Polarization Voltage Characteristics of Li-ion Cells Using a Reduced Electrochemical Model

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Abstract

Advanced battery management systems (BMS) in electric vehicles (EVs) require immediate and accurate internal information of batteries, such as Li-ion concentration, current distribution, and polarization potential across the electrodes for efficient monitoring, control and utilization. In this paper, an electrochemical model was reduced to sufficiently describe each electrode’s instantaneous dynamics without main information loss and it was validated by an experiment from a high-power LiFePO\(_4\)-graphite cell used in EVs. Furthermore, in order to better study and accurately improve the model, the polarization voltage characteristics of Li-ion battery is especially investigated. A sensitivity analysis of up to 6 parameters was carried out using model simulation. A parameter sensitivity matrix was established to describe the parameter sensitivity under constant current discharge condition.

Keywords: electric vehicles (EVs), electrode, polarization voltage, sensitivity analysis

1. Introduction

At present, Li-ion cells has become one of the very attractive candidate in EV's application since they are featured by high power density, high energy density, long service life, non-memory effect and environmental friendliness, etc.[1]. However, Li-ion cells for EVs must operate within the safe and reliable operating area, and improper operating conditions such as exceeding the specified restrictions of temperature and voltage windows can accelerate attenuation processes and even result in the failures. Thus, for safe and reliability of Li-ion batteries, it is required to monitor the batteries operate at reliable operation range through the adoption of model-based BMS in EVs. The core of a BMS is a battery model which identifies the relationship between currents and voltages measured at battery terminals and character the battery state using SOC or SOH [2].

Unfortunately, the main technical challenge for battery state estimation of Li-ion cell comes from the weak observability and the excitation of complex thermo-electrochemical processes in high current applications in EVs [3]. The fundamental challenge exists in the lack of established and readily computable indicators. Multiple metrics have been proposed in the recent literature. Moreover, simultaneous estimation of Li-ion cell in real-time is particularly very challenging due to limited available measurements (voltage, current and temperature). Thus, a rapid, accurate and non-invasive identification method is necessary. This work attempts to study polarization voltage characteristics by analysing a set model parameter sensitivity of cell under constant current discharge condition.

However, the large number of parameters in the full electrochemical models (known as pseudo-two-dimensional (P2D) model makes parameter identification computationally challenging. For example, it takes about three weeks to identify 88 parameters on a cluster of five quad-core PCs using a dynamic test. [4] The identifiability of parameters and identification accuracy are also important issues. Forman et al. used the Fisher information matrix to study parameter identifiability [4], [5]. Identifiability can be indicated by parameter sensitivity, i.e. the influence on battery model output when a parameter changes value. When the value of a highly sensitive parameter changes a little, the model output, i.e. the terminal voltage and surface temperature, will change noticeably. Thus it is easier to identify a highly sensitive parameter from experiments. On the other hand, low sensitivity parameters have very little effect on the model output and are therefore hard to identify correctly from experiments. Insensitive parameters cannot be identified and should be excluded from identification.
Schmidt et al. also used the Fisher information matrix to analyze parameter sensitivity and excluded some unidentifiable parameters to increase the identification quality of the remaining parameters. They also proposed an identification scheme with five different experiments, in which the parameters were grouped and identified stepwise. Using this method the variance and confidence interval can be obtained, but the identifiability matrix needs to be calculated, which is very complex with a multi-physics model. Min et al. and Wang et al. both used model simulation to examine parameter sensitivity for a PEM fuel cell model. They roughly classified the parameters into several groups without a quantitative method. Srinivasulu et al. provided a simple method based on simulated polarization curves to quantify the parameter sensitivity for a PEM fuel cell model. A similar method has not yet been applied to Li-ion batteries. Moreover, there are few established standards for identification experiments [6].

In this paper, we derived SPM from P2D model of a cylindrical Li-ion battery and validated it in order to evaluate the accuracy of the SPM. Furthermore, section 3 analyzes the parameter sensitivity of our SPM model and proposes a feasible method to design simulations for identifying the parameters more accurately using terminal voltage as identification object. A parameter sensitivity matrix to describe the sensitivity of model output was proposed when parameters take different values on operating conditions. Section 4 summarizes the main conclusions of the paper.

2. paper structure

As mentioned earlier, due to the heavy computational resources of the P2D model, a reduced model called the SPM is applied here for designing the estimators. The single particle (SP) approach originally developed by Haran et al. [7] for the metal hydride battery and later extended to the lithium system. This model includes the assumption that each electrode of a lithium ion cell can be approximated by a single spherical particle whose surface area is scaled to that of the porous electrode. Further, concentration and potential changes in the solution phase are ignored, and thermal effects are assumed to be negligible.

2.1 Single particle model

As illustrated in Figure 1 [8], a Li-ion cell model composed of a negative electrode, a separator, a positive electrode and two current collectors at the ends of the two electrodes. Typically, both electrodes consist of a grain structure of quasi-spherical active particles in μm scale. The Li-ions travel inside/outside the active particles via diffusion and migration inside the active particles along the r-axis, which is called solid phase diffusion. The SPM is a simplified, physics based, fundamental model where the current density is assumed to be uniform in each electrodes and all of the active material particles are in parallel. The associated diffusion equations are solved assuming average electrochemical reaction rate. Mathematically, the SPM model consists of two linear solid-state diffusion PDEs for each electrode’s concentration dynamics, where input current enters as a Neumann boundary condition (1), and a nonlinear output voltage function of the state values at the boundary and the input current derived from Butler-Volmer kinetics (2). The details of SPM model are given in the following.

\[
\frac{\partial C_s^i}{\partial t} = \frac{D_s^i}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_s^i}{\partial r} \right) = \frac{D_s^i}{r^2} \frac{\partial}{\partial r} \left( \frac{\partial C}{\partial r} + r^2 \frac{\partial C_s^i}{\partial r} \right), \quad (1)
\]

for \( r \in (0, R_e) \)

The initial conditions (2) and Neumann boundary conditions (3) are introduced:

\[
C_s^i_{\text{at}}, \quad \text{for} \ C > 0 \text{ at } t = 0
\]

\[
\frac{\partial C_s^i}{\partial r} \bigg|_{r=0} = 0, \quad \frac{\partial C_s^i}{\partial r} \bigg|_{r=R_e} = \frac{\pm I}{a_s^i FD_s^i AL_e^i} \quad (3)
\]

The Neumann boundary conditions at \( r = R^e_e \) and \( r = R^s_s \) signify that the flux entering the electrode is proportional to the input current \( I(t) \). The Neumann boundary conditions at \( r = 0 \) are required for well-posedness. Note that the states for the two PDEs are dynamically uncoupled, although they have proportional boundary inputs.

The measured terminal voltage output is governed by a combination of electric overpotential, electrode thermodynamics, and Butler-Volmer kinetics. The end result is
\[ V = \frac{RT}{\alpha F} \sinh^{-1}\left( \frac{t}{2\alpha' \Delta E \sqrt{c_{r,s}^+ (c_{\text{max}}^+ - c_{\text{max}}^-)} - \frac{RT}{\alpha F} \sinh^{-1}\left( \frac{t}{2\alpha' \Delta E \sqrt{c_{r,s}^- (c_{\text{max}}^+ - c_{\text{max}}^-)} - R \Delta E \right)} \right) \]  

(4)

The functions \( U^+(c_{r,s}^+) \) and \( U^-(c_{r,s}^-) \) in Eq. (4) are the equilibrium potentials of each electrode material, given the surface concentration. Mathematically, these are strictly monotonically decreasing functions of their input.

### 2.2 Model validation and verification

Figure 2 compares the voltage responses of the experiments and SPM simulations at 250C ambient temperature with constant current charge/discharge at 0.5C for the 2.3 Ah LFP/gr cells. The lower and upper voltage limits for the cell experiments and simulations are between 2.95 V and 3.6 V. The SPM matches the experimental voltage response very well during the mid SOC operating range. However, the SPM voltage responses at the end of charge and discharge cycles do not match the experiment as well, which possibly can attribute to the simplifying assumptions in our reduced model. The voltage error is still acceptable with a maximum error of less than 30 mV. It is necessary to ensure that the battery operates within a reasonable SOC range in vehicle application owing to the sharp voltage changes.

![Figure 2 Experimental and SPM voltage responses of a high power gr/LFP cell at 220C ambient temperature](image)

### 3. Parameter sensitivity analysis

The battery voltage sensitivity of parameters using single parameter sensitivity analysis was taken in this paper. Each of the 6 parameters to be analysed takes three values within a certain range. The influence degree on the battery voltage was described qualitatively during constant current discharge simulation as the parameter value changes. The parameter definition and values was obtained from LiFePO₄ battery cells with a 2.3 amp-hour capacity, a nominal voltage of 3.3 volts. These cells are designed for transient high power applications including commercial EVs [9]. A 0.2C constant current discharge condition was chosen since SPM is only suitable for small-current discharge. The detailed process of analysis is: Change a parameter of the 6 unknown parameters while keeping the rest parameter values fixed. After that, battery terminal voltage curve were obtained through simulation using these parameters. The sensitivity curves of terminal voltage for the initial stoichiometric numbers, \( \theta_p \) and \( \theta_n \), solid phase diffusion coefficient, \( D_{s,p} \), and \( D_{s,n} \), and the solid phase volume fractions, \( \varepsilon_{s,p} \) and \( \varepsilon_{s,n} \), under this discharge condition were shown as follows:

![Figure 3 Sensitivity analysis of the battery terminal voltage to the electrode SOC: (a) Sensitivity analysis of positive electrode SOC; (b) Sensitivity analysis of negative electrode](image)

### Figure 4 Sensitivity analysis of the battery terminal voltage to the solid phase volume fractions: (a) Sensitivity analysis of solid diffusion coefficient for positive electrode; (b) Sensitivity analysis of solid diffusion coefficient for negative electrode

![Figure 5 Sensitivity analysis of the battery terminal voltage to the solid phase volume fractions: (a) Sensitivity analysis of solid volume fractions for positive electrode; (b) Sensitivity analysis of solid volume fractions for negative electrode](image)
condition. The battery voltage curves are almost coincident under the premise of narrow and magnified 10 times for the solid diffusion coefficient and solid volume fractions. This indicates that the sensitivity value of these two parameters is very low under 0.2C constant current discharge condition and the approximate values can chose for the parameters within its ranges.

4. Conclusions

This paper simplifies a Li-ion electrochemical mechanism model for the purpose of better application in EVs. A SPM are proposed by ignoring the spatial distribution inhomogeneity of local volumetric transfer current density and the Li+ concentration in solid-phase electrode and electrolyte. For validation of the simplified model, a test was carried out with a 2.3 Ah LiFePO4/Gr cell. The sensitivity of terminal voltage to these parameters of the cylindrical Li-ion battery was analyzed based on a SPM in this paper using a constant current discharge simulation. The variation of battery terminal voltage with 6 different parameter values was described under the simulation.

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Reference

[1] Xuebing Han, Minggao Ouyang, Languang Lu, Jianqiu. Simplification of physics-based electrochemical model for lithium ion battery on electric vehicle. Part I: Diffusion simplification and single particle model. J. Power Sources 2015; 278: 802–813.


