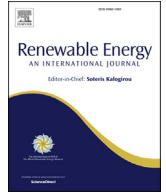




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Li-ion dynamics and state of charge estimation

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ABSTRACT

This paper focuses on real-time estimation of Li-ion State of Charge (SoC). A first-principles model validated by experimental data from literature is chosen to mimic a real Li-ion cell. Its impedance responses at different SoCs are studied by a simulated electrochemical impedance spectroscopy (EIS). An equivalent circuit model is developed for estimator design in which the parameters (including lumped series resistances R_1 , lumped interfacial resistances R_2 and time constant τ) are derived from system identification and compared with the EIS results. The estimator is designed using extended Kalman filtering (EKF) and is implemented in the first-principles model. It is demonstrated by computer simulation that the SoC during charge/discharge cycles can be estimated with a relative error <3%. The accuracy of SoC tracking is improved if it is jointly estimated along with either R_1 or R_2 given that these model parameters vary with SoC as revealed by EIS.

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1. Introduction

Rechargeable Li-ion batteries find a wide variety of applications in satellites, electrical vehicles, portable electronics and stationary power storage. In the renewable energy sector, Li-ion batteries may be used in conjunction of photovoltaics [13,28], thermal solar power [22], wind power [27,12], and geothermal applications [14]. It is envisioned that Li-ion batteries will be the promising means of energy storage in off-grid renewable energy given its longer lifespan than other competing technologies (see paper [3] and references therein for detailed discussions).

A Li-ion battery energy storage system may be composed of numerous cells connected in series and/or in parallel configurations to meet specifications of voltage and power. Because of variations in cell manufacturing, a pack consisting of multiple cells is susceptible to State of Charge (SoC) imbalance during operation. A weaker cell becomes depleted faster during discharge while a stronger cell reaches full charge more quickly during charge. To enhance usable battery capacity and to mitigate cell degradation due to over-charge or over-discharge, cell-wise monitoring and control of SoC is desirable in operating high-voltage, high-power Li-ion battery packs.

While techniques exist for direct measurement of the SoC (see review paper [17] and references therein), they have drawbacks limiting their uses in real-time applications. This motivates

research and development of model-based state estimation techniques utilizing current and voltage measurements that are readily available during battery operation. Because the Li-ion battery is a nonlinear electrochemical system, nonlinear state estimation techniques such as extended Kalman filtering (EKF) [18,19] and unscented Kalman filtering (UKF) [26,23] could be used. Cell-wise management of a high-power, high-voltage Li-ion pack based on EKF has been successfully demonstrated over a long testing period [24]. The real-time estimator usually employs an equivalent circuit model, in which the SoC is one of the internal states. Calibration of parameters in the equivalent circuit model may be done by minimizing difference in voltages measured experimentally and the model predicted values [9].

The mathematical model plays an important role in EKF-based battery estimator design because it is used in the prediction step of the algorithm to calculate battery state. The equivalent circuit model is a type of lumped parameter model that uses classical electrical elements to capture the main input-output dynamics of Li-ion during charging/discharging cycles [29,10]. It can be easily formulated in the state-space form for model-based estimation and control. To shed an in-depth fundamental understanding of the electrochemical transport phenomena in a Li-ion cell, however, nonlinear first-principles models may be required [5,20]. These models are governed by partial differential equations (PDEs) whose parameters may be tuned to match impedance responses of a real Li-ion cell over a wide spectrum of frequencies [2]. If distributed sensors and actuators are available, model reduction and control

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design techniques of PDE systems [1] may be applied to the Li-ion cell.

The focus of this paper is on the input-output dynamics of Li-ion. A detailed PDE-based first-principles model from literature that is validated by experimental data [5] is chosen to mimic a real Li-ion cell. An electrochemical impedance spectroscopy (EIS) study is conducted to obtain impedance responses of the cell over a wide spectrum of frequencies. The EIS helps the understanding of cell impedance which significantly affects cycling performance. Furthermore, it reveals that an equivalent circuit model with constant parameters may not be sufficient to capture Li-ion impedance at all SoCs. This motivates joint estimation of SoC with a time-varying battery parameter in real-time estimator design. The estimator is developed utilizing EKF and an equivalent circuit model whose parameters are derived from EIS and battery cycling data. Finally, the joint state and parameter estimator is compared with the state estimator (assuming constant model parameters during battery charge/discharge cycles) using the true SoC value as a baseline.

2. Approach

2.1. First-principles Li-ion model

A lithium-ion cell consists of five regions: a negative electrode current collector, a porous composite negative insertion electrode, a porous separator, a porous composite positive insertion electrode and a positive electrode current collector. In this work, a one-dimensional model is chosen to simulate a cross section of the battery while the edge effect of height and length is neglected. The model takes into account charge and material balances in the porous electrodes and separator as well as the coupling at the electrode-electrolyte interface. Porous electrode theory is employed so that the medium is treated as a superposition of active material, electrolyte, and filler with known volume fractions [15]. Specifically, the time-dependent PDEs are described as follows:

(i) Charge conservation in homogeneous solid:

$$\nabla \cdot (-\sigma \nabla \phi_s) = -j^{Li} \quad (1)$$

(ii) Mass conservation in homogeneous solid:

$$\frac{\partial c_s}{\partial t} = \nabla \cdot (D_s \nabla c_s) \quad (2)$$

(iii) Mass conservation in homogeneous electrolyte:

$$\varepsilon_e \frac{\partial c_e}{\partial t} + \nabla \cdot (-D_e \nabla c_e) = \left(\frac{1 - t_+^0}{F} \right) j^{Li} \quad (3)$$

(iv) Charge conservation in homogeneous electrolyte:

$$\nabla \cdot (\kappa \nabla \phi_e + \kappa_D \nabla \ln c_e) = -j^{Li} \quad (4)$$

(v) Lithium-ion movement between solid and electrolyte phases accounting for Butler-Volmer kinetics and double layer capacitance:

$$j^{Li} = a_s i_0 \left[\exp\left(\frac{F\eta}{2RT}\right) - \exp\left(-\frac{F\eta}{2RT}\right) \right] + a_s C_{dl} \frac{\partial(\phi_s - \phi_e)}{\partial t} \quad (5)$$

In Eqs. (1)–(5), σ is the solid phase conductivity, ϕ_s is the potential in the solid phase, ϕ_e is the potential in the electrolyte phase, j^{Li} is the reaction current resulting in production or consumption of Li, t is the time, c is the concentration of lithium ion, D is the diffusion coefficient, F is the Faraday constant, ε is volume fraction, t_+^0 is the transference number, κ is the electrolyte phase conductivity, κ_D is the diffusional conductivity, i_0 is the exchange current density, η is the over-potential, a is the specific area and C_{dl} is the double-layer capacitance. Subscript s represents solid phase and e electrolyte phase, respectively. The Bruggeman relationships are adopted to account for the effect of tortuosity on electrolyte diffusion and ionic conductivity in the above equations. Both cathodic and anodic transfer coefficients are 0.5 to evaluate i_0 using the electrode kinetic equation [5].

Model parameters used in this work are based on a $\text{Li}_x\text{C}_6/\text{Li}_y\text{Mn}_2\text{O}_4$ cell studied by Doyle et al. [5]. The double layer capacitance C_{dl} is assumed to be 0.1 F/m^2 [4] and $a_s = 3\varepsilon_s/r_p$, where r_p is the radius of particle in the electrode. The coupled Eqs. (1)–(5) are solved simultaneously using COMSOL Multiphysics, a finite element based numerical solver. The above mathematical model may be enhanced by including side reactions and heat transfer, which will be considered in future work.

2.2. Frequency responses of cell impedance

EIS is a powerful tool to investigate the dynamics of Li-ion cell [2,4,11]. It applies a small excitation voltage or current wave to the electrode and records the resulting response in current or voltage. Excitations at multiple frequencies and various SOCs allow the investigation of several electrochemical transport phenomena occurring at different time scales which facilitates the development of equivalent circuit models for estimator design.

In the EIS simulations, a fully charged cell is first discharged to a specified SoC and then left disconnected for 60 min to allow sufficient relaxation. Subsequently, a small single frequency stimulus current is applied to the positive electrode to observe the response in voltage. A frequency sweep for $f = 10^{-3} - 10^5 \text{ Hz}$ (uniformly distributed in log space) is done to collect 41 sets of data. The whole process is repeated for 11 different SOCs ranging from 0 to 1.

After collecting the current and voltage data, fast Fourier transforms (FFTs) are performed to compute the magnitudes and phase angles of the current and voltage in the transformed domain. For a vector $x = [x_0 x_1 \dots x_{N-1}]$ with length N , its fast Fourier transform, $X = [X_0 X_1 \dots X_{N-1}]$, is calculated as follows:

$$X_k = \sum_{n=0}^{N-1} x_n e^{-j(2\pi kn/N)}, k = 0, 1, \dots, N-1 \quad (6)$$

Given the fact that a single frequency sine wave is used as the stimulus current in each EIS simulation, the voltage output would also be a sine wave with a single frequency assuming quasi-linear response. The magnitude and phase angle of current or voltage are computed as the absolute value and the phase angle of the largest element in the vector of FFT. The complex impedance is then calculated as the transformed voltage divided by the transformed current. The calculation is done for 41 frequencies and 11 SoCs to generate 41×11 data points of cell impedance.

2.3. Equivalent circuit model and parameter identification

There are various forms of equivalent circuits available in literature (see, for example [16,9]). It is acknowledged that the equivalent circuit model shown in Fig. 1 provides a reasonable description of battery dynamics during charge/discharge cycles

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