The Application of the EIS in Li-ion Batteries Measurement

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Abstract. The measurement and determination of the lithium ion battery's electrochemical impedance spectroscopy (EIS) and the application of EIS to battery classification are researched in this paper. The lithium ion battery gets extensive applications due to its inherent advantages over other batteries. For proper and sustainable performance, it is very necessary to check the uniformity of the lithium ion batteries. In this paper, the equivalent circuit of the lithium ion battery is analyzed; the design of hardware circuit based on DSP and software that calculates the EIS of the lithium ion battery is critically done and evaluated. The parameters of the lithium ion equivalent circuit are determined, the parameter values of li-ion equivalent circuit are achieved by least square method, and the application of Principal Component Analysis (CPA) to the battery classification is analyzed.

1. Introduction

The lithium ion battery has the best comprehensive function of all the batteries because of its high voltage, compactness, light mass, no memory effect, no pollution, low self discharge, more cycle life and other advantages. The lithium ion battery has already been applied in many realms, including cell phone, notebook, digital camera and so on [1]. The inconformity of the batteries means that batteries with the same characteristic have differences in their voltage, impedance, electric charge quantity, capacity, self discharge, cycle life and so on [2]. The conformity of the single battery seriously affect the circle life of the battery bank. Therefore it is necessarily to checkout the conformity of the batteries and to classify the batteries according to the measurement result before the batteries are sent to the market. Despite the fact that batteries are produced in the factory with the same materials and production process, their performances are more or less difference. Battery classification is to classify the batteries according to the conformity. We have several means to classify the batteries: by battery voltage, by battery capability, by battery impedance, by battery circle life and so on, each having its own shortcomings.

Electrochemical impedance spectroscopy (EIS), sometimes called AC impedance spectroscopy, is an electrochemical measurement method. EIS is impedance spectroscopy of the electrode system which accords with the basic qualification [3]. This method with wide frequency scope has small disturbance and is a good means of studying the electrode process dynamics, the electrode superficial phenomenon and so on. Since EIS can reflect the electrochemical characteristic and inner structure more accurately, determination of and hence classification of the battery gives accurate results. Due to
large hardware is required to test the battery and the complex algorithm to calculate the EIS and classify the batteries this method is not applied in our country on industrial scale.

2. Equivalent circuit of the li-ion battery

Up to currently, equivalent circuit method is the main analytical technique to EIS. The equivalent circuit of the EIS can be found in the electrochemical of the electrode in most cases. There are 4 equivalent ‘electrical element’ as follows [3]:

- Equivalent resistance R, R represents both the equivalent resistance signal and the value of the resistance parameter as in the electric element. The admittance value of the resistance R has nothing to do with the frequency;
- Equivalent capacitance C, C in electrochemical represents both the signal and value of the Equivalent capacitance as the pure capacitance in electricity;
- Equivalent inductance L, L in electrochemical represents both the signal and value of the Equivalent inductance as the pure inductance in electricity;
- Constant phase element (CPE)Q, the surface between electrode and the liquor equal a capacitance that called double layer capacitance. But the frequency characteristic of the CPE is more or less different from pure capacitance. The impedance of the equivalent Q is

\[ Z_Q = \frac{1}{Y_0} \times (j\omega)^n = \frac{\omega^{-n}}{Y_0} \cos \left( \frac{n\pi}{2} \right) - j \frac{\omega^{-n}}{Y_0} \sin \left( \frac{n\pi}{2} \right) 0 < n < 1 \]

where \( Y_0 \) is the dimension is \( \Omega^{-1} \cdot cm^{-1} \cdot s^n \), \( Y_0 \) always has a positive value, \( n \) is exponent that has no dimension. When \( n=0.5 \), the corresponding electric element is called Warburg impedance. The Warburg impedance relates to low frequency diffuseness and its impedance spectroscopy is a line that is distributed in the first quadrant and the slope is +1.

The equivalent circuit of the li-ion battery is shown in figure 1.

![Figure 1. The equivalent circuit of the li-ion battery.](image)

where Rct, including Rct1 and Rct2, is electrochemical reaction internal resistance. It is also called Faraday resistance and the smaller the value is, the better the battery is. Rs is ohm internal resistance, including materiel resistance and the smaller the value is, the better the battery is. CPE including CPE1 and CPE2 is battery polar plates surface electric double layer capacitance, correlated with battery capability. The lager the parameter \( Y_0 \) is the lager the battery capability. W is Warburg impedance.

3. The hardware design and algorithm of the li-ion battery EIS determination

3.1. The hardware design of the li-ion battery EIS determination

Hardware circuit that based on the DSP is designed to sample and process the battery data accurately in real time in this paper. DSP system and the PC communicate through Ethernet/RS232 module. Also signal conversion and signal detection circuit was designed between the DSP and the battery.

The lower DSP system controls the charging and discharging of the battery, outputs small sinusoidal excitation signals, samples and processes the battery data. The hardware framework of the system is shown in figure 2.
3.2. the concept to calculate the phase difference of EIS

It is the key point to calculate the battery impedance in the whole dsp software system. The difficulty in how to determine the impedance is to calculate the phase difference between the battery ac voltage and ac current. The excitation current signal is

$$Y_1 = A_1 \cos(\omega t + \varphi_1)$$

The response voltage is

$$Y_2 = A_2 \cos(\omega t + \varphi_2)$$

$Y_1$ and $Y_2$ are sampled simultaneously, so

$$Y_1 \times Y_2 = \frac{1}{2} A_1 A_2 \left( \cos(2\omega t + \varphi_1 + \varphi_2) + \cos(\varphi_1 - \varphi_2) \right)$$

$N$ points are sampled every period and $kN$ points data in $k$ periods. The products are accumulated,

$$\sum_{n=1}^{kN} Y_1(n)Y_2(n) = kN \cdot \frac{A_1 A_2}{2} \cos(\varphi_1 - \varphi_2) - \sum_{n=1}^{kN} \cos(2\omega t(n) + \varphi_1 + \varphi_2) = \frac{A_1 A_2 kN}{2} \cos(\varphi_1 - \varphi_2)$$

That is how the phase difference $|\varphi_1 - \varphi_2|$ is determined.

4. Li-ion battery EIS data process

Given that the li-ion battery equivalent circuit contains 9 parameters, 8 are unknown. Twice the unknown parameter number is required at least to fit the data effectively. A total of 35 frequency
points from 0.004Hz to 20000Hz in this experiment are chosen. Figure 3(a) shows the EIS curve diagram obtained from the experiment.

In this paper, the parameter values of li-ion equivalent circuit are achieved by least square method [3]. Proper initial value of the parameters is important to successfully curve fitting. Table 1 shows initial values and parameter values obtained after successful cure fitting where $R_s$, $R_{ct1}$, $R_{ct2}$, $Y_0$ of CEP1, $n$ of CEP1, $Y_0$ of CEP2, $n$ of CEP2, $Y_0$ of W, $n$ of W represent the parameter values in equivalent circuit in figure 1. The EIS curve with fitted parameter values are show in figure 3(b). It can be seen that two curves agree quite with each other.

Table 1. The initial values and fitted values of the equivalent circuit parameters.

| Parameters     | Initial values | Fitted values |
|----------------|----------------|---------------|
| $R_s$          | 0.2000         | 0.2099        |
| $R_{ct1}$      | 0.0200         | 0.03543       |
| $R_{ct2}$      | 0.0400         | 0.08543       |
| $Y_0$ of CEP1  | 1.0000         | 1.1800        |
| $n$ of CEP1    | 0.9000         | 0.9081        |
| $Y_0$ of CEP2  | 1.0000         | 6.5380        |
| $n$ of CEP2    | 0.9000         | 0.8325        |
| $Y_0$ of W     | 10.000         | 31.120        |
| $n$ of W       | 0.5000         | 0.5000        |

5. The basic concept to classify the li-ion battery

In the multivariate statistical analysis with many indexes, all the indexes have complicated correlations with each other. Principal Component Analysis (PCA) is a kind of mature multivariate statistical analysis that convert much more indexes into several complicated indexes. Two requirements are as follows [4]:

- New indexes contain all the information in the original indexes as much as possible;
- New indexes are complete independent; they have no information in common.

In this paper, the equivalent circuit of the lithium ion battery has 8 unknown indexes. First, battery sample is chosen from a passel of batteries made. The equivalent circuit parameter values of the battery sample are determined according to the method in this paper. Principal Component Analysis is applied to the parameters and the batteries are classified and plotted out to different mode according to the distribution of newer parametric variables.

Evaluating indicators of the battery is stored into the database. Principal Component Analysis is applied to the unclassified batteries and the batteries are classified and that means classifications of batteries according to their conformity.
6. Conclusion
In this paper, the electrochemical impedance spectroscopy (EIS) of the li-ion battery is measured and determined and the application of Principal Component Analysis (CPA) to the battery classification is analyzed. It can be concluded from the experiment that the li-ion batteries can be tested and classified quickly and accurately, and this method can be of comprehensive application in the market.

References
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