

Electrochemical Modeling of Lithium Plating of Lithium Ion Battery for Hybrid Application

Zhenli Zhang
Johnson Controls

Zhihong Jin
Johnson Controls Power Solutions

Perry Wyatt
Johnson Controls Inc

ABSTRACT

Lithium plating is an important failure factor for lithium ion battery with carbon-based anodes and therefore preventing lithium plating has been a critical consideration in designs of lithium ion battery and battery management system. The challenges are: How to determine the charging current limits which may vary with temperature, state of charge, state of health, and battery operations? Where are the optimization rooms in battery design and management system without raising plating risks? Due to the complex nature of lithium plating dynamics it is hard to detect and measure the plating by any of experimental means.

In this work we developed an electrochemical model that explicitly includes lithium plating reaction. It enables both determination of plating onset and quantification of plated lithium. We have studied the effects of charging pulses on homogenous plating in order to provide guidance for lithium ion battery design in hybrid applications. By simulation a quantitative analysis of influencing factors on plating and a quantitative map of current limits to prevent lithium plating are provided. Our simulation suggests that a method that combines modeling and three electrode tests could be used to determine the true current limit map to prevent plating. Modeling are also performed to investigate the effects of coating thickness and driving cycles to illustrate the impact of design variables and applications.

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INTRODUCTION

Lithium ion battery with graphite anodes could have plating issue when the battery is charged especially at low temperatures. Lithium plating relates to many problems regarding safety and aging [1, 2, 3]. There is no way to completely prevent plating because in applications the battery will age and very likely they age differently and sometimes they are used in extreme conditions and then it raises questions of how to control plating in service.

A variety of factors influence lithium plating including battery design variables, intrinsic material properties, manufacturing conditions, as well as controls. Understanding these factors has significant value in points of view of design and controls. Using experimental means to investigate plating has limitations in sensitivity and timeliness because in many scenarios plating does not show up in a detectable quantity and sometimes they are not stable [4, 5, 6]. In this work, we develop a model to consider lithium plating. In the framework of electrochemical modeling the lithium plating reaction is explicitly

included. In contrast with literature focusing on continuous charge for energy cell and some heterogeneous plating [7]. Our aim is to use modeling to understand some fundamentals of plating for power cell in hybrid applications, specifically the effects of charge pulses, so that some insights can be drawn for cell and controls designs.

The paper is organized as follows: we first present how the model is developed for plating simulation including equations, battery selection, and parameter determinations. Then we present simulation results including a typical case study to demonstrate some of fundamentals of plating and a qualitative analysis of factors influencing plating which is followed by a quantitative current map to prevent lithium plating. The discussions of the implications of our simulations on battery specifications and controls are included as well. Then we extend the simulations to study coating thickness and driving cycles to elaborate the impacts of design variables and applications on lithium plating. Finally the major findings are summarized.

MODEL DEVELOPMENT FOR LITHIUM PLATING SIMULATION

Figure 1 is the schematic of major reactions involved in lithium plating process: 1) The main reaction of lithium insertion in layered structure of carbon (assuming graphite anode); 2) the plating reaction; 3) plated lithium are oxidized by electrolyte to form passivation layers like SEI; 4) plated lithium accumulates to form dendrites.

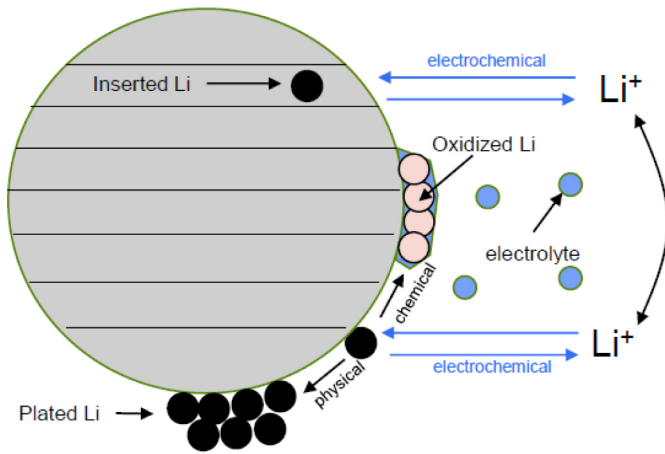


Figure 1. The schematic of lithium plating and related reactions. The top blue arrows indicate main reaction; the bottom blue arrows represent plating reaction;

The four reactions are different in nature and thus may cause different effects as listed in Table 1. Plating reaction may not be harmful if they are reinserted in carbon. But if plated lithium reacts with electrolyte or accumulates it will cause battery degradation. The passivation will cause both capacity loss and resistance increase. The accumulation of plated lithium will cause capacity loss and may lead to safety problem.

Table 1. Reactions involved in lithium plating differ in nature and impacts

Reactions	Nature	Impacts
Lithium insertion	Electrochemical	No impacts on degradation
Lithium plating	Electrochemical	No impacts on degradation if reinserted
Reaction with electrolyte	Chemical	Accelerates aging
Accumulation	Physical	Accelerates aging

In the framework of electrochemical modeling [8] we have considered the lithium plating reaction by adding two equations. Equation 1 describes the Butler-Volmer type kinetics of plating reaction.

$$i_p = a_v i_{0,p} \left[\frac{c_{l,ref}}{c_l} \exp\left(\frac{\alpha_a F \eta_p}{RT}\right) - \frac{c_l}{c_{l,ref}} \exp\left(\frac{-\alpha_c F \eta_p}{RT}\right) \right] \quad (1)$$

where η_p is the over potential of plating reaction. Equation 2 calculates the plated lithium as result of plating reaction and subsequent side reactions.

$$\frac{\partial \varepsilon_{Li}}{\partial t} = -\frac{M_{Li}}{\rho_{Li} F} i_p + f(k, \varepsilon_{Li}) \quad (2)$$

In equation 2 the first term is contributed by plating reaction which may be positive or negative depending on plating over potential, the second term is contributed by side reactions. If it is the physical accumulation the term can be positive or negative. If it is chemical reaction with electrolyte the term will be always negative. In this work we focus on demonstrating the effects of plating and did not simulate any type of side reactions. However the model platform is flexible to consider the battery degradation due to these side reactions.

Most of literature related to plating studied continuous charge for energy cell. Here we focus on investigating effects of charging pulse for power cell. The purpose is to provide some guidance for battery and control design for hybrid application. To relate to state-of-art battery technology we use a product on the market with power cell design as the baseline battery. The battery is NMC/Graphite chemistry. The proprietary cell design information is not disclosed here. First we performed HPPC tests and then determine the electrochemical parameters by fitting to the test results. With the fitted parameters we add the lithium plating reactions. For the two parameters related to plating reaction: plating exchange current and activation energy of this parameter we have referred to literature values [7]. We have used COMSOL to solve the equations and performed 1D simulation that represents a homogeneous plating.

Simulation Results and Discussions

Analysis of a Typical Case

To demonstrate some of the fundamentals of plating dynamics we first present a typical case where a constant current 100A 10s pulse was applied to the cell at T=0C and SOC=50%. Figure 2 shows how the plating happens.

The top figure shows the various potentials in anode for the initial state when current is zero. The $U_{Li+/Li} = 0V$, is the reference potential, the potential of negative electrode, $V_- = OCV_{graphite}$, is about 120mV which corresponds to the open circuit voltage of graphite anode at 50%SOC. Since there is no current the over potential for main anode reaction, $\eta_- = V_- - OCV_{graphite} = 0$. As a result the over potential for plating reaction, $\eta_p = V_- - 0[V] > 0$ indicating the plating has not happened. Note that in equation 1 when $\eta_p > 0$, the anodic term in equation dominates and there is no plating. The middle figure in Figure 2 shows the various potentials at end of the charge pulse. It is seen that the negative electrode potential, V_p , is significantly lowered to maintain a negative over potential η_- and thus supports reacting current in anode. Meanwhile the over potential for plating reaction, η_p , goes to negative as well and then plating happens (the cathodic term in equation 1 wins over anodic term). The bottom figure in Figure 2 shows the evolution of plated lithium which grows along charging time. Note that lithium is plated more at the interface of anode and separator than at the interface between anode and current collector which is reasonable due to the fact that there is a resistance for lithium ions to migrate and diffuse from separator to anode and reactions favor to happen at anode and separator first.