Effects of temperature on electrochemical impedance spectroscopy of the LiFePO₄ battery

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Abstract. Change in temperature affects cycle life and performance of the LiFePO₄ battery. Thus, different temperature (-20°C~45°C) performance of the LiFePO₄ battery was investigated by electrochemical impedance spectroscopy (EIS). The prismatic 40 Ah batteries testing was utilized to show the effect of increasing temperature on ohmic impedance (RΩ) and charge transfer internal resistance (Rct), and evaluate electrical performance consistency of a batch of batteries The results showed that the effect of increasing temperature on RΩ was very slight and on Rct was more obvious. The change was believed to result from ion moving speed, chemical reaction speed and ion charge transfer process at the electrode/electrolyte interface. At low-temperature (-20°C), the standard deviation of R was larger than other higher temperature, indicating that the electrical performance difference of the battery pack was large under low temperature condition.

1. Introduction

The LiFePO₄ battery provided the significant advantages of high specific energy, high specific power, long cycle life, high charge, and discharge efficiency, which were widely used in large-scale energy storage systems, like electric vehicles and energy storage power plants [1]. However, the poor safety and may even be an explosion of the LiFePO₄ batteries cannot be ignored [2]. The circuit of the LiFePO₄ battery need to be protected, and the LiFePO₄ battery cannot be charged with a large current, overcharged or over discharged [3]. Based on the above advantages and disadvantages, the detection of the LiFePO₄ battery has received increasing attention. A series of requirements on the use environment, appearance, technical indicators, and insulation of the LiFePO₄ battery have been put forward. Meanwhile, special regulations on charge and discharge characteristics have also been made. For the national standard of the LiFePO₄ batteries, electrochemical impedance spectroscopy (EIS) technology can be used to monitor the status of the LiFePO₄ battery [4-6].

Electrochemical impedance spectroscopy [7], also known as AC impedance spectroscopy, using small amplitude sine wave potential or current as the disturbance signal to measure changes in impedance of each part in the measurement system [8]. EIS was widely used in the electrochemical energy system [9-11] (fuel cells, supercapacitors, and secondary batteries), especially in predicting the state of the battery [12-14] (SOC, SOH) and determining the limiting electrode performance factors. Because the reaction process of these research objects was usually affected by the electrolyte,
materials, and interface geometry, etc., EIS possesses its very outstanding advantages in the study of the system with these complex factors [15]. Besides the advantages of non-destructive and in-situ testing, EIS possesses wide frequency range, so the measured impedance can reflect more complex electrochemical properties: material transfer, rate constant, diffusion coefficient, and dielectric constant, etc., more dynamic information and electrode interface structure information than other conventional methods. Through the curve obtained by the EIS test, the equivalent circuit [16] of the battery system can be established and the relevant components in the circuit also can be determined, so as to obtain the dynamic parameters of the process or the physical parameters of the system.

In the past 10 years above, there have been many researches on the development of EIS in Li-ion batteries. EIS of graphite-based composites have been extensively reported, like researchers interpreted the impedance profile variations of graphite-based composite electrodes upon Li-ion cell charging and ageing [17]. Nangir et al. investigated the lithium-ion depletiion in the silicon-silicon carbide anode/electrolyte interface in lithium-ion battery via electrochemical impedance spectroscopy [18]. Kurzweil reviewed the state-of-charge monitoring by impedance spectroscopy during long-term self-discharge of supercapacitors and Li-ion batteries. The temperature change has a great impact on the electrochemical kinetic reaction and the transfer of substances. During the EIS test of Li-ion batteries, the process of Li ions charge transfer, ion diffusion and migration was easily affected by temperature. The LiFePO4 battery showed good performance at 20~30°C, which was the best operating temperature, while the high amplitude of temperature variation, the battery pack would show poor performance. Besides, consider the LiFePO4 battery may operate under extreme conditions, the effects of temperature (-20°C~45°C) on EIS parameters (RΩ and Rct) of Li-ion batteries were investigated.

2.  Experiment
The LiFePO4 battery produced by Lixin (Jiangsu) Energy Technology Co., Ltd., has a single cell voltage of 3.2 V and a nominal capacity of 40 Ah, was used in the experiment. Electric charging and discharging tests of Pb-acid battery are conducted by the BTS-5V 600 A battery testing instrument (Shenzhen Xinwei Electronics Co., LTD). The charging and discharging processes of the battery first discharges to 2.5 V with a constant current of 1 C, and then charges to 3.65 V with a constant current of 1 C. After standing for 10~12 hours to ensure the stable state of the battery voltage, followed by putting the battery under different temperature conditions at -20°C, 5°C, 25°C, 45°C for 5~8 hours, which was achieved through Tomino high and low temperature test chamber (Jiangsu Tomino Environmental Testing Equipment Co. LTD), to create different EIS test environments of batteries. The constant potential EIS test was carried out by CS350H Electrochemical Workstation (Wuhan Corrtest Instruments Corp., Ltd.). The potential value set as open circuit voltage, the sinusoidal voltage amplitude set as 5 mV and the scanning frequency range from 1×10^3 Hz to 10 mHz. The Zview software in the electrochemical workstation was used to fit the impedance spectrum data and record the relevant EIS parameters.

3.  Results and discussion
3.1. The electrochemical impedance performance of the LiFePO4 battery
Figure 1 showed the Nyquist plots of cell at fully charged state at 25°C. From left to right in the electrochemical impedance spectroscopy (EIS) were the impedances of the high frequency part, the intermediate frequency part, and the low frequency part. Among them, the EIS in the high frequency part reflected the inductive performance of the power battery, caused by the porosity of the electrode, uneven surface and connecting leads, etc. [19]. Ohmic impedance (RΩ), the junction of the high and middle frequency part, the transfer internal resistance of Li-ion on the electrolyte, diaphragm, and the interface of current collector. Besides, the arc in the intermediate frequency part represented charge transfer impedance of Li ions at the electrode/electrolyte interface. The oblique line in the low frequency part indicated the solid diffusion resistance of Li ions in the electrode active material [20].
3.2. The equivalent circuit of the LiFePO4 battery

To analyze the variation of the EIS behavior of each part of the LiFePO4 battery with the temperature, based on the fitting of EIS, high-frequency, intermediate-frequency and low-frequency equivalent components were combined to obtain the Randles equivalent circuit correction model [21] (Figure 2). The inductance \( L \) represented the performance of reactance, and \( R_\Omega \) was the ohmic impedance. The parallel circuit of the charge transfer internal resistance \( R_{ct} \) and the electric double layer capacitor \( C_{dl} \) represented the charge transfer impedance, but since the electric double layer capacitor was not a pure capacitor, the electric double layer element \( Q \) was used to replace \( C_{dl} \) [22-23]. \( Z_w \) was diffusion resistance. With the equivalent circuit, using the method of nonlinear least squares fitting, the parameter values of the components in the equivalent circuit were obtained. The fitting error of the Li-ion battery was shown in Table 1. The largest fitting error was only 3.09%, most of the errors were less than 2%, which were lower than the conventional standard 5%. So, the model shown in Figure 2 truly reflected the internal state of the cell.

![Figure 2. Equivalent circuit model of the 40Ah LiFePO4 battery.](image)
Table 1. Error values of fitting parameters of Li-ion batteries at different temperature (%).

| Fitting parameter | -20°C | 5°C  | 25°C | 45°C |
|-------------------|-------|------|------|------|
| L                 | 1.25  | 1.33 | 1.58 | 1.63 |
| \(R\Omega\)       | 0.30  | 0.24 | 0.28 | 0.18 |
| Q                 | 2.56  | 3.05 | 2.20 | 2.69 |
| \(R_{ct}\)        | 2.21  | 3.09 | 2.83 | 2.81 |
| \(Z_w\)           | 1.23  | 1.15 | 1.37 | 1.61 |

3.3. Changes on the EIS of the LiFePO4 battery under different temperature conditions

To understand the effect of temperature on EIS, the EIS at 100% SOC was measured and analyzed at -20°C, 5°C, 25°C, 45°C in Figure 3. Though L, \(R\Omega\), Q, \(R_{ct}\) and \(Z_w\) were important parameters, the changes of \(R\Omega\) and \(R_{ct}\) under different temperature were investigated (Table 2). As shown in Figure 3, a comparison between the experimental EIS and the fitted spectra from the circuit was considered, the experimental and fitted solutions were almost identical and the fitting error was less than 5%. When the temperature was raised, ion moving speed and chemical reaction speed increased, followed by \(R\Omega\) reduced. But the electrolyte had good stability, so \(R\Omega\) was not significantly reduced with increasing temperature. Due to temperature made a difference to ion charge transfer process at the electrode/electrolyte interface, \(R_{ct}\) decreased significantly with increasing temperature [24]. Namely, the sluggish kinetics result in the poor low temperature performance [25].

![Nyquist plots of cell at 100%SOC under -20°C, 5°C, 25°C and 45°C, respectively. Inset: Partially enlarged view of Nyquist plots.](image-url)
Table 2. The effect of temperature on the changes of $R_\Omega$ and $R_{ct}$.

| Parameters | -20°C | 5°C  | 25°C | 45°C |
|------------|-------|------|------|------|
| $R_\Omega$ (mΩ) | 4.9223 | 4.6471 | 4.3953 | 4.1748 |
| $R_{ct}$ (mΩ) | 34.0816 | 7.4695 | 4.6068 | 4.2411 |

3.4. $R_\Omega$ and $R_{ct}$ of a batch of the LiFePO4 battery under different temperature conditions

To understand the effect of temperature on $R_\Omega$ and $R_{ct}$, EIS test on the eight prismatic 40 Ah batteries of the battery pack at -20°C, 5°C, 25°C, 45°C was performed, based on the fitting $R_\Omega$ and $R_{ct}$ of each monomer battery, the average value and the standard deviation of $R_\Omega$ and $R_{ct}$ at different temperature was separately calculated. Figure 4 showed that both the average and standard deviation decreased followed by increasing temperature. The eight prismatic 40 Ah batteries showed good consistency at 20~30°C, which was the best operating temperature. With the decreasing temperature, the standard deviation of $R_\Omega$ and $R_{ct}$ showed an obvious increase, so the battery pack would show poor consistency at low temperature. By recording and comparing the impedance, each single battery reflected good electrical performance consistency under normal working temperature conditions, the electrical performance difference was large under low temperature condition. It is suitable for the detection of large batches of batteries to achieve a reasonable combination of batteries and ensure the battery pack had excellent performance at different temperature.

![Figure 4. Average and standard deviation of R at different temperature.](image)

4. Conclusions

EIS characteristics of Li-ion batteries under various temperature were investigated. The results showed that the influence of temperature on $R_\Omega$ and $R_{ct}$, and $R_{ct}$ of the Li-ion battery was more serious than $R_\Omega$, owing to the charge-transfer process of the Faradic reactions taking place on the electrode-electrolyte interfaces. While $R_\Omega$ was slightly affected by change temperature in the range of -20°C~45°C, for the electrolyte had good stability. Besides, as the temperature decreased (from 45°C to -20°C), the increasing standard deviation of $R_\Omega$ (from 0.1749 to 0.3525) and $R_{ct}$ (from 0.1081 to 0.4162) proved the electrical performance difference of the battery pack was large under low temperature condition. The research results can provide theoretical support for more efficient and accurate Li-ion batteries.
sorting scheme design in industrial processes and ensure the battery pack had excellent performance at
different temperature.

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