In Situ Observation of Dendrite Behavior of Electrode in Half and Full Cells

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Lithium dendrites may cause internal short-circuiting, fires, and even explosions. Unfortunately, the study of dendrites has been hindered by the impossibility of in situ observations. This work proposes a new double-scale in situ experimental setup that records the dendrite evolution of half and full cells during small-current-density electrochemical testing. The experiments confirmed that dendritic growth eventually connects the cathode to the anode, with significant effects on the cell voltage. In the full and half-cells, the attached dendrites decreased and increased the voltage, respectively. During discharge, the bubbles generated by the side reaction affected the dendrite evolution in both cells. A detailed model of lithium dendrite evolution mechanism in the anode is also proposed.

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Lithium metal anodes have been extensively researched as an energy-dense power source for high energy-demand applications such as smartphones, smartwatches, activity trackers, tablet/laptop computers, e-bikes, and power tools.1,2 Unfortunately, lithium metal anode batteries are hampered by dendrite growth and low coulomb efficiency during the charging and discharging processes, which have prevented their commercialization.3,4 To improve the electrochemical performance of the battery system, Tripathi et al.5 conducted an in situ analysis of the battery interface. Lithium dendrites are responsible for thermal runaway, fires and explosions in lithium metal anodes.6 A lithium dendrite formed on the anode grows toward the cathode, typically during the battery charging process. When the sharp growing dendrite penetrates the separator and reaches the cathode, it causes electrical contact and short circuit of a working cell.7,8

Dendrites are challenging to study because their evolution results from different combinations of factors.9 Previous researchers have attempted to inhibit the formation of lithium dendrites by modified the electrolyte composition,10 temperature,6,11–13 current density,14–17 and electrode structure.21–23 The interaction among these factors is expected to change the growth rate and morphology of lithium dendrites.

Some researchers have theoretically and numerically simulated the evolution of lithium dendrites. Gibbs et al.24 simulated the three-dimensional morphology of free-growing metallic dendrites by a novel tomographic reconstruction algorithm using experimental morphological datasets. Qin et al.25 analyzed the electron transfer between lithium (100) and lithium cations in the surface proximity by density functional theory. They surmised that the strong heterogeneous electron distribution promotes heterogeneous nucleation and growth of lithium, eventually leading to dendritic behavior. Aryanfar et al.15,26 simulated lithium growth by the Monte Carlo method, and found that the electric field at the sharp tip of a dendrite accelerates the dendrite growth by rapidly drawing lithium ions. Yoon et al.27 simulated the deposition and stripping behavior of lithium in electrochemistry using COMSOL Multiphysics interactive software. They also found an intensified electric field strength at the tip of the dendrite, which attracted many lithium ions and aggravated the dendrite formation. Yan et al.28 and Hong and Viswanathan29 developed phase-field simulations of lithium dendrite growth. Liu and Lu30 presented a comprehensive mathematical model that concurrently couples the lithium dendrite growth, formation and growth of the solid-electrolyte interface (SEI) on the dendrite surface, dendrite penetration of the SEI layer, and SEI regrowth. These theoretical models have replaced the popular graphite electrode with a lithium metal electrode, providing deep physical insights into the formation and growth processes of lithium dendrites.

Other researchers have observed dendrite behavior in ex situ and in situ experiments. Li et al.19 studied the lithium dendrite nucleation and growth process under low and high current densities using in situ optical microscopy. Kong et al.20 also observed dendrite growth by in situ optical microscopy, and concurrently monitored the electrical characteristics of a cell under various current densities. Using a novel X-ray tomographic technique, Gibbs et al.24 determined the three-dimensional morphology of free-growing metallic dendrites. Li et al.30 captured the first atomic dendrite of lithium metal by cryo-electron microscopy. Guo et al.31 studied in situ dendrite growth in a side-by-side arrangement of commercial graphite electrodes. Dolké et al.32 observed the dendritic growth in Li/polymer cells. Wood et al.33 comprehensively investigated the voltage variations during lithium metal cycling, which are directly correlated to dendrite morphology evolution, using operando video microscopy. Shen et al.34 observed the dendritic growth in a graphite anode by operando electrochemical atomic force microscopy. These studies have revealed the evolution of lithium dendrites, especially the deposition of lithium metals, but the dendritic behavior in lithium–graphite half-cells has not been reported.

In most of the theoretical studies,15,24,27–29 and experimental observations,19,20,30,32,33 of lithium dendrites in half-cells, the anode is lithium metal. Lithium dendrite growth in today’s popular commercial graphite electrodes has been rarely addressed, especially under common operating conditions (low charge rates at room temperature). This work proposes a double-scale experimental setup for direct in situ observations of dendrite phenomena in commercial full cells under real operating conditions (small current charge/discharge at room temperature). Previous studies on lithium metal focused exclusively on the deposition process of lithium metal on Li–Li20,32,33 electrodes. To bridge this knowledge gap, we observed dendritic evolution in a lithium–graphite half-cell and a graphite-LiFePO4 full cell in situ. During the electrochemical cycle, we found that the voltage significantly changed when the dendrites connected the anode to the cathode. The bubbles generated by the side reaction during charge/discharge also affected the dendrite evolution.

Experimental

Double-scale in situ experimental observation system.—To observe the growth of lithium dendrites on anode electrodes, we developed a new double-scale (micro-scale and macro-scale) non-destructive experimental test system. The package of our experimental...
Dendrite behavior in the electrodes of a half-cell.—Panels (a)–(d) of Fig. 2 show the evolution of lithium dendrites in the half-cell during the first charge process (insertion of lithium ions into the anode). Fig. 2a shows the surface morphology of the electrodes in the initial charging state of the half-cell and the corresponding voltage traces in the cell. Fig. 2b shows the surface morphology of the anode electrode at the beginning of dendrite appearance, with the corresponding voltage traces. Gradually, the dendrite filled the gap between the cathode and anode and connected the two electrodes (Fig. 2c). Fig. 2d is the state of the dendrite when the half-cell was fully charged. According to the Fig. 2, exclusively dendrite growth and eventually short circuit are observed clearly at the charge rate of 0.2C during the first charging cycle. We need to point out that we don’t know the exact cycle numbers when dendrites appear in real commercial batteries. After disassembled the commercial battery which was used at small current, many dendrites were found.31

As shown in Fig. 2b, the dendrite was initiated in the lithium metal anode (region enclosed by the orange rectangle). As the charging continued, the dendrite size increased along with the voltage (left graph of Fig. 2b). At the end of the half-cell charging, a cluster of dendrites was formed (green solid rectangle in Fig. 2d), and the cathode and anode were connected. Cluster dendrites are smaller than dendritic dendrites because a dendrite tip exerts a strong electric field, attracting more lithium ions than the cluster.27 To clarify the voltage traces in Figs. 2c and 2d, we connect point A in Fig. 2c to point B in Fig. 2d by a vertical dashed line. The voltage begins rising obviously at point B and grows exponentially thereafter. Comparing the photographs of the anode surface captured at this time, one observes that the dendrite has just connected the cathode and the anode in Fig. 2c. As the electroplating progressed, the dendrites continued growing toward the cathode electrode, sharpening until they tightly connected the two electrodes (Fig. 2d). This phenomenon implies that the connected dendrites significantly affected the voltage in the cell. Setting the potential of lithium as 0 V, the potential of the original graphite electrode was 3.05 V during the first charge process, lithium dendrites form and cathodic LiC₆ undergoes a phase transition whereby lithium ions are released from the cathodic graphite. When dendrites connect the cathode and the anode (the dendrite connecting two electrodes was regarded as a fuse),20,32 and the lithium ions transfer from the electrolyte to electrolyte and connected lithium dendrite lead to lithium ions remove from the cathodic LiC₆ more quickly. Hence, a large number of lithium ions are released from the cathodic LiC₆, causing the voltage rise. Zheng et al.36 also showed that the cell voltage rises with the lithium ions remove from in LiC₆.

Fig. 3 shows the complete voltage and current changes during the first charge and discharge of a half-cell. The voltage increased exponentially at the end of charging (green dotted frame in Fig. 3), because the cathode and anode were connected by dendrites. As indicated in the voltage curve, the charging time was shorter than 0.2C, reducing the capacity of the battery. Lithium metal underdoes a notable volume change that damages the SEI and accelerates the loss of cycle-able
Figure 2. In situ observations of lithium dendrites forming on the half-cell during the first charge: (a) before cycling; (b) dendrite region (solid orange rectangle); (c) Dendrite connecting two electrodes; (d) Dendrite state after full charging.

Dendritic growths may be attributed to the inhomogeneity of SEI films at room temperature and with low current density.35

Dendrite behavior of electrodes in a full cell.—Fig. 4 presents images of full cells with a graphite-LiFePO4 electrode during the charge/discharge cycles. Fig. 4a shows the surface morphology of the electrodes in the initial state of full cell charging, and the corresponding voltage traces in the cell. Fig. 4b shows the initial appearance of the dendrite in the first charging process (enclosed in the solid white rectangle), with the corresponding synchronized voltage trace. Eventually, the dendrite filled the gap between the cathode and the anode (Fig. 4c). In Fig. 4d, the dendrites are tightly connected to the two electrodes. Panels (e) and (f) of Fig. 4 show the dendrite states at the ends of the first charge and first discharge, respectively, with their corresponding synchronized voltage traces.

In the double-scale in situ experimental setup, the lithium-ion transport path is clarified by the color change of the graphite electrode surface. As shown in Fig. 4b, lithium ions entered the anode electrode from four sides, and the corresponding voltage trace curve gradually increased. Dendrites were initiated on the anode and grew toward the cathode (Fig. 4b). The voltage trace is much smaller in Fig. 4d than in Fig. 4c. In Fig. 4c, the dendrite had just bridged the anode and the cathode, whereas in Fig. 4d, it had tightly connected the two electrodes, creating an internal circuit. More precisely, during the first
Figure 3. Voltage and current curves during the first charge and discharge of the half-cell. The blue and green dotted frames indicate the initial/nucleation state of the dendrite and the dendritic junction of the cathode and anode until the end of charging, respectively.

Figure 4. In situ observations of lithium dendrites forming in the full cell during the first charge process: (a) before cycling; (b) dendrite region (white solid rectangle); (c) dendrite connecting two electrodes; (d) dendrite state after 240 minutes of charging (e) dendrite state after full charging; (f) dendrite state after full discharge.

Figure 5. Voltage and current curves during the first charge and discharge of the full cell. The blue and green dotted frames indicate the beginning/nucleation of dendrites during the first charge process and the first dendrite bridging between the cathode and anode, respectively. The purple dotted frame indicates when the dendrite tightly connects the anode and cathode, and the red dotted frame indicates the end of the discharge process.

The charge process, lithium dendrites form and lithium ions intercalation into anode graphite from LiFePO₄. The dendrites will be a fuse when they connect the cathode and anode,²⁰,³² the lithium ions transfer path is changed which caused the voltage decrease. Moreover, the dendrites connecting the electrodes reduce the resistance of a battery system,³⁸ causing a voltage drop under constant current conditions. Once it had dropped, the voltage remained stable with small-range fluctuations (cf. Figs. 4e and 4d). This phenomenon is easily understood. Once the two electrodes were connected, the dendrite could be regarded as a fuse.²⁰,³² The current could go through the connecting point and cause a temperature rise that breaks the connection. So, this leads to a small range of voltage recovery. The phenomenon recurs until the charging time terminates (Fig. 4e). A similar voltage-recovery phenomenon was reported by Dollé et al.³² In addition, the anode surface was completely golden indicating the completion of charging.³¹ The irreversible lithium dendrites (the so-called dead lithium) remained on the electrode after the discharge (Fig. 4f). It should be noted that some dead lithium, which increases the surface roughness of the electrode and enhances the lithium growth during deposition in the second charge/discharge cycle, is permanently attached to the electrode.

Fig. 5 plots the voltage and current changes during the first charge–discharge cycle of the full cell. The voltage drop followed by the stable fluctuations (purple dotted rectangle in Fig. 5) indicates that an internal short circuit was formed by dendrites connecting the cathode to the anode. At the end of the discharge (red dotted square in Fig. 5), the residual dendrites reduced the battery capacity.⁵,³¹
Figure 6. Schematic of Li electrodeposition on a lithium metal anode surface: (a) original fully discharged state; (b) random nucleation of Li metal; (c) continuation of dendrite growth and formation of new nucleated lithium; (d) formation of large protuberances or dendritic dendrites; (e) dissolution of connecting dendrites by a high current surge; (f) dendrite state at the end of charging.

Lithium dendrite formation process.—Based on the experimental observations (Figs. 2 and 4), we propose an ideal model of lithium dendrite formation and dissolution processes in battery cells. Here we describe the lithium deposition process on the anode of a lithium–graphite half-cell. Previously, we described lithium deposition and decomposition on the anode of lithium graphite–LiFePO4.31 Our model is especially suitable for graphite electrodes because it accounts for the color change on the graphite surface during the charge–discharge process.

Fig. 6a shows the final discharge and initial charging states of the half-cell. When fully discharged, the surface of the anode electrode is clean and smooth, and the cathode electrode is golden. As the charging reaction proceeds, lithium ions are released from the cathode, enter the electrolyte, and diffuse into the SEI film. When they arrive at the anode–SEI interface, they are reduced and then directly deposited on the anode surface, accompanied by electron transfer. The interface reaction is $\text{Li}^+ + e^- = \text{Li}$. Fig. 6b shows the nucleation of lithium metal. In addition, the cathode surface lightens in color (Fig. 6a), indicating that lithium ions are ejecting from the cathode. As the anode charging reaction continues, the dendrites expand and pierce the SEI film, nucleating at new sites such as sites 1 and 2 in Fig. 6c, while the cathode surface gradually turns black. Attracted by the strong electric field distribution, many lithium ions gravitate to the dendrite tip.27

As the charging reaction continues, the dendrites evolve into a dendritic form (Fig. 6d). Because of the short transport distance, the lithium ions are more attracted to longer dendrites (dendrite 3 in Fig. 6c) than to shorter ones (dendrites 1 and 2 in Fig. 6c). The original nucleation site 1 in Fig. 6c expands as the charging reaction continues, and nucleation site 2 grows dendritically (Fig. 6d). We know that when dendrites connect the cathode to the anode, a large current passes through the half-cell, causing melting and disconnection of the dendrites from the cathode (in the model, the ablated part is shown as the white region of the largest dendrite in the purple dotted frame in Fig. 6e). The simulations of Hong and Viswanathan28 revealed a dynamic competition between ion transport and electrochemical reactions. Therefore, we speculate that when dendrites melt, lithium ions are attracted to the small dendrites at the electrode–electrolyte interface. These minor dendrites then grow as shown in Fig. 6e. As the charging reaction continues, the broken dendrites will reform and reconnect to both electrodes. When the bridging dendrites are re-ablated by another large current surge, the small dendrites will further grow. This cyclic phenomenon of bridging and ablation iterates until the dendrites fill the gap between the cathode and the anode, as shown at the end of the charging reaction (Fig. 6f). Note that at this time, the cathode electrode of the lithium–graphite half-cell is completely black. In addition, when the dendrite connects the cathode to the anode, an internal short circuit may be formed.38

Effect of bubbles on dendrites.—Bubbles are naturally formed in the full cell and half-cell experiments. They are the product of side reactions while generating the SEI film, and mainly consist of CO2 and C2H4.5 Gas in cells forms primarily during the formation cycles.39 Given that bubbles can reduce the battery capacity,39–41 we here explore the effect of bubbles on dendrite formation in in situ full cell and half-cell experiments. Figs. 7 and 8 show the effect of bubbles on the dendrites in a Li–graphite cell and a graphite-LiFePO4 cell, respectively.

Fig. 7a shows the dendrite morphology near a newly released bubble during the discharge cycle of a half-cell. In Fig. 7b, the bubble has gradually enlarged in the transverse direction, establishing close contact with the dendrites. Part of the dendrite separates from the cathode electrode and floats upward. Fig. 7c shows the dendrite morphology when the bubble has disappeared.
Figure 8. Effect of bubbles on dendrites in a graphite–LiFePO₄ cell: (a) dendrite morphology near a newly released bubble; (b) dendrite morphology after disappearance of the bubble; (c) morphology of dendrite 1 pushed upward by bubbles; (d) effect of a flow bubble on dendrite 1; (e) fragmentation of the original dendrite 1.

In Fig. 7a, the bubble initially appeared in the gap between the cathode and the anode. As the discharge continued, the bubble gradually expanded and squeezed the dendrite, partially fragmenting it (blue dotted circle in Fig. 7b). This phenomenon implies that nearby bubbles reduce the size of the dendrites by fragmenting them. As dendrites are hollow structures, they easily break under pressure.42 The formation of dead lithium by dendrite fragmentation is inevitable as the discharge continues. Carefully comparing the dendrite morphologies of Figs. 7a and 7c, one observes that the dendrite is originally perpendicular to the anode, but inclines to the left after the bubble interaction. This process is intuitively shown in supporting Video 1. When the enlarging bubbles penetrate the dendrite space, the dendrite bends to the left to accommodate them.

Panels (a) and (b) of Fig. 8 show the dendrite morphology near a newly released bubble and after disappearance of the bubble, respectively, in the full cell. Fig. 8c shows the upward effect of the bubble on dendrite 1, which subsequently detached from the anode. The flow bubble severely affected dendrite 1 (Fig. 8d), breaking it into many fragments (Fig. 8e).

As shown in Fig. 8a, bubbles appeared on the anode surface and below the dendrite. Comparing the dendrites in the red rectangles in Figs. 8a and 8b, it is found that most of the dendrites were separated from the anode under squeeze pressure from the bubbles at the bottom. Meanwhile, the smaller bubble in Fig. 8b than in Fig. 8a implies a bubble–dendrite interaction. As dendrite 1 was squeezed upward, it floated through the gap between the cathode and the anode (cf. Figs. 8c and 8d). As the charging continued, the floating dendrites were affected...
by more bubbles appearing in the gap, similarly to clay particles in a water flow. Eventually, dendrite 1 was fragmented as shown in Fig. 8e. Inevitably, these floating dendrite fragments dendrites become dead lithium, which increases the surface roughness of the electrode and enhances lithium growth. Supporting Video 2 clarifies the fragmentation process of dendrites near bubbles in the full cell.

Conclusions
We developed and demonstrated a new double-scale in situ experimental setup that records all phenomena (color change, gas generation, lithium dendrite growth, deformation, and other processes) during charge/discharge cycles in battery cells. Within this setup, we observed dendritic evolution in a Li–graphite half-cell and a graphite–LiFePO4 full cell in real time. The experiment confirmed that when dendrites connect the anode to the cathode, the voltage is significantly affected. The voltage decreased in the full cell, but rose sharply in the half-cell. During the discharge process, the dendrite evolution in both cells was disturbed by bubbles generated in the side reaction. The bubbles fragmented the dendrites, releasing the fragments into the electrolyte. It is hoped that by understanding the evolution mechanism of lithium dendrites, we can diminish their adverse effects, thereby improving the electrochemical performance of Li-ion batteries and meeting the high-energy demands of modern society.

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