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Supplementary Information

Revealing the onset condition of Li plating on graphite electrodes

under fast-charging

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Testing protocols

Table S1

No	Step	Operating Value	Cut-off Condition
1	Formation		
1-1	Discharging	C/10	0.005 V
1-2	Resting	30 min	
1-3	Charging	C/5	1.5 V
1-4	Resting	30 min	
1-5	Repeating 1-(1-4)		3 times
2	Pre-cycle		
2-1	Discharging	1C	Specific DOD
2-2	Resting	30 min	
2-3	Charging	C/5	1.5 V
2-4	Resting	30 min	
3	Li plating test		
3-1	Discharging	1C, 2C, 3C, 4C	Specific DOD
3-2	Resting	30 min	
3-3	Charging	C/5	1.5 V
3-4	Resting	30 min	

Testing protocols of graphite-Li cells in Li plating tests.



Figure S1 Voltage and current curves of a graphite-Li cell with an areal capacity of 2.2 mAh/m² in the Li plating tests at 2C. The graphite electrode displays a specific capacity of about 350 mAh/g

according to the last cycle of formation.



Figure S2 Cycling tests of graphite SLPEs and porous electrodes at 0.5C. a, SLPE-based half cell (graphite-Li, 0.09 mAh/cm²). b, Pouch full cell (NMC532-graphite, 2.2 mAh/m²).

Results of Coulombic efficiency



Figure S3 Validation of dOCV method via CE analysis. CE results compared with the dOCV curves of the graphite-Li half cells with an areal capacity of 2.2 mAh/cm² tested at 2C (a,b), 3C (c,d), and 4C (e,f), respectively. The CE at the pre-cycle step can be regarded as a baseline of CE evolution without Li plating.

Calculation of electrolyte overpotential

To estimate the electrolyte overpotential of SLPE-based cells, we divide the electrolyte overpotential into the separator part and the SLPE part. The areal capacity of graphite SLPEs is set to be 100 μ Ah/cm², hence the areal current density at 4C rate is 400 μ A/cm². From the manufacturer, the separator thickness is 25 μ m, the porosity is 0.41 with a tortuosity of about 2 [1], and the ionic conductivity is 0.724 S/m. The thickness between the separator and the current collector is assumed to be 10 μ m, and the porosity is approximately set to be 1 with the tortuosity equal to 1. By ignoring the concentration polarization in such a short distance for mass transport, the electrolyte overpotential can be calculated by

$$\eta_l = \frac{i_a L_{sep} \tau_{sep}}{\kappa_0 \varepsilon_{sep}} + \frac{i_a L_{SLPE}}{\kappa_0}$$
(S1)

equaling 0.0007 V.

Mathematical model of Li plating/stripping on graphite electrodes

The electrochemical model of graphite-Li cells with conventional porous electrodes (~2.2 mAh/cm²) is developed based on Newman's porous electrode theory, the basic assumptions of which have been detailed in our previous work [1, 2]. The mass/charge conservation equations and boundary conditions are briefly given below, and the modeling of Li plating/stripping kinetics is elaborated.

In the solid phase of graphite particles, the Li⁺ diffusion process is described by:

$$\frac{\partial c_s}{\partial t} = D_s \left(\frac{\partial^2 c_s}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial c_s}{\partial r} \right)$$
(S2)

The potential distribution on the solid phase of the porous electrode is governed by:

$$-\sigma_{eff} \frac{\partial^2 \phi_s^{gr}}{\partial x^2} = a_s F i_{ct}^{gr}$$
(S3)

The transport process of Li⁺ ions in the liquid phase (electrolyte) is governed by:

$$\varepsilon \frac{\partial c_l}{\partial t} = \frac{\partial}{\partial x} \cdot \left(D_{l,eff} \frac{\partial c_l}{\partial x} \right) + \frac{(1 - t_+) a_s i_{ct}^{gr}}{V_+}$$
(S4)

The potential distribution in the liquid phase is governed by:

$$-\frac{\partial}{\partial x} \cdot \left(\kappa_{l,eff} \frac{\partial \phi_l}{\partial x}\right) + \frac{2RT\left(1 - t_{+}\right)}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_l}\right) \frac{\partial}{\partial x} \cdot \left(\kappa_{l,eff} \frac{\partial \ln c_l}{\partial x}\right) = a_s F i_{ct}^{gr} \qquad (S5)$$

The interface charge transfer rate of Li⁺ intercalation reaction on graphite particles is calculated by the Butler-Volmer equation:

$$i_{ct}^{gr} = Fk\left(c_{s,\max} - c_s\right)^{0.5} c_s^{0.5} c_l^{0.5} \left[\exp\left(\frac{F}{2RT}\eta_{ct}^{gr}\right) - \exp\left(-\frac{\alpha F}{2RT}\eta_{ct}^{gr}\right)\right]$$
(S6)

where the charge transfer overpotential of Li⁺ intercalation η_{ct}^{gr} at the particleelectrolyte interface is defined as:

$$\eta_{ct}^{gr} = \phi_s^{gr} - \phi_l - E_{eq,surf}^{gr} - \eta_{sei}^{gr}$$
(S7)

The Li plating/stripping reaction is controlled by **equation 8** where the reaction rate constant k_{Li/Li^+} considers the substrates of Li plating. The plated Li is expressed by the

volume fraction ratio, which is calculated by the integration of Li plating current over time

$$\mathcal{E}_{Li} = \int_{t_{pl}}^{t_{end}} \frac{i_{Li/Li^+}^{gr} a_s M_{Li}}{F \rho_{Li}} dt$$
(S8)

In terms of charge conservation, there is

$$I = \int \left(i_{ct}^{gr} + i_{Li/Li^+}^{gr} \right) dA_s \tag{S9}$$

For Li deposition/dissolution reaction on the Li metal electrode, it is also described by the Butler-Volmer equation

$$i_{Li/Li^{+}}^{Li} = \frac{I}{A} = Fk_{Li/Li^{+}}c_{l}^{0.5} \left[\exp\left(\frac{F\eta_{Li/Li^{+}}^{Li}}{2RT}\right) - \exp\left(-\frac{F\eta_{Li/Li^{+}}^{Li}}{2RT}\right) \right]$$
(S10)

The boundary conditions of Li⁺ diffusion within the graphite particles are

$$-D_{s} \frac{\partial c_{s}}{\partial r} \bigg|_{r=0} = 0 \quad -D_{s} \frac{\partial c_{s}}{\partial r} \bigg|_{r=R_{s}} = -\frac{i_{ct}^{gr}}{F}$$
(S11)

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For electron conduction on the solid phase of the porous electrode, the boundary conditions are

$$\frac{\partial \phi_s^{gr}}{\partial x} = 0 \tag{S12}$$

at the electrode-separator interface and

$$-\kappa_{s,eff} \frac{\partial \phi_s^{gr}}{\partial x} = \frac{I}{A}$$
(S13)

at the cathode-current collector interface. The boundary conditions of the mass transport in the electrolyte are

$$\frac{\partial c_l}{\partial x} = 0, \quad -D_{l,eff} \frac{\partial c_l}{\partial x} = \frac{i_{Li/Li^+}^{Li}}{F}$$
(S14)

for the current collector surface and the Li metal surface, respectively. The boundary conditions of the charge transport are

$$\frac{\partial \phi_l}{\partial x} = 0, \quad -\kappa_{l,eff} \frac{\partial \phi_l}{\partial x} = i_{Li/Li^+}^{Li}$$
(S15)

for the current collector surface and the Li metal surface, respectively.

The electrostatic potential of the Li metal anode is also set as

$$\phi_s^{Li} = 0 \tag{S16}$$

Table S2

Model parameters used in the electrochemical simulation of graphite-Li half cells.

Parameters	Graphite electrode	Separator	Li metal	
Porosity ε	0.39 ^a	2.0 ^a		
Turtuosity τ	<i>ɛ</i> ^{-3 a}	0.41 ^b		
Electrode thickness L (µm)	53 a	25 ^b		
Volume fraction of graphite ε_s	0.56 a			
Radii of graphite R_s (D50/2, μ m)	9 в			
Electrode conductivity σ (S m ⁻¹)	2200 °			
Maximum solid-phase concentration $c_{s,max}$ (mol m ⁻³)	31360 ^a	—	—	
Initial <i>x</i>	0.01 ^a			
Solid-phase Li ⁺ diffusivity (m ² s ⁻¹)	1×10 ⁻¹⁵ -5×10 ⁻¹² a			
Reaction rate constant k (m ^{2.5} mol ^{-0.5} s ⁻¹)	5×10 ^{-12 a} (Intercalation) 0.38-7.4×10 ^{-7 a} (plating)		7.4×10 ^{-7 a}	
Density of Li metal ρ_{Li} (kg m ⁻³)		534		
Molar mass of Li metal M_{Li} (kg mol ⁻¹)	6.94×10 ⁻³			
Maximum volume fraction of Li nucleus ε_{nuc}	0.002			

Notes: ^aMeasured or calculated, ^bfrom manufacturers, ^cRef. ^[232]_o

Supplementary simulation results



Figure S4 Simulated charge transfer current density of Li^+ intercalation reaction across the graphite electrode *t*=550 s in the case at 2C rate.

Results of the critical DOD and Li plating reaction overpotentials

Table S3

C-rates.

The critical values of DOD and the corresponding Li plating reaction overpotentials $\eta^{gr}_{_{Li/Li^*}}$ at varied

C-rate	No.	DOD (%)	$\eta^{\scriptscriptstyle gr}_{\scriptscriptstyle Li/Li^*}(\mathrm{V})$
	1	80	-0.0124
1C	2	85	-0.008
	3	80	-0.0091
	1	25	0.0076
	2	35	0.0112
2C	3	40	0.0033
	4	70	-0.0086
	5	40	0.0023
	1	15	0.0254
	2	35	0.0004
20	3	40	0.0102
30	4	40	0.0173
	5	35	-0.0097
	6	30	0.0101
	1	20	0.0214
	2	15	0.0181
	3	20	-0.0053
4C	4	30	0.0068
	5	30	0.0252
	6	30	-0.0043
	7	25	0.0061

Note: the variation of the critical DOD for a fixed C-rate attributes to the different design of electrodes and salt concentrations of electrolyte among the samples.

References

- [1] R. Xiong, Y. Yu, S. Chen, M. Li, L. Li, M. Zhou, W. Zhang, y. Bo, D. Li, H. Yang, Y. Zhang,
- H. Zhou, Journal of Power Sources, 553 (2023) 232296.

[2] R. Xiong, M. Zhou, L. Li, J. Xu, M. Li, B. yan, D. Li, Y. Zhang, H. Zhou, Energy Storage Materials, 54 (2023) 836-844.