



Lithium-Metal Batteries Very Important Paper

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A Diffusion–Reaction Competition Mechanism to Tailor Lithium Deposition for Lithium-Metal Batteries

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Abstract: Lithium metal is recognized as one of the most promising anode materials owing to its ultrahigh theoretical specific capacity and low electrochemical potential. Nonetheless, dendritic Li growth has dramatically hindered the practical applications of Li metal anodes. Realizing spherical Li deposition is an effective approach to avoid Li dendrite growth, but the mechanism of spherical deposition is unknown. Herein, a diffusion-reaction competition mechanism is proposed to reveal the rationale of different Li deposition morphologies. By controlling the rate-determining step (diffusion or reaction) of Li deposition, various Li deposition scenarios are realized, in which the diffusion-controlled process tends to lead to dendritic Li deposition while the reaction-controlled process leads to spherical Li deposition. This study sheds fresh light on the dendrite-free Li metal anode and guides to achieve safe batteries to benefit future wireless and fossil-fuel-free world.

n 1991, the first lithium-ion batteries (LIBs) were sold by a major Japanese electronics company, creating the revolution of wireless and fossil-fuel-free society.^[1] However, after nearly 30 years of relentless research and development, the energy density of current LIBs has gradually reached the summit.^[2] Exploring next-generation high-energy-density batteries is crucial to satisfy the increasing demands of more convenient wireless electronics and cleaner energy technologies.^[3] Replacing the traditional graphite anode in LIBs with metallic Li has great prospects to boost the energy density of rechargeable lithium batteries, because Li metal is recognized as one of the most promising anode materials owing to its ultrahigh theoretical specific capacity (3860 mAh g^{-1}) and low electrochemical potential (-3.04 V vs. standard hydrogen electrode).^[4] Nonetheless, Li metal anode has been severely hindered from practical applications by dendritic Li growth.^[5] The uncontrollable Li dendrites can result in low Coulombic efficiency (CE) and short cycle life of a working battery.^[6] More seriously, the Li dendrites penetrate the separators and

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reach the cathode to cause internal short-circuits, which even lead to thermal runaway and explosions.^[7] However, the continuous conversion between Li metal and Li ions implies the inevitable existence of Li deposition during the plating step. Accordingly, the key to suppress the Li dendrite growth is to tailor Li deposition.^[8]

Compared to available deposition morphologies of Li metal anode, spherical Li deposition endows two important merits from its unique morphology. Firstly, spherical Li deposition features well-defined morphology with smooth surface without any sharp tip, thus avoiding serious safety hazards caused by dendritic Li deposition.^[9] Secondly, Li sphere exhibits minimum surface area per unit volume among all other morphologies, which signifies higher CE and longer cycle life because of forming less solid electrolyte interphase (SEI) by the reactions between fresh Li and electrolyte.^[10]

Based on the above considerations, many researches have focused on regulating Li deposition into spherical shapes. Li and co-workers reported a salt-derived SEI produced by electroreduction of a highly concentrated water-in-salt electrolyte to realize spherical Li deposition with a high CE.^[11] He and co-workers proposed a 3D skeleton with open micrometer-sized pores to promote spherical Li deposition, improving CE and mitigating volumetric change simultaneously.^[12] Even though some strategies have been applied to regulate spherical Li deposition, the underlying mechanism of forming Li spherical deposits has not been clarified yet. If the fundamental rationale behind different morphologies of Li deposition can be unveiled, it is conceivable that safe Li metal batteries can be further achieved based on tailoring Li deposition morphology.^[13]

Herein, we report a diffusion-reaction competition mechanism which can determine the ion concentration beneath the SEI and therefore tailor the morphology of Li deposition. When maintaining the same electrode reaction rate, through modifying the kinetics of Li diffusion from slow to fast, the ratio of sphere/all deposition (including spherical and dendritic Li; denoted as S/D) continuously rises due to the progressively higher Li ion concentration beneath SEI. Changing the electrode reaction rate is found to alter the Li plating morphology, since higher reaction rate can induce ion depletion within SEI. This work provides a deep, fundamental understanding of Li deposition morphology that guides the design of future strategies to enable dendrite-free Li deposition.

The processes of spherical/dendritic Li deposition are schematically illustrated in Figure 1 a. Generally, Li deposition takes place beneath the SEI, including Li ion migrating through SEI and following reduction of a Li ion to a Li atom by obtaining an electron.^[14] At the same electrode reaction

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Figure 1. The diffusion-reaction competition mechanism causing spherical/dendritic Li deposition. a) Scheme of spherical/dendritic Li deposition beneath fast SEI and slow SEI. b) The diffusion and reaction steps influence the Li ion concentration beneath the SEI. c) The Li-ion concentration beneath the SEI determines the Li deposition morphology. Li-ion depletion beneath the SEI induces preferential Li plating on the tip of initial Li deposit and therefore leads to dendritic Li deposition. If sufficient Li ions beneath the SEI obtain electrons uniformly on the surface of Li nucleation bumps, the result is spherical Li deposition.

rate of Li plating process, as the diffusion ability decline, Li ions become difficult to get through the SEI (denoted as slow SEI) and therefore ion depletion easily results in the scarcity of Li ions beneath SEI, making it a diffusion-controlled reaction. Because the initial Li nucleation sites evolve into bumps distributed on the current collector, whose edges are unable to capture Li ions under the electric field,^[15] insufficient Li ions preferentially tend to gather on the tip. Therefore, when the deposition is diffusion-controlled, the scarcity of Li ions beneath the SEI induces dendritic Li deposition. When the Li ion diffusion rate in SEI increases (denoted as fast SEI), Li ions migrate onto the surface of anode with faster kinetics (Figure 1a). As a result, the ratedetermining step of Li deposition transforms to reactioncontrolled and the number of Li ions beneath the SEI remarkably increases even on the edges of Li nucleation bumps. The conversion of Li ion to Li atom can occur

uniformly on Li nucleation bumps,^[16] leading to spherical Li deposition. A phase field model was employed to further describe the lithium spherical/ dendritic deposition under the fast/slow SEI. The harder diffusion of Li ion through the slow SEI induced local current density (the product of Li ion flux and Faraday constant and representing the reaction rate on the surface of Li metal anode) gathered at a dendrite tip, thus generating the dendritic Li deposition under the diffusion-controlled condition (Figure S1b and S1d in the Supporting Information). On the contrary, the spherical Li deposition and uniform local current density around spherical deposition were gained when the ratedetermined step transformed to reaction-controlled under the fast SEI (Figure S1a,c).

Moreover, the diffusion step and reaction step synergistically affect the Li ion concentration beneath the SEI (Figure 1 b,c). Low concentration of Li ions beneath the SEI induces Li ions preferentially plating on the tip of original Li deposition and thus forming dendritic Li deposition. On the contrary, abundant Li ions beneath the SEI obtain electrons at each site of the Li nucleation bumps, achieving spherical Li deposition and avoiding the issues caused by dendritic Li deposition.

To confirm the proposed diffusion-reaction competition mechanism for Li deposition morphology, a series of electrolytes of 1.0 M LiX (X = nitrate (NO₃⁻) and bis(trifluromethanesulfonyl)imide (TFSI⁻)) in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (v/v = 1:1) was selected as the model system to construct SEI with diffusion kinetics gradient. The partial substitution of routine TFSI⁻ anion to NO₃⁻ generates LiN_xO_y and Li₃N in SEI,^[17] thus enhancing the ionic conductivity of SEI. Concretely, electrolytes with LiNO₃:LiTFSI molar ratio of 0:10, 2:8, 4:6, 6:4, and 8:2 were formulated and donated as N0F10, N2F8, N4F6, N6F4, and N8F2, respectively. Correspondingly, N0F10, N2F8, N4F6, N6F4, and N8F2 were employed to fabricate SEI with increasing diffusion kinetics.

The morphology of Li deposition on Cu foil in the half cells at a current density of 0.50 mA cm⁻² with a capacity of 0.125 mAh cm⁻² is presented in Figure 2. In the N0F10 electrolyte, almost all Li depositions were needle-like dendrites with a diameter of 0.70 µm (Figure 2a and Figure S2). When N2F8, N4F6, and N6F4 electrolytes were employed, the spherical Li deposition appeared with increasing proportion. The S/D of N2F8, N4F6, and N6F4 increased to 0.246, 0.554, and 0.846 (Figure 2b,c,d, Figure S2,S3), respectively. The diameter of N2F8, N4F6, and N6F4 correspondingly rose to 0.86, 1.09, and 1.52 μ m (Figure 2 f), respectively. As the content of LiNO₃ in electrolyte reached 0.8 M, all Li tended to deposit into spherical structure in N8F2 electrolyte with a diameter of 1.45 µm (Figure 2 e). The size of Li deposition in series of electrolytes increased under the process transforming to reaction-controlled, and then stabilized limited by other factors, such as surface energy limitation. After second Li plating/stripping, in contrast to the dendritic Li deposition in N0F10 electrolyte (Figure S4), the Li deposition in N8F2



Figure 2. Morphology of spherical/dendritic Li deposition. SEM images of Li deposition at a current density of 0.50 mA cm⁻² with a capacity of 0.125 mAh cm⁻² in N0F10, N2F8, N4F6, N6F4, and N8F2 electrolyte: a) Morphology of dendritic Li deposition in N0F10 electrolyte. Morphology of spherical and dendritic Li deposition in b) N2F8, c) N4F6, and d) N6F4. e) Morphology of spherical Li deposition in N8F2 electrolyte. f) The diameter of Li deposition (dendritic and spherical Li deposition idealized as cylinder and sphere, respectively) and the S/D increase corresponding the amount of LiNO₃.

electrolyte still maintained the spherical structure (Figure S5), suggesting that the morphology of Li deposition is regulated continuously under the competing function of diffusion and reaction control. The transition of Li deposition morphology from dendrite to sphere in N0F10, N2F8, N4F6, N6F4, and N8F2 electrolyte can be attributed to the increase of ion concentration beneath the SEI induced by the increase of diffusion rate at the same electrode reaction rate.

Comprehensive electrochemical characterizations were performed to evaluate the kinetics of Li migrating beneath the SEI.^[18] The Tafel slopes of all samples were probed and obtained from the cyclic voltammetry (CV) profiles in Figure 3a. The exchange current density (j_0) are calculated from the corresponding Tafel plots to reflect charge-transfer kinetics in SEI formed in different electrolytes. As shown in Figure 3b, the N0F10, N2F8, N4F6, N6F4, and N8F2 electrolyte demonstrated increasing exchange current density of 0.41, 0.45, 0.61, 0.68, and 0.69 mA cm⁻², indicating the faster kinetics of SEI and thus adequate Li ion beneath SEI to achieve spherical Li deposition.

The activation energy for Li ion diffusion through the SEI were further investigated by temperaturedependent electrochemical impedance spectra (EIS) in the range of 263 to 293 K (Figure 3c, Figure S6,S7). The activation energy for Li ion diffusion through SEI reduced from $30.70 \text{ kJ mol}^{-1}$ in N0F10, to 29.87 kJ mol⁻¹ in N2F8, 28.84 kJ mol⁻¹ in N4F6, 27.15 kJ mol⁻¹ in N6F4, and 25.76 kJ mol⁻¹ in N8F2 (Figure 3d), respectively. The fast kinetics of Li ion diffusion in N8F2 were due to the ample polycrystalline domains with high ionic conductivity embedded in SEI, which was validated through the double spherical aberration corrected transmission electron microscope (AC-TEM). In contrast to the amorphous phase in SEI formed in N0F10 electrolyte (Figure 3 f), the lattice fringe spacing of domains indicated the existence of Li₃N, LiF, and Li₂N₂O₃ in SEI formed in N8F2 electrolyte (Figure 3e and Figure S8).^[19] Li₃N with high ionic conductivity,^[20] which was induced by the decomposition of LiNO₃ in N8F2 electrolyte,

served as the rapid Li ion pathways in SEI. Consequently, the faster kinetic of diffusion devoted to the higher Li ion concentration beneath the SEI under the same reaction rate, thus regulating spherical Li deposition.

To further verify the presumed diffusion-reaction competition mechanism, more deposition morphologies were evaluated at the adjusted the electrode reaction rate (Figure 4a). At the current density of 5.00 mA cm^{-2} with a capacity of $0.125 \text{ mAh cm}^{-2}$, the morphology of Li deposition in N8F2 electrolyte appeared to be dendritic deposition (Figure 4b,c), instead of all-spherical deposition at the current density of 0.50 mA cm^{-2} (Figure 2e and Figure S3). As the current density increased to 10.0 mA cm^{-2} , the amount of Li dendrite depositions increased (Figure S9), owing to the fast consumption of Li ion upon conversion to Li atom and



Figure 3. Evaluation of kinetics and structure of various SEIs forming in N0F10, N2F8, N4F6, N6F4, and N8F2 electrolyte. a) Tafel plots and corresponding b) exchange current density of N0F10, N2F8, N4F6, N6F4, and N8F2 electrolyte. c) Arrhenius behavior of the reciprocal and d) the activation energy derived for the ion diffusion through the SEI in N0F10, N2F8, N4F6, N6F4, and N8F2 electrolyte. AC-TEM images of e) fast SEI in N8F2 electrolyte and f) slow SEI in N0F10 electrolyte.



Figure 4. Morphology evaluation of Li deposition at various reaction rates. a),b),c) Dendritic Li deposition of fast SEI at the current density of 5.00 mA cm⁻² with the capacity of 0.125 mAh cm⁻². d),e),f) Spherical Li deposition of slow SEI at the current density of 0.05 mA cm⁻² with the capacity of 0.125 mAh cm⁻². g) Li deposition morphology diagram corresponding to the diffusion and reaction rate.

then the dramatic decline of ion concentration beneath the SEI.

While changing the current density of 0.50 to 0.05 mA cm⁻² in N0F10 electrolyte, the electrode reaction rate prominently reduced and therefore the ion concentration beneath the SEI increased. The conversion from Li ions to Li atoms can take place around the surface of Li nucleation bumps, leading to the appearance of spherical deposition (Figure 4e,f). Similar results were also confirmed in the N2F8 and N4F6 electrolyte (Figure S10). The value of S/D noticeably got raised corresponding to the current density declined, which is in accordance with previous reports.^[21] For instance, Zhang et al. revealed that Li deposition at an ultralow local current density turned to sphere in contrast to dendrite at regular current density.^[22] Pei et al. also found the ratio of S/D increased as the current density.^[23] More importantly, based

on the experiment data above (Table S1), the Li deposition morphology diagram was divided into spherical and dendritic deposition zone (Figure 4g), corroborating the diffusionreaction competition mechanism determined ion concentration beneath the SEI to regulate the Li deposition morphology, which shedding a broad light on Li dendrite issue for safe Li metal batteries.

In conclusion, we have presented a diffusion-reaction competition mechanism to reveal the rationale underlying the transition of Li deposition morphology from dendritic to spherical. Based on ingeniously designed model experiment data through controlling the Li ion diffusion and reaction step, a Li deposition morphology map was obtained to confirm that the diffusion and reaction steps determine the ion concentration beneath the SEI and therefore regulate the Li deposition morphology. These observations can afford instructive guidelines for future Li dendrite inhibition strategies, including diffusion improvement by electrolyte engineering and artificial SEI, and reaction enhancement with high-surface-area Li host design. This work constitutes the foundation for tailoring Li deposition to achieve dendrite-free Li metal anode that enables safe, high-energy-density lithiummetal batteries devoting to the future wireless and green society.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: diffusion control · lithium dendrites · lithium-metal batteries · lithium spheres · reaction control

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