Modeling Study for Li-ion Batteries Considering High-frequency Inductance Characteristics Based on Electrochemical Impedance Spectroscopy

Bingxiang Sun\textsuperscript{1,2,*}, Jingji Bian\textsuperscript{1,2,*}, Haijun Ruan\textsuperscript{1,2}, Weige Zhang\textsuperscript{1,2}, Pengbo Ren\textsuperscript{1,2}, Xinwei Cong\textsuperscript{1,2}

1 National Active Distribution Network Technology Research Center, Beijing Jiaotong University, Beijing, 100044, China
2 Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing Jiaotong University, Beijing, 100044, China

Abstract

As a non-destructive test method, electrochemical impedance spectroscopy (EIS) has been widely used in the analysis and diagnosis of Li-ion batteries in recent years. But the study of the high-frequency characteristics of Li-ion batteries is still not enough and the performance of Li-ion batteries at high frequency is not the same with that of the pure capacitance or pure inductance. Based on EIS, a fractional equivalent circuit model considering high-frequency inductance characteristics is established in frequencies from 10mHz to 10kHz in this paper. Then the model is verified and the parameters of the circuit are explored by using differential evolution (DE) algorithm and fractional-order numerical operations. Compared with the traditional equivalent circuit model, a fractional-order model based on EIS can not only describe the characteristics of the battery more comprehensively but also reduce the number of parameters because each component can simulate a certain physicochemical process of Li-ion batteries. The dominant process of the battery reaction is diverse in different frequency bands and therefore the structure of the developed model can be simplified accordingly. For the high-frequency inductive analysis of the battery, results show that the battery's 'inductance-like' phenomenon has a certain relationship with the frequency. This discovery might be implemented in a power electronic circuit to improve understanding of how batteries react to working condition of high-frequency.

Keywords: Li-ion battery, Electrochemical impedance spectroscopy, Fractional-order model, Differential evolution algorithm, ‘inductance-like’ phenomenon

1. Introduction

With the rapid development of science and technology, Li-ion batteries play an increasingly important role in more and more fields due to the high energy, power density and low self-discharge rate. In practical applications, the internal state of the battery is difficult to be measured directly by the sensor.

Therefore, an accurate model implemented to represent these internal states of the battery is the key to ensure safety of the battery and extend the service life. There are many model-based methods to characterize performance of batteries. For example, the black box model [1,3], the electrochemical model [4,5] and the equivalent circuit model [6,8]. The black box model aims to find a nonlinear mapping function between the voltage response and the current excitation, which is based on a large amount of training data without considering the reaction mechanism inside batteries. Due to its lack of physical description and the burden of data, it is not easy to realize in practical application. The electrochemical model is based on the reaction mechanism of batteries. The established dynamic differential equations of electrode and electrolyte can characterize the state of batteries better. But it is too sophisticated to calculate quickly because of the large number of parameters, which is also difficult to popularize in practical applications. The equivalent circuit model that has a certain physical meaning uses ideal voltage source, capacitor, resistor and other components to describe the external characteristics of batteries. The complexity and precision can meet the needs of practical applications, and thus it is widely used.

Although an equivalent circuit model can balance the calculation and precision, the traditional equivalent circuit is essentially lacking an explanation of the physicochemical process inside the battery. As a non-destructive test method, EIS can reflect a large amount of reaction mechanism information, which is used to analyze the interface reaction of electrode/electrolyte [11] and impedance source of the battery [12], and also can be applied as a diagnostic tool of state of health (SOH) [9,10]; therefore, many novel equivalent circuits have been proposed in conjunction with EIS, in which a constant phase element (CPE) is introduced to describe the dispersion of the 'electrical double layer' of the cell, and a Warburg impedance is applied to describe the semi-infinite diffusion of the planar electrode. Due to the characteristics of these two circuit components, the circuit model containing such components is usually
called fractional-order model. In Ref. [13,15], different fractional-order models are established respectively, and genetic algorithm (GA), particle swarm optimization (PSO) and some other optimization algorithms are commonly used to identify parameters by data in time domain. Compared with the one-order RC model, the fractional-order model has higher precision in state of charge (SOC) estimation. In Ref. [16,17], the author used a sliding mode observer to overcome the uncertainty of model, parameters and measurement error which shows good robustness; The fractional-order model is also used to determine the leakage of the battery in combination with random forests [18], as well as to explore the source of battery aging combined with capacity increment analysis [19].

As an energy supply system, batteries often use power electronics to control energy flows so that high frequency disturbances will inevitably occur in the circuit due to fast switching [20]. Alternating current preheating in high frequency is also a promising method that requires constant polarization to reduce the impact on battery life [21]. But there are few satisfactory explanations for the battery’s high-frequency behavior.

In this work, A fractional-order model based on EIS is established. The relationship between the high-frequency parameters of the model and the frequency is also explored which may improve understanding the high-frequency behavior of batteries. The remaining part of this paper is organized as follows. Model building and method of fractional-order numerical calculation are described in the Section 2, the simulation and experimental results and discussions are presented in Section 4, followed by conclusions summarized in Section 5.

2. Fractional-order model

2.1 Electrochemical impedance spectroscopy

EIS technology is to measure the ratio of response signal to disturbance with different frequencies to acquire the real part, imaginary part, Impedance modulus and phase angle at corresponding frequencies, and then these physical quantities are drawn into various forms of curves, among which the most commonly used is the Nyquist diagram of the real and negative imaginary parts. EIS has the following three characteristics: the electrochemical system is perturbed with a small amplitude sinusoidal signal. Therefore, there is a linear relationship between the potential and the current, which simplifies the mathematical processing of the measurement results. the reaction process of the anode and the cathode alternately occurs on the electrode. Even if the measurement is last for a long time, there will be no accumulation of polarization, so it is a kind of 'quasi steady state method'. EIS is a test method of frequency domain that can measure a wide range of frequencies and thus we can obtain more kinetic information and electrode interface information than conventional electrochemical methods.

As shown in Figure1, in the high frequency area, the image below the real axis indicates that the imaginary part of the impedance is positive which represents the inductive properties of the battery. It is usually represented by an inductance element. The intersection of the Nyquist diagram and the x-axis represents a pure ohmic resistor, which indicates the resistance of current collector, electrolyte and connecting portion in a battery. The medium-high frequency band is the response of the solid electrolyte interface (SEI) film, that exists between the electrolyte and the anode blocking the insertion and deintercalation of lithium ions, while the mid-band arc is the response of the charge transfer impedance and the electric double-layer capacitance. The low-frequency region oblique line characterizes the diffusion of Li-ions and it is expressed by Warburg impedance.

![Figure 1 Typical physicochemical reaction and Nyquist diagram (a), equivalent circuit (b).](image)

Finally, the appropriate circuit model can be established according to different Nyquist plots, and each parameter can be obtained by fitting the EIS with some optimization algorithm. In this paper, a differential evolution (DE) algorithm is adopted to get all the parameters of model. The objective function of fitting process is shown below:

\[
E = \frac{\sum_{n=1}^{N} wgt \cdot \log \left( \frac{Z_{\text{cal}}(\omega_n)}{Z_{\text{exp}}(\omega_n)} \right)}{N}
\]

where, \( n = 1,2,\ldots,N \) selected samples

\[wgt(\text{real, imag}) = \frac{\text{real}^2 + \text{imag}^2 \cdot \text{weight}}{\text{weight}}\]

where, \( Z_{\text{cal}} = f(\omega, P_1, P_2, \ldots, P_{k-1}, P_k)\)

A logarithmic distance function ‘wgt’ is introduced to measure the complex deviation between the calculated and the experimental data at a certain frequency \( \omega \). The total error \( E \) minimized during the fitting progress is calculated from the sum of the \( N \) distances between the measured \( Z_{\text{exp}}(\omega_n) \) and calculated data samples \( Z_{\text{cal}}(\omega_n) \) at the frequencies \( \omega_n \). An increasing value of ‘weight’
will increase the weight of the phase angle for fitting (default setting weight=2.2). ‘clog’ denotes the complex logarithm and $P_i$ is the $i$-th parameter of the transfer function which involves $k$ parameters in total. The application of the ‘clog’ operator results in the logarithmic modulus as the real part and the phase angle as the imaginary part. Compared with a linear weighting, a logarithmic distance function is advantageous due to the high dynamic range expected for the parameter values. The logarithmic scaling guarantees an equal weight of small and large parameter values as well. As shown in Figure 2, the EIS is fitted by using the equivalent circuit model of the two structures and frequency range data is 10mHz-10kHz. $E_{FOM}$=0.0030, $E_{IOM}$=0.0031. It can be seen from the results in Figure 3 that the accuracy of the fractional-order model is slightly better than that of the integer-order model. Integer-order model has many parameters and is complex, and there also exists over-fitting of parameters, but the number of parameters of the fractional-order model is reduced by nearly half and are easier to obtain.

2.2 Numerical calculation method of fractional order model

The fractional calculus problem is originated from the letter written to Leibniz by the French mathematician L’Hôpital in 1695. Because of its lack of specific physical explanations, research has always focused on pure mathematical theory. In recent years, the fractional calculus has been used in the control system of engineering by Oustaloup and Podlubny et al.[22]. It is straightforward that the fractional-order models are better than integer order ones to describe process with fractional order characteristics, such as mass transport, diffusion dynamics and memory hysteresis. The continuous integro-differential operator of fractional calculus is defined as:

$$\frac{d^\mu}{dt^\mu}, \quad \mu>0$$

$$1, \quad \mu=0$$

$$\int^t_0 (d\tau)^\mu, \quad \mu<0$$

where $\mu$ is the order of the operation, which can be a fraction or an irrational number, or even all non-integer. It is customary to call this operation a fractional order operation, $a$ and $t$ are the upper and lower limits of the interval. There are three widely used definition methods: Grünwald-Letnikov definition, Riemann-Liouville definition, and Caputo definition.

The definition of Grünwald-Letnikov has a discrete form, which is more suitable for numerical calculation, so the definition method is used here as shown in Eq. (3).

$$\frac{d^\mu}{dt^\mu} f(t) = \lim_{h \to 0} \frac{1}{h^\mu} \sum_{k=0}^{\lfloor (t-a)/h \rfloor} \omega_k^{(\mu)} f(t-kh)$$

$$\omega_k^{(\mu)} = 1 - \frac{\mu+1}{k} \omega_{k-1}^{(\mu)}$$

The above equation indicates that the order $\mu$ derivative is obtained for $f(t)$ in the interval $[a, t]$, where $\mu>0$, $h$ is the sampling interval, $\lfloor (t-a)/h \rfloor$ represents the integral part of the parentheses and $\omega$ is the coefficient. Next, the numerical calculation of fractional-order model
will be introduced by taking the circuit in Figure 2(a) as an example. Here are expressions of components in this circuit:

\[
Z_{crs}(s) = 1/(C_ds^{\alpha_d}) \quad Z_w(s) = 1/(W_ps^{0.5}) \tag{4}
\]

However, in the actual EIS, the order of the Warburg impedance is not fixed at 0.5, so the order is treated as an unknown parameter, and the expression is rewritten as follows:

\[
Z_w(s) = 1/(W_ps^{\alpha_w}) \tag{5}
\]

If the battery impedance can be similarly treated as a system transfer function, the input is current, and the expression in Laplace domain is as follows:

\[
G(s) = \frac{V_{oc}(s) + V(s)}{I(s)} = \frac{R_{OC} + R_{C} + j \omega C_{l} + R_{L} + j \omega C_{p} + R_{P}}{1 + \frac{R_{OC} + R_{C} + j \omega C_{l} + R_{L} + j \omega C_{p} + R_{P}}{1 + \frac{R_{OC} + j \omega C_{l}}{1 + \frac{R_{C} + j \omega C_{p}}{1 + \frac{R_{L} + j \omega C_{p}}{1 + \frac{R_{P} + j \omega C_{p}}{1 + \frac{R_{L} + j \omega C_{p}}{R_{P} + j \omega C_{p}}}}}}}} \tag{6}
\]

In equation (6), All variables except Laplace operator ‘s’ are parameters of model to be solved. Generally, this kind of formula can be written as:

\[
G(s) = \frac{B(s)}{A(s)} = \sum_{i=0}^{\infty} b_i s^{\beta_i} \sum_{i=0}^{\infty} a_i s^{\alpha_i} \tag{7}
\]

\[a, b, \alpha, \beta\] represent the coefficients of denominator and molecule parts, the power of denominator and molecule parts of the transfer function respectively.

The corresponding differential equation is

\[
b_0 s^{\beta_0} u(t) + b_1 s^{\beta_1} u(t) + \ldots + b_\infty s^{\beta_\infty} u(t) + a_0 s^{\alpha_0} y(t) + a_1 s^{\alpha_1} y(t) + \ldots + a_\infty s^{\alpha_\infty} y(t) \tag{8}
\]

The process of obtaining the model output is the process of solving the differential equation in Eq. (8).

The calculation sequence is shown in Figure 4, and an intermediate variable \(x(t)\) is introduced. Then the general expression of the numerical solution of the model output \(y(t)\) can be obtained that is shown in (9).

\[
x(t) = \frac{1}{\sum_{i=0}^{\infty} a_i h_i^\alpha} \left[ u(t) - \sum_{j=0}^{\infty} \frac{\omega_j^{(a_i)}}{h_i^\alpha} \sum_{j=0}^{\infty} \omega_j^{(a_i)} x(t - jh) \right] \tag{9}
\]

\[
y(t) = \sum_{i=0}^{\infty} b_i h_i^\beta \sum_{j=0}^{\infty} \omega_j^{(b_i)} x(t -jh) \]

3. Test bench

In this paper, the NMC type Li-ion battery with nominal capacity of 2.75Ah is selected and its parameters are listed in Table 1. EIS is obtained with a current amplitude of 200mA and a wide frequency range, and a sinusoidal AC current of a single frequency is considered as the input in the verification experiment. The experiment was carried out with VMP-300 that is produced by Bio-Logic Science Instruments and the parameters of the test equipment are listed in Table 2.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>SPECIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>Nominal capacity</td>
</tr>
<tr>
<td>Typical capacity</td>
<td><a href="mailto:2900mAh@0.2C">2900mAh@0.2C</a></td>
</tr>
<tr>
<td>Nominal voltage</td>
<td>3.6V</td>
</tr>
<tr>
<td>Charge voltage</td>
<td>4.20 ± 0.05V</td>
</tr>
<tr>
<td>Discharge cut-off voltage</td>
<td>2.50 ± 0.05V</td>
</tr>
<tr>
<td>Max. charge current</td>
<td>1C (2750mA)25℃</td>
</tr>
<tr>
<td>Max. discharge current</td>
<td>3C (8250mA)25℃</td>
</tr>
</tbody>
</table>

4. Results and discussion

4.1 Model validation

The circuit structure of Figure 2(a) is used to fit the EIS data whose frequency range is from 10MHz to 10kHz. According to the measured EIS, the inductor is replaced by a constant phase element \(Q\) whose equation is (10), and the remaining element have the same meaning as shown in Figure 2(a). All parameters are identified with an objective function as Eq. (1) mentioned in section 2.1. Next, these parameters will be placed in the numerical analytic expression of this model which is similar with Eq. (9) in section 2.2. The fitting results are shown in Table 3, error \(E = 0.0027\).

\[
Z_i(s) = Q_i s^{\alpha_i} \tag{10}
\]
The validation of the mathematical method mentioned in section 2.2 is implemented at first. Two columns sinusoidal current data that have an amplitude of 2A, and frequencies of 10 kHz, 1 kHz are generated by MATLAB® respectively that are considered as excitation. Sampling frequency is set 100 times of the excitation’s frequency, and the voltage response is obtained through the numerical calculation method above. Fast Fourier Transform (FFT) is applied to the current and voltage, respectively. Then the impedance at fundamental frequency can be obtained by voltage divided by current after FFT. The results are shown in Figure 5, Table 4.

From the left figure in Figure 5, it can be clearly observed that the voltage is ahead of the current, which illustrates the inductance characteristics of the circuit at 10kHz. From Table 4 we can see that the difference of both real and imaginary part between $Z_{FFT}$ and $Z_{EXP}$ is under 0.5 miliohm. This small error illustrates that the calculation process of non-integer differential equation has no problems. Next, instead of generated by MATLAB®, we control the electrochemical workstation to emit single frequency current as the excitation while the current and voltage are sampled in current excitation real time. Results at different frequencies are shown in Figure 6 in which the red line represents the measured polarization voltage, and the black line represents output voltage of the model simulation. Results show that at high frequencies, the absolute value of error between the simulated output voltage and the measured voltage is slightly larger, while in the middle and low frequency band, the error is relatively small. In high frequency area ($f > 1$ kHz), we know that imaginary part of the battery's impedance is positive, it means inductance characteristics dominates internal reaction of cells. So, the polarization voltage can be expressed qualitatively by formula $V_p=L\frac{di}{dt}$. Obviously, the error comes from two parts. The first is noise in current sampling. The noise itself is slight, but when divided by the reciprocal of high frequency $dt$, it leads to a noticeable error. Another source of error is the imprecise description of the inductance characteristics of the battery.

**Table 3** Fitting result

<table>
<thead>
<tr>
<th>$Q/\Omega^{-1}\cdot s^n$</th>
<th>$R_i/\Omega$</th>
<th>$R_e/\Omega$</th>
<th>$C_{\omega}/\Omega^{-1}\cdot s^n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5679e-07</td>
<td>0.0181</td>
<td>0.0155</td>
<td>0.6508</td>
</tr>
<tr>
<td>$\alpha_i$</td>
<td>$\alpha_{il}$</td>
<td>$\omega/\Omega^{-1}\cdot s^n$</td>
<td>$\alpha_D$</td>
</tr>
<tr>
<td>0.9190</td>
<td>0.6981</td>
<td>542.6001</td>
<td>0.6346</td>
</tr>
</tbody>
</table>

**Table 4** Comparison of impedance

<table>
<thead>
<tr>
<th>Freq/Hz</th>
<th>$Z_{EXP}/\Omega$</th>
<th>$Z_{FFT}/\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10kHz</td>
<td>0.0215 + 0.0203i</td>
<td>0.0220 + 0.0200i</td>
</tr>
<tr>
<td>1kHz</td>
<td>0.0198 - 0.0003i</td>
<td>0.0200 - 0.0002i</td>
</tr>
</tbody>
</table>

**Figure 5** Voltage and current with 10kHz, 1kHz

**4.2 Discussion**

The impedance spectrum shown in the Figure 7 is obtained from 1Hz to 100kHz. In this frequency range, the Warburg impedance can be ignored to reduce computation and avoid overfitting. $Z$ shown in equation (11) is introduced to model inductance characteristics. Model parameters are listed in Table 5. From the local
magnification in Figure 7, error of the arc fitting in the middle and low frequency segments is smaller than that in high frequency segments. The slope of the inclined line in high frequencies is almost constant, indicating that the value of $m$ remains unchanged. It is speculated that $Q_l$ has changed with frequencies.

**Table 5** Fitting result

<table>
<thead>
<tr>
<th>$Q_l/\Omega^{-1} s^n$</th>
<th>$R_o/\Omega$</th>
<th>$R_c/\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.61e-06</td>
<td>0.0182</td>
<td>0.0195</td>
</tr>
<tr>
<td>Cal/$\Omega^{-1} s^n$</td>
<td>$\alpha_d$</td>
<td>$\alpha_l$</td>
</tr>
<tr>
<td>0.6884</td>
<td>0.6419</td>
<td>0.8807</td>
</tr>
</tbody>
</table>

$$Z_i = (j\omega)^n Q_l$$

\[\text{phase } \tan \varphi = \tan\left(-\frac{m\pi}{2}\right)\]

\[\text{Real } : Z_i = Q_l\omega^n \cos\left(-\frac{m\pi}{2}\right)\]

\[\text{Imag } : Z_i = Q_l\omega^n \sin\left(-\frac{m\pi}{2}\right)\]

![Figure 7](image)

Figure 7 Fitting result (1Hz-100kHz)

Then a method to acquire the relationship between $Z_i$ and frequencies is proposed. Firstly, we subtract real part and imaginary part of all components except $Z_l$ from the original EIS data in whole frequency so that we consider the remaining real part and imaginary part only come from frequency response of $Z_l$. Secondly, as is shown in Figure 8(a), it is a Nyquist plot of $Z_l$ with frequencies ranging from 1kHz to 100kHz. According to equation (11), the value of ‘$\tan(-m\pi/2)$’ is reflected in the graph as the absolute value of slope of the curve. Based on the slope of the curve fitted that is red, the value of $m$ can be obtained. Thirdly, in Figure 8(b), after value of $m$ is known, the value of $Q_l$ at each frequency is obtained by the expression of the imaginary part. Finally, we put $Q_l$ and $m$ into the impedance real part expression to calculate real part $R_{cal}$ in every frequency. There is almost no error compared with the measured data $R_{exp}$ mentioned in the first step which is shown in Figure 8(c).

**Figure 8 Relationship between $Q_l$ and frequencies**

$Q_l$ decreases first and then increases with the increase of frequency. When the frequency is greater than 2kHz, its value is approximately a quadratic function with the natural logarithm of frequency which is shown in Figure 8(d), and the function is shown below, $e$ represents the power of ten.

\[Q_l = -1.343e - 8\ln^2(f) + 3.117e - 7\ln(f) + 3.129e - 7\]

(12)

5. Conclusions

A fractional-order model based on EIS is established and verified at both high and low frequencies with an absolute maximum error about 4~6 mV of polarization voltage. Compared with the traditional equivalent model, fractional-order equivalence model is more suitable to describe the physical process of the battery, such as charge transfer, material transportation and so on. And the model parameters are much less and they are more easily obtained by electrochemical impedance spectroscopy. In the high frequency region, because the fitting error of the real part of the EIS by using a traditional constant phase element is large, a constant phase element with variable parameter is proposed to characterize the ‘inductance-like’ characteristics in frequencies from 1kHz to 100kHz. As the frequency increases, its modulus decreases first and then increases, and reaches a minimum at 2kHz. Above 2kHz, a function between the novel component and frequency is established, which is of practical significance to study the high frequency characteristics of the battery.
Acknowledgement
This work is supported by the “Fundamental Research Funds for the Central Universities” (Grant NO.: 2018JBM053) and the “National Natural Science Foundation of China” (Grant NO.: 61633015).

Reference

Copyright © by ICEEE