Journal of Power Sources 277 (2015) 403–415

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Impedance model of lithium ion polymer battery considering temperature effects based on electrochemical principle: Part I for high frequency

Meng Xiao, Song-Yul Choe*

Mechanical Engineering, 1418 Wiggins Hall, Auburn Univ., AL 36849, USA

HIGHLIGHTS

- Modeled double layer behavior on electrode surface of Li-ion battery.
- Employed modified Gouy-Chapman-Stern method in the model.
- Improved ion transport equation in electrolyte bulk.
- Analyzed the performance of separated sub-models as well as integrated model.

ARTICLE INFO

Article history:
Received 15 May 2014
Received in revised form
11 October 2014
Accepted 13 October 2014
Available online 29 October 2014

Keywords:
EIS
Double layer
Transference number
Pouch type Li-polymer battery
Electrochemical model

ABSTRACT

Measurement of impedance is one of well-known methods to experimentally characterize electrochemical properties of Li-ion batteries. The measured impedance responses are generally fitted to an equivalent circuit model that is composed of linear and nonlinear electric components that mimic behaviors of different layers of a battery. However, the parameters do not provide quantitative statements on charge dynamics considering material properties. Therefore, electrochemical models are widely employed to study the charge dynamics, but have not included high frequency responses predominantly determined by double layers. Thus, we have developed models for the double layer and bulk that are integrated into the electrochemical model for a pouch type Li-ion battery. The integrated model is validated against the frequency response obtained from EIS equipment at different temperatures as well as the time response. The results show that the proposed model is capable of representing the responses at charging and discharging in time and frequency domain.

1. Introduction

1.1. EIS and electric equivalent circuit model

Electrochemical Impedance Spectroscopy (EIS) is the technique that has been widely used to study performance of batteries. In 1986, Laman used the EIS to study effects of the geometry of a cylindrical Li-ion battery on performances [1]. The measured impedance of the terminal of the battery is approximated with that of an electric circuit with parameters derived from electrochemical behaviors of the battery. The electric circuit model was constructed by connecting resistors with capacitors and shows different responses in magnitude and phase when AC current or voltage with different frequency is applied at the terminal. Analysis on Li-ion batteries using the EIS conducted by Munichandraiah in 1998 revealed existence of three semicircles in complex domain. The semicircle formed at the high frequency range is caused by film resistance and its capacitance, and the one at the middle frequency range is from charge-transfer resistance and double layer (DL) capacitance, while the one at the low frequency range is due to diffusional impedance [2]. Effects of degradation on battery performance have not considered. Capacity fade of 18650 Li-ion cells at different operating conditions was investigated by Ning using the EIS, where an equivalent electric model was used and the parameters were extracted from the impedance data [3,4]. Analysis of the

---

* Corresponding author.
E-mail addresses: mzx0001@auburn.edu (M. Xiao), choe@auburn.edu (S.-Y. Choe).

http://dx.doi.org/10.1016/j.jpowsour.2014.10.157

Nomenclature

A	Helmholtz free energy (J cm^{-3})
a	specific surface area for electrode (cm^{-1})
b	ion mobility (cm^2 V^{-1} s^{-1})
c	concentration (mol cm^{-3})
D	diffusion coefficient (cm^2 s^{-1})
F	Faraday's constant (96,487C mol^{-1})
e	energy storage density (J cm^{-1})
i_0	reference exchange current density (A cm^{-2})
I	load current (A)
j	transfer current density(A cm^{-3})
SOC	state of charge
N	ion flux (mol s^{-1} cm^{-2})
R	universal gas constant (8.3143 J mol^{-1} K^{-1})
T	cell temperature (K)
U	standard potential affected by solid concentration (V)
x	stoichiometric number in negative electrode or coordinate
y	stoichiometric number in positive electrode or coordinate

Greek symbols

ε	porosity of a porous medium
E	permittivity (F cm^{-1})
ϕ	potential in a phase (V)
η	surface overpotential (V)
σ	conductivity of solid active material (S cm^{-1})
μ	chemical potential (J mol^{-1})

Subscripts

a	anode reaction
B	bulk
c	cathode reaction
D	double layer
e	electrolyte phase
E	boundary between DL and bulk
eff.	effective
s	solid phase
S	boundary between DL and electrode particle
ST	stern plane
$+$	cathode
$-$	anode

parameters showed that the radius of the semicircle formed at low frequency range gets larger when cycled because of the increased interfacial resistance of both electrodes [5]. Another study using symmetric coin cells showed that the increased charge-transfer resistance is the main reason for degradation, where the charge-transfer resistance in cathode is larger than that in anode [6,7]. There has been another attempt to characterize interfacial behaviors for use of different solvents and salts along with different concentrations using the EIS [8]. Better correlation between the impedance and the parameters of the electric model was accomplished by replacing capacitors with constant phase elements (CPE) that are made of combined resistors and capacitors [9]. Other authors applied Kalman filter to correct the errors of the model [10,11].

All of the studies using EIS are based on the equivalent circuit model, which has several drawbacks. The electric equivalent circuit model (EECM) are constructed using lumped parameters that do not consider any effects of SOC or aging phenomena as well as locations, so that internal detailed mechanism associated with charge dynamics is hard to understand. The impedance is generally measured at an operating point with a perturbation of a small AC signal. When the operating point is changed, the impedance varies because of nonlinear behavior of the battery. Therefore, physical battery states cannot be accurately estimated by the linear parameters of electric equivalent circuit EIS model.

1.2. Current electrochemical model

Electrochemical model proposed by Doyle [12] has widely accepted to analyze static and dynamic behavior of ions in time domain. In frequency domain, however, the model does not show responses of impedance in high frequency range. The equations used for the model are summarized in table as below. These partial differential equations (PDEs) are discretized in two coordinates; spherical one for the radial direction (R direction) of particles and Cartesian one for through-the-plane direction (L direction) of the cell. The resulting matrices are solved with an implicit method. Details can be found in previously published papers [13,14].

Reaction kinetics

$$j^{\mathrm{Li}} = a_S \cdot i_0 \left(\exp\left(\frac{\alpha_a \cdot n \cdot F}{R \cdot T} \left(\eta - \eta_{\mathrm{SEI}} \right) \right) - \exp\left(- \frac{\alpha_c \cdot n \cdot F}{R \cdot T} \left(\eta - \eta_{\mathrm{SEI}} \right) \right) \right) \tag{1}$$

Electrolyte conductive

$$\frac{\partial}{\partial l}\left(\kappa_e^{\mathrm{eff}} \cdot \frac{\partial}{\partial l} \phi_e \right) + \frac{\partial}{\partial l}\left(\kappa_{D,e}^{\mathrm{eff}} \cdot \frac{\partial}{\partial l} \left(\ln c_e \right) \right) + j^{\mathrm{Li}} = 0 \tag{2}$$

Solid conductive

$$\frac{\partial}{\partial l}\left(\sigma^{\mathrm{eff}} \cdot \frac{\partial}{\partial l} \phi_s \right) = j^{\mathrm{Li}} \tag{3}$$

Electrolyte ion transport

$$\frac{\partial(\varepsilon_e c_e)}{\partial t} = \frac{\partial}{\partial l}\left(D_e^{\mathrm{eff}} \cdot \frac{\partial}{\partial l} c_e \right) + \frac{1 - t_+^0}{F} j^{\mathrm{Li}} \tag{4}$$

Solid ion transport

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_s}{\partial r} \right) \tag{5}$$

In order to obtain frequency responses, AC signals with different frequencies are applied to the model and a pouch type lithium polymer battery using EIS equipment. The amplitude is 1 A and frequency ranges from 0.01 Hz to 900 Hz at 50% SOC. The results of the frequency responses are plotted in Fig. 1, where the real and imaginary parts of the calculated impedances in the low frequency range match fairly well with that of experiments, but not in the frequency that is larger than 20 Hz. The model does not respond on the high frequency excitations and remains constant even though the frequency increases. This discrepancy is more obvious at Nyquist plot that the simulation result with the current model shows a linearly increasing part, but completely misses the semicircle that represents high frequency responses.