluded that when the retention capacities of the LFP batteries are higher than 90%, the $R_s$ and $R_1$ values would increase and the $R_2$ values would decrease during cycling. It can be deduced that when the retention capacities of the LFP batteries are lower than 80% and decrease rapidly during cycling, the $R_s$, $R_1$ and $R_2$ values would increase significantly.

Figure 4. The $R_s$ of the LFP batteries during cycling. The cycling currents of the group a, b and c LFP cells were 0.32, 0.8 and 1.6 A, respectively.

Figure 5. The $R_1$ of the LFP batteries during cycling. The cycling currents of the group a, b and c LFP cells were 0.32, 0.8 and 1.6 A, respectively.

Figure 6. The $R_2$ of the LFP batteries during cycling. The cycling currents of the group a, b and c LFP cells were 0.32, 0.8 and 1.6 A, respectively.

3.4. The SOC influence on the patterns of ECM for LFP batteries
The $R_s$, $R_1$ and $R_2$ values of the LFP batteries at various SOC during 0.32 A current cycling are showed in Figure 7. It can be seen that when the LFP batteries were discharged from 100% SOC to 0% SOC during one single cycle, the $R_s$, $R_1$ and $R_2$ values of the batteries kept increasing. It indicates that the sum ohmic resistance, the Li$^+$ diffusion through the SEI layer resistance and the charge transfer resistance keep increasing during the LFP batteries discharging.
4. Conclusion
An equivalent circuit model including one capacitor element in parallel with resistor and one constant phase angle element in parallel with resistor elements is established to study the electrochemical behaviors of LFP batteries. When the LFP batteries cycle currents are 0.32 and 0.8 A (the cycle rates are 0.2 and 0.5 C, respectively), the retention capacities could keep higher than 90% even after 600 cycles. In the meanwhile, the parameters $R_s$ and $R_1$ of the LFP batteries cycling under 0.2 and 0.5 C have been found to increase slowly during cycling, and the $R_2$ values kept decreasing. The capacities of the LFP batteries fade fast during cycling under 1.6 A (the cycle rate is 1 C) and are lower than 80% after 200 cycles. There are two stages for the values of the $R_s$, $R_1$ and $R_2$ of the LFP batteries cycling under 1 C. In the first stage, the values of $R_s$ and $R_1$ increase slightly and the values of $R_2$ decrease during the first 100 cycles. In the second stage, all the $R_s$, $R_1$ and $R_2$ values keep increasing during cycling and they dramatically increase after 200 cycles. It indicates that the sum ohmic resistance and the Li$^+$ diffusion through the SEI layer resistance keep increasing and the charge transfer resistance drop during the cycling when the retention capacities are higher than 90%. While the LFP batteries cycle under 1 C, the charge transfer resistance of them drops in the first stage when the retention capacities are higher than 90%, and it increases significantly in the second stage when the retention capacities are lower than 80%. It can be concluded that when the LFP batteries are discharged from 100% SOC to 0% SOC during one single cycle the sum ohmic resistance, the Li$^+$ diffusion through the SEI layer resistance and the charge transfer resistance keep increasing.

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