FUNDAMENTAL UNDERSTANDING OF LITHIUM PLATING IN LITHIUM-ION BATTERIES: MECHANISM, MODEL AND MITIGATION STRATEGIES

by

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ABSTRACT

JIANI LI. Fundamental Understanding of Lithium Plating in Lithium-ion batteries:
Mechanism, Model and Mitigation Strategies
(Under the direction of DR. JUN XU)

During the normal charging process of lithium-ion batteries (LIBs), lithium ions are extracted from the cathode, transported through the electrolyte, and finally intercalated into the anode. However, abusive conditions such as overcharging, fast charging, and low-temperature charging can lead to the occurrence of lithium plating on the anode, which facilitates capacity fade, lithium dendrite growth, and even an internal short circuit in LIBs. Therefore, detecting the onset of lithium plating, understanding its mechanism, and avoiding this unwanted side reaction is significant for the safe design of LIBs.

Firstly, detecting the initiation of lithium plating on graphite electrodes is of paramount importance in ensuring battery safety. To achieve this, Graphite/Li cells with consistent and reliable electrochemical performance are manufactured and selected. Discharging tests with various capacities are conducted on these cells to intentionally induce lithium plating on the graphite electrode. By comparing the voltage analysis and morphology analysis results of Graphite/Li coin cells with different discharging capacities, the localization of the lithium plating onset is detected within a narrow discharge capacity range.

An electrochemical model applied to the experimental Graphite/Li coin cells is proposed to further determine the precise onset of lithium plating and provide a deep understanding of its mechanism. The model incorporating a concentration criterion can precisely predict the onset of lithium plating on graphite and elucidate the underlying mechanisms governing its occurrence. Moreover, comparative analysis reveals that the model incorporating a concentration criterion is more suitable for predicting the onset of lithium plating than a model relying on a potential criterion, particularly under high C-rate conditions. Based on the concentration criterion model, a parametric study is conducted to obtain an optimized discharging protocol with high discharging efficiency but no occurrence of lithium plating.

Furthermore, a 2D physics-based model considering the actual winding structure of the battery is established to investigate the distribution of lithium plating among the winding structure in a cell. The model is validated based on the voltage-time curves of charging tests with different C-rates. By analyzing the lithium plating current density and lithium plating overpotential at different layers, it is shown that lithium plating tends to occur in the inner layers of the battery. Based on this validated model, a parametric study is conducted to clarify the influence of governing factors, including the electrochemical properties of the materials, tab arrangement, and charge protocols. According to the results, appropriate designs and use of the battery are proposed to reduce the risk of lithium plating.

This study comprehensively investigates the behavior of lithium plating, including its onset, mechanism, and mitigation strategies. The results provide powerful tools for designing the next generation of long cycle-life batteries.

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NOMENCLATURE

Nomenclature

φ_{anode}	Anode potential	M_{pla}	Molar weight of the plated li metal
c_l	Li concentration in liquid phase	ρ_{pla}	Density of the plated li metal
c_s	Li concentration in solid phase	σ_{film}	Conductivity of the plated Li metal
$E_{eq,int}$	Equilibrium potential of lithium intercalation	ε_s	Solid phase volume fraction
U	Voltage	σ_s	Solid phase conductivity
Q	Capacity	R_s	Particle radius
σ_s^{eff}	Effective electrical conductivity of solid phase	$c_{s.1}$	Li concentration parameter
φ_s	Potential of solid phase	$c_{s.2}$	Li concentration parameter
j_{total}	Total volumetric current density	c_{li}	Concentration of the plated Li metal
i_{app}	Applied current density	t_{M}	Simulated onset of lithium plating
σ_l^{eff}	Effective electrical conductivity of liquid phase	t_{E}	Experimental onset of lithium plating
SOC	State of charge	Φ_{li}	Flux of Li-ion across the particle surface
φ_l	Potential of liquid phase	ε	Prediction error of lithium plating onset
R	Gas constant	$\eta_{pla\_\min}$	Minimum over-potential of lithium plating among the graphite electrode
T	Temperature	$c_{s,surf\_\max}$	Maximum surface concentration of Li-ion among the graphite electrode
F	Faraday parameter	$k_{0,SEI}$	Kinetic rate constant of SEI formation
t^+	Transport number of Li^+	c_{EC}^s	Concentration of solvent Molecules ethylene carbonate (EC) on the graphite surface
f	Activity coefficient	$E_{eq,SEI}$	Equilibrium potential of SEI formation
c_l	Li^+ concentration in the liquid phase	D_{EC}	Diffusivity of EC
D_s	Solid phase diffusion coefficient	c_{EC}^0	Concentration of EC in electrolyte
r	Radius of the particle	c_{SEI}	Concentrations of SEI

j_{int}	Local current density of lithium intercalation	χ	Fraction of plated lithium that is oxidized to form new SEI
a_s	Specific surface area of particle	M_{SEI}	Molar weight of SEI
ε_l	Volume fraction of liquid phase	ρ_{SEI}	Density of SEI
J_l	Li$^+$ flux density in liquid phase	w_{SEI}	Fraction of SEI in the surface film
i_l	Liquid phase current density	κ_{SEI}	Ionic conductivity
j_{pla}	Current density of lithium plating	H	Thickness of single sided active material
$i_{0,pla}$	Exchange current density of lithium plating	W	Width
$c_{s,surf}$	Li concentration at the particle surface	$\alpha_{c,SEI}$	Anodic charge transfer coefficient of SEI
$c_{s,max}$	Maximum value of solid Li concentration	H_C	Thickness of active material on cathode
$\alpha_{c,pla}$	Charge transfer coefficient of the cathode for lithium plating	σ_l	Conductivity of liquid phase
$\alpha_{a,pla}$	Charge transfer coefficient of the anode for lithium plating	D_C	Diffusivity of Li-ion in cathode
k_{pla}	Reaction rate constant for lithium plating	D_A	Diffusivity of Li-ion in anode
η_{pla}	Over-potential of lithium plating	δ_{pla}	Thickness of plated li metal
$E_{eq,pla}$	Equilibrium potential of lithium plating		
R_{film}	Resistance of the surface film		
$i_{0,int}$	Exchange current density of lithium intercalation		
η_{int}	Over-potential of lithium intercalation		
k_{int}	Reaction rate constant for lithium intercalation		
$c_{l,ref}$	Reference Li$^+$ concentration in the liquid phase		
$\alpha_{c,int}$	Charge transfer coefficient of the cathode for lithium intercalation		
$\alpha_{a,int}$	Charge transfer coefficient of the anode for lithium intercalation		

CHAPTER 1 INTRODUCTION

1.1 Background

Li-ion batteries (LIBs) have been playing an increasingly significant role in our mobile society, including consumer electronics [1] and electric vehicles [2] due to their relatively high energy and power density [3, 4], long lifecycle, and lower cost. However, the current bottleneck for the wide application of lithium-ion batteries is the performance deterioration and safety issues during cycling, and lithium plating is one of the most challenging and dominant factors [2, 5]. As an undesired side reaction, the lithium plating facilitates capacity fade, li-dendrite growth [6], and even an internal short circuit [7, 8]. Hence, understanding the mechanism of lithium plating and avoiding side reactions is significant for the safe design of Li-ion batteries.

1.2 Literature review

1.2.1 Lithium plating behavior

During battery charging, the Li ions are extracted from the cathode, transported through the electrolyte, and finally intercalated into the anode. The insertion potential of Li in the graphite is in the range of 200 to 65 mV (vs. Li/Li^+), slightly higher than 0 V [3, 9]. However, abusive conditions such as overcharging [10, 11], fast charging [12-15], and low temperature-charging [16-18] may contribute to the high polarization of the anode and drop the anode potential below 0 V (vs. Li/Li^+) [19], making lithium plating thermodynamically feasible. Therefore, there are two electrochemical reduction reactions taking place at the electrode/electrolyte interface during battery charging: li intercalation and lithium plating (Fig.1). As an unwanted side reaction, lithium plating has adverse effects on battery safety. Firstly, the plated lithium will partially react with electrolyte solvents to form a new SEI layer [18], which consumes the active lithium and further induces capacity degradation. Besides, partial-plated lithium may lose electrical contact with the anode (known as dead Li). Both the formation of SEI and dead Li are responsible for capacity degradation and poor Coulombic efficiency during cycling. Secondly, the internal resistance will increase due to the pore clogged by plated Li metal, which hinders the transport of Li ions in the electrode. The increasing internal resistance contributes to larger polarization during the intercalation and deintercalation of Li ions [20]. Thirdly, with the accumulation of plated Li metal, the continuous growth of dendritic or needle-like lithium is prone to penetrate the separator and cause an internal short circuit and even thermal runaway of the battery. Hence, understanding the mechanism of lithium plating and avoiding side reactions is significant for the safe design of Li-ion batteries.

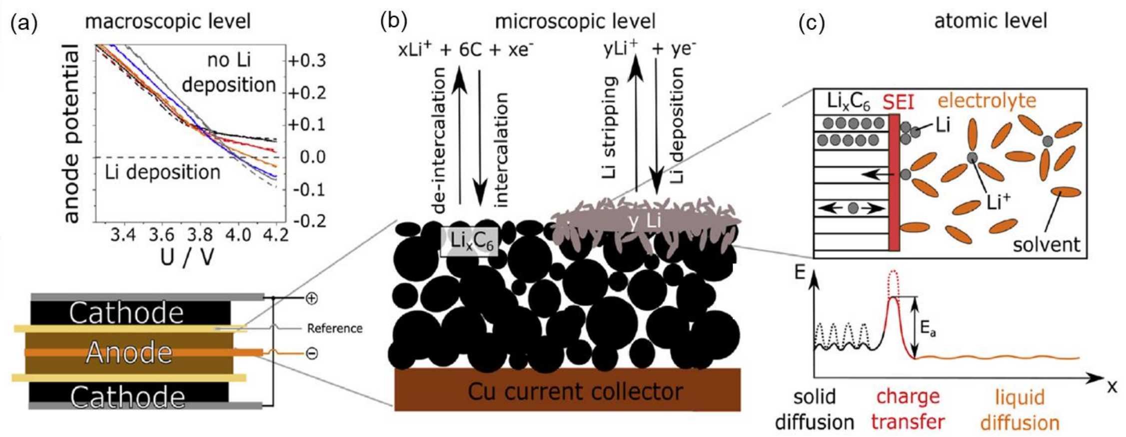

Figure 1 Scheme of lithium plating on the (a) macroscopic, (b) microscopic, and (c) atomic level [21].

Plenty of research has discovered that lithium plating is more likely to occur under extreme conditions such as fast charging, low-temperature charging, and overcharging. Therefore, a deeper understanding of the behavior and underlying mechanism of lithium plating under these extreme conditions is necessary. During a desirable charging process, the Li ions are transported through the electrolyte, intercalated into the active particles, and finally diffused from the surface of the active particles to their inside driven by the concentration gradient. It is generally believed that the limited Li ions solid diffusion in active particles is responsible for the high lithium plating risk at a high charging rate [22]. When charging at a high rate, the Li ions tend to accumulate at the active particle surface since the Li ions diffusion in the solid phase is less than that in electrolytes [23, 24]. As a consequence, the saturation of Li ions at the interface contributes to the occurrence of lithium plating (Fig. 2(a)). The influencing factors of lithium plating at low temperatures are charge-transfer resistance and Li-ion diffusion in solid phase [25-27]. When charging under a low temperature, the sluggish charge transfer kinetics and slow Li ions diffusion in the solid phase hinder the intercalation reaction and facilitate lithium plating. Indeed, investigations from experiments [17, 21, 28-31] and simulations [17, 19] all showed that the anode potential becomes lower with decreasing temperature, facilitating the occurrence of lithium plating. As an example in a commercial battery (Fig. 2(b)), lithium plating occurs when the charging rate is larger than 2C under 50 °C but 0.5C under 12 °C [32], indicating that lowering temperature reduces the critical charging rate of lithium plating. The intercalation of Li ions into graphite tends to be slowed down with a higher state of charge (SOC) since the solid diffusion barrier is increased with x in Li_xC_6 [33]. For overcharging conditions [34, 35], when the anode has been fully lithiated, the Li ions will no longer intercalate into the anode but plate on the surface of the anode (Fig. 2(a)).

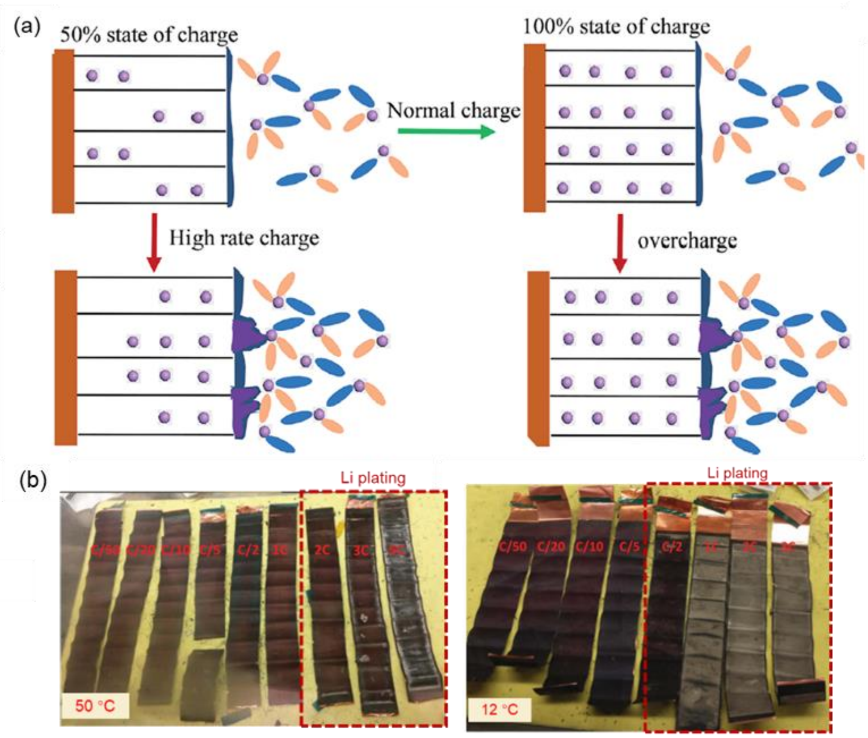

Figure 2 (a) Illustration of the lithium plating under extreme charging protocols (b) Photograph of the anodes after cycling at different charging rates under 12 °C and 50 °C [32].

1.2.2 Detection of lithium plating

Various experimental methods have been employed to detect the occurrence of lithium plating and comprehensively understand lithium plating, encompassing electrochemical techniques and physical characterization methods [36].

The electrochemical methods adopted for lithium plating detection include the measurement of graphite electrode potential and cell voltage during discharging/rest process [37-40]. The graphite electrode potential measured in cells with 2-electrode [41] and 3-electrode [29, 31, 41-43] setup (Fig. 3(a)) can directly serve as the indicator of lithium plating according to the traditional criterion of lithium plating [2, 44, 45]. Besides, the detection of lithium plating can be realized by monitoring and analyzing the cell voltage vs time curve [37, 40, 46-48]. The occurrence of voltage plateau at the beginning of the discharging/rest process (Fig. 3(b)) is caused by the stripping of plated Li metal, which can demonstrate that lithium plating occurred during the preceding charging process. These electrochemical methods are nondestructive and convenient for engineering applications, however, they can only confirm the occurrence of lithium plating indirectly and fall short of *in-situ* detection of the precise onset of lithium plating [36].

To detect the occurrence of lithium plating directly, *ex-situ* and *in-situ* physical characterization methods have been proposed and applied. For the *ex-situ* physical characterization method, the cells are disassembled and the morphology of graphite electrode surface [38, 49-52] are characterized by optical microscopy [53, 54], scanning electron microscopy (SEM) [55] and transmission electron microscopy (TEM) [56] to determine the existence of plated Li metal. However, the microscopic plated Li metal may not be observed by these ex-situ observation techniques since the plated Li metal may dissolve and intercalate back into the graphite electrode during the disassembling process. To solve this problem, *in-situ* optical microscopy and electrochemical measurement were simultaneously performed on half cells to monitor the voltage of the graphite electrode and the occurrence of lithium plating (Fig. 3(c)) during battery cycling [57]. Although the *ex-situ* and *in-situ* physical characterization methods offer direct detection of plated Li metal, they are hindered by expensive equipment and implementation challenges. Consequently, there exists a need for an economical, convenient, nondestructive, and accurate *in-situ* method for detecting the onset of lithium plating.

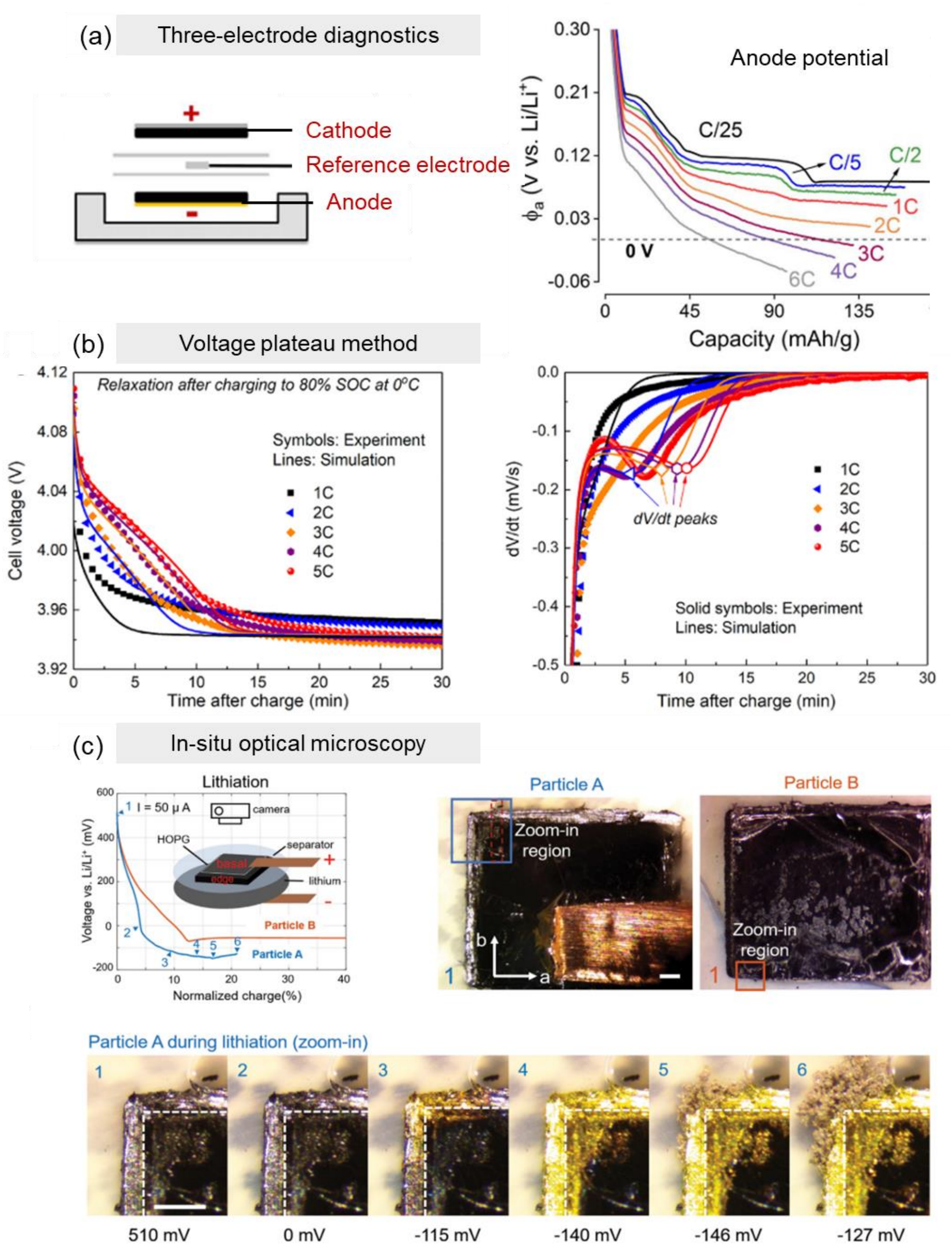

Figure 3 (a) Three electrode diagnostics: three-electrode set-up and individual anode potentials during charging with different rates [41]. (b) Voltage plateau method: voltage-time curves and corresponding differential voltage during the relaxation process after charging with different rates. [40]; (c) In-situ optical microscopy: voltage profile and in-situ optical images during lithiation and plating [57].

1.2.3 Criteria of lithium plating

Understanding the mechanism of lithium plating is imperative for determining its onset. Conventionally, it is held that lithium plating becomes thermodynamically possible once the over-potential of the lithium plating reaction reaches smaller than 0 V vs. Li/Li$^+$ ($\eta_{pla} < 0\,\mathrm{V}$) (Fig. 4(a)) [2, 44, 45]. The elevated polarization resulting from high C-rates [41] and low temperatures [17] contributes to a reduction in graphite potential, thereby promoting the occurrence of lithium plating. However, while the potential criterion ($\eta_{pla} < 0\,\mathrm{V}$) is considered a necessary condition for lithium plating, it is insufficient as demonstrated in several experiments [43, 48, 57-59]. Uhlmann et al. [48], for instance, subjected Graphite/Li cells to charging pulses with varying C-rates after reaching a certain State of Charge (SOC). Results indicated that during charging pulses at 5C and 10C, lithium plating did not manifest until the graphite potential fell significantly below 0 V. Gao et al. [57], utilizing *in-situ* optical microscopy coupled with electrochemical measurements on a single graphite particle, observed that the graphite particle could withstand a negative potential of -115 mV before any plated Li metal was observed during the discharging of 0.6C. The above experiments were conducted on cells with a 2-electrode setup, which may affect the measurement accuracy of graphite potential due to the polarization on the counter electrode. Based on this, Wandt et al. [43] performed the forced lithium plating on cells with a 3-electrode set up. Employing *operando* electron paramagnetic resonance (EPR) spectroscopy, they observed that the onset of lithium plating was also identified at a negative graphite potential measured with a reference electrode setup. Besides, the electrolyte concentration gradient between the graphite electrode and reference electrode was less significant due to the low C-rate of 0.1C, guaranteeing the measurement accuracy of graphite potential. It has been demonstrated that the potential criterion ($\eta_{pla} < 0\,\mathrm{V}$) alone is inadequate in determining lithium plating onset.

Factors beyond potential, such as concentration, may play vital roles in lithium plating occurrence. Using in situ optical microscopy, some researchers [57, 60, 61] found that the lithium plating occurred exclusively on the fully lithiated parts of the graphite electrode, while the onset voltage is much below 0 V versus Li/Li^{+} [57, 60]. Such observations illustrates that the Li concentration in graphite is a more accurate indicator of lithium plating than graphite potential, which has been rationalized by analyzing the energetics and kinetics of the lithium intercalation and lithium plating [57]. During the charging process, lithium intercalation is always more favorable than lithium plating energetically and kinetically even when the potential criterion of lithium plating is satisfied ($\eta_{pla} < 0\,\mathrm{V}$). The tipping point occurs when the graphite surface becomes saturated with intercalated Li-ions ($c_{s,surf} \geq c_{s,\max}$). At that time, lithium intercalation is energetically equally favorable but kinetically less favorable than lithium plating due to the lack of sites for Li-ions to intercalate and drop off of nucleation barrier for lithium plating. As a result, the intercalation reaction is restrained and the applied current is redirected towards lithium plating.

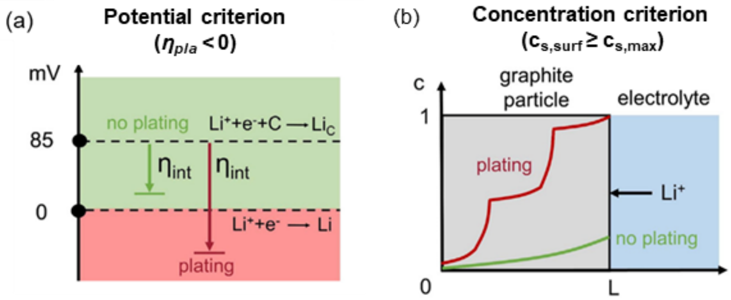

Figure 4 Proposed criteria of lithium plating on Graphite electrode [57].

1.2.4 Modeling of lithium plating

Numerical simulation can provide quantitative information to predict the onset of lithium plating and help analyze the underlying mechanism. Arora et al. [44] firstly described the reaction of lithium plating during overcharge. They proposed a mathematical model to predict lithium plating behavior under a variety of operating conditions based on the classical electrochemical model developed by Doyle et al. [62, 63]. The influence of key design parameters (particle size, electrode thickness, and mass ratio) on lithium plating was investigated to minimize the safety hazards and capacity fade problem. To study the lithium plating behavior at low temperatures, Ge et al. [64] extended Arora's model with the temperature sensitivity of the electrochemical properties. The model was validated by comparing the simulation and experimental data in terms of the amount of plated metallic lithium under various conditions. Yang et al. [65] proposed a lithium-plating-induced aging model able to predict the aging characteristics of Li-ion batteries. They discovered that the drop of anode porosity due to SEI (solid electrolyte interface) growth was attributed to the larger gradient of electrolyte potential in the anode, which lowered the lithium plating over-potential and finally led to the onset of lithium plating. Furthermore, Yang et al. [40] modified their electrochemical-thermal model with lithium stripping to gain a fundamental understanding of the voltage plateau behavior. Similar research has also been reported by other groups [45]. In their work, the amount of plated lithium could be evaluated according to the shape of the simulated voltage plateau due to lithium stripping. Mei et al. [7, 66] combined experimental and numerical methods to investigate the overcharge-caused lithium plating comprehensively. They found that lithium plating started at the graphite/separator interface and the lithium plating capacity and overcharge are linear-dependent.

It can be found that most researchers have traditionally adopted graphite potential ($\eta_{pla} < 0\,\mathrm{V}$) as the primary indicator of lithium plating when establishing the models [18, 45, 66-68], signifying lithium plating occurrence when the graphite potential falls below 0 V vs. Li/Li$^+$. However, it is emphasized that the potential criterion ($\eta_{pla} < 0\,\mathrm{V}$) is not universally applicable under all conditions, as mentioned previously. Therefore, the Li concentration in graphite emerges as an equally critical parameter in modeling and predicting lithium plating onset. Besides, current models focus on limited-sized materials or adopt a homogenization strategy for the cell to give a qualitative description of the lithium plating [69]. Such a model cannot provide enough detailed information and mechanism understanding of lithium plating observed at the cell level due to the lack of the quantitative relationship of “material-structure-performance”. Therefore, models considering lithium plating growth in the actual winding structure of the battery are still lacking.

1.2.5 Mitigation strategies

As an undesired side reaction, lithium plating on graphite electrode can be inhibited by various mitigation strategies (Fig. 6) such as anode modification, cell design and modified charging protocols.

For graphite electrodes, adding amorphous carbon coating [70-72] and metal coating (Cu, Sn) [73, 74] can improve the kinetics of intercalation reaction on graphite electrodes, thus restraining the lithium plating reaction. Besides, adopting graphite electrodes with nanostructured graphene structure [75, 76] can facilitate the lithium diffusion in the solid phase, accelerate the intercalation reaction, and finally inhibit the plating reaction. For Li anode, surface modification such as constructing a patterned Li anode [77] can realize the selective Li deposition in the patterned grooves, which suppresses the formation of Li dendrite.

The risk of lithium plating can be effectively reduced by optimizing the cell design. Firstly, increasing the residual capacity and width of graphite electrodes helps suppress lithium plating [59]. However, increasing the capacity of graphite electrodes may result in the capacity loss of cells, which needs to be considered when designing practical LIBs. Besides, adjusting the position and number of the current collecting tabs can obviously influence the current distribution and lithium plating distribution among the cells. To realize the uniform distribution of current density and lower the risk of lithium plating, the configuration of cathode and anode tabs needs to be designed appropriately [78] and the number of tabs is suggested to be increased [79] (Fig. 6(b)).

Compared to the mitigation strategies of anode modification and cell design which require the improvement of the manufacturing process of LIBs, the adoption of modified charging strategies is more convenient and applicable in battery management systems (BMS). Several optimized charging strategies have been proposed to restrain the lithium plating on graphite electrodes based on the graphite potential obtained from the 3-electrode setup and numerical model (Fig. 6(c)). According to the graphite potential measured with a reference electrode, a stepwise charging strategy was raised by Waldmann et al.[12]: charging with a high C-rate until the graphite potential reached 0 V vs. Li/Li^+, followed by the charging with a low C-rate to the cut-off voltage. Besides, based on the electrochemical model with the potential criterion of lithium plating ($\eta_{pla} < 0\,\mathrm{V}$), Tippmann et al. proposed a detailed CC-CV charging strategy to avoid lithium plating on graphite electrodes at low temperatures [80]. However, the current charging strategies are optimized and mainly focus on the inhibition of lithium plating without the consideration of the charging efficiency of the battery. A comprehensive charging strategy is needed to realize the restraint of lithium plating and enhancement of charging efficiency simultaneously.

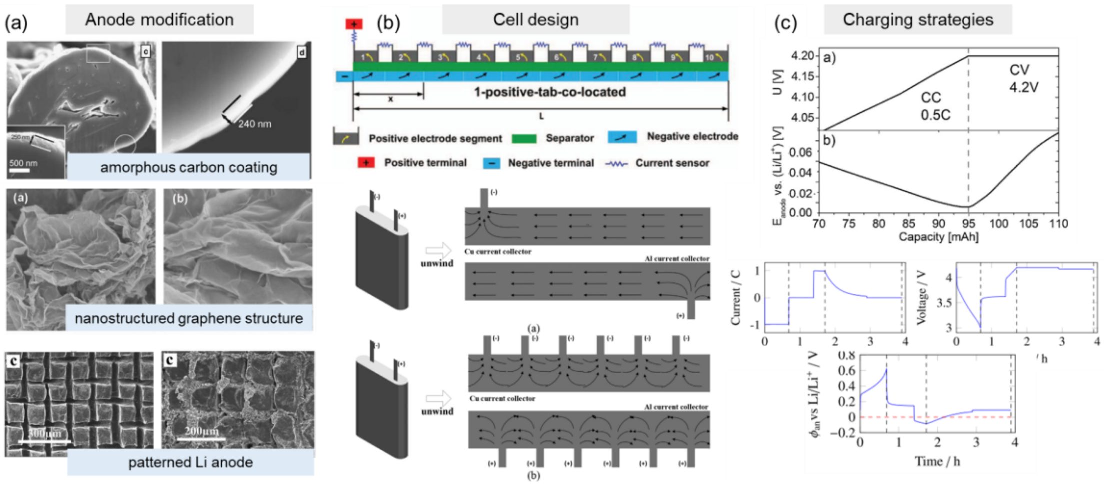

Figure 5 Proposed mitigation strategies to prevent lithium plating: (a) anode modification, (b) cell design [78], and (c) charging strategies.

1.3 Challenges and motivation

As mentioned above, a large number of studies have been carried out to investigate the onset detection, criterion, modeling, and mitigation strategies of lithium plating, providing us with a basic understanding of this unwanted side reaction in LIBs. However, there are still some limitations to the results of these studies, which need to be figured out and improved in the following research. For onset detection of lithium plating, the current electrochemical techniques [37-40] are convenient for engineering applications but fall short of accuracy. The *in-situ* physical characterization methods [57] can detect the plated Li metal accurately but are hindered by expensive equipment and implementation challenges. Thus, an economical, convenient, nondestructive, and accurate *in-situ* method is still lacking for the detection of lithium plating onset. For the criterion of lithium plating, most researchers adopt the potential criterion to describe the occurrence of lithium plating [2, 44, 45], while some researchers [57, 60, 61] claim that the concentration criterion is more accurate and convincing.

To compare the reliability and accuracy of these two criteria, a comprehensive analysis is needed combining the experimental and simulation methods. The existing electrochemical models [7, 44, 62, 63, 66] mainly adopt a homogenization strategy for the cell without the consideration of a detailed battery winding structure. Such models can only provide a qualitative description of the lithium plating rather than the detailed distribution of lithium plating in the cell level. Therefore, it's necessray to develop models considering lithium plating distribution in the actual winding structure of the battery. For mitigation strategies, optimizing the charging strategy [12, 80] has been widely adopted due to its convenience and applicability in battery management systems (BMS). However, except for the aim of lithium plating restraint, the enhancement of charging efficiency also needs to be considered when modifying the charging strategy. As mentioned above, the current studies of lithium plating still have some limitations among the onset detection, criterion, modeling and mitigation strategies of lithium plating, which will be further studied in my thesis work.

1.4 Chapter arrangement

Chapter 2 presents a synergistic integration of experiments to precisely detect the onset of lithium plating. Chapter 3 develops electrochemical models incorporating different lithium plating criteria (potential criterion and concentration criterion) to analyze the underlying mechanism governing the onset of lithium plating. Besides, the optimization of the discharging strategy is conducted based on the model with concentration criterion. Chapter 4 presents a 2D physics-based model considering the distribution of lithium plating in the actual winding structure of pouch cells. Chapter 5 summarizes the conclusions of this dissertation.

CHAPTER 2 DETECTING THE ONSET OF LITHIUM PLATING

In this chapter, our primary objective is the precise detection of the lithium plating onset on the graphite electrode through a synergistic integration of experiments. To achieve this, the Graphite/Li cells with excellent electrochemical performance were manufactured and the discharging tests with varying capacities were conducted, intentionally inducing lithium plating on the graphite electrode. The onset of lithium plating was discerned by analyzing both indirect differential voltage curves and direct morphology characterization of disassembled cells.

2.1 Experimental

2.1.1 Preparation of coin cells

The experimental cells were meticulously assembled in a glove box under an Argon atmosphere, with the graphite as the working electrode and an ample Li plate as the counter electrode. The detailed preparation procedure and nominal capacity ($Q_n = 2.03\ mAh$) of the Graphite/Li coin cell are described in APPENDIX A. The nominal capacity of the cells was calculated from the materials loading of the graphite electrode (Supplemental Information). Before the formal tests, the experimental cells underwent a pre-cycling process at 0.1C, spanning from 0.005 V to 2 V, repeated for three cycles. The charging capacity observed during the third cycle was the rated capacity. Subsequently, only cells exhibiting a rated capacity within the 1.81-1.92 mAh range were selected for the subsequent formal tests. This stringent selection criterion ensures consistency and reliability in the electrochemical performance evaluation of the graphite electrode. Besides, discharging tests were conducted on the selected Graphite/Li cells at 0.01C to obtain the equilibrium potential of intercalation $E_{eq,int}$ on the graphite electrode (Figure 6 (a)), which was adopted for the model establishment in Chapter 3.

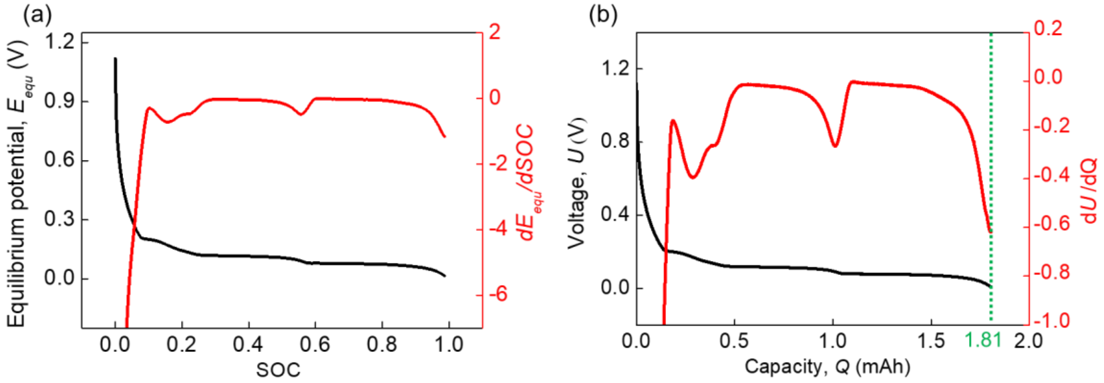

Figure 6 (a) Equilibrium potential of intercalation on graphite and its differential curve as a function of SOC (b) Voltage and its differential curve as a function of capacity during the discharging test of Graphite/Li cells at 0.01C to 1.81 mAh;

2.1.2 Method to detect the lithium plating onset

The electrochemical performance of the graphite electrode during overdischarge was assessed using Graphite/Li coin cells on an electrochemical workstation (Metrohm Autolab). In the formal experiments, the selected cells with similar rated capacities were discharged at 0.5C to different extents by setting different discharging capacities from 1 to 5 mAh. Subsequently, without any relaxation period, the cells were promptly charged at 0.1C, reaching a cut-off voltage of 2V. The differential analyses of voltage [37, 38, 81] were then applied to the discharging and charging curves mentioned above, employing an indirect detection method to assess the occurrence of lithium plating. Furthermore, the morphology of the disassembled cells was characterized to detect lithium plating directly.

Specifically, cells with different capacities were initially discharged at 0.5C and immediately disassembled within the confines of a glove box to prevent the stripping of plated Li metal and the potential reaction between Li metal and air. This comprehensive experimental approach, encompassing indirect and direct detection methods, contributes to a precise detection of lithium plating onset on the graphite electrode.

2.2 Results and discussion

2.2.1 Voltage analysis

As mentioned above, to induce lithium plating on graphite electrode and detect the onset of lithium plating, overdischarge tests were conducted on Graphite/Li cells with the electrolyte of 1.0 M $LiPF_6$ /EC+PC+EDC (1:1:1). The four cells A1-A4 were discharged at 0.5C to different extent by setting different discharging capacities (A1: 4.53 mAh, A2: 2.14 mAh, A3: 1.70 mAh, and A4: 1.38 mAh), then immediately charged at 0.5C to 2 V with no relaxation. The U_Q and $\mathrm{d}U/\mathrm{d}Q\_Q$ curves during the discharging process (Figure 7(a)) show the reliable repeatability of cell performance. The curves during the subsequent charging process (Figure 7(b)) can be further analyzed to help determine the onset of lithium plating. Lithium stripping plateaus can be observed in the starting stage of U_Q curves for cells A1 and A2. These stripping plateaus are attributed to the preferential stripping of plated Li metal, due to its lower standard potential than intercalated lithium inside graphite [82]. Besides, the peaks at $\mathrm{d}U/\mathrm{d}Q\_Q$ curves of cells A1 and A2 correspond to the transition from lithium stripping to lithium deintercalation, which indicates that the capacity at the d*U*/d*Q* peak can be regarded as the amount of reversible Li metal. The lithium stripping plateau and peak indicate that lithium stripping occurs during the initial charging process of cells A1 and A2. Furthermore, it demonstrates that lithium plating occurs during the overdischarging process of A1 and A2. Cells A3 and A4 have no obvious Li stripping plateau and peak in the charging process (Figure 7(b)). There are two possible explanations for this phenomenon, *i.e.*, (i) Lithium stripping does not occur during charging; (ii) Lithium stripping occurs, but the amount of plated Li metal is too small to be detected. As a result, it is challenging to determine if lithium plating occurs during the discharging process of cells A3 and A4.

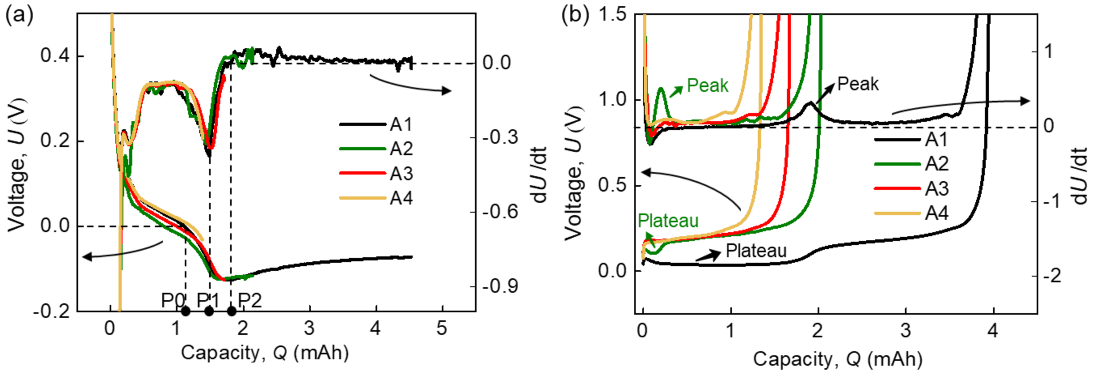

Figure 7 The *U*_*Q* and d*U*/d*Q*_*Q* curves during (a) discharging tests with different capacities and (b) charging tests.

It has been confirmed that lithium plating occurs during the discharging of cells A1 and A2. On this basis, three possible locations for lithium plating onset can be defined as P0, P1 P2 according to characteristics of *U*_*Q* and d*U*/d*Q*_*Q* curves during discharging (Figure 7(a)). P0 is defined at *U* = 0V since most researchers [7, 44, 45, 66] believe lithium plating occurs when the graphite voltage drops below 0 V (based on potential criterion).

P1 is defined at the valley of dU/dQ_Q. By comparing the dU/dQ_Q curves of the overdischarge test with 0.5C (Figure 7(a)) and normal discharge test with 0.01C (Figure 1(b)), an additional valley is found at around 1.63 mAh in Figure 7(a), which may result from the occurrence of lithium plating. Besides, P2 is defined at dU/dQ = 0, representing the onset of the final plateau stage of U_Q curve. Generally, the plateaus of U_Q curve represent the coexisting phase regions since the chemical potential of Li in coexisting phases is equal [83]. Accordingly, the plateau after P2 represents the coexisting phase region of LiC_6 and Li metal.

2.2.2 Morphology analysis

To further determine the onset of lithium plating, the morphologies of disassembled cells with varying discharging capacities were systematically characterized (Figure 8). Cells B1 and B2 were discharged to capacities exceeding P2 (Figure 8(a)) and promptly disassembled within the glove box. Evident silver Li metal deposits were observed on the graphite surface of both B1 and B2 (Figure 8(b)). Cell B3, discharged to a capacity surpassing P1 yet falling short of P2 ((Figure 8(a)), exhibited a modest presence of Li metal on its graphite surface ((Figure 8(b)). In contrast, Cell B4, discharged to a capacity below P1, displayed no discernible plated Li metal on the disassembled graphite electrode. Consequently, it can be inferred that the onset of lithium plating is situated between B3 and B4, proximate to or precisely at P1. This characterization allows for precise localization of the lithium plating onset within the specific discharge capacity range defined by cells B3 and B4. Besides, the graphite voltage range between B3 and B4 (-0.076 ~ -0.021V) indicates that lithium plating occurs at a negative graphite voltage, which can not be explained by the traditional potential criterion [2, 44, 45]. As described in some references [57, 84, 85], Li concentration in graphite is considered as the indicator of lithium plating instead of graphite voltage. In this case, lithium plating may be induced since the Li concentration at the graphite particle surface reaches the saturation level.

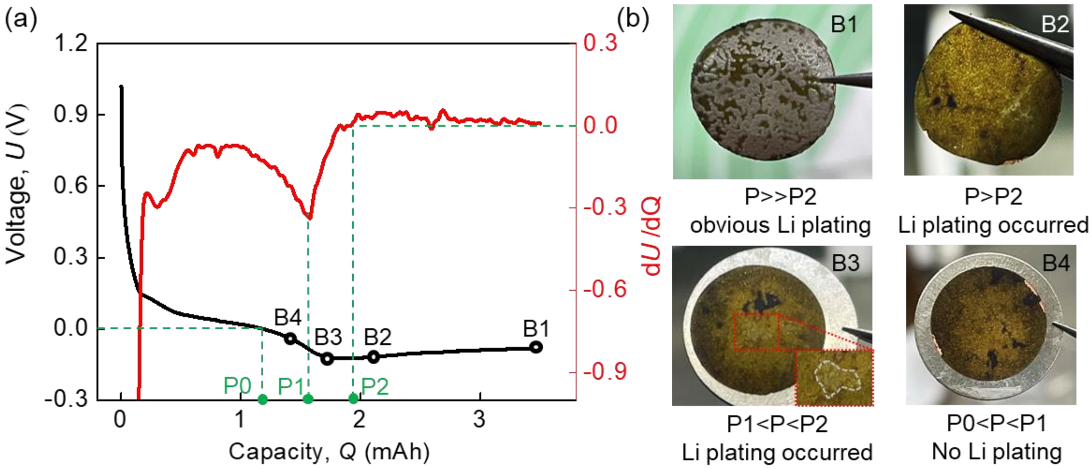

Figure 8 (a) Cells B1-B4 were discharged at 0.5C to different capacities. (b) The morphology of graphite electrodes disassembled from cells B1-B4.

2.3 Conclusion

Detecting the initiation of lithium plating on graphite electrodes holds paramount importance in ensuring the safety of batteries. In this study, the Graphite/Li coin cells with consistent and reliable electrochemical performance were prepared and selected. To precisely locate the onset range of lithium plating on graphite, a comprehensive experimental investigation including voltage analysis and morphology analysis was conducted on the Graphite/Li coin cells. By comparing the experimental results of

Graphite/Li coin cells with different discharging capacities, the precise localization of the lithium plating onset was detected within a narrow discharge capacity range. Besides, the negative graphite voltage at the lithium plating onset indicates that Li concentration in graphite needs to be considered as the indicator of lithium plating instead of graphite voltage in this case.

CHAPTER 3 MODIFYING THE CRITERION OF LITHIUM PLATING

In this chapter, electrochemical model applied to the experimental Graphite/Li coin cells was proposed to compensate for experiments and provide a comprehensive understanding of the mechanism governing the onset of lithium plating. Electrochemical models incorporating different lithium plating criteria, such as the potential criterion and concentration criterion, were developed and systematically compared across different C-rates. Comparing to the traditional potential criterion, the modified concentration criterion in our proposed model serves as a nuanced improvement, allowing for a more accurate depiction of the onset of lithium plating. Building upon the insights gleaned from our models, we propose optimal discharging protocols designed to enhance efficiency while mitigating the occurrence of lithium plating.

3.1 Simulation

The electrochemical model applied in this work is developed based on the pseudo-two-dimensional (P2D) model established by Doyle and Newman et al. [62, 86, 87], which consists of a one-dimensional representation of the cell and a second dimension representing the spherical active material particles. The basic equations in model consist of charge conservation equations which describe the potential distribution in the solid and liquid phases, mass conservation equations to describe the Li concentration distribution in the solid and liquid phase, and electrochemical kinetic equations that describe the reaction rates of lithium intercalation and lithium plating. In most cases [7, 44, 45, 65, 66], the potential of graphite is commonly used as the indicator of lithium plating. Lithium plating started when the graphite potential dropped below 0 V vs. Li/Li$^+$. However, according to the assumption of solid diffusion limitation in graphite [9, 57], lithium plating is triggered when the inserted Li-ions saturate the graphite surface due to the slow solid diffusion compared to intercalation. Accordingly, the criterion of Li concentration needs to be considered in some cases. In the present work, model with concentration criterion is established to predict the onset of lithium plating on graphite electrode of Graphite/Li coin cells and analyze the underlying mechanism.

3.1.1 Charge conservation equations

In the battery, the solid phase potential distribution is governed by Ohm's law [62, 88]:

$$\nabla \cdot \left(\sigma_s^{eff} \nabla \varphi_s \right) = j_{total} \tag{1}$$

where σ_s^{eff} is the effective electrical conductivity of solid phase, φ_s denotes the potential of solid phase and j_{total} is defined as the total volumetric current density of all electrochemical reactions. The boundary conditions at the current collector/graphite interface and graphite/separator interface are listed as below, where i_{app} represents the applied current density.

$$-\sigma_s^{eff} \nabla \varphi_s \Big|_{cc/gr}^{interface} = -i_{app} \tag{2}$$

$$-\sigma_s^{eff} \nabla \varphi_s \Big|_{gr/sep}^{interface} = 0 \tag{3}$$

The governing equation for the liquid phase potential distribution and the corresponding boundary conditions at the current collector/graphite interface and graphite/separator interface as follows:

$$-\nabla\cdot\left(\sigma_l^{eff}\nabla\varphi_l\right)+\frac{2RT\left(1-t^+\right)}{F}\left(1+\frac{d\ln f}{d\ln c_l}\right)\nabla\cdot\left(\sigma_l^{eff}\nabla\ln c_l\right)=j_{total} \tag{4}$$

$$-\sigma_l^{eff}\nabla\varphi_l\Big|_{cc/gr}^{interface}=0 \tag{5}$$

$$-\sigma_l^{eff}\nabla\varphi_l\Big|_{gr/sep}^{interface}=-i_{app} \tag{6}$$

where σ_l^{eff} is the effective electrical conductivity of liquid phase, φ_s is the potential of liquid phase. R, T and F are gas constant, temperature and Faraday parameter, respectively. t^+ represents the transport number of Li^+, f is the activity coefficient and c_l denotes the Li^+ concentration in the liquid phase.

3.1.2 Mass conservation equations

The distribution of Li concentration inside the solid active material particles follows Fick's law [16] (Equation (7)). c_s denotes the Li concentration in the solid phase, D_s represents the solid phase diffusion coefficient (APPENDIX B) and r is the radius of the particle. The boundary condition at the particle center (r=0) (Equation (8)) indicates that no Li source exists at the center of particle. At the particle surface (r=R_s), the Li flux is determined by the local current density of lithium intercalation (j_{int}). Here a_s represents the specific surface area of the particle.

$$\frac{\partial c_s}{\partial t}=D_s\left(\frac{2}{r}\frac{\partial c_s}{\partial r}+\frac{\partial^2 c_s}{\partial r^2}\right) \tag{7}$$

$$\frac{\partial c_s}{\partial r}\Big|_{r=0}=0 \tag{8}$$

$$-D_s \frac{\partial c_s}{\partial r}\Big|_{r=R_s} = \frac{j_{int}}{a_s F} \tag{9}$$

The Li$^+$ distribution in the liquid phase is directed by the Nernst-Plank equation (Equation (10)) [4]. The related boundary condition at the current collector/graphite interface can be expressed as Equation (11).

$$\varepsilon_l \frac{\partial c_l}{\partial t} = -\nabla \cdot \left(J_l\right) + \frac{j_{total}}{F} \tag{10}$$

$$-\nabla c_l \Big|_{cc/gr}^{interface} = 0 \tag{11}$$

where c_l and ε_l represent the Li$^+$ concentration and volume fraction of the liquid phase, respectively. J_l is defined as the Li$^+$ flux density in the liquid phase, which is related to c_l and i_l (liquid phase current density) as follows:

$$J_l = -D_l^{eff} \nabla c_l + \frac{t_+}{F} i_l \tag{12}$$

$$i_l = -\sigma_l^{eff} \nabla \varphi_l + \frac{2RT\left(1-t^+\right)}{F}\left(1+\frac{d\ln f}{d\ln c_l}\right)\left(\sigma_l^{eff} \nabla \ln c_l\right) \tag{13}$$

3.1.3 Electrochemical kinetic equations

During the overdischarging process of Graphite/Li cell, lithium intercalation is the main electrochemical reaction at the surface of the graphite particle, while lithium plating is regarded as the side reaction that will take place if the criterion of lithium plating is satisfied. Accordingly, the total volumetric current density j_{total} includes the current densities of lithium plating j_{pla} and lithium intercalation j_{int}:

$$j_{total} = j_{pla} + j_{int} \tag{14}$$

As mentioned above, j_{total} is used in the charge conservation Equations (1) (4) and mass conservation Equation (10) as the reaction sources. However, only j_{int} is applied as a reaction source in Equation (9) since the lithium inside the particle comes entirely from the lithium intercalation at the particle surface, irrelevant to lithium plating.

The volumetric current density of lithium plating j_{pla} is expressed by the Butler-Volmer equation as written in Equation (15). Unlike the widely used model which adopts graphite potential as the indicator of lithium plating [7, 44, 45, 65, 66], the Li concentration criterion is applied in the present model. Specifically, the expression for exchange current density of lithium plating $i_{0,pla}$ (Equation (16)) indicates that lithium plating is induced when the Li concentration at the particle surface $c_{s,surf}$ exceeds the maximum value $c_{s,max}$.

$$j_{pla} = a_s i_{0,pla}\left[\exp\left(\frac{\alpha_{a,pla}F\eta_{pla}}{RT}\right) - \exp\left(-\frac{\alpha_{c,pla}F\eta_{pla}}{RT}\right)\right] \tag{15}$$

$$i_{0,pla} = Fk_{pla}c_l \left(c_{s,surf} \geq c_{s,max}\right) \tag{16}$$

$$\eta_{pla} = \varphi_s - \varphi_l - E_{eq,pla} - \frac{j_{total}}{a_s}R_{film} \tag{17}$$

$\alpha_{c,pla}$ and $\alpha_{a,pla}$ is the charge transfer coefficient of the cathode and anode, respectively. k_{pla} represents the reaction rate constant for lithium plating. η_{pla} is the over-potential of lithium plating and $E_{eq,pla}$ is the equilibrium potential of lithium plating, which equals 0 V vs. Li/Li$^+$. R_{film} represents the resistance of the surface film.

The volumetric current density of lithium intercalation j_{int} is also expressed by the

Butler-Volmer equation [44]:

$$j_{int} = a_s i_{0,int} \left[\exp\left(\frac{\alpha_{a,int} F \eta_{int}}{RT} \right) - \exp\left(-\frac{\alpha_{c,int} F \eta_{int}}{RT} \right) \right] \tag{18}$$

where $i_{0,int}$ represents the exchange current density of lithium intercalation:

$$i_{0,int} = F k_{int} c_{s,surf}^{\alpha_{c,int}} \Delta c_s^{\ \alpha_{a,int}} \left(\frac{c_l}{c_{l,ref}} \right)^{\alpha_{a,int}} \tag{19}$$

$$\Delta c_s = \min\left\{ \max\left[\left(c_{s,max} - c_{s,surf} \right), c_{s1} \right], c_{s2} - c_{s,surf} \right\} \tag{20}$$

η_{int} is the over-potential of lithium intercalation:

$$\eta_{int} = \varphi_s - \varphi_l - E_{eq,int} - \frac{j_{total}}{a_s} R_{film} \tag{21}$$

The general expression of Δc_s in traditional P2D model with potential criterion is $\Delta c_s = c_{s,max} - c_{s,surf}$ [45, 66] (black line in Figure. 9), which will lead to a non-convergence problem in the present model with concentration criterion. Specifically, Δc_s will be infinitely close to 0 when $c_{s,surf}$ increases and approaches $c_{s,max}$, which will lead to the approach to 0 of $i_{0,\text{int}}$ according to Equation (19). At this moment, j_{pla} still remains as 0 since lithium plating hasn't been triggered (Equations (15-16)), j_{int} is therefore equal to j_{total} which remains unchanged under constant current discharging (Equations (14)). According to Equation (18), the unchanged j_{int} and the approach to 0 of $i_{0,\text{int}}$ will lead to the infinite increment of η_{int}, which will finally result in the non-convergence of the model. When applied with the concentration criterion in the present model, to avoid the computational conflict and simulate the transition from lithium intercalation to lithium plating during discharging progress, the expression of Δc_s needs to be modified as Equation (20). c_{s1} and c_{s2} are parameters to define Δc_s which are adjusted through the calibration of experimental and simulated voltage. As depicted in Figure. 9, compared to the traditional expression of Δc_s (black line), modified Δc_s (blue line) is not infinitely close to 0 but remains at a small constant value when $c_{s,surf}$ increases and approaches $c_{s,max}$ so that the non-convergence can be avoided.

Besides, k_{int} is the reaction rate constant, $c_{l,ref}$ represents the reference Li^+ concentration in the liquid phase. $\alpha_{c,int}$ and $\alpha_{a,int}$ is the charge transfer coefficient of the cathode and anode, respectively. $E_{eq,int}$ is the equilibrium potential of lithium intercalation on graphite (Figure 6(a)), which was derived from the discharging test conducted on Graphite/Li coin cells at 0.01C.

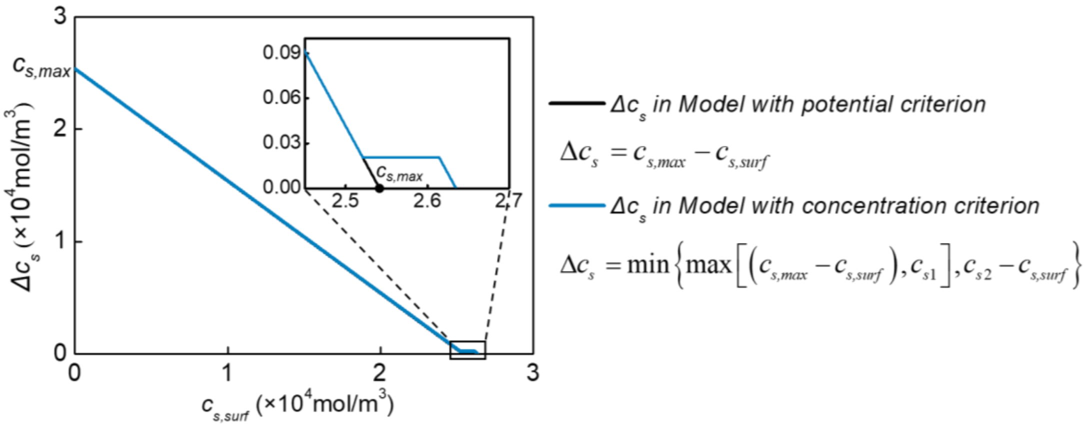

Figure 9 The comparison of Δc_s as a function of cs_surf between the model with concentration criterion and the model with potential criterion.

Following the mass conservation, the thickness of the plated li metal δ_{pla} can be expressed as:

$$\frac{\partial \delta_{pla}}{\partial t} = -\frac{j_{pla} M_{pla}}{a_s \rho_{pla} F} \tag{22}$$

where M_{pla} and ρ_{pla} represent the molar weight and density of the plated li metal. Then, the resistance of the Li metal film can be determined by the thickness δ_{pla} and conductivity σ_{film} of the plated Li metal:

$$R_{film} = \frac{\delta_{pla}}{\sigma_{film}} \tag{23}$$

Besides, the pore of the graphite electrode is occupied by plated li metal. As a result, the porosity of graphite can be written as:

$$\varepsilon_l = \varepsilon_{l,0} - a_s \delta_{pla} \tag{24}$$

The model was established and presented in COMSOL Multiphysics. The electrochemical parameters applied in model are listed in Table. 1.

Table 1 Electrochemical parameters of the model.

Symbol	Unit	Value
Li intercalation		
ε_l		44.4%
ε_s		38.3%
σ_s	S/m	100
R	m	5e-6
$\alpha_{a,int}$		0.5
$\alpha_{c,int}$		0.5
lithium plating		
k_{pla}	m/s	7e-10 ^{ad}
$c_{s.max}$	mol/m^3	25414
$c_{s.1}$	mol/m^3	205.9^{ad}
$c_{s.2}$	mol/m^3	26350 ^{ad}

$\alpha_{c,pla}$		0.5
$E_{eq,pla}$	V	0
M_{pla}	kg/mol	6.94e-3
ρ_{pla}	kg/m^3	534

^{ad} Adjusted

3.2 Results and discussion

3.2.1 Mechanism of lithium plating onset

The experiments in Chapter 1 have provide a relatively narrow range for lithium plating onset, yet the precise location of lithium plating onset and the underlying mechanism need to be confirmed and interpreted by simulation. Considering the fact that the potential criterion is not suitable to illuminate the occurrence of lithium plating in this case, the model was established with the concentration criterion for lithium plating. Figure 10(a-c) shows the model predictions, where the dash lines correspond to the experimental results while the simulated results are shown with the solid lines. The results show that the simulated *U_t* and d*U*/d*t_t* curves of overdischarging cases at 0.1C, 0.2C, and 0.5C can fit the experimental results well, which validates the accuracy of the model. Besides, according to the variation rate of the plated Li metal concentration $\mathrm{d}c_{li} / \mathrm{d}t$, the turning point of $\mathrm{d}c_{li} / \mathrm{d}t$ can be determined as the simulated onset of lithium plating, which is denoted as t_{M}. When lithium plating occurs at t_{M}, valley points appear on the simulated d*U*/d*t_t* curves in all cases, indicating that the valley point P1 on d*U*/d*t_t* arises from the occurrence of lithium plating. Based on this, the valley points on the experimental d*U*/d*t_t* curves can be determined as the experimental onset of lithium plating t_{E}. The model with concentration criterion can precisely predict the actual lithium plating onset ($t_{\mathrm{E}} \approx t_{\mathrm{M}}$) at various C-rates.

Further analysis is conducted to interpret the relationship between lithium plating occurrence and valley point on d*U*/d*t*_*t* curve (Figure 10(d)). When lithium plating occurs, the current density of plating i_{pla} starts to increase from 0 while the current density of intercalation i_{int} starts to decrease. As a result, the flux of Li-ion across the particle surface Φ_{li}, determined by i_{int}, starts to decrease. With the decreasement of Φ_{li}, the Li concentration and *SOC* at the particle surface keep increasing, but the corresponding variation rates ($\mathrm{d}c_{s\_surf} / \mathrm{d}t$, $\mathrm{d}SOC / \mathrm{d}t$) begin to decrease. Since the equilibrium potential of intercalation E_{equ_int} is the function of *SOC*, the decrease of $\mathrm{d}SOC / \mathrm{d}t$ leads to the decrease of $\mathrm{dE}_{equ\_int} / \mathrm{d}t$, which finally causes the valley on the d*U*/d*t*_*t* curve.

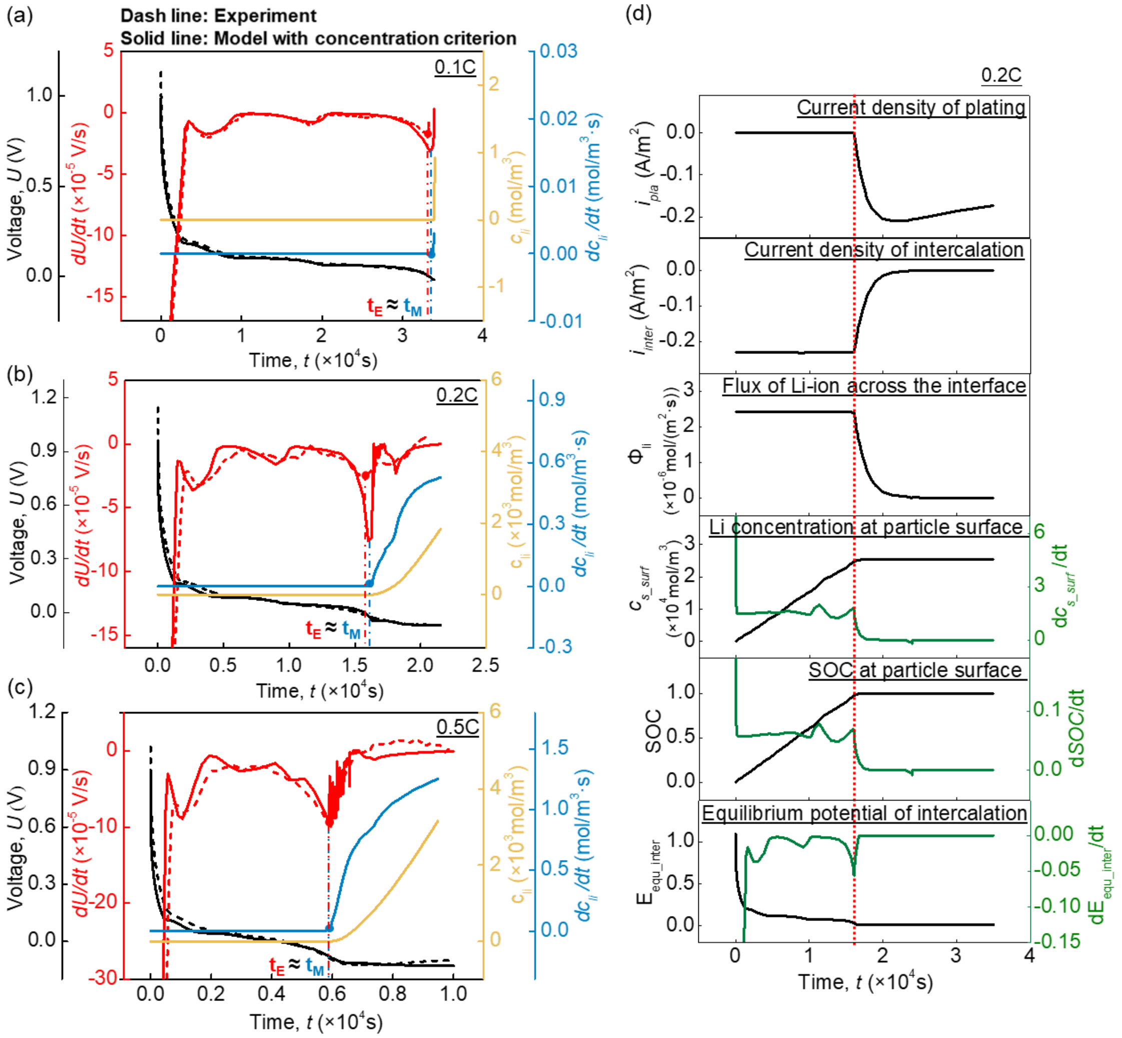

Figure 10 The comparison of results between the model with concentration criterion and overdischarging tests at (a) 0.1C, (b) 0.2C, and (c) 0.5C. (e)The underlying mechanism of valley point

3.2.2 Comparison of models with different criteria of lithium plating

As described above, the model with concentration criterion is able to predict the onset of lithium plating precisely. To further demonstrate the superiority of concentration criterion in lithium plating onset prediction, the simulated results are compared between the models with concentration criterion and potential criterion. To quantify the the accuracy of model in lithium plating onset prediction, the prediction error of lithium plating onset

ε is defined as the ratio of the interval between simulated and experimental lithium plating onset ($|t_{\mathrm{M}} - t_{\mathrm{E}}|$) to the experimental lithium plating onset (t_{E}). As shown in Figure 11(a), for the model with potential criterion, the prediction error of lithium plating onset ε generally increases from 1.21% to 8.34% as C-rate varies from 0.1C to 0.5C. By comparison, the ε of model with concentration criterion firstly increases from 0.84% to 2.27% as C-rate changes from 0.1C to 0.2C, then ε remains at this level while C-rate increases from 0.2C to 0.5C. The results demonstrate that the concentration criterion is more suitable to predict the actual lithium plating onset under a high C-rate compared to the potential criterion. The adoption of the concentration criterion can keep the prediction error of lithium plating onset at a relatively low level for all C-rates, indicating that the experimental lithium plating is more likely to be induced by saturated concentration at graphite particle surface rather than negative over-potential of lithium plating.

Furthermore, the evolution process of minimum over-potential of lithium plating $\eta_{pla\_\min}$ among the graphite electrode and maximum surface concentration of Li-ion $c_{s,surf\_\max}$ among the graphite electrode are extracted and analyzed in Figure 11(b). $\eta_{pla\_\min}$ continues to decrease as time increases and the potential criterion is triggered as $\eta_{pla\_\min}$ reaches 0 V (red circle). $c_{s,surf\_\max}$ continues to increase with time, the concentration criterion is triggered when $c_{s,surf\_\max}$ reaches $c_{s\_\max}$ (blue circle). It can be observed that the potential criterion is triggered prior to the concentration criterion in all cases. As C-rate increases, the difference between the triggering time of the potential criterion and concentration criterion becomes larger since $c_{s,surf\_\max}$ at the potential criterion triggering time (red circle) becomes smaller. As a result, the predicted lithium plating onset of the model with potential criterion is obviously prior to the actual lithium plating onset at a high C-rate of 0.5C.

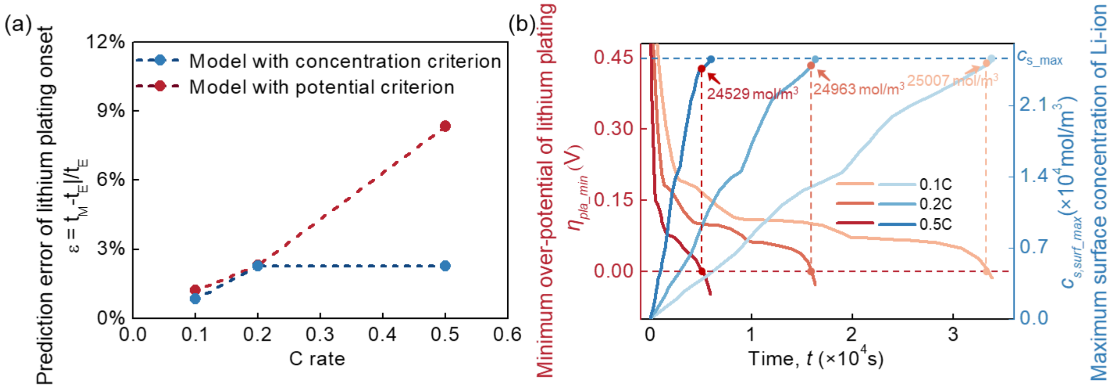

Figure 11 (a) The comparison of results between models with concentration criterion and potential criterion at different C-rates. (b) The evolution process of minimum over-potential of lithium plating η_{pla_min} among the graphite electrode and maximum surface concentration of Li-ion $c_{s,surf\_max}$ among the graphite electrode at different C-rates.

3.2.3 Optimal charging protocol

By applying the concentration criterion of lithium plating, the model can precisely predict the lithium plating onset under various C-rates. Based on this, the optimization of the discharging protocol can be conducted on the model with concentration criterion to restrain lithium plating and enhance discharging efficiency. Firstly, two typical protocols CC(0.5C)_CV and CC(0.5C)_CC(0.4C) are proposed (Figure 12(a)(b)). For CC(0.5C)_CV, the cell is discharged with a constant current of 0.5C (grey part) until the concentration criterion of lithium plating is triggered ($c_{s,surf} = c_{s,\max}$), then the cell is discharged with constant voltage to a certain SOC (green part). The result of the current density of lithium plating i_{pla} shows that lithium plating occurs at the starting point of CV process since $c_{s,surf}$ continues to increase and remains larger than $c_{s,\max}$ during the CV process. The traditional CC_CV protocol can not restrain lithium plating. For CC(0.5C)_CC(0.4C) in Figs 12(b), the cell is discharged with 0.5C (grey part) until $c_{s,surf} = c_{s,\max}$, then the cell is discharged with 0.4C to a certain SOC (green part). During the CC(0.4C) process, $c_{s,surf}$ firstly decreases from $c_{s,\max}$ and then increases to exceed $c_{s,\max}$. As a result, the onset of lithium plating is postponed in CC(0.5C)_CC(0.4C) compared to the CC(0.5C)_CV.

Furthermore, different C-rates *n*C(*n* = 0.1, 0.2, 0.3 and 0.4) are adopted for the second CC process and the effect of C-rate (*n*C) are analyzed in Figure 12(c-f). As the C-rate decreases from 0.4C to 0.1C, the voltage recovery at the starting point of CC(*n*C) process increases from 0.02 V to 0.11 V. Besides, while the C-rate decreases from 0.4C to 0.2C, the onset of lithium plating is postponed from t_1 (6027 s) to t_3 (7340 s) (Figure 12(d)) since that the triggering time of concentration criterion $c_{s,surf} \geq c_{s,\max}$ is postponed from t_1 (6027 s) to t_3 (7340 s) (Figure 12(e)). It should be noted that lithium plating doesn't occur in CC(0.5C)_CC(0.1C) case since the concentration criterion is not triggered during the whole discharging process. Although the decrease of C-rate on the second CC process contributes to the delay of lithium plating, the discharging efficiency also becomes poorer since it takes more discharging time to reach the set discharging SOC. Besides, when lithium plating occurs respectively at t_1 (6027 s), t_2 (6400 s), and t_3 (7340 s) for cases with *n* = 0.4, 0.3 and 0.2 (Figure 12(d)), the valley points appear on d*U*/d*t_t* curves (Figure

12(c)). The specific valley points on dU/dt_t curves can be recognized as the signal of concentration saturation at the graphite particle surface and lithium plating occurrence. Accordingly, the lithium plating onsets can be detected in situ by monitoring the data of dU/dt_t, which is simple and suitable for engineering applications.

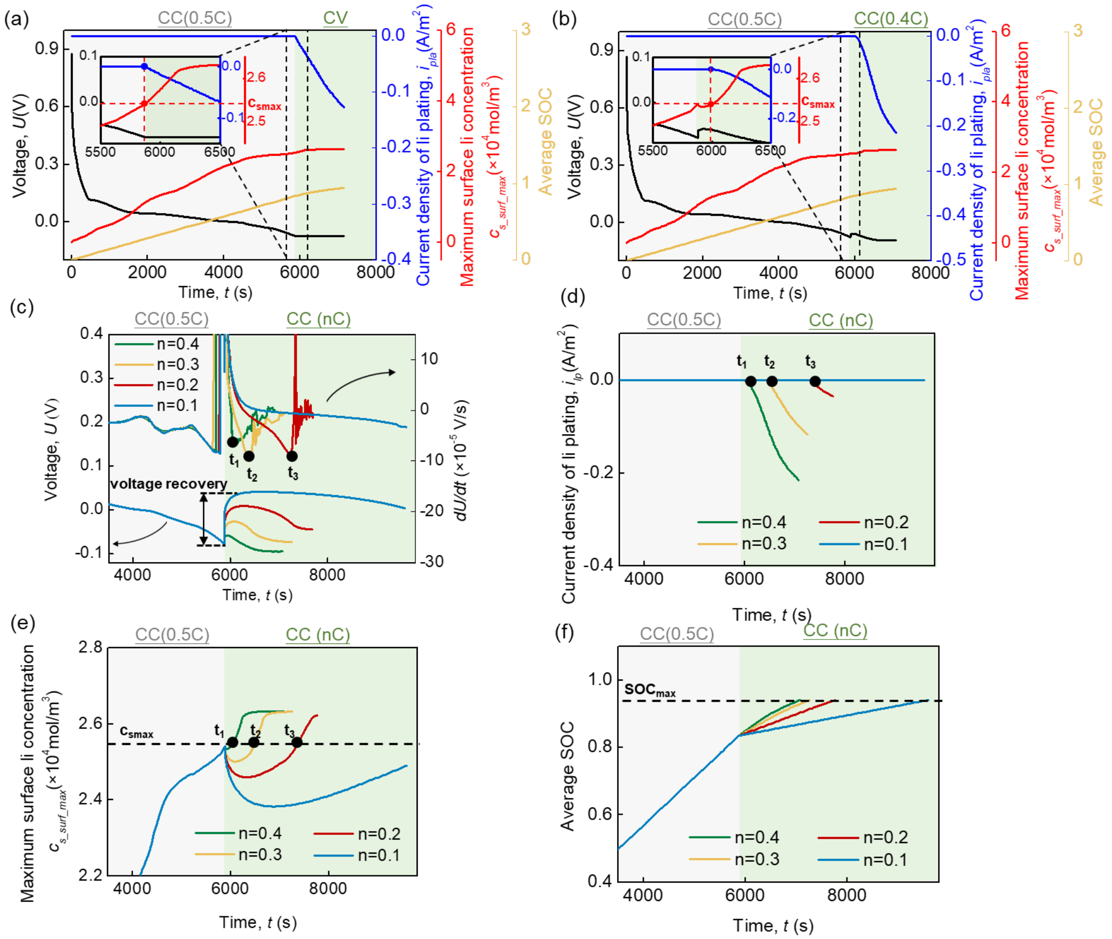

Figure 12 The results of (a) CC(0.5C)_CV and (b) CC(0.5C)_CC(0.4C) based on the model with concentration criterion. The (c) voltage, (d) current density of lithium plating, (e) maximum surface Li concentration, and (f) average soc of the CC(0.5C)_CC(nC) protocols with different *n* values.

As mentioned above, lithium plating is not induced when the cell is discharged with CC(0.5C)_CC(0.1C). Based on this protocol, four multi-CC discharging protocols (Table 2, Modes 1~4) are proposed by inserting CC steps between CC(0.5C) and CC(0.1C) and performed on the model with concentration criterion. ΔC-rate is defined as the difference of C-rates between the adjacent CC steps. The multi-CC discharging protocols are performed based on the concentration criteria of lithium plating. Specifically, the transition between two adjacent CC steps is induced when the concentration criteria is triggered ($c_{s,surf} = c_{s,\max}$). It can be found that no lithium plating occurs in these four modes (Figure 13(b)) since $c_{s,surf}$ remains lower than or equal to $c_{s,\max}$ during the whole discharging process (Figure 13(c)). Besides, as ΔC-rate decreases from 0.4C (Mode 1) to 0.05C (Mode 4), the discharging time to reach the set discharging SOC becomes shorter (Figure 13(d)). It indicates that decreasing the ΔC-rate of multi-CC protocol can enhance the discharging efficiency of cell with no lithium plating.

Table 2 Multi-CC discharging protocols.

Name	C-rate of each CC step	ΔC-rate
Mode 1	0.5C_0.1C	0.4C
Mode 2	0.5C_0.3C_0.1C	0.2C
Mode 3	0.5C_0.4C_0.3C_0.2C_0.1C	0.1C
Mode 4	0.5C_0.45C_0.4C_0.35C_0.3C_0.25C_0.2C_0.15C_0.1C	0.05C

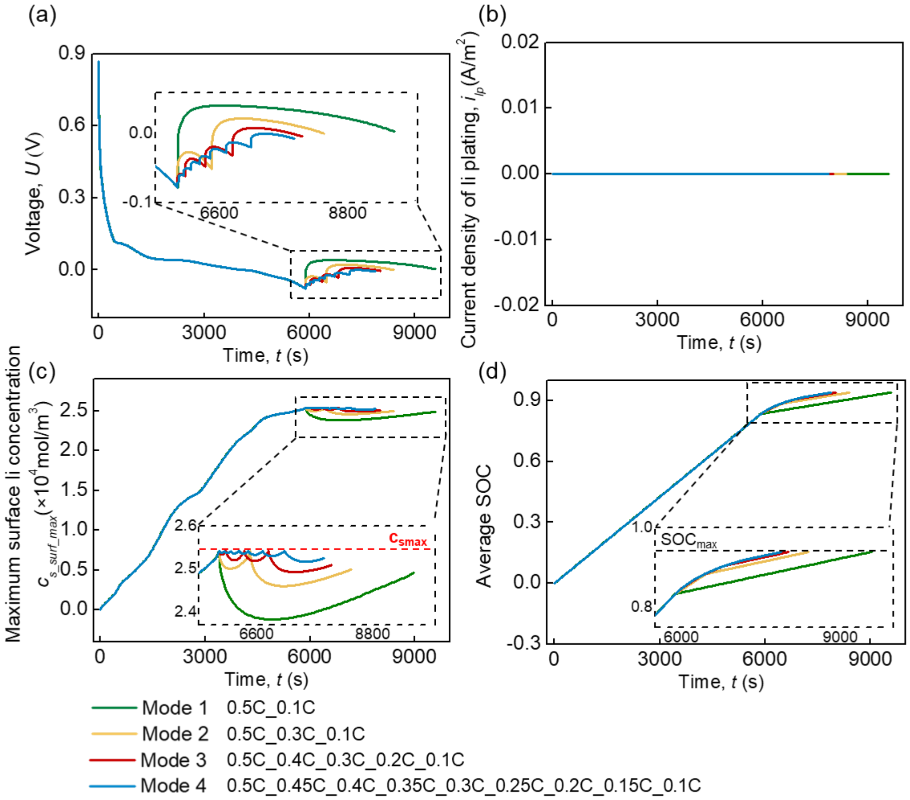

Figure 13 The (a) voltage, (b) current density of lithium plating, (c) maximum surface li concentration, and (d) average soc of the multi-CC discharging protocols with different ΔC-rates.

3.3 Conclusions

In this study, we performed a simulation investigation to obtain a comprehensive understanding of lithium plating onset on graphite. Firstly, we developed an electrochemical model employing concentration criteria to precisely determine the onset of lithium plating on graphite and elucidate the underlying mechanisms governing the initiation of lithium plating. Besides, Comparative analysis revealed that the model incorporating a concentration criterion, demonstrated superior suitability in predicting the onset of lithium plating, particularly under conditions of elevated C-rates, when contrasted with the model relying on a potential criterion. Employing the model with modified criterion, a parametric study was undertaken to derive an optimized discharging protocol that not only exhibits high discharging efficiency but also mitigates the occurrence of lithium plating. This finding underscores the significance of protocol design in achieving optimal battery performance with minimal risk of lithium plating.

CHAPTER 4 INVESTIGATING THE DISTRIBUTION OF LITHIUM PLATING IN LITHIUM-ION BATTERIES

The 1D electrochemical model in Chapter 3 adopts a homogenization strategy for the Graphite/Li coin cells to give a qualitative description of the lithium plating initiation. In this chapter, we extend the 1D electrochemical model into 2D physics-based model considering the distribution of lithium plating in the actual winding structure of pouch cells. Based on this validated model, a parametric study is conducted to quantify the influence of governing factors, including the electrochemical properties of the materials, tab arrangement, and charge protocols.

4.1 Simulation

4.1.1 Finite element modeling

The $Li_xC_6/LiCoO_2$ battery with a capacity of 4 Ah supplied by CosMX is chosen as the target sample in this study. The electrolyte is dissolved $LiPF_6$ salt in carbonate solvents. The target pouch cell is composed of battery casing and jellyroll, and the jellyroll is a spiral winding structure with an anode-separator–cathode–separator sequence. The 2D electrochemical model is established based on the jellyroll of the sample cell via the COMSOL platform (Figure. 14). The spiral winding structure with 8 cycles is built according to the actual geometric dimensions of separator, cathode, and anode active material, cathode and anode current collectors. The anode and cathode tabs are separately located at the innermost anode and cathode layers. To enhance the computational efficiency and convergence, we adopt the mapping method is to mesh the entire model in quadrilateral elements with the total number of 7,570.

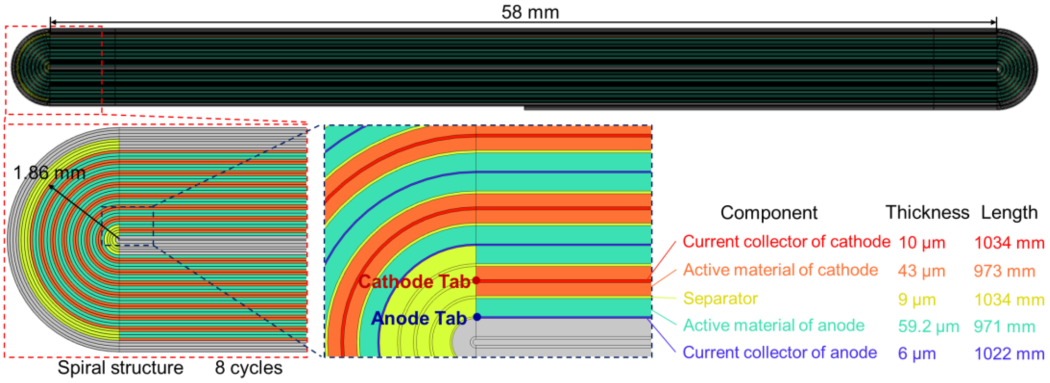

Figure 14 The geometry of the 2D battery model. The spiral winding structure is of 8 cycles with an anode-separator–cathode–separator sequence. The sizes of cathode, anode, separator, collectors, and the positions of tabs are defined based on the actual battery.

4.1.2 Modeling of lithium plating and SEI growth

In the present model, the governing equations of charge conservation and mass conservation are identical to those in Chapter 2 (Equations (1-13)). Besides, three electrochemical reactions are considered in this model. Lithium intercalation into graphite is the main reaction, while the lithium plating and SEI growth are regarded as side reactions. Lithium plating would occur if the local anode potential becomes smaller and finally negative vs. Li/Li^+. The formation of SEI is attributed to the decomposition of electrolyte solvent at the graphite anode surface due to the low anode potential.

The total volumetric current density is equal to the sum of the current density of all three reactions:

$$j_{total} = j_{int} + j_{SEI} + j_{pla} \qquad (25)$$

The volumetric current density of lithium intercalation is calculated by the Butler-

Volmer equation:

$$j_{int} = -a_s i_{0,int} \left\{ \exp\left[\frac{\alpha'_{a,int} F \eta_{int}}{RT} \right] - \exp\left(-\frac{\alpha'_{c,int} F \eta_{int}}{RT} \right) \right\} \tag{26}$$

where a represents the specific surface area, $i'_{0,int}$ is the exchange current density of lithium intercalation, and η_{int} indicates the over-potential, which denotes as:

$$\eta_{int} = \varphi_s - \varphi_l - E_{eq,int} - \frac{j_{total}}{a_s} R_{film} \tag{27}$$

where φ_s and φ_l indicate potentials of the solid and liquid phase; $E_{eq,int}$ is the thermodynamic equilibrium potential for lithium intercalation, and R_{film} is the resistance of the surface film.

The side reactions for SEI formation and lithium plating are described by the cathodic Tafel expression [89]:

$$j_{SEI} = -a_s F k_{0,SEI} c_{EC}^{s} \exp\left(-\frac{\alpha_{c,SEI} F}{RT} \left(\varphi_s - \varphi_l - E_{eq,SEI} - \frac{j_{total}}{a_s} R_{film}\right)\right) \tag{28}$$

$$j_{pla} = -a_s i'_{0,pla} \exp\left(-\frac{\alpha'_{c,pla} F}{RT} \left(\varphi_s - \varphi_l - E_{eq,pla} - \frac{j_{total}}{a_s} R_{film}\right)\right) \tag{29}$$

where $k_{0,SEI}$ is the kinetic rate constant, c_{EC}^{s} represents the concentration of solvent molecules ethylene carbonate (EC) on the graphite surface, $E_{eq,SEI}$ and $E_{eq,pla}$ indicate the equilibrium potential of SEI formation and lithium plating reaction, $i'_{0,pla}$ is the exchange current density of lithium plating. c_{EC}^{s} can be obtained from the mass conservation of EC:

$$-D_{EC} \frac{c_{EC}^{s} - c_{EC}^{0}}{\delta_{film}} = -\frac{j_{SEI}}{aF} \tag{30}$$

where D_{EC} is the diffusivity of EC, c_{EC}^{0} is the concentration of EC in electrolyte, δ_{film} represents the thickness of the particle surface film.

The mass conservation of SEI and lithium metal can be expressed as:

$$\frac{\partial c_{SEI}}{\partial t} = -\frac{j_{SEI}}{2F} - \frac{j_{pla}}{2F}\chi \tag{31}$$

$$\frac{\partial c_{Li}}{\partial t} = -\frac{j_{pla}}{F}(1-\chi) \tag{32}$$

where c_{SEI} and c_{Li} are the concentrations of SEI and lithium metal. χ denotes the fraction of plated lithium that is oxidized to form a new SEI.

The surface film of graphite particles is composed of SEI and lithium metal. The thickness of the surface film can be derived as follows assuming that the surface film is uniform:

$$\delta_{film} = \frac{1}{a}\left(\frac{c_{SEI}M_{SEI}}{\rho_{SEI}} + \frac{c_{Li}M_{Li}}{\rho_{Li}}\right) \tag{33}$$

where M_{SEI}, M_{Li}, ρ_{SEI}, and ρ_{Li} are molar weights and densities of SEI and lithium metal. The resistance of the surface film can be expressed as:

$$R_{film} = w_{SEI}\frac{\delta_{film}}{\kappa_{SEI}} \tag{34}$$

The resistance of lithium metal is neglected here due to the much larger conductivity of lithium metal compared to SEI. w_{SEI} indicates the fraction of SEI in the surface film, and κ_{SEI} represents ionic conductivity.

In this work, cell design information and key model parameters related to Li intercalation, SEI growth, and lithium plating are summarized in Table 3.

Table 3 Key parameters of the finite element model.

Symbol	Unit	Anode	Cathode	Separator
Appearance parameters				
H	m	5.92e-5	4.3e-5	N/A
W	m	7.78e-2		
Li intercalation				
R_s	m	5e-6	6e-6	N/A
$\alpha'_{a,int}$		0.5 [45]	0.5 [45]	N/A
$\alpha'_{c,int}$		0.5 [45]	0.5 [45]	N/A
SEI and lithium plating				
$k_{0,SEI}$	m/s	2e-12 [ad]	N/A	
c_{EC}^{0}	mol/m^3	4541 [89]	N/A	
D_{EC}	m^2/s	2e-19 [ad]	N/A	
$\alpha_{c,SEI}$		0.5 [89]	N/A	
κ_{SEI}	S/m	1.8e-6 [ad]	N/A	
M_{SEI}	kg/mol	0.162[89]	N/A	
ρ_{SEI}	kg/m^3	1690 [89]	N/A	
$i'_{0,pla}$	A/m^2	0.0001 [ad]	N/A	
$\alpha'_{c,pla}$		0.5 [65]	N/A	
$E_{eq,pla}$	V	0	N/A	
M_{pla}	kg/mol	6.94e-3	N/A	
ρ_{pla}	kg/m^3	534	N/A	

[ad] Adjusted

4.2 Model validation and results

4.2.1 Model validation

The charging and discharging experiments were performed on the commercial prismatic LIB by the BK6808AR rechargeable battery performance tester. All C rates in this work were assigned relative to the nominal capacity of 4 Ah. Two types of charging protocols, e.g., CC-CV charging and step charging were adopted to comprehensively validate the accuracy of the model.

(1) CC-CV charging. The cells were charged with a constant current (CC) of various C rates (0.1C, 0.5C, 1C, and 2C) from 3.2 V to the cut-off voltage of 4.4 V, followed by a constant voltage (CV) stage at 4.4 V until the charge current dropped below 0.025C. Afterward, the cells were discharged with 0.1C to 3.0 V. Besides, the discharging current could be changed to 0.5C, 1C, and 2C while the current of CC charging was maintained as 0.1C.

(2) Step charging. The charging period can be divided into four steps. a). The cell was CC charged with 8A to the upper voltage limit of 4.25 V, followed by CV charged until the charge current dropped below 6A. b). The cell was CC charged with 6A to the upper voltage limit of 4.30 V, followed by CV charged until the charge current dropped below 5A. c). The cell was CC charged with 5A to the upper voltage limit of 4.35 V, followed by CV charged until the charge current dropped below 1C. d). The cell was CC charged with 1C to the upper voltage limit of 4.40 V, followed by CV charged until the charge current dropped below 0.025C. Finally, the cells were discharged with 0.7 C to 3.0 V.

We are able to observe the satisfied agreement of the results from the established model and experimental characterization results in various charging protocols (Figure 15).

The developed 2D model is capable of predicting the electrochemical behavior of the battery.

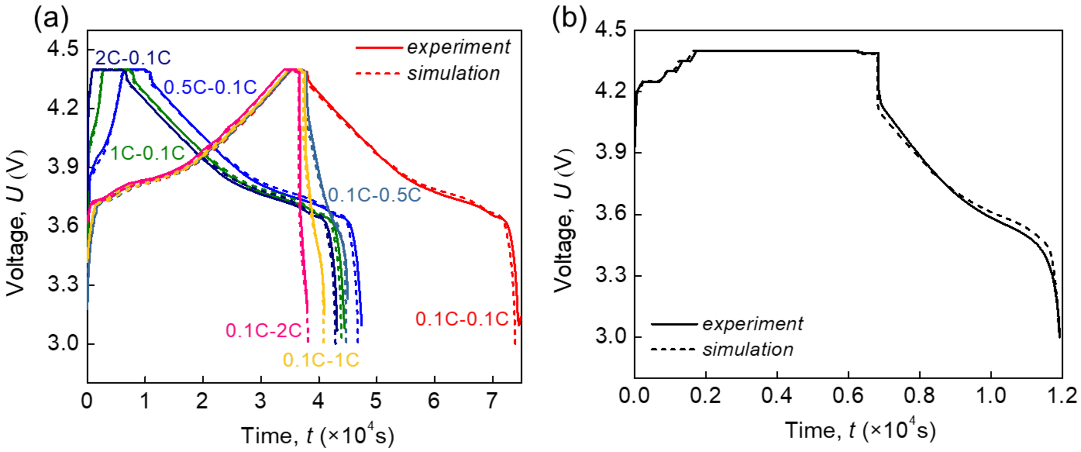

Figure 15 Comparison of the simulated and experimental cell voltages of (a) CC-CV charging and discharging with 0.1C, 0.5C, 1C, 2C and (b) step charging.

4.2.1 Distribution of lithium plating

During the charging process, the Li intercalation is the main reaction that determines the reaction rate compared with SEI formation and lithium plating by comparing the current densities of these reactions (Figure 16(a)). Further analysis is conducted to clarify the possible area of lithium plating. For step charging, the distribution of lithium plating over-potential (Figure 16(b)) in anode at charging time $t = 350$ s is extracted. The lithium plating over-potential in the inner layer is smaller than that in the outer layer, which means that lithium plating is more likely to occur in the inner layers of the winding anode. Besides, the lithium plating over-potential at the separator/anode (sep/an) interface is smaller than that at the anode/current collector (an/cc) interface ((Figure 16(b))), indicating that lithium plating is prone to occur at the separator/anode (sep/an) interface. As indicated by Equation

(27), lithium plating over-potential is determined by the solid-phase potential φ_s, liquid-phase potential φ_l, and resistance of the surface film R_{film}. The resistance of the surface film is small at room temperature [65]. Among the two remaining factors φ_s (Figure. 16(c)) and φ_l (Figure 16(d)), the distribution of φ_s in anode associated with the anode tab position is the dominant factor of the smaller over-potential in the inner layers. Besides, compared with the unchanged solid-phase potential along the thickness direction, the varying φ_l along the thickness direction (Figure 16(d)) due to varying Li-ion concentration is the primary effect contributing to the tendency that the lithium plating over-potential is smaller at the separator/anode (sep/an) interface.

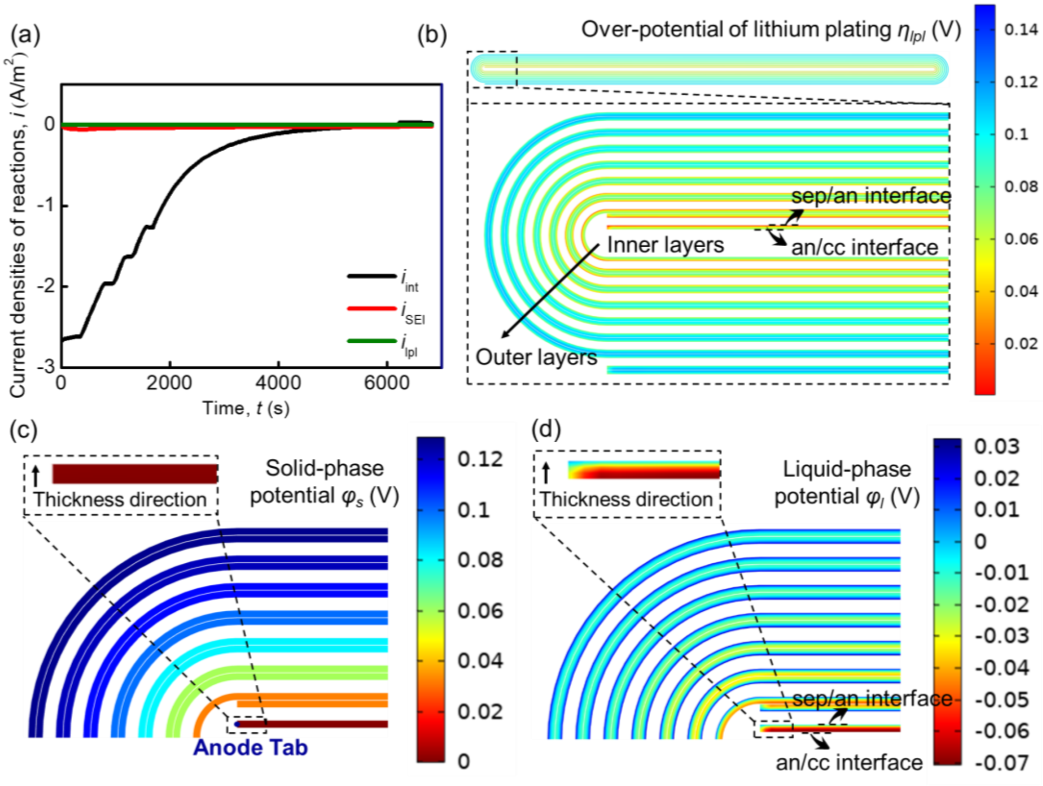

Figure 16 Distribution of the (a) over-potential of lithium plating, (b) solid-phase potential and (c) liquid-phase potential in anode at the charging time t = 350 s.

4.3 Discussion

4.3.1 Effect of design parameters on lithium plating

The thickness of active material on the cathode H_C is parametrically studied from 38.7 to 47.3 μm. The charging time increases with H_C (Figure 17(a)) since larger cathode material mass leads to higher cathode capacity, which determines the battery capacity in the situation of anode excess. During the charging period, the local over-potential reaches the minimum (the risk of lithium plating reaches the highest) at the end of CC charging with 8A (t = 350 s). Therefore, the distribution of the lithium plating over-potential (η_{pla}) in anode at 350 s is worth studying to help analyze the effect of H_C on lithium plating (Figure 17(c)). In all cases, η_{pla} in the inner layers are smaller than those in the outer layers, while η_{pla} at the sep/an interface is smaller than that at the an/cc interface. It indicates that lithium plating is most likely to occur at the sep/an interface of the innermost layer. As mentioned before, the distribution pattern of φ_s is responsible for the smaller η_{pla} in inner layers while the distribution pattern of φ_l along the thickness direction is the main reason for the smaller η_{pla} at the sep/an interface. As H_C increases, the overall distribution pattern of η_{pla} is unchanged while the decreasing φ_s and increasing φ_l contribute to smaller η_{pla}, whereas φ_l plays the primary role. lithium plating occurs at position P in cases of $H_C = 45.15, 47.30\ \mu\text{m}$. The average η_{pla} of the innermost anode layer decreases so that the risk of lithium plating increases with increasing H_C (Figure 17(b)).

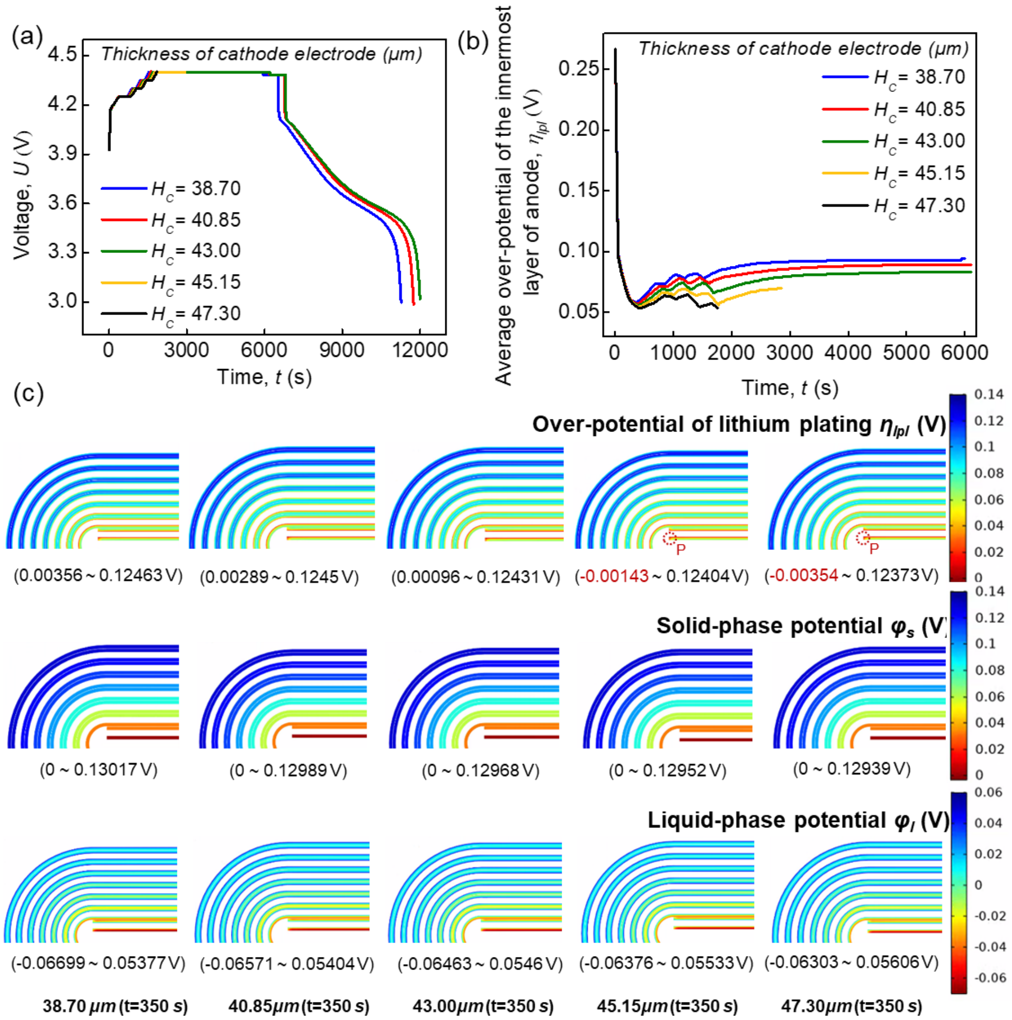

Figure 17 (a) Charge and discharge curves of batteries with different thicknesses of the active material on the cathode; (b) Average lithium plating over-potential of the innermost layer of anode of batteries with different thickness of cathode active material; (c) Distribution and ranges of lithium plating over-potential, solid-phase potential and liquid-phase potential in the anode of batteries with different thickness of cathode active material at the end time of CC charging with 8A;

4.3.2 Effect of material property on lithium plating

The material properties of electrodes and electrolytes can significantly influence the rate of lithium plating reaction [82]. Among all the material properties, the influences of the conductivity of the electrolyte, and diffusivity of Li-ion in cathode and anode electrodes are studied. The conductivity of electrolyte σ_l changes with the range from 0.1 S/m to 10 S/m; the diffusivities of Li-ion in cathode and anode electrode are set from 10^{-15} to 10^{-11} m^2/s and 10^{-14} to 10^{-10} m^2/s, respectively.

The charging time (especially the charging time of CV period) is shortened when increasing D_C, while the change of σ_l and D_A hardly influences the voltage-time curves of the battery (Figure 18(a), (d), (g)). It indicates that the diffusion rate of Li-ions in the cathode limits the overall charging rate of the battery in these cases. The distribution of η_{pla} in the anode (Figure 18(c), (f), (i)) shows that the lithium plating is more likely to occur at the sep/an interface of the innermost layer of the anode, independent of the material properties. The average η_{pla} in the innermost anode layer (Figure 18(b), 5(e), 5(h)) shows that the risk of lithium plating increases while increasing σ_l, D_C and decreasing D_A. Increasing the diffusion rate of Li-ions in the cathode, increasing the conductivity of Li-ions in the cathode, and decreasing the diffusion rate of Li-ions in the anode all contribute to the massive accumulation of Li-ions on the anode/electrolyte interface and finally leads to lithium plating. Indeed, lithium plating occurs at position P in the following cases: $\sigma_l = 5{,}10$ S/m, $D_C = 10^{-13}, 10^{-12}, 10^{-11}$ m^2/s and $D_A = 10^{-14} m^2/s$.

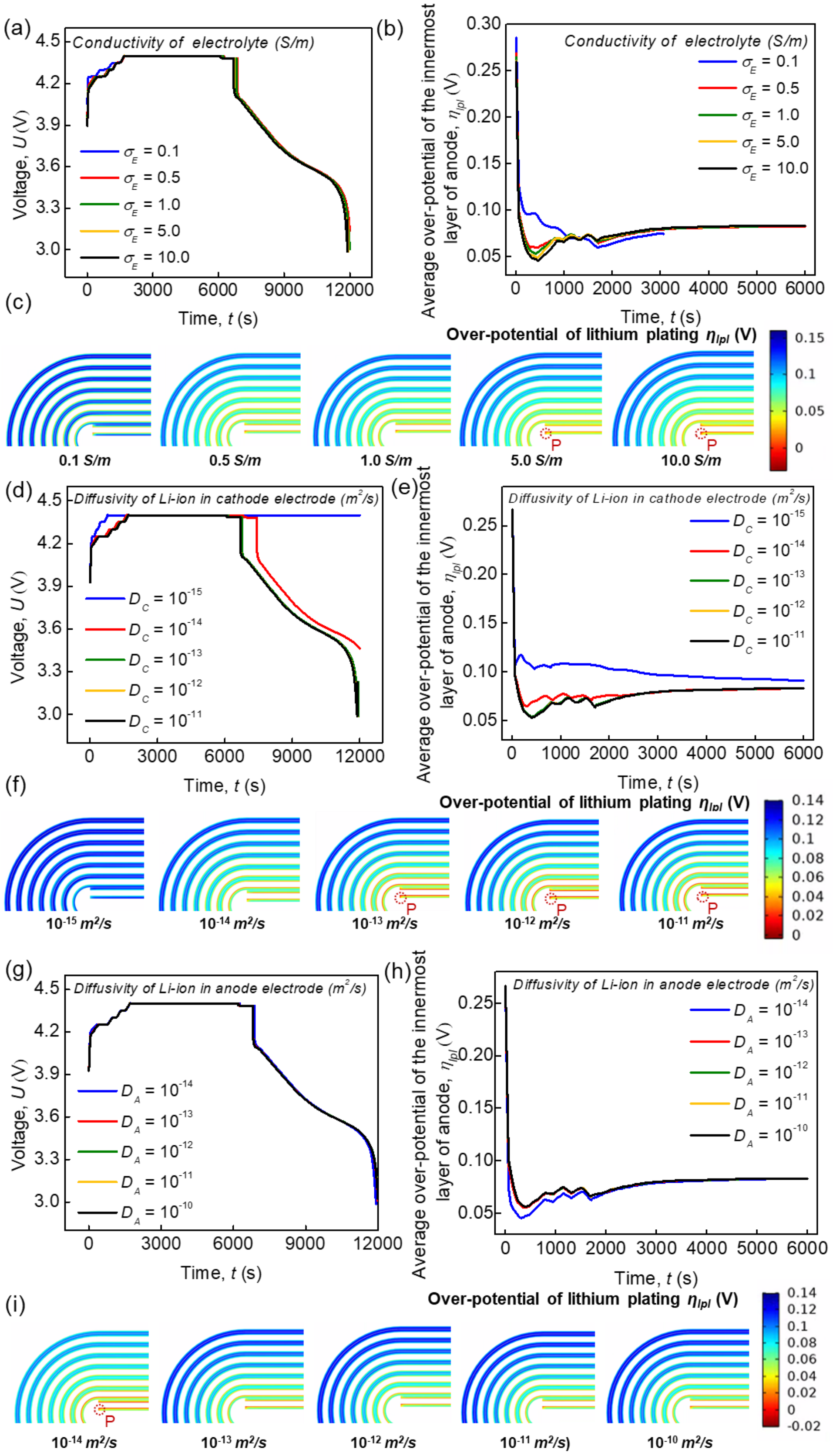
(a)
Conductivity of electrolyte (S/m)
Voltage, U (V)
Time, t (s)
σ_E = 0.1
σ_E = 0.5
σ_E = 1.0
σ_E = 5.0
σ_E = 10.0
(b)
Average over-potential of the innermost layer of anode, η_{lpl} (V)
(c)
Over-potential of lithium plating η_{lpl} (V)
0.1 S/m
0.5 S/m
1.0 S/m
5.0 S/m
10.0 S/m
P
(d)
Diffusivity of Li-ion in cathode electrode (m^2/s)
$D_C = 10^{-15}$
$D_C = 10^{-14}$
$D_C = 10^{-13}$
$D_C = 10^{-12}$
$D_C = 10^{-11}$
(e)
(f)
10^{-15} m^2/s
10^{-14} m^2/s
10^{-13} m^2/s
10^{-12} m^2/s
10^{-11} m^2/s
(g)
Diffusivity of Li-ion in anode electrode (m^2/s)
$D_A = 10^{-14}$
$D_A = 10^{-13}$
$D_A = 10^{-12}$
$D_A = 10^{-11}$
$D_A = 10^{-10}$
(h)
(i)
10^{-14} m^2/s
10^{-13} m^2/s
10^{-12} m^2/s
10^{-11} $m^2/s)$
10^{-10} m^2/s

Figure 18 Charge and discharge curves of batteries with different (a) electrolyte conductivity, (d) diffusivity of Li-ion in cathode electrode and (g) diffusivity of Li-ion in anode electrode; Average lithium plating over-potential of the innermost anode layer with different (b) electrolyte conductivity, (e) diffusivity of Li-ion in cathode electrode and (h) diffusivity of Li-ion in anode electrode; Distribution of lithium plating over-potential in the anode of batteries with different (c) electrolyte conductivity, (f) diffusivity of Li-ion in cathode electrode and (i) diffusivity of Li-ion in anode electrode at the end time of CC charging with 8A (t = 350 s);

4.3.3 Effect of charge protocol on lithium plating

The optimization of the charging protocol can restrain the lithium plating of the anode [82]. Various charging protocols have been proposed (Figure 19(a), 6(d), 6(g)) and carried out to study the influence of charge protocol on lithium plating, including constant current charge (4 modes) and step charge (7 modes) (Table 4).

Table 4 Summary of the charging protocol

Constant current charge				
C rate	0.1C	0.5C	1C	2C
Step charge				
	Upper limited voltage of each constant current phase			
	8 A	6 A	5 A	3.92A
Base	4.25	4.30	4.35	4.40
①	4.23	4.30	4.35	4.40
②	4.27	4.30	4.35	4.40
③	4.25	4.28	4.35	4.40
④	4.25	4.32	4.35	4.40
⑤	4.25	4.30	4.33	4.40
⑥	4.25	4.30	4.37	4.40
⑦*	4.20	4.32	4.27	4.40

Above all, the risk of lithium plating in the innermost layer of the anode becomes higher as C rate increases (Figure 19(a)). For constant current charging with low C rates, η_{pla} is high and even distributed among the entire anode except for the part of the corner (Figure 19(c)). The smaller N/P (capacity ratio of the negative electrode to the positive electrode) at the corner due to geometric factor leads to the massive accumulation of Li-ions (higher concentration of Li-ions) in the liquid phase of anodes at the corner, which contributes to the higher φ_l and finally lower η_{pla} at the corner. For constant current charging with high C rates, lithium plating is more prone to be triggered at the sep/an interface of inner layers (Figure 19(c)). On the one hand, the high C rate increases the sensitivity of φ_s distribution to the anode tab position. The distribution pattern of φ_s is the dominant factor leading to the lower η_{pla} in the inner layers. On the other hand, massive Li-ions accumulate on the anode/separator interface at high C rates (Figure 19(c)) due to the significant difference between the diffusion rates of Li-ion in graphite and electrolyte, the higher c_l (concentration of Li-ions) leads to higher φ_l and finally lower η_{pla} at the sep/an interface.

For step charge, the effect of the upper-limited voltage of each constant current phase on lithium plating is discussed. The upper-limited voltages of three CC charging stages are adjusted respectively (charging modes ①~⑥) (Figure 19(d)). The distribution pattern of η_{pla} (Figure 19(f)) indicates that lithium plating is more obvious in the inner layers under these six charging protocols. It is interesting that the risk of lithium plating increases when raising the upper-limited voltage of CC charging with 8A (Figure 19(e)). The extended stage of CC charging with 8A leads to a lower minimum η_{pla} during the whole charging process.

Based on the results, charge mode ⑦* is proposed to suppress lithium plating by shortening the stage of CC charging with 8A. Compared to the basic charge mode, the upper limited voltages of the high-rate charging step are reduced, and the upper-limited voltages of the low-rate charging step are raised in ⑦*. According to the distribution pattern of η_{pla} (Figure 19(i)), lithium plating is more obvious in the inner layers under mode ⑦*, and the battery has a lower risk of lithium plating when charged under ⑦* overall.

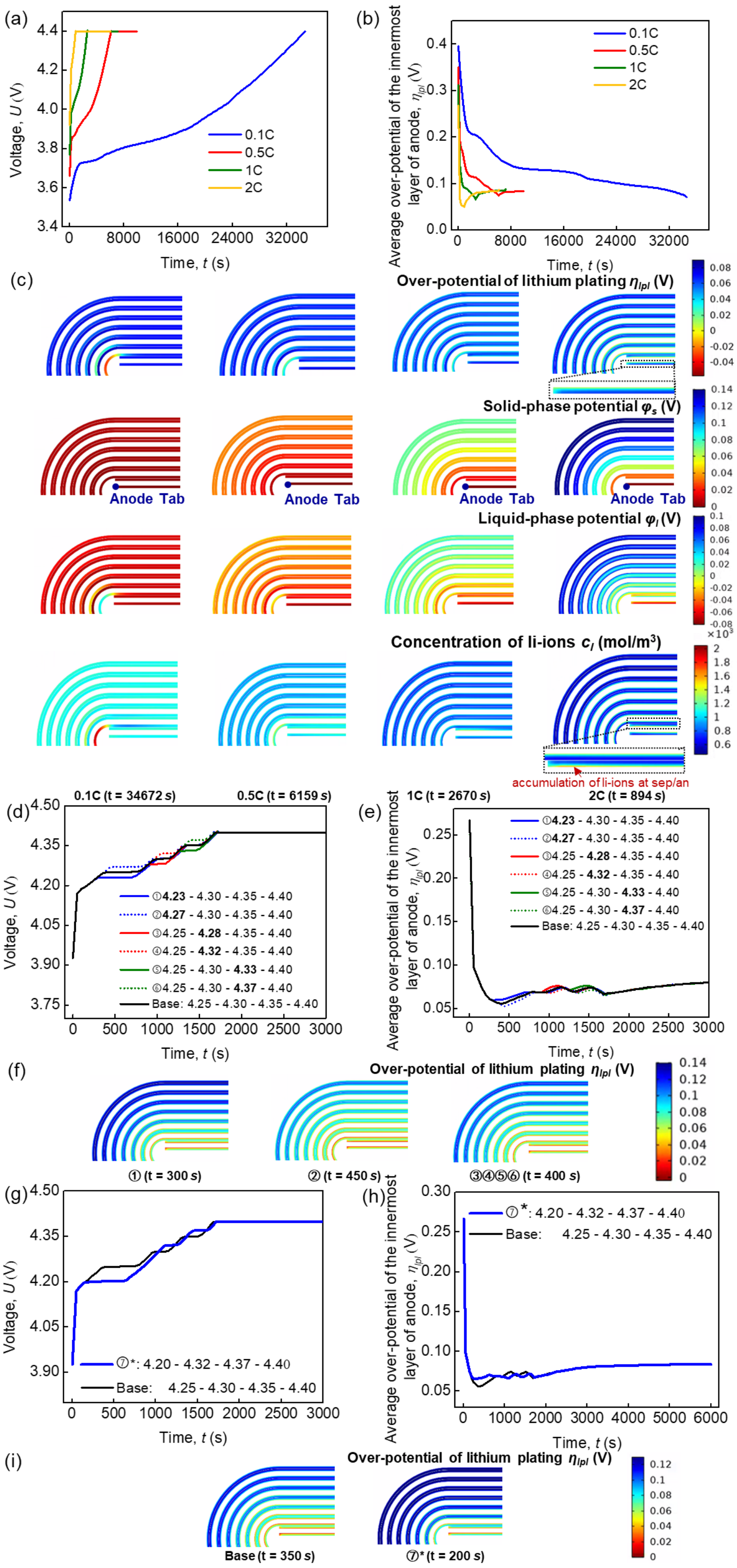
(a)
Voltage, U (V)
Time, t (s)
0.1C
0.5C
1C
2C
(b)
Average over-potential of the innermost layer of anode, η_{lpl} (V)
Time, t (s)
0.1C
0.5C
1C
2C
(c)
Over-potential of lithium plating η_{lpl} (V)
Solid-phase potential φ_s (V)
Anode Tab
Liquid-phase potential φ_l (V)
Concentration of li-ions c_l (mol/m^3)
×10^3
accumulation of li-ions at sep/an
0.1C (t = 34672 s)
0.5C (t = 6159 s)
1C (t = 2670 s)
2C (t = 894 s)
(d)
Voltage, U (V)
Time, t (s)
①4.23 - 4.30 - 4.35 - 4.40
②4.27 - 4.30 - 4.35 - 4.40
③4.25 - 4.28 - 4.35 - 4.40
④4.25 - 4.32 - 4.35 - 4.40
⑤4.25 - 4.30 - 4.33 - 4.40
⑥4.25 - 4.30 - 4.37 - 4.40
Base: 4.25 - 4.30 - 4.35 - 4.40
(e)
Average over-potential of the innermost layer of anode, η_{lpl} (V)
Time, t (s)
(f)
Over-potential of lithium plating η_{lpl} (V)
① (t = 300 s)
② (t = 450 s)
③④⑤⑥ (t = 400 s)
(g)
Voltage, U (V)
Time, t (s)
⑦*: 4.20 - 4.32 - 4.37 - 4.40
Base: 4.25 - 4.30 - 4.35 - 4.40
(h)
Average over-potential of the innermost layer of anode, η_{lpl} (V)
Time, t (s)
⑦*: 4.20 - 4.32 - 4.37 - 4.40
Base: 4.25 - 4.30 - 4.35 - 4.40
(i)
Over-potential of lithium plating η_{lpl} (V)
Base (t = 350 s)
⑦* (t = 200 s)

Figure 19 Charge curves of batteries (a) with different C rates, (d) with different upper limited voltages of CC charge stages in step charge (g) with charging mode ⑦*; Average lithium plating over-potential of the innermost layer of the anode (b) with different C rates, (e) with different upper limited voltages of CC charge stages in step charge (h) with charging mode ⑦*. (c). Distribution of lithium plating over-potential, solid-phase potential, liquid-phase potential, and concentration of Li-ions with different C rates at the end time of CC charging; Distribution of lithium plating over-potential (f) with different upper limited voltages of CC charge stages in step charge and (i) with charging mode ⑦* at the end time of CC charging with 8A;

4.3.4 Effect of tab arrangement on lithium plating

By changing the position and number of the cathode and anode tabs, the effect of tab arrangements on the lithium plating are studied (Figure 20). The tabs move from inner layers to outer layers as the position changes from P1 to P4. Table 5 shows the different arrangements of tabs.

Table 5 Summary of the tab arrangement

Type	Case (cathode tab position_anode tab position)			
Changing cathode tab position	P1_P1	P2_P1	P3_P1	P4_P1
Changing anode tab position	P1_P1	P1_P2	P1_P3	P1_P4
Changing Cathode & Anode tab position	P1_P1	P2_P2	P3_P3	P4_P4
Multiple Cathode & Anode tabs	P1_P1	P3_P1P4	P1P4_P3	P1P4_P1P4

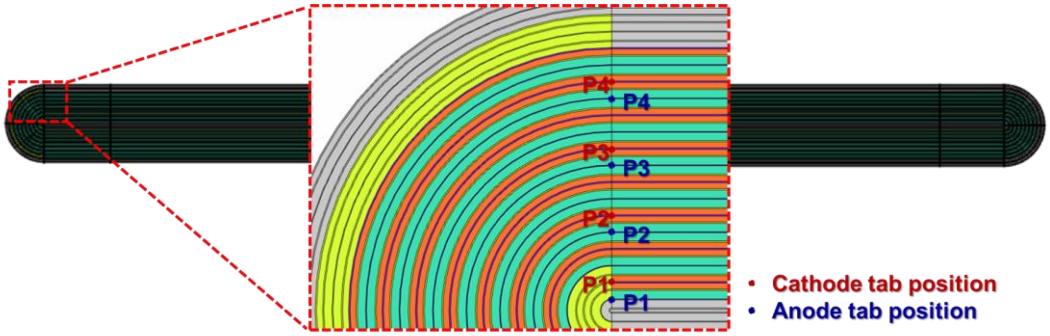

Figure 20 Available positions for cathode and anode tabs in 2D model.

The influence of the cathode tab position on lithium plating is investigated by changing the cathode tab position from P1 to P4, while the anode tab is maintained at P1. The charging time tends to be shorter when the cathode tab moves from P1 to P4 (Figure 21(a)), and changing the position of the cathode tab obviously influences the distribution of η_{pla} (Figure 21(b)). When cathode and anode tabs are both located at the innermost P1, lithium plating is more likely to occur in the inner layers. As the cathode tab moves outward and the anode tab remains unchanged, the risk of lithium plating in the inner layers decreases while that of the outer layers increases (however, the risk in the inner layer is always higher than the outer layers). For the case of P4_P1, the even distribution of η_{pla} indicates the consistent risks of lithium plating in the inner and outer layers. As mentioned before, the distribution of η_{pla} among anode is the result of the interaction of φ_s and φ_l. Further analysis reveals that the distribution of φ_s in the anode is determined by anode tab position which remains unchanged in these cases, while the distribution of φ_l in the anode is slightly influenced by outward-moving cathode tab. In the case of P4_P1, the unevenly distributed φ_s and φ_l lead to evenly distributed η_{pla} .The average η_{pla} curves of the innermost layer of the anode show that the risk of lithium plating in the innermost anode layer gradually decreases as the cathode tab moves from inner layers to outer layers (P1 to P4) (Figure 21(c)).

Besides, the results of the parametric study for different anode tab positions are shown in Figure 21(d-f). As the anode tab moves outward while the cathode tab remains unchanged, the uneven distribution of η_{pla} gradually changes into an even distribution. It can be observed that the distribution of φ_s in the anode changes with outward-moving anode tab, and the distribution of φ_l in the anode is also influenced by outward-moving anode tab. Compared with the cathode tab position (Figure 21(b)), the anode tab position (Figure 21(e)) dominates the distribution of φ_s and φ_l. For cases with anode tab in P1 and P2, both φ_s and φ_l increase with the increase of layer number of the winding structure. For cases with anode tab in P4, both φ_s and φ_l decrease with increasing layer number.

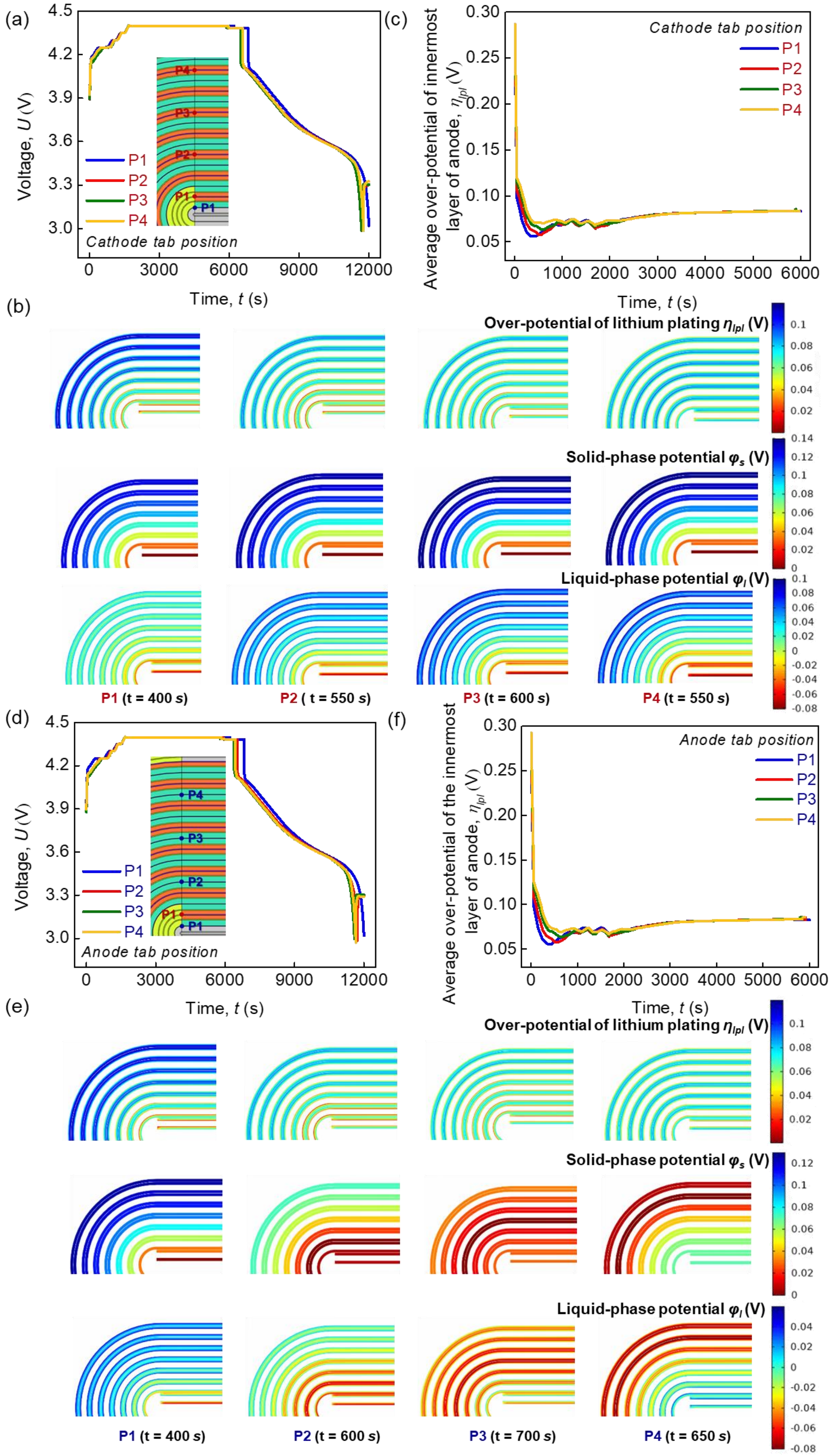
(a)
Voltage, U (V)
Time, t (s)
P1
P2
P3
P4
Cathode tab position
(c)
Average over-potential of innermost layer of anode, η_{lpl} (V)
Time, t (s)
Cathode tab position
P1
P2
P3
P4
(b)
Over-potential of lithium plating η_{lpl} (V)
Solid-phase potential φ_s (V)
Liquid-phase potential φ_l (V)
P1 (t = 400 s)
P2 (t = 550 s)
P3 (t = 600 s)
P4 (t = 550 s)
(d)
Voltage, U (V)
Time, t (s)
P1
P2
P3
P4
Anode tab position
(f)
Average over-potential of the innermost layer of anode, η_{lpl} (V)
Time, t (s)
Anode tab position
P1
P2
P3
P4
(e)
Over-potential of lithium plating η_{lpl} (V)
Solid-phase potential φ_s (V)
Liquid-phase potential φ_l (V)
P1 (t = 400 s)
P2 (t = 600 s)
P3 (t = 700 s)
P4 (t = 650 s)

Figure 21 Charge and discharge curves of batteries with (a) different cathode tab positions (d) different anode tab positions; Distribution of lithium plating over-potential, solid-phase potential and liquid phase potential in anode with (b) different cathode tab positions, (e) different anode tab positions at the end time of CC charging with 8A; Average lithium plating over-potential of the innermost layer of anode of batteries with (c) different cathode tab positions (f) different anode tab positions;

In addition, the cases of changing cathode and anode tabs simultaneously are discussed (Figure 22). It can be observed that the charging time tends to be shorter when the cathode and anode tabs both move from P1 to P4. In P1_P1 case, the risk of lithium plating is higher in the inner layers. As the cathode and anode tabs move outward simultaneously (P1 to P4), the risk of lithium plating in the inner layers and outer layers respectively decreases and increases. In P4_P4 case, the risk of lithium plating in the outer layers is higher than inner layers. The average η_{pla} curves show that the risk of lithium plating in the innermost layer of the anode gradually decreases as the positions of the cathode and anode tabs move from the inner layer to the outer layer at the same time.

Finally, considering the actual situation in industry manufacturing, the cases of multiple cathode and anode tabs are discussed (Table 5) (Figure 22). Among all the cases, the charging time is shortest in the case of P1P4_P1P4, i.e., two cathode tabs are respectively located at P1P4, and two anode tabs are respectively located at P1P4. According to the η_{pla} distribution of all cases, the six cases can be divided into two categories: P1_P1, P1P4_P1, P1_P1P4, and P1P4_P1P4, P3_P1P4, P1P4_P3. For the first category, the cathode and anode tabs are not distributed symmetrically with respect to the middle layer. As a result, the distributions of η_{pla} are uneven. Taking the case of P1P4_P1, for example, the cathode tabs are symmetrically located at P1 and P4, but the anode tab is located at the innermost P1. Therefore the lithium plating is more likely to take place in the inner layers. The distribution of η_{pla} is uniform, and the risk of lithium plating is low for the entire anode due to the symmetric distribution of the tabs. The average η_{pla} curves show that the risk of lithium plating in the innermost layer of the anode is lowest in the cases of P3_P1P4 and P1P4_P3.

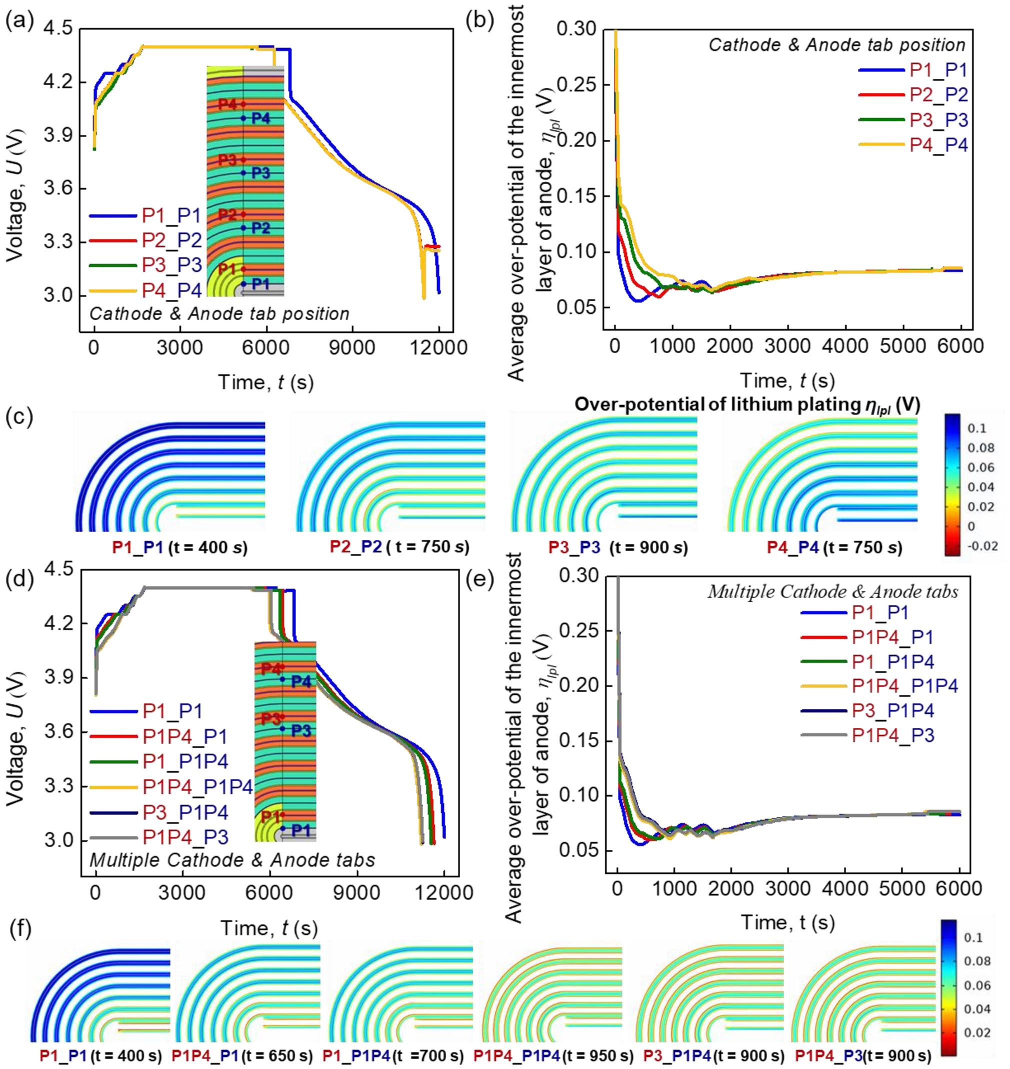

Figure 22 Charge and discharge curves of batteries with (a) different cathode & anode tab positions and (d) multiple cathode & anode tabs; Average lithium plating over-potential of the innermost layer of anode of batteries with (b) different cathode & anode tab positions and (e) multiple cathode & anode tabs; Distribution of lithium plating over-potential in anode of batteries with (c) different cathode & anode tab positions and (f) multiple cathode & anode tabs at the end time of CC charging with 8A;

4.4 Conclusion

In this study, a 2D model considering the actual winding structure of the battery is established to investigate the distribution of lithium plating risk within the winding structure in a cell. The model is validated based on the voltage-time curves of charging experiments with different rates. The analysis of lithium plating current density and lithium plating over-potential at different layers illustrates that lithium plating tends to occur in the inner layers of the battery. Further research on lithium plating is conducted by the parametric study of the numerical model. The relationship between the risk of lithium plating and vital design parameters is clarified. In conclusion, the distribution of η_{pla} among anode is the result of the interaction of φ_s and φ_l. Whereas the distribution of φ_s in the anode is dominated by anode tab position, especially in cases of high C rates, and the distribution of φ_l in the anode is dominated by c_l distribution in the anode which can be affected by other factors including cathode active material thickness, material properties, charging rate and tab position. According to the results, appropriate design and use of the battery is proposed to reduce the risk of lithium plating which can be summarized as follows:

(1) Decreasing the cathode thickness, the conductivity of the electrolyte, diffusivity of Li-ion in the cathode;

(2) Increasing the diffusivity of Li-ion in anode;

(3) Adopting the charge protocol mode I;

(4) Adopting appropriate tab arrangements under which the tabs are symmetrically distributed with respect to the middle layer.

This study mainly focuses on the influence of battery design parameters on lithium plating, to guide the safety of battery designs. Results establish a mechanistic model for describing the lithium plating at the cell level and provide powerful tools for designing the next-generation long cycle-life batteries.

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CHAPTER 5 CONCLUDING REMARKS

In this work, we developed a comprehensive study of the lithium plating reaction in lithium-ion batteries. Firstly, we prepared the Graphite/Li coin cells and selected the cells with consistent and reliable electrochemical performance for the experiments of lithium plating onset detection. The onset range of lithium plating on graphite electrodes was determined through a comprehensive experimental investigation including voltage analysis and morphology analysis. By comparing the experimental results of Graphite/Li coin cells with different discharging capacities, the precise localization of the lithium plating onset was determined within a narrow range. Besides, the negative graphite voltage at the lithium plating onset indicates that Li concentration in graphite needs to be considered as the indicator of lithium plating instead of graphite voltage. Furthermore, electrochemical models incorporating different lithium plating criteria (potential criterion and concentration criterion) were developed to further determine the precise onset of lithium plating and interpret the mechanism governing the occurrence of lithium plating. The comparative analysis revealed that the model with concentration criterion was more suitable to predict the lithium plating onset than the model with potential criterion, especially under conditions of high C-rates. Based on the model with concentration criterion, optimized discharging protocols were proposed considering both the restraint of lithium plating and the enhancement of discharging efficiency. Finally, we extend the 1D electrochemical model into 2D physics-based model considering the distribution of lithium plating in the actual winding structure of pouch cells. The model was validated and the results of lithium plating current density and lithium plating over-potential at different layers indicated that lithium plating was more likely to occur in the inner layers of the battery. A parametric study was conducted based on the validated 2D physics-based model to clarify the relationship between lithium plating distribution and vital battery parameters including electrochemical properties of the materials, tab arrangement, and charge protocols. According to the results, appropriate strategies of cell design were proposed to mitigate lithium plating among the winding structure of the battery.

This work provided a comprehensive and deep understanding of lithium plating including the onset detection method, mechanism, modeling, and mitigation strategies. The related experimental and modeling methods also provide an innovative solution for onset detection, mechanism evaluation, and mitigation of lithium plating.

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APPENDIX A: Preparation Procedure and nominal capacity of CR2032 Coin Cells

A. Preparation Procedure of CR2032 Coin Cells:

The CR2032 Coin Cells are assembled in glove box in argon atmosphere with graphite as the working electrode, an ample Li plate as the counter electrode and 1.0 M LiPF6 /EC+PC+EDC (1:1:1) as the electrolyte. The detail preparation procedure is decribed as follows:

(1) Wash the spring, spacer, positive and negative caps with ethanol by ultrasonic cleaning. Then the components are heated and dried in the vacuum drying oven

(2) Cut the copper sheet coated with sigle side graphite into round tablets with a diameter of 12 mm. The tablets without graphite debonding were picked out as working electrodes, they were heated and dried in the vacuum drying oven at 80°C for 4 hours.

(3) Cut the Celgard 2400 seperator into round tablets with a diameter of 16 mm.

(4) Transfer all components of Graphite/Li coin cells into the glove box. During the assembly process, the water content and oxygen content in the glove box need to be less than 0.01 ppm to keep the Li plates from being oxidized and nitrided.

(5) Li plates need to be stored in an oxygen-free and nitrogen-free environment, the well-stored Li plates with silver surface can directly serve as counter electrodes. If there is an oxide layer on the surface of Li plate, it is necessary to scrape off the oxide layer at first. Then the Li plates with silver surface can be adopted.

(6) Assemble the coin cells in the following order: negative cap, Li plate, electrolyte (20

µL), seperator, electrolyte (20 µL), graphite (copper side up), spring, spacer and positive cap.

(7) Transfer the coin cell onto the sealing machine with the negative cap side up. The coin cell was sealed with the pressure of 50 kg/cm^2.

B. Nominal capacity of CR2032 Coin Cells

The nominal capacity of the Graphite/Li cells Q_n was calculated from the materials loading of the graphite electrode as follows:

$$\begin{aligned} Q_n &= (m_{ge} - \sigma_{cc} S_{cc})\omega\psi \\ &= (14.5mg - 7.3mg/cm^2 \times 1.13cm^2) \times 95.7\% \times 340mAh/g = 2.03mAh \end{aligned} \tag{A1}$$

where m_{ge} represents the mass of the graphite electrode, σ_{cc} and S_{cc} denote the surface mass density and surface area of the current collector of the graphite electrode, ω is defined as the mass fraction of the active material, ψ represents the capacity per unit weight of the active material.

APPENDIX B: Procedure to obtain the solid phase diffusion coefficient

The solid phase diffusion coefficient D_s of the graphite electrode was obtained from the GITT (Galvanostatic Intermittent Titration Technique) tests (Table 6) [66] on the experimental Li/Graphite cells. Firstly, the cell was charged at 0.1C to the cut-off voltage of 1 V and rested for 2 h. Then, the cell underwent 36 cycles which consisted of the discharge at 0.1C for 20 min and rest for 2 h. The voltage-time curves during the overall cycling process and a single GITT step are shown in Figure 23 (a-b). According to the values of ΔE_t and ΔE_s obtained from each GITT step (Figure 23 (b)), the solid phase diffusion coefficient D_s at this SOC can be calculated as follows:

$$D_s = \frac{4}{\pi\tau}\left(\frac{n_m V_m}{S}\right)\left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \tag{B1}$$

where τ is denoted as the galvanostatic current pulse time, n_m and V_m represent the molar number and molar volume of graphite, S is the area of the electrode-electrolyte interface. ΔE_s represents the variation of the steady-state voltage after a single GITT step, while ΔE_t is the variation of the voltage during a galvanostatic current pulse. Finally, the calculated D_s as the function of average SOC (Figure 23 (c)) can serve as the input parameter in the model.

Table 6 Experimental procedure to obtain the solid phase diffusion coefficient

Number	Step	Value	Cut-off voltage/Time
1	Charge	0.1C	1 V
2	Relaxation	/	2 h
3	Discharge	0.1C	20 min
4	Relaxation	/	2 h
5	Cycle	3 and 4	36 times

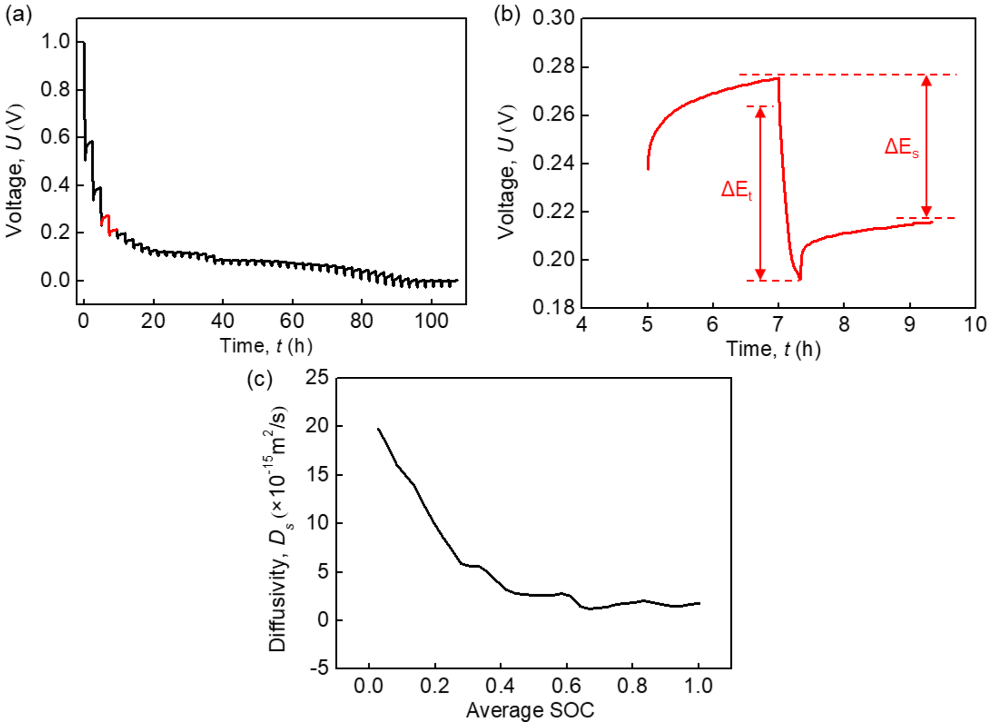

Figure 23 The voltage-time curves during the (a) overall cycling process and (b) a single GITT step. (c) the calculated solid phase diffusion coefficient as the function of average SOC;

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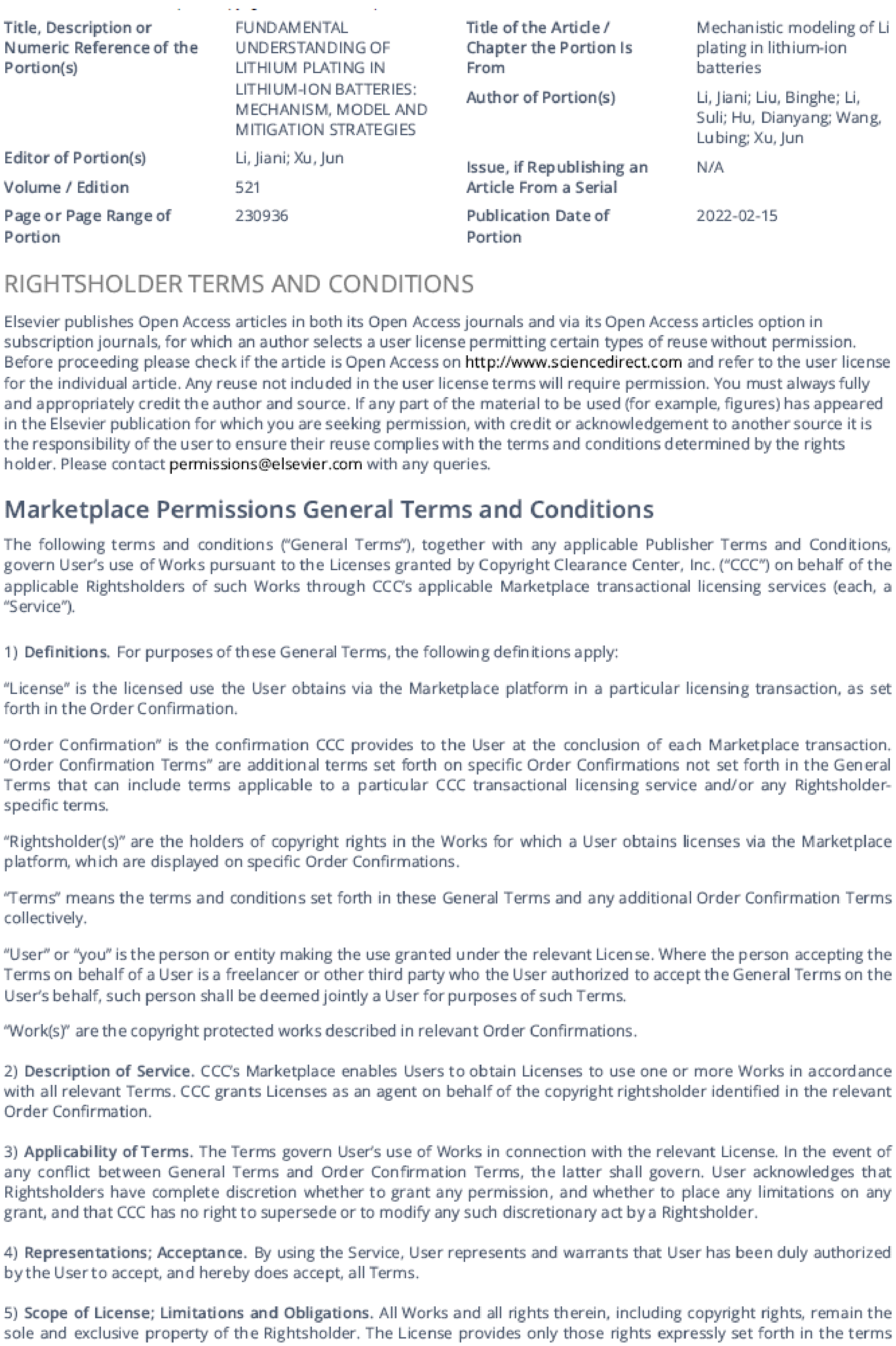

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Editor of Portion(s)	Li, Jiani; Xu, Jun	**Author of Portion(s)**	Li, Jiani; Liu, Binghe; Li, Suli; Hu, Dianyang; Wang, Lubing; Xu, Jun
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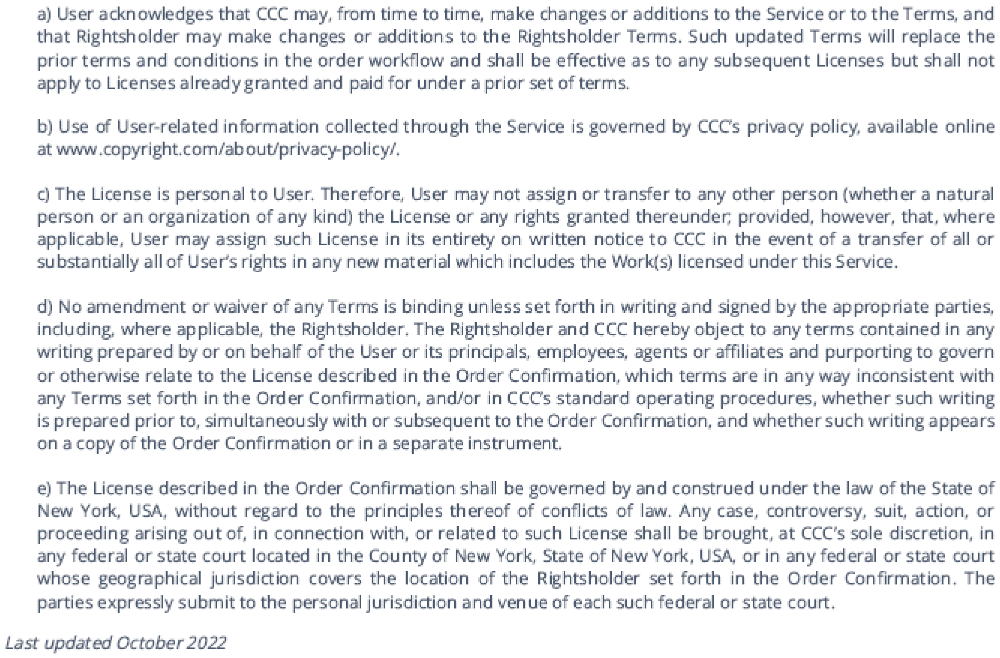

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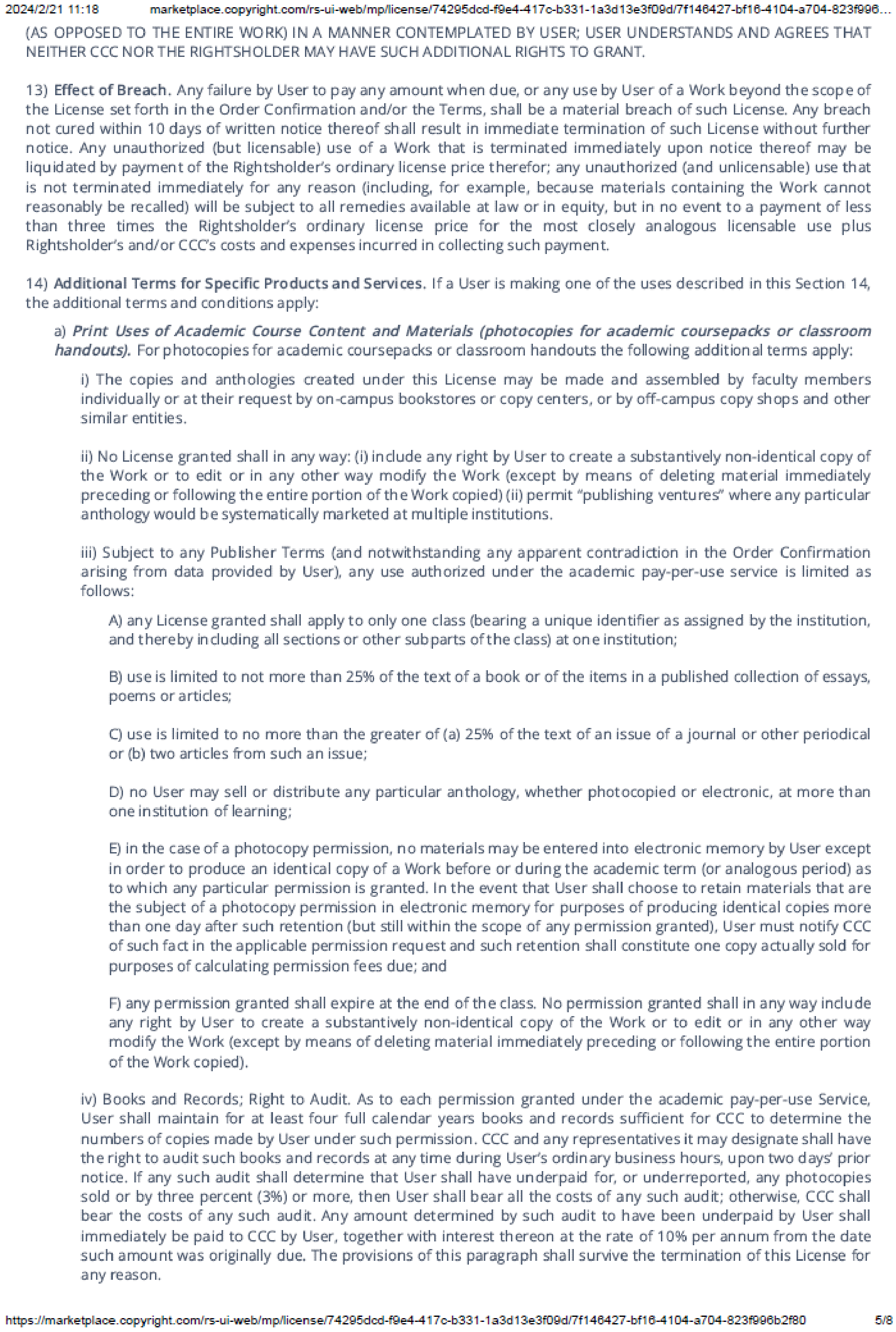

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