



A practical framework of electrical based online state-of-charge estimation of lithium ion batteries



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HIGHLIGHTS

- We develop an electrical model based on the principle of electrochemistry.
- This model agrees well with its experimental EIS spectra and discharging curve.
- The maximum initial capacity can be obtained simply through its discharging curve.
- Enable on-line estimation of the capacity used to indicate the SoC.

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ABSTRACT

State of charge (SoC) is an important parameter for Li ion battery (LiB) cells, and its estimation should be done online as its continuous operation before recharge depends on its SoC. While Coulomb counting method (also called Coulometry) is useful to estimate the SoC online, its accuracy depends on the value of its initial maximum capacity. Presently, this capacity is obtained by the periodic discharge of the cell fully but this can introduce damage to the cell and shorten its lifespan. In this work, an electrical model is developed for LiB cells based on the principle of electrochemistry from its discharge curve (i.e. the change in terminal voltage over time within a discharge cycle). This model is able to compute the internal parameters of a cell, including its maximum initial capacity at the beginning of each discharge cycle. With the internal parameters computed, it can also produce its Nyquist plot and the plot is found to agree well with its experimental electrochemical impedance spectroscopy (EIS) spectra. With this model, the status of a LiB cell and its maximum charge capacity can be determined in real time.

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1. Introduction

Batteries are playing an increasingly significant role in our daily life as electronic technology is occupying in more aspects of our lives such as portable communication devices including smart phones and laptops etc, portable medical information devices, and now electrification transportation systems. For light weight and long life applications, and clean environmental consideration, LiB stand up among various existing rechargeable batteries, due to its largest energy-to-weight ratio and long life as well as its memory-less property. Hence, it is a prime candidate for the portable devices' battery as well as electrical vehicles (EVs) of different kinds [1].

In all battery operated devices and system that require continuous operations, estimation of the battery SoC is important so that user can have a clue on the remaining useable time they can use further. Uncertainties in SoC estimation can cause the user to be highly conservative, but frequent re-charging can shorten the lifespan of the battery [2]. On the other hand, if re-charging is done too late, an over-discharge may occur which also shorten the life of the battery.

Methods of SoC estimation can be classified into electrical, stochastic and thermodynamic methods [3]. In electrical methods, the commonly employed methods today are the Coulomb counting and open circuit voltage (OCV) methods. The Coulomb counting method integrates the current over time and thus the accumulated charge delivered can be obtained and used to estimate the SoC [4]. This method is simple and easy to be implemented, but its drawback is that its maximum capacity at the start of each discharge cycle must be known and this capacity degrades with prolonged charge–discharge cycle. Thus, this method often requires periodic

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capacity calibration where a full discharge of the cell will be performed, but such action can shorten the life of the battery significantly [5]. Another common method on the estimation of SoC is the OCV method [6], this method is not an online estimation as OCV can only be measured at open circuit. Also, OCV vs. SoC profiles can be very flat, and thus large uncertainty can be generated by using OCV to estimate SoC.

As errors can occur during the SoC measurement due to noise and external disturbance, Kalman filter (KF) has also been applied to estimate the battery's SoC as a stochastic method. It has become popular due to its self-regulated and online nature. As the SoC pattern with discharging is not linear, extended Kalman filter (EKF) and sigma-point Kalman filter (SPKF) are introduced, and they have been used for the lithium polymeric battery (LiPB)-based hybrid electric vehicle (HEV) battery [7–11]. As all the stochastic methods require an accurate model of the battery's discharging behaviour, various battery models [12] have been developed based on the battery electrical performances at the beginning, and these models are empirical instead of being derived based on the principle of electrochemistry, rendering their limited applicability to specific battery type without performance ageing being taken into account. Although there is a fully described model which takes into account of all the electro-chemical processes [13], it is very difficult to implement in real time application as complex solution of simultaneous partial differential equations is needed.

Thermodynamics based method computes the entropy of a cell based on the variation of the terminal voltage and temperature, from which the cell's SoC can be deduced [14]. Unfortunately its in-situ online measurement is yet to be developed.

Among all the online SoC measurement methods, Coulomb counting method is the most intuitive and simple. In order to remove the necessity of calibration to determine its maximum capacity at the start of each discharge cycle, an in-situ method is proposed to provide an accurate online estimation of the maximum capacity in this work.

As only the battery discharge curve is available during battery operation, the estimation will be done by extracting the information contained in the discharge curve. Thus decomposition of the curve into different components is necessary and it is the first step in the model development.

2. Decomposition of battery discharge curve

The discharging terminal voltage contains much information about the battery's working state. It is well understood that the terminal voltage can be decomposed into the electromotive force (emf) and the over-potential.

2.1. Derivation of emf expression

The emf represents the battery's ability to provide a certain voltage. It is the difference in equivalent potentials between the two electrodes. The emf is often measured as the OCV of the battery and is described by the Nernst's equation [13].

To model the emf voltage change during discharging, Coleman et al. [4] presented a linear relationship between the emf voltage and SoC based on their experimental data, but such linear relationship is applicable to a limited range of SoC, and it is empirical with the data set they have.

In fact, during discharging, the active mass concentrations at the electrodes reduces, render the reduction in its emf, and such active mass concentration reduction need to be taken into account to reflect the mechanism underlying.

Limit the work to the LiB of intercalation type reaction instead of displacement or conversion type reaction, the emf expression

derived by Pop et al. [15] is employed, based on the Nernst Equation as given below:

$$V_{\text{emf}} = E_{\text{eq}}^+ - E_{\text{eq}}^- \quad (1)$$

where

$$E_{\text{eq}}^+ = E_0^+ - \frac{RT}{F} \left[\ln \left(\frac{x_{\text{Li}}}{1 - x_{\text{Li}}} \right) + U_j^+ x_{\text{Li}} - \zeta_j^+ \right] \quad (2)$$

$$E_{\text{eq}}^- = E_0^- - \frac{RT}{F} \left[\ln \left(\frac{z_{\text{Li}}}{1 - z_{\text{Li}}} \right) + U_j^- z_{\text{Li}} - \zeta_j^- \right] \quad (3)$$

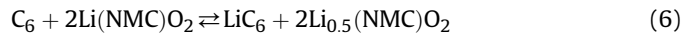
Here R is the gas constant, F is the Faraday constant, T is temperature at the electrode in K , x_{Li} and z_{Li} are the mole fraction of Li^+ ion inside the positive and negative electrodes respectively. U_j^+ and U_j^- are the dimensionless interaction energy coefficient in the respective electrodes, and ζ_j^+ and ζ_j^- are dimensional constant accounting for the phase transition in the equilibrium potential of the two electrodes. Superscripts $+$ and $-$ refer to positive and negative electrodes respectively. Subscript j is used to represent the phase change at the electrodes, and such phase change is found to occur at SoC below 50% (i.e. x_{Li} below 0.75 and z_{Li} below 0.25) [15]. As the terminal voltage of LiB will drop abruptly when SoC is below 50% for the ageing battery [2], the situation of SoC >50% is considered for practical consideration and hence the subscripts in Eqs. (1)–(3) are dropped in the subsequent equations.

If Q_{m} is the maximum amount of electrochemically active Li^+ ion inside a battery, and the maximum capacities of the positive and negative electrodes are denoted as Q_{max}^+ and Q_{max}^- , then according to the work of Pop et al. [15].

$$Q_{\text{max}}^+ = m_1 Q_{\text{m}}, \quad m_1 \leq 1 \quad (4)$$

$$Q_{\text{max}}^- = m_2 Q_{\text{m}}, \quad m_2 \leq \frac{1}{2} \quad (5)$$

Here $m_1 = 1$ and $m_2 = 2$ for fresh battery, and corresponds to the chemical reaction of the full cell as schematized below:



In Eq. (6) C_6 and $\text{Li}(\text{NMC})\text{O}_2$ denote the composition of the anode and the cathode at the cell discharge state respectively, whereas LiC_6 and $\text{Li}_{0.5}(\text{NMC})\text{O}_2$ refer to the same electrodes composition at the cell' charge state.

Denote Q_0^- as the amount of Li^+ ions inside the negative electrode in a fully discharged battery, and Q_z^- as the charge stored in the negative electrode for a given SoC, and consider the minimum SoC for practical application to be above 50% (in order to prevent over-discharge so as to maintain the battery lifespan), equation in Ref. [15] becomes

$$Q_z^- = Q_0^- + \text{SoC} \times \left(Q_{\text{m}} - Q_0^- - \frac{Q_{\text{max}}^+}{2} \right) = \text{SoC} \times Q_{\text{m}} \left(1 - \frac{m_1}{2} \right) \quad (7)$$

since $Q_0^- \ll Q_{\text{m}}$ and for $\text{SoC} > 50\%$.

But z_{Li} and x_{Li} are given as [15],

$$z_{\text{Li}} = \frac{Q_z^-}{Q_{\text{max}}^-} \quad (8)$$

$$x_{\text{Li}} = \frac{Q_{\text{m}} - Q_z^-}{Q_{\text{max}}^+} \quad (9)$$

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