

A Single Particle Thermal Model for Lithium Ion Batteries

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Abstract: COMSOL[®] *Single Particle Model for Lithium-Ion Batteries* (Model ID: 14527) is generalized to include an energy balance. This is accomplished by approximating the solution phase polarization as a function of current and temperature. The theoretical approach for this work is similar to Guo et al. [*Journal of the Electrochemical Society*, 158, (2) A122-A132 (2011)] for modelling lithium ion cells. The COMSOL isothermal model run at 0.1 A provided the baseline for the open circuit potentials (OCPs).

Keywords: Lithium Ion Batteries, Single Particle Model.

1. Introduction

A disadvantage common to fully dimensional lithium ion battery models is the long simulation time due to the large number of nonlinear equations, so these models become computationally inefficient for simulating conditions in real time [Ref. 1 and 2]. To improve computational run time without compromising accuracy, the single particle model (SP model) has been proposed [Ref. 3 and 4].

The single particle model for a lithium-ion battery is a simplification of the one dimensional (1d) model, subject to several simplifying assumptions. In the single particle model formulation, the local potential and concentration gradients in the electrolyte phase are ignored and accounted for using a lumped solution resistance term [Ref. 5 and 6]. Similarly, the potential gradients in the solid phase of the electrodes are also neglected and the porous electrode is treated as a large number of single particles all being subjected to the same conditions. The single particle formulation accounts for solid diffusion in the electrode particles and the intercalation reaction kinetics.

In this work, the existing single-particle model: COMSOL “Single Particle Model for Lithium-Ion Batteries” (Model ID: 14527) is extended to include thermal effects by adding the energy balance equation to the SP model.

2. Mathematical Model

Generally, a lithium ion battery consists of the current collector, the positive electrode, the separator and the negative electrode. A lithiated organic solution fills the porous components and serves as the electrolyte. A schematic of a lithium ion battery is shown in Figure 1 [Ref. 7].

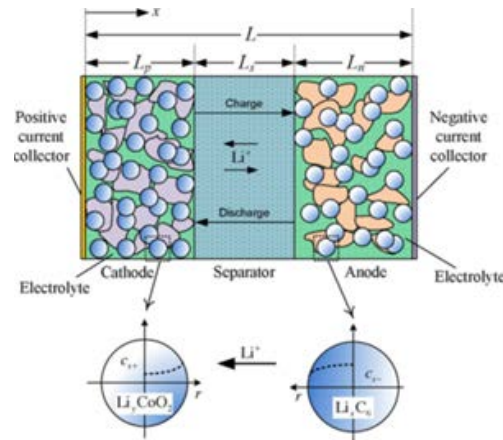


Figure 1: Schematic of lithium ion battery

The material balance for lithium ions in the batteries solid electrodes is governed by Fick’s second law in spherical coordinates:

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

The flux is zero at the center of the particle and is equal to the flux from the spherical particle at the particle surface. This gives boundary conditions

$$D_{s,j} \frac{\partial c_s}{\partial r} = 0 @ r = 0 \text{ and } D_{s,j} \frac{\partial c_s}{\partial r} = j(t) @ r = R_s \quad \text{Eq. 2}$$

and initial conditions

$$c_{s,j}(r, 0) = c_{s,j,0}$$

Where $j = p, n$ for the positive and negative electrode respectively, D_s is the solid phase lithium ion diffusion coefficient, R_s is the solid particle radius and $j(t)$ is the pore wall molar flux of lithium ions. The molar flux is related to the applied cell current as:

$$j(t) = \frac{i_{loc}}{F} = \frac{i_{applied}}{(F(3/R_s)\epsilon_s L)} \quad \text{Eq. 3}$$

Where $i_{applied}$ is the applied current density, ϵ_s is the volume fraction of the solid phase active material in the electrode, and L is the thickness of the electrode. In this model formulation, discharge current densities are taken to be positive and charge current densities are taken to be negative.

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

$$SOC = \frac{c_s^{surf}}{c_s^{max}} \quad \text{Eq. 4}$$

where $c_s^{surface}$ and c_s^{max} are the surface and maximum concentration, respectively, of lithium in the electrode particles. The Butler-Volmer expression describes the intercalation reaction kinetics,

$$i_{loc} = i_0 \left(\exp\left(\frac{0.5F\eta}{RT}\right) - \exp\left(-\frac{0.5F\eta}{RT}\right) \right) \quad \text{Eq. 5}$$

and the overpotential η is defined as:

$$\eta = \phi_s - \phi_l - E_{eq} \quad \text{Eq. 6}$$

where ϕ_s and ϕ_l are the potential of the solid and solution phase, respectively.

The exchange current i_0 is defined as:

$$i_0 = Fk \sqrt{(c_s^{max} - c_s) c_s \left(\frac{c_l}{c_{l,ref}}\right)} \quad \text{Eq. 7}$$

where k is the reaction rate constant, c_l is the solution phase concentration which is taken to be equal to a constant value in the single particle model, and $c_{l,ref}$ is the reference solution phase concentration (taken to be equal to 1 mol/m³).

The Butler-Volmer kinetic expression is re-written in terms of the inverse hyperbolic function in order to improve computational efficiency. An expression for the solid phase potential for each electrode can be obtained as:

$$\phi_s = E_{eq} + \phi_l + \frac{RT}{0.5F} \operatorname{asinh}\left(\frac{i_{loc}}{2i_0}\right) \quad \text{Eq. 8}$$

The potential drop in the solution phase between the positive and negative electrode is:

$$\phi_{l,positive} - \phi_{l,negative} = i_{applied} R_{solution} \quad \text{Eq. 9}$$

where $R_{solution}$ is the solution phase resistance which is actually determined from coupled mass and charge transfer processes. In the single particle model $R_{solution}$ is an adjustable parameter which could depend on cell temperature and applied current.

The cell potential is determined as follows:

$$E_{cell} = \phi_{s,positive} - \phi_{s,negative} \quad \text{Eq. 10}$$

In the energy balance used for this model formulation, the spatial temperature distribution in cell is neglected, so the cell temperature T is a function of time only. The general energy balance equation is given as Eq. 24 in Ref. 8, and is written as:

$$\rho v C_p \frac{dT}{dt} = IT \left[\frac{\partial U_p}{\partial T} (SOC_{p,surface}) - \frac{\partial U_n}{\partial T} (SOC_{n,surface}) \right] + I(\eta_p - \eta_n + IR_{solution}) \quad \text{Eq. 11}$$

The initial cell temperature is assumed to be same with the ambient temperature where T is the cell temperature, v is the volume of cell, p is the density of cell, C_p is the specific heat capacity of cell, and q is the rate of heat transfer between cell and surroundings. In this work, heat flux at cell surface are assumed to follow Newton's law of cooling, so the term q is expressed as

$$q = hA(T - T_{amb}) \quad \text{Eq. 12}$$

where h is the advection heat transfer coefficient and A is the cell surface area.

2.1 Model Parameterization

All the model parameters required by the thermal single particle model are identical to the parameters used in the COMSOL isothermal model example except for parameters impacted by the thermal balance. This was done for the purpose of comparison of the discharge voltage profiles between the two formulations. The temperature dependence of the diffusion coefficient, reaction rate constant and the open circuit potentials (OCP) are given by

$$D_{s,j}(T) = D_{s,j} \exp \left[\frac{E_{a,d,j}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad \text{Eq. 12}$$

$$k_j(T) = k_j \exp \left[\frac{E_{a,r,j}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad \text{Eq. 13}$$

$$U_j(SOC_j, T) = U_j(SOC_j, T_{ref}) + \frac{\partial U_j}{\partial T} (T - T_{ref}) \quad \text{Eq. 14}$$

where $j = p, n$ for the positive and negative electrodes.

The entropy change coefficient profiles from Ref. 9 are shown in Figure 2 and 3. These curves were incorporated into the COMSOL model as interpolations in SOC.

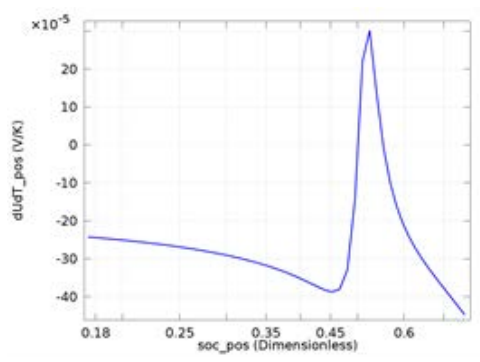


Figure 2: The entropy change coefficient for the positive electrode.

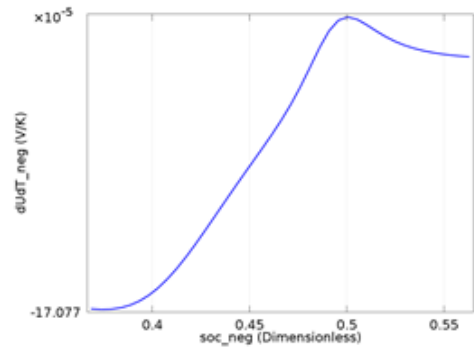


Figure 3: The entropy change coefficient for the negative electrode.

3. Results and Discussion

Figure 4 shows the 1C discharge curves at different cooling rates for the thermal single particle model as compared with the corresponding discharge profile for the isothermal model. Note that the discharge data from the isothermal model is imported into COMSOL as text files for the purpose of comparison.

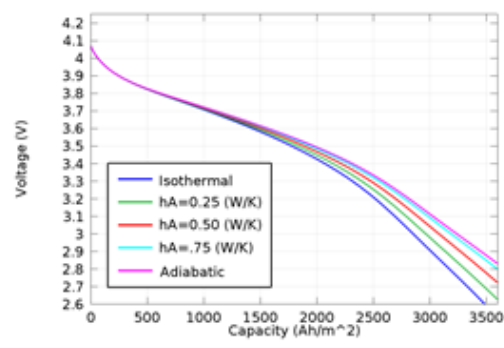


Figure 4: Cell Voltage for 1C discharge at different cooling rates.

Figure 5 shows the temperature profiles on the skin of the cell for a 1C discharge rate and different cooling rates. Figure 6 shows the reversible and irreversible heat generation and the heat loss to the cell's surroundings at a cooling rate given by $hA = 0.25 \text{ (W/m}^2\text{)}$.

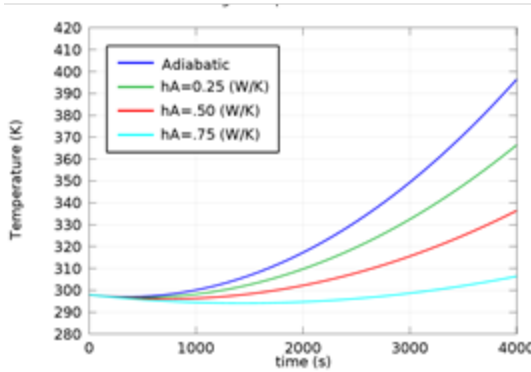


Figure 5: Temperature profiles on the cell skin for a 1C discharge and different cooling rates.

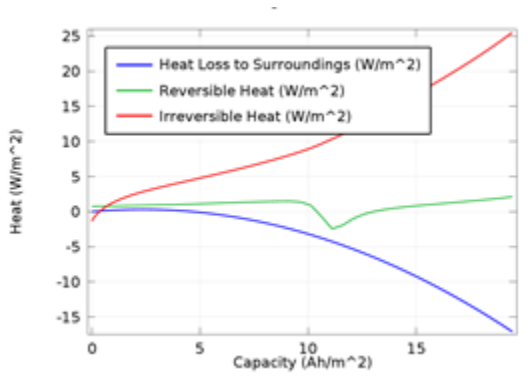


Figure 6: Cell Heat Balance for different Cooling Rates.

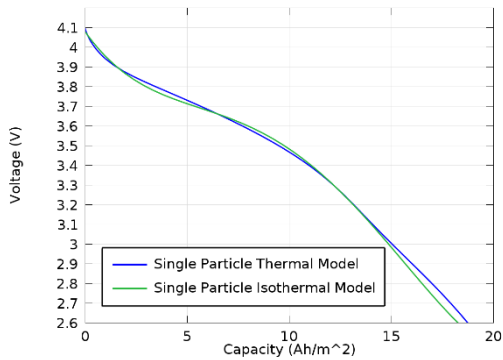


Figure 7: Comparison of 1C Discharge Profiles for Thermal Model and Isothermal Model.

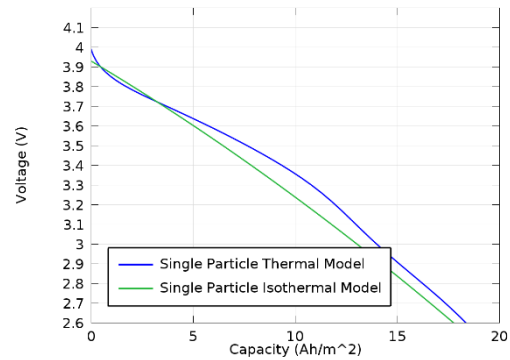


Figure 8: Comparison of 2C Discharge Profiles for Thermal Model and Isothermal Model.

The COMSOL model was used to conduct parameter sweeps with respect to ambient temperature (T_{amb}) applied discharge rates ($i_{applied}$) and the rate of cooling as reflected by the magnitude of the advection heat transfer coefficient (h). The resulting temperature profiles from the thermal balance were then fitted by conducting multiple nonlinear regression in terms of $i_{applied}$ and h using Oakdale Engineering Datafit 9.0 software. The lowest order model with good approximation of the single particle thermal model is:

$$T = 298 + (1 - hA)1.0^{-6}t^2i_{applied} - 1.0^{-5} - .0054 \quad \text{Eq. 15}$$

This allowed the COMSOL model to represent $R_{solution}(i_{applied}, T)$ as a simulation in time since there is no spatial component associated with $R_{solution}$ for the single particle thermal model and because the dependence of $R_{solution}$ on $i_{applied}$ and T is reflected by the regression in T . The resulting statistical model is capable of approximating the thermal behavior of lithium ion batteries as reflected in the preceding figures. The model is not capable of directly modelling the macro spatial battery thermal characteristics but the heat balance depicted in Figure 6 can be used in conjunction with geometric and thermal conductivity information of battery components to approximate a batteries spatial thermal behavior.

This modelling approach is stochastic in nature and the simplifying assumptions that form the basis of the single particle model represent a gross departure from existing robust models. However, even robust dimensional lithium ion

battery models rely heavily on empirical data because the complex mass transfer and electrochemical kinetics involved are not completely understood. The virtue of the single particle model and other reduced order models is that they have the potential to provide real time modelling and control of battery processes where the accuracy of more sophisticated models is not required.

4. References

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