



A look into the voltage plateau signal for detection and quantification of lithium plating in lithium-ion cells



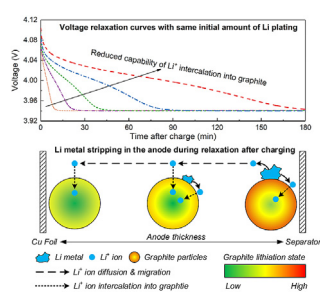
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HIGHLIGHTS

- We present a Li-ion battery model incorporating both Li plating and stripping.
- Voltage plateau after charging due to Li stripping is captured and analyzed.
- Length of voltage plateau depends highly on capability of graphite intercalation.
- Anode splits into two parts during Li stripping.
- Differential voltage approach to quantify Li plating amount is assessed.

GRAPHICAL ABSTRACT



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ABSTRACT

Voltage plateau during relaxation or discharge after charging is a distinct signal associated with stripping of deposited Li metal and hence a feasible tool for online detection of Li plating in Li-ion batteries. Here, we present a physics-based model with incorporation of Li plating and stripping to gain a fundamental understanding of the voltage plateau behavior. Specifically, we focus on the internal cell characteristics when voltage plateau occurs and on key factors affecting the shape and duration of voltage plateau. Furthermore, the validity of using the duration of voltage plateau for estimating Li plating amount is assessed. It is found that the duration of voltage plateau depends on the rate of Li stripping, while the stripping rate is restricted by the capability of Li⁺ intercalation into graphite. Parameters like intercalation kinetics, solid-state diffusivity of graphite and cell temperature can substantially influence the voltage curves even with the same amount of Li plating. Further, we report an interesting phenomenon that during Li stripping one part of anode near the separator has net oxidation current (local stripping rate > intercalation rate), providing Li⁺ ions and electrons to the other part of anode near the foil which has net reduction current.

1. Introduction

The last decade has witnessed an unprecedented penetration of Li-ion batteries (LiBs) into the market in various applications like electric vehicles and energy storage systems. These applications require LiBs to be of great durability and safety [1–6]. Carbon-based materials, in particular, graphite, are utilized as anode materials in most state-of-the-

art LiBs. A critical challenge to the use of graphite anode is metallic Li deposition, also known as Li plating, which can induce drastic capacity loss as well as safety hazards [7–11]. Detection of Li plating is therefore crucial, especially for real-world applications.

Today's methods for detection of Li plating can be divided into the following categories: a) *Measurement of anode potential vs Li/Li⁺ with a reference electrode* [12–15]. A general criterion is that Li plating occurs

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at anode potential < 0 V. b) *Post-mortem imaging of anode morphology* [16, 17]. c) *Electron paramagnetic resonance* [18, 19] and *nuclear magnetic resonance* [20, 21] to detect a particular range of resonance frequency corresponding to metallic Li. d) *High precision measurement of coulombic efficiency* [22, 23]. Dahn's group [22] proposes that the plots of coulombic inefficiency per hour versus time fall on the same curve for different tests if cell aging is dominated by solid electrolyte interphase (SEI) growth. Deviation from this curve indicates Li plating. e) *Measurement of cell thickness* [24–27]. Li metal deposition is revealed to induce larger volume change than Li^+ intercalation into graphite, estimated to be $0.37 \text{ cm}^3/\text{Ah}$ [24]. It is also reported that thickness change becomes irreversible when Li plating occurs. f) *Measurement of graphite lithiation degree via in-situ neutron diffraction* [28]. Zinth et al. [28] found that the lithiation degree of graphite increased by 17% in the relaxation process after C/5 charge at -20°C , indicating that at least 17% of Li was plated in the charging process. g) *Detection of a distinct voltage plateau after charging* [29–36]. The voltage plateau is ascribed to stripping of deposited Li metal and thus indicates that Li is plated during charging. The voltage plateau can occur either at the beginning of discharge [29–31] or of relaxation [32–36] after charging. A brief summary of the above works are given in Table 1.

Among the above methods, voltage plateau is the most feasible method for online detection of Li plating in real-world applications, as it is nondestructive and does not require special and expensive equipment. Smart et al. [29, 30] were among the first to apply discharge voltage plateau after low temperature (-40°C) charging as a tool for Li plating detection. They also proposed that the length of plateau can be used as a metric for evaluating Li metal amount. Petzl and Danzer [31] presented a differential voltage approach to detect and quantify Li plating. In their tests, a cell was charged with 1C rate at $< -20^\circ\text{C}$ and discharged immediately after charging. A voltage plateau appeared at the beginning of discharge. Plotting the derivative of voltage over capacity (dV/dQ), they found a distinct dV/dQ peak at the beginning of discharge. They proposed that this dV/dQ peak indicates the end of Li metal stripping, and the discharge capacity at the dV/dQ peak corresponds to the total amount of Li plated during charging. Later, Uhmman et al. [32] proposed to detect voltage plateau during relaxation rather than during discharge, which is advantageous as the cell has no net current at open-circuit, making the plateau more pronounced and easier to detect. This method was then adopted by many other researchers [33–36]. Schindler et al. [33] extended their differential voltage approach to the relaxation process by plotting the derivative of voltage over time (dV/dt), and found a similar peak in dV/dt curve attributed to Li stripping. Bauer et al. [34] applied a similar method to study the impacts of charging temperature on Li plating and found that the

duration of voltage plateau was longer at lower charging temperatures. This work is more close to real-world applications as the tested cell is a commercial large-size (16Ah) cell and the testing temperature is more practical ($-7.5^\circ\text{C} \sim +27.5^\circ\text{C}$, other than extreme cold temperature in the past). Luders et al. [35] further applied the voltage relaxation method along with in-situ neutron diffraction to examine the impacts of charge rate on Li plating, with a 1.95Ah 18650 cell charged at -2°C . A very interesting finding is that the increase of Li plating amount, estimated by the gain in graphite lithiation degree during cell relaxation measured by neutron diffraction, is proportional to the increase of the duration of voltage relaxation plateau, estimated by the time to reach the dV/dt peak. These results indicate that the time to reach dV/dt peak can be used for assessing the Li plating amount in different tests.

Overall, the prior work demonstrated the feasibility of adopting voltage plateau as a method for Li plating detection. Despite the significant progress in the past several years, there is still lack of fundamental understanding of the voltage plateau behavior. For instance, it is known that the distinct voltage plateau is ascribed to Li metal stripping, but how fast can Li metal be stripped? What factors affect the rate of Li stripping? Which factor is the rate-limiting step? Further, either the discharge capacity at dV/dQ peak or the time to reach dV/dt peak has been proposed as metrics for comparing Li plating amount. Are these methods valid under most circumstances? The objective of the present work is to answer the above questions by a fundamental study of the voltage plateau behavior with the help of mathematical modeling.

Mathematical models have been extensively applied to predict performance and life of LiBs and gain fundamental insights into the internal cell characteristics.[37–44] Several works have been reported to study Li plating during overcharge [45, 46] or during charge at high rates and/or low temperatures [21, 47], and to study the capacity loss induced by Li plating [48]. These models, however, only considered Li plating process and neglected Li stripping process; thus cannot capture the voltage plateau behavior. To the best of our knowledge, only the work of Hein and Latz [49] in the literature ever attempted to simulate Li stripping and the associated voltage plateau behavior, using a 3D microscopic model. It is shown that Li metal distribution is highly non-uniform in the anode. The predicted voltage plateau in this work, however, only lasts a few seconds, rather than tens of minutes as reported in experimental studies.

Here, we present a mathematical model incorporating both Li plating and stripping and apply it to study the voltage plateau behavior after charging at low temperatures. Both the plateau during relaxation and that during discharge are studied. We also perform experiments to validate the model in terms of voltage curves during charge, relaxation, and discharge. The main objectives are to gain fundamental insight into

Table 1
A brief summary of literature work on Li plating detection and quantification

Methods	Description of physics/criteria for Li plating detection	Refs
Three-electrode diagnostics	<ul style="list-style-type: none"> Li plating occurs at anode potential $< 0\text{V}$. 	[12–15]
Electron paramagnetic resonance (EPR)	<ul style="list-style-type: none"> The EPR signal of Li metal is much narrower and its signal center is slightly upfield compared with the EPR signal of Li_xC_6. The magnitude of EPR signal is related to Li metal amount. 	[18, 19]
^7Li Nuclear magnetic resonance (NMR)	<ul style="list-style-type: none"> The chemical shift of Li metal in NMR spectra (245–270 ppm, depending on Li metal structure) is markedly different from the chemical shift of Li in graphite (~ 40 ppm). The peak intensity in NMR spectra is proportional to Li amount and is used to quantify Li plating. 	[20, 21]
Measurement of coulombic efficiency (CE)	<ul style="list-style-type: none"> If SEI growth is the only aging mechanism, plots of coulombic inefficiency (1-CE) per hour versus time shall fall on the same curve regardless of charge rate. Li plating leads to additional capacity loss and hence to deviation from this curve. 	[22, 23]
Measurement of cell thickness	<ul style="list-style-type: none"> For the same amount of charge (e.g. 1Ah), the volume change of Li metal is 0.49 cm^3, much larger than graphite (0.12 cm^3). Hence, Li plating leads to a larger increase in cell thickness than Li^+ intercalation. 	[24–27, 34]
In-situ neutron diffraction	<ul style="list-style-type: none"> The intensity of neutron diffraction data is used to calculate graphite lithiation degree. The increase of graphite lithiation degree in the relaxation process after charging indicates the amount of Li stripped. 	[28, 35]
Detection of voltage plateau	<ul style="list-style-type: none"> The mixed potential associated with simultaneous Li stripping and Li^+ intercalation leads to a voltage plateau. 	[29–36]

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