Supplementary information

1. Nominal capacity of Graphite/Li cells

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

$$\begin{aligned} Q_n &= (m_{ge} - \sigma_{cc} S_{cc})\omega\psi \\ &= (14.5mg - 7.3mg/cm^2 \times 1.13cm^2) \times 95.7\% \times 340mAh/g = 2.03mAh \end{aligned} \tag{1}$$

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.

2. Model with concentration criterion

2.1. Model parameters

The equilibrium potential of intercalation $E_{eq,int}$ on the graphite electrode (Figure S1. (a)) was obtained from the discharging test conducted on Graphite/Li cells at 0.01C (Figure S1. (b)).

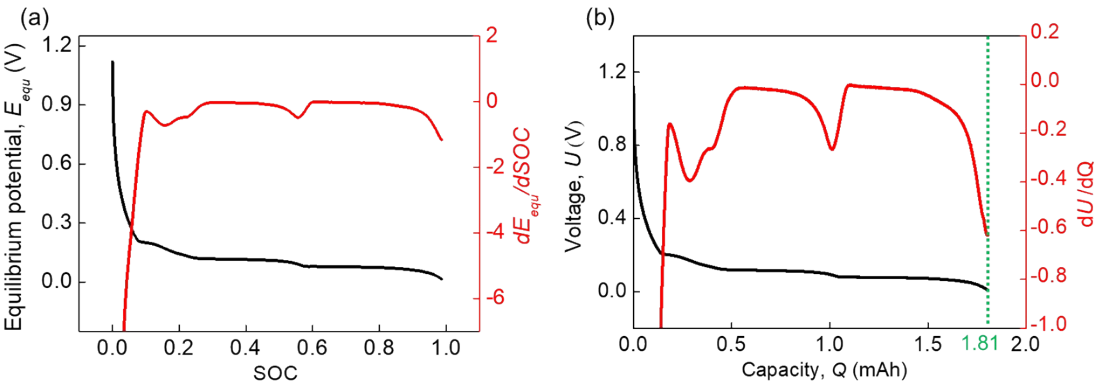

Figure S1. (a) Equilibrium potential of intercalation on graphite and its differential curve (b) Voltage and its differential curve during the discharging test of Graphite/Li cells at 0.01C to

1.81 mAh;

The solid phase diffusion coefficient D_s of the graphite electrode was obtained from the GITT (Galvanostatic Intermittent Titration Technique) tests (Table S1) [1] 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 S2 (a-b). According to the values of ΔE_t and ΔE_s obtained from each GITT step (Figure S2 (b)), the solid phase diffusion coefficient D_s at this SOC can be calculated as follows:

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

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 S2 (c)) can serve as the input parameter in model.

Table S1. 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

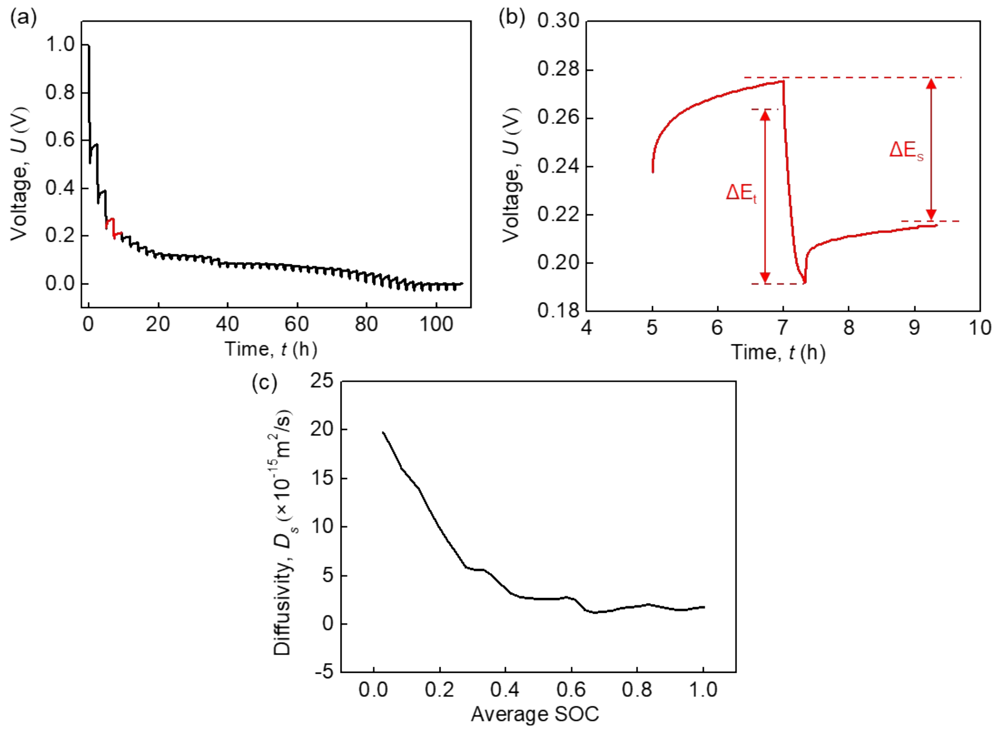

Figure S2. The voltage-time curves during the (a) overall cycling process and (b) a single GITT step. (c) the calculated solid phase diffusion coefficient as the function of average SOC;

Compared to the model with potential criterion, the expression of Δc_s needs to be modified in model with concentration criterion to avoid the computational conflict. As shown in Figure S2, the general expression of Δc_s in model with potential criterion is $\Delta c_s = c_{s,max} - c_{s,surf}$ (black line). 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 increasement of η_{int}, which will finally result in the non-convergence of the model. When applied with concentration criterion, 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 $\Delta c_s = \min\left\{\max\left[\left(c_{s,max} - c_{s,surf}\right), c_{s1}\right], c_{s2} - c_{s,surf}\right\}$. As depicted in Fig. S2, 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.

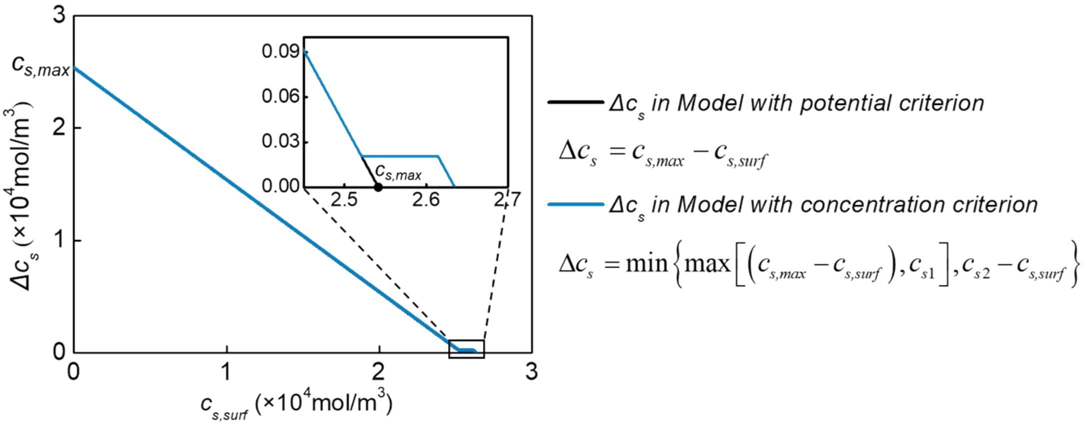

Figure S3. The comparison of Δc_s as function of c_{s_surf} between model with concentration criterion and model with potential criterion.

The key parameters applied in the model with concentration criterion are listed in Table S2.

Table S2. Key parameters of the model.

Symbol	**Parameter**	**Unit**	**Value**
	Li intercalation		
ε_l	Electrolyte phase volume fraction		44.4%

ε_s	Solid phase volume fraction		38.3%
σ_s	Solid phase conductivity	S/m	100
R	Particle radius	m	5e-6
$\alpha_{a,int}$	Anodic charge transfer coefficient		0.5
$\alpha_{c,int}$	Cathodic charge transfer coefficient		0.5
	Li plating		
k_{pla}	Kinetic rate constant	m/s	7e-10 [ad]
$c_{s.max}$	Maximum Li concentration in solid phase	mol/m^3	25414
$c_{s.1}$	Li concentration parameter	mol/m^3	205.9[ad]
$c_{s.2}$	Li concentration parameter	mol/m^3	26350 [ad]
$\alpha_{c,pla}$	Anodic charge transfer coefficient of Li plating		0.5
$E_{eq,pla}$	Equilibrium voltage of Li plating	V	0
M_{pla}	Molar mass of metallic Li	kg/mol	6.94e-3
ρ_{pla}	Density of metallic Li	kg/m^3	534

[ad] Adjusted

3. Model with potential criterion

3.1. Critical governing equations

Compared to the model with concentration criterion, the overpotential of lithium plating was adopted as indicator in the model with potential criterion. Specifically, the volumetric current density of lithium plating j_{pla} is expressed by the Butler-Volmer equation while the expression for exchange current density of lithium plating $i_{0,pla}$ indicates that lithium plating occurs when the over-potential of lithium plating η_{pla} drops below 0 V (potential criterion).

$$j_{pla} = a_s i_{0,pla}\left[\exp\left(\frac{\alpha_{a,pla}F\eta_{pla}}{RT}\right) - \exp\left(-\frac{\alpha_{c,pla}F\eta_{pla}}{RT}\right)\right] \tag{3}$$

$$i_{0,pla} = Fk_{pla}c_l \;\left(\eta_{pla} \leq 0\right) \tag{4}$$

$$\eta_{pla} = \varphi_s - \varphi_l - E_{eq,pla} - \frac{j_{total}}{a_s}R_{film} \tag{5}$$

Besides, the volumetric current density of lithium intercalation j_{int} is also expressed by the Butler-Volmer equation:

$$j_{int} = a_s i_{0,int}\left[\exp\left(\frac{\alpha_{a,int}F\eta_{int}}{RT}\right) - \exp\left(-\frac{\alpha_{c,int}F\eta_{int}}{RT}\right)\right] \tag{6}$$

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

$$i_{0,int} = Fk_{int}c_{s,surf}^{\alpha_{c,int}}\Delta c_s^{\alpha_{a,int}}\left(\frac{c_l}{c_{l,ref}}\right)^{\alpha_{a,int}} \tag{7}$$

$$\Delta c_s = c_{s,max} - c_{s,surf} \tag{8}$$

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

$$\eta_{int} = \varphi_s - \varphi_l - E_{eq,int} - \frac{j_{total}}{a_s}R_{film} \tag{9}$$

3.2. Results

The results of model with potential criterion are shown in Fig. S3. For cases with low C-rates (0.1C and 0.2C), the simulated onsets of lithium plating correspond to the actual onsets of lithium plating which are denoted as valley points on the experimental dU/dt_t curves ($t'_M \approx t_E$). For case with high C-rate of 0.5C, the simulated onset of lithium plating in this case is obviously prior to the actual onset of lithium plating ($t'_M < t_E$), which means that the potential criteria of lithium plating is not applicable for high C-rate. Beisdes, comparing to the experimental dU/dt_t curve, there exists additional oscillations at around t'_M on computed dU/dt_t curve which are caused by the lithium plating triggered in advance, which further demonstrates the inaccuracy of model with potential criterion.

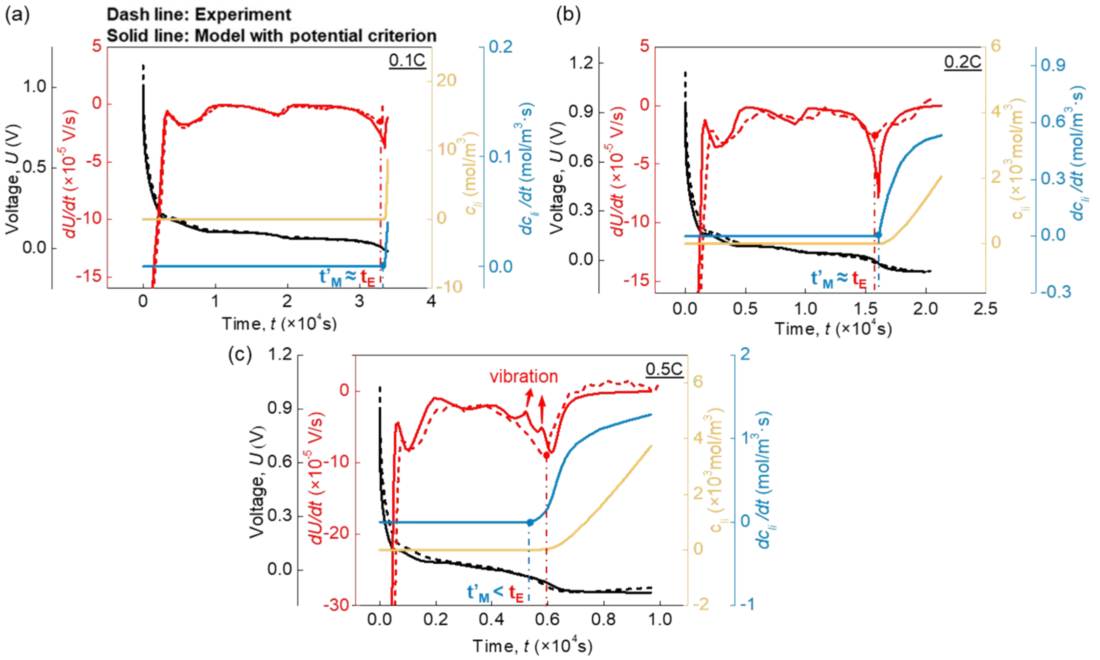

Figure S4. The comparison of results between the model with potential criterion and overdischarging tests at (a) 0.1C, (b) 0.2C, and (c) 0.5C.

Reference

1 W. Mei, L. Jiang, C. Liang, J. Sun and Q. Wang, *Energy Storage Materials*, 2021, **41**, 209-221.