

Unravelling the Mechanism of Lithium Nucleation and Growth and the Interaction with the Solid Electrolyte Interface

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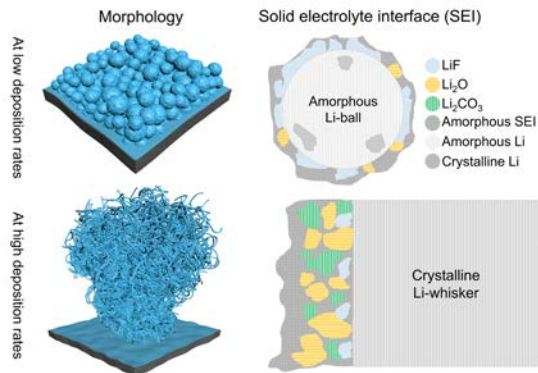
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Abstract

Limited understanding of the lithium (Li) nucleation and growth mechanism has hampered the implementation of Li metal batteries. Herein, we unravel the evolution of the morphology and inner structure of Li deposits using focused ion beam scanning electron microscopy (FIB/SEM). Ball-shaped Li deposits are found widespread and stacking up at a low current density. When the current density exceeds the diffusion-limiting current, bush-shaped deposition appears that consists of Li-balls, Li-whiskers and bulky Li. Cryogenic transmission electron microscopy (cryo-TEM) further reveals that Li-balls are primarily amorphous while the Li-whiskers are highly crystalline. Additionally, the solid electrolyte interface (SEI) layers of the Li-balls and whiskers show a difference in structure and composition, which is correlated to the underlying deposition mechanism. The revealed Li nucleation and growth mechanism and the correlation with the nanostructure and chemistry of the SEI provide insights towards the practical use of rechargeable Li metal batteries.

TOC Graphic



Lithium (Li) metal anodes are regarded as the “holy grail” for next-generation Li batteries because they can largely improve the energy density of Li batteries by replacing conventional graphite anodes.¹⁻³ However, the successful implementation of Li metal anodes in rechargeable Li batteries is hindered by the low Coulombic efficiency (CE) and dendritic (fibre-, whisker- or needle-shaped) Li electrodeposition that induces safety issues. The low CE originates from the irreversible formation of a solid electrolyte interface (SEI) layer⁴⁻⁵ and “dead” Li (electrically isolated Li), while Li dendrites stem from the non-uniform charge distribution at the Li/electrolyte interface. To address these issues, various approaches have been explored, including structured electrode design⁶⁻⁸, surface engineering of Li and separator⁹⁻¹⁰, and electrolyte modification¹¹⁻¹⁵. Although remarkable progress has been achieved in stabilizing Li electrodeposition, an in-depth and comprehensive understanding of the underlying mechanism of Li nucleation and growth is still underdeveloped but is crucial for the practical use of Li metal batteries.¹⁶

Therefore, intensive efforts, both experimentally and theoretically, have been devoted to understanding the Li electrodeposition behavior. For instance, *in situ* optical microscopy¹⁷⁻²⁰, which provides a real-time and non-destructive observation of the growth of Li at the sub- μm resolution, has been employed to correlate the morphological evolution to the voltage variations during Li plating/stripping. *Operando* transmission electron microscopy (TEM) and transmission X-ray microscopy (TXM)²¹ enable the visualization of the dynamic evolution of Li electrodeposition at the nm-scale, which is particularly inspiring to clarify the elusive nucleation stage that determines the following Li growth. Furthermore, TEM conducted at cryogenic conditions (cryo-TEM)²² has been demonstrated to be able to minimize beam damage and to resolve the structure and chemistry of Li deposits and the SEI layer thereon at the nanometer scale. Meanwhile, classical nucleation theory²³⁻²⁴ and several mathematical models²⁵⁻²⁶ based on the thermodynamics and kinetics of Li deposition have also been developed to describe the electrochemical nucleation of Li and the following growth. Among these theoretical models, a space-charge theory suggests that a large electric field near the electrode surface induced by anion depletion leads to the formation of dendritic Li electrodeposits.²⁷⁻²⁸

Based on previous studies, the morphology of Li electrodeposits can be concluded as a function of the operating conditions (i.e. current, temperature and stack pressure) and is immensely influenced by the local chemistry and nanostructure of the electrode/electrolyte interface. Two typical morphologies, namely ball-shaped and whisker-shaped Li electrodeposits have been widely reported. Generally, in carbonate electrolytes that are commonly used in Li-ion batteries, the Li electrodeposit mostly appears to be whisker-shaped²⁹, while that in ether-based electrolytes particularly those with LiNO_3 ³⁰ or fluorine-containing additives^{14, 31} forms a spherical or granular shape. Moreover, the SEI layer, which originates from the side reactions between the electrolyte and Li, also plays a decisive role in the formation of Li electrodeposits.³² It has been reported that a compact and LiF-rich SEI layer obtained by using fluorine-enriched electrolytes or additives could facilitate uniform Li-ion migration and thus suppress dendritic deposition.^{14, 33} This can be clarified by a recently proposed diffusion-reaction competition mechanism³⁴ which states that a fast diffusion rate of Li-ions through the SEI induces a spherical Li deposition while a slow one results in a dendritic form.

These pioneering investigations and proposed theories have advanced our understanding of the Li electrodeposition process. Nevertheless, the fundamental mechanism of Li nucleation and growth remains elusive and how an SEI layer shapes the Li deposits during the electrodeposition process is still unclear. In particular, several primary questions need to be addressed, including 1) How do Li deposits evolve towards the two typical morphologies, i.e. Li balls and whiskers?; 2) What is the relationship between Li balls and whiskers?; 3) How are Li deposits shaped by the SEI layer?

To address these questions, in this work, we performed multi-scale morphological and structural characterization of Li deposits and the SEI layer using focused ion beam scanning electron microscopy (FIB/SEM) and cryo-TEM. The Li deposits are found to be ball-shaped where the local charge density is low, while Li whiskers appear where a high flux of Li-ions and electrons exists. The Li-whiskers are highly crystalline and are concluded to have evolved from amorphous and ball-shaped deposits. Moreover, we discovered that the nanostructures and compositions of the SEI layer on Li balls and whiskers are different, and the differences have been correlated with the morphological evolution of Li deposition. These results provide a fundamental understanding of the electrochemical behaviors of Li deposition and SEI growth, which is of vital importance for the development of stable Li metal anodes.

Morphology and structure transition at varying deposition rates

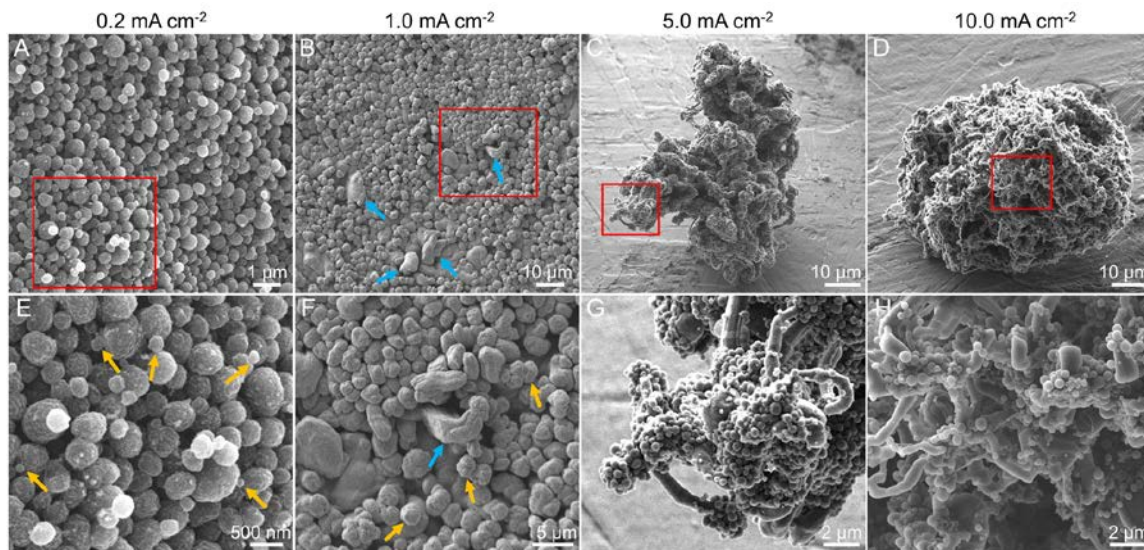


Figure 1. Li morphology transformation with increasing deposition current. (A-D) SEM images showing morphological features of Li deposition on Li substrates at current densities of 0.2, 1.0, 5.0, 10.0 mA cm⁻² for a fixed capacity of 1.0 mAh cm⁻²; (E-H) Corresponding magnified images of the red squared regions in (A-D), respectively; Some small Li balls that may act as deposition embryos at 0.2 mA cm⁻² are marked by orange arrows in (E); Blue and orange arrows in (B, F) highlight the columnar and granular deposits at 1.0 mA cm⁻², respectively.

Figure 1 shows Li electrodeposits formed at various current densities ranging from 0.2 mA cm⁻² to 10.0 mA cm⁻² at a fixed deposition capacity of 1.0 mAh cm⁻² (cell configuration: Figure S1, Li deposition voltage profiles: Figure S2). At 0.2 mA cm⁻², ball-shaped roughly 500 nm large Li electrodeposits as shown in Figure 1A and 1E, can be found spreading across the Li electrode (Figure S3). Additionally, smaller balls (< 300 nm) can be observed as highlighted by orange arrows in Figure 1E. These smaller Li-balls are likely the newly generated Li electrodeposits and are expected to grow or expand if electrodeposition continues. The widely distributed thin deposition and the ball-shaped morphology indicate a high homogeneity of the local current density at the Li/electrolyte interface during electrochemical deposition. When the current density is increased to 1.0 mA cm⁻², the Li electrodeposits (Figures 1B, 1F and S4) become increasingly less uniform and two different morphologies co-exist, namely granular- and columnar shapes, indicated by orange and blue arrows, respectively. Compared to the deposits shown in Figure 1A, the less spherical and bigger Li deposits (μm-scale), as shown in

Figure 1B, indicate a bigger average size of deposits at 1.0 mA cm^{-2} , and thus a decreased total amount of nuclei after a deposition capacity of 1.0 mA cm^{-2} .

A further increased current density of 5.0 mA cm^{-2} gives rise to bush-shaped Li deposits consisting of ball-shaped and dendritic structures as shown in Figures 1C, 1G and Figure S5. Note that the ball-shaped particles can also be observed on the bush branches instead of spreading across the surface of the Li substrate as for the deposition generated at 0.2 mA cm^{-2} . Similarly, Li electrodeposits generated at 10.0 mA cm^{-2} are also bush-shaped but tend to have fewer balls covering the intertwined whiskers (Figures 1D and S6).

It is evident that the Li electrodeposits formed at 0.2 and 1.0 mA cm^{-2} appear to be dense and spread out over the whole electrode while porous bush-shaped deposits were obtained at and above 5.0 mA cm^{-2} . This result can be rationalized by the space-charge theory. Assuming negligible convection in the symmetric Li||Li cell during electrochemical cycling, the diffusion-limiting current (J_{lim}), which is used to define a current at which the Li^+ concentration near the cathode electrode decreases to zero, is calculated to around 2.1 mA cm^{-2} (see Figure S1 related text in supporting information). This mechanism can explain the observed morphologies in Figure 1 that a current density below J_{lim} (2.1 mA cm^{-2}) induces a relatively flat deposition while exceeding J_{lim} brings in a dendritic deposition.

A meso-scale computational model of the electrode-electrolyte interface³⁵⁻³⁷ using the smoothed particle hydrodynamics (SPH) method also supports the experimental findings. As seen in Figure S7, lower current density leads to a more even distribution of Li-ions on the surface. When the current density is increased, mass transport limitations reduce the Li-ions available at the interface. The concentration of Li-ions near the top of the dendrite structures is higher than that at the base, leading to favorable conditions for vertical growth instead of lateral spreading at high current densities. The SPH simulations provide detailed insights into how electrodeposition evolves at different electrodeposition rates (Figure S7), and supports the observations obtained from SEM probing.

FIB/SEM enables us to further reveal the internal morphology and structure of the Li electrodeposits that has been rarely reported. Figure 2 shows the cross-sectional views of two representative morphologies, namely ball-shaped and bush-shaped electrodeposits that are generated at current densities of 0.2 and 5.0 mA cm^{-2} , respectively. In Figures 2A and 2B, ball-shaped Li particles are found stacked up and covered with white shells. These shells could be attributed to SEI layers that arise from the side electro-/chemical reactions between Li and the electrolyte³⁸.

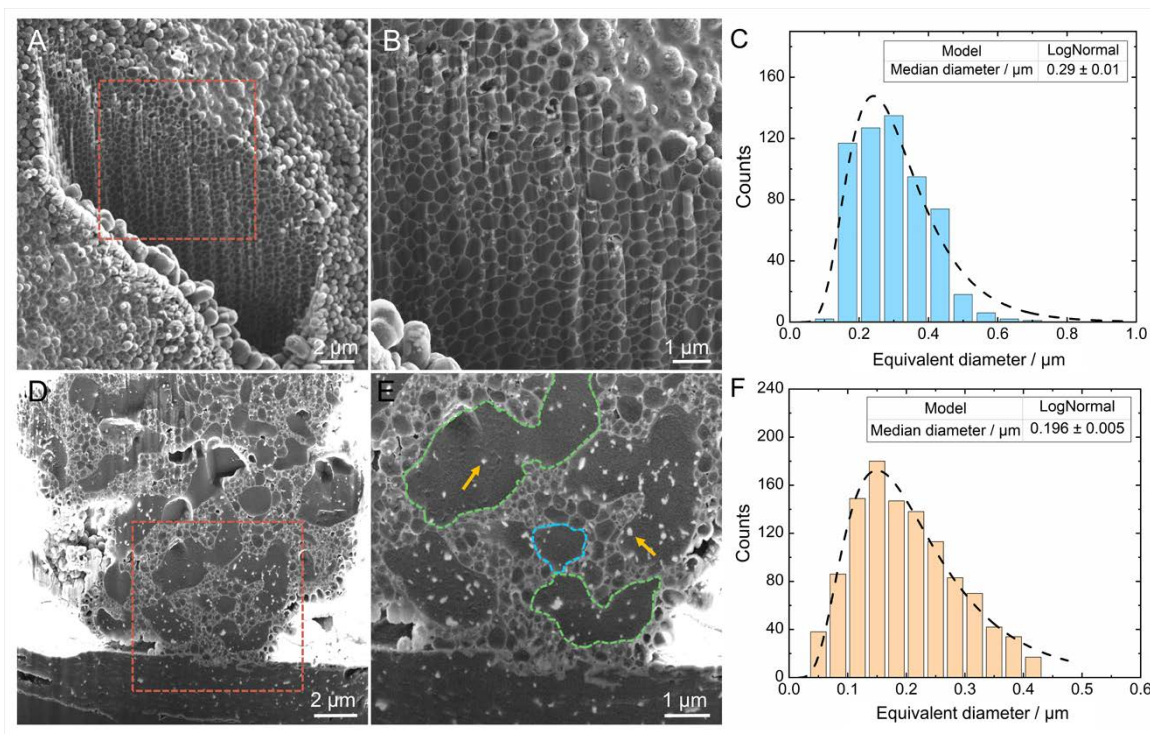


Figure 2. The internal structure of the granular and bush-shaped Li deposition obtained by FIB/SEM. (A) A cross-sectional view and (B) the magnified view of the ball-shaped deposition formed at a current density of 0.2 mA cm^{-2} ; (C) the diameter distribution of the Li-balls obtained from the cross-sectional area in (B) after FIB cutting; (D) A cross-sectional view and (E) the magnified view of the bush-shaped deposition formed at a current density of 5.0 mA cm^{-2} ; The white dots marked with orange arrows in (E) could be attributed to the removed electrodeposition chips that fall off during FIB-cutting; The dashed green and blue lines highlight the columnar and granular deposits in the Li-bush, respectively; (F) Diameter distribution of the ball-shaped deposits obtained from the cross-sectional area in (D) after FIB cutting.

The bush-shaped Li electrodeposits generated at 5.0 mA cm^{-2} feature a different structure. Micrometer-sized bulky electrodeposits were found within the Li-bush (Figures 2D and S8). These bulky deposits can be classified into two shapes, namely columnar and granular, and are analogous to the deposits obtained at 1.0 mA cm^{-2} regarding morphology and size (μm -scale). Besides, nm-sized Li-balls exist in between these two bulky structures as well as at the surface of a Li-bush. From the diameter distribution (Figures 2C and 2F) of particles in the cross-sectional view, one can conclude that the average diameter of the ball-shaped deposits from the Li-bush is smaller than that of the Li-balls formed at 0.2 mA cm^{-2} . This result agrees well with the classic nucleation theory and further demonstrates the inverse relationship²⁹ between nucleation size and deposition overpotential. The Li-bushes generated at 10.0 mA cm^{-2} are shown in Figures S6 and S9 and they possess a similar structure to that obtained at 5.0 mA cm^{-2} . Therefore, combined with the SEM results from Figures 1G and 1H, we conclude that at 5.0 and 10.0 mA cm^{-2} the electrodeposits possess mixed morphologies, including Li-balls, μm -sized Li-granules and columns, as well as the typical Li-whiskers.

Structural and chemistry evolution at a high current density

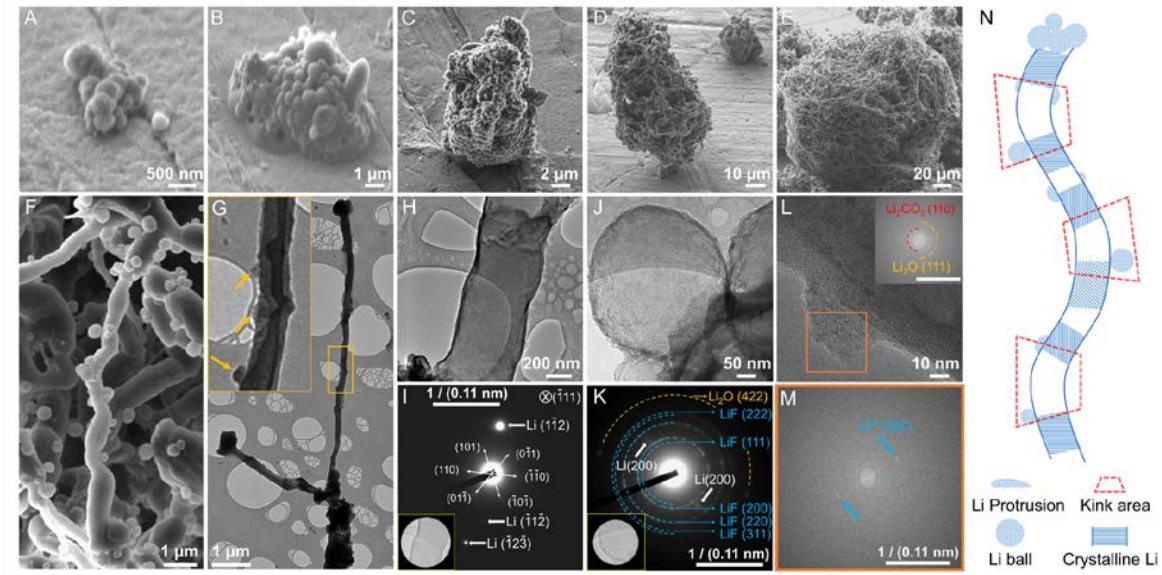


Figure 3. The structure and chemical compounds of Li deposits at 5.0 mA cm⁻². (A-E) SEM images illustrating Li deposits of different sizes and structures that were obtained at a deposition capacity of 1.0 mAh cm⁻². These Li deposits were categorized as different stages of the morphological evolution based on their sizes and structures: (A) Initial spherical nuclei, (B) A cluster of Li-nuclei forming a hemisphere, (C) A "mossy" Li dendrite, i.e., an irregularly shaped Li deposit with its surface covered dominantly by Li-balls without Li-branches, (D) A small Li-bush consisting of intertwined Li-whiskers and Li-balls at the kinks and tips of Li-whiskers; (E) A large bush-shaped deposit (>100 μm) mainly consisting of Li-whiskers with few Li-balls; For clarity, enlarged images of (D) and (E) are included in Figure S12F and S12H, respectively. (F) SEM and (G) cryo-TEM images of Li-whiskers with spherical deposits at the tips and kinks of the whiskers as well as small Li-spheres and protrusions on the Li-whiskers (inset); (H-K) Cryo-TEM characterization of Li deposits of two typical morphologies: Li-whisker and Li-ball; (H) & (J): micrographs and (I) & (K): SAED patterns and their aperture area (insets) of the Li-whisker and the Li-ball in (I) and (K), respectively; (L) HRTEM image of a protrusion adhering to a Li-whisker and the FFT pattern as an inset (scale bar: 1/(0.11 nm)); (M) FFT results from the orange boxed area in (L); (N) Schematic of a crystalline Li-whisker with amorphous protrusions and Li-balls on the tip and kink area of the Li-whisker rich in crystalline defects.

To further understand the underlying mechanism of Li nucleation and growth especially at a high current density, the morphological and structural evolution of Li electrodeposits generated at 5.0 mA cm⁻² ($> J_{lim} = 2.1 \text{ mA cm}^{-2}$) were further elaborated. Li electrodeposition of five capacities (from 0.05 to 1.0 mAh cm⁻²) was performed and the SEM images are displayed in Fig. S10. It clearly shows that Li deposits of different sizes/morphologies co-exist at every deposition capacity and deposits of comparable sizes exhibit a similar morphology. Therefore, deposits of various sizes from a single deposition capacity can represent the morphological evolution process of Li electrodeposition. In Figures 3A-E and S11-12, Li electrodeposits obtained from 1.0 mAh cm⁻² that were categorized as different stages of the morphological evolution based on their sizes and structures are displayed. At the initial Li nucleation stage, single or clusters of spherical Li nuclei (diameter 200-600 nm) are found (Figure 3A), which are similar to the ball-shaped Li deposits formed at 0.2 mA cm⁻². As a starting point for subsequent growth, the spherical nuclei could aggregate to hemispheres made of Li-balls and Li-columns (Figures 3B and S11), and subsequently form a sapling-shaped deposit with Li-balls covering the surface (Figure 3C). Meanwhile, mature bush-shaped Li deposits (Figure 3D) can be observed with Li-whiskers and Li-balls appearing on the surface, as an enlarged image shows in Figure S12. Moreover,

“giant” deposits that are much bigger than that in Figure 3D are also evident. They are dominated by Li-whiskers at the surface with few Li-balls visible on the surface (Figures 3E and S12).

The distinctly different morphologies allow for the straightforward identification of the Li-balls and Li-whisker as the initial and grown stages of Li deposits, respectively. This agrees well with results from an *in situ* observation of the dynamic evolution of Li-whiskers.³⁹⁻⁴⁰ Micrographs of the Li deposits characterized by SEM (Figure 3F) and TEM (Figures 3G and S13) both show that ball-shaped Li deposits appear mostly at the tips/kinks of the Li-whiskers rich in crystalline defects. It has been suggested that at the kinks and tips, the Li nuclei are preferentially spherical.⁴¹ On the other hand, smaller protrusions on the Li-whiskers can be found, as indicated by the arrows in the inset of Figure 3G. These Li protrusions may act as the subsequent active spots where ball-shaped Li electrodeposit would occur. The growth of Li protrusions could be associated with the heterogeneity of the SEI on Li-whiskers, which will be discussed in the last part of this work.

Cryo-TEM based selected area electron diffraction (SAED) data in Figures 3H and 3I show that the whisker-shape Li electrodeposits are dominated by single crystalline Li phases. No signals related to the SEI are evident in Figure 3I due to the extremely low SEI content compared to Li. However, the SAED pattern corresponding to the surface of a Li-whisker in Figure S14 reveals the presence of polycrystalline Li_2CO_3 , Li_2O and LiF , apart from single crystalline Li. These Li-salts constitute the inorganic content of the SEI layer grown on Li-whiskers. In comparison, the Li-balls are concluded to be dominantly, though not completely, amorphous, given the disproportion of signals from the SEI and metallic Li (Figures 3J-K). Specifically, in the SAED pattern, strong signals of polycrystalline LiF and Li_2O are evident, but originate from the thin SEI shell of the Li-ball; In contrast, with much more volume/mass of Li being probed, only faint and barely perceptible electron diffraction spots of Li (200) are recognized. Besides, small protrusions were also found adhering to the Li-whiskers (Figures 3G and 3L). Similar to Li-balls, these protrusions are found to be amorphous with LiF -rich SEI layers, as seen from the fast Fourier transform (FFT) results in Figure 3M, and hence are concluded as the embryos of Li-balls. In brief, electrodeposits in their primordial stage (protrusions and Li-balls) are amorphous, but become crystalline as the balls evolve to Li-whiskers (Figure 3N), while their corresponding SEI layers are also distinct with disparity profiles that will be discussed in the next section.

SEI of Li-balls and Li-whiskers

The distinct morphologies of Li-balls and Li-whiskers allow us to identify the discrepancies of the SEI layer on their primordial stage (Li-balls) and the SEI layer on the grown stage (Li-whiskers), which are hereafter referred to as SEI-I and SEI-II, respectively. The HRTEM and FFT results in Figures 4A and 4B show that the SEI-I layer (on Li-balls, ~10 nm thick) is mainly crystalline (Figure S14) with the major contribution from polycrystalline LiF , which is consistent with the SAED results (Figure 3K). Besides, weak signals of polycrystalline Li_2O can also be recognized in the SAED pattern, but are not visible in the HRTEM/FFT. This can be ascribed to the low content of Li_2O in the SEI layer, particularly in the much smaller imaging region of HRTEM (in Figure 4A) compared with that of SAED (Figure 3K). In contrast, the HRTEM/FFT results in Figures 4C and 4D and the SAED pattern (Figure S14) demonstrate that the SEI-II layer (on Li-whiskers) consists of two layers (~20 nm thick), including an inner predominantly inorganic layer consisting mostly of Li_2O , Li_2CO_3 and LiF crystallites and an outer amorphous and organic stratum.

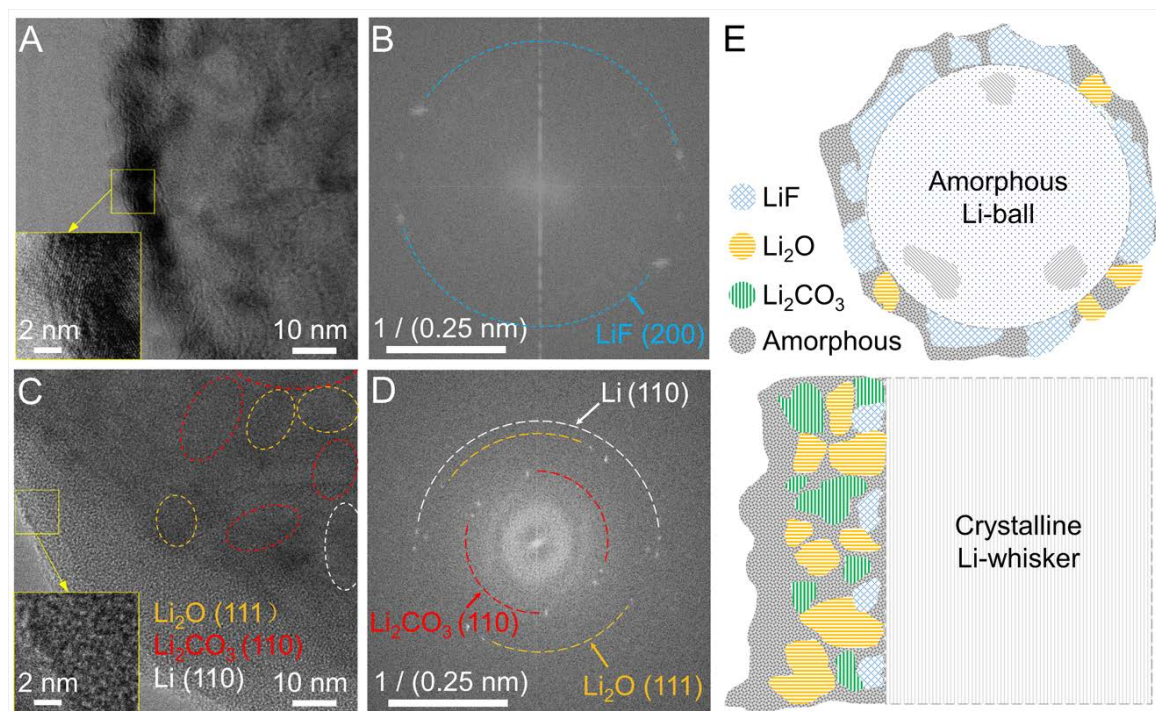


Figure 4. Cryo-TEM characterization and schematic of the SEI layer. (A, C) HRTEM images of the SEI layers on a Li-ball and a Li-whisker, respectively; The insert in (A), which is enlarged in Figure S15, displays the crystalline structure of the SEI layer on the Li-ball; An overview in Figure S16 shows the location of (C). (B, D) FFT patterns of the corresponding HRTEM images in (A, C); (E) Schematic illustrations of the SEI layer structures of Li-balls and Li-whiskers (not to scale).

The dominance of LiF in the initially formed SEI-I layer can be attributed to the decomposition of LiPF_6 on the surface of the Li-balls.⁴² Meanwhile, the organic solvents would be further reduced upon contact with Li, forming amorphous and organic compounds consisting of mainly lithium ethylene dicarbonate (LEDC). Thus, it is believed that LiF and LEDC constitute the primary components of the SEI-I layer. Similar to the evolution of SEI on graphite anode in Li-ion batteries,⁴² the chemically unstable LEDC could decompose into a complex mixture of organic and inorganic compounds (e.g. Li_2CO_3 , Li_2O and polycarbonate) with the progressing Li deposition, which eventually leads to a thicker SEI-II layer. The detailed structures of SEI-I and SEI-II are illustrated in Figure 4E.

Correlation between the SEI layer and the Li growth mechanism

Based on the aforementioned results, we propose a mechanism of Li nucleation and growth during electrodeposition in carbonate-based electrolytes, as shown in Figure 5. Due to the existence of surface cracks, pits, and subsurface impurities on practical Li electrodes, Li-ions and electrons would preferentially gather at the interface of these sites and form Li nuclei as a result of a high local electron density at these inhomogeneous sites from the onset of deposition. This is supported by the site-favored electrodeposits found at the surface cracks and subsurface impurities revealed by SEM and synchrotron X-ray tomography (Figures S17 and S18), as well as supported by simulation results (Figure S19).

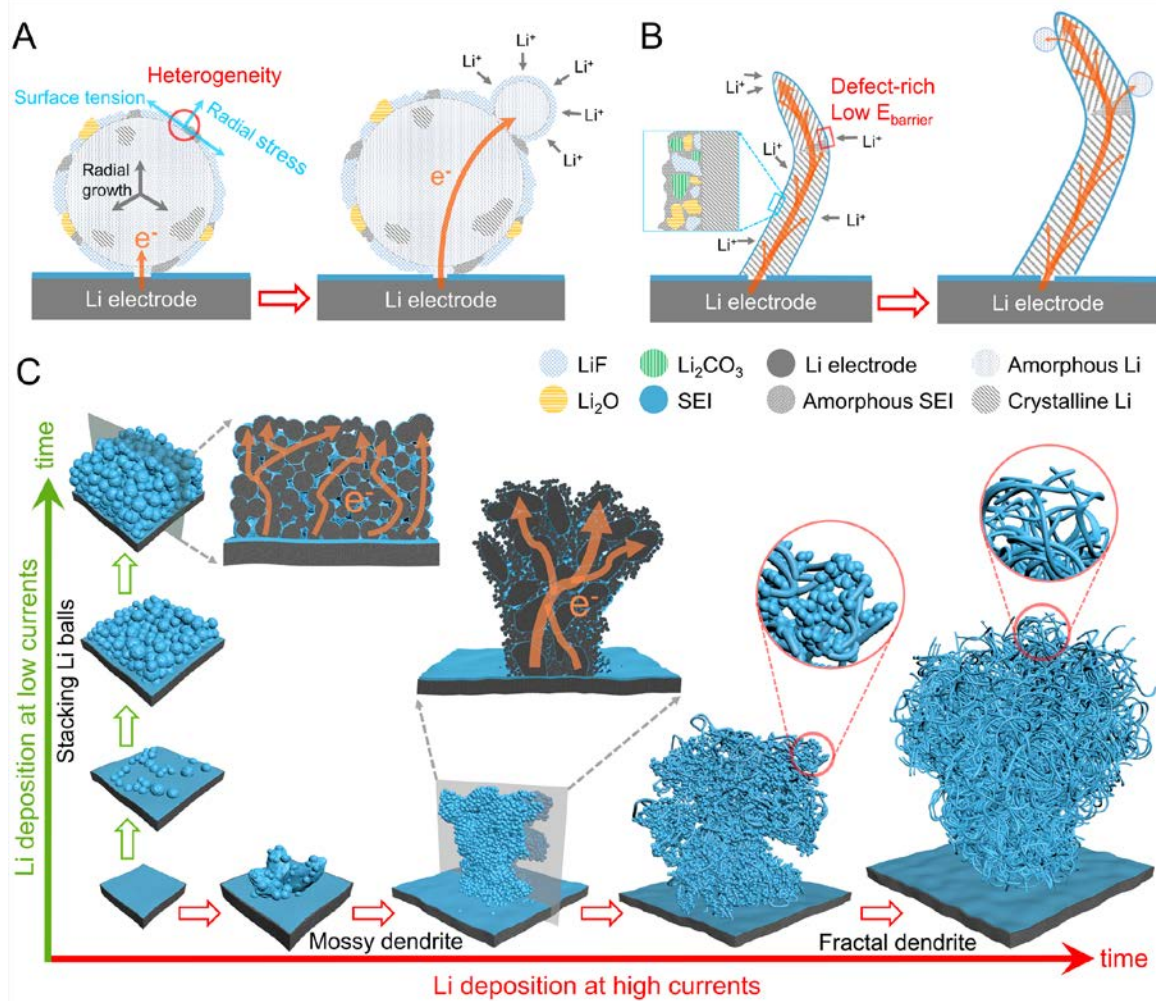


Figure 5. Schematics illustrating the proposed Li nucleation and growth mechanism. (A) A schematic of a new nucleus forming on Li-balls where the SEI-I layer is heterogeneous in terms of structure and chemistry. (B) Two favored preferential deposition sites on Li-whiskers: tips with newly formed SEI layer and kinks where defects are rich. (C) Illustration of the evolution of Li deposition at low and high currents.

After the initial nucleation, the subsequent growth determines the morphology of deposits. When electrodeposition is performed at a low current density, the overpotential of Li nucleation is low and electrodeposition is kinetics controlled. Therefore, the initial nuclei tend to be spherical due to low surface energy and amorphous due to the insufficient driving force to overcome the activation energy for Li crystallization. The SEI layer of these Li nuclei is thin and LiF-dominated (i.e. SEI-I), which has a low Li⁺ diffusion barrier⁴³, thus facilitating fast and uniform Li-ion diffusion. As a result, the Li nuclei grow radially beneath the SEI-I layer. Upon continuous expansion, the radial stress and surface tension induced by the expansion of Li-balls would cause the breakage of the SEI-I layer in which structural and chemical heterogeneities are pronounced as, for example, LiF and organic Li salts⁴⁴ co-exist in some areas (Figure 5A). The breakage would facilitate Li-ion and electron transport and serves as an active site for the formation of new Li nuclei. Therefore, Li-balls could appear next to each other across the electrode surface due to the relatively homogenous Li-ion distribution at a low deposition rate and stack up as deposition proceeds (Figure 5C).

When the current density exceeds the rate of Li-ion diffusion, in other words, the Li deposition is diffusion-limited, the initially formed Li deposits tend to be whisker-shaped driven by a high overpotential²⁵. With the Li-whisker growing, the accumulating mechanical strain of metallic Li beneath the SEI layer and crystallographic defects formed during Li electro-crystallization could result in kinks on the Li-whisker (Figures S20-21), where the energy barrier for Li-ion nucleation is low. Charge transport is facilitated at these kinks owing to the deformed/cracked SEI layer. As a result, new Li nuclei form at the kinks, which are rather ball-shaped than whisker-like, due to the significantly decreased local current density as a result of the increase of real surface area (Figure 5B). Another active site for Li nucleation is the tip of Li-whiskers where newly formed SEI layers are still thin, and thus induce a relatively fast Li⁺ migration through SEI and the forming of nuclei. In the following stage, Li-whiskers grow both in length and diameter, forming Li-whiskers with increased aspect ratios (i.e., growth is preferentially axial) or bulky Li (preferential radial-growth); In the meantime, as observed in previous reports^{39-40, 45}, some Li balls may evolve towards Li-whiskers along specific Li-facets (e.g., (110) and (200) in Figures S20 -21) driven by a high overpotential. Eventually, bush-shaped deposits form, consisting of Li-whiskers, sub- μm -sized Li-balls and μm -sized bulky Li, among which the bulky and whisker-shaped ones serve as the bush trunk and branches, respectively (Figure 5C).

Although whisker-like Li deposits are more commonly reported, our results suggest the co-existence of spherical and whisker-like Li deposits during Li electrodeposition in carbonate-based electrolytes. This is consistent with the observations in previous studies⁴⁶⁻⁴⁸ using carbonate-based electrolytes. At a high deposition rate, amorphous ball-like deposits grow towards highly crystalline Li-whiskers, which agrees well with the observed crystallinity transition of Li deposition from glassy to crystalline⁴⁹. Meanwhile, it has been demonstrated that amorphous Li exhibits a higher plating/stripping Coulombic efficiency than that of crystalline Li.⁴⁹ In light of this, an improved cycling stability of Li metal anodes can be anticipated through controlling the morphologies of Li deposition and facilitating spherical and amorphous Li deposition using approaches like electrolyte optimization and surface engineering, etc.

In addition, we for the first time, to the best of our knowledge, uncovered the differences in chemistry and nanostructure of the SEI on Li-balls and whiskers using cryo-TEM. Given the electric insulating nature of SEI, the high heterogeneity of the SEI is attributed to the root cause that enables new nucleation on the insulating SEI, as potential breakage of the heterogeneous SEI (e.g., as a result of the expansion of Li-balls) could open up pathways for electron transfer to the Li/electrolyte interface at the breakage areas and thus lead to the reduction of Li-ions and nucleation at the interface.

Compared to two dimensional (2D) or surface imaging techniques (e.g. standard SEM/TEM/TXM), FIB/SEM enables us to reveal the rarely reported inner structures of Li deposits that consist of the different Li morphologies (e.g., ball- and whisker-like), enabling three-dimensional depiction of Li deposits of different evolution stages. Furthermore, this allows us to reveal the morphological evolution process of Li electrodeposition, providing new fundamental understanding towards Li deposition. Compared to efforts devoted to Li deposition, the electro-dissolution process of Li remains relatively less explored. Therefore, further study on the electro-dissolution process of Li is also required to get a panoramic view of the plating-stripping mechanism of Li metal anode.

In summary, this work investigates Li nucleation and growth, the solid/electrolyte interface, and their correlation during Li electrodeposition in a carbonate-based liquid electrolyte using FIB/SEM and cryo-TEM. The morphological evolution of Li deposits is determined by the varying distribution of Li-ions near the electrode-electrolyte interface at different current densities, as computational modeling

corroborates. With the increase of current density, electrodeposited Li transforms from Li-balls to granule- or column-like deposits and finally to bush-like objects. Study of the interior structures of Li deposits reveals that Li-balls stack up and spread across the electrode surface at a low deposition rate of 0.2 mA cm^{-2} , while at higher current densities exceeding the diffusion-limiting current, bush-shaped deposits form with sub- μm -sized Li-whiskers/balls as branches and μm -sized bulky Li as the trunk. Meanwhile, Li-balls are concluded to be the origin of the Li-whiskers. The ball-shaped deposits are dominated by amorphous Li, while the Li-whiskers are highly crystalline. Moreover, the Li-balls are covered with a thin and LiF-dominated SEI layer, which is heterogeneous and may induce the formation of new Li nuclei. In comparison, thick and organic-enriched SEI appears on the dendritic Li and hinders charge transport across the SEI layer. As a result, new Li nuclei preferentially form at defect-rich regions (e.g. kinks) and the tips of the Li whisker. The proposed Li nucleation and growth mechanism as well as its relationship with the SEI growth provides fundamental insights into the electrochemical Li deposition behaviors.

Experimental Methods

1. Materials

Li metal chips were purchased from MTI Corp. USA. The electrolyte of 1 M LiPF₆ with a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:1, v/v) and anhydrous dimethyl carbonate (DMC) were received from Sigma-Aldrich. A Swagelok derived cell consisting of a polyamide-imide housing is described in our previous report⁵⁰.

2. Battery assembly and electrodeposition

The Li chips (0.45 mm thick) were punched into disks with a diameter of 2.0 or 3.0 mm and used for cell assembly without further treatments. The Swagelok-type cell was employed to build symmetrical Li||Li cells in an argon-filled MBraun glovebox using two Li chips with a diameter of 3 mm and 2 mm as the working and counter electrode, respectively. To observe the evolution of Li electrodeposition, no separator but a distance of around 1.3 mm between the two Li disks was used without any external stack pressure, thus avoiding mechanical compression and flattening of Li deposition that usually happens in coin cells. After assembly, cells were subjected to galvanostatic charging at different current densities with the bottom Li (3 mm) acting as the cathode for Li deposition. Galvanostatic charging of the cells was conducted using a Neware BTS4000 battery cycler.

3. FIB/SEM and Cryo-TEM characterization

Sample preparation: After electrodeposition at various current rates, the cells were disassembled in an argon-filled MBraun glovebox (O₂ and H₂O < 5 ppm), where the working electrodes were removed from the cell. Before drying under vacuum, the electrode samples were rinsed by anhydrous DMC to remove residual electrolyte. After this, the whole electrode or the electrodeposits were mounted on a sample holder or transferred onto TEM grids. The TEM grids with Li electrodeposits were sealed in 1 mL plastic Eppendorf tubes inside an Ar-filled glovebox before cryo-TEM characterization. To avoid degradation, sealed samples were transported and protected by argon gas using a sealed container for the FIB/SEM and cryo-TEM measurements.

FIB/SEM imaging: The morphological and structural characteristics of the as-grown Li deposits on the electrode were investigated using a focused ion beam scanning electron microscope (FIB/SEM, Zeiss Crossbeam 340) at room temperature. SEM images were taken primarily at 2 kV. FIB cutting and milling were performed with a gallium ion beam voltage of 30 kV. The current used for FIB cutting was 7, 15, or 30 nA depending on the cutting area. While for fine milling, the current applied was 0.3 or 0.7 nA, thus minimizing potential ion beam damage. The diameter analysis of ball-shaped deposits from the cross-sectional views was conducted using ImageJ/Weka segmentation⁵¹.

Cryo-TEM imaging: The Eppendorf tubes containing TEM grids with Li deposits were plunged into a dewar containing liquid nitrogen (LN₂), and were then rapidly crushed with a cutter plier while immersed in LN₂ in order to avoid the exposure of the TEM grids to the ambient air. The grids were then either transferred directly to a JEOL JEM-2100 transmission electron microscope (JEOL GmbH, Eching, Germany) using a cryo-transfer holder (Gatan 914, Gatan, Munich, Germany) or stored in LN₂. During the insertion of cryo-transfer holder into the TEM column, the sample was protected by a built-in shutter on the holder. Throughout the sample preparation and transfer, the Li deposits were protected by Ar gas or LN₂ without

exposure to the ambient air. Imaging was carried out at temperatures around 90 K and the TEM was operated at an acceleration voltage of 200 kV. Cryo-TEM micrographs were recorded at several magnifications with a bottom-mounted $4k \times 4k$ CMOS camera (TemCam-F416, TVIPS, Gauting, Germany) and the total electron dose in each micrograph was kept below $20 e^-/\text{\AA}^2$. Image processing was done with the ImageJ software.

4. Simulations

Smoothed particle hydrodynamics (SPH), which is a particle-based Lagrangian method, was used to simulate reactive transport near the electrode-electrolyte interface.⁵² SPH is a continuum-based method and solves equations for the mass transport and surface reactions of Li-ions near the interface. Based on previous works^{35-37, 53}, this model has included verification of the numerical model and validation with literature data. A detailed description of the model is provided in the supporting information.

Supporting information

The supporting information is available free of charge at:

Additional FIB/SEM, cryo-TEM images; simulation and electrochemical results (PDF)

Supporting Movie S1: FIB-cutting of a bush-shaped deposit obtained at 10 mA cm^{-2} (AVI)

Supporting Movie S2: Beam damage to an amorphous deposit under cryo-TEM (electron dosage: $500 e^-/\text{\AA}^2$ per image; frame rate: 7 frames per second) (AVI)

Supporting Movie S3: Beam damage to a Li-whisker and protrusions under cryo-TEM (electron dosage: $500 e^-/\text{\AA}^2$ per frame; frame rate: 7 frames per second) (AVI)

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Author Contributions

K.D. and Y.X. contributed equally to this work. K.D., F.S. and I.M. conceived the idea and designed the experiments. M.O. conducted the FIB/SEM measurement and data analysis. K.D., Y.X. and Z.K. performed the cryo-TEM experiments. Y.X. and Z.K. interpreted the cryo-TEM data. J.T. and E.R. conducted the simulations. C.Y., S.M. and A.H. helped prepare and perform experiments. K.D. and Y.X. co-wrote the manuscript with input from other authors. Y.L. and I.M. supervised the project.

Notes

The authors declare no competing financial interest.

References

1. Xu, W.; Wang, J.; Ding, F.; Chen, X.; Nasybulin, E.; Zhang, Y.; Zhang, J.-G., Lithium metal anodes for rechargeable batteries. *Energy Environ. Sci.* **2014**, *7* (2), 513-537.
2. Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Zhang, Q., Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem Rev* **2017**, *117* (15), 10403-10473.
3. Lin, D.; Liu, Y.; Cui, Y., Reviving the lithium metal anode for high-energy batteries. *Nature Nanotechnology* **2017**, *12*, 194.
4. Aurbach, D.; Markovsky, B.; Salitra, G.; Markevich, E.; Talyossef, Y.; Koltypin, M.; Nazar, L.; Ellis, B.; Kovacheva, D., Review on electrode–electrolyte solution interactions, related to cathode materials for Li-ion batteries. *Journal of Power Sources* **2007**, *165* (2), 491-499.
5. Liu, B.; Zhang, J.-G.; Xu, W., Advancing Lithium Metal Batteries. *Joule* **2018**, *2* (5), 833-845.
6. Li, G. X.; Liu, Z.; Huang, Q. Q.; Gao, Y.; Regula, M.; Wang, D. W.; Chen, L. Q.; Wang, D. H., Stable metal battery anodes enabled by polyethylenimine sponge hosts by way of electrokinetic effects. *Nature Energy* **2018**, *3* (12), 1076-1083.
7. Wang, S. H.; Yin, Y. X.; Zuo, T. T.; Dong, W.; Li, J. Y.; Shi, J. L.; Zhang, C. H.; Li, N. W.; Li, C. J.; Guo, Y. G., Stable Li Metal Anodes via Regulating Lithium Plating/Stripping in Vertically Aligned Microchannels. *Adv Mater* **2017**, *29* (40), 1703729.
8. Li, N.; Wei, W.; Xie, K.; Tan, J.; Zhang, L.; Luo, X.; Yuan, K.; Song, Q.; Li, H.; Shen, C.; Ryan, E. M.; Liu, L.; Wei, B., Suppressing Dendritic Lithium Formation Using Porous Media in Lithium Metal-Based Batteries. *Nano Lett* **2018**, *18* (3), 2067-2073.
9. Becking, J.; Grobmeyer, A.; Kolek, M.; Rodehorst, U.; Schulze, S.; Winter, M.; Bieker, P.; Stan, M. C., Lithium-Metal Foil Surface Modification: An Effective Method to Improve the Cycling Performance of Lithium-Metal Batteries. *Advanced Materials Interfaces* **2017**, *4* (16), 1700166.
10. Zhang, H.; Liao, X.; Guan, Y.; Xiang, Y.; Li, M.; Zhang, W.; Zhu, X.; Ming, H.; Lu, L.; Qiu, J., Lithiophilic-lithiophobic gradient interfacial layer for a highly stable lithium metal anode. *Nature communications* **2018**, *9* (1), 1-11.
11. Basile, A.; Bhatt, A. I.; O'Mullane, A. P., Stabilizing lithium metal using ionic liquids for long-lived batteries. *Nat Commun* **2016**, *7*, ncomms11794.
12. Wang, C.; Zhao, Y.; Sun, Q.; Li, X.; Liu, Y.; Liang, J.; Li, X.; Lin, X.; Li, R.; Adair, K. R.; Zhang, L.; Yang, R.; Lu, S.; Sun, X., Stabilizing interface between Li₁₀SnP₂S₁₂ and Li metal by molecular layer deposition. *Nano Energy* **2018**, *53*, 168-174.
13. Lewis, J. A.; Cortes, F. J. Q.; Boebinger, M. G.; Tippens, J.; Marchese, T. S.; Kondekar, N.; Liu, X.; Chi, M.; McDowell, M. T., Interphase Morphology between a Solid-State Electrolyte and Lithium Controls Cell Failure. *ACS Energy Letters* **2019**, *4* (2), 591-599.
14. Zhang, X.-Q.; Cheng, X.-B.; Chen, X.; Yan, C.; Zhang, Q., Fluoroethylene Carbonate Additives to Render Uniform Li Deposits in Lithium Metal Batteries. *Advanced Functional Materials* **2017**, *27* (10), 1605989.
15. Ding, F.; Xu, W.; Graff, G. L.; Zhang, J.; Sushko, M. L.; Chen, X.; Shao, Y.; Engelhard, M. H.; Nie, Z.; Xiao, J.; Liu, X.; Sushko, P. V.; Liu, J.; Zhang, J. G., Dendrite-free lithium deposition via self-healing electrostatic shield mechanism. *J Am Chem Soc* **2013**, *135* (11), 4450-4456.
16. Wood, K. N.; Noked, M.; Dasgupta, N. P., Lithium Metal Anodes: Toward an Improved Understanding of Coupled Morphological, Electrochemical, and Mechanical Behavior. *ACS Energy Letters* **2017**, *2* (3), 664-672.
17. Wood, K. N.; Kazyak, E.; Chadwick, A. F.; Chen, K. H.; Zhang, J. G.; Thornton, K.; Dasgupta, N. P., Dendrites and Pits: Untangling the Complex Behavior of Lithium Metal Anodes through Operando Video Microscopy. *ACS Cent Sci* **2016**, *2* (11), 790-801.
18. Nishida, T.; Nishikawa, K.; Rosso, M.; Fukunaka, Y., Optical observation of Li dendrite growth in ionic liquid. *Electrochimica Acta* **2013**, *100*, 333-341.

19. Steiger, J.; Kramer, D.; Mönig, R., Microscopic observations of the formation, growth and shrinkage of lithium moss during electrodeposition and dissolution. *Electrochimica Acta* **2014**, *136*, 529-536.
20. Bai, P.; Li, J.; Brushett, F. R.; Bazant, M. Z., Transition of lithium growth mechanisms in liquid electrolytes. *Energy & Environmental Science* **2016**, *9* (10), 3221-3229.
21. Cheng, J.-H.; Assegie, A. A.; Huang, C.-J.; Lin, M.-H.; Tripathi, A. M.; Wang, C.-C.; Tang, M.-T.; Song, Y.-F.; Su, W.-N.; Hwang, B. J., Visualization of Lithium Plating and Stripping via in Operando Transmission X-ray Microscopy. *The Journal of Physical Chemistry C* **2017**, *121* (14), 7761-7766.
22. Li, Y.; Li, Y.; Pei, A.; Yan, K.; Sun, Y.; Wu, C.-L.; Joubert, L.-M.; Chin, R.; Koh, A. L.; Yu, Y., Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy. *Science* **2017**, *358* (6362), 506-510.
23. Ely, D. R.; Garcia, R. E., Heterogeneous Nucleation and Growth of Lithium Electrodeposits on Negative Electrodes. *Journal of the Electrochemical Society* **2013**, *160* (4), A662-A668.
24. Nucleation and Growth Models. In *Fundamentals of Electrochemical Deposition*, pp 113-138.
25. Jana, A.; Woo, S. I.; Vikrant, K. S. N.; García, R. E., Electrochemomechanics of lithium dendrite growth. *Energy & Environmental Science* **2019**, *12* (12), 3595-3607.
26. Chen, L.; Zhang, H. W.; Liang, L. Y.; Liu, Z.; Qi, Y.; Lu, P.; Chen, J.; Chen, L.-Q., Modulation of dendritic patterns during electrodeposition: A nonlinear phase-field model. *Journal of Power Sources* **2015**, *300*, 376-385.
27. Chazalviel, J.-N., Electrochemical aspects of the generation of ramified metallic electrodeposits. *Physical review A* **1990**, *42* (12), 7355.
28. Fleury, V.; Chazalviel, J.-N.; Rosso, M.; Sapoval, B., The role of the anions in the growth speed of fractal electrodeposits. *Journal of electroanalytical chemistry and interfacial electrochemistry* **1990**, *290* (1-2), 249-255.
29. Pei, A.; Zheng, G.; Shi, F.; Li, Y.; Cui, Y., Nanoscale Nucleation and Growth of Electrodeposited Lithium Metal. *Nano Lett* **2017**, *17* (2), 1132-1139.
30. Liu, Y.; Lin, D.; Li, Y.; Chen, G.; Pei, A.; Nix, O.; Li, Y.; Cui, Y., Solubility-mediated sustained release enabling nitrate additive in carbonate electrolytes for stable lithium metal anode. *Nat Commun* **2018**, *9* (1), 3656.
31. Choudhury, S.; Archer, L. A., Lithium Fluoride Additives for Stable Cycling of Lithium Batteries at High Current Densities. *Advanced Electronic Materials* **2016**, *2* (2), 1500246.
32. Yu, X.; Manthiram, A., Electrode-electrolyte interfaces in lithium-based batteries. *Energy & Environmental Science* **2018**, *11* (3), 527-543.
33. Qian, J.; Xu, W.; Bhattacharya, P.; Engelhard, M.; Henderson, W. A.; Zhang, Y.; Zhang, J.-G., Dendrite-free Li deposition using trace-amounts of water as an electrolyte additive. *Nano Energy* **2015**, *15*, 135-144.
34. Chen, X.-R.; Yao, Y.-X.; Yan, C.; Zhang, R.; Cheng, X.-B.; Zhang, Q., A Diffusion-Reaction Competition Mechanism to Tailor Lithium Deposition for Lithium-Metal Batteries. *Angewandte Chemie International Edition* **2020**, *59* (20), 7743-7747.
35. Tan, J.; Tartakovsky, A. M.; Ferris, K.; Ryan, E. M., Investigating the Effects of Anisotropic Mass Transport on Dendrite Growth in High Energy Density Lithium Batteries. *Journal of The Electrochemical Society* **2015**, *163* (2), A318-A327.
36. Tan, J.; Ryan, E. M., Computational study of electro-convection effects on dendrite growth in batteries. *Journal of Power Sources* **2016**, *323*, 67-77.
37. Tan, J.; Ryan, E. M., Structured electrolytes to suppress dendrite growth in high energy density batteries. *International Journal of Energy Research* **2016**, *40* (13), 1800-1810.
38. Peled, E.; Menkin, S., Review—SEI: Past, Present and Future. *Journal of The Electrochemical Society* **2017**, *164* (7), A1703-A1719.

39. He, Y.; Ren, X.; Xu, Y.; Engelhard, M. H.; Li, X.; Xiao, J.; Liu, J.; Zhang, J.-G.; Xu, W.; Wang, C., Origin of lithium whisker formation and growth under stress. *Nature Nanotechnology* **2019**, *14* (11), 1042-1047.
40. Zhang, L.; Yang, T.; Du, C.; Liu, Q.; Tang, Y.; Zhao, J.; Wang, B.; Chen, T.; Sun, Y.; Jia, P., Lithium whisker growth and stress generation in an in situ atomic force microscope–environmental transmission electron microscope set-up. *Nature nanotechnology* **2020**, *15* (2), 94-98.
41. Yamaki, J.-i.; Tobishima, S.-i.; Hayashi, K.; Keiichi, S.; Nemoto, Y.; Arakawa, M., A consideration of the morphology of electrochemically deposited lithium in an organic electrolyte. *Journal of Power Sources* **1998**, *74* (2), 219-227.
42. Heiskanen, S. K.; Kim, J.; Lucht, B. L., Generation and evolution of the solid electrolyte interphase of lithium-ion batteries. *Joule* **2019**, *3* (10), 2322-2333.
43. Ozhables, Y.; Gunceler, D.; Arias, T. A., Stability and surface diffusion at lithium/electrolyte interphases with connections to dendrite suppression. **2015**, *arXiv:1504.05799*.
44. Xu, Y.; Wu, H.; Jia, H.; Zhang, J.-G.; Xu, W.; Wang, C., Current Density Regulated Atomic to Nanoscale Process on Li Deposition and Solid Electrolyte Interphase Revealed by Cryogenic Transmission Electron Microscopy. *ACS Nano* **2020**, *14* (7), 8766-8775.
45. Kushima, A.; So, K. P.; Su, C.; Bai, P.; Kuriyama, N.; Maebashi, T.; Fujiwara, Y.; Bazant, M. Z.; Li, J., Liquid cell transmission electron microscopy observation of lithium metal growth and dissolution: Root growth, dead lithium and lithium flotsams. *Nano Energy* **2017**, *32*, 271-279.
46. Shi, F.; Pei, A.; Vailionis, A.; Xie, J.; Liu, B.; Zhao, J.; Gong, Y.; Cui, Y., Strong texturing of lithium metal in batteries. *Proc Natl Acad Sci USA* **2017**, *114* (46), 12138-12143.
47. Stark, J. K.; Ding, Y.; Kohl, P. A., Nucleation of Electrodeposited Lithium Metal: Dendritic Growth and the Effect of Co-Deposited Sodium. *Journal of The Electrochemical Society* **2013**, *160* (9), D337-D342.
48. Ju, Z.; Nai, J.; Wang, Y.; Liu, T.; Zheng, J.; Yuan, H.; Sheng, O.; Jin, C.; Zhang, W.; Jin, Z.; Tian, H.; Liu, Y.; Tao, X., Biomacromolecules enabled dendrite-free lithium metal battery and its origin revealed by cryo-electron microscopy. *Nat Commun* **2020**, *11* (1), 488.
49. Wang, X.; Pawar, G.; Li, Y.; Ren, X.; Zhang, M.; Lu, B.; Banerjee, A.; Liu, P.; Dufek, E. J.; Zhang, J.-G., Glassy Li metal anode for high-performance rechargeable Li batteries. *Nature Materials* **2020**, 1-7.
50. Dong, K.; Osenberg, M.; Sun, F.; Markötter, H.; Jafta, C. J.; Hilger, A.; Arlt, T.; Banhart, J.; Manke, I., Non-destructive characterization of lithium deposition at the Li/separator and Li/carbon matrix interregion by synchrotron X-ray tomography. *Nano Energy* **2019**, *62*, 11-19.
51. Arganda-Carreras, I.; Kaynig, V.; Rueden, C.; Eliceiri, K. W.; Schindelin, J.; Cardona, A.; Sebastian Seung, H., Trainable Weka Segmentation: a machine learning tool for microscopy pixel classification. *Bioinformatics* **2017**, *33* (15), 2424-2426.
52. Monaghan, J. J., Smoothed particle hydrodynamics. *Reports on progress in physics* **2005**, *68* (8), 1703.
53. Tan, J.; Cannon, A.; Ryan, E., Simulating dendrite growth in lithium batteries under cycling conditions. *Journal of Power Sources* **2020**, *463*, 228187.