



Dynamic Electrochemical Impedance Spectroscopy of a Three-Electrode Lithium-Ion Battery during Pulse Charge and Discharge



Jun Huang, Hao Ge, Zhe Li*, Jianbo Zhang

Department of Automotive Engineering, State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 6 March 2015

Received in revised form 20 June 2015

Accepted 3 July 2015

Available online 9 July 2015

Keywords:

Dynamic electrochemical impedance spectroscopy

Inductive behavior

Stationary condition

Charge transfer resistance

Lithium-ion battery

ABSTRACT

The dynamic electrochemical impedance spectroscopy (DEIS) of a three-electrode pouch type lithium-ion battery is measured using a series of sine wave perturbations super-imposed on pulse charge and discharge. The DEIS reveals noticeable differences between charge and discharge at frequencies corresponding to the charge transfer reaction. The charge transfer resistance during intercalation is generally found to be larger than that during deintercalation for the battery chemistry in this study. This result is mainly attributed to the decreased Li ion concentration in the electrolyte during intercalation. At low frequencies, an abnormal inductive behavior is also observed. Such abnormality is found to result from the violation of stationary condition, *i.e.* the state of the battery under pulse charge or discharge deviates significantly from its initial condition for the perturbation of low frequencies. To analytically define the stationary condition, we develop electrochemical models of a single active particle in both time and frequency domain, which describes the transport of lithium ions in both active particle and electrolyte phase and the interfacial charge transfer reactions at their interface. The lower frequency limit is a key parameter to ensure a quasistationary state during the DEIS measurement. An explicit formulation of the stationary condition predicts a positive correlation between the lower frequency limit and the DC pulse current.

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1. Introduction

Electrochemical impedance spectroscopy (EIS) technique is being widely used as a characterization and diagnosis method in the study of the lithium-ion batteries. The main advantage of EIS is its capability in resolving multiple processes of different time scales. Usually, the EIS is measured when the battery is at a steady or stationary state, for which there is no direct current (DC). The battery is first adjusted to a certain state of charge (SOC). After a long period of rest when the battery is stabilized at an equilibrium state, the impedance measurement is carried out with a zero DC current. Such EIS is referred to as steady EIS (SEIS).

In contrast to the SEIS, dynamic EIS (DEIS) measures the impedance response of lithium-ion batteries during charge/discharge at finite DC currents. The state of the batteries changes slightly during the measurement (quasistationary). The merits and potential applications of DEIS include but not limit to: (1) information in batteries under operation can be obtained, which

can be used to parameterize precise battery models for use in battery management systems (BMS) [1–6] and to track the in-situ evolution of interfacial reactions and species (more details below) [7,8]; (2) the differences between charge and discharge (that is, intercalation and deintercalation reactions) can be distinguished, which finds its application in a precise estimation of heat generation rates [9,10], helps to explain why charging is so difficult at low temperatures [11], and provides insights into the limiting factors of intercalation and deintercalation processes, respectively.

In 1985, Stoynev et al. [12] conducted an impedance study at quasistationary state for the first time. In 1989, Chenebault et al. [13] measured the impedance of a Li metal electrode in $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte while the system was under charging. The DEIS method was later applied to lithium metal battery by Osaka et al. in 1994 [14], and to lithium-ion battery by Buller et al. [2] and Itagaki et al. [7] around 2000.

The methods to measure the DEIS of lithium-ion batteries can be categorized into two types: one measures the DEIS during continuous charge/discharge [4,7,8,11,15,17], hereafter referred to as CDEIS, the other measures the DEIS during pulse charge/discharge [2,5,6,16], hereafter referred to as PDEIS.

* Corresponding author. Tel.: +86 6278 6918.

E-mail address: lizhe02@mails.tsinghua.edu.cn (Z. Li).

Nomenclature

A_{pe}	Surface area of a porous electrode, m^2
c_e	Lithium ion concentration in electrolyte phase, $mol\ m^{-3}$
c_s	Lithium ion concentration in solid phase, $mol\ m^{-3}$
c_s^{max}	Maximum lithium-ion concentration in solid phase, $mol\ m^{-3}$
C_{dl}	Double layer capacitance, $F\ m^{-2}$
C_{sei}	SEI film capacitance, $F\ m^{-2}$
D_s	Diffusion coefficient in solid active material phase, $m^2\ s^{-1}$
f	Frequency, Hz
F	Faradaic constant, $C\ mol^{-1}$
i_0	Exchange current density, $A\ m^{-2}$
i	Applied current density, $A\ m^{-2}$
j	Imaginary unit
j_{ct}	Current density of charge transfer reaction, $A\ m^{-2}$
k_{ct}	Reaction kinetic constant, $A\ m^{2.5}\ mol^{-1.5}$
L_{pe}	positive electrode thickness, m
N	number of measured frequency points, or moles of lithium ions, mol
R_s	Particle radius, m
R	Universal gas constant, $J\ mol^{-1}\ K^{-1}$
R_{ct}	Charge transfer resistance, $\Omega\ m^2$
t_+	Transference number
t	Time, s
T	Temperature, K, or target function in global search algorithm
U	Equilibrium potential, V
Y_s	Transfer function defined in Eq.id=6#(B-3)
Z	Impedance, $\Omega\ m^2$
Z_p	Impedance of active particle, $\Omega\ m^2$
Z_{sei}	Impedance of SEI film, $\Omega\ m^2$

Greek

α_a, α_c	Transfer coefficients
ϕ	Potential, V
ψ	Tuning parameter to determine the weight of the imaginary part in the target function
ω	frequency
Ω_s	$\Omega_s = \omega R_s^2 / D_s$

Subscript

ct	charge transfer reaction
dl	electric double layer
f	filler
pp	primary particle
pe	positive electrode
real	real part of complex number
imag	imaginary part of complex number
sei	solid electrolyte/electrode interphase
ref	reference
e	electrolyte phase
s	electrode phase
+	cations
-	anions

Superscript

exp	experimental
over-bar	dimensionless variable or constant value of variables
over-tilde	variables in frequency domain or the perturbation of variables
sim	simulation
suf	surface

Employing the CDEIS technique, Itagaki et al. [7,8] studied the formation mechanism of the solid electrolyte interphase (SEI) film on the graphite and $LiCoO_2$ electrode in lithium-ion batteries during the first cycle. They also found the differences between the charge transfer resistance obtained from the SEIS and that from the DEIS. Later on, they explored the differences between intercalation and deintercalation reactions using a three-electrode lithium-ion battery [17].

Applying the PDEIS method, Buller et al. [2] parameterized the electrical circuit model for the battery while considering the differences between charge and discharge. The model parameterized in frequency domain was used to predict the battery performance under real operating conditions in time domain. To avoid violating the stationary requirement in the PDEIS, the magnitude of DC current should be limited to a certain level. Therefore, the parameters in the electrical circuit model for high current are difficult to obtain. A method combining the DEIS method at low current and charge/discharge curves at high current has been proposed to solve this problem by Dong et al. [6].

Karden et al. [4] compared the impedance spectra measured using CDEIS and PDEIS at the same temperatures, SOC and DC currents. Remarkable differences were revealed and attributed to the different species and electrochemical reactions distributions in the two situations. In addition, we believe that, at a same SOC in the CDEIS, the open-circuit voltage (OCV) during charging cycle is different from that during discharging cycle according to the widely reported voltage hysteresis. In this regard, it is difficult to study the differences between charge and discharge by using CDEIS method as the cell states are different. Therefore, the PDEIS method is more preferable to investigate the electrochemical reactions as it has much less accumulated distributions of species, temperature and reactions which tend to obscure the purely electrochemical reactions, and the cells are stabilized at a same state and have a same OCV before they are subjected to the EIS measurement embedded in a short pulse charge/discharge.

Despite decades of advances in application of the DEIS method in lithium-ion batteries, several key issues still remain as unsolved:

- (1) The characteristics of impedance spectrum in the DEIS measurement are not well understood. Inductive behavior at lower frequencies has been reported by researches [1,2,17]. However, the corresponding causes are controversial, as discussed in Ref.[17] (see section 3.2).
- (2) A quantitative formulation of the stationary condition in DEIS test is missing. As pointed out by Karden et al. [4] and Huang et al. [16], the lower frequency limit in PDEIS measurement is controlled by the magnitude of DC current in order to fulfill the quasistationary condition. However, there is no explicit formula relating the lower frequency limit with the DC current.
- (3) The causes for the differences between charge and discharge capability of the battery, especially at low temperatures [11], are still not well understood. Employing a three-electrode lithium-ion battery and the CDEIS method, Itagaki et al. revealed that the charge transfer resistance during intercalation process is smaller than that during deintercalation process for both electrodes [17]. They explained this finding as follows: first, during intercalation, the reactants are lithium ions in the electrolyte phase which are assumed to have a constant concentration; second, during deintercalation, the reactants are "lithium atoms" in the active particle with a decreasing concentration from the core to the electrode/electrolyte interface; third, the rate of charge transfer reaction depends on the surface concentration of reactants. As a consequence of the decreasing surface concentration in the active particle, the charge transfer resistance is larger for the deintercalation process. The deficiencies in the above explanation are: First,

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