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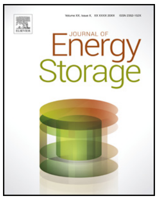

Equivalent circuit model parameters extraction for lithium ion batteries using electrochemical impedance spectroscopy

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ABSTRACT

Numerical modelling is the method by virtually testing and verifying the functionality of a specific product or component. The primary goal is to get approximate results of how the system behaves in a given time and environment. We are able to accept a certain numerical error from a real experiment, thus significantly speeding up part of the development of the device. In the field of electrochemistry of lithium-ion accumulators, several variants of numerical models have been proposed that yield satisfactory results in modelling certain physical fields of these batteries (electric field, temperature field, current field).

One model is the battery model with its equivalent circuit, which is represented by passive components, namely a resistor and a capacitor. This is a model that describes the internal behaviour of a battery by RC circuit. However, the problem is to find or measure these parameters. One way to get the parameters of this spare circuit is by means of electrochemical impedance spectroscopy (EIS).

This article deals with the application this method to obtain the parameters of the equivalent battery circuit and comparing the charging and discharging curves of a specific battery with the ECM model.

1. Introduction

Electrochemical Impedance Spectroscopy (EIS) allows the observation of the electrochemical and physical processes occurring in the monitored system. This is a very sensitive method in which the interpretation of results is rather complex due to its high sensitivity. The total measurement result consists of a mixture of responses from all the events that occur in the measured system, which often leads to ambiguity of the result [1].

For a good interpretation of the results, it is necessary to understand the physical and chemical essence of the measured system. Then compare the results with other analytical methods, both electrochemical and physical. The basic principle of this method is to set up a small sinusoidal AC voltage of a given frequency with offset of a certain value of the polarization voltage (mostly between 1 and 10 mV) [2].

2. EIS basics

The impedance value of the system is calculated using the ratio of alternating voltage and alternating current. This is composed of amplitude and phase shift values that are dependent on the set frequency. Thanks to this, the dependence of the system impedance on the frequency is obtained. The individual chemical elements that make up the measured system differ from each other by the time constant of the polarization, which causes the individual components of the impedance to vary with frequency variations [3] and [4].

These components are: Z' which is the real impedance, jZ'' the imaginary impedance and $|Z|$ – the total impedance. The ratio of impedances "Z'/Z'' / Z is called the loss factor tgδ. EIS requires stable system, which is difficult in practice due to the possibility of influencing the measurement by external noise, the temperature change and contamination. It is necessary to perform the measurement in the moment when the electrochemical response of the system is stable. The impedance is described by the formula according to [5–7]:

$$Z = Z' + jZ'' \tag{1}$$

Alternatively, using polar coordinates:

$$Z = |Z|e^{j\varphi} = |Z|\cos\varphi + j{*}|Z|\sin\varphi \tag{2}$$

Thanks to these parameters, we are able to describe the electrochemical process with the help of spare electrical circuits.

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These circuits consist of several basic elements, passive or active, which can be connected serial, parallel or mixed. These type are resistor R, capacitor C and several others. In these circuits, the capacitor with polarization processes and a resistor with conductivity of the sample are related.

2.1. Resistor R

This is an element that is reflected in the impedance chart, the so-called Nyquist graph, only by the real axis shift (see Fig. 1). This shift corresponds to the value of the real resistance. The real resistance may by dependent on the conductivity of used electrolyte. The overall impedance of the model represented by the resistance is:

$$Z = R \tag{3}$$

2.2. Capacitor C

Unlike resistivity, the capacity is frequency dependent and the phase change is −90° (see Fig. 2). This is an element that appears in the Nyquist graph in the negative values of the imaginary axis as a half-line. With an increasing frequency, the value decreases towards zero at an infinite frequency. The capacitor corresponds to two layers at the electrode-electrolyte interface and its capacity is inversely proportional to the thickness of this double layer. The overall impedance of the model represented by the capacitor is:

$$Z = -\frac{1}{j\omega\Psi} \tag{4}$$

2.3. Inductor L

Inductance, like capacitance, is frequency dependent and also changes phase, but unlike capacity + 90° (see Fig. 3). This element, like the capacitor, will appear in the Nyquist graph as a half-line, but in the positive values of the imaginary axis. Inductive behaviour may be due to a different current distribution and a potentiostatic error, indicating an error in the EIS measurement. The total impedance of the model represented by the inductor is:

$$Z = j\omega\Lambda \tag{5}$$

2.4. Constant phase element (CPE)

It is an element that is similar to a capacitor but, unlike it, the phase is changed at a different angle than 90° (see Fig. 4). In the Nyquist chart, it is again represented as a semi-line which forms the angle α with the real axis. As with a capacitor with increasing frequency, the value decreases towards zero at infinite frequency. CPE therefore behaves as a non-ideal capacity, it provides information on the surface structure. The overall impedance of the CPE model is therefore:

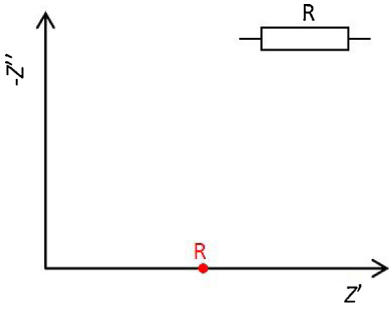

Fig. 1. Nyquist graph for resistor.

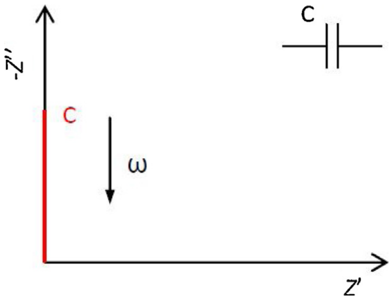

Fig. 2. Nyquist graph for capacitor.

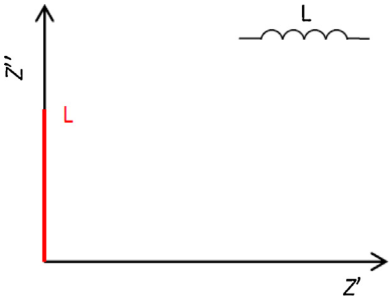

Fig. 3. Nyquist graph for inductor.

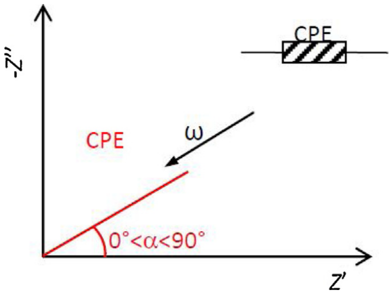

Fig. 4. Nyquist graph for CPE.

$$\frac{1}{Z} = Y = Q^0 \cdot (j\omega)^n \tag{6}$$

where Q° is numerically equal to admittance at ω = 1 rad/s refers to the unit $[S \cdot s^n]$, n is the slope of the semi-line from 0 to 1. For n = 1 it is a capacitor and for n = 0 it is a resistor.

2.5. Warburg W

Warburg impedance is a special case of CPE, occurring when the angle α in the Nyquist chart is equal to 45° (see Fig. 5). This element is used to model the diffusion of ions. It consists of frequency-dependent CW capacity and RW resistance in a serial combination. The total impedance of model W corresponds to CPE when n = 0.5:

$$\frac{1}{Z} = Y = Q^0 \cdot (j\omega)^{0.5} \tag{7}$$

A simplified overview of the processes taking place in the lithium-ion battery captured by EIS is shown in Fig. 6. These storages are divided into three parts according to the speed at which they proceed. Each part is assigned a corresponding portion of the progress in the Nyquist chart [8] and [9].