Journal of Power Sources 325 (2016) 482–494

Contents lists available at ScienceDirect

Journal of Power Sources

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

Parameter sensitivity analysis of a simplified electrochemical and thermal model for Li-ion batteries aging

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HIGHLIGHTS

- Sensitivity Analysis of a multi-physics model of graphite/$LiFePO_4$ battery.
- Determination of most critical parameters for voltage and temperature simulation.
- Parameters value influence on loss of capacity simulated by the model in aging mode.
- Step-wise method for minimizing influence of parameters while identifying others.

ARTICLE INFO

Article history:
Received 2 November 2015
Received in revised form
3 June 2016
Accepted 7 June 2016

Keywords:
Lithium-ion
Batteries
Aging
Modeling
Sensitivity analysis
Parameter identification

ABSTRACT

In this work, a simplified electrochemical and thermal model that can predict both physicochemical and aging behavior of Li-ion batteries is studied. A sensitivity analysis of all its physical parameters is performed in order to find out their influence on the model output based on simulations under various conditions. The results gave hints on whether a parameter needs particular attention when measured or identified and on the conditions (e.g. temperature, discharge rate) under which it is the most sensitive. A specific simulation profile is designed for parameters involved in aging equations in order to determine their sensitivity. Finally, a step-wise method is followed to limit the influence of parameter values when identifying some of them, according to their relative sensitivity from the study. This sensitivity analysis and the subsequent step-wise identification method show very good results, such as a better fitting of the simulated cell voltage with experimental data.

1. Introduction

Due to their high power and energy densities, Li-ion batteries are the leading systems for the new generations of electric vehicles. In such demanding applications, it is essential to have the optimum cell design, management and configuration. Unfortunately, internal resistance rise and capacity fade over calendar and cycle life are still a major barrier [1] and despite intensive studies on electrolytes and positive and negative electrode chemistries, the underlying aging mechanisms are still not well understood. Modeling provides tools to perform complex analysis of the performance of Li-ion batteries and reduces the amount of time spent on experimental testing. The aim of our research is to use a physics-based model that can predict battery behavior and aging under various conditions to specify experimental tests to accelerate aging of Li-ion cells.

Initially developed by Newman and Tiedemann [2], the Pseudo Two-Dimensional (P2D) model is the reference in electrochemical battery models in terms of theoretical integration of mechanisms and prediction capabilities [3–8]. An in-house simplified and computationally efficient electrochemical and thermal model has been developed based on the P2D model [9,10]. Although it was already calibrated for the $LiFePO_4$-graphite Li-ion chemistry and shows good results compared to experimental data, the parameter identification process is still a challenging step because of the interdependence of the parameters during the calibration. The problem is even more difficult with multi-physics modeling that requires several parameters.

Parameter sensitivity analysis has already been used in Li-ion

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http://dx.doi.org/10.1016/j.jpowsour.2016.06.030
0378-7753/

batteries modeling research [11–14] in order to find out the influence of a parameter variation on the model output, such as terminal voltage or cell skin temperature, and identify those parameters with the most accurate and efficient method. Zhang et al. [15,16] carried out a sensitivity analysis of up to 30 parameters of their $LiFePO_4$ based multi-physics model without aging and proposed a feasible method to design experiments for identifying those parameters more accurately. In the current work we present a study of 41 physical parameters of our model, whether they are measured, estimated or involved in aging phenomena. Even if a parameter can be identified or measured with relative confidence, it is still useful to know if its variation on a certain range has an impact on the model output. Thus, it becomes easier to identify a parameter under the conditions where it has the greatest influence on the model output (i.e. higher sensitivity). A parameter with low sensitivity will not be identified since no experiment will be able to determine its value correctly. After the sensitivity analysis was performed, a stepwise method has been followed for the identification of the sensitive parameters.

In the first section of the paper, the hypotheses and the mathematical structure of the model are presented. In the secondpart, the sensitivity analysis method is detailed resulting in a sensitivity matrix that describes the influence of the parameters on the model output under different conditions. A specific simulation profile was also defined in order to study the sensitivity of parameters involved in aging equations. Finally, the third part is dedicated to the stepwise identification method of the sensitive parameters in order to improve the calibration process.

2. Multi-physics model

2.1. Electrochemical model

A single particle (SP) electrochemical model coupled to a thermal model has been developed from the simplification of the Pseudo-2D mathematical structure. The complete electrochemical

Table 1
1D electrochemical model equations [2].

Physical and chemical mechanism	Eq.		Boundary conditions
Solid phase conservation of Li^+ species	$\frac{\partial}{\partial t}c^s - \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D^s \frac{\partial}{\partial r}c_s\right) = 0$	(1)	$D^s\frac{\partial}{\partial r}c^s\Big\|_{r=0} = 0 - D^s\frac{\partial}{\partial r}c^s\Big\|_{r=R^s} = \frac{j_f}{a^s F}$
Electrolyte phase conservation of Li^+ species	$\frac{\partial}{\partial t}\varepsilon^e c^e - \frac{\partial}{\partial z}\left(D_e^{eff}\frac{\partial}{\partial z}c_e\right) - \left(1-t^+\right)\frac{j_f}{F} = 0$	(2)	$\frac{\partial}{\partial z}c^e\Big\|_{z=0} = \frac{\partial}{\partial z}c^e\Big\|_{z=L} = 0$
Electrochemical kinetics	$j_f^n = a_s^n i_0^n\left(exp\left(\frac{\alpha\widetilde{\kappa}}{RT}\overline{\eta}_n^k\right) - exp\left(-\frac{(1-\alpha)\widetilde{\kappa}}{RT}\overline{\eta}_n^k\right)\right)$ $j_f^p = a_s^p i_0^p\left(exp\left(\frac{\alpha\widetilde{\kappa}}{RT}\overline{\eta}_p^k\right) - exp\left(-\frac{(1-\alpha)\widetilde{\kappa}}{RT}\overline{\eta}_p^k\right)\right)$ $i_0^n = k_0^n \cdot c_e^{\alpha_{ox,n}}\left(c_{n,max}^s - c_n^s\right)^{\alpha_{ox,n}} c_n^{s\alpha_{ox,n}}$ $i_0^p = k_0^p \cdot c_e^{\alpha_{ox,p}}\left(c_{p,max}^s - c_p^s\right)^{\alpha_{ox,p}} c_p^{s\alpha_{ox,p}}$	(3)	
Electrode overpotential	$\overline{\eta}_n = \overline{\eta}_n^k + \overline{\eta}_n^{diff}$ $\overline{\eta}_p = \overline{\eta}_p^k + \overline{\eta}_p^{diff}$	(4)	
Kinetic overpotential	$\overline{\eta}_n^k = \frac{RT}{\alpha F} ln\left(\xi_n + \sqrt{\xi_n^2 + 1}\right)$ $\overline{\eta}_p^k = \frac{RT}{\alpha F} ln\left(\xi_p + \sqrt{\xi_p^2 + 1}\right)$	(5)	
Diffusion overpotential in the particles	$\overline{\eta}_n^{diff} = U_n\left(\theta_n^s\right) - U_n\left(\theta_n^b\right)$ $\overline{\eta}_p^{diff} = U_p\left(\theta_p^s\right) - U_p\left(\theta_p^b\right)$	(6)	
Mass transport overpotential in the electrolyte	$\overline{\eta}_e^{mt} = \varphi_e(L) - \varphi_e(0) = (1-t_+)\frac{2RT}{F} ln\frac{c^e(L)}{c^e(0)} - \frac{I}{2A}\left(\frac{\delta_n}{\kappa_n^{eff}} + 2\frac{\delta_{sep}}{\kappa_{sep}^{eff}} + \frac{\delta_p}{\kappa_p^{eff}}\right)$	(7)	
Cell voltage	$V(t) = U_p\left(\frac{c_p^s}{c_{p,max}^s}\right) - U_n\left(\frac{c_n^s}{c_{n,max}^s}\right) + \frac{2RT}{F} ln\left(\frac{-\frac{R_p^s}{6\epsilon_p^s i_{0_p}^0 A\delta_p} I + \sqrt{\left(\frac{R_p^s}{6\epsilon_p^s i_{0_p}^0 A\delta_p} I\right)^2 + 1}}{\frac{R_n^s}{6\epsilon_n^s i_{0_n}^0 A\delta_n} I + \sqrt{\left(\frac{R_n^s}{6\epsilon_n^s i_{0_n}^0 A\delta_n} I\right)^2 + 1}}\right) +$ $(1-t_+)\frac{2RT}{F} ln\frac{c^e(L)}{c^e(0)} - \frac{I}{2A}\left(\frac{\delta_n}{\kappa_n^{eff}} + 2\frac{\delta_{sep}}{\kappa_{sep}^{eff}} + \frac{\delta_p}{\kappa_p^{eff}}\right)$	(8)	