

# Parameter Estimation of Single Particle Model Using COMSOL Multiphysics® and MATLAB® Optimization Toolbox

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**Abstract:** In order to study the behavior of the secondary batteries, physics-based models are more representative of the real behavior than equivalent circuit models, especially for the estimation of the life and capacity fading. On the other hand, the complexity and computational cost of sophisticated physics-based models like pseudo two-dimensional (P2D) models justify the use of more simplified models such as single particle model (SPM). In this work, COMSOL Multiphysics® *Single Particle Model for Lithium-Ion Batteries* (Model ID: 14527) was linked to MATLAB® through LiveLink™ for MATLAB® and a regression technique was applied to estimate the parameters of the model. Moreover, an empirical equation was introduced for the solution phase resistance to account for concentration and potential influences at higher applied currents.

**Keywords:** Lithium-Ion Batteries, Single Particle Model, LiveLink™ for MATLAB®, Parameter Estimation

## 1. Introduction

Equivalent circuit models (ECMs) are among the most widely used empirical models in simulation of batteries [1, 2]. They have the advantage of low computational cost, which makes them more appropriate for online simulations. However, ECMs do not consider physical phenomena occurring in batteries. On the other hand, physics-based models, like Pseudo Two Dimensional (P2D), account for electrochemical kinetics and transport phenomena. These models can predict the behavior of the cells better than empirical models, at the cost of higher complexity and longer computation time. Single particle model (SPM) has been introduced to simplify P2D model by ignoring local concentration and

potential of the solution phase and using a lump solution resistance instead. The most important assumption in SPM is its uniform current distribution along the thickness of the porous electrode, which results to treatment of porous electrode as a large number of single particles, all of which being subject to the same conditions. Although SPM is applicable for low applied current densities, thin electrodes, and highly conductive electrodes [3], they are still one of the best alternatives for ECMs if we want to have physical insights of phenomena inside the cell. Moreover, the number of parameters needed for SPM is less than P2D, which makes it a better candidate for online simulation and optimization.

In this work, the existing single-particle model: COMSOL “Single Particle Model for Lithium-Ion Batteries” (Model ID: 14527) will be run with known parameters to obtain a solution that will be considered as our base of comparison. Then, the model will be linked to MATLAB® through LiveLink™ for MATLAB®. Then parameters of the model will be estimated by means of regression methods. In the next section, an equation for the solution phase resistance will be introduced to improve the results of SPM especially for higher applied currents. This equation is based on fitting the results of SPM and P2D by means of same technique mentioned above.

## 2. Modeling Approach

### 2.1 Use of COMSOL Multiphysics®

Figure 1 is a schematic of a typical Li-ion cell, consisting of two current collectors, a negative electrode, a positive electrode, a separator between electrodes, and an electrolyte that fills the porous components [4].

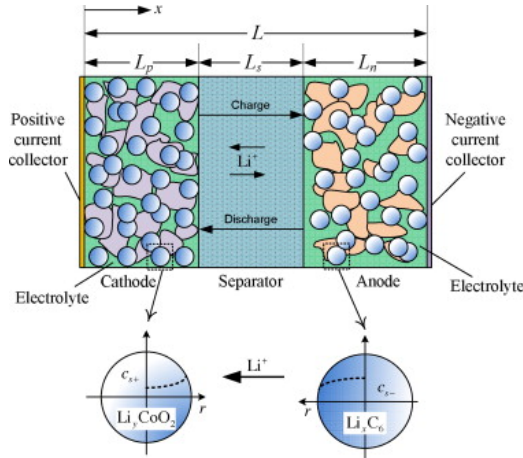


Figure 1. Schematic of lithium ion battery [4]

Assuming uniform current distribution along the thickness of the porous electrode in SPM makes it possible to represent the entire porous electrode (positive/negative) by a single intercalation particle [3]. The material balance for lithium ions inside electrode active material is described by Fick's second law in a spherical coordinate system as

$$\frac{\partial c_{s,j}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_{s,j} r^2 \frac{\partial c_{s,j}}{\partial r} \right) \quad (1)$$

with initial conditions as

$$c_{s,j}(t = 0, r) = c_{s,j}^0 \quad (2)$$

The boundary conditions are zero flux of lithium ions at the center of the spherical particle and  $J_j$  molar flux of lithium ions at the surface of particle. These conditions can be expressed respectively as

$$D_{s,j} \frac{\partial c_s}{\partial r} \Big|_{r=0} = 0 \quad (3)$$

$$-D_{s,j} \frac{\partial c_s}{\partial r} \Big|_{r=R_j} = J_j \quad (4)$$

Where  $j = p, n$  for the positive and negative electrodes respectively,  $D_s$  is the solid phase lithium ion diffusion coefficient, and  $R_j$  is the solid particle radius.

The molar flux of lithium ions in SPM is related to total current  $I$  passing through the cell as

$$J_j = \frac{I}{FS_j} = \frac{i_{loc,j}}{F} \quad (5)$$

Where  $F$  is Faraday number and  $S_j$  is the total electroactive surface area of electrode  $j$

$$S_j = \frac{3\varepsilon_j V_j}{R_j} \quad (6)$$

Where  $\varepsilon_j$  is the volume fraction of solid phase active material in electrode  $j$  and  $V_j$  is the total volume of that electrode.

A state of charge (SOC) variable for the solid electrode particles is defined as follows:

$$SOC_j = \frac{c_s^{surf}}{c_s^{max}} \quad (7)$$

Where  $c_s^{surf}$  and  $c_s^{max}$  are the surface and maximum concentration, respectively, of lithium in the electrode particles.

The dependency of the local electrochemical reaction rate on concentration and potential is usually determined by the Butler-Volmer rate equation:

$$i_n = i_0 \left[ \exp\left(\frac{0.5F\eta}{RT}\right) - \exp\left(\frac{-0.5F\eta}{RT}\right) \right] \quad (8)$$

Where  $R$  is universal gas constant and  $T$  is absolute temperature. The surface overpotential,  $\eta$ , is the deviation from the thermodynamic potential difference between the solid and the solution at the existing surface concentrations:

$$\eta = \phi_s - \phi_l - E_{eq} \quad (9)$$

Where  $\phi_s$ ,  $\phi_l$ , and  $E_{eq}$  are the potential of the solid, potential of the solution phase, and open-circuit potential of the solid material evaluated at the surface concentration respectively.

The exchange current density,  $i_0$ , is a function of lithium concentrations in electrolyte and solid active materials, i.e.:

$$i_0 = Fk \left( \frac{c_l}{c_{l,ref}} \right)^{0.5} \left( c_s^{max} - c_s^{surf} \right)^{0.5} \left( c_s^{surf} \right)^{0.5} \quad (10)$$

Where  $c_l$  is the solution phase concentration which is taken to be equal to a constant value in the SPM, and  $c_{l,ref}$  is the reference solution phase concentration (taken to be equal to 1 mol/m<sup>3</sup>).

By using inverse hyperbolic form of Butler-Volmer expression, solid phase potential is defined as follows:

$$\phi_s = E_{eq} + \phi_l + \frac{\eta RT}{0.5F} \operatorname{asinh}\left(\frac{i_{loc}}{2i_0}\right) \quad (11)$$

The potential drop in the solution phase between the positive and negative electrode can be obtained as:

$$\phi_{l,positive} - \phi_{l,negative} = IR_{solution} \quad (12)$$

Where  $R_{solution}$  is the solution phase resistance determined by coupled mass and charge transfer processes [5]. This variable is an adjustable parameter in SPM. The approximation of  $R_{solution}$  is discussed later.

Finally, the difference between solid phase potential of positive and negative electrodes equals to the cell voltage.

$$E_{cell} = \phi_{s,positive} - \phi_{s,negative} \quad (13)$$

## 2.2 Parameter Estimation

Physical and chemical parameters are needed for the simulation of lithium-ion cells. Although finding some parameters such as physical dimensions and chemistry of materials are practicable from experimental measurements, it is not convenient to measure some others. These parameters include design parameters (such as porosity, particle size, etc.), electrode specific parameters (like diffusion coefficients, electrical conductivity, contact resistance, etc.), and kinetics parameters (such as transfer coefficients, concentration exponential etc.). Parameter estimation might be a useful approach to find kinetic and transport parameters from the experiment charge/discharge data. Such techniques are typically formulated as the minimization of the sum-of-squared differences between the model outputs and their experimentally measured values for each cycle  $i$  [6]

$$\min_{\theta_i} \sum_{j=1}^{n_i} [y_i(t_j) - y_{model,i}(t_j; \theta_i)]^2 \quad (14)$$

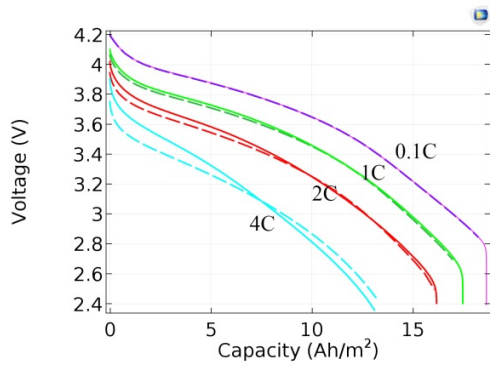
Where  $y_i(t_j)$  is the measured voltage at time  $t_j$  for cycle  $i$ ,  $y_{model,i}(t_j; \theta_i)$  is the voltage computed from the battery model at time  $t_j$  for cycle  $i$  for the vector of model parameters  $\theta_i$  (the parameters being estimated from the experimental data), and  $n_i$  is the number of time points in cycle  $i$ . Solving this equation is known in the literature as least-squares estimation [6].

Here, the goal is to evaluate the capability of COMSOL and its interfacing module to find these unknown parameters. First, we run Single Particle Model for Lithium-Ion Batteries (Model ID: 14527) with known parameters such as effective diffusion coefficient of lithium in the solid phase for the negative and positive electrodes ( $D_{sn}$  and  $D_{sp}$ ), and electrochemical reaction rate constants for the negative and positive electrodes ( $k_n$  and  $k_p$ ). Thereafter, we assume the results of SPM as exact solutions ( $y_i(t_j)$  in eq.(14) in order to assess the performance of the estimation techniques in recovering the parameters, based on the voltage curve this time. As a matter of fact, the next step is to consider some parameters as unknown ( $\theta_i$  in eq.(14) and try to identify them by minimizing the difference between the exact solutions and the experimental results from new sets of parameters. This was done by connecting the COMSOL model with MATLAB and using optimization techniques to minimize the errors.

The estimated parameters in this work were chosen to be the effective diffusion coefficient of lithium in the solid phase for the negative and positive electrodes ( $D_{sn}$  and  $D_{sp}$ ), initial state of charge of electrodes ( $SOC_{0,n}$  and  $SOC_{0,p}$ ), and volume fraction of active materials ( $\varepsilon_n$  and  $\varepsilon_p$ ).

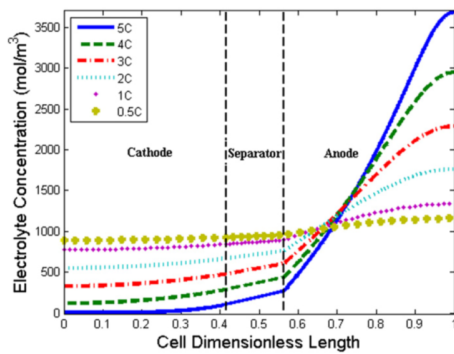
## 2.2 Solution Phase Resistance

Despite the advantages of SPM, its accuracy is limited at high charge/discharge current where the concentration gradient of solution phase is large and cannot be neglected. Figure 2 shows the difference between SPM and P2D in various applied current. Obviously, this difference is more and more important at higher applied currents.



**Figure 2.** SPM model (dashed line) compared to P2D model (solid line) at different applied currents

There are several ways to improve SPM and make it applicable in higher current. Among those possibilities, the refinement of  $R_{solution}$  seems more straightforward. Due to the fact that  $R_{solution}$  takes into account the solution phase concentration gradient, it is natural to assume that its value increases with the C-rate of discharge process. This can be illustrated in Figure 3 [7].



**Figure 3.** Electrolyte Li ion concentration inside cell at end of discharge for different rates, P2D model [7]

After trying several mathematical forms, an empirical equation for  $R_{solution}$  was introduced to improve the performance of SPM:

$$R_{solution} = A(SOC_{pos})^B \quad (15)$$

Finding the constant coefficients  $A$  and  $B$  is discussed in the next section.

### 3. Results and Discussion

As it was discussed in Parameter Estimation section, we assumed that some parameters are

unknown and regression was conducted by minimizing the difference between the output of model with unknown parameters and the results from previous simulation where the parameters are known. Regression was accomplished using 20 points taken from the voltage curve of discharge process from beginning to the end of discharge, after each 30 minutes. The MATLAB optimization toolbox function  $fmincon$  was selected as the solver, which is defined for constrained nonlinear multivariable functions. Table 1 shows the constraints and the initial guesses for parameters. The relative error in the table is defined as

$$\text{Relative error} = \frac{|P_{\text{exact}} - P_{\text{estimated}}|}{P_{\text{exact}}} \quad (16)$$

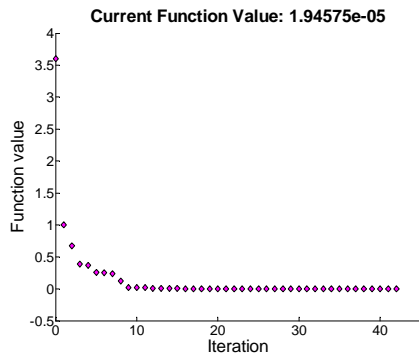
As it is showed, the values of  $\varepsilon_n$ ,  $\varepsilon_p$ ,  $SOC_{0,n}$ , and  $SOC_{0,p}$ , have been estimated with a very good accuracy. This is due to the fact that the results are more sensitive to these parameters. However, the situation is different for the evaluation of the diffusion coefficients. In this case, an accurate estimation can be achieved only when both bounds and initial guesses are taken close enough to the exact values. One suggestion is to increase the number of points where the regression is taking place. Running some experiments (e.g. Electrode Impedance Spectroscopy) to define the range of these parameters is also an appropriate way for estimating them correctly.

**Table 1.** Exact and estimated parameters

Parameters	Lower bound	Upper bound	Initial guess	Estimated	Exact	Relative Error %
$D_{Sn}$ [m <sup>2</sup> /s]	2.73 e-14	11.7 e-14	2.73 e-14	2.23 e-14	3.9 e-14	17.18
$D_{Sp}$ [m <sup>2</sup> /s]	0.7 e-13	3 e-13	0.7 e-13	1.2 e-13	1e-13	20
$\varepsilon_n$	0.2	0.6	0.2	0.357	0.357	0
$\varepsilon_p$	0.2	0.6	0.2	0.444	0.444	0
$SOC_{0,n}$	0.5	0.7	0.5	0.5642	0.5635	0.12
$SOC_{0,p}$	0.1	0.3	0.1	0.1709	0.1706	0.059

Figure 4 depicts the optimized function value which is a summation of all differences between estimated and exact solution data for the whole

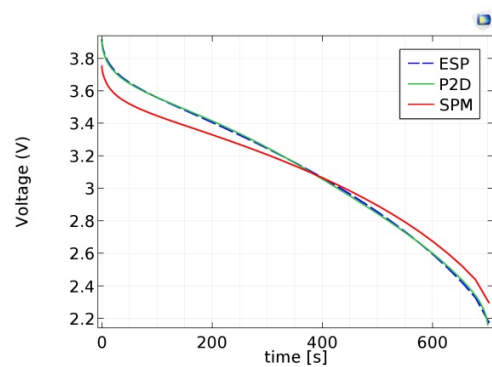
timespan (20 time points). Although estimated diffusion coefficients differ from exact values, the difference in the voltage of two models (function value of regression problem) converges to really small values.



**Figure 4.** Differences between the results using the exact parameters and those obtained with estimated parameters

To improve the behavior of the SPM, we then propose to fit discharge curves (with 2C, 4C, 6C, 8C, and 10C discharge rates) in order to find coefficients of solution resistance equation (Eq. 15). The same regression technique was chosen to minimize the difference between exact solution and estimated solution. However, in this step, we had to base our regression on a more representative solution. Consequently, the results from P2D model (where concentration and potential of solution phase are explicitly calculated) has been chosen as for our new “exact solution”. Figure 5 shows a comparison between P2D, SPM, and ESP (enhanced single particle), the later being the modified SPM with  $R_{solution}$  equation in discharge process. A sufficiently high current (4C) was applied to compare the performance of these models. Obviously, there is a significant improvement in predicting voltage of the cell with ESP model. The relative errors of the ESP are less than 1% for each time step.

Regression was performed for various applied currents and constant coefficients  $A$  and  $B$  in equation 15 were estimated for each current (Table 2).



**Figure 5.** Comparison between various models for 4C discharge process

**Table 2.**  $A$  and  $B$  for different applied currents

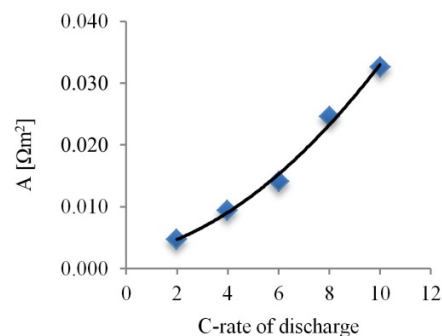
Applied current I	$A[\Omega \cdot m^2]$	$B$
2C	4.750e-3	0.579
4C	9.387e-3	1.168
6C	1.400e-2	1.498
8C	2.458e-2	2.073
10C	3.255e-2	2.370

Figure 6 and Figure 7 show values for  $A$  and  $\alpha$ , respectively. As it can be seen, it is possible to fit two equations for  $A$  and  $\alpha$  as a function of applied current:

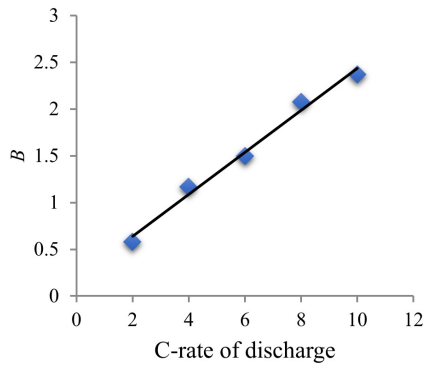
$$A = 2.2556e - 4c^2 + 8.3298e - 4c + 2.1308e - 3 \quad (17)$$

$$B = 0.2244c + 0.1915 \quad (18)$$

where  $c$  is c-rate of the discharge process.

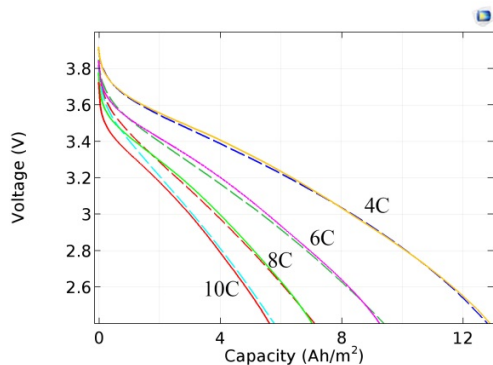


**Figure 6.** Values for  $A$  from Table 2



**Figure 7.** Values for  $B$  from Table 2

Figure 8 compares the result from P2D model and ESP considering equation 17 and equation 18 for  $A$  and  $B$ , respectively. Clearly, ESP model can predict discharge voltage with a good accuracy. It should be noted that defining  $A$  and  $B$  from Table 2 improves the results and their accuracy. However, using equation 17 and 18 makes the model more flexible as it can be applicable for all discharge currents.



**Figure 8.** Comparison between results from ESP (dashed line) and P2D model (solid line) for higher applied currents

#### 4. Conclusion

In this work, “Single Particle Model for Lithium-Ion Batteries” (Model ID: 14527) was linked to MATLAB<sup>®</sup> and some parameters of the model were estimated by the optimization toolbox in MATLAB<sup>®</sup>. The parameters, which the model is more sensitive to, were calculated with a good precision (error < 0.1%). Then, by using the same regression technique, an empirical equation for the solution phase resistance was introduced to reduce the errors of SPM in case of higher applied currents.

Predictability of the improved SPM (called ESP) was evaluated by comparing its results with those obtained with P2D model at high applied currents (up to 10C). In all cases, a good conformity was observed between the P2D and ESP. Consequently, ESP can be used to simulate realtime status of secondary cells and battery packs.

#### 5. References

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