Analysis on Electrochemical Impedance Data Based on Computer Fitting

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Abstract. With the development of technology, the demand for batteries in all walks of life is increasing, such as electric vehicles. Therefore, battery research has become one of the most important topics, which requires us to study electrochemical impedance. With the development of a new generation of energy-saving and environmental protection vehicles, electric vehicles have been gradually applied. Among them, LiFePO4 battery has high safety, which has been widely used in electric vehicles. Power battery is the basic unit of energy storage and supply, which requires more effective monitoring and management. In battery management, the modeling of battery characteristics is one of the key technologies, which leads to the study of nonlinear system impedance of LiFePO4 battery. In this paper, an equivalent circuit is established based on electrochemical impedance spectroscopy (hereinafter referred to as EIS). Finally, the data are fitted and analyzed.

Keywords: Computer Fitting, Electrochemical Impedance, Data Analysis

1. Introduction
Lithium ion battery has many advantages, such as long life cycle, good stability, high energy density, which has become the most valuable energy storage equipment. SOQ and SQH are the key parameters of battery management system (hereinafter referred to as BMS) \cite{1}. Through SOQ and SQH, we can predict various states of lithium battery. Through mathematical model and state estimation, we can predict SOC estimation and SOH, which is also the most important research direction of BMS. However, the optimum operating temperature of lithium battery is 298 K \cite{2}. If the temperature is lower than the optimal temperature, the internal chemical reaction rate will be slowed down, which will affect the charge transfer and lithium ion diffusion coefficient. EIS is an accurate method, which is mainly used to simulate the electrochemical system of batteries. Based on the equivalent circuit model (hereinafter referred to as ECM), the electrochemical impedance spectra, including inductance, resistance, capacitance and phase angle element, are obtained. Therefore, this paper constructs an appropriate ECM, which can predict the invisible SOC impedance spectrum and circuit parameters. Battery impedance model can reflect many performance information of battery. Therefore, the study of electrochemical impedance is very important \cite{3}. Through the impedance spectrum characteristics of the equivalent components, we can measure the characteristics of the battery impedance spectrum
curve, which will better correct the equivalent circuit. Therefore, this paper constructs a battery impedance model in accordance with the measured results [4].

2. Basic theory of EIS

2.1. Impedance

If we take a sine wave electric signal \( X \) with angular frequency \( \omega \) as the excitation signal of a stable system. When \( X \) passes through the system, we can get the same frequency sine wave signal \( Y \) at the other end of the system [5]. If the frequency response function of the system is \( g \), then the relationship between \( X \) and \( Y \) is shown in Formula 1.

\[
Y = G(\omega)X
\]  

Among them, \( G \) is the stable impedance of the system.

2.2. EIS

When an electrode system is in a steady state, the sinusoidal polarization signals of different frequencies can excite the electrode system, which can measure the corresponding response output electrical signal. The ratio of the output signal to the input signal is the impedance spectrum of the electrode system, which is the electrochemical impedance spectrum. Inside the battery is a complex system. The dynamic process of an electrode system is generally controlled by two kinds of variables, namely state variable and control parameter. Among them, the main control parameters are reaction rate constant, Tafel constant and diffusion coefficient. In the measurement of electrode system, the battery itself is a nonlinear system, which will complete the measurement of electrode impedance spectrum. EIS is considered to be one of the best methods to describe the characteristics of batteries [6]. Therefore, the EIS of lithium-ion battery will change with the charging state, as shown in Figure 1.

![Figure 1](image)

**Figure 1.** The impedance spectra of Li ion batteries under different charging states were studied. In different charging States, the impedance spectra of lithium batteries are not consistent, but their basic shapes are highly consistent. In the impedance spectrum, the high frequency section intersects with the real axis to characterize the ohmic resistance of lithium battery. In the middle frequency part,
it shows a flattened semicircle, which indicates the charge transfer on the SEI film. In the low frequency part, it is a part of flattened semicircle, which indicates the diffusion behavior of ions in lithium battery at low frequency [7].

2.3. Battery equivalent circuit
In this paper, different impedance spectra are normalized to a simple equivalent circuit, as shown in Figure 2. Where $R_{ser}$ is the ohmic resistance of the lithium battery, which corresponds to the high frequency band of the impedance spectrum. $V_{ser}$ was used to characterize the partial pressure of $R_{ser}$ in lithium battery. The parallel connection of $R_i$ and $C_{CPE1}$ indicates the active polarization phenomenon of lithium battery, which corresponds to the middle frequency section of impedance spectrum. $V_1$ is the partial pressure at the parallel connection of $R_i$ and $C_{CPE1}$. The parallel connection of $R_2$ and $C_{CPE2}$ indicates the concentration polarization phenomenon of lithium battery, which corresponds to the low frequency band of impedance spectrum. $V_2$ is the partial pressure at the parallel connection of $R_2$ and $C_{CPE2}$.

Figure 2. The equivalent circuit of lithium-ion battery based on EIS.

3. The experiment of EIS

3.1. Experimental instrument and environment
In this paper, the data of AC impedance spectroscopy were measured by chi650d electrochemical workstation of Shanghai Chenhua company. Chi650d is a general electrochemical measurement system. The frequency range of AC impedance measurement is $10^3 - 10^5$ Hz. The four electrodes can be used in electrochemical measurement of liquid / liquid interface, which is suitable for high current or low impedance electrolytic cell.

3.2. Experiment and experimental results
The specific steps of impedance spectrum measurement are as follows. First, the lithium battery after voltage response sampling experiment is placed for one hour. By stabilizing the double-layer self-discharge of the battery, we can accurately measure the measurement results of impedance spectrum. Secondly, an EIS measurement system was established. Through the four electrode system, we can connect the positive electrode of the battery to the working electrode of the electrochemical workstation, which will be connected to the auxiliary electrode and the reference electrode at the negative electrode of the battery. Third, parameter setting. Select technique in the setup option of chi650d upper computer interface. By selecting impedance A.C., we can select parameter in the setup item, which includes the parameter settings before impedance spectrum measurement, mainly
including E-init, frequency high, frequency low, amplitude. Fourth, measure and store the data results. The EIS measurement interface is shown in Figure 3.

![EIS measurement interface](image)

**Figure 3.** EIS measurement interface.

### 3.3. Data fitting process and result diagram

Through the electrochemical impedance software zsimpwin, the experimental data can be fitted and analyzed in this paper. Zsimpwin software is widely used in the field of electrochemistry, which has the functions of simple operation and fast measurement. Before measurement, we need to specify the specific battery impedance model, which is the data processing method of known impedance model. Through the prediction model, we can obtain the sample output data. In this paper, a group of battery impedance data are used for fitting, and the fitting results are shown in Figure 4. The impedance spectrum curve of the battery is in good agreement with the corresponding impedance model.

![Data fitting process and result diagram](image)

**Figure 4.** Data fitting process and result diagram.

### 4. Conclusion

With the development of a new generation of energy-saving and environmental protection vehicles, electric vehicles have been gradually applied. Among them, LiFePO4 battery has high safety, which
has been widely used in electric vehicles. Through the kinetic reaction mechanism of lithium battery, we can analyze the contribution of battery electrode to battery impedance spectrum. The increase of battery electrode impedance mainly comes from the increase of battery positive electrode impedance. The relationship between the parameters of impedance model and temperature and SOC is analyzed. The ohmic internal resistance decreases with the increase of temperature, but it does not change with SOC. The polarization resistance will not decrease with the increase of temperature, but will decrease with the increase of SOC.

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