



# Modeling of lithium plating induced aging of lithium-ion batteries: Transition from linear to nonlinear aging



Xiao-Guang Yang<sup>a,\*</sup>, Yongjun Leng<sup>a</sup>, Guangsheng Zhang<sup>a</sup>, Shanhai Ge<sup>b</sup>,  
Chao-Yang Wang<sup>a,b,\*\*</sup>

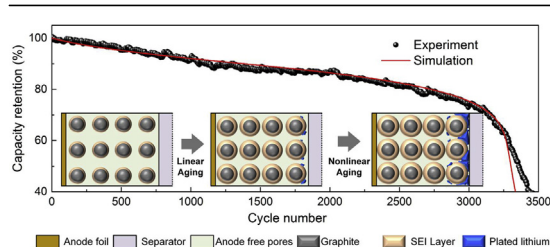
<sup>a</sup> Department of Mechanical and Nuclear Engineering and Electrochemical Engine Center (ECEC), The Pennsylvania State University, University Park, PA 16802, USA

<sup>b</sup> EC Power, State College, PA 16803, USA

## HIGHLIGHTS

- We present a Li-ion battery model capable of predicting Li plating induced aging.
- The model is able to capture the transition from linear to nonlinear aging.
- Nonlinear aging is attributed to exponential increase of Li plating rate.
- Anode porosity drop due to SEI growth is response for onset of Li plating.
- There is positive feedback btw porosity drop and Li plating rate increase.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 4 April 2017  
Received in revised form  
13 May 2017  
Accepted 30 May 2017

### Keywords:

Li-ion battery  
Lithium plating  
Solid electrolyte interphase  
Aging  
Pore clogging

## ABSTRACT

A physics-based Li-ion battery (LIB) aging model accounting for both lithium plating and solid electrolyte interphase (SEI) growth is presented, and is applied to study the aging behavior of a cell undergoing prolonged cycling at moderate operating conditions. Cell aging is found to be linear in the early stage of cycling but highly nonlinear in the end with rapid capacity drop and resistance rise. The linear aging stage is found to be dominated by SEI growth, while the transition from linear to nonlinear aging is attributed to the sharp rise of lithium plating rate. Lithium plating starts to occur in a narrow portion of the anode near the separator after a certain number of cycles. The onset of lithium plating is attributed to the drop of anode porosity associated with SEI growth, which aggravates the local electrolyte potential gradient in the anode. The presence of lithium metal accelerates the porosity reduction, further promoting lithium plating. This positive feedback leads to exponential increase of lithium plating rate in the late stage of cycling, as well as local pore clogging near the anode/separator interface which in turn leads to a sharp resistance rise.

© 2017 Elsevier B.V. All rights reserved.

\* Corresponding author.

\*\* Corresponding author. Department of Mechanical and Nuclear Engineering and Electrochemical Engine Center (ECEC), The Pennsylvania State University, University Park, PA 16802, USA.

E-mail addresses: [xuy19@psu.edu](mailto:xuy19@psu.edu) (X.-G. Yang), [cwx31@psu.edu](mailto:cwx31@psu.edu) (C.-Y. Wang).

## 1. Introduction

Aging of lithium ion batteries (LIBs) is a critical issue for applications requiring long life such as electric vehicles (EVs) [1–8].

When expecting a lifespan of 10–15 years for an EV, the durability of LIBs is typically the bottleneck. In general, aging of LIBs involves loss of capacity, rise of impedance, and reduction of power. A fundamental understanding of aging characteristics, such as the evolutions of cell capacity and resistance over the lifetime, is of critical significance for development of reliable life-prediction methods for battery management systems (BMS) [9–11].

Various aging mechanisms have been proposed in the literature, including formation and growth of solid electrolyte interphase (SEI) [3–5], mechanical breakup of electrode materials [12–14], dissolution of transition metals from the cathode [15–17], and deposition of metallic lithium in the anode [18–21]. Among them, SEI growth has been recognized as the dominant aging mechanism in most scenarios, especially for commercially available LIB cells [22–25]. SEI is a layer formed on the surface of electrode materials during the first charge (formation) process. Its role is to protect electrode from further reaction with the electrolyte. Owing to the porous nature of SEI, however, a small amount of electrolyte can still diffuse across the SEI layer and be reduced on the electrode surface after the formation cycle, leading to continuous thickening of the SEI layer and thus loss of active lithium. Dominated by the SEI growth, the capacity decay of LIBs exhibits a square root dependency on time if in storage [26]. If under load, capacity decay is revealed to be linear with respect to the charge throughput [25,26]. Furthermore, both calendar and cycling aging accelerate with the increase of operating temperature, following the Arrhenius law.

In recent years, however, many studies have reported aging behaviors that are in contrast to the above SEI-dominated aging characteristics. One example is the nonlinear capacity drop after prolonged cycling. Schuster et al. [27] cycled a set of commercial 1.95Ah 18650 cells at moderate temperatures and charging rate. Capacity decay and impedance rise were found to be linear with the charge throughput at the beginning, indicating SEI-dominated aging. After prolonged cycling, however, the cell capacity dropped abruptly and cell impedance increased sharply, indicating that some other mechanism took over the aging process. Similar nonlinear aging behaviors have also been reported by other groups [26,28–36]. Based on these research efforts, some major characteristics can be concluded regarding the nonlinear aging phenomenon. First, it occurs for cells of various cathode chemistries, including  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC111) [26–29],  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC622) [29],  $\text{LiFePO}_4$  [30–33],  $\text{LiCoO}_2$  [34,35], and  $\text{LiMn}_2\text{O}_4$ /NMC111 blend [36]. It is therefore reasonable to expect that this nonlinear aging behavior is mostly related to aging mechanisms of the anode. Second, it is revealed that the transition point from linear to nonlinear aging is strongly affected by the current and cut-off voltage of the charging process [27], and also by the composition of the electrolyte [28,34]. Third, through post-mortem analysis of electrodes taken from cells after serious nonlinear aging [27,30–33], thick films were observed near the anode/separator interface, whereas no apparent morphology change was observed for the cathode material. Using energy dispersive X-ray spectroscopy (EDX), Klett et al. [31] showed that the thick films in the anode contain similar composition as the SEI layer. With the help of Osmium tetroxide ( $\text{OsO}_4$ ) staining approach, Zier et al. [37] revealed existence of a large amount of metallic lithium at the anode/separator interface. Broussely et al. [34] also stated that a large deposit of lithium metal was observed after dismantling the deeply cycled cell. Based on the above characteristics, it is believed that the nonlinear aging after prolonged cycling is attributed to lithium plating.

The equilibrium potential of lithium intercalation into graphite is fairly close to, only ~100 mV higher than, the equilibrium potential of lithium deposition reaction. These two reactions therefore compete during cell charging. Under harsh conditions, the anode

potential can become negative with respect to  $\text{Li}/\text{Li}^+$  [18], leading to deposition of lithium onto the surface of graphite particles instead of intercalation, which is called lithium plating. The plated lithium can react with electrolyte to form a new SEI layer, or can become isolated from the electron-conductive matrix, leading to loss of lithium inventory. Furthermore, the plated lithium metal can be in the form of dendrites, which, in the worst scenarios, may pierce the separator, induce internal short circuit and result in hazardous consequences.

Previously, lithium plating was considered to be a serious issue only under harsh charging conditions like high C-rate and/or low temperatures. Recent work as mentioned above, however, indicates that lithium plating can also occur at mild charge conditions in cells after extended cycling, leading to rapid aging of the cell. One plausible reason for the onset of lithium plating after extended cycling is continuous growth of the SEI layer, which may clog the electrode pores [34] and reduce anode ionic kinetics [27]. The SEI layer can grow considerably after long-term operation. Using focused ion beam (FIB) and scanning electron microscopy (SEM), Yoshida et al. [5] reported that thickness of SEI layer in the tested cells increased from 40 nm at the beginning to as high as 450 nm after storage at 40 °C for 392 days. Lee et al. [38] also revealed via FIB-SEM measurement that the SEI layer of a cell became more than 300 nm thick after 12.5% capacity loss. This significant increase of SEI thickness can greatly reduce the anode porosity, as reported by Frisco et al. [39] most recently. In their work, nano-scale X-ray computed tomography was applied to visualize the pore structure of graphite anode taken from fresh and aged commercial 18650 cells. Dramatic reduction of average pore diameter was observed in the aged cell, with the anode porosity reducing from 0.25 in the fresh cell to 0.12 in the aged cell. This considerable drop of anode porosity can exert strong impacts on cell performance, as discussed by Sikha et al. [40]. However, research efforts on the evolutions of anode porosity and the ensuing impact on cell performance in the aging process are rather scarce in the literature.

Numerical modeling is a useful tool for investigating the aging behavior of LIBs. Numerous physics-based aging models have been proposed in the literature [41–47], most of which focus on capacity fade due to SEI growth. Research on modeling of lithium plating, however, is rather limited [48–52]. Arora et al. [48] proposed the first lithium plating model by incorporating the lithium deposition reaction as a side reaction into the macroscopic LIB model developed by Doyle et al. [53]. The scenario of overcharge was studied and the concentrations of plated lithium at various operating conditions were predicted. Tang et al. [49] extended Arora's model to two dimensional and found that lithium deposition is prone to occur near the edge of anode if the two electrodes are evenly aligned. The importance of using a larger anode than a cathode therefore was stressed. Perkins et al. [50] proposed a method to reduce the complexity of Arora's model in order to develop a control-oriented model suitable for BMS. Most recently, Ge et al. [51] extended Arora's model to the scenario of low temperature charging. The amount of lithium plating is predicted and compared with experiment data measured by nuclear magnetic resonance. To the best of our knowledge, no physics-based aging model has ever been reported in the literature with the ability to predict lithium plating induced aging.

Here, we present a physics-based LIB aging model able to predict aging behaviors associated with lithium plating. It will be demonstrated in the present work that this model is able to capture the above-mentioned transition from linear to nonlinear aging after prolonged cycling. In a companion paper following the present one, the model is applied to study the effects of ambient temperature and electrode thickness on cell aging, as it is known that lithium plating is more prone to occur in cells at low temperatures

Download English Version:

<https://daneshyari.com/en/article/5148974>

Download Persian Version:

<https://daneshyari.com/article/5148974>

[Daneshyari.com](https://daneshyari.com)