THE PROCESS MODEL DEVELOPMENT OF LITHIUM-ION BATTERIES: AN ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY SIMULATION

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ABSTRACT

In this study, a simulation of an electrochemical impedance spectroscopy for lithium-ion batteries was proposed. The electrochemical process was developed from battery electrode kinetics and mass transfer of mobile Li^+ ion through negative and positive electrodes and electrolyte. The phenomena used in this process were represented by an equivalent electrical circuit. A mathematical model was designed using the equivalent circuit and its elements which are in fact battery parameters. The parameter values were presented as compared with real experimental impedance result.

Keywords- Li-ion battery, impedance spectroscopy, equivalent electrical circuit, porous electrode, solid electrolyte interphase

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I. INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is a broadly used noninvasive technique for variety of systems including batteries [1-5], fuel cells [6-9], corrosion detecting [10-14], biosensors [15-19], and so on [20].

Figure 1. Typical impedance response of a Li-ion battery at 3.6 V cell potential [21]

Typical representation of EIS of an electrochemical system is complex Nyquist diagram. The Nyquist plot a Li-ion battery shown in Figure 1 can be divided into two regions of high frequency and low frequency. The high frequency region is between points corresponding to 100 kHz and 0.5 Hz. The low frequency region is between points corresponding to 0.5 Hz and 20 mHz. Initial examination of the Nyquist plot the following points can be attested as:

1. The high frequency zone corresponds to the interfacial charge transfer kinetics on electrodes.
2. The low frequency zone corresponds that of a diffusion process in a solid phase.

II. PROCESS DEVELOPMENT

Two prominent theories explain the process of a Li-ion battery. The theory by Doyle et al. [22,23], describes the battery process as given in Figure 1. The battery is considered to include a porous negative electrode, a separator, and a porous positive electrode. Li^+ ions from the positive electrode are released, travel through the electrolyte in the separator region, and are then intercalated into the negative electrode. The following processes may be considered to take place:

1. The de-intercalation reaction of the Li^+ ions in the porous positive electrode.
2. The diffusion of Li^+ ions in the solid phase of positive electrode.
3. Transport of solution in the porous electrode in the positive electrode.
4. Transport of Li^+ ions through the electrolyte in separator region.
5. Transport of solution in porous electrode in the negative electrode.
6. Diffusion of Li^+ ions in the solid phase in the negative electrode.
7. Intercalation reaction of the Li^+ ions in the porous negative electrode.

Along with the above processes, charging of the double layer takes place at both the electrodes. In the analysis charging and Faradaic currents are assumed to be separable, side reactions at the electrode-electrolyte interface are neglected, and Butler-Volmer kinetics are assumed to apply for the reactions at both electrodes. For a single reversible electrochemical reaction, the Butler-Volmer equation is expressed as

$$i = i_0 \left\{ \exp \left[\frac{(1-\alpha)nF}{RT} \eta_s \right] - \exp \left(-\frac{\alpha nF}{RT} \eta_s \right) \right\} \quad (1)$$

where i is the current density, i_0 is the exchange current density, η_s is the surface overpotential representing the departure from an equilibrium potential, α (symmetry factor) is the fraction of the

surface overpotential that promotes the cathodic reaction, n is the number of electrons transferred in electrochemical reaction, F is the Faraday's constant, R is the universal gas constant, and T is temperature [24].

Doyle et al. [22,23] used a set of equations for the above process and, solving those equations with specific set of conditions, established various parameter relations which enabled them to simulate the impedance spectra and compare it with those of experimental spectra. The complete analysis of the impedance spectra by Doyle et al. enabled them to distinguish the various factors of the battery by separating the terms of the equations which symbolized different processes of the battery. The analysis revealed that the high frequency region of the impedance spectra was mainly due to the interfacial kinetic resistance contributed primarily by the intercalation reaction. It also depended on the depth of discharge of the Li-ions. The charge transfer resistance of the de-intercalation reaction is a primary contributor when the depth of discharge was >80% or <20%. The low-frequency region was attributed to the diffusion impedance in the solution phase and the solid phase and to the capacitive double layers at the interface. The summation of all the above regions gave impedance spectra similar to that of the low frequency region.

The other theory, as represented by Aurbach [25], considers a different lithiated graphite electrode structure. This theory places more importance to the reactions at the electrode–electrolyte interface. These reactions lead to the development of an additional film at the interface called the solid electrolyte interphase (SEI). This film also explains the rise in impedance response on cycling of the cell due to continuous formation of additional film during the operation of the battery. The model envisions transport of Li^+ ions through different phases of the film and the final assimilation of Li^+ ions in the negative electrode. Unlike the process described by Doyle et al., interfacial kinetics in the porous electrode is not considered. Instead, diffusion of the Li^+ ions is assumed to occur in the electrode until they reach their final destination. This leads to development of capacitance inside the electrode. Also films on the surface provide different phases; hence, they too contribute to capacitance.

III. MATHEMATICAL MODEL

A mathematical model of the battery was developed considering aspects of the two theories. The stages of the battery process are assumed to include:

1. The formation of an SEI due to Li^+ ions reductive strength on the electrode surface,
2. The de-intercalation of Li^+ ions from the positive electrode,
3. Diffusion of Li^+ ions in the solid phase,
4. Transport of solution through the porous electrode and then across the SEI, and
5. Diffusion of Li^+ ions through the electrolyte in the separator.

Figure 2. Proposed equivalent electrical circuit for EIS of Li-ion battery

Similar processes are added from stage 1 to 4 in reverse order across the negative electrode with de-intercalation replaced by intercalation reaction in the negative electrode. The capacitance is

assumed to exist at both the SEI and the double layer at the electrode surface. The corresponding equivalent circuit is presented as Figure 2.

The impedance of the above circuit can be expressed as

$$Z = R_e + Z_1 + Z_2 \quad (2)$$

where R_e is the electrolyte or ohmic resistance; Z_1 and Z_2 are the equivalent impedances of the negative and positive electrodes, respectively, and are expressed as:

$$Z_1 = \frac{R_{f,1}}{1 + j\omega R_{f,1} C_{f,1}} + \frac{R_{t,1} + Z_d}{1 + j\omega(R_{t,1} + Z_d)C_{d,1}} \quad (3)$$

and

$$Z_2 = \frac{R_{f,2}}{1 + j\omega R_{f,2} C_{f,2}} + \frac{R_{t,2} + Z_d}{1 + j\omega(R_{t,2} + Z_d)C_{d,2}} \quad (4)$$

where R_f refers to the SEI film resistances, R_t refers to the charge transfer resistances for the intercalation and de-intercalation reactions, C_f refers to the SEI capacitance, C_d is the double layer capacitance, and Z_d is the diffusion impedance.

Diffusion might play a role in the proposed process across the SEI, through the solution phase in the electrode, and through the solid phase of the electrode. Each of these may be treated explicitly. For the present model, a simplified treatment is assumed in which diffusion takes place through a stagnant layer, i.e.,

$$Z_d(\omega) = Z_d(0) \frac{\coth(\sqrt{jK})}{\sqrt{jK}} \quad (5)$$

where $Z_d(0)$ is the diffusion impedance at zero frequency, and K is the dimensionless frequency given as

$$K = \frac{\omega \delta^2}{D_{Li^+}} \quad (6)$$

where δ is the Li^+ ion diffusion layer thickness, and D_{Li^+} is the diffusion coefficient of Li^+ ions. In above Equations (2-6), ω is the angular frequency, and j refers to the imaginary number.

IV. RESULTS AND DISCUSSION

A typical simulation is presented in Figure 3 using the frequency range between 10 kHz to 10 mHz. The model parameters used to obtain this result are presented in Table 1.

Figure 3. Simulation result for the impedance model in Equations (2-6) shown with the line. The corresponding frequencies are indicated with dots.

A certain amount of positive imaginary impedance (Z_j) values can be observed in Figure 1 at a typical impedance response of the Li-ion battery. That type of response is generally interpreted to an inductive behavior of the electrochemical system interested in. However, it is not a case for an energy storage device such as batteries. This inductive behavior at very high frequencies is attributed to noise or impedance related to connection cables in the experimental setup of the Li-ion battery cell. Therefore, only negative values of imaginary impedance forming capacitive loop at high frequencies are observed in the simulation shown in Figure. While doing regression on impedance data, like applied in previous studies [26-28], one should keep in mind that the positive values of Z_j could be truncated. Thus, no inductive loop could be observed in the simulation result in Figure 3. Also, there are three capacitive loops combined in the simulation constituting a compressed circle like shape similar to the experimental data shown in Figure 1. The large capacitance values in Table 1 forming the capacitive loops here are consistent with assumption of a porous electrode. The capacitive loops are corresponding to the negative electrode, the SEI layer, and the positive electrode. The interception the line of this loop with real impedance (Z_r) axis represents the electrolyte resistance (R_e). If the line is extrapolated to Z_r axis at lower frequencies at the high frequency region, e.g. 10 Hz in Figure 3, the value here is equal to sum of all resistances in the equivalent circuit that are R_e , $R_{f,1}$, $R_{t,1}$, $R_{f,2}$, and $R_{t,2}$. The straight line at low frequencies is attributed to diffusion impedance (Z_d). The values of all above mentioned parameters are indicated in Table 1.

Table 1. Model parameters used for the simulation result presented in Figure 3

Parameter	Value
R_e	$1.0 \Omega\text{cm}^2$
$R_{f,1}$	$0.15 \Omega\text{cm}^2$
$R_{f,2}$	$0.15 \Omega\text{cm}^2$
$R_{t,1}$	$0.20 \Omega\text{cm}^2$
$R_{t,2}$	$0.20 \Omega\text{cm}^2$
$C_{f,1}$	$3.16 \times 10^{-3} \text{ F/cm}^2$
$C_{f,2}$	$1.00 \times 10^{-2} \text{ F/cm}^2$
$C_{d,1}$	$3.16 \times 10^{-2} \text{ F/cm}^2$
$C_{d,2}$	$1.00 \times 10^{-1} \text{ F/cm}^2$
D_{Li}^+	$1.5 \times 10^{-10} \text{ m}^2/\text{s}$
δ	$1.5 \times 10^{-4} \text{ m}$
$Z_d(0)$	$1.5 \Omega\text{cm}^2$

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