

# Investigation of the Dynamic Process of Direct Contact Pre-lithiation in Graphite Anode of Lithium-ion Batteries

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## ABSTRACT

Lithium-ion batteries (LIBs) experiences a significant loss of initial capacity due to the formation of solid electrolyte interface (SEI) layer for the initial charge-discharge cycle, and weaken the advantages of LIBs. Pre-lithiation (Pr-Li) has emerged as an effective strategy to compensate for such lithium loss in the initial cycles. We employed in-situ research techniques to investigate the direct contact Pr-Li process in graphite anode, and utilizing ultrathin lithium foil structures. Results show that the specific evolution process of direct contact Pr-Li in the graphite anode. Notably, when the lithiation state is 50%, the lithiated graphite electrode undergoes a distinct color transformation from the initial black-gray to dark blue color ( $\text{LiC}_{18}$ ). It is investigated the Li transport pathway primarily involves convert into  $\text{Li}^+$  followed by diffusion within the electrolyte. This intricate process eventually results in the lithiated graphite electrode was obtained. By employing ultra-thin lithium foil structure as the lithium source and exploring with in-situ techniques, this study reveals the complex pre-lithiation dynamics inside the graphite anode using the direct contact Pr-Li method. This study contributes to more deeply understanding the mechanism of the direct contact Pr-Li, and have potential implications for the in-depth study and application of pre-lithiation technology in LIBs.

**Keywords:** Direct-contact Pr-Li, Graphite anode, Solid electrolyte interface, Lithium-ion batteries

## NONMENCLATURE

### Abbreviations

|       |  |
|-------|--|
| LIBs  | Lithium-ion batteries                      |
| SEI   | Solid electrolyte interface                |
| Pr-Li | Pre-lithiation                             |
| DC-Pr | Direct contact Pr-Li with metallic lithium |

## 1. INTRODUCTION

Lithium-ion batteries (LIBs) as a key energy storage technology, have been widely used in portable electronic devices and electric vehicles (EVs) owing to their long cycle life, impressive high energy density, high working voltage, and no memory effect<sup>[1-7]</sup>. LIBs are unable to meet the rapid growth of daily life and more commercialized applications. High-energy-density LIBs are still desirable to extend the driving range with the electric vehicle market continues prosperously<sup>[8,9]</sup>. In this context, it is particularly significant to develop lithium-ion batteries with higher energy density, faster charging, and improved safety performance.

Unfortunately, solid electrolyte interphase (SEI) forms at the anode due to the consumption of  $\text{Li}^+$  from the cathode during the first charging process, resulting in high irreversible capacity loss (ICL) and low initial Coulombic efficiency<sup>[10]</sup>. If the initial irreversible cycle loss cannot be compensated, the efficiency and recyclability of the energy storage device will be seriously affected<sup>[11, 12]</sup>. To alleviate this issue, additional  $\text{Li}^+$  sources can be added to the LIBs to compensate for the  $\text{Li}^+$  loss in the first cycle. The extra  $\text{Li}^+$  helps to maintain a higher reversible capacity, prevents the anode from deep cycling, and stabilizes the anode so that capacity retention is improved. Pre-lithiation (Pr-Li) has been suggested and extensively researched in different LIBs to supply extra lithium sources, and compensate for such lithium loss<sup>[13-15]</sup>. In the last decade, the Pr-Li strategy has been developed using different mechanisms to offset the initial Li loss<sup>[16-18]</sup>. Currently, various Pr-Li technologies are being surveyed popularly can be classified into anode or cathode Pr-Li methods<sup>[19]</sup>. Due to the low initial efficiency of anode materials being a major obstacle to their application in LIBs, anode Pr-Li is necessary and the main task. Anode Pr-Li mainly involves electrochemical Pr-Li (EC-Pr)<sup>[20]</sup>, chemical Pr-Li (C-Pr)<sup>[21]</sup>, physical mixing

Pr-Li (PM-Pr)<sup>[22]</sup>, Pr-Li using additives (A-Pr)<sup>[23]</sup>, and direct contact Pr-Li with metallic lithium (DC-Pr)<sup>[24]</sup>.

Direct contact Pr-Li, also known as “internal short circuit method”, of the anode with metallic lithium is a concept to perform Pr-Li. This is a simple and an efficient method because it does not require any re-arrangement or any special structural requirements of electrodes, thereby reducing device assembly time and manufacturing costs<sup>[25]</sup>. The principle of the direct contact Pr-Li with lithium metal, which requires an electrical pathway between the anode and lithium metal as well as the presence of an electrolyte. This method utilizes the potential difference between the metal lithium and the anode for the lowest potential of lithium (~ 3.04 V vs. SHE). Moreover, driven by the potential difference, lithium is oxidized into Li<sup>+</sup> and diffused into the electrolyte, where electrons enter the anode material<sup>[26]</sup>. To maintain the electrolyte's electrical neutrality, the Li<sup>+</sup> intercalate into the anode and pass through the surface SEI, and combine with the electrons in the electrode to ultimately generate lithium compounds to achieve the effect of Pr-Li. Direct contact Pr-Li can be achieved by using a lithium foil<sup>[27, 28]</sup>, lithium powder<sup>[29]</sup> or through applying lithium metal by physical vapor deposition<sup>[30]</sup>.

This work reports the Li-source loading on graphite anodes for achieving the direct contact Pr-Li step was performed using following the thin Li foil. With utilizing 50% prelithiated lithium content in the graphite anode, the transformation of graphite anode from gray black to final dark blue was achieved (LiC<sub>18</sub>). Therein, the composition changes the center to the final stage of the entire electrode, from LiC<sub>6</sub> to LiC<sub>12</sub> and then to LiC<sub>18</sub>. This study explored and revealed the complex pre lithiation kinetics of the direct contact Pr Li method inside graphite anodes using in-situ technology. Moreover, it was observed that takes approximately 48 h for the Li metal to fully embed into the graphite electrode, forming a dense and continuous SEI on the graphite surface. The spatial distribution of lithiation was studied the lithiation occurs on a macroscopic level (electrode) and on the microscopic level (particle). Therefore, this paper aims research a dynamic change to explore the process of Pr-Li by direct contact Pr-Li with graphite electrodes.

## 2. MATERIAL AND METHODS

Pr-Li electrode: the graphite electrode (Shenzhen Kejing Star Technology Company Ltd.) was used after preheating at 80 °C for 24 h in a vacuum oven. The graphite electrodes were punched to the desired dimensions of 2 cm × 4 cm (active area) for real-time

visual observation, and thin Li foil (~ 20 μm) was cut to an area of approximately 2 cm<sup>2</sup> (calculated based on the 50% capacity of graphite electrode). 1 M LiPF<sub>6</sub> electrolyte was used with the EC and DMC (1:1 in wt%) solvents. The material morphologies were characterized through optical microscopy. The Energy Dispersive Spectrometer (EDS) was analyzed the element composition. The physical properties such as crystallinity and phase purity were recorded using X-ray diffractometer (XRD). The morphologies and structures of the SEI on pre-lithiated graphite electrodes were characterized by Scanning electron microscopy (SEM).

## 3. RESULTS AND DISCUSSION

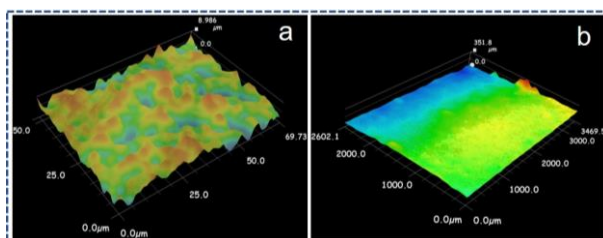


Fig. 1. Optical microscopy images of lithiated graphite electrode. (a) the area covered by Li foil on the graphite electrode with add electrolyte for 0 h. (b) graphite electrode after adding electrolyte for 2 h

Fig. 1 present the optical microscopy images of graphite electrode with direct contact Pr-Li. After the electrolyte is added, at the beginning of Pr-Li, it is found that a relatively uniform height distribution with the area covered by the Li metal (Fig. 1a). This result indicate that the Li metal is evenly covered on the surface of the graphite electrode. In the following, select the area from the center of the Li metal to the edge of the graphite electrode for observation at a reduced height after Pr-Li for 2 h, the height distribution of electrodes surface indicates the changes in Pr-Li (Fig. 1b). Meanwhile, with the progress of Pr-Li proceeds, it will cause changes in the composition of the graphite electrode.

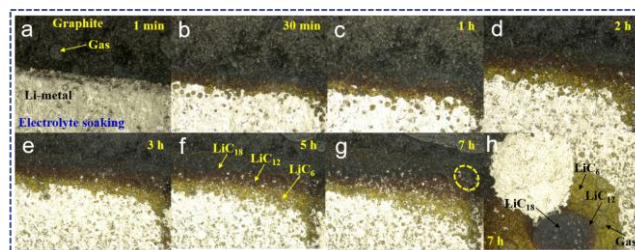


Fig. 2. Magnified images of graphite anodes undergoing color transformation during direct contact Pr-Li

The high-resolution magnified images of the soaked graphite electrode loaded with Li metal in Fig. 2. The color change of the Gr electrode is very prominent, it is

initiating immediately at the process of Pr-Li with the injection of electrolyte (Fig. 2a). It can be observed that Li metal slowly disappears from the edge of the Gr electrode, indicating that Li metal tends to solvate to  $\text{Li}^+$ , and as  $\text{Li}^+$  is inserted (embedded), the electrode begins to change color. Shown in Fig. 2b-g, extensive color changes were emerged with the increase of Pr-Li time, the gold and red colors evident indicating the  $\text{LiC}_{18}$  (dark blue color),  $\text{LiC}_{12}$  (dark red color),  $\text{LiC}_6$  (gold color) and stage co-existence in the Gr-Li electrode after introduction of electrolyte, and there is also evidence of gas formation. From the Fig. 2h, to further analysis of the changes in various components during the process of Pr-Li, and the color of graphite transform from gray black to dark blue color ( $\text{LiC}_{18}$ ), continuing to transform into dark red color ( $\text{LiC}_{12}$ ), and eventually turns into gold color ( $\text{LiC}_6$ ).  $\text{LiC}_{18}$  is ultimately formed throughout the entirely electrode for uniform the electrode with 50% lithium intercalation.

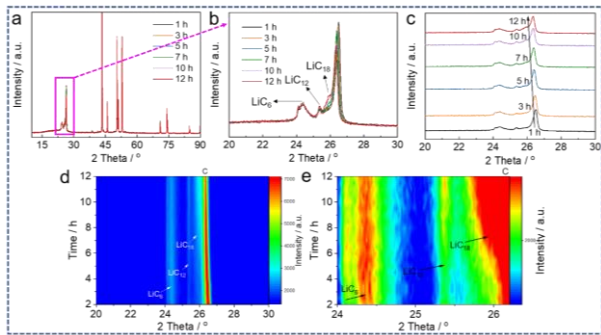


Fig. 3. In-situ XRD patterns for lithiated graphite electrodes at different time (0 - 12 h). (a)  $10^\circ$  to  $90^\circ$ , (b-d)  $20^\circ$  to  $30^\circ$ , (e)  $24^\circ$  to  $26.2^\circ$

The change of the present phase can be detected for all degrees of Pr-Li with in situ XRD (Fig. 3). A significant change in diffraction peaks can be observed within the range of  $20 - 30^\circ$ , and this is the range of variation of  $\text{LiC}_x$  compounds for Pr-Li (Fig. 3a). The reflection at  $24.2^\circ$  ( $\text{LiC}_6$ ),  $25.3^\circ$  ( $\text{LiC}_{12}$ ), and  $25.9^\circ$  ( $\text{LiC}_{18}$ ) great change with the time increase for Pr-Li (Fig. 3b and 3c). Fig. 3d and 3e show the characteristic reflection of graphite (002) at  $\sim 26.8^\circ$  is observed of graphite electrode, and the reflection peaks of  $\text{LiC}_6$  and  $\text{LiC}_{12}$  are getting weaker, while the highest lithiated graphite phase ( $\text{LiC}_{18}$ ) is observable after 12 h, indicating that more  $\text{LiC}_{18}$  are being converted with the increase of Pr-Li graphite electrode. Therefore, this Pr-Li behavior gives evidence for the Pr-Li of graphite to form the SEI.

The process of Pr-Li is gradually progressing from the periphery towards the center of covered by Li metal (Fig. 4a). It is clearly observed that as time goes on, the process of Pr-Li is gradually progressing from the

periphery towards the center of covered by Li metal, until the Li metal completely disappears ( $\sim 48$  h), indicating the completion of Pr-Li. This phenomenon may be caused by the preferential insertion of Li metal near the graphite electrode. Among them, the Li metal around the graphite electrode is preferably embedded in the graphite, and the progress of Pr-Li increases with the distance between the Li metal and the graphite electrode. The above two steps occur almost simultaneously, resulting in the slowest insertion of the outermost Li metal changes  $\text{Li}^+$  and into graphite, and the insertion speed of the graphite edge is greater than that of the Li metal in the middle. Moreover, to investigate the surface micromorphology after Pr-Li (Fig. 4f) was analyzed and compared with un-Pr-Li graphite electrode (Fig. 4b). As shown in the surface morphology of the un-Pr-Li graphite electrode in Fig. 4c-e, the surface of the electrode is smooth, and the boundary between the bulk graphite is clearly. On the contrary, the surface of the lithiated graphite electrode displays rougher, and the surface becomes blurred in Fig. 4g-i. This is due to the passivation layer formed during the Pr-Li process. To further examine the element composition of passivation layer on the lithiated graphite electrode by EDS (Fig. 4j), from which one can observe the presence of C, O, F, and P elements, compared with the unPr-Li electrode only have C element (Fig. 4k). This result further proves that will generate a SEI layer on the surface of lithiated graphite.

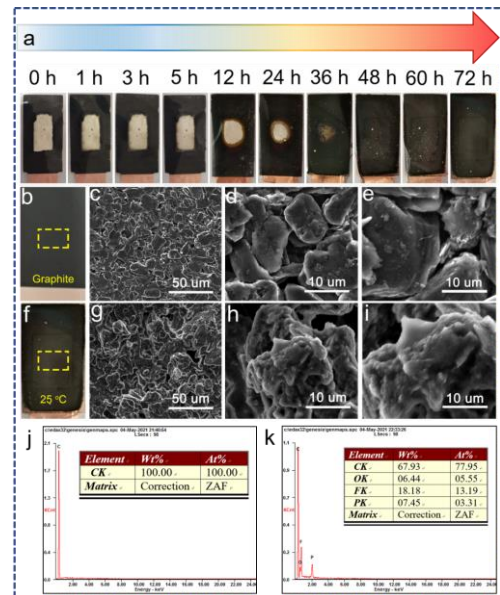


Fig. 4. (a) Photographs at difference Pr-Li time for garphite electrodes. SEM images of (b-e) original graphite electrode, and (f-i) the lithiated graphite electrode corresponding 48 h, (j, k) EDS analysis

As shown in Fig. 5, it can be concluded that there may be several processes for direct contact Pr-Li based on the above analysis, which in the reaction of Li metal with a graphite electrode. Firstly, dissolution of Li metal into  $\text{Li}^+$  in electrolyte (ionization,  $\text{Li}_s \rightarrow \text{Li}^+ + \text{e}^-$ ), and solvation  $\text{Li}^+$  is removed from desolvation intercalation into graphite (solvation,  $\text{Li}^+ \rightarrow \text{Li}_{\text{solv}}$ ; de-solvation,  $\text{Li}_{\text{solv}} \rightarrow \text{Li}^+$ ). Secondly, Li metal insert into graphite electrode in direct contact. Thirdly,  $\text{Li}^+$  de-intercalation from graphite, and intercalation into to other graphite particles.

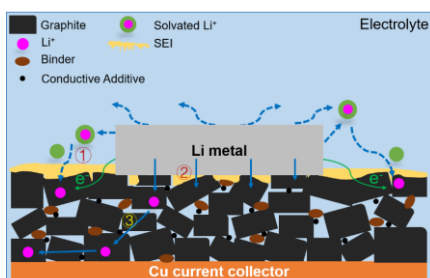


Fig. 5. Possible Li transport pathways in the reaction of Li metal with a graphite electrode

#### 4. CONCLUSIONS

The Pr-Li step is crucial for compensating for the initial loss of recyclable Li and improving the working potential of LIBs. In this study, the Pr-Li ability of graphite electrodes was evaluated by the direct contact Pr-Li method. The orderliness of graphite structure generates phase and color transitions, which enables visualization of the progress of lithiation and phase transition. The surface of the graphite electrode is  $\text{LiC}_{18}$  with 50% lithiation state is selected for direct contact Pr-Li. We present a systematic study on the Li transport pathways in the spontaneous reaction of Li metal in graphite electrode. The main Li transport pathway is the lithiation of graphite via  $\text{Li}^+$  diffusion through the electrolyte. The present study showed important new insights into the reaction mechanism of Li metal with graphite electrodes, which are valuable for Pr-Li.

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#### DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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