

MEGN 570  
Electrochemical Systems Engineering  
Final Report  
Studying the dynamic effects of diffusion parameters on  
Li-ion battery

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# 1 Introduction

Li-ion batteries are becoming increasingly popular in society. To further advance this technology, a better understanding of internal dynamics is necessary. Many have used RC equivalent circuit models to estimate the behavior of batteries. These models are useful if using the model to control the battery since once fitted, they are quick to solve for any condition they are exposed to. What they lack is a physical understanding of battery operations [1]. As a battery degrades, the previously fitted model no longer matches with the current battery. Of course the fit can be performed again on the battery but that doesn't provide an answer to what is causing the battery degradation. It is for this reason, physically based battery models are created. In this study, a physically-based pseudo-2D (P2D) model is created for an A123, 18650 cell containing a graphite anode and a  $\text{LiFePO}_4$  cathode. This model will then be used to study the effects solid-state diffusion parameters have on the dynamic response of the battery.

## 2 Model Formulation

As mentioned in Section 1, this model is based on an A123 cell. The battery is modeled using a P2D framework. In this framework, the anode, separator, and the cathode are discretized into mesh nodes using the cartesian coordinate system. Each mesh node contains electrolyte and a solid particle discretized using spherical coordinates. These two coordinate systems are coupled by the charge-transfer reactions that occur at the surface of each solid particle. In this model, positive current will be designated as current that discharges the battery. Each node tracks the following state variables:  $C_{\text{Li}}^+$ ,  $C_{\text{Li}}$ ,  $\phi_s$ ,  $\phi_{el}$ , and  $T$ , the concentration of Li ions in the electrolyte, concentration of Li in each node of the solid particle, electric potential of the solid (s) and electrolyte (el) phase, and temperature of the mesh node respectively.

### 2.1 Governing Equations

In each phase, conservation of mass, charge, and energy govern the results for each mesh node. Currently in this model, temperature is assumed to be constant over the course of the simulation. Therefore, the following set of equations will only concern conservation of mass and charge.

#### 2.1.1 Electrolyte Phase

*Conservation of Mass:*

$$\frac{\partial C_{\text{Li}^+}}{\partial t} = -\nabla_x \cdot \mathbf{N}_{\text{Li}^+} + A_{fac} \dot{S}_{\text{Li}^+} \quad (1)$$

*Conservation of Charge:*

$$\frac{\partial (\phi_s - \phi_{el})}{\partial t} = -\nabla_x \cdot \mathbf{i}_{el} + A_{fac} \dot{S}_{\text{Li}^+} F \quad (2)$$

where

$$\mathbf{N}_{\text{Li}^+} = -D_{\text{Li}^+}^{eff} \nabla_x C_{\text{Li}^+} - D_{\text{Li}^+, intf}^{eff} \frac{z_{\text{Li}^+} F}{RT} \nabla_x \phi_{el} \quad (3)$$

$$\mathbf{i}_{el} = -\sigma_{el} \nabla \phi_{el} \quad (4)$$

### 2.1.2 Solid Phase

In the solid particle, the electric potential of the solid does not change in the radial direction. There is flux of charge between the adjacent mesh nodes.

*Conservation of Mass:*

$$\frac{\partial C_{Li}}{\partial t} = -\nabla_r \cdot \mathbf{N}_{Li} \quad (5)$$

*Conservation of Charge:*

$$\frac{\partial \phi_s}{\partial t} = 0 \quad (6)$$

$$\nabla_x \cdot \mathbf{i}_s = A_{fac} \dot{s}_{Li} \quad (7)$$

where

$$\mathbf{N}_{Li} = -D_{Li}^{eff} \nabla_r C_{Li} \quad (8)$$

$$\mathbf{i}_s = -\sigma_s \nabla \phi_s \quad (9)$$

### 2.1.3 Charge-Transfer

The solid and electrolyte phases are linked by the charge-transfer reactions that occur at the surface of the particle. The reaction at the surface is simplified to



This single charge transfer reaction is governed by the Butler-Volmer equation

$$i_{BV} = i_o \left[ \exp \left( \frac{-n\beta F}{RT} \eta \right) - \exp \left( \frac{n(1-\beta)F}{RT} \eta \right) \right] \quad (11)$$

where

$$\eta = (\phi_s - \phi_{el}) - (\phi_s - \phi_{el})^{eq} \quad (12)$$

## 3 Results

Nothing to show unfortunately.

## 4 Discussion

Since the model is not working, I will discuss what I think the effect these parameters would have on the battery. Also, I will discuss the simplifications made to the model and their validity.

### 4.1 Effects of changing $r_p$

On a geometrical standpoint, as the radius of the particle is decrease, the ratio of surface area to volume is increased. From this, I would expect the rate of  $\text{Li}/\text{Li}^+$  production from the charge transfer reaction to change. Also, with a larger area it is expected that a capacitance value would increase. This could be tested using EIS. I wouldn't expect the capacity of the battery to change from a change in particle radius. If the porosity of the solid material stays constant, then the volume of the solid will also be constant. This volume determines the amount of lithium that can be stored in the electrode.

## 4.2 Effects of changing $D_o$

Opposite to a change in particle radius, the diffusion coefficient would greatly impact the cell's capacity. The overpotential of the particle is calculated based on the concentration of lithium at the surface. Lithium that is produced at the surface of the particle takes up a vacancy that could be used for another charge-transfer reaction. If the lithium does not diffuse into the particle, the capacity is only as good as the max surface concentration. This reduction in capacity can be seen in a real battery that has a very high charge/discharge current applied.

## 4.3 Model Simplification

One area that is simplified is the model geometry. This cell is a spiral cell. When wrapped, the outer electrode will have a larger surface area to transmit electrons to the current collector than the inner electrode. This model also assumes smooth spherical solid particles. In reality, there is some surface roughness associated with the active material, providing more surface area for the charge transfer to occur. Another mechanism not modeled is the voltage drop across the SEI layer. This voltage drop is non-linear and would effect the overpotential used in the Butler-Volmer equation.

$$\eta = (\phi_s - \phi_{el}) - (\phi_s - \phi_{el})^{eq} - V_{SEI} \quad (13)$$

In the Butler-Volmer equation,  $i_o$  is currently modeled as being a constant value. This is not true as  $i_o$  is a function of the concentrations of the Li and  $\text{Li}^+$ . Another parameter that is a function of concentration is the solid-state diffusion coefficient. As mentioned above, The solid-state diffusion coefficient could effect the batteries capacity.

## 5 Conclusions

While physically based models provide more information, they are also harder to develop. Developing this model has been a learning experience on its own. It has made me think of the mechanisms going on inside the battery and how they have been modeled historically.

[1] M. Jun, et al., Journal of Power Sources (2014),<http://dx.doi.org/10.1016/j.jpowsour.2014.02.063>